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REVIEW ARTICLE

Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene

Ekaterina V. Makshina,*[a] Michiel Dusselier,[a] Wout Janssens,[a] Jan Degrève,[b] Pierre A. Jacobs[a] and Bert F. Sels*[a]

Increasing demand for renewable feedstock-based chemicals is driving the interest of both academic and industrial research to substitute petrochemicals with renewable chemicals from biomass-derived resources. The search towards novel platform chemicals is challenging and rewarding, but the main research activities are concentrated on finding efficient pathways to produce familiar drop-in chemicals and polymer building blocks. A diversity of industrially important monomers like alkenes, conjugated dienes, unsaturated carboxylic acids and aromatic compounds are thus targeted from renewable feedstock. In this context, on-purpose production of 1,3-butadiene from biomass-derived feedstock is an interesting example as its production is under pressure by uncertainty of the conventional fossil feedstock. Ethanol, obtained *via* fermentation or (biomass-generated) syngas, can be converted to butadiene, although there is no large commercial activity today. Though practised on a large scale in the beginning of the 20th century, there is a growing worldwide renewed interest in the butadiene-from-ethanol route. An alternative route to produce butadiene from biomass is through direct carbohydrate and gas fermentation or indirectly *via* the dehydration of butanediols. This review starts with a brief discussion on the different feedstock possibilities to produce butadiene, followed by a comprehensive summary of the current state of knowledge regarding advances and achievements in the field of the chemocatalytic conversion of ethanol and butanediols to butadiene, including thermodynamics and kinetic aspects of the reactions with discussions on the reaction pathways and the type of catalysts developed.

1. General introduction

1.1. Setting the scene

1,3-Butadiene (C_4H_6 or BD) is the most important conjugated diene, being the basis of a wide variety of synthetic rubbers, elastomers and polymer resins upon polymerisation by itself or in conjunction with other polymerizable monomers. The global BD demand in 2012 was approximately 10 million metric tons with an incremental growth of 1–2% per year.

The synthetic BD industry started in 1920–1930; the synthetic rubber was proposed as an alternative for the manufacture of automobile tires. Sodium-butadiene rubber was the first synthetic rubber industrially produced worldwide. In Russia, the S.K. synthetic rubber production (abbreviation from Russian

"Sinteticheskii Kauchuk" – synthetic caoutchouc) was made in a one-stage process from grain ethanol, often referred to as the Lebedev process. In addition to Russia, synthetic rubber from ethanol (KER: abbreviation of Polish – "kauczuk erytrenowy" – erythrene caoutchouc) was also produced in Poland in the early 1930s. Germany produced the rubber under the brand name "Buna-S" and two routes starting from coal-derived acetylene were employed. The main route was the condensation of acetaldehyde *via* 1,3-butanediol with an overall BD yield on acetylene of 60%;[1] the second route proceeded *via* 1,4-butynediol with an overall yield on acetylene of 70–75%.[1] The first process involved the hydration of acetylene to acetaldehyde, which is subsequently converted into the aldol product, hydrogenated to 1,3-butanediol and dehydrated to butadiene, while the second (Reppe) process used formaldehyde and acetylene to produce 1,4-butynediol, which was hydrogenated to 1,4-butanediol and dehydrated partly *via* tetrahydrofuran to BD. These routes are no longer practicable. In the US, BD routes employed were from oil sources and ethanol by a two-step process using a mixture of ethanol and acetaldehyde.[2]

In the US and most of Europe, the ethanol and acetylene routes have been abandoned after the world war because of the

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emerging production of BD from petroleum sources. The ethanol route only survived up to now in China and India. In the US, a large percentage of BD production is obtained by dehydrogenation of *n*-butane and *n*-butenes.[2] Direct extraction from C_4 streams arising from naphtha crackers (ethylene plants) is substantially practised in Europe since the early seventies. The separation of BD from C_4 streams though requires an expensive extractive distillation with a selectivity of only 4–5% due to its azeotrope formation with butane.

The growth of ethylene production outpaced that of BD demand resulting in an oversupply of BD. Although this situation has led to a shut-down of many on-purpose BD production units, it also stimulated the development of chemical processes using BD as the building block. BD is thus considered as a high value by-product of ethylene production from steam crackers without clear production economics. Since many years, the BD supply and price have been influenced by the demand for ethylene.

Table 1 Butadiene content (kg kg^{-1} ethylene) for various feedstocks[2,3]

Feedstock	Butadiene/ethylene
Ethane	0.02
Propane	0.07
Butane	0.07–0.11
Naphtha	0.13
Gas oil	0.26

Recent trends in steam cracking show a lightened feedstock as a result of lower costs and larger availability of ethane from natural gas like shale gas, this change in feedstock affecting the supply and price of BD. Table 1 illustrates the lower BD yield from lighter feedstock relative to naphtha and light atmospheric gas oil in the steam cracker.[2,3] Whereas an ethane-only cracker has the lowest capital cost and the highest selectivity towards ethylene, it shows the lowest BD yield. As a consequence, restrictions on the availability of BD and high BD prices are expected in

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the near future. Moreover, lightening of the feedstock for the purpose of ethylene production leads to a deficit of C3, C4, C5 and pygas supply. Shortage of these chemicals, partially introduced due to the shale gas revolution, may create new opportunities for the production of biobased chemicals from renewable feedstock like sugars, glycerin *etc.* One could argue about the price of such chemicals, but their production cost will decrease as the process technologies evolve and the sustainability benefits should also not be overlooked.[4,5] The worldwide change in feedstock usage asks for a revisit of on-purpose BD production. Future BD production will probably be diverse, highly depending on the local availability and price of the different feedstocks such as coal, oil, gas and biomass. Most relevant on-purpose BD synthesis strategies are summarized in Scheme 1.

Biomass routes to butadiene. A return to the old BD production routes from ethanol currently is gaining renewed interest, since in a short time frame ethanol is one of the most relevant sources of ''bio''-carbon for the chemical industry.[6] As supplies of ethanol increased rapidly in the last few years, mostly with regard to its usage as a renewable fuel, its production is expected to grow continuously. To illustrate its volume, the global ethanol production amounts to more than 100 billion litres in 2012,[7] which is an order of magnitude higher than the BD demand. Usually, ethanol is made by fermentation of carbohydrates such as starch (*e.g.* from corn) or sugar (*e.g.* from sugar cane and sugar beet),[8,9] though hydration of petroleum-based ethylene is still practised. Chemical and fermentative routes *via* syngas to ethanol have also been investigated (see below).

Obviously, the success of the ethanol-to-BD route will depend on the cost of the upstream ethanol process. While the exploitation of the Brazilian sugarcane currently delivers the cheapest ethanol, over time cellulosic-based second generation ethanol in Asia,
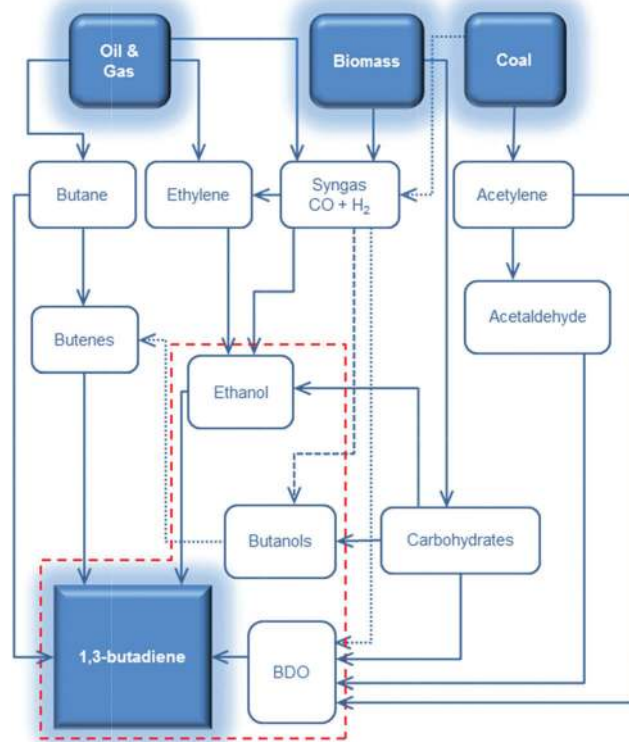
Scheme 1 Synthesis of 1,3-butadiene (BD) from various carbon-containing feedstocks. The focus of this review is shown in the red dashed line. BDO = butanediols.

Europe and United States may well surpass the techno-economic performances. Many research efforts are presently undertaken developing more efficient ethanol production technologies from

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Bert F. Sels

Bert F. Sels obtained his PhD in 2000 at KU Leuven in the field of oxidation chemistry with heterogeneous catalysis. He was awarded the DSM Chemistry Award in 2000, and in 2005 the Incentive Award by the Societè Chimique Belge for his research achievements. In 2005 he was appointed assistant professor at KU Leuven, and full professor in 2008. He now teaches courses on spectroscopic tools in organic chemistry, sustainability of chemical processes, spectroscopic tools in surface chemistry and heterogeneous catalysis. He heads a research group in the Center for Surface Chemistry and Catalysis (KU Leuven). His current field of research interest focuses on synthesis, characterization and use of heterogeneous catalysis, mainly in transformation of renewable resources to chemicals. He was recently elected the co-chair of the IZA Catalysis Commission.

low-cost and non-food/feed biomass feedstocks.[10] Ethanol from cellulosic and algal sources, the so-called 2nd and 3rd generation ethanol, is promising in this respect.[11–17]

While the industrial feasibility of the ethanol-to-BD route has been proven long time ago, a number of improvements both from an engineering and catalytic point of view is still vital to attain high BD yield and high BD productivity. In order to compete with existing oil- and gas-based technologies like C_4 dehydrogenation, issues related to carbon efficiency, catalyst cost, toxicity, catalyst performance, feedstock tolerance, back-end optimization, catalyst lifetime and stability require further optimization. So, it seems that extensive research is necessary to improve the viability of the ethanol route to BD vis-à-vis the conventional routes. In 2013, Axens, IFPEN and Michelin have launched their joint research program to develop an economically competitive process to produce bio-sourced synthetic rubber from bioethanol.[18,19]

Next to ethanol, other bio-derived chemicals like butanols (BuOH), viz. n-butanol and Gevo's isobutanol, 2,3-butanediol (2,3-BDO) and 1,4-butanediol (1,4-BDO) may also be useful to produce BD. Most of the C_4 alcohols are now available from renewable feedstocks via fermentation of biomass or syngas (e.g. biomass derived).[20,21] For instance, Genomatica – a company designing microorganisms for the conversion of sugars and cellulosic biomass to sustainable chemicals – is currently producing 1,4-BDO at a demonstration plant. The first commercial-scale plant is scheduled, with Novamont as a partner.[22,23] Together with Versalis, Eni's chemicals subsidiary leader in the production of elastomers, they recently announced the establishment of a strategic partnership to enable the production of BD from renewable feedstocks. Main incentive of the collaboration is the successful direct production of million pound quantities of bio-based 1,4-BDO from biomass resources in 2011 by Genomatica.[24]

Acid catalysed dehydration of (bio-based) butanols leads to a mixture of n-butenes, requiring further dehydrogenation to produce BD with existing technology.[2] Next to dehydration of monohydric alcohols direct butanediol (BDO) dehydration to BD was also performed. This strategy has the advantage of avoiding the expensive dehydrogenation step. The reaction involves a double dehydration, preferably employing a catalytic process, the catalyst and the reaction conditions employed differing with the position of the alcohol groups. Dehydration of 1,4-BDO is well-known from the acetylene-based Reppe route.[2] It is carried out at 280 °C by a rather complex method using an excess of steam and THF in the presence of a sodium phosphate catalyst. The dehydration chemistry of 1,3-BDO is slightly different. High BD yields above 80% were obtained at 400 °C using the same catalyst in the presence of steam. Dehydration of the other diols is less selective. So, 2,3-BDO easily dehydrates to methyl ethyl ketone, while its diacetate can be pyrolysed in high yield to BD upon heating to 475–600 °C, the acetic acid co-product being recycled.[25] New catalytic advances in the dehydration of diols and polyols in detail will be described below.

Gasification routes to butadiene. New chemical and biochemical technologies producing BD from syngas are currently under development. Syngas may originate from reforming of natural gas such as shale gas, although gasification of biomass or waste gases from the steel industry are valid alternatives. One route to BD runs via the production of 2,3-BDO followed by its dehydration. It was announced for technical implementation by 2016 in the frame of new technology for adiponitrile (ADP) and nylon-6,6 production by LanzaTech and Invista.[26] The butanediol is produced from syngas via fermentation, for instance from the waste gases of a steal producer or from natural gas steam reforming.[27] In the long term the direct gas fermentation of CO to BD is envisaged. In a partnership with Orochem Technologies, both companies claim an economically viable thermocatalytic 2,3-BDO dehydration process to BD with high selectivity. While the CO gas fermentation lifts the process out of the sugar value chain (food – chemicals), the batch sugar production is replaced by continuous CO gas production.

Other routes to BD from natural gas were investigated. They mainly focused on the direct and indirect production of chemical and fermentation ethanol, which is converted to BD. Several papers and reviews have been published on the catalytic conversion of syngas to ethanol and higher alcohols using chemocatalysis.[28–31] Three chemocatalytic routes are known in the literature to convert syngas to ethanol: (i) the direct conversion via selective CO hydrogenation on a solid catalyst, (ii) methanol homologation, which involves reductive carbonylation of methanol over a redox catalyst, and (iii) a multistep process, wherein classical methanol production from syngas, is followed by carbonylation to acetic acid, and subsequent hydrogenation to ethanol. None of these routes have been commercially practised. The carbonylation of methanol to ethanol is the most promising route, while the direct formation of ethanol from syngas is probably commercially less interesting due to a low ethanol yield and selectivity.[32] A recent example of the methanol–acetic acid route (TCX technology) is reported by Celanese.[33]

The fermentative production of ethanol from syngas has also gained considerable attention. The syngas could be an industrial waste gas or it may be obtained by natural gas reforming or gasification of biomass. The utilization of the whole biomass of low quality and the elimination of biomass fractionation are major advantages here. The state-of-the art and the most important challenges recently have been critically reviewed.[34–38]

Hydrocarbon and natural gas routes. Synthetic ethanol, produced by the direct or indirect hydration of ethylene from the cracker or dehydrogenation of ethane in natural gas resources, may be converted to BD. However, the capacity of worldwide production of synthetic ethanol is rather limited and represents less than 10% of the global production.

Dehydrogenation of butane from natural gas is a better economical solution to BD production. This well-established technology has been practiced until the 1990's in Russia and the US. The main disadvantages of the process are the high endothermicity and the high process temperature (600–700 °C) to achieve an economical equilibrium conversion. As the reaction runs at incomplete conversion, separation of feed and products is mandatory. Due to coke formation, catalysts usually run for only 5 to 15 minutes. As heat from catalyst regeneration

fuels the endothermic dehydrogenation, the overall lifetime of the catalysts is much longer. The Houdry-Catadiene process using a mixture of Al oxide and Cr oxide typically shows a reactor outlet with 15 vol% butadiene, and about 50% carbon yield.[39] Somewhat higher yields (65%) are reported for the two-step Phillips Petroleum technology, involving butane dehydrogenation to *n*-butenes with Cr/Na/Al oxide, followed by their extractive distillation and conversion to butadiene over Fe/K/Al oxide.[39] Application of vacuum or addition of water are used to reduce the partial pressure (Le Chatelier) and to overcome coke formation by stimulating the water gas shift reaction, respectively (see also technologies from Dow and Shell). The conversion and selectivity of the process are also greatly improved by hydrogen removal. In the presence of dioxygen, water is formed, the exothermicity partly being used to compensate the energy required for the dehydrogenation. Whereas the presence of water and O_2 increases catalyst lifetime, O_2 also helps the difficult abstraction of allylic hydrogen. With Phillips O–X–D at 480–600 °C, 80% conversion and 90% BD selectivity were obtained. The Oxo-D process of PetroTex shows 93% BD selectivity at 65% conversion.[2] Both processes run only on *n*-butenes since the addition of oxygen to butane would result in products oxidation at the temperature required for butane dehydrogenation. Although use of iodine to remove H_2 as HI (Idas process, Shell France) has been proposed, serious corrosion has been encountered. The yield of BD on butane was said to be 70%. Butenes could be also resourced from dehydrating biobutanols to produce bio-based BD, though the price of the bioalcohols is currently too high for commercial use.

The dehydrogenation processes are competitive with the cracking process when BD price is high and raw C_4 is available. Honeywell UOP in partnership with TPC group and BASF in collaboration with Linde recently announced the development and licensing of such a process for the on-purpose BD production from butane.[40–42]

1.2. Scope of the review

The introductory section already partly reveals many feedstock possibilities for future on-purpose production of BD. Routes from butane and *n*-butenes are probably the most developed ones. Although they will not be described in this review, they should be regarded as benchmark to alternative routes. The most promising competitive routes are BD from ethanol and BDOs. They form the main subject of this review.

Research on ethanol conversion to BD has been performed intensively in the twenties to sixties of the 20th century. A possible reaction mechanism and promising catalytic systems have been presented in previous reviews.[43–48] With the decreasing industrial interest for this reaction at that time, the scientific interest also faded, while only a few publications analysing recent achievements appeared.[49–52] Yet, there is now a steadily growing interest of academia and industry in producing bio-ethanol and using it as a platform molecule for various base chemicals,[53–61] BD being an important chemical among them. Therefore, a comprehensive review paper of old and recently published reports on the catalytic conversion of ethanol to BD

is attempted in the first part. The contribution includes details of the reaction network, mechanistic and thermodynamic considerations and compares catalytic data (in terms of BD yield, ethanol conversion, carbon yield and volume productivity) of various catalyst types. Catalytic properties and structure/activity–selectivity relationships were made as much as possible, if appropriate, in order to guide and inspire the reader.

Routes to BD from 4-carbon diols (BDO) have attracted much recent attention and this evolution is mainly explained by the availability of bio-derived BDOs from renewable and waste feedstocks. Though the chemistry seems less complicated and has already been described in part of the old BD processes from acetylene and ethanol, the selective double dehydration of BDOs to BD under milder conditions remains challenging requiring unique catalysis. The second part of the review is therefore devoted to summarize and describe the most important catalytic achievements to dehydrate such diols including the mechanistic proposals and thermodynamics, the type of catalyst developed and the current status.

## 2. Ethanol-based butadiene

2.1. The technological options: one *vs.* two-step processes

In 1903 the catalytic synthesis of BD from ethanol was first performed by Ipatiev in Russia.[62] Low BD yield of about 1.5% was obtained by passing ethanol at 550–600 °C vapour over Al powder. Filippov obtained a BD yield of 5% from diethyl ether at 400–500 °C on the same catalyst.[63] Ostromyslensky proposed a catalytic route from a mixture of ethanol and acetaldehyde over alumina or clay catalysts at 440–460 °C, yielding 18% BD.[64] Maximoff claimed the formation of BD from a mixture of ethanol with acetaldol (or crotonaldehyde) over aluminium hydroxide.[65] Later, Lebedev[66–68] proposed his first process on a mixture of zinc oxide and alumina at 400 °C. He achieved a BD selectivity of 18%, directly from ethanol according to following reaction (1):

$$2 \ \diagup\!\!\diagdown_{OH} \longrightarrow \diagup\!\!\diagdown\!\!\diagup + 2H_2O + H_2 \qquad (1)$$
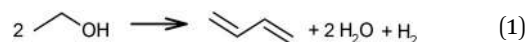
Improvements by Lebedev's group with an undisclosed catalyst composition showed higher yields with up to 70% BD selectivity at 350 °C and atmospheric pressure.[69] The process was examined both in Germany and in the US, but was not taken to the full scale. I.G. Farbenindustrie tested supported magnesia catalysts promoted by Co or Cr and reported 60% yield at 300 °C and atmospheric pressure.[1] In the US a similar catalyst containing 59% magnesia, 2% chromic acid and 39% silica gel was also examined.[1] This catalyst gave 38% BD yield per pass with 56% selectivity at 400–425 °C.

In addition to the direct ethanol conversion according to (1), BD from a mixture of ethanol and acetaldehyde (or a so-called two-steps process according to Ostromyslensky's pathway) was studied. Union Carbide and Carbon Chemicals Corporation performed the industrial manufacturing of BD from ethanol in the USA over tantalum oxide on silica using this two-step process (Scheme 2). This process includes the partial dehydrogenation of
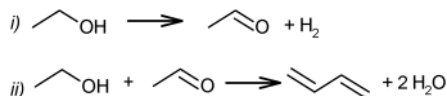
Scheme 2   Two-step process of BD from ethanol.

ethanol to acetaldehyde, followed by the transformation of the mixture of ethanol and acetaldehyde into BD. The yield of ethanol was 18% at a conversion of 30% per pass.[70]

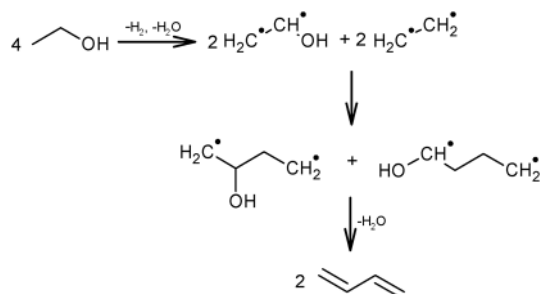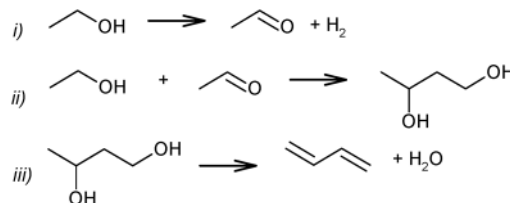## 2.2.   Routes and chemistry from ethanol to BD

Ethanol as a building block can be converted into BD. The reaction network involves a series of reactions, leading *via* multiple pathways to a variety of products that are controlled differently by kinetics and thermodynamic restrictions. Before describing the thermodynamic and kinetic aspects, the different reactions involved and the complex reaction network in the synthesis of BD from ethanol will be clarified first.

Butadiene formation. Since the successful industrial production of BD from ethanol (or a mixture of ethanol and acetaldehyde), the study of the reaction mechanism has been performed extensively. Many reaction mechanisms proposed before 1945 have been discussed in depth in the review by Egloff and Hulla.[44] This review briefly mentions the most important statements and conclusions of that period, but we will focus more on the recently anticipated reaction schemes.

Initially, Lebedev *et al.* proposed a radical mechanism to describe the direct formation of BD from ethanol, in accordance with the reactions in Scheme 3.[68] A few years later, Balandin argued that this radical reaction mechanism was energetically possible.[71] All possible combinations of molecules in the reaction mixture were analysed based on the multiplet theory. Whereas the formation of 49 different possible reaction products was predicted, only 21 of them could be detected. Acetaldehyde was identified as a primary product, while BD was assumed to be a third generation product. Baladin concluded that the reaction proceeded *via* 1,3-BDO according to the following reaction sequence (Scheme 4).

This scheme was essentially similar to the mechanism proposed earlier by Ostromyslensky for his two-step process using a mixture of ethanol and acetaldehyde.[64] Egloff and Hulla supported the intermediate formation of 1,3-BDO.[44]

The above mechanistic proposals were all rejected a few years later by different research groups.[69,72–76] By studying the


Scheme 4   BD formation mechanism according to Balandin.[71]

transformation of various reactants and mixtures thereof, the authors considered that the reactions, including the Lebedev and Ostromyslensky synthesis, all proceeded through the intermediate formation of crotonaldehyde.[69,72,73,77,78] The mechanism includes the formation of acetaldol *via* the aldol condensation of two acetaldehyde molecules, followed by dehydration of the aldol to crotonaldehyde, in accordance with reaction (2):
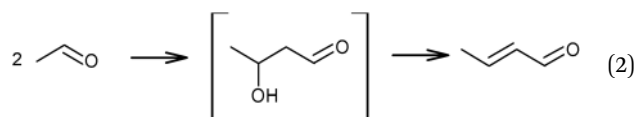
Further transformation of crotonaldehyde to BD has been the subject of many discussions for a long time. According to Quattlebaum *et al.*, crotonaldehyde is deoxygenated with ethanol, as presented in Scheme 5(i).[73] Moreover, the authors for the first time attempted a description of the mechanism taking into account the participation of surface atoms of the catalyst. They assumed a synthesis route *via* hydrogen transfer from ethanol to the enol-form of crotonaldehyde.[73] It has been suggested that the reactive bridged siloxane of the silica-based catalyst participated in the deoxygenation process by reacting with ethanol and the enol, thereby supporting an intermolecular hydride shift (Scheme 5ii–iv), while the oxide promoter (*e.g.*, tantalum, zirconium or niobium oxides) performs the aldol condensation. The latter reaction was identified as the rate-controlling step for the Ostromyslensky process.[73]

Scheme 3   BD formation mechanism according to Lebedev.[68]
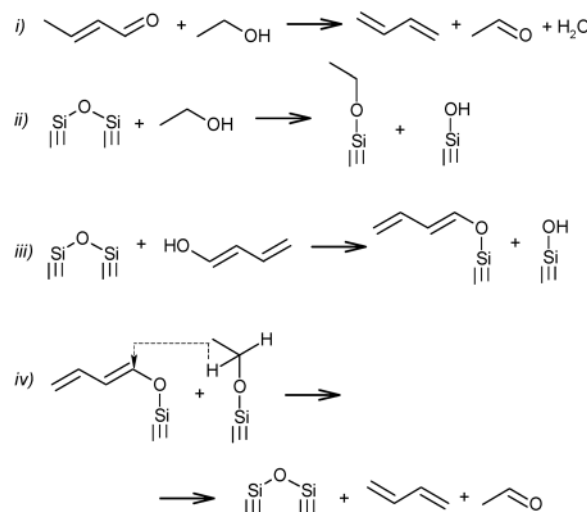
Scheme 5   BD formation mechanism according to Quattlebaum *et al.*[73]
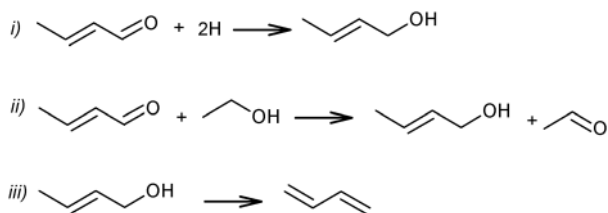
Scheme 6   Pathways of crotonaldehyde to BD.[69,72]

Jones et al.[76] studied the reaction mechanism of the two-step process over the same catalyst, viz. 2%Ta$_2$O$_5$–SiO$_2$. They suggested an opposite effect from the catalyst's components, the unmodified silica being more effective for acetaldehyde condensation and the 2%Ta$_2$O$_5$–SiO$_2$ material being more active for feed mixtures requiring deoxygenation of the aldehyde. Thus, the proposed mechanism of the process (in Scheme 5i) was supported, while reaction sequence ii–iv was rejected (Scheme 5), because participation of the Ta promoter was not included.

At the same time, a slightly different pathway for crotonaldehyde transformation was proposed (Scheme 6).[69,72] Crotonaldehyde was first reduced to crotyl alcohol (Scheme 6i and ii), followed by its dehydration to BD (Scheme 6iii). Ethanol (or any other alcohol present in the system) served as a hydrogen donor.

Kagan et al. over Lebedev type catalysts showed BD production by the direct reduction of crotonaldehyde with hydrogen.[72] In view of the overall scheme of the reaction mechanism, it was concluded that this hydrogenation process is less likely than the hydrogen transfer from the alcohol to the aldehyde (Scheme 6ii). Natta and Rigamonti[74] and later Bhattacharyya and Sanyal,[75] based on thermodynamic calculations of the proposed reaction scheme (Scheme 6), have confirmed that the formation of BD proceeded via the selective reduction of crotonaldehyde by ethanol to crotyl alcohol, the direct reduction of crotonaldehyde by hydrogen being thermodynamically less favourable. In the overall reaction network (Scheme 7), crotonaldehyde formation from acetaldehyde, i.e. the aldol condensation step, was indicated as the rate-controlling step.[72,75]

The reaction network in Scheme 7 was also confirmed by Vinogradova et al. using C^{14} labelled acetaldehyde.[79] They showed
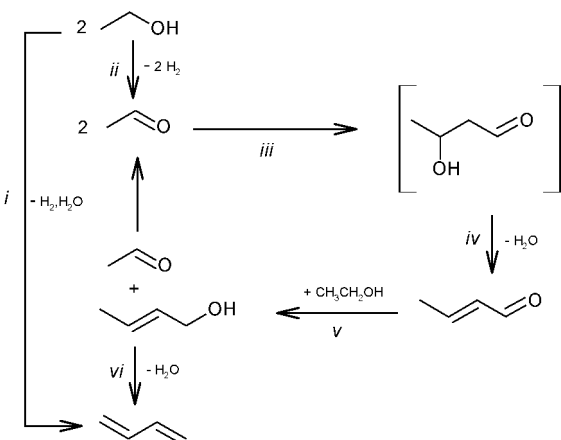
the conversion of crotonaldehyde into crotyl alcohol in the presence of an excess of ethanol due to the repartition of hydrogen, which occurs via the formation and decomposition of an intermediate complex between ethanol and the aldehyde.

Later, Niiyama et al. studied the ethanol to BD conversion over MgO–SiO$_2$ catalysts. They assumed the ethanol dehydrogenation as a rate-determining step on the basic catalyst.[80] They postulated for the first time that the intermolecular hydrogen transfer between ethanol and crotonaldehyde proceeded via a Meerwein–Pondorf–Verley mechanism (MPV), requiring the participation of acid and basic sites. High BD yields necessitate a balanced ratio between the acidity and basicity.[80]

Kvisle et al. also using the MgO–SiO$_2$ catalyst[81] concluded that the rate-limiting step consists in the condensation of acetaldehyde occurring prior to the hydrogen transfer step, rather than the dehydrogenation of ethanol to acetaldehyde. In the absence of quantitative details, they also emphasized the synergic effect of the catalyst's components for active and selective catalysis.

Separately, the possible formation of 1,3-BDO as an active intermediate was studied in more detail.[73,74,82] Based on the transformation of pure butanediol or its mixture with ethanol, it was concluded that the former did not participate in BD formation from ethanol.[73,82] The analysis by Natta and Rigamonti supported the thermodynamically impossible formation of 1,3-BDO from ethanol and acetaldehyde.[74]

Although the route of BD formation (Scheme 7) is generally accepted, alternative schemes were proposed as well. In Scheme 8 it is suggested that BD formation results from an interaction between acetaldehyde and ethylene via the Prins reaction.[83,84] Thermodynamically, the Prins mechanism is energetically possible but less favourable than the generally accepted mechanism via aldol condensation.[51,74] However, no experimental studies confirming the involvement of the Prins reaction have been performed.

In the literature, all mechanistic and reaction network studies were based on the experimental results of catalytic tests using various feed combinations, temperatures and contact times. There has been only one attempt studying BD formation from ethanol by IR spectroscopy.[86] Ethanol adsorption and its chemical transformation were studied over an alumina–zinc catalyst in the temperature range of 20–400 °C. Above 300 °C a decrease of surface alkoxy-species in the region 1080–1120 cm^{-1} with increasing reaction temperature was observed at the expense of several new vibration bands. The most intense signal was assigned to the characteristic vibrations of C=O (1750 cm^{-1}) and C=C–O (1035 and 1680 cm^{-1}), while the origin of other, less intense bands was not specified. However, a conclusive mechanism was not proposed.

Scheme 7   Overall scheme of ethanol conversion to BD.
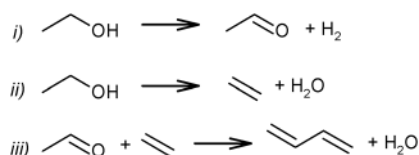
Scheme 8   Prins reaction scheme for BD formation from ethanol.[83–85]

Identification and origin of by-products. Reaction of ethanol to BD generates several by-products. Their formation has been studied intensively.[73,87,88] Quattlebaum *et al.* proposed a classification of the by-products according to their formation mechanism,[73] one group including the products formed by simple dehydration or ester-forming disproportionation, another one containing the products formed similarly as in the reaction cascade towards BD. The flow chart of the most important by-products is presented in Scheme 9.

According to this classification, the first group includes ethylene and diethyl ether, being products of the direct ethanol dehydration (reaction (1) and (2), Scheme 9). Ethyl acetal is a condensation product in the reaction between ethanol and acetaldehyde (reaction (3)). Ethyl acetate is a product of acetaldehyde disproportionation, also known as the Tishchenko reaction (reaction (4), Scheme 9). Finally, acetic acid is a product of ethyl acetate hydrolysis (reaction (5), Scheme 9).[73]

The second group of by-products consists of crotonaldehyde, a product of acetaldehyde condensation to acetaldol (reactions (iii), Scheme 9) and its subsequent dehydration (reaction (iv)); crotyl alcohol, a product of the reduction of crotonaldehyde (reaction (v)). Methyl ethyl ketone (butan-2-one) could be a

product of deoxygenated acetaldol with subsequent rearrangement (reaction (6))[73] or it may result from dehydration of 1,3-BDO (see below, Section 3.2), or it could result from crotyl alcohol isomerization.[90] Butanal can be an isomerization product of crotyl alcohol (reaction (7)), while butenes and butanol may be produced from butanal *via* deoxygenation (reaction (8)) and reduction (reaction (9)), respectively.[73] 1,3-BDO was considered as a product of acetaldol reduction (reaction (10)). Furthermore, C_6-hydrocarbons and C_6-oxygenated products were formed by the condensation of C_4-aldehydes such as butanal and crotonaldehyde with acetaldehyde *via* similar mechanisms (reaction sequence, ii–vi).[73]

The presence of molecules containing three and five carbon atoms was rationalized by the cleavage of 1,3-BDO into propylene and formaldehyde (reaction (11), Scheme 9). The occurrence of the last reaction explains the formation of C_3-hydrocarbons and C_3-oxygenated compounds as a result of an interaction of formaldehyde with ethanol and acetaldehyde, as well as C_5-hydrocarbons and C_5-oxygenated products as a result of an interaction of formaldehyde with C_4-oxygenated compounds.[73] Also the reduction of formaldehyde could be a source of methanol (reaction (12)), which further reacts with other alcohols resulting in ether formation and ultimately in aromatics according to the Methanol-to-Gasoline concept.[91]

An almost similar scheme of by-product formation was proposed by Gorin *et al.*[87,88] Despite the experimental evidence of reaction (11) (Scheme 9),[82] an alternative mechanism was proposed to explain the formation of by-products with an odd number of carbon atoms.[88] The steps proposed are the ketonization of acetic acid, formed *via* reaction (5), resulting in acetone with release of CO_2 (reaction (13)). Acetone is further reduced to isopropyl alcohol (reaction (14)), which is likely the origin of propylene *via* dehydration (reaction (15)). Acetone and isopropanol could participate in the formation of the C_5-hydrocarbon pool[92,93] *via* mechanisms similar to those proposed for BD formation (Scheme 9, reactions (ii)–(vi)).

Alternatively, it has been suggested that *n*-butanol is formed directly *via* hydrogenation of crotonaldehyde (reaction (16), Scheme 9)[53,59,89] by surface hydrogen atoms resulting from ethanol dehydrogenation (reaction (ii)), whereas the butenes can be obtained by dehydration of *n*-butanol (reaction (17)).[59] Furthermore, it has been also proposed that acetone could be produced from acetaldol (reaction (18)).[94–96] Reaction proceeds *via* formation of surface carboxylate intermediate $CH_3CH(OH)CH_2COO(s)$ followed by dehydrogenation and decarboxylation.

All compounds identified as by-products in both Lebedev's and Ostromyslensky's processes are summarized in Table 2.

2.3. Thermodynamic considerations

The thermodynamics for the conversion of ethanol to BD have been described by several authors.[43,51,74,75] The first attempt was performed by Natta and Rigamonti[74] in 1947, aiming at unravelling the reaction mechanism. Seven different mechanisms were discussed in this study. Based on the experimental data and on the data for the Gibbs free energy of the different reaction steps in the temperature range 400–430 °C, the authors
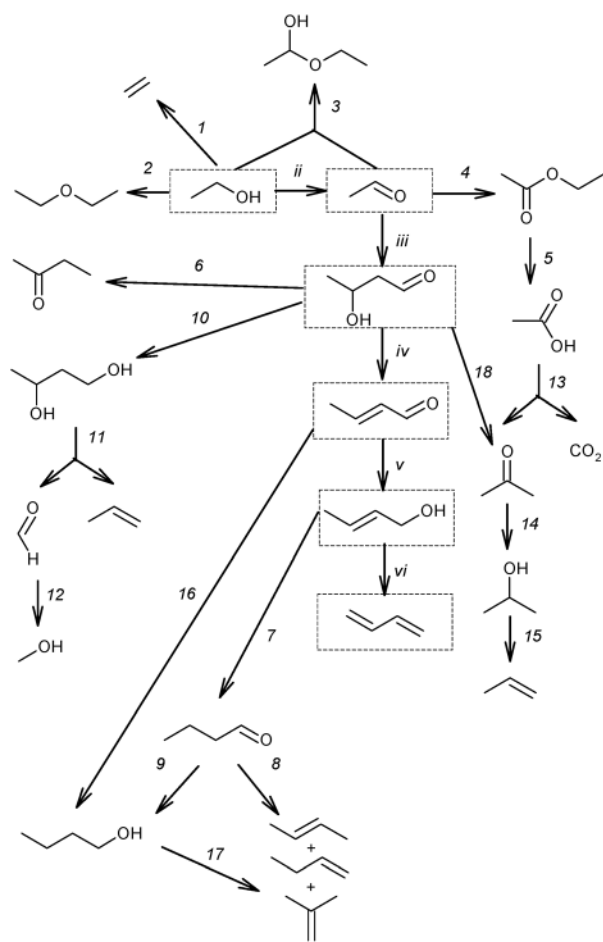
Scheme 9 Reaction network of the main by-products.[53,59,73,87–89] Reactions (ii)–(vi) and the products (in boxes) represent the generally accepted reaction pathway towards BD.

Table 2 By-products of ethanol conversion into butadiene[48,73,78,87,88,97]

Number of carbon atoms	Hydrocarbons	Oxygenated compounds
1	Methane	Carbon monoxide Carbon dioxide Formaldehyde Methanol
2	Ethylene Ethane	Acetaldehyde Acetic acid
3	Propylene Propane	Methyl ethyl ether Acetone Propanol and isopropanol
4	Butadiene Butenes: 1-butenes, trans-2-butene, cis-2-butene; iso-butene	Ethers: ethyl ether, ethyl vinyl ether Esters: ethyl acetate Aldehydes: butanal, crotonaldehyde Ketones: butanon Alcohols: butanol, crotyl alcohol Ethyl acetal
5	Pentenes: 2-pentene, 1-pentene, 2-methyl-2-butene, 2-methyl-1-butene and 3-methyl-1-butene Pentadienes: 1,3-pentadiene; 2-methyl-1,3-butadiene	Amyl alcohol
6	Hexanes: both branched and strait-chain isomers Hexadienes: 1,3-cyclohexadiene, 2,4-hexadiene, 3-methyl-1,3-pentadiene and 1,3-hexadiene benzene	Ethers: butyl acetate Aldehydes: hexaldehyde and hexenal Alcohols: hexanol; 2-hexen-1-ol
7	Toluene	
8	4-Vinylcyclohexene; p-xylene	n-Octyl alcohol

concluded that the reaction sequence of reactions (ii) to (vi) in Scheme 7 is the most probable pathway to form BD from ethanol. Later, several groups carried out a more comprehensive thermodynamic analysis as shown in Scheme 7.[43,51,75]

An Ellingham-type plot (Fig. 1) displays the change in Gibbs free energy (ΔG, kJ mol^{-1}) between 25 and 530 °C for the different reactions shown in equation (i) to (vi). Calculations were done in Aspen Plus$^{\text{®}}$ software for pure components in their real, and not standard states at the given reaction temperature and pressure. The ethanol to BD reaction is endothermic by 102–109 kJ mol^{-1} from 200 to 500 °C (not shown). The Gibbs free energy change for the direct conversion of ethanol to BD shows that the reaction (i) is favourable above 150 °C. Higher temperature shifts the equilibrium of the endothermic reaction to higher conversions. Since the number of moles of products is higher than that of the reagent, the reaction is pressure dependent, low pressures being favourable for high equilibrium conversion.

Inspection of the individual reactions shows different thermodynamic behaviour. The condensation of acetaldehyde to crotonaldehyde ((iii) + (iv) in Fig. 1 and Schemes 7, 9) is characterized by very low values of the Gibbs energy (ΔG). The reaction is unfavourable above 200 °C, whereas the formation of acetaldehyde from ethanol (ii) and the dehydration of crotyl alcohol to BD (vi) are favourable above 250–300 °C. Thus, in the usual temperature range applied for BD synthesis, viz. 350 to 430 °C, the equilibrium of reaction (vi) (Fig. 1) is clearly shifted to
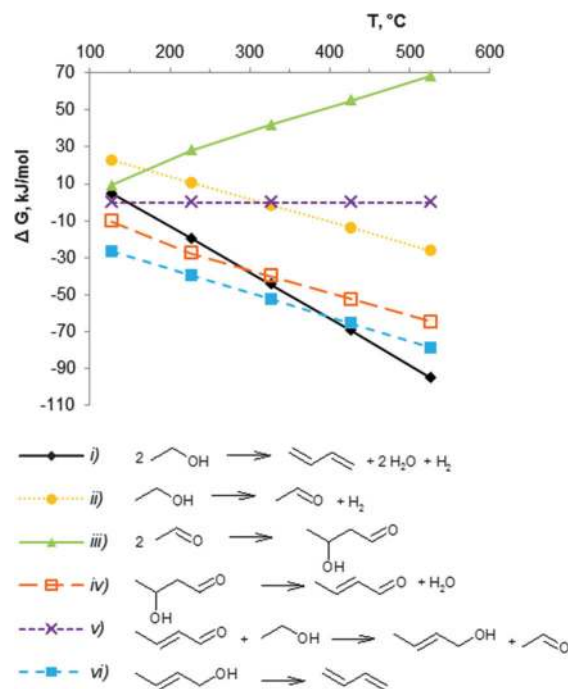

Fig. 1 Calculated thermodynamic data for ethanol transformation into BD, ΔG values of the overall reaction (i) and the intermediate steps (ii–vi). The calculations were performed with Aspen Plus$^{\text{®}}$ software for mixtures of pure components at given temperature, p = 1 atm (ΔG is calculated in the real state and thus different from ΔG^0).

BD formation. One reaction, *viz.* the bimolecular MPV ((v) in Fig. 1 and Schemes 7, 9), forming crotyl alcohol (CrOH), shows very low Δ*G* values over the entire temperature range. However, as long as CrOH is consumed by dehydration in the consecutive reaction to BD (vi), the MPV reaction (v) will be consuming crotonaldehyde (CrH) to form new CrOH. Furthermore, as the equilibrium of reaction (ii) is in favour of acetaldehyde formation, an excess of acetaldehyde in the system also stimulates reaction (iii) + (iv) to continuously produce crotonaldehyde.

It may thus be concluded that the choice of the temperature range for BD formation from ethanol will be defined by kinetic factors, and thus by the ability of the catalyst components to accelerate the individual reactions.[43]

Fig. 2 shows the equilibrium compositions (mole fractions) in the direct conversion of ethanol to BD. These data were
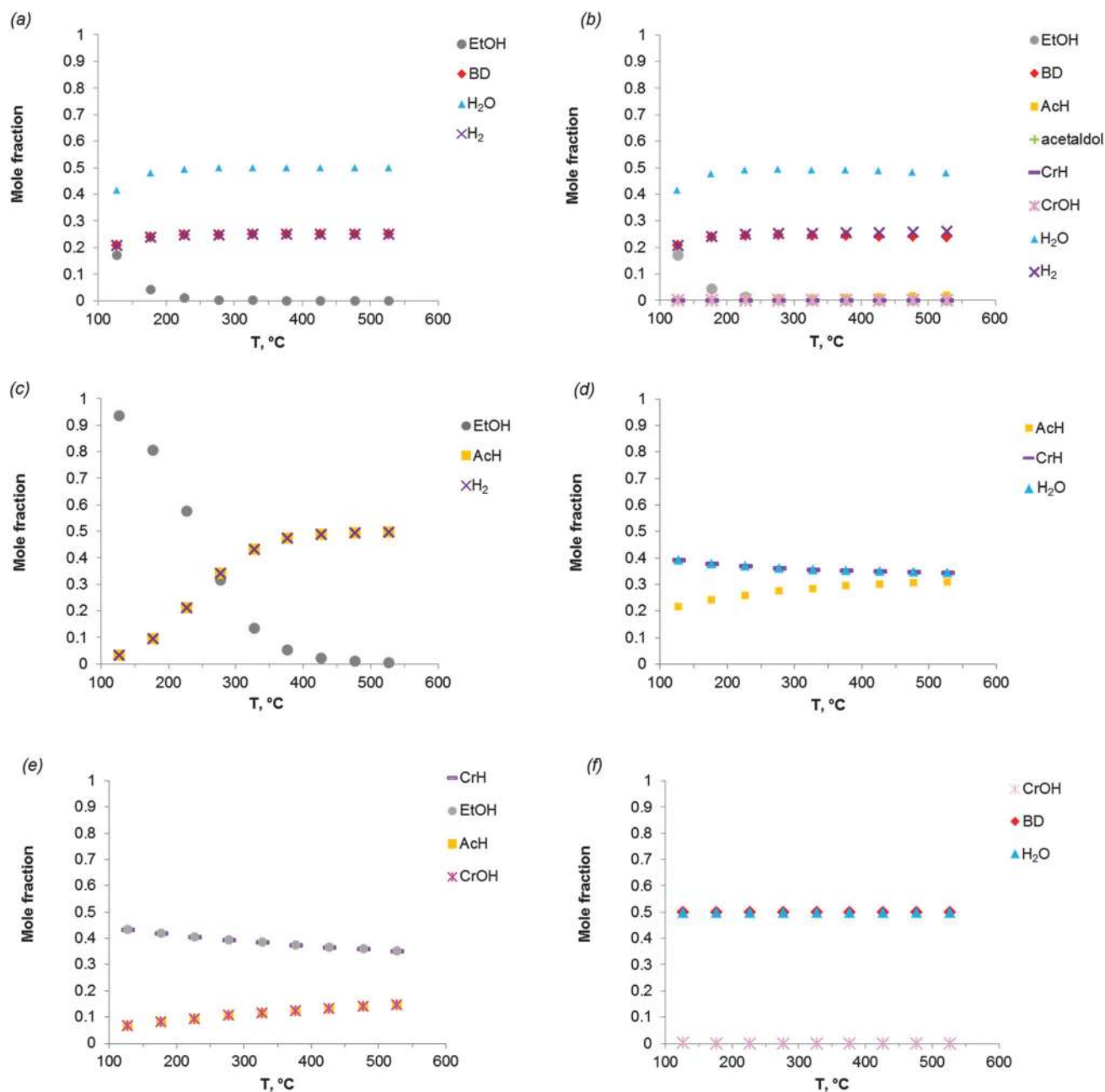
Fig. 2   Equilibrium compositions calculated for: (a) the overall reaction of ethanol to BD, reaction (i); (b) the reaction of ethanol to BD taking into account the reaction sequence, reactions (ii) to (vi); (c) ethanol dehydrogenation to acetaldehyde, reaction (ii); (d) aldol condensation of acetaldehyde to crotonaldehyde, reaction (iii) + (iv); (e) MPV reaction of ethanol with crotonaldehyde to synthesize crotyl alcohol, reaction (v), with a mixture of ethanol and crotonaldehyde (molar ratio is 1:1); (f) dehydration of crotyl alcohol to BD, reaction (vi). The pressure in the calculations is assumed 1 atmosphere. The simulation is performed using Equilibrium based reactor (REquil) in Aspen Plus® software. The reactions (i) to (vi) are in line with the reactions in Fig. 1 and in Scheme 7. (CrOH = crotyl alcohol; CrH = crotonaldehyde; AcH = acetaldehyde; BD = 1,3-butadiene).

calculated at one atmosphere pressure using the Equilibrium based reactor (REquil) in Aspen Plus® software. The results indicate that an almost complete EtOH conversion could be obtained above 227 °C (Fig. 2a). A very similar result is obtained when the thermodynamic analysis was approached *via* the reaction sequence (ii) to (vi) in Schemes 7 and 9 (Fig. 2b). Only a slight decrease in BD concentration was found for temperatures higher than 340 °C due to unconverted acetaldehyde and crotonaldehyde (Fig. 2b).

The different steps of the reaction network (Schemes 7 and 9) were also individually analysed with respect to the equilibrium compositions and conversion. Ethanol dehydrogenation is thermodynamically favored by an increase in temperature,[43,51,74,75] a temperature higher than 430 °C being required to obtain full ethanol conversion (Fig. 2c). In the commercially applied temperature range of 325 to 430 °C, a 76 to 96% (on carbon basis) thermodynamic yield of acetaldehyde (AcH) can be reached.

Further transformation of acetaldehyde into crotonaldehyde proceeds *via* acetaldol (Scheme 7(iii)). The aldol reaction is thermodynamically unfavourable (Fig. 1),[51,75] but the subsequent aldol dehydration into crotonaldehyde (CrH) (iv) is highly favorable (Fig. 1). The thermodynamics show full conversion of the aldol over the entire temperature domain. The overall transformation of acetaldehyde into CrH (reactions (iii) + (iv)) inhibited by an increase in temperature shows low ΔG values over the entire temperature domain. Consequently, the equilibrium conversion of acetaldehyde is 72% at 330 °C (on carbon basis) and decreases with increasing temperature (Fig. 2d). Subtle acid–base catalysis is required to assist this condensation reaction.

The subsequent step with crotonaldehyde is the MPV reaction (v), which is also characterized by very low ΔG values.[43,51,74] The conversion of crotonaldehyde (CrH) into crotyl alcohol (CrOH) is 23–27% (from 325 to 430 °C, calculated on CrH basis) in the case of an equimolar substrate feed (Fig. 2e). The equilibrium conversion could be increased by increasing the molar ratio of EtOH to CrH, with a value of 77%, when the molar ratio of EtOH to CrH is 20. CrOH formed as a product of the MPV reaction is then dehydrated to BD (Fig. 2f). This reaction is thermodynamically favorable irrespective of the temperature applied.

The thermodynamics were also analysed taking into account the presence of side-products (Table 2). The effect of ethylene and diethyl ether (DEE) on the thermodynamics was specified first. Fig. 3a shows the equilibrium composition of the reaction mixture in the case where ethanol dehydration occurs together with ethanol-to-BD. Ethylene is clearly the most thermodynamically stable product, whereas diethyl ether is formed at temperatures below 150 °C. The BD yield is considerably lower when ethanol dehydration is included in the thermodynamic analysis (compare Fig. 3a with Fig. 2a and b). When the temperature increases from 325 to 430 °C, in the presence of ethylene in the product mixture, the thermodynamic yield of BD is reduced to 24–27% (on carbon basis). When the reaction temperature is increased to 530 °C, the BD yield only slightly increases (up to 30%). Thus dehydration of ethanol to ethylene should be avoided kinetically to attain high BD yields. As the reaction is catalysed by the acidity of the catalyst or the support,
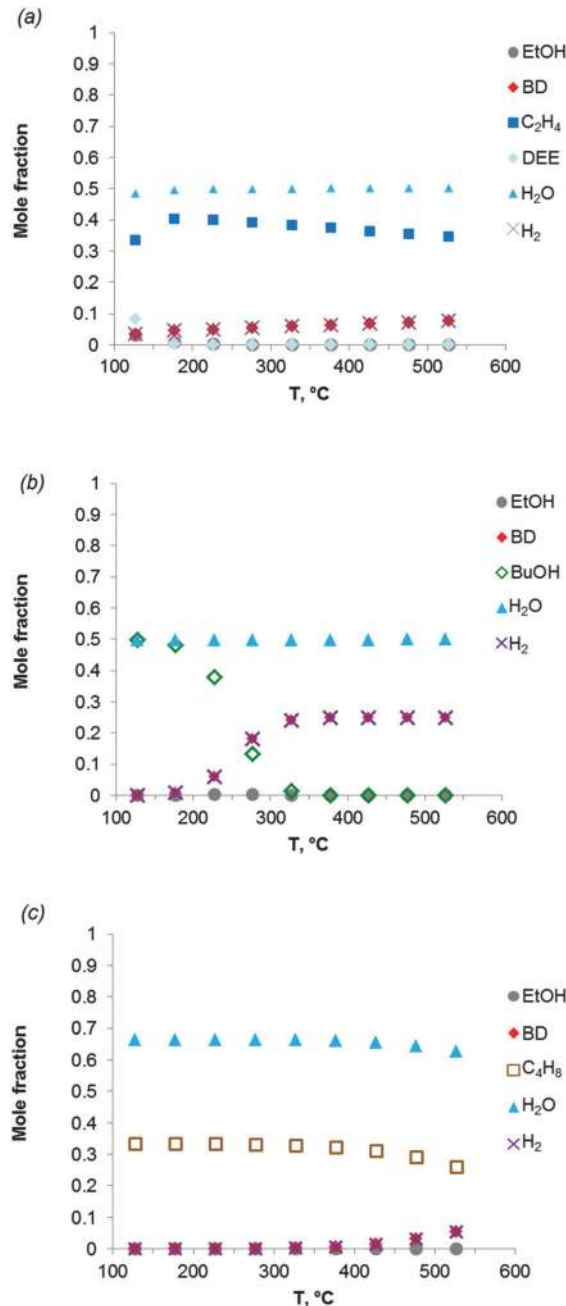
Fig. 3 Equilibrium composition calculated for the conversion of ethanol to BD in case following by-products are allowed: (a) diethyl ether and ethylene; (b) 1-butanol; (c) butenes (1-butene, *cis*-2-butene, *trans*-2-butene). The pressure in the system is 1 atmosphere. Simulation is performed using the Equilibrium based reactor (REquil) in Aspen Plus® software. (BuOH = 1-butanol; DEE = diethyl ether).

the choice of the appropriate catalyst plays a significant role in the BD selectivity of the overall ethanol-to-BD process.

For reaction temperatures ranging from 350 to 430 °C, co-production of 1-BuOH in the ethanol-to-BD reaction is of little importance, BD being formed preferentially according to the thermodynamics (Fig. 3b). Conversely, all isomers of butenes thermodynamically more favorable than BD (Fig. 3c) may be formed by acid catalysed dehydration of butanols.
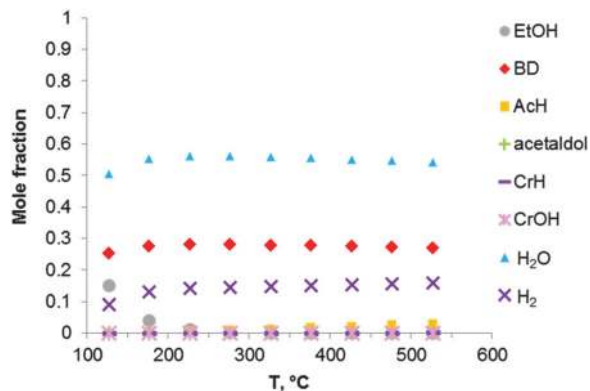
Fig. 4 Equilibrium compositions calculated for the synthesis of BD from an ethanol–acetaldehyde mixture with a molar ratio of EtOH to AcH of 3, via the reaction sequence (ii) to (vi) of Fig. 1 and Scheme 7. The pressure in the system is 1 atmosphere. The simulation is performed using the Equilibrium based reactor (REquil) in Aspen Plus® software.

Thus, optimization of catalyst properties is of key importance to obtain high BD yields.

Thermodynamic simulation was also carried out for the two-step Ostromyslensky process, co-feeding a mixture of ethanol and acetaldehyde to the catalyst (Fig. 4). Butadiene is the most favorable product in the reaction mixture. It seems that there is no thermodynamic advantage when performing ethanol-to-BD in two steps. The increase in BD yield and selectivity of the two-stage process can thus only be explained by kinetic factors, related to the properties of the catalyst.

Summarizing the thermodynamic aspects, reaction temperatures between 325 and 430 °C are preferred, since lower temperatures lead to restricted acetaldehyde formation, whereas higher temperatures disfavor the aldol condensation. In the preferred temperature range, BD yield and selectivity are kinetically determined, the choice of the active catalyst being of utmost importance.

2.4 Catalyst development and reaction conditions

The preceding analysis does not include the choice of the catalyst. The sequence of reactions (ii) to (vi) (Schemes 7 and 9) converting ethanol to BD is favoured at high temperature, most side-reactions (hydrogenation and dehydration) being more affected. Therefore the catalyst must be particularly active in reactions like dehydrogenation, aldol condensation and MPV, while avoiding side-reactions such as ethylene and butene formation.

The data in the literature on agents capable of activating the ethanol-to-BD conversion are abundant. They will be summarized for both the one-step and two-step processes in the next section. Further classification is based on the support type and the increasing number of modifiers in the catalyst composition. Where possible, focus will be on structure–activity/selectivity relationships.

2.4.1 Catalysts in the Lebedev one-step process. Lebedev
et al. were the first to comment on the compositional requirements of the catalyst. Based on inspection of the net reaction, it has been concluded that the catalyst should be able to remove water and hydrogen simultaneously. Therefore, dehydration and dehydrogenation were the prime targeted reactions for catalyst's components selection.[68]

In the first patents, Lebedev et al.[66,67] have been referring to a mixture of zinc oxide and alumina, yielding BD with a selectivity of 18 wt%. Other compositions containing uranium oxide[98] and mixtures of aluminium hydrosilicate[98,99] or floridin (Fuller's earth)[98,100] with zinc or manganese oxide were suggested as well. The dehydrogenation and dehydration components should be present in an optimal ratio, viz. 25% dehydration and 75% dehydrogenation component, in order to attain a high BD yield.[68] However, this optimal ratio strongly depending on the catalyst nature has been the subject of many discussions in the more recent literature. Unfortunately, the elemental composition of the preferred catalyst, showing up to 42 wt% BD selectivity (or close to 70% on carbon basis), remained undisclosed.[68,69] The composition of a Lebedev industrial catalyst became available in 1941 after occupation of a factory for synthetic rubber production in the Russian city of Yefremov by the German army.[43,74] Chemical analysis revealed the presence of 44.6 wt% of magnesia and 10 wt% of silica, next to a large number of small amounts of different elements.[43,74] XRD analysis has shown the presence of magnesium oxide, silica and kaolin. Later on, in the literature an abundant number of catalyst combinations has been described and tested. Note that the definition of a "Lebedev catalyst" is ambiguous as in the literature two compositions, viz. $ZnO-Al_2O_3$ and $MgO-SiO_2$, have often been used by different authors as a reference to Lebedev's catalyst. The present review categorises the catalysts into three groups, encompassing (i) doped alumina catalysts (Table 3 and Fig. 5), (ii) pure and promoted magnesia–silica containing catalysts (see Table 4 and 5; Fig. 6–11), and (iii) other catalysts (Table 6). Comparison between the catalysts is made based on BD selectivity and yield, total carbon conversion in the product stream (TC, %), activity (g_{BD} g_{cat}^{-1} h^{-1}) and volume productivity (g_{BD} l_{cat}^{-1} h^{-1}).

Doped alumina catalysts. Early publications by Lebedev have claimed a BD selectivity of 31% with a $ZnO-Al_2O_3$ catalyst (Table 3, entry 1).[67] Several authors failed to reproduce this BD selectivity. Natta and Rigamonti reported a BD yield of 5.6% with $40\%ZnO-60\%Al_2O_3$, although a high selectivity to ethylene was observed (Table 3, entry 2).[74] Reduction of the dehydration activity of the alumina by treatment with sodium carbonate increased the BD yield to 9%. Variations of Zn and Al ratios were investigated. The catalyst $25\%ZnO-75\%Al_2O_3$ showed a BD yield of 10% (Table 3, entry 3),[101] while with a $75\%ZnO-25\%Al_2O_3$ catalyst a BD yield of 15% with a selectivity of 20% has been reported (Table 3, entry 4).[102] Despite the improvements, the selectivity was lower than commercially acceptable levels. Many authors therefore considered the unpromoted $ZnO-Al_2O_3$ composition as "*not very promising*".

Natta and Rigamonti reported enhanced catalytic results with $MgO-Al_2O_3$ catalysts rich in magnesia, yielding 10% BD with a selectivity of 11% (Table 3, entry 5).[74] This result was explained by the higher condensation activity of magnesia, compared to zinc oxide. Corson et al.[101] have varied the

Table 3 Catalytic activity of doped alumina materials in the direct butadiene synthesis from ethanol

Entry	Catalyst	T/°C	WHSV/ h^{-1}	LHSV/ h^{-1}	TC^a/ %	Yields/ C%	Selectivity/ C%	Activity/ $g_{BD}\ g_{cat}^{-1}\ h^{-1}$	Volume productivity/ $g_{BD}\ l_{cat}^{-1}\ h^{-1}$	Ref.
1	$ZnO–Al_2O_3$	400	—	—	—	—	31	—	—	67
2	$40\%ZnO–60\%Al_2O_3$	360–380	—	0.3	—	5.6	—	—	8	74
3	$25\%ZnO–75\%Al_2O_3$	425	0.25	0.4	67	10	15	0.01	17	101
4	$75\%ZnO–25\%Al_2O_3$	445	—	0.3	75	15	20	—	23	102
5	$80\%MgO–20\%Al_2O_3$	430	—	0.3	95	10	11	—	12	74
6	$2\%PbO–98\%Al_2O_3$	425	0.6	0.6	—	18	—	0.06	46	101
7	$1\%TiO_2–9\%\ ZrO_2–90\%Al_2O_3$	425	0.5	0.6	—	17	—	0.05	43	101
8	$30\%Sb_2O_3–70\%Al_2O_3$	425	0.9	0.6	—	14	—	0.07	36	101
9	$10\%Cr_2O_3–90\%Al_2O_3$	425	0.5	0.6	—	8	—	0.02	20	101
10	$70\%\ MgO–30\%Al_2O_3$	450	2.0	—	86	18	21	0.20	—	59
11	$40\%ZnO–60\%Al_2O_3$	425	1.5	1.6	94	56	59	0.50	421	104
12	$20\%MgO–80\%Al_2O_3$	425	1.5	1.5	—	48	—	0.40	322	104
13	$40\%Cr_2O_3–60\%Al_2O_3$	450	1.5	1.6	—	47	—	0.40	365	104
14	$30\%ZnO–1\%K_2O–4\%SiO_2–4\%MgO–Al_2O_3$	420	—	2.5	43	34	80	—	395	105

^{a} TC = Total conversion of ethanol.
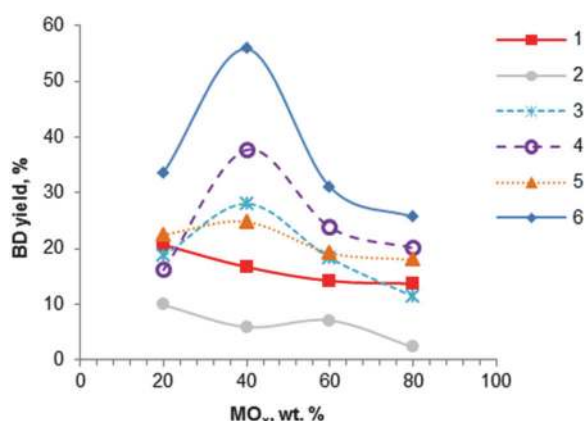
Fig. 5 Effect of $MO_x–Al_2O_3$ catalyst composition on butadiene yield: (1) $MgO–Al_2O_3$ (400 °C); (2) $SiO_2–Al_2O_3$ (425 °C); (3) $ZrO_2–Al_2O_3$ (425 °C); (4) $Fe_2O_3–Al_2O_3$ (425 °C); (5) $Cr_2O_3–Al_2O_3$ (425 °C); (6) $ZnO–Al_2O_3$ (425 °C), WHSV ~ 1.5 h^{-1}.[104]

$MgO:Al_2O_3$ ratios between 0.3 and 2.2 by co-precipitation of magnesium and aluminium salts. However, such mixed oxides showed poor activity, yielding less than 7% BD. Among other alumina containing catalysts, the following oxide systems were found to be more active producing BD in yields higher than 8%: $PbO–Al_2O_3$, $TiO_2–ZrO_2–Al_2O_3$, $Sb_2O_3–Al_2O_3$ and also $Cr_2O_3–Al_2O_3$ (Table 3, entries 6–9). Conversely, $SiO_2–Al_2O_3$, $ZrO_2–Al_2O_3$, $Fe_2O_3–Al_2O_3$ and $NiO–Al_2O_3$ yielded less than 7% BD. Thus, none of the alumina-based materials were considered as a promising catalyst.[101]

Hydrotalcite-derived mixed oxides are often used as basic catalysts, especially when a high dispersion of the elements in the composition is needed.[103] León et al.[59] using a MgAl hydrotalcite precursor with a Mg:Al atomic ratio of 3:1 obtained at 450 °C using a WHSV of 2 h^{-1} a moderately high BD selectivity of about 21% at an ethanol conversion of 86%. Tuning the acid–base properties of the catalyst by changing the synthesis procedure by precipitation of hydrotalcites under low or high supersaturation conditions or under sonication, over catalysts with low acidity and basicity an accumulation of acetaldehyde

was found, besides a low activity to ethylene and C_4 side-products. Conversely, catalysts with moderate basicity and high acidity showed next to superior BD yields also high amounts of other thermodynamically stable dehydration products like ethylene and butenes (Section 2.3). Substitution of Fe for Al in the hydrotalcite precursor, adjusting the acidity without affecting the MgO-related basicity, yielded less acidic catalysts showing at the same conversion high 1-butanol yields amounting to 3 and 11% with Mg–Fe and Mg–Al catalysts, respectively, as well as decreasing BD yield. Clearly, tuning of the acid–base properties of the catalysts both in strength and number seems to be the preferred way to attain high BD yields.

Extensive work on alumina-based catalysts containing mono-, binary and ternary oxides has been performed by Bhattacharyya et al.[75,104,106–108] None of the studied ternary oxide-based catalysts gave better results than the binary oxides. Among the binary oxides, mixtures of alumina with magnesia, zirconia, chromium oxide, calcium oxide, manganese oxide, silica, iron oxide, zinc oxide and nickel oxide were investigated (Fig. 5).[104] Most binary systems showed an optimum composition corresponding to a 40:60 weight ratio for $MO_x:Al_2O_3$: for $MgO–Al_2O_3$ and $SiO_2–Al_2O_3$ materials, catalysts containing 80% of alumina showed enhanced catalytic performance (Fig. 5 and Table 3, entries 11–13). The best catalytic results were found with ZnO-containing alumina, yielding at 425 °C and atmospheric pressure 56% BD with a selectivity of 59% to BD, corresponding to a volume productivity of 421 g_{BD} L h^{-1} (entry 11). The catalyst showed a very high activity of 500 g_{BD} kg_{cat} h^{-1}. Iron oxide on alumina was the second best catalyst (Fig. 5). In addition, the materials containing nickel oxide and manganese oxide (not shown) were found to be active only in the dehydrogenation of ethanol, irrespective of the catalyst preparation method and the composition.

Binary oxide systems prepared by co-precipitation of the corresponding salts with aqueous ammonia showed higher activity relative to mechanically blended samples and/or individual oxides, likely due to synergetic effects of the various active sites.[104] Unfortunately, no physicochemical information of the different catalytic systems was available proving this statement. Furthermore, metal nitrate precursors are preferred over chlorides

and sulphates, because the anion could be completely removed by washing and calcination. In addition, substitution of aqueous ammonia as a precipitating agent by sodium or potassium hydroxides resulted in adverse effects.[107] Optimal contact times attaining maximum BD yields were reported for the binary systems. A WHSV of 1.5 h^{-1} showed the highest BD yields for most catalysts, except for the SiO$_2$–Al$_2$O$_3$ catalyst which showed the highest BD yields at a WHSV of 1 h^{-1}. Note that many authors were using much higher contact times.[74,101,102] Bhattacharyya et al. have clearly demonstrated the remarkable importance of an optimal WHSV. In the case of ZnO–Al$_2$O$_3$, BD yield dropped from 56 to 34% with a WHSV decreasing from 1.5 to 1 h^{-1}, or to 12% with an increase of WHSV from 1.5 h^{-1} to 2 h^{-1}.[104] It is worth mentioning that high BD selectivity and yields at a high EtOH feed rate is beneficial because high space-time yields can be reached (Table 3, compare entries 11–13 with entries 2–9). With regard to the temperature, the highest BD yield was observed at 425 °C for most binary systems. Over the ZnO–Al$_2$O$_3$ catalyst a decrease of the temperature from 425 to 375 °C showed a BD yield decrease from 56 to 14%.[104] Furthermore, it has been shown that use of a fluidized bed reactor allowed us to significantly increase BD yield up to 73% compared to 56% obtained with a fixed bed reactor.[108]

Tret'yakov et al. reported a similar zinc–alumina catalyst promoted with a small percentage of potassium oxide, silica and magnesia, viz. 30%ZnO–1%K$_2$O–4%SiO$_2$–4%MgO–Al$_2$O$_3$.[105] They reported 34% BD yield with 80% selectivity at 420 °C and low contact time, e.g. LHSV of 2.5 h^{-1} (Table 3, entry 14). Catalysts were synthesised by mixing of zinc, aluminium and potassium oxides with suspension of magnesia and silica. The catalyst composition contained all the necessary active elements to catalyse the sequence of transformations such as dehydrogenation (reaction (ii), Scheme 7) with Zn, the base-catalysed condensation (iii and iv) with MgO, the MPV reaction (v) with Zn or MgO, and the dehydration (vi) with SiO$_2$. The dehydration of ethanol to ethylene is avoided possibly due to poisoning of

the most acidic sites by K$_2$O. Addition of hydrogen peroxide (0.8–1.5 wt%) in the feed significantly improved the catalytic results. A BD yield of 48% was found over the same catalyst under similar conditions showing 90% selectivity for BD, corresponding to a productivity of 550 g$_{BD}$ l$_{cat}$$^{-1}$ h^{-1}. The promoting effect of peroxide was explained, on one hand, by hydroxylation of the catalyst surface during the reaction with peroxide and, on the other hand, by cleaning of the surface from coke by radicals resulting from peroxide decomposition.

In conclusion, numerous catalysts of the Zn–alumina type were not retained because of low activity or selectivity. High activity was reached after modification with promoters, facilitating simultaneously the five elemental reactions for fast BD formation, avoiding formation of the thermodynamically more favourable side-products such as ethylene and butenes. High temperature and low contact times were beneficial for the BD yield. Synthesis procedures and choice of precursors were essential to reproduce the best performing catalysts.

Magnesia–silica catalysts. Magnesia on silica has long been studied for converting ethanol in BD. Many catalytic studies have been reported to reproduce the catalytic experiments and to better understand the active sites on the magnesia–silica catalyst type. Table 4 compares the most important catalytic data for un-promoted systems.

Szukiewicz[109–111] has reported between 350 and 450 °C the production of BD from ethanol over a MgO–SiO$_2$ catalyst with a BD selectivity of 30–40%, using a LHSV of 0.3 h^{-1} (Table 4, entry 1). Unfortunately, ethanol conversion data were absent. The catalyst had a MgO:SiO$_2$ weight ratio of 60:40 and was prepared by wet-kneading of a physical mixture of the dry oxide powders in water, the amount of water added only specified as 1.5–4 parts of water to one part of powder mixture by weight. The aging time (2 to 12 h) was not essential. At 410 °C and with a LHSV of 0.4 h^{-1}, Corson et al.,[101] with a similar MgO–SiO$_2$ catalyst, having a molar Mg/Si ratio of 2.2, were able to

Table 4 Catalytic activity of MgO–SiO$_2$ materials in the direct butadiene synthesis from ethanol

Entry	Mg/Si	Preparation	T/°C	WHSV/ h^{-1}	LHSV/ h^{-1}	TC^a/ %	Yields/ C%	Selectivity/ C%	Activity/ g$_{BD}$ g$_{cat}$$^{-1}$ h^{-1}	Volume productivity/ g$_{BD}$ l$_{cat}$$^{-1}$ h^{-1}	Ref.
1	2.2	Wet-kneading, MgO + SiO$_2$	350–400	—	0.3	—	—	30–40	—	—	109–111
2	2.3	Impregnation of SiO$_2$ hydrogel by Mg-salt	410	0.5	0.4	25	9	36	0.02	15	101
3	2.2	Wet-kneading, MgO + SiO$_2$	430	—	0.3	84	35	41	—	48	112
4	2.2	Wet-kneading, MgO + SiO$_2$ with NH$_4$OH	415	—	0.3	55	27	50	—	37	112
5	2.2	Wet-kneading, MgO + SiO$_2$ with H$_3$COOH	415	—	0.3	34	18	54	—	25	112
6	5	Mg(OH)$_2$ + SiO$_2$	400	—	0.3	52	28	54	—	33	113
7	5	Same as entry 6, after hydrothermal treatment	400	—	0.3	64	37	58	—	44	113
8	2	Commercial	440	0.30	0.2	70	37	48	0.06	31	114
9	3	Mg(OH)$_2$ + colloidal SiO$_2$	380	0.40	—	46	28	62	0.06	—	80
10	1	Wet-kneading, Mg(OH)$_2$ + SiO$_2$	350	0.15	—	50	42	84	0.04	—	115
11	0.83	Wet-kneading, Mg(OH)$_2$ + SiO$_2$	350	0.03	—	53	16	30	0.003	—	81
12	1	Wet-kneading, Mg(OH)$_2$ + SiO$_2$	350	0.20	—	76	15	20	0.02	—	116
13	6	Wet mixing MgO + SiO$_2$	400	—	—	66	32	48	—	—	117

^{a} TC = Total conversion of ethanol.

reproduce the data, *viz.* a BD yield of 9% and a BD selectivity of 36% (Table 4, entry 2).

A variety of procedures is known to synthesize magnesia–silica catalysts. A comprehensive study of the preparation of MgO–SiO$_2$ catalysts (with constant Mg to Si molar ratio of 2.2 according to the method proposed by Szukiewicz[109–111]) was carried out by Natta and Rigamonti.[112] It was postulated that the activity and selectivity of the magnesia–silica catalysts strongly should be dependent on the synthesis procedure, including the amount of water added, the time and temperature of aging, the drying and calcination procedure. XRD-analysis demonstrated the requirement of a high dispersion of magnesia on silica and the presence of a limited amount of amorphous magnesia hydrosilicate phase (less than 10 wt% based on Mg), resulting from the interaction of dissolved Mg^{2+} with the silanols of the silica surface. Wet kneading, followed by calcination at 450 °C, thus provided superior magnesia silica catalysts, at 430 °C showing an ethanol to BD yield of 35% and a selectivity of 41% or volume productivity of 48 g$_{BD}$ l^{-1} h^{-1} (Table 4, entry 3). Mechanical blending or mixing of the oxide powders in alcohol preventing silicate formation showed poor catalytic performance.

Stability is one of the key problems of magnesia–silica catalysts. The formation of crystalline silicate from the amorphous magnesium hydrosilicate during the catalytic process was found to be responsible for the decrease in BD yield after regeneration.[112] During catalyst synthesis, prevention of extensive formation of magnesium hydrosilicate is possible by reduction of the Mg^{2+} solubility when cold water is used or acetic acid or aqueous ammonia is added. Such catalysts showed a high stability upon regeneration. Though slightly less active, a high BD selectivity between 41 and 54% is reached (Table 4, entries 3–5).

Hydrothermal treatment between 100 and 200 °C significantly improved activity and selectivity of magnesia–silica catalysts.[113] Such treatment increased the specific surface area and pore volume of the catalyst. Hydrothermal treatment of a magnesia–silica catalyst, at 400 °C yielded 37% BD with a selectivity of 58% for a LHSV of 0.3 h^{-1} (Table 4, compare entries 6 and 7). This mild hydrothermal treatment was also proposed for regeneration of deactivated catalysts. The catalytic result is close to the commercial MgO–SiO$_2$ catalyst (with a molar ratio of Mg to Si of 3) (Table 4, entry 8). A 2 h pretreatment between 400 and 500 °C was defined as preferable. Higher temperatures resulted in a decreased BD yield.[114]

Niiyama *et al.*[80] studied the effect of the Mg/Si molar ratio in the catalyst. Catalysts were prepared by kneading magnesium hydroxide with colloidal silica, followed by drying and calcination at 600 °C for 3 h. Note that this pre-treatment temperature is higher than the previously recommended one.[112,114] At 380 °C a butadiene yield of 28% with a selectivity of 62% was reported over the catalyst with a Mg to Si molar ratio of 3 (Table 4, entry 9). The acid–base properties of the magnesia–silica catalysts in terms of the Mg to Si ratio have been investigated as well.[80] Whereas the formation rate of ethylene was too high for samples with MgO content below 75 mol% (67 wt%), pure MgO was inactive for both dehydration and BD formation, the latter requiring a balance between acidic and basic sites.
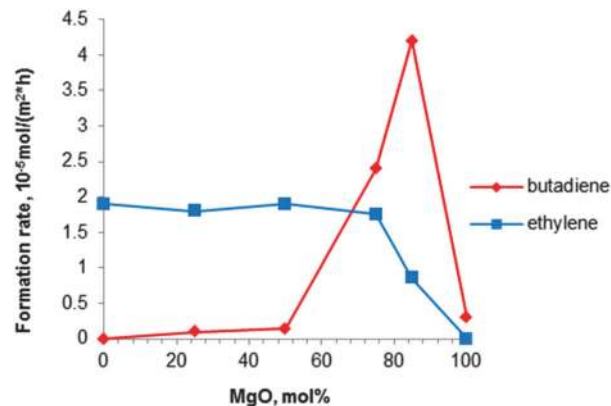

Fig. 6 Formation rates of BD and ethylene at 380 °C with a MgO content of MgO–SiO$_2$ catalysts (ethanol concentration of 10 vol%).[80]

The catalyst with 85 mol% (79 wt%) of MgO (Mg to Si molar ratio of 5.7) possessed an optimal acid–base balance reaching a high BD formation rate of 42 µmol$_{BD}$ m^{-2} h^{-1} (Fig. 6). Unfortunately, BD yield and selectivity were not reported.[80]

Ohnishi *et al.* probably reported the highest BD yields ever over magnesia–silica.[115] At 350 °C after 10 min-on-stream the butadiene yield and selectivity amounted to 42 and 84%, respectively (Table 4, entry 10). The catalysts were prepared by wet-kneading of precipitated magnesium hydroxide and silica gel derived from tetraethyl orthosilicate (TEOS). The nature of the reagents was shown to be important, as substitution of magnesium nitrate and nitric acid for magnesium chloride and hydrochloric acid, respectively, showed reduced BD formation. This was rationalised by incomplete removal of chloride ions during washing of the precipitates, in agreement with earlier results reported by Bhattacharyya *et al.*[107] for alumina catalysts. Maximum activity and BD selectivity were obtained for a Mg to Si molar ratio of 1.

Many authors attempted reproducing such excellent data. In the hands of Kvisle *et al.*[81] samples prepared according to the Ohnishi method failed to show excellent performance. The better results at 350 °C only amounted to a BD yield of 16% with a selectivity of 30% (Table 4, entry 11).

From time-on-stream studies only showing steady-state behaviour and acceptable carbon mass balance after 20 to 50 minutes on-stream, it was concluded that any catalytic result corresponding to shorter times-on-stream, *viz.* 10 min as used by Ohnishi *et al.*, should be interpreted with caution. Recently, with a similar unmodified magnesia–silica catalyst, we only could reach at 350 °C and a WHSV of 0.2 h^{-1} a BD yield of 15% with a BD selectivity of 20% (Table 4, entry 12).[116] This catalyst performance is similar to that reported by Kvisle *et al.*[81] Analysis with UV-vis and XRD showed that wet-kneading of the sample induces structural perturbations in the highly dispersed MgO, forming Mg–O–Si interactions like in amorphous magnesia hydrosilicate.[81] Both criteria were already proposed by Natta[112] and Kovařík[113] as a fingerprint of active and selective catalysts.

Recently, Tong *et al.* reported the formation of BD from ethanol with 48% selectivity over magnesia–silica catalysts obtained by

wet-mixing (Table 4, entry 13).[117] An optimal calcination temperature of 500 °C was suggested, which is in good agreement with data reported earlier. The best performance was obtained with a MgO content of 80 wt% (or a molar Mg to Si ratio of 6).

In addition to the catalyst composition and synthesis procedure, reaction conditions also affect catalytic activity and BD selectivity. With the commercial catalyst (Table 4, entry 8) increasing BD yields are obtained at reaction temperatures up to 460 °C in agreement with thermodynamics, while the BD selectivity reaches a maximum of 48% at 430–440 °C and then decreases.[114]

Kvisle et al. have investigated the effect of the ethanol concentration on its conversion to BD at 350 °C with their magnesia–silica catalyst (entry 11) at a constant carrier gas flow rate of 18 ml min^{-1}. The authors observed higher BD yields at lower ethanol partial pressures (3000 ppm), in agreement with the increase in the number of product molecules in the chemical reaction of ethanol to BD (eqn (1)).[81] Lowering the partial pressure obviously leads to lower volume productivity, while an increase of the carrier gas flow rate (or decrease of the contact time) at constant ethanol concentration in the feed leads to a lower butadiene yield.[80]

Summarizing the results mentioned, it follows that high BD yields (up to 30–40%) and selectivity (40 to 60%) are possible over the un-promoted binary magnesia–silica materials of Table 4 at temperatures ranging from 350 to 400 °C, using space velocities from 0.3 to 0.5 h^{-1}. For low partial pressures of ethanol, a value of 10 vol% is a compromise between BD yield (selectivity) and volume productivity. Higher partial pressures require higher reaction temperatures resulting in the formation of more side-products. Although contradictory data are reported on the optimal Mg to Si molar ratio and the preferred synthesis recipe, it appears that the catalytic performance of the MgO–SiO$_2$ catalysts is very sensitive to the acid–base properties of the synthesized material. There is agreement that the synthesis procedure should promote formation of Mg–O–Si species, at the same time keeping the remaining MgO highly dispersed. However, for the design of improved catalysts, more systematic characterization of the surface properties of the active catalysts is a prerequisite.

Magnesia–silica materials doped with a dehydrogenation promoter. The commercial magnesia–silica catalysts industrially used in USSR contained various dopants affording high and stable BD yields. These dopants were initially thought to improve the dehydrogenation capacity of the commercial catalyst, resulting in faster conversion of ethanol to acetaldehyde. According to the patents of Szukiewicz,[109–111] modification with chromium oxide up to 10 wt% led to a significant increase in BD selectivity of about 5%. The Cr modification reduced the formation of some by-products like ethylene, while others, like butenes, were increasing. The effect of different dopants on the catalytic performance has been studied in detail.

Natta and Rigamonti[74,112] have employed the addition of chromic acid as a promoter of a MgO–SiO$_2$ catalyst with an atomic Mg : Si ratio of 2.2. At 415 °C and with a LHSV of 0.2 h^{-1} (entry 1, Table 5) ethanol was converted to a high yield and selectivity of BD of 43 and 52%, respectively. With the Cr-free catalyst only the respective values of 35 and 41% were obtained. The positive effect of the Cr-promotion was connected to the formation of magnesium chromate preventing excessive formation of magnesium silicate. It appears that modification with chromium oxide has an effect similar to that of ammonia or acetic acid (see before).

Corson et al.[101] showed that among the more than 500 tested materials, the 2%Cr$_2$O$_3$–59%MgO–39%SiO$_2$ catalyst was superior. In a fixed-bed reactor at 400 °C with a WHSV of 0.4 h^{-1}, it exhibited a BD yield of 38% with 56% selectivity (Table 5, entry 2), corresponding to a volume productivity of 65 g$_{BD}$ l$_{cat}$$^{-1}$ h^{-1}.

Fig. 7 shows an overview of the promotion with 2 wt% Cr of MgO–SiO$_2$ catalysts with varying atomic ratios of Mg : Si, as prepared and tested by different authors.[101,102,112,116,118]

Table 5 Catalytic activity of modified MgO–SiO$_2$ materials and related clay minerals in the direct butadiene synthesis from ethanol

Entry	Catalyst composition	T/°C	WHSV/ h^{-1}	LHSV/ h^{-1}	TC^a/ %	Yield/ C%	Selectivity/ C%	Activity/ g g$_{cat}$$^{-1}$ h^{-1}	Volume productivity/ g l$_{cat}$$^{-1}$ h^{-1}	Ref.
1	2%Cr$_2$O$_3$–59%MgO–39%SiO$_2$	415	—	0.2	82	43	52	—	42	112
2	2%Cr$_2$O$_3$–59%MgO–39%SiO$_2$	400	0.4	0.4	68	38	56	0.08	65	101
3	2%Cr$_2$O$_3$–79%MgO–19%SiO$_2$	435	—	0.3	75	40	52	—	58	102
4	2%Cr$_2$O$_3$–79%MgO–19%SiO$_2$	400	—	0.3	60	37	62	—	44	118
5	3%Cr$_2$O$_3$–54%MgO–43%SiO$_2$	350	0.2	—	65	34	53	0.04	23	116
6	2%Cr$_2$O$_3$–76%MgO–11%SiO$_2$–11% kaolin	435	—	0.3	76	48	63	—	82	102
7	2%Cr$_2$O$_3$–76%MgO–11%SiO$_2$–11% kaolin	400	—	0.3	75	47	63	—	56	118
8	30%ZnO–30%MgO–40%SiO$_2$	365	—	0.2	95	26	27	—	25	74
9	ZnO–MgO–SiO$_2$–kaolin	<410	—	0.3	67	46	69	—	64	121
10	3%ZnO–56%MgO–42%SiO$_2$	400	0.7	—	98	45	46	0.19	117	116
11	2%Ta$_2$O$_5$–60%MgO–38%SiO$_2$	420	0.4	0.4	68	34	50	0.08	58	101
12	10%NiO–28%MgO–62%SiO$_2$	280	—	—	59	53	90	—	—	122
13	3%CuO–56%MgO–42%SiO$_2$	400	0.7	—	86	44	53	0.20	123	116
14	4%Ag–55%MgO–41%SiO$_2$	400	0.7	—	92	49	54	0.22	130	116
15	MgO/bentonite	440	—	0.4	—	—	31	—	—	123
16	Li$^+$-containing fluorohectorite	375	0.3	—	32	16	48	0.03	—	124
17	6%Ag/Al–sepiolite	280	0.8	—	63	5.5	9	0.03	—	83

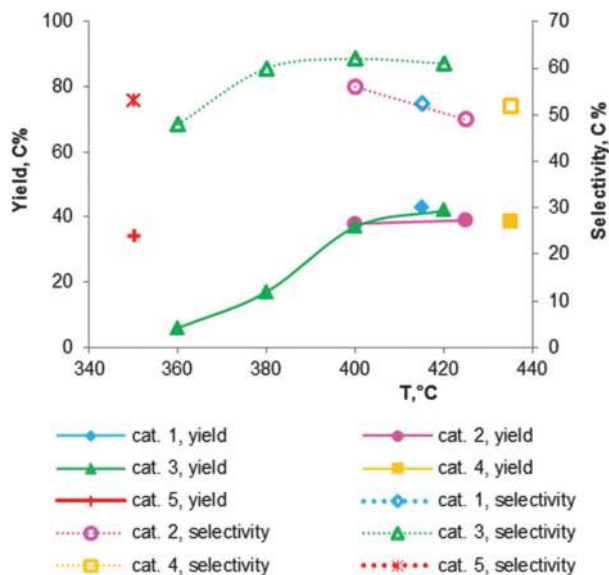^{a} TC = Total conversion of ethanol.

Fig. 7 Catalytic performance of chromium oxide doped MgO–SiO$_2$ materials, containing 2 wt% of Cr$_2$O$_3$: cat. 1 – Mg : Si = 2.2;[112] cat. 2 – Mg : Si = 2.3;[101] cat. 3 – Mg : Si = 6;[118] cat. 4 – Mg : Si = 6;[102] cat. 5 – Mg : Si = 2[116] (see Table 5 for the reaction conditions).

Modification of magnesia–silica materials with a small amount of chromium oxide clearly results in higher BD yield and selectivity in comparison with the unmodified MgO–SiO$_2$ samples (compare Table 5, entries 1–5 and the corresponding data in Table 4). Some authors reported a decrease in selectivity at temperatures higher than 400 °C, despite the higher BD yield.[101,118] Comparison of the catalysts is difficult due to the different reaction conditions.

László and co-workers[102] have studied the Mg content for 2 wt% Cr$_2$O$_3$ doped MgO–SiO$_2$ materials at 435 °C with a LHSV of 0.3 h^{-1}. The catalytic data are summarized in Fig. 8. They observed that a lower silica content leads to a higher BD yield and selectivity, while ethylene formation decreased. The observation again proofs the requirement of an optimal balance of the surface acid–base properties. They obtained the highest BD
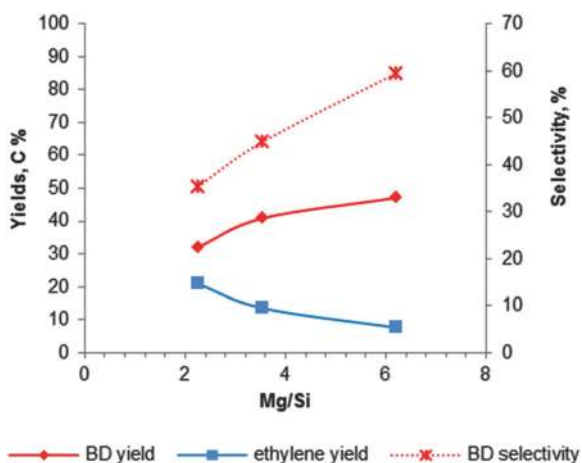

Fig. 8 Influence of the magnesium content on the activity and BD selectivity of 2%Cr$_2$O$_3$–MgO–SiO$_2$ at 435 °C and a WHSV of 0.3 h^{-1}.[102]
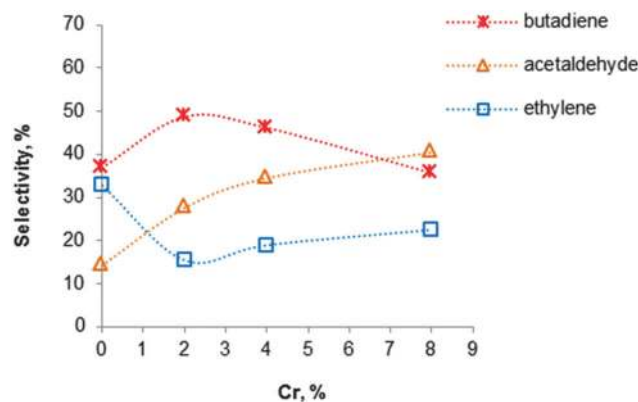

Fig. 9 Influence of the chromium loading on the BD selectivity for Cr$_2$O$_3$–MgO–SiO$_2$ materials with an atomic Mg : Si ratio of 3, carried out at 400 °C.[119]

yield of 40% with a selectivity of 52% over the magnesia–silica catalyst with an atomic Mg : Si of 6 (Fig. 8; Table 5, entry 3).

An increase of the chromium content of these catalysts resulted in an increase of the BD yield.[102] Silva et al.[119] have been studying the influence of the chromium loading on the catalytic performance of MgO–SiO$_2$ materials in the conversion of ethanol to BD at 400 °C. The Cr$_2$O$_3$–MgO–SiO$_2$ materials were prepared by conventional impregnation on magnesia–silica catalysts. A steadily increasing activity was observed with increasing Cr content, the effect on the BD selectivity being displayed in Fig. 9. Clearly, an increase of Cr enhances acetaldehyde selectivity. Whereas BD selectivity first increases until 50% upon addition of Cr up to 2 wt%, it drops with further enhanced Cr content.

The opposite effect is seen for the ethylene selectivity. Cr was noted to promote ethanol dehydrogenation and to adjust the acid–base properties of the magnesia–silica material, by eliminating strong acid sites with $H_0 \leq 3.3$, thus avoiding the formation of thermodynamically more favourable ethylene. Too high Cr contents should be avoided as well, since they introduce new acid sites related to the presence of Cr(III) species with distorted octahedral symmetry or to Cr(VI) species, as evidenced by UV-reflectance bands at 27 000 and 37 000 cm^{-1}, respectively.[119]

Zinc oxide has also been used as a promoter for Lebedev's industrial magnesia–silica catalyst.[120] Natta et al.,[74] partially substituting zinc oxide for magnesium oxide, reported lower BD yield and selectivity in comparison to unmodified MgO–SiO$_2$. At 365 °C and a LHSV of 0.2 h^{-1}, with a 30%ZnO–30%MgO–40%SiO$_2$ catalyst, a BD yield of about 26% at almost complete ethanol conversion was obtained (compare entry 3 of Table 4 with entry 8 in Table 5). The ZnO modified materials were prepared either by co-precipitation of the carbonates of magnesium and zinc or by mechanical mixing of the oxides, followed by wet-kneading with silica. The lower BD yield and selectivity were due to a reduced dehydrogenation and condensation capacity as a result of the formation of a solid solution between MgO and ZnO.

Berak et al., studying the influence of the zinc oxide promoter loading on the performance of the magnesia–silica catalysts,[121] reported an increase of the activity with increasing Zn content. The reaction temperature to reach 66% ethanol conversion decreased with an increase of the zinc oxide content.
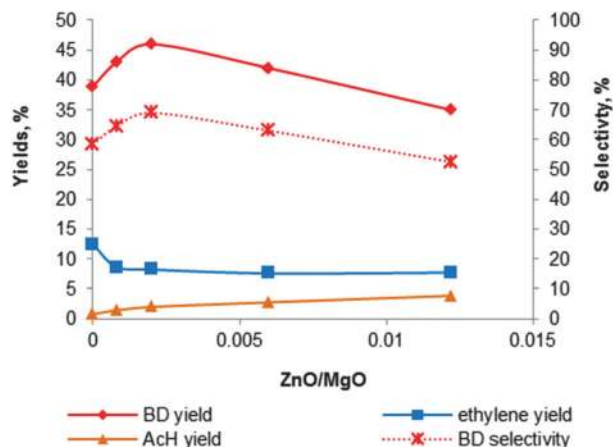
Fig. 10 Effect of the content of zinc promoter on the activity and selectivity of the MgO–SiO$_2$ catalyst at a total ethanol conversion of 67% with a WHSV of 0.3 h^{-1}.[121]

Fig. 10 shows the effect of the Zn promoter loading on the BD yield and product selectivity. With increasing Zn content, the BD yield first increased to 46% with a selectivity of 69% at a molar ZnO : MgO ratio of 0.002 (entry 9, Table 5). Further increase of the Zn loading resulted in a decreased BD yield at the expense of acetaldehyde, ethylene and other by-products formation.

Makshina et al.[116] recently confirmed that the modification of silica by co-impregnation with both zinc and magnesium salts results in a poor activity, yielding 17% of BD with a selectivity of 31%, in comparison to similar materials obtained by consecutive modification of silica with MgO and ZnO.[116] At 400 °C and with a WHSV of 0.7 h^{-1}, the latter catalyst showed a BD yield of 52% at almost full ethanol conversion, corresponding to a record volume productivity of more than 100 g$_{BD}$ l$_{cat}^{-1}$ h^{-1} (entry 10, Table 5). Inspection of the side products pointed to high levels of unconverted acetaldehyde with the co-impregnated catalyst, indicating that impregnation leads to an un-balance between the dehydrogenation and aldol condensation capacity. Possibly, the formation of new phases in the co-impregnated sample blocks or prevents the creation of the active basic sites. XRD analysis showed the presence of mixed Zn–Mg silicates in the co-impregnated sample. Further spectroscopic work is needed to confirm the rationalisation.

Furthermore, Ta, Ag, Ni, Mn, Cu, Mo, Fe, Co, and Zr oxides were also used as promoters for MgO–SiO$_2$ catalysts in the ethanol to BD reaction.[101,113,116,122,125–128]

Among these redox dopants, tantalum oxide was found to be an efficient promoter for magnesia–silica catalysts.[101] These catalysts showed a butadiene yield of 34% with a selectivity of 50% at 420 °C with a WHSV of 0.4 h^{-1} (Table 5, entry 11), corresponding to a volume productivity of 58 g$_{BD}$ L^{-1} h^{-1}. Similar to chromium oxide, an amount as low as 2 wt% of tantalum oxide was sufficient to boost the butadiene yield to higher values relative to the unmodified catalyst. Variation of the magnesium content was also studied for the Ta promoted samples. By changing the atomic Mg : Si ratio from 0.6 to 2, an increase of the BD yield from 7 to 34% has been reported.

Kitayama et al.[122] have shown that NiO promoted MgO–SiO$_2$ is highly selective to BD. At 280 °C about 90% BD selectivity at 59% ethanol conversion (entry 12, Table 5) was found with a 10 wt% NiO supported on MgO–SiO$_2$ with an atomic Mg : Si ratio of 0.7. Catalysts were synthesized via impregnation of Mg(OH)$_2$–aerosil mixtures with nickel nitrate followed by calcination at 400 °C for 2 h. They were shown to possess optimal acid–base properties, although X-ray analysis still revealed the presence of magnesium silicate. Whereas higher levels of Mg resulted in the appearance of pure MgO phases, a decreased surface area was found, leading to lower activity. It was claimed that substituted Ni is present as Ni^{2+} cations, dispersed into the silicate and MgO lattice. However, no characterisation of acid–base properties has been provided.

Makshina et al.[116] have performed a comparative study of magnesia–silica materials modified with various transition metal oxides and metallic silver. Among the oxides, Ni, Cu and Zn were promising with regard to the BD yield and selectivity, while Fe and Mn showed insufficient performance. At 400 °C and a WHSV of 0.7 h^{-1}, Cu-loaded magnesia silica with an atomic Mg : Si ratio of 2 showed a BD yield of 47% at almost complete ethanol conversion, corresponding to a remarkable volume productivity of 123 g$_{BD}$ l$_{cat}^{-1}$ h^{-1} (entry 13, Table 5). Sequential impregnation is essential for keeping the specific activity of the individual elements as high as possible. The atomic Mg : Si ratio influenced selectivity and activity, a value of 2 being optimal. The presence of metallic Ag had a similar beneficial effect on the catalytic performance. under similar experimental conditions, the Ag promoted catalyst exhibited a high selectivity of 54% for BD at full conversion, corresponding to a formation rate of 220 g BD per kilogram catalyst per hour (entry 14, Table 5).

Recently it has been reported that modification of the magnesia–silica catalyst with Zr and Zn oxides (1.5 and 0.5 wt% respectively) leads to a significant increase in selectivity, e.g. at 325 °C and WHSV = 0.3 h^{-1} doped catalyst with a Mg : Si ratio of 85 : 15 showed 63 mol% selectivity towards BD at 40% of ethanol conversion while unpromoted material yielded butadiene with only 26 mol% selectivity at the same level of conversion.[128]

Concluding this part, promotion of the magnesia silica catalyst with elements showing dehydrogenation activity, generally improves both the catalyst activity and selectivity to BD. The higher activity may be rationalised by faster acetaldehyde formation. However, the promoter loading is crucial since a balance with the basic sites, related to the highly dispersed MgO, is important as unconverted acetaldehyde otherwise causes a decrease in BD yield. Some of the dopants may introduce strong acidity or may block the mild acidity of the silica, e.g., by silicate formation. These effects need to be avoided to prevent diethyl ether but mainly ethylene formation from ethanol or to facilitate the dehydration of the aldol and crotyl alcohol to BD. Once used in the optimal content, the nature of the element seems somewhat less crucial, since Cr, Zn, Ta, Cu, Ni, Zr oxides and Ag show beneficial effects. However, a sequential loading of the silica with the base, and the dopant using intermediate calcination or not, is crucial to attain high yield of and

selectivity to BD. Co-impregnation often forms additional silicate phases or causes blockage or creation of acid sites. There is no consensus on the optimal atomic ratio of Mg : Si in the doped catalysts, probably resulting from differences in the preparation methods and in the nature of the dopant. It is therefore recommended to compare the different catalysts based on their surface properties like acid–base relationship (in terms of amounts, strength and location) rather than on the basis of the elemental composition only. Today, systematic studies with advanced surface characterization tools in combination with catalytic measurements are missing for the ethanol-to-BD reaction.

Magnesia–silica catalysts promoted by alkaline metal cations and clay minerals. As ethylene is thermodynamically favoured in the reaction of ethanol to BD, promotion of magnesia-silica with alkaline metal oxides has been studied. Accordingly, Butterbaugh and Spence[125,126] have reported active MgO–SiO_2 catalysts, yielding BD from ethanol with a selectivity up to 48% at 435 °C, by contacting the precursor mixture of magnesium hydroxide and silica with an alkaline solution at 90–100 °C for 1–2 h. The alkaline treatment improved the BD selectivity at the expense of the ethylene selectivity. The most promising results were obtained with alkali-digested MgO–SiO_2 materials containing 20 to 50 wt% magnesia, corresponding to an atomic Mg : Si ratio of 0.4 to 1.5.

Later, Ohnishi *et al.* used post-impregnation with sodium or potassium hydroxide followed by calcination at 500 °C, resulting in the formation of highly active MgO–SiO_2 catalysts. At 350 °C and with a WHSV of 0.2 h^{-1}, Na_2O/MgO–SiO_2 and K_2O/MgO–SiO_2 yielded 87 and 70% BD, respectively.[115] Though the post-synthetic selective poisoning of acid sites by addition of alkali is similar to that proposed by Butterbaugh and Spence,[125,126] the catalytic performance reported by Ohnishi *et al.* was almost twice as high. The different time-on-stream behaviour of the catalyst possibly is at the origin of the different catalytic data. In our experience, early sampling under non-steady state conditions often leads to higher conversions. Within one to two hours BD yield and selectivity converge to lower steady state values, followed by slow deactivation at longer time-on-stream.

László *et al.*[102] have studied ethanol to BD conversion with magnesia–silica catalysts mixed with clays or clay-related minerals. Replacement in a 2 wt% chromium oxide promoted catalyst of half of the silica by kaolin, at 435 °C and with a LHSV of 0.3 h^{-1} showed a BD yield and selectivity increase from 40 to 48% and from 54 to 63%, respectively, while the ethylene selectivity decreased (compare entries 3 and 6, Table 5). Kovařík *et al.*[118] using a similar catalyst reported a similar increase of the BD yield with partial substitution of silica for kaolin. At 400 °C and with a LHSV of 0.3 h^{-1}, 37 and 47% BD yields were obtained with $2\%Cr_2O_3$–MgO–SiO_2 and $2\%Cr_2O_3$–MgO–SiO_2–kaolin, respectively (compare entries 4 and 8, Table 5). A complete substitution of silica for kaolin resulted in a reduced BD yield and enhanced ethylene yield. Under the same conditions, a MgO–kaolin catalyst yielded 22.5% BD, while the MgO–SiO_2 catalyst produced 35% BD yield.[74] Complete substitution of

silica by other layered silicates such as talc and kaolinite showed similarly reduced BD yields.[129] Generally, both MgO and SiO_2 components being essential in the catalyst composition should not be replaced for more than 20 wt% by the layered silica to attain BD yields of 35 to 40%.[129]

The situation is somewhat different when $MgO\cdot3SiO_2\cdot3H_2O$, an amorphous magnesium hydrosilicate, is used as a catalyst precursor.[129] At 400 °C and with a LHSV of 0.3 h^{-1} it gives up to 80% yield of ethylene from ethanol. After precipitation of magnesium hydroxide with aqueous ammonia or sodium hydroxide (MgO > 60 wt%) and subsequent calcination at 550 °C, BD yields of over 50% were noticed. Based on X-ray diffraction, a partially crystalline phase, *viz.* composition, $3MgO\cdot4SiO_2\cdot2H_2O$, could be identified next to MgO. Whereas the presence of free MgO has been suggested to be essential to ensure fast dehydrogenation of ethanol to acetaldehyde, the precise catalytic role of the Mg silicate phase has not been clarified.

Aleixandre *et al.*[123] have reported the effect of clay-modified MgO on the BD selectivity. At 440 °C and using a LHSV of 0.4 h^{-1}, four different clay minerals, *viz.* bentonite A and B, halloysite, and kaolin, were physically mixed with a variable amount of MgO (Fig. 11). Bentonite B was obtained from bentonite A by extracting free silica. The MgO–clay catalyst containing 57 wt% of bentonite A exhibited the highest BD selectivity (31%). Unfortunately, no ethanol conversions were reported (entry 15, Table 5). Catalytic differences were rationalised by taking into account the number of accessible active acid–base sites on the clay mineral. Compared to halloysite and kaolin, montmorillonite – the main component of bentonites – is known for its large interlamellar voids and high cation-exchange capacity. However, the presence of different impurities in bentonites like iron oxides which likely could promote ethanol dehydrogenation was not taken into consideration.

In conclusion, the catalytic performance of magnesia–silica catalysts can be promoted with alkaline metal cations, by suppressing (too) high acidity, thus reducing/blocking the ethanol to ethylene dehydration. Whereas modification of the magnesia–silica catalyst with layered silicates or clay minerals also results in an increase of BD selectivity, the catalytic role of
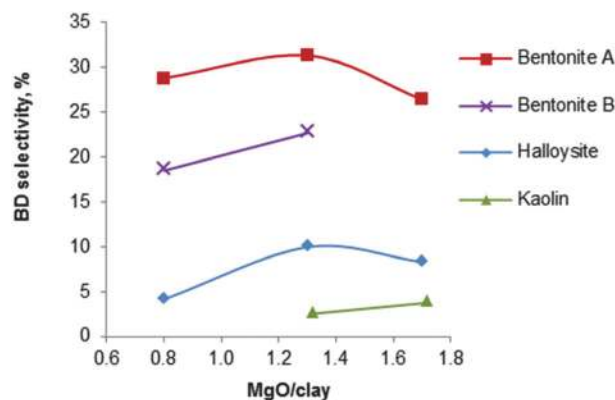

Fig. 11 Influence of the nature of various clay minerals on the selectivity of the MgO/silicate catalysts (T = 440 °C, LHSV = 0.4 h^{-1}).[123]

the silicates is less clearly defined. Despite these improvements, addition of dehydrogenation modifiers is more effective to reach high BD yields.

Magnesium silicate clay minerals. A series of unmodified Mg and Si containing clay minerals have also been used in the ethanol to BD reaction. Dandy *et al.* demonstrated BD formation over sepiolite for temperatures ranging from 200 to 300 °C.[130]

Higher BD yields were generally obtained after modification of the clay with dopants, affecting the acid–base and dehydrogenation properties of the catalyst. Suzuki *et al.*[124] have employed synthetic Li modified fluorohectorite as a catalyst in the ethanol to BD reaction at 375 °C using a LHSV of 0.3 h^{-1}. The catalyst exhibited an excellent BD selectivity of 48% at 33% ethanol conversion (Table 5, entry 16). An IR study with adsorbed pyridine and CO_2 showed that the presence of Li^+ and F^- in the catalyst modified the Lewis and Brønsted acid sites, thus optimising the dehydration properties of the catalyst. Oxygen atoms bound to Mg^{2+} at the edge of the layers were responsible for the dehydrogenation activity.

To further improve the dehydrogenation ability of the clay catalysts, various metal oxide dopants have been explored. Cd, Zn and Cu oxide promoters have been tested to improve the BD yields with smectite and bentonite clays.[131] Smectite clay modified with Cd showed better results than other catalysts yielding BD with 17% selectivity. Kitayama *et al.*[132–137] used sepiolites modified by impregnation with various transition metal oxides as ethanol conversion catalysts in a recirculation reactor at 320 °C. For the unmodified sepiolite ethylene selectivity was very high, while after doping BD was one of the major products, the nature and amount of the precursor salt of the promoter determining the BD yield. With manganese content increasing from 39 to 79 mol% in the MnO_2–sepiolite, the BD yield increased spectacularly from 8.4 to 33.4%. The catalyst prepared from manganese acetate showed better activity than that from manganese chloride.[135] Superior results were obtained with ZnO modified sepiolite containing 4.4 wt% Zn, yielding 63.5% of BD at full conversion after 2 h of reaction at 260 °C.[133] High BD yields ranging from 33 to 58% were obtained over sepiolites modified with copper, nickel, cobalt and vanadium

oxides[132,134,136] or with mixtures of vanadium oxide with tungsten or molybdenum oxides.[137]

Gruver *et al.*[83] have reported that a 6 wt% Ag promoted sepiolite is able to produce BD from ethanol. At 280 °C and a WHSV of 0.8 h^{-1}, they obtained about 9% BD yield at 63% ethanol conversion. As the major product was acetaldehyde, obtained at about 20% yield, the catalyst probably lacks appropriate basicity needed to compensate for the fast dehydrogenation caused by the presence of metallic silver (entry 17, Table 5).

In summary, clay minerals like magnesia–silica catalysts require careful promotion of the dehydrogenation activity and fine-tuning of the acid–base properties in order to achieve high BD yields from ethanol. While the aforementioned modified magnesia–silica catalysts generally show better BD yields and selectivity than the promoted clays, individuals like ZnO promoted sepiolite also exhibited promising catalytic properties.

Other catalysts. Catalysts free of Mg^{2+} and Al^{3+} have been reported as well. Spence and Butterbaugh[138] have reported the use of 20 wt% zinc oxide supported on silica (like diatomaceous earth) for butadiene formation from ethanol, showing a selectivity of 58% and a yield of 29% at 450 °C using a LHSV of 1 h^{-1} (Table 6, entry 1). The reaction temperature for BD formation was lowered by modifying the Zn catalyst with phosphate or tungstate. ZnO on silica and ZnO/Zn(II)phosphate on silica showed BD yields of 29 and 22% and a BD selectivity of 58 and 63%, at 450 and 415 °C, respectively. Corson *et al.*[101] have found a BD yield of 20% at 425 °C using 0.6 h^{-1} LHSV with a 10 wt% ZnO on a silica catalyst (Table 6, entry 3).

Thorium and zirconium oxides on silica exhibit catalytic activity for BD formation from ethanol as well, at 445 °C amounting to BD selectivities of 35 and 44%, respectively (Table 6, entries 4 and 5). Unfortunately, no details about ethanol conversion were reported.[127,139] Corson *et al.* reported 23% of BD yield using a ZrO_2–SiO_2 catalyst (Table 6, entry 6).[101]

Spence *et al.*[127,139] have claimed copper and molybdenum oxides as potential dopants for the ZrO_2–SiO_2 catalyst. Unfortunately, most of the catalytic data refer to catalytic compositions for which detailed information on the synthesis procedure and the physicochemical properties of the catalyst surface is missing.

Table 6 Catalytic activity of various catalysts

Entry	Catalyst composition	T/°C	WHSV/ h^{-1}	LHSV/ h^{-1}	TC^a/ %	Yield/ C%	Selectivity/ C%	Activity/ g g$_{cat}^{-1}$ h^{-1}	Volume productivity/ g l$_{cat}^{-1}$ h^{-1}	Ref.
1	20%ZnO/diatomaseous earth	450	—	1	50	29	58	—	127	138
2	ZnO + Zn–phosphate/diatomaceous earth	415	—	1.3	35	22	63	—	123	138
3	10%ZnO–90%SiO$_2$	425	—	0.6	—	20	—	0.13	51	101
4	21% ZrO$_2$/diatomaceous earth	445	—	—	—	—	44	—	—	127,139
5	21% ThO$_2$/diatomaceous earth	445	—	—	—	—	38	—	—	127,139
6	9,5%ZrO$_2$–90,5%SiO$_2$	425	1.0	0.6	—	23	—	0.13	59	101
7	ZrO$_2$/ZnO/SiO$_2$–60Å	375	—	1.5	46	18^b	39^b	—	—	140
8	ZrO$_2$/ZnO/SiO$_2$–150Å	375	—	1.5	48	23^b	48^b	—	—	140
9	CuO/ZrO$_2$/ZnO/SiO$_2$–60Å	375	—	1.5	39	19	50^b	—	—	140
10	Ag/ZrO$_2$/SiO$_2$	325	0.3	—	34	24	72	0.04	—	141
11	2%Ta$_2$O$_5$–98%SiO$_2$	425	—	0.6	—	16	—	—	41	101
12	1.1% CuO on 2%Ta$_2$O$_5$–98%SiO$_2$	425	0.5	0.4	83	25	30	0.06	43	101
13	ZrO$_2$–Fe$_2$O$_3$ (40:60)	425	1.5	—	—	40	—	0.34	—	104

^{a} TC = Total conversion of ethanol. ^{b} Yield and selectivity are calculated in mol%.

Conversion of ethanol to BD has recently been reported by Jones et al.[140] over silica doubly promoted with metal oxides of zinc, zirconium, copper, cobalt, manganese, cerium and hafnium. Emphasis was on the effect of the nature of the promoters and the texture of the silica on the catalytic activity and BD selectivity. The best results were obtained over a $ZnO–ZrO_2/SiO_2$ catalyst containing 1.5 and 0.5 wt% ZrO_2 and ZnO, respectively. Higher ethylene selectivity occurred in parallel with higher promoter contents. At 375 °C and a space velocity of 1.5 h^{-1}, the catalyst showed 18 mol% BD yield with a BD selectivity of 39 mol%, corresponding to a high volume productivity of 124 g_{BD} l_{cat}^{-1} h^{-1} (entry 7, Table 6). Using this catalyst as reference, it could be shown that impregnation of the promoters rather than sol–gel synthesis is the preferred synthesis method to achieve high BD yields. High ethylene yields were observed as well.

Selective poisoning of acid sites with alkali metal cations, as proposed by Ohnishi[115] for the $MgO–SiO_2$ system, was not very successful for the Zn/Zr oxide silica system. In contrast, adding a third element like Cu oxide to the Zn–Zr doped silica significantly improved the BD selectivity, yielding 19 mol% BD with a BD selectivity of 50 mol% (compare entries 7 and 9 in Table 6). Finally, an increase in BD yield and selectivity with pore size of the silica support increasing from 40 to 150 Å was noticed for the Zn–Zr modified silica. Doped large pore silica yielded 23% BD with 48% BD selectivity under the same reaction conditions (compare entries 7 and 8, Table 6). According to authors[140] the large pore silica catalyst contained lower proportion of acidic silanols, as measured by the fractions of Q^4 vs. Q^2 and Q^3 in ^{29}Si MAS NMR that results in the decrease of ethylene yield. However diffusional effects and dispersion of supported metal oxides particles were not taken into account to explain the changes in selectivity. Catalytic tests at different space velocities showed that a decrease of the space velocity from 1.5 to 0.75 h^{-1} results in a slight increase in BD yield, albeit with lower BD productivity. No explanation of the contact time effect was advanced. It should be stressed that the preferred LHSV of 1.5 h^{-1} used is similar to that used by Bhattacharyya et al.[104,107,108] for the superior modified alumina catalysts. This contact time is several times higher than that usually applied for the magnesia–silica and other related catalytic systems (compare Table 6, entries 7–9 with the entries in Tables 4 and 5).

Recently, Ordomskiy et al.[141] have claimed that silver, cerium, tin and antimony oxide promoted $ZrO_2–SiO_2$ are highly selective for BD. At 325 °C and with a WHSV of 0.3 h^{-1}, 72% BD selectivity at an ethanol conversion of 34% was obtained over a 0.4 wt% Ag modified catalyst, corresponding to a productivity of 40 g kg_{cat}^{-1} h^{-1} (entry 10, Table 6). A remarkably low temperature was used compared to the usual temperature window for ethanol conversion to BD.

Furthermore, a high BD yield has been observed over a tantalum oxide doped silica – the commercial catalyst developed for the two-step process.[101] Good yields of BD up to 16% have been observed over the catalysts with 2 wt% Ta_2O_5 on silica at 425 °C and 0.6 h^{-1} (Table 6, entry 11).[101] Under similar reaction conditions, an increase in BD yield up to 25% with 30% BD selectivity was found upon doping the Ta oxide catalyst with Cu oxide, likely due to an improved dehydrogenation capacity of the

catalyst (Table 6, entry 12). Although lead and cadmium oxide silica promoters have been proposed, no systematic approach to variations in catalyst composition was present nor was detailed information concerning the preparation methods available. Finally, although it has been postulated that modification of silica gel with 0.5–10 wt% titanium oxide should give suitable catalysts for ethanol transformation into BD, no catalytic data were presented to support this.[142]

Next to the reported silica supported oxide materials, silica-free catalysts have been found to be active in the direct conversion of ethanol to BD. Bhattacharyya et al. studied binary systems containing zirconium or thorium oxides.[104] Among the tested materials, $ZrO_2–Fe_2O_3$, having a weight ratio of 40 to 60, showed a high BD yield of 38% with 45% selectivity at 450 °C and a space velocity of 1.5 h^{-1} (Table 6, entry 13). Arata et al.[143] have shown that promotion of zirconia with weakly basic TiO_2 catalysed the ethanol to BD reaction, yielding 12.4% BD at 330 °C.

Tsuchida et al.[53] have employed hydroxyapatite to produce BD from ethanol at 350 °C and 1 h^{-1}. The acid–base properties of the catalyst surface were controlled by changing the Ca to P ratio in the hydroxyapatite composition. Catalysts with a molar Ca : P ratio larger than 1.62 possessed the appropriate acid–base balance, yielding 24% BD at an ethanol conversion of 20%.

2.4.2 Two-step process. The two-step process of ethanol to BD involves the dehydrogenation of ethanol to acetaldehyde in a separate step, followed by BD production in the second stage by co-feeding ethanol and acetaldehyde. The latter reaction was a discovery of Ostromyslensky at the beginning of the 20th century.[64] In this way, dehydrogenation of ethanol is decoupled from aldol condensation, MPV reduction and dehydration.

Commercialized by Union Carbide, the process has been supplying the major amount of synthetic BD in the US during 1943 to 1944.[1] Although many studies on the two-step process were not showing much pertinent information, most of the available bibliographic data refer to reactions of co-fed ethanol and acetaldehyde in the presence of catalysts, previously developed for the one-step process. It was attempted mostly to elucidate the reaction mechanism or to evaluate the effect of the presence of the different components on the catalyst composition. In this respect, various authors noticed that addition of acetaldehyde results in an increase of BD yield. However, it remains undecided whether the two-step process should be preferred over the one-step process.

Corson et al. have reported that BD formation from ethanol via the two-step process is preferable.[101] This preference is based on the enhanced flexibility for selection of appropriate conditions for each reaction separately and on the decreased catalyst complexity with respect to composition and properties of the two catalyst types used in each stage. The two-step process allowed a reduction of the reaction temperature from 400–425 °C to 350 °C. The purity of BD extracted from the 4-carbon cut amounting to 98% BD in the two-step process was only 80% in the one-step process.

Conversely, Bhattacharyya et al. have claimed that the one-step process is preferable.[108] Under appropriate conditions, the amount of formed BD is high enough so that it is easily separated from other gases.[108] Jones et al. showed that the

addition of acetaldehyde next to ethanol does not result in any improvement of BD yield for catalysts that are able to produce significant amounts of acetaldehyde (AcH) from ethanol.[140]

Ostromyslensky has reported that a higher yield of BD was obtained over aluminium oxide at 440–460 °C using an equimolar mixture of EtOH and AcH.[64,144] Later, Maximoff and Canonici[145,146] have shown that aluminium sulphate, and basic aluminium sulphate alone or deposited on pumice-stone or Kieselguhr, were capable of catalysing the formation of BD from EtOH–AcH mixtures at a reaction temperature ranging from 280 to 450 °C yielding a BD selectivity of 33% with a molar EtOH to AcH ratio of 2.

The two-step process of BD formation has been studied intensively at Union Carbide and Carbon Chemical Corp. as early as 1947 with tantalum, zirconium or niobium oxide promoted silica.[70,78] The first step proceeded over a standard copper dehydrogenation catalyst. The best results of the second step were obtained over a catalyst containing 2 wt% tantalum oxide on silica. At 325–350 °C and a space velocity of 0.4–0.6 h^{-1}, the catalyst produced 35% BD yield with a selectivity of 67% using a mixture of 69% by weight ethanol, 24% acetaldehyde and 7% water. Higher Ta_2O_5 contents in the catalyst resulted in a further increase of the BD yield but at the expense of BD selectivity. It has been stated that the activity of catalysts containing less than 1 wt% of tantalum oxide was not reproducible.[101]

The catalytic activity of zirconium and niobium oxides on silica was lower than the Ta_2O_5–SiO_2 material. 1.6 wt% ZrO_2 on SiO_2 showed a BD selectivity of 59% under comparable reaction conditions.[78] Corson *et al.* have reported that hafnia promoted silica gel was selective and active in the two-step production of BD. At 300 °C a BD yield of 30–40% and a BD selectivity of 50–60% could made from an ethanol–acetaldehyde mixture.[101]

Ordomskiy *et al.* have claimed that zirconium, titanium, tantalum, niobium or magnesium oxides supported on silica promoted by silver, gold, copper, cerium, tin or antimony oxides are highly active and selective catalysts for the production of BD from a mixed acetaldehyde–ethanol feed at 325 °C.[141] Among the Ag promoted MO_x–SiO_2 catalysts, mildly basic titanium oxide was found to be the most selective catalyst showing a BD yield of 25% and a BD selectivity of 72%. Ag promoted MgO-containing catalyst produced more BD, yielding 29%, but with a BD selectivity of only of 64%. Among the zirconium containing materials, M–ZrO_2–SiO_2 doped with different metals, gold was claimed to be the best choice producing BD with a yield of 25% and a selectivity of 82%. Promotion of a Ag modified ZrO_2–SiO_2 with cerium oxide further increased the BD yield when compared to tin, antimony and sodium dopants, yielding 33% BD with 81% selectivity. Silica was the best support, and use of promoted alumina and aluminosilicate resulted in lower BD yields, 18 and 25%, respectively, and selectivity was 57 and 74%, respectively.

Chae *et al.*[147] have studied the effect of the pore size, pore volume and pore organisation on the catalytic conversion of an ethanol–AcH mixture at 350 °C and a LHSV of 1 h^{-1} by using 2 wt% Ta_2O_5 on several mesoporous silica like SBA-15, KIT-6 and MCM-41 type materials. The BD yield increased from 22–24 till 37% when a SBA-15 silica support was used instead of a commercial silica gel, while the BD selectivity increased from 72–75 to 80%. Moreover, Ta_2O_5 supported on ordered silica exhibited a better coke tolerance and stability with time-on-stream. The best catalytic results in terms of activity and selectivity were obtained using silica support material with nano-sized morphology and large pore sizes, indicating the importance of efficient pore diffusion. 2D or 3D organization of the mesopores like in SBA-15 or KIT-6 was found to be less important. The advantage of hierarchical mesoporous silicas is related to the ability of reaching higher dispersion of tantalum making more active sites available and preventing agglomeration of Ta oxide during synthesis and catalytic reaction.

Romanovsky and Jordan[148–150] have reported that the addition of phosphate modifiers to magnesia–rich MgO–silica catalysts with an atomic Mg to Si ratio of 5 resulted in a higher conversion of the ethanol–acetaldehyde mixture and a higher BD selectivity. Key promoters for silica–magnesia were 5 to 25 wt% calcium or calcium–nickel phosphate complexes having molar Ca to Ni ratio of 7.5–9.2. The best results were obtained at 400 °C using a LHSV of 0.4–1.0 h^{-1}, yielding 21 and 23% BD with 56 and 58% selectivity, respectively.

In addition to the catalyst composition, the reaction operating conditions like temperature, contact time and feed molar ratio of ethanol to AcH also played an important role in the catalytic activity and BD selectivity. The old commercial process operating between 325 and 350 °C used a mixture of 7 wt% water and 93 wt% feed with a molar ethanol to AcH ratio of 2.7.

Toussaint *et al.*[78] investigated the influence of the reaction temperature, the molar ratio of EtOH to AcH and the space velocity on the catalyst activity and BD selectivity of a commercial 2 wt% Ta_2O_5 on silica. High BD selectivity was obtained at 325 °C for a feed mixture with a EtOH to AcH ratio of 3, whereas better results were found at 350 °C with a feed mixture ratio of EtOH to AcH of 2–2.5. Catalyst deactivation was less pronounced at lower temperature. Though an increase in BD yield was observed at 350 °C with a EtOH to AcH feed molar ratio of 2, a considerable loss in activity was detected after 160 h on stream, when compared to a reaction at 325 °C using a feed molar ratio of 3, the latter conditions being considered as optimal. Corson *et al.* have reported that for a 2%Ta_2O_5–SiO_2 the optimal conditions for BD production were achieved at 350 °C, using a LHSV of 0.6 h^{-1} and a molar EtOH to AcH molar feed ratio of 2.75.[151] The amount of coke deposited on the catalyst was significantly higher when the EtOH to AcH molar ratio was decreased below 2.75, resulting in faster catalyst deactivation.

The old commercial process with 2 wt% Ta_2O_5 on silica used 7 wt% water in the feed. Romanovsky and Jordan employed 40 to 60 wt% water with the phosphate supported magnesia–silica catalyst to reach the highest BD yield of 23% at 410 °C using a LHSV of 0.4 h^{-1}. However, the precise role of water has not been investigated.[148–150]

In conclusion, 2 wt% Ta_2O_5 on silica seems to be the preferred catalyst for converting a mixture of ethanol and acetaldehyde to BD contains. High ethanol to acetaldehyde molar ratios are required to obtain high BD selectivity and to avoid coke formation. Likely, water in the feed mixture has a

beneficial though not further determined role in the catalysis. High catalyst stability and high BD yield are obtained for reaction temperatures between 325 and 350 °C, the preferred contact times corresponding to a LHSV ranging from 0.3 to 1 h^{-1}. Use of large pore size mesoporous silica is beneficial for the BD yield and selectivity due to high Ta oxide dispersion and efficient pore diffusion. Best BD yield and selectivity were reported to be about 25 and 80% respectively, corresponding to a volume productivity of 350 g$_{BD}$ l^{-1} h^{-1}.

3. Dehydration of C$_4$ alcohols to BD

3.1 Introduction and the feedstock origin

Next to the ethanol-based route, alternative paths to on-purpose production of BD have been demonstrated. These routes are based on the (deoxy)dehydration of mono- and polyols with a four-carbon (C$_4$) backbone. In the literature the catalytic processing of 1-butanol, several butanediols (BDOs) and even tetritols were reported for BD production *via* a direct or multi-step process. Scheme 10 provides an overview of the C$_4$-based alcohol routes and summarizes the major chemical transformations involved.

Double dehydration of several BDOs, *viz.* 1,3-, 2,3- and 1,4-BDO, leads to the formation of BD. In the search for novel on-purpose BD routes independent of the fossil oil feedstock, the origin of the

Scheme 10 Overview of 4-sugar alcohol based BD production routes.

different BDOs is addressed first. 1,4-BDO is a versatile intermediate in the chemical industry with an annual production in the range of 1 million metric tons.[2] The main synthesis route is based on the Reppe process starting with the reaction of acetylene with formaldehyde to form 2-butyne-1,4-diol, followed by hydrogenation to 1,4-BDO. The latter is not only a feedstock for tetrahydrofuran (THF), but it is also used for polyurethanes and poly(butylene) terephthalate. Very recently, Genomatica unveiled an inventive bio-based route towards 1,4-BDO, using a metabolically engineered *Escherichia coli*, which is capable of directly producing 1,4-BDO by fermenting different biomass-derived sugars.[152–154] Although this technology is immature, it has been proven on a 2000 ton scale. Major players have already licensed the technology for scale-up, paving the path for replacing the non-renewable 1,4-BDO production.[24]

Next to the 1,4-isomer, 2,3-BDO (Scheme 10) is also a potential feedstock for BD. Though 2,3-BDO production by bacterial sugar fermentation has been reported,[155–157] its production was replaced by petrochemical routes based on sequential butene chlorohydrination and chlorohydrin cyclization, followed by hydrolysis of the resulting epoxides and their subsequent fractionation.[155] A recently discovered approach to 2,3-BDO is gaining more importance. The route is based on the fermentation of syngas by acetogenic organisms.[158] Feedstock syngas not only can be derived from biomass gasification, but also from industrial gas waste, *e.g.* from a steel mill. Several companies are actively exploring gas fermentation to liquid fuels, mainly to ethanol, Lanzatech being a pioneer in gas fermentation to 2,3-BDO.[26,159]

1,3-BDO is the third BDO isomer in Scheme 10. This diol is the intermediate in the old synthesis of BD based on acetaldehyde from acetylene, followed by aldol condensation and reduction of the intermediately formed 3-hydroxybutanal, a route also included in Scheme 1.[155] For this diol, no sustainable production technology has been demonstrated at the commercial level. However, numerous patents were filed in this domain, using engineering of fermentative pathways.[21,160–162]

On the left-hand side of the lower part of Scheme 10, another route to BD is shown, based on butanol dehydration. *n*-Butanol and its isomers are dehydrated *via* a straightforward acid-catalysed gas phase approach, leading to 1-butene (and isomers).[163–166] This could be an alternative way to biomass-derived BD, as it plugs directly into the state-of-the-art industrial dehydrogenation process of 1-butene.[2,39] Though the latter process has been practiced by Shell, Phillips and Petro-Tex, most plants have been closed due to the high operational costs originating from the elevated temperatures (up to 700 °C) needed to compensate for the endothermicity. The catalyst is composed either of oxides of Cr, Fe and/or Al (*e.g.*, Fe$_2$O$_3$/bauxite) or of (Ca–Ni) phosphates.[2,39] Often, besides steam, oxygen is added to reduce coking, oxidize hydrogen gas to water and generally to shift the equilibrium away from the hydrocarbons. The oxidative variant usually runs with mixed oxides based on Bi/Mo or Sn/Sb.[2]

The production of renewable butanol is experiencing a true revival. The production of butanols relies on the fermentation of carbohydrates in the so-called ABE fermentation,[165,167] named after its major products, *viz.* acetone, butanol and ethanol.
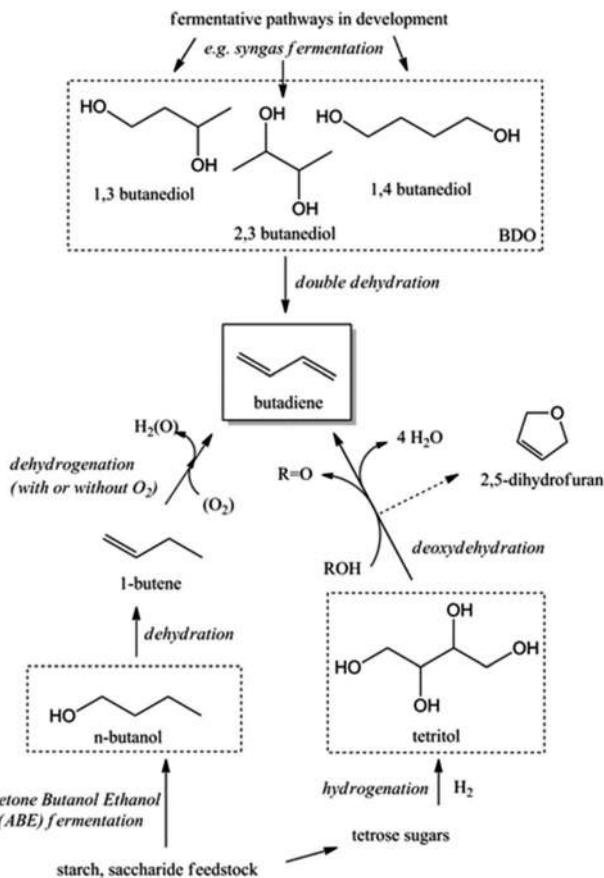
The process was operated commercially in the first half of the 20th century, but abandoned again in favour of fossil alternatives.[168] The focus of recent developments is aimed at the synthesis of butanol, due to its high added-value and its proven efficiency as a liquid transportation fuel with a high substitution potential for both ethanol and biodiesel.[168–170] Solventogenic *clostridia* organisms are used to produce the acetone : butanol : ethanol mixtures in a fixed 3 : 6 : 1 molar ratio. Large scale economic breakthrough of this technology is hampered by the high cost of the carbohydrate feedstock. Use of cheaper lignocellulosic biomass may present a great opportunity, though considerable efforts are required to improve the performance of the fermentation and to make the butanol recovery more sustainable.[168–170] As both ABE fermentation and the oxidative dehydrogenation of butenes to BD have been applied commercially in the past, a combined revival of these technologies could potentially lead to bio-based BD, given the current drivers in this market.[171] One should however include the additional catalytic dehydration to transform butanol to butenes. Although this reaction is considered rather easy, butanol is produced in water and its preceding recovery is a major issue.[21,165,166] Due to its biofuel potential and incentives therein, bio-butanol production could likely increase dramatically on a short timescale,[165] rapidly followed by BD production from the butanols.

Scheme 10 also shows a one-step route based on the deoxydehydration (DODH) reaction of 4-carbon sugar alcohols. These tetritols are produced *via* hydrogenation of natural tetrose sugars. As recently demonstrated in an efficient way by Shiramizu and Toste, the liquid phase one-pot double DODH approach towards BD is based on homogeneous rhenium catalysts and involves the (transfer) hydrogenation with a sacrificial reductant. Unfortunately, tetrose sugars are not produced on a large scale today and remain an expensive and elusive feedstock.[154,172–175]

In conclusion, the introduction clearly points to the availability of on-purpose routes towards BD *via* 4-carbon mono-, di- and tetrols, which are derived from a renewable feedstock or syngas. The main driver for the breakthrough is the success of engineering organisms to ferment carbohydrates or syngas to available bio-butanols and BDOs. Selective dehydration is thus an essential step. The purpose of the next part is therefore to review and assess various catalytic dehydration processes for the conversions of BDOs reported in the recent past with an emphasis on BD production, including the chemistry and thermodynamics of the reactions, the reaction network and the type of catalysts developed. In what follows, the DODH approach applied to tetritols will be assessed as well.

3.2.   Mechanistic, catalytic and thermodynamic aspects of BDO to BD dehydration chemistry

Double catalytic dehydration of 1,3-BDO, 1,4-BDO and 2,3-BDO leads to BD. The dehydration reaction with the different BDOs leads to a mix of overlapping intermediates – originating from the first dehydration – and side-products, resulting from competing reactions. The routes and chemistry of BDO double dehydration are schematically represented in Scheme 11, and will be discussed for each type of BDO.
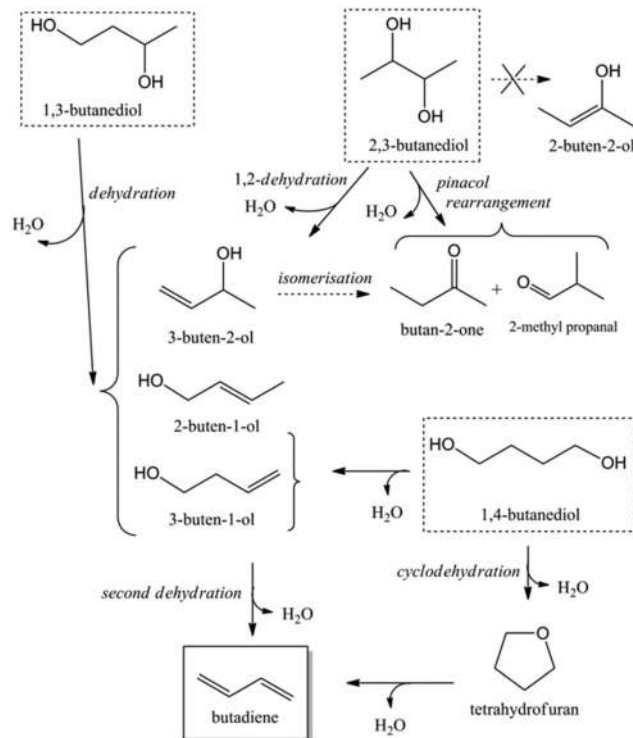
Scheme 11   BDO to BD reaction scheme with the major intermediate and side products.

Dehydration of 2,3-BDO. Technically, the acid-catalysed dehydration of vicinal diols in the liquid phase covers a large field of research in the literature, mainly in the context of pinacol rearrangement, as first discovered by Fittig.[176] Dehydration of pinacol or 2,3-dimethyl-2,3-butanediol, is the most studied substrate and leads to 3,3-dimethylbutan-2-one in the presence of acid catalysts. The reaction proceeds *via* dehydration according to a 1,2-rearrangement mechanism.[177] The rearrangement occurs by shifting a methyl group to the initially formed carbocation. Dehydration of 2,3-BDO follows the same chemistry, a hydride being shifted, leading to the formation of butan-2-one (Scheme 11). When a methyl shifts, 2-methyl propanal is formed as a minor side product (Scheme 11). The classic pinacol chemistry is described *via* the formation of an enol and thus hypothetically suggests the formation of 2-buten-2-ol, which then isomerizes into the ketone. However, the enol in the case of 2,3-BDO has never been observed and its existence is thought to be highly unlikely. Rather, the dehydration mechanism more likely occurs either *via* OH⁻ abstraction with formation of a carbocation intermediate (E1) or in a concerted fashion, *via* a protonated hydroxyl group (oxonium, E2).[178]

Next to butan-2-one formation *via* the pinacol route, dehydration of 2,3-BDO also follows another reaction mode, often denoted as 1,2-elimination, forming an alkene upon elimination of water. If one water molecule is removed, the unsaturated 3-buten-2-ol will be formed, which may further dehydrate to BD. The ratio of the two dehydration types, presented in parallel in Scheme 11, depends on the chemical structure of the diol, the acidic property of the catalysts and the experimental conditions.[178,179]

Most reports on the conversion of 2,3-BDO in the gas or liquid phase show a predominant pinacol type dehydration. The pinacol reaction is accompanied by BD formation in the liquid phase only under non-classical conditions. For instance, Waldmann *et al.* have studied the dehydration of 2,3-BDO to BD in excess of pthalic anhydride with benzenesulfonic acid.[178,180] The pyrolysis of 2,3-acetoxy derivatives of 2,3-BDO into BD is also known.[181] The use of amines also helps in guiding the dehydration to BD, while avoiding butan-2-one formation from 2,3-BDO.[182] Hereto, a vapour phase reaction over a catalyst, containing silica and tungsten oxide on alumina, succeeded yielding 48% of BD from 2,3-BDO in a single pass at 330 °C. However, this high yield was only possible by co-feeding butan-2-one, water and triethylamine. Later, a patent was filed on a similar catalyst composition regarding the formation of 2-methyl-butadiene (isoprene) in high yields (>90%) from 2-methyl-2,3-butanediol in the vapour phase without co-feeding additional reagents. Unfortunately, the patent did not demonstrate the conversion of 2,3-BDO to BD.[178,183]

The first real attempts on the single-step 2,3-BDO-to-BD conversion without sacrificial or stoichiometric reagents date back to the 1940s. Bourns *et al.* have assessed a Morden bentonite clay as a catalyst and they noticed full conversion of 2,3-BDO into butan-2-one below 350 °C. Between 450 and 700 °C, more gaseous products were formed containing small quantities of BD. Dilution of the feed stream with steam increased the BD yield to 25%.[184] Winfield was the first who truly aimed at making BD form 2,3-BDO in as single step and thoroughly screened a range of catalysts including several metal oxides and salts such as SiO_2, B_2O_3, ThO_2, BeO, $CaHPO_4$, $CaCO_3$ and $CaSO_4$ in a vapour phase reactor setup in 1945.[185] The author aimed at a reaction step, proceeding *via* 1,2-elimination towards 3-buten-2-ol, and further dehydration to BD (Scheme 11). While most catalysts promoted pinacol dehydration with almost exclusive formation of butan-2-one, ThO_2, prepared according to a specific synthesis protocol, produced selectively BD. The best result was obtained over the ThO_2 catalyst at 350 °C in a fixed-bed reactor under reduced pressure, yielding 60% BD and 20% 3-buten-2-ol. According to the authors, the rate of the second dehydration step, converting 3-buten-2-ol to BD, appears inversely proportional to the applied pressure. Winfield then thoroughly investigated the adsorption equilibria of his catalytic system to elucidate the profound effect of water adsorption and the concomitant retardation of the second dehydration.[186]

The work of Winfield on ThO_2 may be considered as the breakthrough in converting 2,3-BDO to BD, since most other catalytic materials produced butan-2-one.[178,187] Bartok *et al.* have reported that the pinacol route is the preferred dehydration pathway in the presence of zeolites like Na^+ and Na^+/H^+ exchanged X and Y type faujasites at 250 °C.[188,189] The authors noticed that a lower acidity within X-type zeolites not only led to more pronounced 1,2-elimination and thus BD, but also to a decreased conversion rate.[188] For instance, at 250 °C, use of the NaH–X zeolite showed 59% conversion, distributed over 78% butan-2-one, 4% 2-methyl-propanal and 16% BD.[179,188] Zeolites generally require high reaction temperatures for dehydration and therefore they also tend to catalyse fragmentation of the

carbon backbone.[189] Other zeolite topologies have also been investigated. Lee *et al.* have investigated a series of zeolites with different Si/Al ratios within MFI, MOR, BEA and FAU topologies. They noted that the small pore zeolites favoured butan-2-one formation,[190] whereas the large pore zeolites mostly yielded acetals and ketals. However, no significant formation of BD was reported. Very recently, Zhang *et al.* have studied the influence of boric acid modification of H-ZSM-5 zeolites[191] in a study concerned with the effect of acid site density and strength. In all cases however, BD yields were in the range of 1%.[190–192]

Olah *et al.* in a study on the use of H-Nafion, a perfluorinated resin with sulfonic acid groups, reported that this superacid mainly catalysed the pinacol route.[179] In a reactive distillation setup, 1,3-dioxolane derivatives were predominantly formed *via* acetalisation of butan-2-one with 2,3-BDO, while butan-2-one was the main product in a continuous flow reactor setup. At 150 °C, the conversion of 2,3-BDO was about 78%, while the selectivity to BD only reached 4%. Butan-2-one and its acetals accounted thus for about 94% of the recovered products. At 175 °C, the yield of BD increased to 8% at full BDO conversion.

Other strong acids like heteropolyacids examined by Török *et al.* showed a dominant pinacol pathway.[193] The preference for pinacol formation with acid catalysts is attributed to the strength of the acid sites. Strong acidity better stabilises the oxonium ion transition state (thus the carbocation formed from 2,3-BDO), hence favouring the 1,2-hydride (and also some 1,2-methyl) shift. Ironically, when 2,3-dimethyl-2,3-butanediol (actual pinacol) is the substrate instead of 2,3-BDO, pinacol rearrangement is less dominant and diene formation is more pronounced. Ironically, when 2,3-dimethyl-2,3-butanediol (actual pinacol) is the substrate instead of 2,3-BDO, pinacol rearrangement is less dominant and diene formation is more pronounced. This change in the reaction pathway is likely related to the relative ease of pinacol rearrangement with 2,3-BDO, since the migration of the hydride as in 2,3-BDO is easier than the shift of a methyl group as in 2,3-dimethyl-2,3-butanediol.[188,189]

Sato *et al.* have reported the use of basic CeO_2 to dehydrate 2,3-BDO at 425 °C, noting the formation of butan-2-one as the major product, while no BD was formed (Table 7, entry 7B).

Next to the unique ThO_2 catalyst of Winfield, a recent patent showed promising dehydration of 2,3-BDO to BD in the presence of an hydroxyapatite–alumina catalyst at 320 °C, yielding BD yields above 45%.[194]

Finally, an alternative and original strategy was recently proposed, which tries to bridge the fermentative production of 2,3-BDO with its conversion to BD. The strategy is composed of (i) the esterification of the diol with formic or acetic acid – which are naturally present in glucose-to-BDO fermentation liquors-, followed by (ii) the pyrolysis of the di-esters formed with production of BD at 500 °C. The yields of step 1 are in the range of 70–85% depending on the acid, whereas the pyrolysis of the pure di-esters yields BD in the range of 82–94%. This appears to be an effective way of avoiding pinacol type reactions, but requires pyrolysis at elevated temperatures.[195]

In conclusion, direct dehydration of 2,3-BDO into BD in high yields is very challenging due to the competitive butan-2-one

Table 7 Exemplary catalytic conversions of BDOs in gas phase processing

Entry	Feedstock	Catalyst	T/°C	WHSV/ h^{-1}	TC/ %	S_{BD}/ mol%	S_{THF}/ mol%	$S_{3\text{-buten-1-ol}}$/ mol%	$S_{3\text{-buten-2-ol}}$/ mol%	$S_{2\text{-buten-1-ol}}$/ mol%	Ref.
1	1,4-BDO	Al_2O_3	200	9.0	17	70	30	0	—	—	202
2	1,4-BDO	Al_2O_3	275	9.0	100	0	99	0	—	—	202
3	1,4-BDO	SiO_2–Al_2O_3	200	9.0	100	5	92	0	—	—	202
4	1,4-BDO	ZrO_2	275	9.0	15	49	37	0	—	—	202
5	1,4-BDO	CeO_2	275	6.0	6	87	0	0	—	—	202
6	1,4-BDO	CeO_2	425	6.0	73	5	7	56	—	—	202
7A	1,4-BDO	CeO_2	425	1.8	91	24	—	36	—	—	202
7B[a]	2,3-BDO	CeO_2	425	13.2	51	0	—	—	3	—	203
8	1,4-BDO	Yb_2O_3	375	20.3	40	—	3	82	—	—	208

Entry	Feedstock	Catalyst	T/°C	WHSV/ h^{-1}	TC/ %	Sel.$_{BD}$/ mol%	$S_{formaldehyde}$/ mol%	$S_{3\text{-buten-1-ol}}$/ mol%	$S_{3\text{-buten-2-ol}}$/ mol%	$S_{2\text{-buten-1-ol}}$/ mol%	Ref.
9	1,3-BDO	SiO_2–Al_2O_3	200	11.4	19	20	0	44	2	14	214
10	1,3-BDO	SiO_2–Al_2O_3	250	11.4	74	36	8	28	3	3	214
11	1,3-BDO	Al_2O_3	250	11.4	49	0	28	15	0	4	214
12[b]	1,3-BDO	TiO_2	350	11.4	56	0	5	21	3	11	214
13[c]	1,3-BDO	ZrO_2	350	11.4	57	3	3	18	13	15	214
14	1,3-BDO	CeO_2	325	6.7	73	0	0	0	58	36	216
15	1,3-BDO	Yb_2O_3	325	6.7	33	0	0	1	51	35	216
16	3-Buten-1-ol	SiO_2–Al_2O_3	250	5.7	42	13	58[d]	—	—	—	214
17	2-Buten-1-ol	SiO_2–Al_2O_3	250	5.7	77	93	—	—	—	—	214
18	3-Buten-2-ol	SiO_2–Al_2O_3	250	5.7	71	93	—	—	—	3	214

[a] 2,3-BDO as feed: major product is 64 mol% butan-4-one (thus pinacol rearrangement). [b] Other major product was 3-buten-2-one: 19 mol%/11 mol%. [c] Other major product was 3-buten-2-one: 19 mol%/11 mol%. [d] Major product is 58% propene instead of formaldehyde. TC presents the total conversion of substrate (in %)

formation according to the pinacol rearrangement. While the latter is catalysed preferably by most acid catalysts, Winfield's work of 1945 using ThO_2 and recent work with hydroxyapatite prove that the competitive dehydration of 2,3-BDO to BD is possible, provided that the appropriate catalyst is used. Therefore, research urgently needs further and deeper exploration to clarify the required catalytic properties and surface reactions. Some companies[159] very recently have announced development of such new catalytic technology, in light of the recent breakthroughs in the production of 2,3-BDO from syngas and biomass fermentation.[158]

Dehydration of 1,4-BDO. The acidic dehydration of 1,4-diols (γ-diols) such as 1,4-BDO almost always leads to the formation of cyclic ethers under medium temperature conditions. As summarized in a comprehensive chapter by Bartok and Molnar,[178] the 1,4-cyclodehydration reaction is nearly independent of the chemical structure and the degree of substitution of the BDO. It has been demonstrated with countless acidic catalysts,[196] ranging from organic to mineral acids, metal salts like $ZnCl_2$ and oxides like alumina and phosphates in both liquid and gas phase conditions.[178] Cyclodehydration of 1,4-BDO leads to the formation of tetrahydrofuran (THF, in Scheme 11). As this dehydration process is highly selective to the cyclic ether, it is obviously one of three commercially practiced processes to produce THF. In the vapour phase, the dehydration of 1,4-BDO over chromium oxide, alumina or calcium phosphate at 250–320 °C almost quantitatively leads to THF.[2]

Production of BD from 1,4-BDO demands a higher reaction temperature. The formation of THF over $Ca_3(PO_4)_2$ is selective in the temperature window of 250 to 320 °C. At higher temperatures, the formation of some BD was observed along with high concentrations of unsaturated alcohols like 3-buten-1-ol and 2-buten-1-ol. Further increase of the temperature above 400 °C led to the predominant formation of BD.[178] According to Freidlin et al., with phosphate type catalysts THF was said not to isomerise into the butenols, but to convert directly into BD at temperatures above 360 °C.[197]

BD is thus formed both from THF and 3-buten-1-ol, as visually presented in Scheme 11. The primary pathway is said to occur via 3-buten-1-ol, which is the product of dehydration via the catalysed 1,2-elimination mechanism.[178] The work by Reppe et al. has confirmed that the 1,4-cyclodehydration is mildly exothermic and rather easy, while the conversion of THF to BD reaction is highly exothermic and is much more difficult.[198] Nevertheless, they have described a process converting 1,4-BDO vapours mixed with steam, over a supported H_3PO_4 catalyst bed, containing sodium phosphates. The residence time could be optimized to form almost quantitative yields of THF, including small percentages of BD. By separating BD and recycling THF over the catalyst bed, BD yields of over 90% were shown.[198,199] The reverse process, viz. 1,4-BDO production from BD, is currently commercially practiced. This process proceeds via 1,4-diacetoxybutene formation from BD and acetic acid and subsequent hydrogenation followed by a final acid hydrolysis. Acetic acid can be recycled and, next to 1,4-BDO, THF is formed.[2,200,201]

Sato et al. have studied the dehydration of 1,4-BDO to unsaturated alcohols. A wide range of oxides such as Al_2O_3, SiO_2–Al_2O_3, ZrO_2, MgO were screened as well as plethora of lanthanide oxides, with a special focus on CeO_2.[202,203] Logically, the different catalytic behaviour of SiO_2–Al_2O_3 and Al_2O_3 showed that acidity influences the dehydration activity. The dehydration reaction over alumina at 200 °C (entry 1 in Table 7)

shows a conversion of 1,4-BDO of 17%, whereas full conversion is obtained with SiO_2–Al_2O_3 at the same temperature (entry 3, Table 7). While at low conversions the selectivity to BD was high, viz. 70% for alumina, THF is the dominant product at full BDO conversion (entries 2 and 3), while no unsaturated alcohols were formed.

Yamamoto et al.[204,205] have investigated the use of ZrO_2 for the selective dehydration of 1,4-BDO to produce THF and 3-buten-1-ol at 275 °C and a WHSV of 9 h^{-1} (entry 4, Table 7). The competitive formation of both products is likely due to the presence of both acid and basic sites on ZrO_2.[204] This surface composition is able to compete for 1,4-cyclodehydration to THF and 1,2-elimination to unsaturated alcohols. In order to avoid the formation of THF, the authors decided to investigate purely basic cerium oxides. Usage of CeO_2 completely avoided the formation of THF. At 275 °C and a WHSV of 6.0 h^{-1}, only 6% 1,4-BDO conversion was noticed with a high BD selectivity close to 90%, while a 73% conversion was obtained at 425 °C albeit with a selectivity shift from BD to 3-buten-1-ol (compare entries 5 and 6 of Table 7). Upon increasing the contact time with a factor of three, BD selectivity increased from 5 to 24% at the expense of 3-buten-1-ol (entry 7A, Table 7), while a 91% conversion of 1,4-BDO was obtained. These results highlight the importance of tuning the contact time to promote single or double dehydration. The excellent redox properties of CeO_2 is responsible for a selective stimulation of dehydration to the unsaturated alcohol.[202,206] A similar behaviour was noticed with In_2O_3[207] and weakly basic, heavy rare earth oxides[202,203,206,208–210] such as Yb_2O_3 (entry 8, Table 7). The latter catalyst was very active and selective for dehydrating 1,4-BDO selectively to 3-buten-1-ol at 375 °C and a WHSV of 20.3 h^{-1} with a selectivity of 82% at a conversion of 40%. The very high WHSV (and thus low contact time) reveals a high activity of Yb_2O_3. Although rather basic in nature, the catalytic action of the rare-earth oxides likely proceeded via a concerted acid–base mechanism, as hinted from gas poisoning experiments.[211] Sato et al. recently reviewed their efforts in the dehydration of diols with rare-earth oxides.[211]

In conclusion, the most favourable dehydration route of 1,4-BDO is cyclodehydration, rendering the formation of THF. Although THF may be further dehydrated to BD, this reaction requires severe thermal conditions. The more straightforward route from 1,4-BDO follows the double 1,2-elimination with intermediate formation of 3-buten-1-ol. This pathway is less dominant over acidic catalysts. Neutral to basic catalysts like phosphates, ZrO_2, CeO_2 and Yb_2O_3 favour the formation of the unsaturated alcohol, BD being formed at high enough contact time and increased reaction temperature. However, since the formation of BD was never the purpose of the aforementioned catalytic studies, we anticipate that much better catalytic results are expected soon once the contact time, catalyst composition and other engineering parameters are fine-tuned with focus on 1,4-BDO dehydration to BD.

Dehydration of 1,3-BDO to BD. Dehydration of 1,3-BDO is the textbook example of 1,3-diols dehydration. As mentioned above, 1,3-BDO is the intermediate in the Reppe acetylene-based route to BD. In fact, the double acidic dehydration for a long time has been an industrially practiced route.[2,39,178] The reaction, which proceeds mainly via the 1,2-elimination mechanism, is catalysed by a plethora of acids, acid anhydrides and metal salts.

Different products such as BD, intermediately dehydrated enol products, and other side-products have been encountered in the dehydration of 1,3-BDO. Their pathways are depicted in Scheme 11. The intermediate products are the result of a different regioselectivity in the first dehydration step. According to the classic acid-catalysed 1,2-dehydration mechanism, the diol should transform to 2-buten-1-ol, the most stable alkene in agreement with Zaitsev's rules. The anti-Zaitsev product, 3-buten-1-ol, is formed abundantly with 1,3-BDO. In addition, while the elimination of water from a secondary alcohol is usually easier than from a primary one due to the higher stability of the more substituted carbocation, the terminal hydroxyl in the case of 1,3-BDO also undergoes serious dehydration, rendering the formation of 3-buten-2-ol, as a third enol product in the mixture. BD formation via dehydration of the three enols occurs with different reactivity for each enol type. Competitive isomerization with the formation of butan-2-one is an unwanted side-reaction in view of BD production. Another mode of dehydration, namely 1,3-cyclodehydration resulting in the formation of the cyclic 2-methyl oxirane, is usually not encountered for 1,3-BDO. Next to dehydration, fragmentations may occur via retro-aldolisation if one of the hydroxyls is able to undergo dehydrogenation to yield a carbonyl group.

Patent literature on the synthesis of BD from 1,3-BDO is ample. The patents describe the conditions and catalyst compositions, which favour BD formation such as supported and unsupported acidic and neutral phosphates like Na-(poly)-phosphates (at 270 °C)[2] and $CePO_4$ (at 320 °C).[212] Supported H_3PO_4 and more complex compositions have also been used.[213] BD yields over 90% are not uncommon in these patents.

Sato et al.[211] have thoroughly investigated the conversion of 1,3-BDO in the vapour phase with focus on the production of the unsaturated alcohol, 3-buten-2-ol, rather than on BD (Scheme 11). Such enols are important raw materials for the synthesis of custom and added-value specialty chemicals. Although not aimed at producing BD, these studies are relevant for gaining mechanistic insight into the dehydration of 1,3-BDO over solid acid and base catalysts. A selection of the catalytic data is displayed in Table 7 (entries 9 to 18). Strongly acidic catalysts such as SiO_2–Al_2O_3 were more active and yielded BD next to the enols (entries 9 to 13, Table 7). 19% of 1,3-BDO could be converted into 20% BD, 44% 3-buten-1-ol and 14% 2-buten-1-ol over SiO_2–Al_2O_3 at 200 °C and WHSV of 11.4 h^{-1}. Increasing the reaction temperature to 250 °C, both the conversion and the BD selectivity increased to 74% and 36%, respectively, (compare entries 9 and 10, Table 7). Interestingly, and in contrast to dehydration of 1,4-BDO, dehydration of 1,3-BDO is more selective to BD in the presence of acid catalysts.

Less acidic oxides like alumina tend to catalyze other reaction channels. In the presence of alumina, formation of formaldehyde and 4-methyl-1,3-dioxane with 28 and 18% selectivity was noticed next to some 3-buten-1-ol (entry 11). Formaldehyde likely

originated from 1,3-BDO dehydrogenation towards 4-hydroxy-butan-2-one, followed by retro-aldol fragmentation. Formaldehyde further reacts with a new 1,3-diol molecule to form 1,3-dioxane.[214]

In the case of Zr and Ti oxides (entries 12 and 13), mainly unsaturated alcohols were found, next to 3-buten-2-one, indicative of the formation of 4-hydroxy-butan-2-one and its dehydration, reaction temperatures as high as 350 °C being required to achieve comparable 1,3-BDO conversions. CeO_2 and Yb_2O_3 were very selective for the formation 3-buten-2-ol (from primary alcohol dehydration) and 2-buten-1-ol (Zaitsev's product from a secondary alcohol dehydration) (entries 14 and 15). Unfortunately no BD was formed over the mildly basic oxides.[206,211,214,215] At 325 °C and a WHSV of 6.7 h^{-1}, 73% 1,3-BDO is converted into 3-buten-2-ol and 2-buten-1-ol with a selectivity of 58 and 36%, respectively.

The same authors have also investigated the dehydration of the intermediate enols to BD using acidic SiO_2–Al_2O_3. Interestingly, 3-buten-2-ol and 2-buten-1-ol are selectively converted to BD at 250 °C and a WHSV of 5.7 h^{-1}, 2-buten-1-ol being slightly more reactive, while the anti-Zaitsev's product 3-buten-1-ol is less reactive, primarily forming propylene under the same conditions (entries 16 to 18, Table 7). Clearly, the intermediate formation of the latter enol should be limited as much as possible, as almost no BD is formed from it.

In conclusion, dehydration of 1,3-BDO has been commercially practiced at 400 °C in the presence of steam using a mixture of $NaPO_3$ and $Na_2P_2O_7$, the pyrophosphate being the dehydrating agent, yielding 80% of BD. Conversion of 1,3-BDO in the presence of acid catalysts mainly follows three parallel pathways in the first dehydration step, leading to a peculiar product regioselectivity with three enol intermediates. While 3-buten-2-ol and 2-buten-1-ol are selectively converted to BD, intermediate formation of 3-buten-1-ol should be avoided since its transformation into BD is unselective. Here, the use of mildly basic rare earth metal oxides like CeO_2 may be interesting to apply in a two-stage approach with Brønsted acids like silica–alumina, since it converts 1,3-BDO exclusively into the two preferred enols, which are further dehydrated over the silica–alumina to attain high yields of BD. Despite the promising dehydration of 1,3-BDO to BD, production of 1,3-BDO from sustainable resources is less developed when compared to the other BDOs. Its limited availability *via* renewable routes presents a major bottleneck.

Thermodynamic considerations. The thermodynamics of the BDO routes have been assessed by Aspen software based on available Gibbs free energies for all three BDOs. In the simulation of the overall reaction, *viz.* one molecule of BDO converting to one molecule BD and two H_2O molecules (eqn (3)), the molar composition at steady state equilibrium showed only the presence of BD in the range of 100 to 500 °C, demonstrating that the reaction is favourable over a large temperature window (data not shown). The reaction is slightly endothermic by 62 kJ mol^{-1}, 56 kJ mol^{-1} and 111 kJ mol^{-1} (at 250 °C) for 1,3-, 1,4-, and 2,3-BDO, respectively calculated in Aspen Plus$^®$ software for pure components at given temperature,
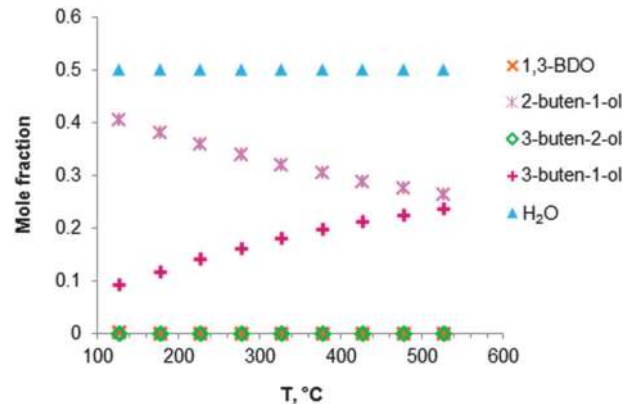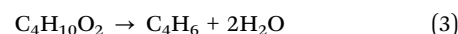

Fig. 12 Equilibrium composition calculated for 1,3-BDO to *x*-buten-*y*-ol, performed using the Equilibrium based reactor (REquil) in Aspen Plus$^®$ software.

p = 1 atm (ΔH calculated in the real state and thus different from ΔH^0).

$$C_4H_{10}O_2 \rightarrow C_4H_6 + 2H_2O \tag{3}$$

The equilibrium composition shown in Fig. 12 for the dehydration of 1,3-BDO to its three enol products shows that 2-buten-1-ol is favoured thermodynamically at low temperature, whereas the formation of 3-buten-1-ol gains importance at higher temperature. 3-Buten-2-ol will be highly unfavourable over the whole temperature range, if formation of the other two enols is possible. Clearly, the selective formation of BD from 1,3-BDO is a kinetic issue only.

As explained before, dehydration of 2,3-BDO shows the dominant formation of butan-2-one rather than BD, due to the presence of an easy pinacol reaction channel. Fig. 13 shows the variation of the equilibrium composition with respect to temperature. It should be noted that butan-2-one is the most favourable product up to 500 °C. At higher temperatures, further dehydration according to the 1,2-elimination mechanism is favoured, resulting in the formation of BD. This means that tuning the catalytic properties towards 1,2-elimination is of utmost importance to attain BD selectively. If not, butan-2-one will be predominantly formed.
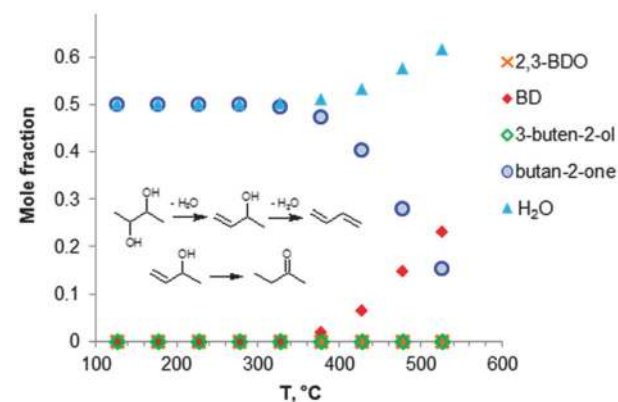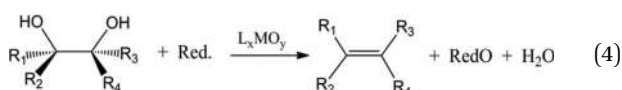

Fig. 13 Equilibrium composition calculated for 2,3-BDO to 3-buten-2-ol, BD and butan-2-one, using the Equilibrium reactor (REquil) in Aspen Plus$^®$ software.

In the thermodynamic simulations of 1,4-BDO dehydration to BD, the presence of THF in the equilibrium composition was unimportant (data not shown). Thus THF is not thermodynamically favoured, while its abundant formation in the catalytic experiments demonstrates the fast kinetics of the 1,4-cyclodehydration. In the long run, BD formation is favoured, albeit with a high energy barrier. Lowering the energy barrier will be a great challenge for catalytic scientists if production of BD from 1,4-BDO is aimed at.

3.3. Mechanistic and catalytic chemistry of deoxydehydration

Besides the dehydration route for converting BDOs into BD, there also exists a catalytic deoxydehydration (DODH) methodology, involving dehydration with concomitant oxygen transfer to a reductant (Red.). This approach is generalized for vicinal diols in eqn (4), L and M being ligand and (transition) metal, respectively.

$$\begin{array}{c}\text{HO} \quad \text{OH} \\ \text{R}_1 \cdots \overset{}{\underset{\text{R}_2 \quad \text{R}_4}{\diagdown}} \cdots \text{R}_3 + \text{Red.} \xrightarrow{\text{L}_x\text{MO}_y} \overset{\text{R}_1 \quad \text{R}_3}{\underset{\text{R}_2 \quad \text{R}_4}{\diagup}} + \text{RedO} + \text{H}_2\text{O} \end{array} \quad (4)$$

The metal-catalysed single stage DODH has first been reported by Cook et al. based on a 1,2,3,4,5-pentamethylcyclopentadienyl–ReO₃ catalyst (Cp*ReO₃) and triphenyl phosphine (PPh₃) as the sacrificial reductant.[217] Although some homogeneous catalysts based on Ru,[218] Mo[219] or V[220] have since then been examined for DODH potential, most reports focus on the use of Re[221–231] as the catalytic centre. Most DODH work was published in view of deoxygenation of biomass derived oxygen-rich substrates to produce new biofuels.[232,233] Although erythritol was included as a substrate in the original report by Cook and Andrews,[217] the application of DODH to sugar alcohols and real biomass substrates such as glycerol and tetritols and not merely to aliphatic or aromatic 1,2-diols, recently received much interest.[221,222,227,229,234,235] Cook et al. have worked under biphasic conditions for DODH of erythritol at 135 °C, using chlorobenzene as a solvent, yielding after 28 h about 80% of BD (entry 1, Table 8). Next to BD as the major product, 3-butene-1,2-diol and cis-2-butene-1,4-diol were formed as well in a molar ratio of 85 : 15. The latter enolic products are the result of a single DODH reaction on either one of the 1,2 or 2,3-diol couple. Scheme 12 i summarizes all possible enol products that can be derived from erythritol via a single DODH reaction, viz. 3-butene-1,2-diol (1), cis-2-butene-1,4-diol (2) and trans-2-butene-1,4-diol (3). Since 3-butene-1,2-diol is a vicinal diol, it may undergo a second DODH resulting in BD formation. Cook and Andrews have verified the BD formation route by feeding 3-butene-1,2-diol to the catalytic system.[217] They observed fast BD formation, whereas no direct DODH was observed when feeding cis-2-butene-1,4-diol. They have noticed some isomerisation of cis-2-butene-1,4-diol into 3-butene-1,2-diol under the catalytic conditions indicating indirect formation of BD, albeit very slow. In the end, because the solubility of the three butenediols is much higher in chlorobenzene than the erythritol reagent, sequential DODH is favoured promoting BD formation. Cook et al. also applied the DODH protocol to xylitol.[217]

Arceo et al.[208] have studied the use of Re₂(CO)₁₀ in 3-octanol, acting as solvent and the reductant for the conversion of

Table 8 Catalytic results for the DODH approach applied to erythritol

E	Catalyst	Solvent/red.	Feed	BD^a	1^a	2^a	3^a	4^a	5^a	Ref.
1^b	Cp*ReO₃	C₆H₅Cl/PPh₃	ery	80	obs.^b	obs.^b	—	—	—	217
2^c	Re₂(CO)₁₀	3-Octanol^f	ery	—	—	—	—	—	62	221
3^d	Bu₄NReO₄	benzene/SO₃	ery	27	0	3	0	0	6	222
4^e	MeReO₃	3-Octanol^f	ery	89	0	0	0	0	11	234
5^e	MeReO₃	3-Octanol^f	threi^g	81	0	0	0	13	0	234
6^h	HReO₃	3-Octanol^f	ery	73	0	0	0	0	7	234
7^e	MeReO₃	3-Octanol^f	2^i	70	0	0	0	6	0	235
8^e	MeReO₃	3-Octanol^f	3^i	70	0	0	0	0	0	235
9^j	XReO₃^k	PhCl/PPh₃	ery	18	0	6	2	—	—	229
10^l	XReO₃^k	Pyridine/PPh₃	ery	30	4	3	5	—	—	229
11^e	XReO₃^k	3-Octanol^f	ery	67	0	0	0	—	7	229

[a] Yields of BD and compounds 1–5, as seen in Scheme 12i, are expressed in mol%. [b] 0.044 M erythritol (ery), 1.5 mol% Re, 0.044 M PPh₃, 135 °C, 28 h obs = observed. [c] 1 M ery, 1.25 mol% Re, 1.7 mol% TsOH, 160 °C, 12 h, air. [d] 0.2 M ery, 10 mol% Re, 0.3 M Na₂SO₃, 155 °C, 100 h. [e] 0.3 M ery, 2.5 mol% Re, 170 °C, 1.5 h, N₂. [f] 3-Octanol plays the role of solvent and reductant. [g] Reaction with DL-threitol instead of erythritol, main side product is a diastereoisomer of compound 4. [h] Conditions as e but at 155 °C for 5.5 h. [i] Resp. intermediates from Scheme 12i as substrate, 0.5 h of reaction. [j] 0.1 M erythritol, 2 mol% Re, 0.22 M PPh₃, 180 °C, 24 h, N₂. [k] X = 1,2,4-tri(tert-butyl)cyclopentadienyl. [l] Conditions as j but 15 h. E = Entry.
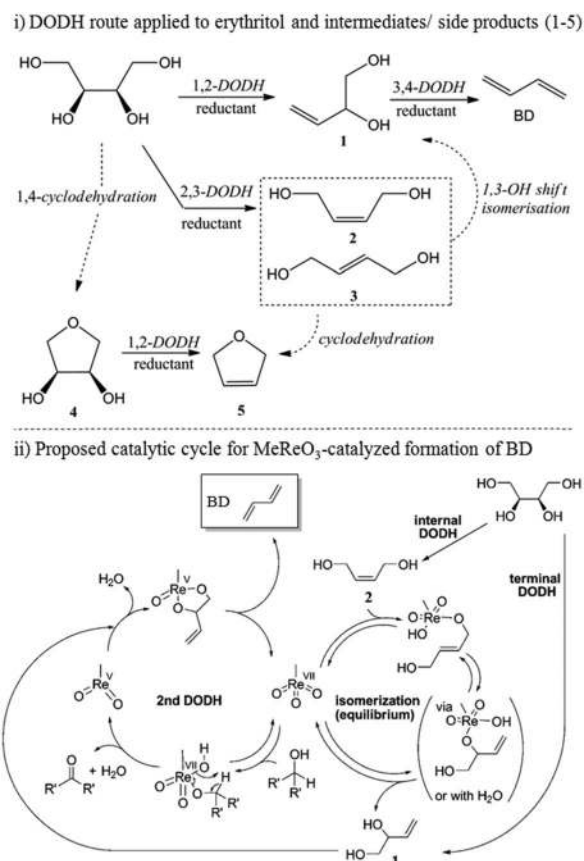
Scheme 12 Tetritol to BD route: (i) main products: 3-butene-1,2-diol (1); cis-2-butene-1,4-diol (2), 3: trans-2-butene-1,4-diol (3); 1,4-anhydroerythritol (4); 2,5-dihydrofuran (5). (ii) Proposed catalytic cycle, adapted from Shiramizu et al.[235]

erythritol in the presence of p-toluenesulfonic acid. The reaction (entry 2, Table 8) mainly showed 2,5-dihydrofuran formation. Erythritol underwent a sequential 1,4-cyclodehydration

yielding 1,4-anhydroerythritol (**4** in Scheme 12), followed by a vicinal DODH reaction leading to the formation of 2,5-dihydrofuran (**5** in Scheme 12). The presence of the acid additive was suggested to be the driver for cyclisation to 1,4-anhydroerythritol. Such a mechanism corroborates with the well-established substitution-independent acidic cyclisation of γ-diols (see the 1,4-BDO section).[178]

In 2011, Ahmad *et al.* have investigated a sulphite driven oxorhenium catalysed approach.[222] Bu$_4$NReO$_4$ (perrhenate salts) was tested with a Na$_2$SO$_3$ reductant in benzene for the DODH of erythritol (entry 3, Table 8) at 155 °C. BD, *cis*-2-butene-1,4-diol and 2,5-dihydrofuran were encountered, with BD being the major product (24%). MeReO$_3$ was also used in combination with sulphites, but this Re catalyst performed less well. The reaction products of these DODH reactions are fully in line with the proposed Re reaction system of Cook *et al.* with PPh$_3$ (entry 1), and helped corroborating the reaction path in Scheme 12i.
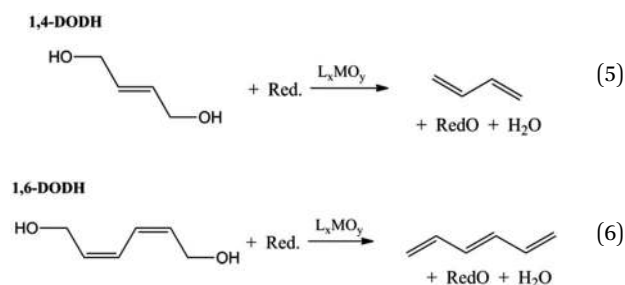
However, Nicholas *et al.*[209] attributed the formation of 2,5-dihydrofuran *via* fast 2,3-DODH, followed by a 1,4-cyclodehydration. Given the long reaction times, the sulphite[225] system seemingly presents a less active DODH system for tetritols. Mechanistically, the first 1,2-diol DODH transforming erythritol into 3-butene-1,2-diol is generally considered faster than a 2,3-DODH (Scheme 12i). The second DODH, of 3-butene-1,2-diol into BD, is considered to be even faster, because this diol was never noticed in the initial reaction stage. Although considerably slower, and thus not a major pathway, the initial 2,3-diol DODH leading to the *cis* rather than to the *trans* form of 2-butene-1,4-diol, further confirms the preference of oxorhenium for a *syn*-oriented elimination.

Both Shiramizu and Toste[234] and Yi *et al.*[227] independently have further explored the DODH reaction on erythritol, both with a less complex and commercially available MeReO$_3$ catalyst. The former authors have provided a breakthrough in the frame of BD production, by adopting a closed system in excess of a sacrificial alcohol reductant – as in the work of Bergman[221] – with the significantly simpler MeReO$_3$ catalyst to assist the DODH. This transfer hydrogenation, here demonstrated with 3-octanol to 3-octanone, is useful in view of the production of bio-alcoholic solvents like isobutanol. Moreover, the formed ketone is easily reduced and recycled, if necessary, or may be used in other reactions like aldol condensation. The authors have reported very efficient double DODH on erythritol and DL-threitol at 170 °C, yielding BD in 89% yield at high conversion (entries 4 and 5, Table 8). The major side-product from erythritol was 2,5-dihydrofuran in line with the Bergman's report, suggesting a dominant 1,4-cyclodehydration activity (see Scheme 12i). In the case of DL-threitol, the major side-product was a *trans* isomer of 1,4-anhydroerythritol, a cyclic internal *trans*-diol. Its formation demonstrates the need for *cis*-diol substrates to get an efficient vicinal-directed DODH. To check whether the introduction of Brønsted acidity would result in an increase of the 2,5-dihydrofuran yield *via* the acidic 1,4-cyclodehydration path (Scheme 12i), a reaction with HReO$_4$ as a catalyst was performed under similar conditions (entry 6). However, no changes in the product distribution were noted, while BD remained the

main product. This points to the high preference of catalytic DODH rather than cyclodehydration under the conditions used.

Yi *et al.* also used MeReO$_3$, but mainly reported on a solvent-less DODH approach, practiced with glycerol.[227] To remove and collect the gaseous products, a continuous distillation setup was used, mainly producing allyl alcohol from glycerol. The latter is not only the reactant, it also participates in transfer hydrogenation with co-production of dihydroxyacetone. With 2 mol% of MeReO$_3$ and 1.5 molar equivalents of 1-heptanol as a transfer reagent, erythritol and threitol were converted mainly into gaseous products.[214] Using the continuous distillation procedure, no BD was condensed in the collector. Erythritol mainly yielded 2,5-dihydrofuran and *cis*-but-2-enal, while meso-threitol was converted into (3*S*,4*S*)-tetra-hydrofuran-3,4-diol, an isomer of compound **4** in Scheme 12i.[227] Differences with the results of Shiramizu and Toste[234] (entries 4 and 5, Table 2) may originate either from the excess of sacrificial alcohol used or, more likely, from the differences in setup; *viz.* an open distillative system *versus* a closed approach. It appears that the open reactor promotes 1,4-cyclodehydration, next to DODH chemistry, preferably leading to the cyclic species of Scheme 12 rather than to BD. The resemblance with the product spectrum of the Bergman system is obvious.[221] However, rather than being the effect of Brønsted acidity (Bergman), here a plausible explanation could be a shift in reaction equilibria, caused by the open distillation, hereby promoting dehydration.

To expand the scope of the oxorhenium catalyzed DODH, Shiramizu and Toste have investigated different substrates.[235] Oxorhenium compounds not only catalyse DODH chemistry, but in parallel accelerate 1,3-OH shifts in allylic alcohols. The latter reaction thus formally presents 1,4-DODH and 1,6-DODH (eqn (5) and (6), respectively), rather than classic *cis*-vicinal or 1,2-DODH (eqn (4)).

$$+ \text{Red.} \xrightarrow{L_xMO_y} \qquad + \text{RedO} + H_2O \qquad (5)$$

$$+ \text{Red.} \xrightarrow{L_xMO_y} \qquad + \text{RedO} + H_2O \qquad (6)$$

For intermediates like *cis*- and *trans*-2-butene-1,4-diol (**2** and **3**, Scheme 12i) tested under conditions similar to those of the original tetritol, very smooth progression of 1,4-DODH chemistry has been noticed for both isomers.[222] The catalytic results (entries 7 and 8, Table 8) indicate that the formation of a 7-membered rhenium-diolate from the catalyst and the 1,4-diol is excluded as both isomers showed identical reactivity. On this basis, the 1,3-OH shift causing isomerisation of allylic alcohols may be included in Scheme 12i (dotted line). Note that Cook *et al.*[217] already noticed the formation of 3-butene-1,2-diol from *cis*-2-butene-1,4-diol, though at a much slower rate than the DODH reaction. Shiramizu and Toste have proposed a catalytic cycle for their tandem isomerisation/DODH protocol, which is

in fact the combination of a 1,4 and 1,2-DODH (Scheme 12ii). In the tentative catalytic cycle it is proposed that the 1,4-DODH reaction proceeds through a 5-ring rhenium^V-diolate before expelling the isomerised olefin, *i.e.* 3-butene-1,2-diol (**1**) in the case of erythritol. This intermediate is identical to the one in the last step of the final 1,2-DODH reaction, just before BD expulsion (Scheme 12ii). This merged isomerisation-DODH mechanism might explain the high overall DODH efficiency of the MeReO$_3$–3-octanol system, in conjunction with the high substrate solubility. Theoretical density functional studies by Qu *et al.* have demonstrated the possibility of a pathway involving a MeReO(OH)$_2$ species formed from MeReO$_3$ and the reducing alcohol,[231] coordinating diols through double dehydration. Thus, the alcohol may act as a shuttle facilitating various hydrogen-transfer steps. Other mechanistic proposals, elaborated for the synthesis of *trans*-stilbene, involve a rhenium^{III}-diolate, formed from 3-octanol reduction of methyl-dioxorhenium^V.[228] Finally, Raju *et al.* reported the conversion of erythritol *via* DODH with a bulky 1,2,4-tri(*tert*-butyl)cyclo-pentadienyl-ReO$_3$ catalyst.[229] Entries 9 and 10 in Table 8 show these results, using PPh$_3$ as a reductant in chlorobenzene or pyridine. Low BD yields were noticed and several intermediates, including *trans*-2-butene-1,4-diol, were obtained, pointing to an inefficient DODH protocol. Under the conditions of Shiramizu and Toste, 67% BD yield was noticed with the aforementioned bulky catalyst (entry 11), underlining the importance of solvent and the reductant in DODH reactions, as well as the appropriateness of using a sacrificial alcohol such as 3-octanol.[221,223,234]

As mentioned before, the four-carbon sugar-based feedstock is currently not produced on a large scale and certainly not on the scale requested for BD production. Therefore, it seems unlikely that it will become shortly a viable feedstock for BD *via* DODH chemistry. Alternatively, the development has been reported for new routes to tetritols *via* decarbonylation,[236] or to tetroses *via* decarboxylation[237] of larger carbohydrates such as pentoses and hexoses and *via* aldol condensation of glycolaldehyde.[173] Pentose and hexoses are abundantly present in (hemi-)-cellulosic biomass,[238–240] while glycol aldehyde is a dominant compound in bio-oils from biomass pyrolysis.[173,241,242] Interestingly, the elegant DODH approach was also performed with glucose-derived sugar alcohols such as mannitol and sorbitol, leading to a hexatriene as the major product.[234] Such hexitol feedstocks can be directly derived from cellulosics.[175,243,244]

A second issue of current DODH next to feedstock availability and cost lies in the use of the expensive complex Re catalysts. Taking into account their turnover rate, their use on a large scale appears uneconomical for the production of BD. Note however that NH$_4$ReO$_4$ has a significantly lower cost.[223] For an industrial breakthrough of the DODH approach, research should be directed to the development of stable and practical heterogeneous catalysts. Denning *et al.* have recently ventured into this area, with the synthesis of a carbon supported perrhenate DODH catalyst.[224] In addition, the solventless distillation of Ji *et al.*,[214] which was mainly applied to convert glycerol, could be envisioned occurring in a full continuous mode. It seems that such open and continuous DODH

systems are worthy of exploring for BD production from tetritols, provided 2,5-dihydrofuran formation can be suppressed.

4. Conclusions and perspectives

On-purpose synthesis of BD has received a recent revival of interest because its availability from naphtha and gas crackers is diminishing. Worldwide investment in BD extraction capacity at the crackers and dehydrogenation of the butane fraction, either as a component of natural gas and shale gas or as a waste fraction from petrorefinery, are two obvious ways to satisfy the needs of a firm BD market. Although the butane dehydrogenation route to BD is an energy consuming process because of its endothermicity, state-of-the-art technology has proven its reliability in the past and new initiatives were recently announced. However, driven by the shortage of light alkanes due to lightening of cracker feeds and the increasing global demand for bio-derived chemicals, biomass-based conversion might offer new avenues for on-purpose BD production from renewable feedstock. The major technical challenge here is to produce BD from biomass and/or biomass-derived syngas that will be cost competitive with fossil oil-based BD. Several research and development needs are required to answer critical questions regarding the technical, *viz.* process (operational) costs, and economic, *viz.* feedstock price and BD price, feasibility to integrate a bio-derived BD in the chemical industry.

Ethanol can be converted to BD. This route has been practised on the industrial scale long before fossil oils and gases found general use. The industrial production of bio-ethanol is under extensive development, enabling production of large amounts of ethanol in the near future. Other encouraging developments show ethanol production from syngas, either derived from natural gas, waste gas or biomass feedstock. Also methanol carbonylation, followed by acetic acid hydrogenation might turn out promising for ethanol production. Meanwhile, fermentation became a very competitive process to ethanol.

The conversion of ethanol to BD is thermodynamically feasible and proceeds *via* a sequence of reactions, receiving general acceptance, *viz.* ethanol dehydrogenation, aldol condensation, MPV reduction, and dehydration. Clearly, a subtle balance of the four reactions is required to achieve high BD yield.

The literature overview indicates that a strong base like MgO or ZnO is essential to catalyse the aldol coupling, while Ag and CuO are good candidates to assist the dehydrogenation step. The catalytic system tolerates the presence of weak Brønsted acidity, *e.g.* surface hydroxyls of silica, alumina or clays, catalysing dehydration, though its amount and strength should be limited, to avoid the thermodynamically favourable ethylene as the side-product. The activity of the MPV hydrogen transfer reaction is likely most difficult to understand at the molecular level, but it is related to the presence of Lewis acid sites, on incompletely coordinated Mg^{2+} in MgO and some clays or on Al^{3+} in alumina and clays. The addition of ZrO$_2$ is an interesting option to assist aldol condensation and MPV reduction.

Current BD selectivity with such catalysts ranges from 50 to 80%, the latter being obtained at modest conversion, thus showing room for improvement and development. Hydrocarbons like ethylene and butenes and oxygenates like acetaldehyde are produced, thereby reducing total BD selectivity. While ethylene may be valorised, the formation of butenes is unfortunate because of separation issues with BD. Another challenge of the ethanol-to-BD reaction consists in its low volume productivity and often low BD concentration in the product stream. Current values range from 50 to 400 g_{BD} h^{-1} per litre catalyst volume, with values below 100 being reported most frequently. Thus one faces the challenging task to develop more active and selective catalysts at higher ethanol concentration. A low ethanol conversion should not always be an inconvenience *per se* as efficient recycling of unconverted ethanol is optional, as well as a product recycle since many by-products can be formed from the various intermediates in the reaction sequence. Besides recycling reactors, reactor types like a fluidized bed could favour the cascade of consecutive reactions to BD due to better heat supply and back-mixing;[108] there has been no systematic study of the influence of the reactor design and reactor type on the production of BD from ethanol. Most of the research and catalyst developments were devoted to experiments in plug flow reactors.

There is also little information available about the importance of the purity of the ethanol for BD production. Sporadically, a beneficial effect of water is reported, possibly as a dilute of ethanol or as a reactant that poisons strong acid–base sites. Others reported on the usage of diethyl ether in the feed stream as a better reagent for BD production. The presence of impurities of larger alcohols like isoamyl alcohol in the bio-ethanol feed has not been investigated in the context of on-purpose BD production.

Catalysts of particular interest for further improvement would include a combination of the abovementioned elements. Catalyst preparation and pretreatment techniques are very important in order to maintain high dispersion and ideal mixtures/phases of the different functions. Structural modifiers are likely required to stabilize the high dispersion against sintering. Scalability and cost of catalyst preparation/modification are important factors to consider as well with these multi-component catalysts.

Whereas whole series of catalyst compositions have been tested, many reports unfortunately lack thorough physicochemical characterization and kinetic approaches defining the ideal catalyst in terms of acid–base and redox properties. Studies of individual reaction types in the conditions of BD formation are highly welcome,[90,245,246] but this is not always possible due to the thermodynamic constraints. They will form a first step in the deeper understanding of the correlation between the active sites. A better understanding of the adsorption phenomena and surface chemistry is crucial, especially of the critical reaction steps determining selectivity and rate limiting events. Advanced (*in situ* and *operando*) spectroscopic tools are available today to better monitor the reaction processes at the microscopic and molecular level and the catalyst behaviour with nanoscale resolution under reaction conditions. Crucial information on the overall catalyst behaviour, in terms of textural and chemical

(redox, acid–base) properties, is needed, ultimately helping improving overall catalytic performance.

Next to ethanol, there have been recent developments in producing bio-derived 4-carbon alcohols, like *n*-butanol, iso-butanol and various butanediols such as 1,3-BDO, 1,4-BDO and 2,3-BDO using fermentation of sugars. Also fermentation of syngas from natural gas or biomass has been demonstrated to provide some of the diols. Dehydration of the monohydric alcohols provides bio-derived butenes, which could be dehydrogenated to BD, preferably in the presence of oxidants to compensate for the endothermicity. Availability of cheap alcohols will allow commercialization of the ODH technology.

Dehydration of butanediols to BD has received increasing interest given the availability of bio- and gas-derived BDO's. Each diol has its own unique features and challenges. Dehydration of 2,3-BDO faces a facile pathway to butan-2-one, following a pinacol-type rearrangement. Whereas higher temperatures will stimulate BD formation thermodynamically, kinetic control is key to achieve high BD yields. This remains the key challenge for the catalytic chemist, especially with the renewable production of 2,3-BDO just around the corner. For as such unknown reasons, a ThO_2 catalyst currently delivers the best catalytic performances.

Dehydration of 1,4-BDO suffers from the production of THF. Again, use of higher temperatures is part of the thermodynamic solution, although kinetics to a major extent still determine the selectivity. THF can be further processed into BD, albeit at high temperatures. There is another challenging route proceeding according to a double dehydration with intermediate formation of 3-buten-1-ol. Suitable catalysts are neutral to basic like CeO_2 and Yb_2O_3. Combination of effective catalysis with the recent breakthrough in fermentative 1,4-BDO production is a route to BD that probably will be picked up in the very near future.

Dehydration of 1,3-BDO is a classical route, as this diol was the key intermediate in the acetylene-based industrial BD production long time ago. Therein, cheap Na–polyphosphate catalysis allowed good catalytic dehydration results.[2] Alternatively, a two-step reaction with CeO_2 may be envisioned producing selectively 2-buten-1-ol and 3-buten-2-ol, followed by their dehydration to BD using common Brønsted acid catalysts like silica–alumina. However, the bottleneck in this approach resides in the development of a renewable production of 1,3-BDO.

Finally, the pioneering work of deoxydehydration of butanediols and tetritols is an elegant chemistry to produce BD. Although this route is probably far from commercialisation, it shows that creative thinking could lead to original catalytic pathways towards useful drop-in chemicals from bio-derived chemicals. Development of cheap catalysts is essential though, and perhaps heterogeneous catalysis may offer the solution.

Acknowledgements

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