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Heterogeneous Catalysis for the Valorization of CO_2: Role of Bifunctional Processes in the Production of Chemicals

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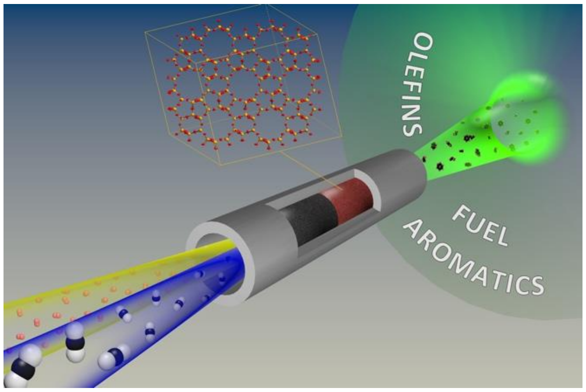
ABSTRACT: Carbon dioxide is an abundant carbon feedstock, and there exists a sustained interest in methods for its utilization. At the moment, several routes that rely on the use of renewable energy for the valorization of CO_2 are being considered, with a strong emphasis on fully electrocatalytic routes. In this perspective, we highlight the role that heterogeneous catalysis may play in hybrid processes in which H_2 is obtained via electrolysis and CO_2 valorized in a second, dark step. Targeting high selectivity to value added products (olefins and aromatics), we cover CO_2 to chemicals routes that involve cascade multifunctional processes. In doing so, we highlight the main advantages of this approach along with the most important challenges and remaining questions.



Global warming solutions come down to reducing the alarming CO_2 levels[1]. Within this context, the transformation of CO_2 into high value chemicals is gaining a lot of attention and may result in a paradigm shift in which CO_2 turns from waste to commodity[2].

In this scenario, several technologies able to convert CO_2 and water, with help of renewable energy, to economically attractive products have been proposed. In short, these technologies can be divided into the following categories: biochemical, photochemical, electrochemical and thermochemical[3]. The first three approaches rely on the simultaneous conversion of CO_2 and water in a ‘single pot” process. As a consequence, competition between water splitting and CO_2 reduction along with the low solubility of CO_2 in water bring a number of challenges that researchers are trying to address (i.e. by reactor engineering[4]). However, in spite of high faradaic efficiencies to certain products like CO or ethylene, achieving high conversion per pass and economically attractive production rates have proved challenging[5]. On the other hand, given the maturity of water electrolysis technologies, the use of traditional heterogeneous catalyzed processes for the hydrogenation of carbon dioxide may become a very attractive technology.

To this extent, some excellent reviews highlighting the conversion of CO_2 to various useful chemicals have been published recently. Prieto[6] described the importance of CO_2 hydrogenation with renewable hydrogen targeting chemicals having high volumetric energy density. These high energy compounds are great platform chemicals having positive compatibly with current energy infrastructures. Yang and coworkers[7] discussed the conversion of CO_2 specifically to C_{2+} hydrocarbons. They covered the different catalytic routes to transform CO_2 into useful chemicals touching upon bifunctional routes as well. W. Li and coworkers[8] reviewed the valorization of CO_2 to methane. They described the supported metallic catalysts employed in this process (with Ni being the most common active phase) along with the mechanisms of CO_2 methanation. They also briefly touched upon bifunctional hydrogenation of CO_2 and highlighted possible mechanisms of C-C coupling over Fe based and Cu based catalysts. Finally, J. Li and coworkers[9] illustrated the conversion of CO_2 to ethanol via hydrogenation. This is much more challenging than methanol synthesis due to the requirement of direct C-C coupling. Additionally, they briefly described the synthesis of other value added products from CO_2 including acetic acid, dimethylether, olefins and gasoline.

Traditionally thought of as processes in which either less valuable products are made (i.e. methane), that require unaffordable pressures (i.e. methanol synthesis) or that result in a very wide spectrum of products (Fischer Tropsch like chemistry), over the last few years, the use of cascade thermochemical processes involving multifunctional catalysts or the combination of several catalysts in a single reactor vessel for the valorization of CO_2 has gained a lot of attention. More specifically, the use of bifunctional catalysis (a combination of a metal/metal oxide and a zeolite) for the heterogeneous gas phase hydrogenation of CO_2 to value added compounds (especially olefins and aromatics) is one of the most attractive technologies[10-25]. Olefins are key components of the chemical industry, being fundamental building blocks for many different derivatives, while aromatic compounds such as benzene, toluene and xylenes are in the top 20 chemicals produced in the world.

The greatest advantage of this bifunctional metal-zeolite configuration is that the product selectivity can be shifted to either light olefins[11-18, 21-24] (C_2-C_4) or aromatics[10, 19-20, 25] by selecting the appropriate zeolite, overcoming many limitations of the standalone metal catalyst (i.e. thermodynamic limitations and/or product distribution)[21]. However, multiple reactions are involved (oligomerization, cracking, dehydrogenation, cyclization, alkylation, isomerization, etc.) and many intermediates can serve as reactants for other reaction pathways, limiting the total olefin or aromatics selectivity and impeding the complete understanding of the global reaction mechanism[26-28]. This complex reaction network is likely the main reason of the limited number of publications available in the open literature. Additionally, despite some promising results, there are important issues to overcome, like the high CO selectivity (frequently higher than 50%[21, 25]) and the zeolite selection and fine-tuning.

In this perspective, we first analyze the possible reactions that are likely to occur under these conditions. Subsequently, we critically review the most promising works especially pertaining towards production of light olefins and/or aromatics and, finally, we discuss future challenges, emphasizing possible approaches to overcame the present limitations and reach the desired commercial viability.

MECHANISTIC CONSIDERATIONS

The conversion of CO_2 to hydrocarbons can proceed through two different routes: i) the transformation of CO_2 into CO via reverse water gas shift (RWGS route) followed by the conversion of CO to hydrocarbons by a classical Fischer-Tropsch (FTS) mechanism[29] and the subsequent hydrocarbon cracking/isomerization/aromatization, and (ii) the transformation of CO_2 into methanol[30] followed by its conversion into hydrocarbons (MeOH route)[31-32]. Figure 1 provides a scheme comparing the two mechanistic routes.

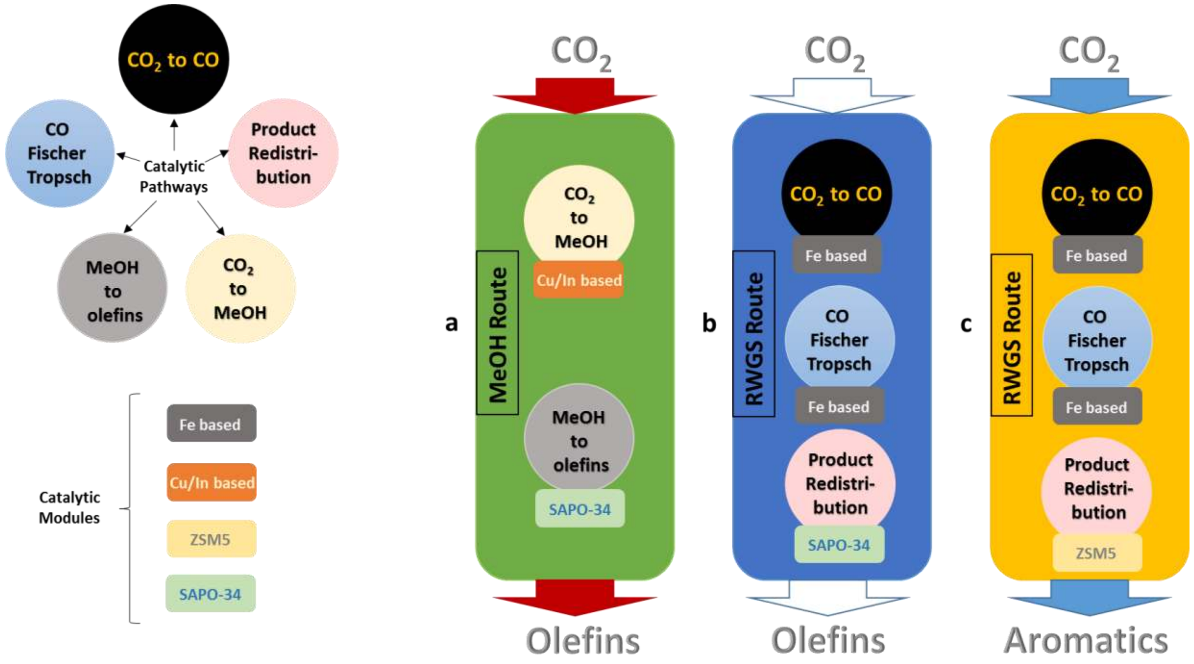


Figure 1. Mechanistic pathways for CO_2 hydrogenation and conversion to (a) olefins using the MeOH route (b) olefins using the RWGS route (c) aromatics using the RWGS route

These conversion routes can also be applied towards syngas ($CO+H_2$)[33-34]. It is comparatively easy to activate CO and therefore more straightforward to produce chemicals from this feedstock. However, there exist other practical challenges mainly coming from CO toxicity. Analogous to the RWGS route, the first step for CO conversion is the Fischer-Tropsch synthesis itself. This can then be followed by the coupling of the FTS catalyst with a zeolite in order to allow for product re-distribution and selectively produce olefins and/or aromatics[35]. Similarly, for the MeOH route it is an advantage to directly use syngas since it is already employed for the industrial production of methanol. Combining with a zeolite for the MTH reaction can, once again, allow for the production of value added chemicals via CO hydrogenation[34]. It should be noted that while the two processes (CO_2 hydrogenation *vs* CO hydrogenation) do share similarities, they also carry essential differences in their reaction mechanisms as elucidated below for CO_2. The reader is invited to refer to Cheng and coworkers[36] for a detailed overview of CO hydrogenation to hydrocarbons. While syngas utilization can lead to higher productivities as compared to CO_2 hydrogenation, the main source of syngas currently is methane steam reforming which does not help in alleviating CO_2 levels. Thus, direct valorization of CO_2 is of great importance for climate change and has the additional benefit of providing a non-fossil fuel alternative for the production of chemicals.

Hydrocarbon synthesis from CO_2 *via* MeOH

Methanol synthesis from carbon dioxide has been extensively studied for the last four decades. However, a full agreement about the reaction pathway for this transformation has not been achieved yet. The most widely used and studied catalyst – Cu/ZnO based – is still a topic of intensive research[2]. It is typically assumed that CO_2 is hydrogenated on the copper sites, but there exist a number of reports on the bifunctional Cu-Zn systems. Another research discrepancy is laying in the methanol carbon source – whether it is CO_2 or CO. Though there is a large amount of carbon monoxide being produced via the RWGS reaction, CO_2 is more generally accepted to be acting as the carbon source. The reaction intermediate is also a topic of a debate – some researchers support the formation of formate species (HCOO*) as the first hydrogenated species in the mechanism, whereas others propose the formation of hydrocarboxyl (COOH*).

Considering the thermodynamics of the reaction, it has to be noted that methanol synthesis via hydrogenation of CO_2 is a moderately exothermic reaction, which means that it is favored thermodynamically at low temperatures. That fact limits its conversion since a recycling reactor is required to reuse the accumulated heat.

The subsequent transformation of methanol to hydrocarbons (MTH reaction) is a domain of zeolite catalysis, usually HZSM-5 and SAPO-34[31]. The mechanism of the MTH reaction has been the subject of vast amount of research. More than 20 possible mechanisms have been proposed, encompassing a variety of reactive intermediates. The dual hydrocarbon-pool (HCP) mechanism is nowadays the most accepted one (see Figure 2). This hydrocarbon pool, with an initially specified overall stoichiometry $(CH_2)_n$, represents an adsorbate (containing several polycondensed aromatic species) which has many characteristics in common with ordinary coke and contains less hydrogen than indicated. Initially, researchers assumed that the presence of impurities in the feed/catalyst/carrier gas caused the formation of the first direct C-C bond[32]. Recent research has refined this theory by proving that the MTH reaction goes through two phases: (i) a short induction period followed by the (ii) autocatalytic dual cycle mechanism. In the induction period, formation of the direct C-C bond takes place (i.e. the coupling of two methanol and/or dimethylether (DME) molecules) via a surface methoxy species[37]. Then the dual cycle (consisting of methylation and cracking of olefins, methylation and dealkylation of aromatics, hydrogen transfer and cyclization [32]) takes control, governing catalyst lifetime and product selectivity. Product distribution depends on the zeolite topology, acidity and the operating conditions, causing either the aromatic or the olefinic cycle to propagate more than the other cycle. Nevertheless, the mechanism of the methanol to olefins (MTO) process is still a matter of investigation and discussion.

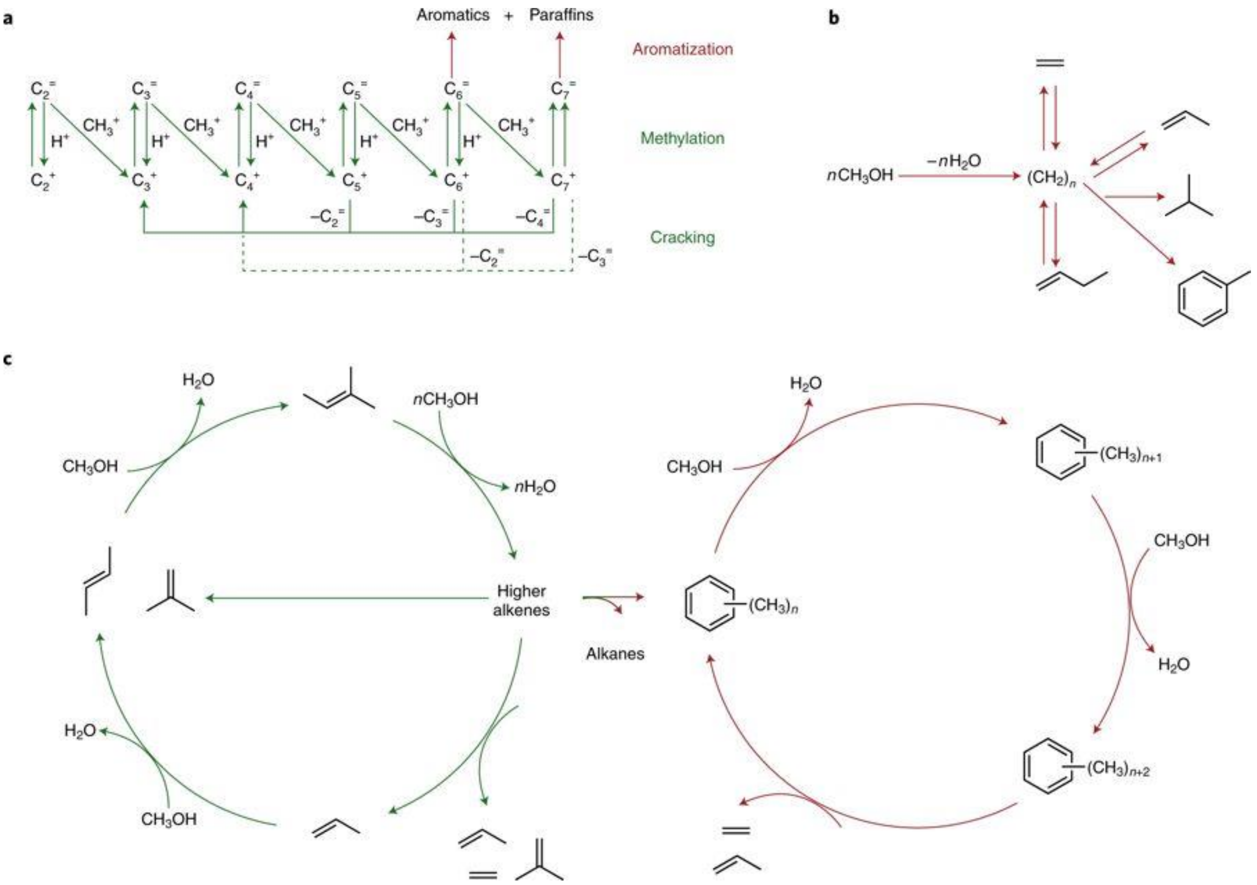


Figure 2. a) Dessau and LaPierre described steady state kinetics of MTH reaction over ZSM-5. b) Dahl and Kolboe HCP concept over SAPO-34. c) The dual-cycle mechanism, where two competing cycles run in the zeolite channels governed by olefins and aromatics, both acting as co-catalysts for MTH and being active HCP species. Reproduced with permission from [32].

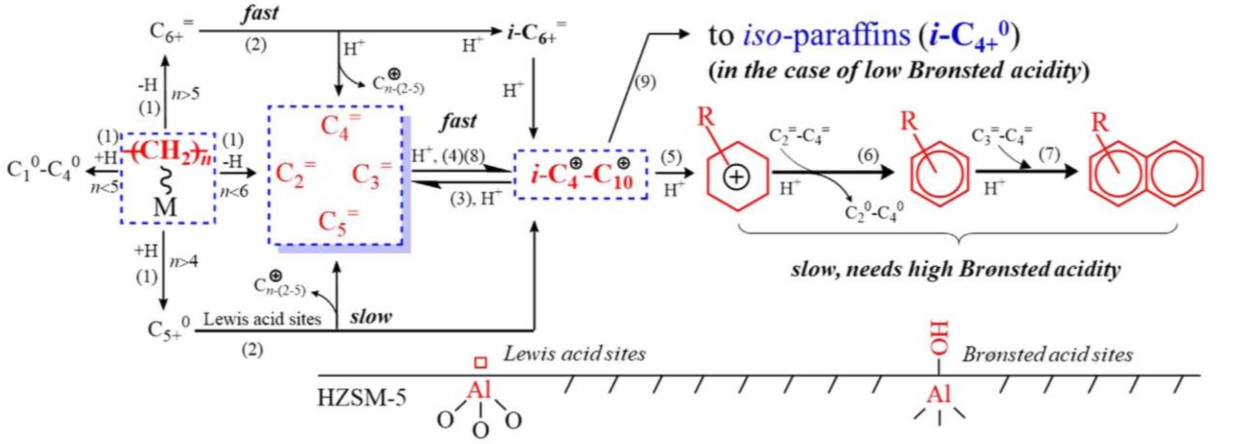
Hydrocarbon synthesis from CO_2 via RWGS

Among all possible catalysts for the transformation of CO_2 via RWGS, iron materials are the most popular ones, as Fe can catalyze both the RWGS and the FTS reactions[38]. According to the proposed mechanism for this process, CO_2 is initially reduced to CO *via* RWGS, followed by a subsequent hydrogenation of CO to olefins and paraffins *via* FTS over Fe carbide active sites[29].

The formed olefins and paraffins can then be converted into aromatics, short chain olefins, and paraffins *via* hydrocracking, hydroisomerization, oligomerization, cyclization, and H transfer over acidic zeolites in the bifunctional system. This reaction chemistry is complex, as it involves many reaction networks with different reaction intermediates[26-28].

Paraffins can be activated by two mechanisms: a monomolecular and a bimolecular one. In the monomolecular mechanism, proposed by Haag and Dessau[39], alkanes are protonated to form carbonium ions that can undergo either C–C bond cleavage yielding paraffins or C–H bond cleavage yielding hydrogen and carbenium ions. These carbenium ions can subsequently form olefins *via* back donation of a proton to the zeolite. In the bimolecular mechanism, a paraffin is protonated by the Bronsted acid and forms a dimer with another olefinic hydrocarbon. In case of olefins, the carbenium ion can readily be formed *via* addition of a proton, supplied by Bronsted acid sites[40]. Therefore, activation of paraffins requires much higher temperatures than activation of olefins, needing temperatures above 500 ºC to obtain conversions higher than 20%[41].

Once activated, the catalytic cracking can proceed through a monomolecular and/or a bimolecular mechanism. The bimolecular pathway prevails at mild temperatures (below 350 ºC), while at higher temperatures the monomolecular mechanism is predominant[42]. The aromatic formation is suggested to start with polymerization reactions to form dienes[43], followed by cyclization into alkyl-cyclohexanes in the zeolite channels, and then multistep H transfer with olefins yielding alkylbenzenes and paraffins. P-xylene is likely to be the first aromatic formed[44], and the final aromatics distribution is controlled by their interconversion reactions, such as isomerization, disproportionation and dealkylation/alkylation, all catalyzed by the zeolitic protons (see Figure 3). Nevertheless, more mechanistic studies are needed to unravel the complete reaction network, especially when involving a feed with high content of CO_2, CO, H_2 and H_2O. Recent investigations have even highlighted the presence of ketene intermediates in zeolite-catalyzed hydrocarbon conversions[45]. This presents a compelling case to simulate the complex reaction network by carrying out studies wherein possible intermediates are co-fed with reactants and the ensuing product distributions can help to pinpoint the extent of their influence on the reaction.



(1) desorption; (2) hydrocracking/isomerization; (3) hydrocracking; (4) oligomerization; (5) cyclization; (6) H transfer; (7) polycondensation; (8) isomerization; (9) hydrogenation.

Figure 3. Reaction routes for aromatics and iso-paraffins over H-ZSM-5 zeolite. Reproduced with permission from [28].

OVERVIEW OF THE STATE OF THE ART

Catalytic performance results for the production of hydrocarbons from CO_2 *via* bifunctional catalysis from research available in open literature are presented chronologically in Table 1. While additional publications exist[46-49], owing to their lack of distinction between the olefinic, paraffinic and aromatic components of the products formed, they have not been included in this abridgment.

Table 1. Comparison of bifunctional catalyst performance towards olefin and/or aromatic production.

Ref	Catalyst	Reaction Conditions[a]			Catalytic route	Catalytic Performance				
		T(°C)	P(bar)	GHSV ($ml.gcat^{-1}.h^{-1}$)		Conversion (%)	Sel$_{C2-C4=}$ (%)[b]	Sel$_{Arom.}$ (%)[b]	Sel$_{CO}$ (%)	Sel$_{CH4}$ (%)
[10]	Fused Fe/ HZSM5	350	21.7	60	RWGS	38.1	0.7	18.2	14.5	8.6
[11]	Cu-Zn-Cr/HY	400	50	3000	MeOH	35.5	~1.0[c]	--	~85.1	0.4
[12]	Fe-ZnO/HY	350	50	3000	RWGS	13.3	~6.0[c]	--	61.6	2.9
[13]	Fe-K/KY	300	10	1900	RWGS	21.3	23.2	--	26.5	11.2
[14]	Fe-Cu-Na/H-Mordenite	250	20	3000	RWGS	11.8	5.7	--	23.7	17.6
[15]	Fe-Zn-Zr/HY	360	50	3000	MeOH	17.2	4.7	--	53.2	1.4
[16]	Fe/NaY	300	10	1900	RWGS	20.8	22.6	--	29.4	10.2
[17]	Fe-Ce/KY	300	10	1900	RWGS	20.1	24.0	--	34.6	5.8
[18]	Zn-ZrO_2/ Zn-SAPO-34	380	20	3600	MeOH	~18.0	32.0	--	~48.0	2.1
[19]	Na-Fe_3O_4/ HZSM5	320	30	4000	RWGS	~34.0	~3.4	~36.5	~15.0	~6.9
[20]	In_2O_3/ HZSM5	340	30	9000	MeOH	13.1	~2.0	8.2	44.8	0.6
[21]	In_2O_3-ZrO_2/ SAPO-34	400	15	12000	MeOH	21.5	~9.0	--	90.0	0.8
[22]	$ZnGa_2O_4$/ SAPO-34	370	30	5400	MeOH	13.0	46.4	--	~49.0	--
[23]	In_2O_3-ZrO_2/ SAPO-34	400	30	9000	MeOH	35.5	~11.5	--	85.0	0.6
[24]	In-Zr/ SAPO-34	380	30	9000	MeOH	26.2	26.9	--	63.9	0.7
[25]	$ZnAlO_x$/ HZSM5	320	30	2000	MeOH	9.1	--	31.5	57.4	0.4

[a] CO_2:H_2 is equal to 1:3 in all cases except the first one where it is 1:2

[b] Total selectivity

[c] Selectivity of ethylene+propylene

To the best of our knowledge, Fujimoto and coworkers[46] were the first authors to combine a methanol synthesis catalyst with a zeolite in order to produce hydrocarbons from CO_2. Their focus was on the production of C_2-C_5 hydrocarbons by combining a Cu-Zn catalyst with a dealuminated Y zeolite. Analogously, Kuei and coworkers[10] were among the first authors to try to produce hydrocarbons from CO_2 via the RWGS route using multi-functional catalysis. They combined a fused Fe catalyst with an H-ZSM-5 zeolite and produced aromatics directly from CO_2. They were the first authors to report product yields of olefinic, paraffinic and aromatic components from CO_2 hydrogenation using bifunctional catalysis.

Fujiwara and coworkers[11] also reported the olefinic, paraffinic and aromatic components of their products using the MeOH route for hydrocarbon production from CO_2. Their catalyst was a combination of the multi-metallic Cu-Zn-Cr catalyst and the proton form of zeolite Y[12]. They reported high conversion of CO_2 (33.5%) but poor hydrocarbon yields due to high CO selectivities (>80%). This high CO selectivity is an intrinsic characteristic of the MeOH route and limits the hydrocarbon yield obtained *via* methanol intermediate. They followed up this work with an investigation into the RWGS route using an Fe-ZnO catalyst instead of Cu-Zn-Cr with zeolite Y. Although, the authors claim that the composite catalyst (Fe-ZnO+HY) is working as a methanol synthesis catalyst (as compared to standalone Fe-ZnO catalyst that is working as a FTS catalyst), we believe that the simple addition of a zeolite is unlikely to change the mechanism of CO_2 hydrogenation over the Fe-ZnO catalyst. The decrease in performance is likely due to the poisoning of Fe sites as hypothesized by Wei and coworkers[19] (*vide infra*). Due to milder temperature conditions, (350 ºC instead of 400 ºC) they obtained lower CO_2 conversion. However, owing to the switch to the RWGS route, they achieved less selectivity to CO (~60%) compared to their previous work and higher selectivity to light olefins.

Kim and coworkers[13] presented a very interesting configuration of a bifunctional catalyst. They impregnated alkali ion exchanged zeolite Y with potassium doped Fe to hydrogenate CO_2 via the RWGS route. They reported quite low selectivity to CO (26.5%) and among the highest selectivity to light olefins (23.2%) available in open literature using the RWGS route. Again, due to milder temperatures (300 ºC), they did not achieve very high conversion of CO_2. Their follow-up works achieved similar results with an Fe impregnated alkali ion exchanged zeolite Y[16] (using Na instead of K in this case) and an Fe-Ce impregnated alkali ion exchanged zeolite Y[17].

Until this point in time, the most commonly used zeolite in this area of research was zeolite Y. Xu and coworkers[14] were the first to report the use of mordenite zeolite in combination with a metallic catalyst for CO_2 hydrogenation. Since they used an Fe-Cu-Na catalyst together with the zeolite, the RWGS route dominated and consequently they obtained low CO selectivity (23.7%). Once again, due to the low temperatures used, they reported low conversion of CO_2 with modest selectivity to light olefins.

Tan and coworkers[15] combined a methanol synthesis catalyst with a zeolite for hydrogenation of CO_2. Their focus, however, was on the production of isobutane from CO_2 and therefore they did not obtain high olefin or aromatics selectivity. They studied various multi-metallic catalysts (combining Cr, Al, Ga, Zr with Fe-Zn) and concluded that the Fe-Zn-Zr catalyst combined with HY zeolite gave the best yield for isobutane.

Li and coworkers[18] used a combination of Zn modified ZrO_2 and Zn modified HSAPO-34 in order to achieve selective conversion to lower olefins from CO_2 via the MeOH route. Figure 4 gives a summary of their results. From Figure 4a, it can be inferred that in the tandem catalyst, ZnZrO generates methanol from CO_2 hydrogenation and the SAPO zeolite is responsible for the methanol to lower olefins conversion. These authors were able to further enhance the selectivity of lower olefins from 80% to 93% in the hydrocarbon fraction by increasing the space velocity from 3600 to 20000 mL/gcat/h, but the conversion is drastically reduced (see Figure 4c). Liu and coworkers[22] obtained similar results by using a combination of $ZnGa_2O_4$ and SAPO-34. However, in the latter case the selectivity towards light olefins was more pronounced (46.4%) in exchange for lower CO_2 conversions (see Table 1).

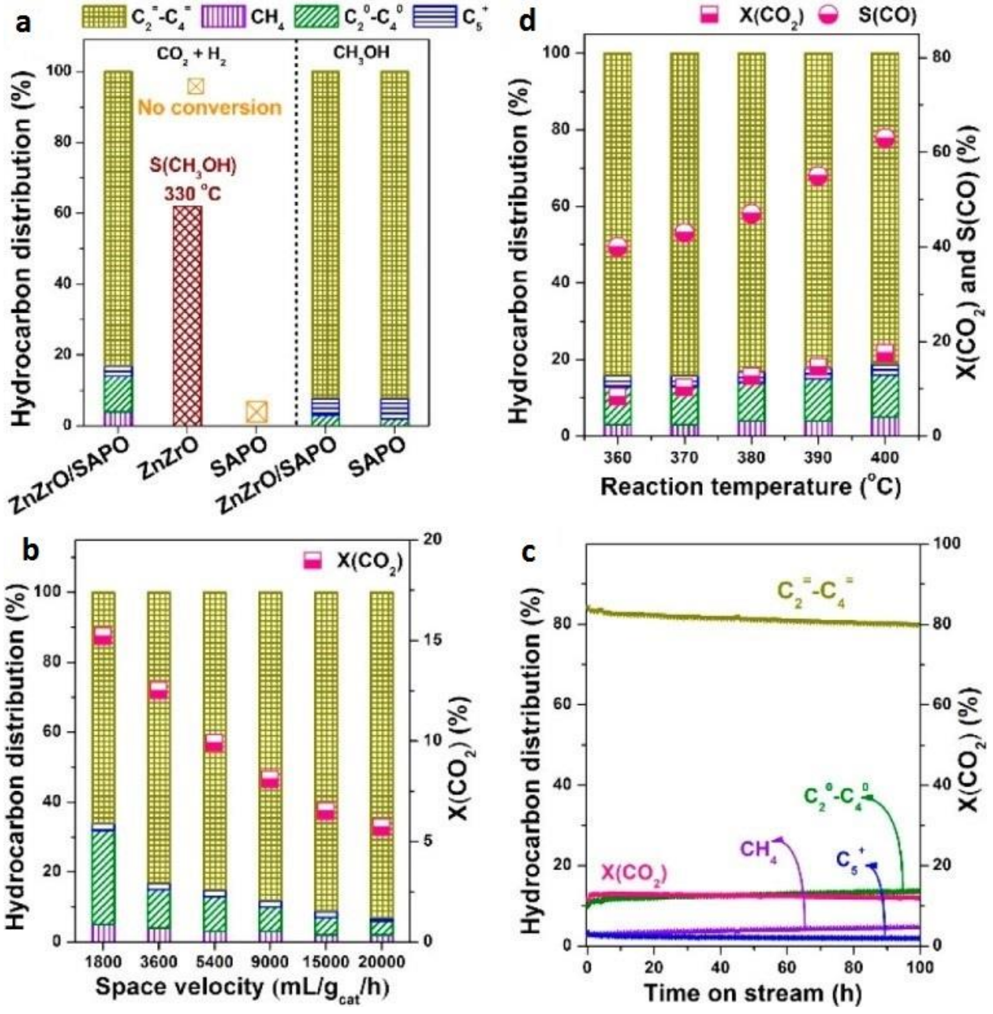


Figure 4. Catalytic performance in CO_2 hydrogenation: a) CO_2 hydrogenation on ZnZrO/SAPO, ZnZrO and SAPO and methanol conversion on ZnZrO/SAPO and SAPO. b) Hydrocarbon distribution and CO_2 conversion over ZnZrO/SAPO with different space velocity. c) CO_2 conversion over ZnZrO/SAPO, hydrocarbon distribution and CO selectivity at different reaction temperatures. d) Stability test for ZnZrO/SAPO. Reproduced with permission from [18].

Wei and coworkers[19] used a combination of Na modified Fe_3O_4 and ZSM5 to give one of the best results in terms of hydrocarbon yield from CO_2 hydrogenation to date. They achieved a high selectivity of ~61% towards the gasoline fraction (C_5-C_{11}) and the lowest CO selectivity reported until now (~15%). Figure 5 gives a summary of their catalytic performance results. It can be observed that the three types of zeolites with 10 member ring (MR) channels exhibit higher C_5–C_{11} selectivities, suggesting that 10 MR channels can favor the oligomerization of olefins and the production of C_5–C_{11} hydrocarbons.

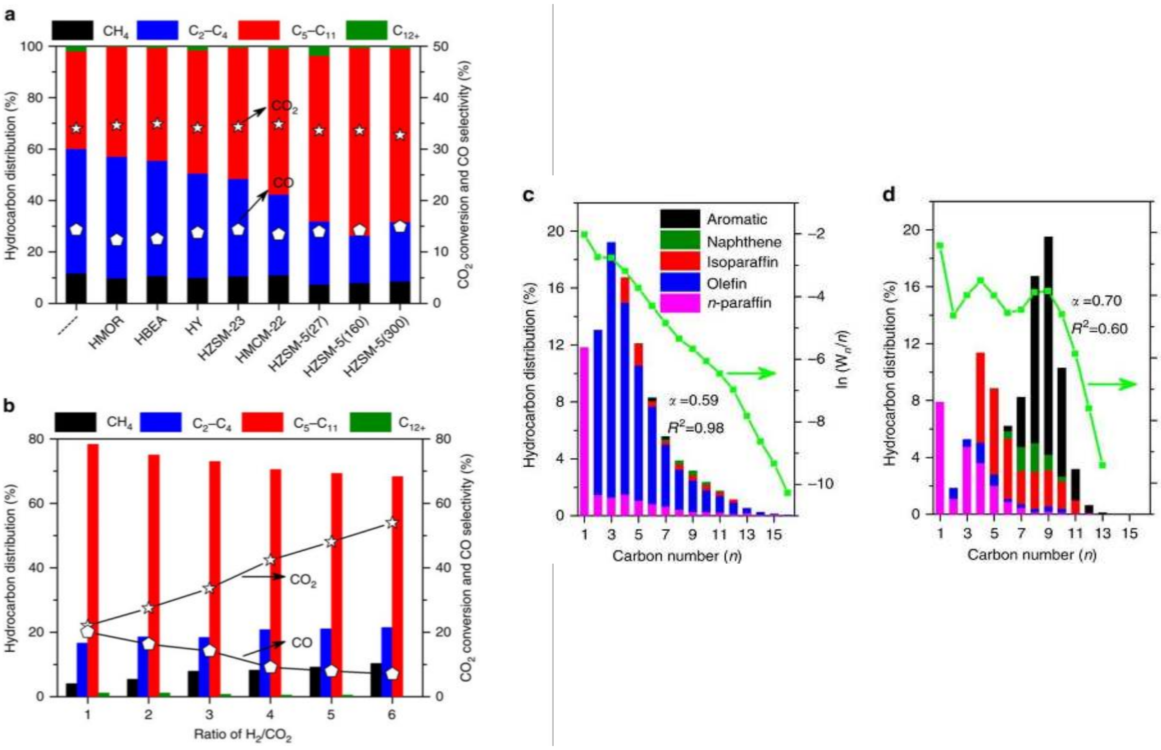


Figure 5. Catalytic performance in CO_2 hydrogenation: a) CO_2 conversion and product selectivity over different Na–Fe_3O_4/Zeolite catalysts. b) CO_2 conversion and product selectivity at different H_2/CO_2 ratios over Na– Fe_3O_4/HZSM-5(160) catalyst. c), d) The detailed hydrocarbon product distribution obtained over Na–Fe_3O_4 (c) and Na–Fe_3O_4/HZSM-5(160). d) catalysts, an additional ASF plot and a value comparison of above two catalysts are also depicted; W_n is the weight fraction of a product with n carbon atoms. Reproduced with permission from [19].

Gao and coworkers[20] also worked on production of hydrocarbons from CO_2 with a focus towards gasoline fraction selectivity. They, however, chose to take the MeOH route using a combination of In_2O_3 and HZSM-5. Although they achieved good selectivity towards the gasoline fraction in the hydrocarbon portion of products (~78%), owing to the high selectivity towards CO (~45%) their overall selectivity towards the gasoline fraction was limited (~43%). Additionally CO_2 conversion was much lower when compared with the RWGS route[16, 19].

The same group[23] and the group of Liu *et al.*[21] also studied the MeOH route to selectively produce light olefins (C_2-C_4) from CO_2 using a combination of In_2O_3-ZrO_2 and HSAPO-34. Although they achieved a high proportion of light olefins in the hydrocarbon fraction (~90% and ~80% respectively), the selectivity to CO was too high (>80%), limiting therefore the applicability of these catalysts. Recently, the former group[24] has improved the performance of its bifunctional catalyst by varying the In-Zr ratio. They reported their best yield of light olefins at an In:Zr ratio of 4:1. Moreover, they significantly improved their selectivity towards hydrocarbons by reducing CO selectivity from ~90% to ~64%.

Finally, Ni and coworkers[25] have recently reported a combination of ZnAlOx and HZSM-5, which yields high aromatics selectivity (73.9%) in the hydrocarbon fraction by following the MeOH route. However, the CO_2 conversion is only 9.6% and the CO selectivity is more than half of the total products (57.4%).

SUMMARY AND FUTURE OUTLOOK

With the use of zeolites, the products distribution obtained from classical CO_2 hydrogenation (either methanol or hydrocarbons *via* FTS) can be tuned by choosing the appropriate zeolite (with properties like particle size, pore size and Si/Al ratio affecting the product distribution).

The selection of the ideal route is complicated, as both have their advantages and disadvantages. The RWGS route has proven to be more productive with higher yields of olefins and/or aromatics, as high methanol selectivity from CO_2 can only be achieved at low reaction temperatures (usually lower than 300 ºC[30]), which in turn limits the CO_2 conversion and consequently the yield of products *via* the MeOH route. Moreover, the RWGS route has led to significantly lower selectivities to CO as compared to the MeOH route due to CO undergoing FTS reaction[19]. However, methane production is much more pronounced in the case of RWGS route owing to the mechanism of the FTS reaction, alongside the wider product distribution in comparison with the MeOH route. In addition, we have to take into consideration that aromatization reactions require higher temperatures (300-400 ºC olefins, 500-600 ºC paraffins) than Fisher-Tropsch (~300 ºC)[28], limiting the aromatics selectivity in the RWGS route. Therefore, the development of catalytic materials that can work at higher temperatures seems to be mandatory to achieve commercial implementation for both routes (*i.e* to achieve higher conversion in the MeOH route and to couple aromatization with FTS in the RWGS route).

The selection of the most suitable zeolite is another key parameter. H-ZSM-5 has proven to be unbeatable in aromatic production, while SAPO-34 is the preferred choice for olefin production. However, a very limited number of different zeolites have been studied (see Table 1), pointing to the possibility of there being a hidden winner among the more than 200 types of discovered zeolites[50]. Moreover, surface modification, acidity tuning and incorporation of secondary metal are also features to take into consideration. Surface modification and acidity tuning can affect the product distribution, as it has been reported that BTX selectivity can be enhanced by suppressing isomerization, disproportionation and dealkylation/alkylation reactions via surface/acidity modification[25, 34].

Incorporation of metals into zeolites can also assist in aromatization, involving a bifunctional process where metal species provide dehydrogenation sites leading to olefins, which are further converted to aromatics. For example, over gallium doped zeolites, gallium catalyzes the dehydrogenation of paraffins while the protonic sites catalyze olefin oligomerization and diene cyclization. However, gallium species can also catalyze undesired reactions like cracking and hydrogenation of olefins[51].

The configuration of the bifunctional catalyst also plays a major role in the product selectivity. Some authors have reported that the increasing the proximity of the two components shifts the equilibrium toward the desired products and hence increases the conversion[20, 34]. On the other hand, Wei and coworkers[19] reported that, when their Na–Fe_3O_4 and HZSM-5 catalyst were integrated by powder mixing, the close proximity between iron-based sites and zeolite acid sites turned out to be detrimental due to zeolite acid sites poisoning the alkali sites on the iron catalyst. The spatial arrangements of the metal oxide/zeolite bifunctional catalyst investigated have ranged from mortar mixing[20] (representing the closest proximity between metal catalyst and zeolite acidic sites) to dual bed configuration[19-20] (representing the furthest proximity) with powder mixing and granule stacking as the intermediate proximity options[19]. The optimal spatial arrangement could very well depend upon the hydrogenation route followed (RWGS or MeOH). Although not all the authors have explored the various spatial arrangements, very close proximity (i.e. mortar mixing) is usually detrimental to the catalytic performance regardless of the route. On the other hand, granule stacking and dual bed configurations seem to provide optimal site separation with the conversion and product distribution depending slightly on the configuration chosen. In summary, more comparative studies varying the spatial arrangement need to be carried out before a general conclusion can be arrived at.

Thus, unraveling the complicated reaction mechanism seems to be mandatory in order to develop more active and selective catalysts. Experimental and theoretical investigations involving model reactants in an atmosphere with CO_2, CO, H_2 and H_2O are needed, as these compounds can drastically change the classical MTH or aromatization networks. For example, CO not only functions as a reactant in the FTS pathway but also as a hydrogen acceptor to accelerate aromatization of dienes[34].

Looking forward, as research in all the fields involved – methanol synthesis from carbon dioxide, MTH and FTS – develops; strategic bifunctional catalyst development should also become more feasible. Bifunctional catalysis is a unique model; it requires at least double the effort for catalyst design – there are obviously more parameters to consider compared to a single catalyst system. It is imperative that this field continues to develop, as obtaining value-added chemicals from abundant greenhouse gas is a promising (partial) solution for a series of modern issues, such as global warming and fossil fuels depletion.

On an additional note, it has become common practice to not take the CO selectivity into account when presenting the product selectivities. Although some authors clarify that the selectivities reported are in the hydrocarbon fraction (i.e. selectivity on a "CO free" basis), the values reported still paint an unreliably optimistic picture of the catalyst performance. This practice can become especially fraught when "product distribution" and "selectivity" are used interchangeably. The CO produced implies a net CO_2 consumption and thus to avoid confusion, it behooves researchers to include the CO fraction in the overall selectivities. Last but not the least, we would like to emphasize that these approaches will only be of scientific curiosity unless efficient routes for the green generation of H_2 are developed. If this is achieved, we strongly believe that the combination of electrocatalysis for the production of H_2 in combination with thermal catalysis approaches as the ones described here have the potential to strongly impact our society.

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Notes

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QUOTES

"The greatest advantage of this bifunctional metal-zeolite configuration is that the product selectivity can be shifted to either light olefins (C_2-C_4) or aromatics by selecting the appropriate zeolite, overcoming many limitations of the standalone metal catalyst."

"Bifunctional catalysis is a unique model; it requires at least double the effort for catalyst design – there are obviously more parameters to consider compared to a single catalyst system."

"The CO produced implies a net CO_2 consumption and thus to avoid confusion, it behooves researchers to include the CO fraction in the overall selectivities."

"These approaches will only be of scientific curiosity unless efficient routes for the green generation of H_2 are developed"

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