

Review

Recent Advances in Catalysis for Methanation of CO₂ from Biogas

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Abstract: Biogas, with its high carbon dioxide content (30–50 vol%), is an attractive feed for catalytic methanation with green hydrogen, and is suitable for establishing a closed carbon cycle with methane as energy carrier. The most important questions for direct biogas methanation are how the high methane content influences the methanation reaction and overall efficiency on one hand, and to what extent the methanation catalysts can be made more resistant to various sulfur-containing compounds in biogas on the other hand. Ni-based catalysts are the most favored for economic reasons. The interplay of active compounds, supports, and promoters is discussed regarding the potential for improving sulfur resistance. Several strategies are addressed and experimental studies are evaluated, to identify catalysts which might be suitable for these challenges. As several catalyst functionalities must be combined, materials with two active metals and binary oxide support seem to be the best approach to technically applicable solutions. The high methane content in biogas appears to have a measurable impact on equilibrium and therefore CO₂ conversion. Depending on the initial CH₄/CO₂ ratio, this might lead to a product with higher methane content, and, after work-up, to a drop in-option for existing natural gas grids.

Keywords: CO₂ methanation; biogas; catalysts; deactivation; sulfur resistance



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1. Introduction

Carbon dioxide (CO₂) is the greenhouse gas that is considered to be the main cause of human-induced climate change [1]. It is one of the main by-products of industrial processes and energy production, such as power, heat, and transportation [2,3]. The main goal has to be the reduction of these emissions in order to eventually stop global warming. Whenever possible, biogenic energy sources should be used, as the CO₂ emitted from these processes was previously bound from the air during plant growth, thus creating an emission-neutral cycle of carbon use instead of releasing CO₂ from fossil energy sources. If the emissions from such processes cannot be reduced further by increasing efficiencies, reducing consumption, or using biogenic energy sources, it is also possible to capture and use the CO₂ produced in the process [3,4].

The conversion of CO₂ in carbon capture and utilization (CCU) processes to molecules like methanol, dimethyl ether, urea, or methane (CH₄) creates added economic value and reduces the consumption of the initially used, mostly fossil, energy sources by maximizing the utilization of carbon [5]. In this way, a reduction of emissions through a circular economy of CO₂ can be achieved. A major step towards defossilization can be taken by replacing fossil fuels with biogenic sources, and subsequently CCU for further processes, attaining so-called bioenergy with CCU processes (BECCU) [6,7].

Power-to-gas (PtG) processes, linking the electricity grid to the gas grid, are a promising way to produce fuels from CO₂ [8]. Even in a defossilized and heavily electrified future, some sectors are going to be reliant on carbon-based fuels due to their low potential for

electrification, such as aviation or heavy-duty transport on land and sea. In methanation processes, CH₄ is produced from CO₂ (or carbon monoxide, CO) and hydrogen (H₂), which stems from the electrolytic splitting of water (H₂O) into H₂ and oxygen (O₂) [9]. The production of methane from CO₂ is a relatively simple and robust synthesis, which can be carried out in small-scale plants and without the necessity of a large CO₂ point source. While methanation of CO is state of the art, using CO₂ as carbon source for synthesis of CH₄ only exists on a pilot scale today. One of the main arguments for technical methanation is that the existing large natural gas grid in many countries fulfills both the distribution and storage requirements of methane very efficiently [10].

To avoid greenhouse gas emissions from methanation, the electrolysis must be powered by electricity from renewable energy sources. At best, a biogenic source of CO₂ should be used to avoid greenhouse gas emissions. A promising biogenic CO₂ source is biogas. CO₂ is already present in biogas at high concentrations of 15–60 vol% [11]. Due to the high CO₂ content, the conventional carbon capture technologies can be used to separate CO₂ and use it in a downstream process. However, it is also possible to save the energy intensive step of carbon capture and to hydrogenate the biogas—including CH₄ and CO₂—directly [12].

CO₂ is thermodynamically very stable due to the highest oxidation state of the carbon atom and the linear structure of the molecule. Therefore, in direct biogas methanation, CO₂ must be activated biologically by suitable microorganisms or thermo-catalytically by high energy input and/or suitable catalysts in order to react with other molecules [13,14].

In addition to CO₂, biogas contains minor concentrations of sulfur compounds, ammonia, and organosilicon compounds known as siloxanes [15]. Such compounds, which often act as catalyst poisons, must be removed to use the biogas in a subsequent catalytic process. Sulfur-containing molecules are especially harmful, due to sulfur's high affinity for transition metals, occupying the active sites of methanation catalysts [16,17]. For the fine desulfurization of biogas, the adsorption process with activated carbon and/or metal oxides has become widely accepted, as this is one of the simplest and most cost-effective solutions for H₂S removal [18]. With such adsorbents, the H₂S concentration of biogas can be reduced to sub-ppm range [19]. Even after fine desulfurization, the catalysts are exposed to low concentrations of H₂S. Ni in particular is sensitive to sulfur-containing molecules down to the ppb range [20]. This shows that fine purification of the biogas is essential before catalytic utilization.

The major challenge in biogas methanation involves the catalyst-damaging trace components in biogas and the search for a catalyst resistant to those poisons. An additional interesting question is the impact of large amounts of CH₄ in biogas on methanation, when CO₂ is not separated from CH₄ prior to the reaction.

This article concentrates on the chemical processes in thermo-catalytic methanation. The goal of this review is to evaluate current research on the influences of various biogas components on CO₂ methanation catalysts, and to draw conclusions regarding which catalysts are suitable for direct biogas methanation.

2. Biogas Composition

The presence of catalyst poisons in biogas can be explained by the processes of biomass decomposition. Biogas is produced by the digestion of organic substrates by microorganisms under anaerobic conditions [21]. Any type of biomass composed of carbohydrates, cellulose and hemicellulose, proteins, and fats, can serve as the substrate for biogas production. During anaerobic digestion, the macromolecules mentioned are broken down by different microorganisms in four basic degradation steps, namely hydrolysis, acidogenesis, acetogenesis, and methanation, as shown in Figure 1 [22,23]. The resulting biogas is generally composed of 40–75 vol% CH₄, 15–60 vol% CO₂, and traces of H₂O, H₂, H₂S, O₂ (from desulfurization with air) and NH₃ [11].

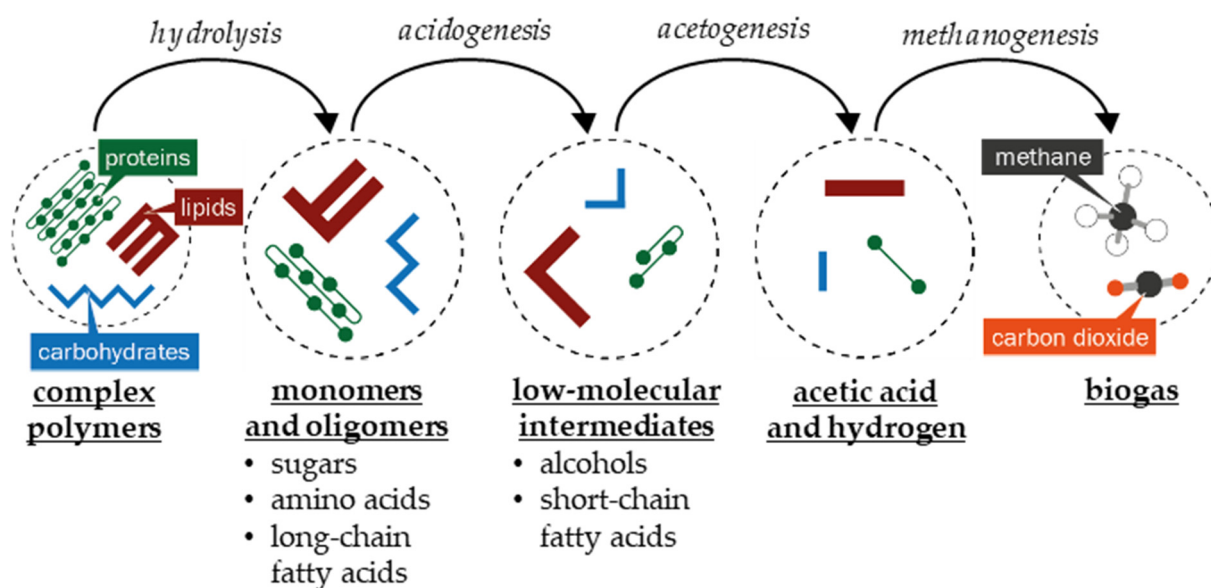


Figure 1. Sequence of decomposition products from the four steps of biogas production: hydrolysis, acidogenesis, acetogenesis, and methanation [23].

Waste biomass from agricultural or urban areas is particularly suitable for biogas production, as this avoids competition with the use of biomass as food. The exact composition of biogas is highly dependent on the used substrate or substrate mixture. For example, increased levels of H_2S and other volatile sulfur-containing compounds such as mercaptans (R-SH) are seen in biogas when agricultural waste materials are used. The use of animal waste, e.g., chicken manure, results in high NH_3 concentrations in the product gas [24]. Both H_2S and NH_3 are degradation products of proteins and their amino acids during acidogenesis [23,25]. H_2S is only formed from the sulfur-containing amino acids cysteine and methionine, and NH_3 is, among other reactions, a product of the Stickland reaction. In this redox reaction, two amino acids are degraded to acetate over several reaction steps [23].

Utilizing urban biomass such as municipal waste or sewage sludge adds other components to the biogas. For example, more halogenated hydrocarbons can be detected in the biogas from the fermentation of unsorted municipal waste, which can be traced back to plastic waste. In biogas from sewage sludge fermentation, particularly high concentrations of siloxanes are found. They enter the wastewater, for example, through the use of detergents and in the production of cosmetics [24]. In some cases, low concentrations of O_2 and N_2 can also be found in biogas. These are due to biological desulfurization, in which air is usually fed directly into the digester to oxidize sulfur-containing components to solid sulfur, thus separating them from the produced gas [11].

More detailed specifications of the expected biogas compositions obtained from agricultural waste, residual waste, biowaste, and sewage sludge are summarized in Table 1. The concentration ranges given in the table refer to the middle 60% of the measurement results [25,26]. The concentrations measured in each case were sorted in ascending order and evaluated without the highest and lowest 20% of the measured values. Thus, the table shows the mainly occurring concentration of the individual components. For a more detailed evaluation, including the maximum and minimum measured values and the median, please refer to [26].

Table 1. Average concentrations of the individual biogas components for different substrate groups, according to [26].

Compound	Unit	Agricultural Waste ¹	Residual Waste ²	Bio Waste ³	Sewage Sludge ⁴
CH ₄	vol%	52–57	59–64	58–61	63–65
CO ₂	vol%	36–48	33–38	39–41	35–37
O ₂	vol%	<2	<0.5	<0.6	<0.2
N ₂	vol%	0–4.5	0–2.2	1.4–1.6	0.2
H ₂ S	mg/m ³	10–560	5–320	390–860	5–20
R-SH	mg/m ³	0–5	1–8	3–5	1–2
NH ₃	mg/m ³	0–12	2–15	<2	<1
H ₂	ppmv	10–500	50–390	100–190	120–350
BTEX	mg/m ³	<2	<90	<3	<39
Si	mg/m ³	<2	<2	<2	4–15

¹ including renewable resources and farm manure; ² e.g., residues from food and feed production, residues from processing agricultural commodities or garden waste; ³ from organic waste garbage can; ⁴ from municipal wastewater treatment.

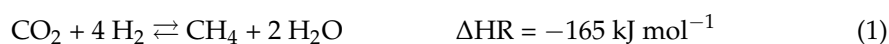
Should biogas be used for direct combustion of the methane fraction in combined heat-and-power plants, the minor components of biogas would lead to adverse properties of the gas. The presence of CO₂, H₂O, NO_x, and N₂ results in a reduction of the calorific value [27]. Therefore, these components should be separated or, in case of CO₂, be upgraded by the addition of H₂ to raise the CH₄ content. Components that should be considered critical for downstream processes include H₂S, NH₃, halogenated components, and siloxanes. H₂S, NH₃, and halogenated components have a corrosive effect on reactors or combustion engines in combination with water, and must be removed from the biogas to enable a long service life of the equipment [28]. The harmful effect of siloxanes arises from the reaction to microcrystalline SiO₂, which is deposited on hot surfaces, where it causes abrasion or blocking [27,29,30]. Siloxanes are also possible catalyst poisons for downstream processes, as they might cover catalyst surfaces and block active sites [27].

The most prominent catalyst poisons in biogas are H₂S and sulfur-organic compounds. Due to the high affinity of sulfur for transition metals, active sites of the catalyst are irreversibly occupied by strong chemisorption, leading to catalyst deactivation [17].

Knowledge of the biogas composition is important for selecting a suitable cleaning step prior to subsequent combustion or catalytic processing. To exploit biogases with a high content of sulfur-containing substances for catalytic downstream processes, further research should be conducted on sulfur-resistant catalysts.

3. CO₂ Methanation

CO₂ methanation (Equation (1)) can run directly or via CO as gaseous intermediate. In the second case, CO is formed by reverse water gas shift reaction (Equation (2)) followed by CO methanation (Equation (3)).



There is no consensus on the reaction mechanism of CO₂ methanation. For the direct CO₂ methanation, two main mechanisms are described. For one, the CO route with surface CO* intermediate species, and for the other, the formate route without intermediate CO [31]. However, if the reaction proceeds via CO as an intermediate (so-called carbide mechanism), reaction networks in which formate or carboxyl intermediates are formed have also been observed [32]. The carbide mechanism proceeds from CO₂ via CO either to C (carbide) + O (not shown here) or to OCH₂ and OCH₃ as intermediates, which are hydrogenated to CH₄

(Figure 2) [31,33,34]. The formate mechanism proceeds from CO_2 via CO , HCOO^- , and C to CH_4 [31]. Some groups also describe a formate route via methanol (Figure 3) [35]. However, the actual mechanism depends strongly on the catalyst's properties.

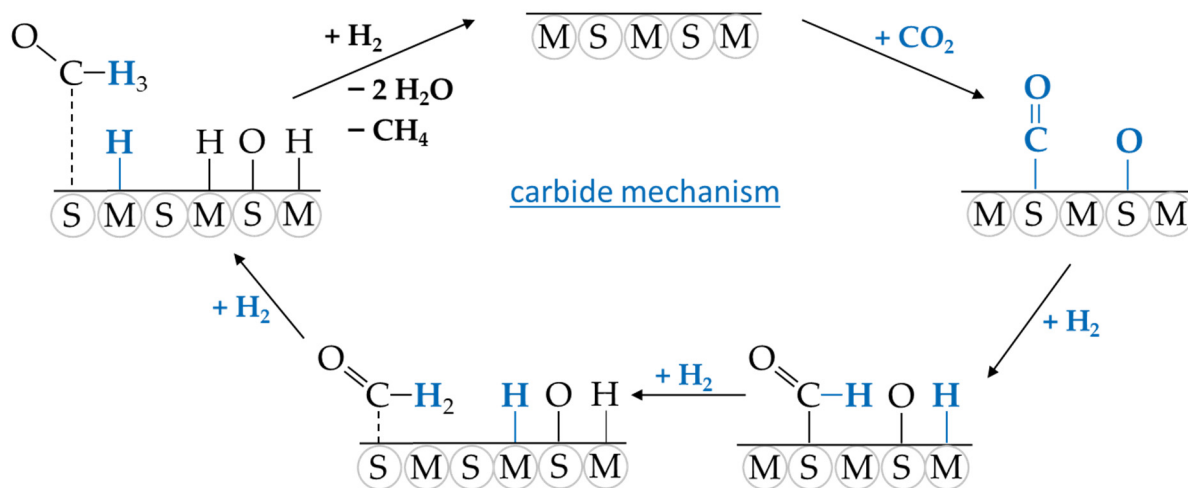


Figure 2. Proposed elementary steps with M = active metal and S = support for H_2 -assisted carbide mechanism [34].

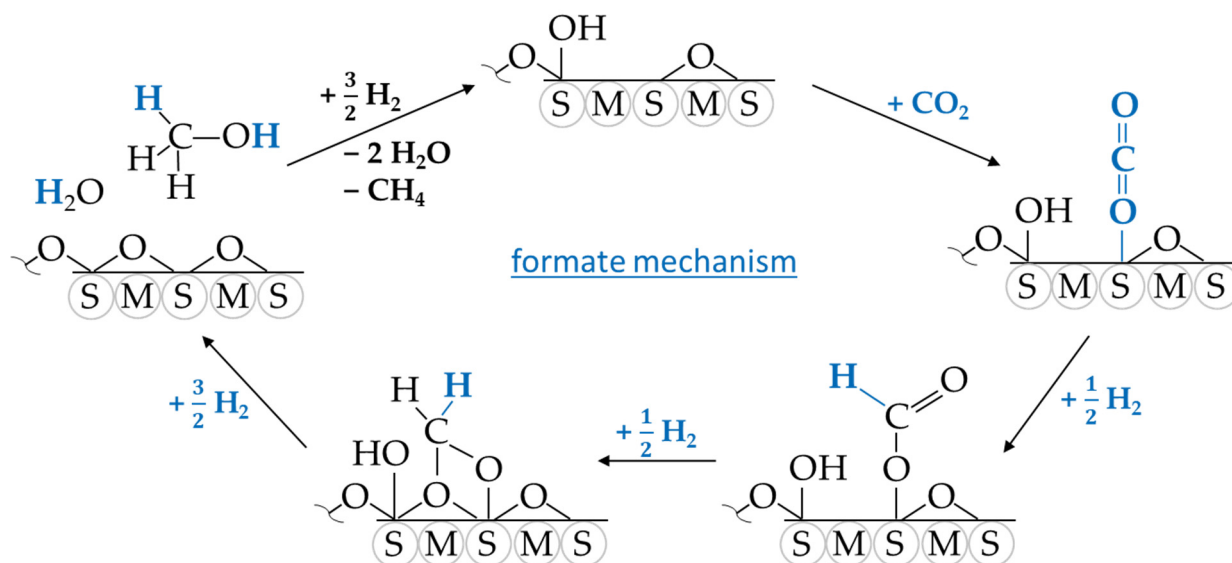


Figure 3. Proposed elementary steps with M = active metal and S = support for formate mechanism over Ru/CeO_2 [35].

Due to the exothermic character and the volume reduction during CO_2 methanation, the equilibrium is shifted towards CH_4 , according to Le Chatelier's principle, at low temperatures and high pressures. Nevertheless, the thermodynamically very stable structure of CO_2 requires high activation energy. This is based on the fulfillment of the octet rule for each of the three atoms by the double bonds between carbon and oxygen atoms, and the two lone pairs at the oxygen atoms [36]. In addition, the reduction of CO_2 to CH_4 represents an eight electron process, which limits the reaction kinetically at low temperatures [37]. Therefore, temperatures above $200\text{ }^\circ\text{C}$ are necessary to achieve sufficiently high reaction rates [38]. To overcome these activation barriers and to reach high CO_2 conversions at sufficiently low temperatures, which is preferred because of the conditions of equilibrium, catalysts are required [39].

The key challenge for catalytic methanation with CO₂ is finding a suitable catalyst with high activity at low temperatures [40,41]. Considering the high exothermic heat of the reaction, an effective heat management in the reactor is essential. Temperature hot spots might shift the equilibrium to unfavorable conditions, leading to catalyst deactivation by sintering, active metal agglomeration, coking via methane decomposition, or end in the worst case with reactor runaway.

4. Catalysts for Biogas Methanation

The direct methanation of biogas without prior separation of CO₂ from CH₄, which is referred to in the following as direct biogas methanation, is intended to take place at biogas plant sites and thus at small CO₂ point sources. Besides having efficient plant conditions for the technology to be commercially viable, a high-performance catalyst providing high conversions, high selectivity, long lifetime, and a competitive price is crucial. Due to the possible presence of catalyst poisons such as sulfur-containing components even in purified biogas, the catalysts used for direct biogas methanation require a certain resistance to sulfur.

In most cases, methanation catalysts are composed of active metal particles that are finely distributed on an oxidic support material [42]. By supporting the catalytically active particles and thus dispersing them well on the surface of the support, the active surface area and the respective number of active sites is increased. The resulting interface between the substrate and the active metal also plays an important role, since H₂ dissociation occurs at the active metal, and CO₂ is mainly activated by the support [43,44]. Due to the spatial proximity of the activated species, the methanation reaction can proceed more easily at this interface. The introduction of one or more additional metals as promoters can improve both the dispersion of the active metal and the catalytic performance in general [45]. Besides the selection of the active metal, a suitable support, and optional promoters, the concentrations of the respective components play a major role [42,45]. Likewise, the preparation method can influence the catalytic activity, as it affects the particle size of the active component and the metal-support interactions [42,46]. Since the composition of a suitable catalyst is crucial for achieving high conversions and yields in methanation, the individual components of methanation catalysts are discussed in more detail (Sections 4.1–4.3). Materials, which can lead to improved S-compatibility of the catalyst, are discussed in Section 4.5.

4.1. Active Metal

There are several metals that catalyze CO₂ methanation, especially transition metals from groups 8 to 10 [46]. Below are the descending series of activity and methane selectivity [46,47]:

$$\text{Activity Ru} > \text{Fe} > \text{Ni} > \text{Co} > \text{Rh} > \text{Pd} > \text{Pt} > \text{Ir}$$
$$\text{Selectivity Pd} > \text{Pt} > \text{Ir} > \text{Ni} > \text{Rh} > \text{Co} > \text{Fe} > \text{Ru}$$

Noble metals such as Ru, Rh, and Pd lead to high CH₄ yields, because these metals are active in H₂ activation at low temperatures. This correlates well with the low temperature level of the thermodynamic equilibrium, leading to an easy formation of CH₄ [48]. Despite the high activity or selectivity of noble metals, they are rarely applied in industry due to their high cost [41,46]. If the price is neglected, Ru would be the most suitable active metal for methanation, especially at low temperatures [46]. Cheaper alternatives include Fe, Co, and Ni, with Ni being the most studied active metal for methanation to date, because of its competitive high activity and selectivity to CH₄ [49,50]. In experiments up to 800 °C, other transition metals (Mo, Ag, Os, Ir, Pt) also showed methanation activity for carbon oxides. However, the list of important metals for methanation can be shortened due to the high cost by most of the noble metals to Fe, Co, Ni, Mo, and Ru [51]. Of these metals, the methanation activity of Ru is the highest, followed by Ni, Co, Fe, and Mo [51].

4.2. Support Material

Supports influence the adsorption capacity and morphology of the active phase, which can increase the catalytic activity [45]. Acidic or basic sites are often provided by supports rather than the metals. The related metal-support interaction might strongly affect metal activity, dispersion, and stabilization [52]. High basicity is also advantageous for CO₂ activation as CO₂ chemisorption is facilitated [48]. In some cases, active metals might even form new crystalline phases with support materials, e.g., highly stable Ni spinels [53]. Among the most studied supports are Al₂O₃, SiO₂, TiO₂, MgO, CeO₂, and ZrO₂ [41,42]. The use of mixed oxides composed of two of the aforementioned support materials may potentially increase the reducibility of the active phases or the stability of the catalysts [1].

The formation of spinels and solid solutions, e.g., between Al₂O₃ and MgO, is well known [53]. Their presence can stabilize Ni/Al₂O₃ [54], and thus high dispersion at high temperature stability can be achieved. Another example is the combination of CeO₂ and ZrO₂, which has already been studied [42,55–57]. Synergistic effects occur between the two oxides, bringing out the advantages of both support materials. CeO₂ in general is a special support material due to its fluorite crystal structure. These crystal structures consist of a face-centered cubic packing of Ce⁴⁺ cations with all tetrahedral vacancies occupied by O²⁻. The reduction of CeO₂ leads to the formation of free oxygen vacancies on the surface of the crystal lattice, where oxygen can be easily stored and released. They also facilitate the adsorption and activation of other oxygen-containing molecules, such as CO₂ [35,57,58]. It was found that the methanation reaction with CeO₂-supported Ru catalysts proceeds via the formate mechanism, in which formate is formed as an intermediate and hydrogenated subsequently (Figure 3). In contrast, this reaction pathway was not observed in an analogous experiment with Ru supported on Al₂O₃. Instead, CO was formed as intermediate (Figure 2) [35]. The addition of ZrO₂ to CeO₂ changes the crystal structure from a cubic lattice to a tetragonal crystal lattice with increasing ZrO₂ concentration [57]. This results in an enhanced formation of oxygen vacancies due to easier reducibility and higher oxygen mobility in the crystal lattice [1,57]. In addition, cations of the active metals can be better incorporated into the lattice, where ZrO₂-induced defects are present [57]. In summary, this leads to a high concentration of oxygen vacancies, high dispersion of the metal, and basic properties with the mixed CeO₂-ZrO₂ support [55].

4.3. Promoters

Generally, alkali and alkaline earth metals, transition metals, and rare earth metals are used as promoters. They can incorporate into the crystal lattice in ionic form, or deposit on the surface of the catalyst as oxides [48]. Such compounds act either electronically or as the structural promoter for metal dispersion and thermal stability. Another powerful effect is the modification of acid/basic sites on the catalyst surface by selective blocking (poisoning). The effects of the most investigated promoters for CO₂ methanation are listed in Table 2. The active metals described in Section 4.1 can also be used as promoters. The promoter weight percentage is typically far below that of active metal or support [42].

An example of a promoting effect is the facilitated activation of CO₂ due to increased basicity at the surface of the catalyst [48]. The dispersion of the active metal is also improved by most promoters, as well as the metal-support interactions in general [45].

Table 2. Common promoters used in catalysts for CO₂ methanation and their effects.

Promoter	Effect	Source
Fe	<ul style="list-style-type: none"> • higher activity at low temperature • higher reducibility of Ni • facilitated CO₂ adsorption 	[1,48]
Co	<ul style="list-style-type: none"> • higher activity at low temperature • facilitated CO₂ adsorption • lower carbon deposition and sintering of metal particles • lower activation energy required for CO₂ activation 	[1,48]
Ru	<ul style="list-style-type: none"> • higher dispersion of active metal • higher reducibility of Ni • higher basicity • higher activity at low temperature • facilitated CO₂ and H₂ activation 	[48]
Mg	<ul style="list-style-type: none"> • lower carbon deposition and metal particle sintering • resistance to water • higher thermal stability • stabilization of Al₂O₃ support when H₂O is present • facilitated CO₂ activation 	[2,44,45,59]
Mn	<ul style="list-style-type: none"> • higher adsorption capacity for CO₂ • higher reducibility of Ni and stabilized metal surface of Ni⁰ • higher dispersion of active metal • higher number of moderate basic sites 	[1]
Ce	<ul style="list-style-type: none"> • higher dispersion of active Ni phase • higher activity at low temperature • lower metal particle sintering • lower S deposition on active metal • stabilization of Al₂O₃ support when H₂O is present 	[42,60–62]
Zr	<ul style="list-style-type: none"> • higher dispersion of active metal • higher reducibility of Ni 	[39]
Mo	<ul style="list-style-type: none"> • higher sulfur resistance 	[63]

In addition to improving effects, however, promoters can also have inhibiting effects. The concentration of the used promoter and the type of promoter itself play an important role. For example, if K is added to Ni, the reaction to higher hydrocarbons is facilitated [36,46]. The methanation is thus inhibited, which is why K is not suitable for CO₂ methanation. Adding Cu is also unsuitable for CO₂ methanation with Ni-based catalysts, as the NiCu alloy does not adsorb H₂, and thus inhibits the hydrogenation reaction [48]. Regarding the concentration of promoters, volcano-shaped curves are often observed for the activity of the catalyst, meaning that the activity increases up to a certain concentration of promoter and then decreases at higher concentrations [36,64].

4.4. Deactivation of Catalysts

The relevant chemical, thermal, or mechanical mechanisms of catalyst deactivation are deeply discussed in, e.g., [63]. These effects might be reversible or irreversible, and Table 3 gives a short overview.

Most metal catalysts with acceptable methanation activity (cf. Section 4.1) are extremely sensitive to sulfur-containing compounds, and will inevitably deactivate over time in presence of H₂S. Such chemical poisoning occurs predominantly via the dissociative adsorption of H₂S on metal surfaces.

This effect was extensively investigated for Ni, as it serves as an active metal in highly important processes for hydrogenation of feedstocks contaminated with sulfur compounds. The poisoning by H₂S is evident in the ppm range and even below. At such low partial pressures with a low degree of surface coverage, sulfur is up to three times more strongly bound to Ni than in bulk sulfides, and blocks the surface very effectively, as a single S atom interacts with several Ni atoms [63,65]. Sulfur preferably adsorbs at the defect sites of Ni particles, which are the active sites [66]. In the worst case, nearly complete coverage can occur at 0.1–1 ppm H₂S. This hinders the desired adsorption and activation of H₂, and explains the extreme deactivation of Ni by sulfur. The poisoning effect of H₂S is very strong and almost irreversible, as stable sulfides like NiS or Ni₃S₂ can eventually form [63].

Similarities exist between methanation and the dry or steam reforming of methane (reductive mixtures of CO₂, CH₄, H₂, CO, H₂O at high temperature, Ni catalysts, traces of sulfur). The presence of various sulfur compounds adsorbed on Ni and Rh catalysts supported on CeO₂-Al₂O₃ during steam reforming was proven by XANES (X-ray absorption near edge structure) measurements [67]. At temperatures up to 800 °C, four major sulfur species were detected: metal sulfides, organic sulfides with C-S-C bonds, sulfonates -RSO₂O⁻, and sulfate. Rh clearly outnumbered Ni regarding S resistance at 800 °C. In that study, some sulfur compounds were formed exclusively on either Ni or Rh. This points to a much higher complexity of surface S chemistry and poisoning. In the absence of sulfur, the carbon formation rate was low, while in the presence of sulfur the carbon deposition contributed 2/3 to deactivation. This points to a strong effect of sulfur on the carbon chemistry of Ni catalysts, which lowers the number of reactive carboxyl groups necessary for carbon gasification compared to Rh. Within a few hours the initial deactivation by S poisoning of Ni leads to sulfides, and subsequently unreactive carbon is formed [67].

Carbon formation, as the second major deactivation mechanism over Ni-based catalysts, leads to different types of deposits (filaments, encapsulating and pyrolytic carbon) [63]. Almost each of the effects described in Table 3 is relevant: chemisorption, physisorption, blocking the active metal surface by coverage, encapsulation, or pore plugging. The presence of hydrocarbons in the biogas feed will drastically increase the formation of carbon filaments. This can be partially suppressed by high Ni dispersion.

CO₂ methanation typically runs at a high temperature and concentration of formed H₂O as described in Section 3. Both are known to cause Ni sintering. Effective catalysts should be active at temperatures below 400 °C (at the cost of poor energy recovery) and stable against sintering and coking up to 700 °C [42]. Carbon formation and sintering can be prevented mainly by two approaches: setting optimum reaction conditions (temperature, pressure, H₂ partial pressure) and catalyst modification.

In contrast to poisoning by sulfur, some of the carbon-mediated effects are reversible, and deposited carbon can be removed by gasification with H₂, O₂ or H₂O at high temperature. Comparing the deactivation effects caused by S-compounds and C-compounds, the first is the bigger challenge in the application of metal catalysts for biogas methanation, since the deactivation effect is strong and catalyst regeneration is difficult.

In this context, it must be mentioned that sulfur compounds also interact with the metal surfaces of metallic construction materials (including Ni) following the described mechanisms. This may require additional measures, such as the inertization of pipes, reactors, and analytical equipment. On such sulfided surfaces, hydrocarbons may react to oligomers and finally carbon deposits [68].

Ni catalysts react under certain conditions with CO and may form volatile Ni carbonyl Ni(CO)₄ at temperatures up to 300 °C [63]. Thus, the CO partial pressure must be minimized as far as possible.

4.5. Increasing Sulfur Resistance

The sulfur resistance can be modified by measures that either focus on the catalyst or the process [65]. Considering the described sensitivity of the conventional methanation catalysts against sulfur, a proper process design is the most effective way to lower the sulfur

content to 0.1 ppm at the reactor inlet. This can be achieved at comparatively low cost with upstream ZnO adsorbers operated at 200 °C, which trap sulfur as ZnS. Thereby, the catalysts can reach lifetimes of 1–2 years. Alternatively, with an oversized bed of a cheap catalyst, the lifetime of the reactor load might be elongated as well [63].

Based on these ideas, several advanced catalyst concepts have been discussed. The trapping concept was demonstrated with a Ru/CeO₂ catalyst immobilized in a micro-structured reactor by adding Ni as sulfur trapping component. This improved the catalyst stability in CO₂ methanation with 1 ppm H₂S [69]. Changing the reaction conditions (temperature, pressure, feed composition) offers some potential to influence the adsorption equilibria on the catalyst surface. Other sulfur adsorbing sites such as Zn or Ce may be added to the catalyst to decrease the poisoning. This could have a similar protective effect as upstream traps. A similar approach is to create mass transfer limitations that stop poisons at the surface before entering the pores with the active metal sites (core-shell catalysts, protective layers [63]). Interestingly, among several Al₂O₃-supported mono- and bimetallic Ni and Co catalysts, monolith-type catalysts showed higher S tolerance compared to pelletized or powder catalysts at 525 °C with 10 ppm H₂S in the feed, although complete deactivation was reached within 2–3 days [70].

When modifying the catalyst, proper choice of the active metal, and the support and promoters, are possible factors to achieving higher stability. Numerous studies varied the innumerable compositions as well as the preparation and pretreatment parameters, e.g., to reduce the strength of poison adsorption by catalyst modification.

4.5.1. Active Metal

Several strategies have been reported to prepare monometallic Ni catalysts with improved sulfur resistance. Avoiding defect sites, e.g., by using plasma techniques, has been proposed [42,71–73]. Thereby, improved S-tolerance of a 10% Ni/SiO₂ catalyst for CO methanation with smaller Ni particle size, less defects, and enhanced metal-support interaction was obtained. The catalyst was tested with 10 ppm H₂S up to 500 °C. In particular, the low-temperature activity was improved, and carbon formation (encapsulation) was decreased [71].

Weakening the interaction between sulfur and the metal can be improved by using bimetallic catalysts like Ni-Ru with small cluster sizes. The lifetime of a Ni-Ru/SiO₂ catalyst for CO methanation was significantly improved by using polyethylene glycol as an additive during preparation, and exceeded the stability of separated Ru and Ni/SiO₂ catalysts [74]. This was explained by geometric factors: H₂S adsorption was weaker when interacting with Ni and Ru simultaneously, and the small metal particles were more stable against sintering, which lowered the carbon formation. Thus, catalyst lifetime was extended to 400 h.

Regarding energetic and electronic aspects, DFT (density functional theory) calculations are an excellent approach to estimating the adsorption energies of sulfur or carbon containing compounds on metal surfaces. Adding Ni to a Rh catalyst for CO methanation significantly changes the S adsorption and CO dissociation energies, which results in lower sulfur coverage, thereby increasing catalyst stability [75]. The combination of DFT calculations and experiments in steam reforming on Ni-Ru, Ni-Sn, and Ni catalysts (Ni/M = 3) supported on Al₂O₃ in the presence of H₂S, identified bimetallic surfaces with lower H₂S adsorption energies and enhanced adsorption of hydrocarbons [76].

Beyond the mentioned metals used in hydrogenation catalysts, which are deactivated by sulfur, some metals such as Mo or W can form various materials with different oxidation states, which promote redox reactions as well. Some of them are known to form active phases with much better sulfur tolerance. Co-Mo and Ni-Mo (W) supported on γ -alumina are state-of-the-art hydrodesulfurization (HDS) catalysts, which can cope with sulfur contents of 1000 ppm and more [67,68,77]. The active phase MoS₂ is easily accessible from MoO₃ precursor via in situ sulfurization, e.g., with dimethyl disulfide or H₂S, and shows highest HDS efficiency in the temperature range of 380–400 °C. This matches the preferred

temperature range of methanation. MoO_3 precursors might form tetrahedral, octahedral, and crystalline phases on Al_2O_3 depending on preparation and calcination methods. In addition, $\text{Al}_2(\text{MoO}_4)_3$ species form above 600 °C [78]. MoS_2 is catalytically active in methanation. A special advantage of Mo catalysts is that they can be operated in methanation at much lower H_2/CO ratios than Ni-based materials unless steam is added to prevent carbon deposition [79]. These findings offer the potential to develop S-resistant catalysts [42,80,81]. However, the activity of Mo for methanation is still lower compared to other metals. The highest CO conversion of 46% was achieved at 560 °C with a $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst obtained via the incipient wetness method. Moderate deactivation was observed over 45 h on stream in the presence of 0.24 vol% H_2S [78]. Modification of a Ni/ Al_2O_3 catalyst for methanation of CO with Mo led to improved activity even with 10 ppm H_2S [70]. The combination of 50% Ni and MoO_3 on Al_2O_3 support showed acceptable catalytic performance in the methanation of CO_2 -rich gas from biomass gasification in the presence of 10 ppm H_2S [82]. The nature and amount of the poisoning sulfur species (sulfide, sulfate) were analyzed by XANES and temperature-programmed oxidation, respectively. It was observed that the poisoning was due to thiophene, but not H_2S . Total run times of 100 h were achieved.

To develop such sulfide catalysts, several obstacles must be tackled: (1) classical HDS catalysts permanently lose sulfur during hydrogenation in form of H_2S , which must be replenished by continuously feeding low concentrations of S compounds; (2) the possible activity of such catalysts in the oligomerization of carbon species on the catalyst surface; and (3) the acidity of such metal sulfides.

4.5.2. Support

One very important support feature is acidity, which governs the adsorption and desorption of sulfur compounds [74]. With Ni as active metal, the sulfur tolerance decreases in the order $\text{CeO}_2 > \alpha\text{-Al}_2\text{O}_3 > \text{TiO}_2 > \text{MgO}$ [44,69]. CeO_2 is known for its redox properties, and introduces basic sites for CO_2 activation [83], while Al_2O_3 provides high surface area and thermal stability. The effect of the promoter CeO_2 on the S-resistance of Ni/ Al_2O_3 was investigated in CO_2 methanation [84]. As with other promoters, CeO_2 helps in dispersing Ni by forming smaller crystallites and hindering their growth. Such mixed $\text{CeO}_2\text{-Al}_2\text{O}_3$ supports are effective at slowing down Ni deactivation during CO_2 methanation at 300 °C in the presence of 0.4 ppm H_2S [85]. The improved sulfur resistance was explained by the formation of $\text{Ce}_2\text{O}_2\text{S}$. This phase is thermodynamically preferred over NiS, with the reaction to sulfided CeO_2 occurring spontaneously over the entire temperature range. As a result, the catalytically active Ni sites remain stable for a longer time, even in the presence of S compounds [62]. However, the Ni/ $\text{CeO}_2\text{-Al}_2\text{O}_3$ catalyst deactivated rapidly in less than 60 h. Interestingly, CeO_2 doped with rare-earth metal (La, Gd, Sm, Nb, Y) was reported to be active and stable in the steam reforming of biogas and other feeds in the presence of H_2S , even at 900 °C [86]. This proves the importance of O mobility in the catalysts.

TiO_2 -supported noble metals Pt and Rh were also described as S-resistant catalysts, which was attributed to oxygen vacancies such as those present in the CeO_2 lattice. H_2S can be incorporated into these vacancies [71,87]. In general, the acidity of the support material plays a major role in sulfur adsorption, with the less S being deposited, the more acidic the surface.

Using Ru as active metal (5 wt%) on various supports in micro-structured reactors showed an activity ranking $\text{SiO}_2 > \text{CeO}_2, \text{TiO}_2$ in CO_2 methanation with 1 ppm H_2S [69]. However, the initial activity of the catalysts drastically dropped within 50 h at the latest.

As mentioned above, the obvious combination of sulfur-resistant MoO_3 with $\gamma\text{-Al}_2\text{O}_3$ gives comparatively low activity. A more suitable support is required, since Mo strongly interacts with the basic OH sites of Al_2O_3 support, which is disadvantageous for the formation of the active MoS_2 phase [88]. Using MoO_3 and a binary $\text{CeO}_2\text{-Al}_2\text{O}_3$ support via co-precipitation preparation, stable CO methanation over 40 h was achieved [89].

Table 3. Types and mechanisms of catalyst deactivation [63].

Mechanism	Type	Description
Poisoning	Chemical	Species adsorb strongly on catalytic sites and block them for reaction
Fouling	Mechanical	Physical deposition of species on catalytic surface and in pores
Thermal degradation and sintering	Thermal Thermal/chemical	Thermally induced loss of catalytic surface area, support area, and active phase support reactions
Vapor formation	Chemical	Loss of catalyst compounds by reaction with gas
Vapor-solid and solid-solid reactions	Chemical	Reaction of catalyst compounds among each other or with gas leading to deactivation
Attrition/crushing	Mechanical	Loss of active material due to abrasion and crushing

4.5.3. Promoters

For the most preferred transition metals (Pt, Pd, Ni, Rh, Mo, W), sulfur withdraws charge from the metal, which decreases the ability to adsorb CO and to dissociate H₂. Suited promoters that counteract S poisoning, e.g., in the reforming process, are Cu, Ag, Au, Al, Zn, and Sn, which form bimetallic phases with the active metals [65]. Another beneficial effect of these promoters might be that they are able to increase the activity of Mo and W in HDS. Here, Ni is an outstandingly effective promoter, as it accelerates the formation of MoS₂. Since the composition of the catalysts is the same as that preferred for CO₂ methanation, these promoters could also be suitable in this case.

Likewise, alkaline promoters can increase the S-tolerance of a supported Ni catalyst. An obvious effect would be the inactivation of acid sites (electronic effect). In a Ni/SiO₂ catalyst for benzene hydrogenation, the use of alkali metals (Li, Na, and K) led to the partial blocking of Ni surface, which was explained by geometric effects. This decreased the adsorption of H₂S and thiophene [90].

So far, few studies have been conducted on the development of S-resistant catalysts for CO₂ methanation. However, such catalysts are important for the direct use and upgrading of existing gases, such as biogas. By developing effective S-resistant catalysts, the biogas can be used without the need for fine purification. This would make direct methanation of biogas more economical.

Apart from the mentioned active compounds, other types of catalysts with remarkable methanation activity and sulfur resistance have been developed. Well-known are supported noble metal catalysts. During the last decades, some new phases such as carbides, nitrides, and phosphides have been investigated in combination with various active metals [68,91]. Nevertheless, these concepts are still far away from realization [42], but the findings might be the starting point for catalyst preparation with such materials and advanced methods (cf. Section 4.5).

4.6. Catalyst Regeneration

Sulfur poisoning determines the overall deactivation rate compared to carbon formation. As mentioned, sulfides, sulfates, and other structures can form during methanation and sulfur poisoning in general. As a final means to prolong the catalyst lifetime, regeneration by oxidation or reduction was proposed by several authors [63,92,93]. This is very difficult however, as the effectivity is hindered by several effects. By reduction, the removal rate is far too low for technical applications. Raising the temperature might be helpful, but this is only possible with thermally stable catalysts. The same is true for oxidative treatment, which might additionally lead to the formation of NiSO₄ as the most stable structure [69]. Another option, steam treatment, might be applied. More sophisticated protocols have been tested, e.g., for the regeneration of a Ni/SiO₂ catalyst poisoned by

thiophene using a sequence of oxidation–reduction treatments at low O_2 partial pressure and 1 atm H_2 . Temperatures above 700 °C would be necessary in all cases, which causes sintering of Ni metal particles.

Apart from that, some treatments with oxidants such as permanganate, hypochlorite and N_2O were reported, which are only applicable *ex situ*.

5. Review Criteria and Catalyst Nomenclature

This review aims to analyze scientific literature on experiments with catalysts for direct biogas methanation. Hence, only studies on CO_2 methanation are regarded. The selected publications include tests with simulated biogas as feed, which contains CH_4 in addition to CO_2 , and studies on catalyst poisoning by H_2S . Other catalyst poisons, for example NH_3 , are not considered, because not enough experimental studies on them were found. The focus of the selected studies is set on the catalyst and its composition of metal, support material, and, where relevant, promoters. For this purpose, only studies with specified catalyst composition were evaluated. For uniformity and better readability, the naming of catalysts is adjusted in this review when necessary. When naming catalysts in the following, the active metal will be named first, followed by promoters after a hyphen, if applicable. The support material follows a slash character, as in the following example: Ni20-Cu5/ Al_2O_3 . The numbers after the metals indicate the targeted loading in weight percent. The results of the selected studies are based on experiments. Simulation studies were only considered as support for the experimental findings.

6. Influence of CH_4 in the Feed Gas

Several studies state that the separation of CO_2 from CH_4 is unnecessary when biogas is used for CO_2 methanation [12,14,94,95]. However, not many studies have experimentally tested the influence of CH_4 in the feed on methanation. On the one hand, the high CH_4 content in the gas could shift the reaction equilibrium towards the reactants according to Le Chatelier's principle. This would decrease the conversions of CO_2 and H_2 , and consequently lead to a lower CH_4 yield. On the other hand, in industrial processes CH_4 is recycled to the inlet gas to act as a diluent and to contribute to a better temperature distribution in the reactor during the exothermic reaction of CO_2 and H_2 [96]. This avoids hot spots in the reactor bed.

To summarize the current knowledge of the CH_4 impact on CO_2 methanation, this section outlines and evaluates four experimental studies with different catalysts. The CO_2 yield and CH_4 selectivity achieved in these studies are displayed in Table 4 for respective CH_4/CO_2 ratios in the feed.

6.1. Influence of CH_4 on Ni/ Al_2O_3

The performance of Ni/ Al_2O_3 catalysts, with promoters or non-promoted, has been investigated in three studies with CH_4 in the inlet gas.

In the first study, four incipient wetness impregnated catalysts with 12 or 20 wt% Ni, either non-promoted or with 0.5 wt% Ru on Al_2O_3 , were studied [97]. The two better performing catalysts with higher Ni loading were selected for the investigation of CH_4 influence under the reaction conditions given in Table 5.

In a first experiment with unpromoted Ni20/ Al_2O_3 , the composition of the gas was varied by changing the concentration of $CH_{4,in}$ from zero via 14 to 29 vol% and back to zero, holding each value for 2 h [97]. The addition of CH_4 was compensated by the reduction of N_2 content in the feed to leave the inlet content of H_2 and CO_2 unaffected. With increasing CH_4 concentrations in the inlet gas, the CO_2 conversion decreased slightly from 71.5% to 70.8% to 70.6% (Table 4). The initial CO_2 conversion was well reproduced at 71.4% in the last 2 h without CH_4 addition. The CH_4 selectivity always remained high without much variation [97].

Table 4. Experimental conditions (catalyst composition, temperature, CH₄/CO₂ ratio, and feed gas composition with CH₄ concentration in bold type) and results (CO₂ conversion and CH₄ selectivity) of different studies. All experiments were performed at 1 bar except where indicated.

Reaction Conditions	Catalyst	T/°C	CH ₄ /CO ₂	H ₂ /CO ₂ /CH ₄ /N ₂ /vol% ¹	X (CO ₂)	S (CH ₄)	Ref.
Table 5	Ni20/Al ₂ O ₃	350	0/100	57/14/ 00 /29	71.5%	99.7%	[97]
			50/50	57/14/ 14 /14	70.8%	99.5%	
			67/33	57/14/ 29 /00	70.6%	99.4%	
Table 5	Ni20-Ru0.5/Al ₂ O ₃	350	0/100	57/14/ 00 /29	82% ²	>99%	[97]
			67/33	57/14/ 29 /00	81% ²	>99%	
Table 6	Ni20-Mg3/Al ₂ O ₃	400	0/100	80/20/ 00 /00	74% ²	96% ²	[98]
			40/60	71/18/ 12 /00	67%	97% ²	
			50/50	67/17/ 17 /00	64%	97% ²	
			65/35	58/15/ 27 /00	54%	97% ²	
Table 7 ³	Ni20/Al ₂ O ₃	350	0/100	62/15/ 00 /23 ⁵	88.5%	100%	[99]
			50/50	62/15/ 15 /08 ⁵	82% ²	79% ²	
Table 7 ³	Ni40/Al ₂ O ₃	350	0/100	62/15/ 00 /23 ⁵	91.4%	100%	[99]
			50/50	62/15/ 15 /08 ⁵	81% ²	79% ²	
Table 7 ³	Ni20/CeO ₂	350	0/100	62/15/ 00 /23 ⁵	91.7%	100%	[99]
			50/50	62/15/ 15 /08 ⁵	81% ²	75% ²	
Table 8 ⁴	Ni20/Al ₂ O ₃	350	50/50	62/15/ 15 /08 ⁵	93.7%	100%	[99]
Table 8 ⁴	Ni40/Al ₂ O ₃	350	50/50	62/15/ 15 /08 ⁵	95.7%	100%	[99]
Table 8 ⁴	Ni20/CeO ₂	350	50/50	62/15/ 15 /08 ⁵	94.6%	100%	[99]
Table 9	Ni15-Co3/CeO ₂ -ZrO ₂	350	0/100	80/20/ 00 /00	71% ²	98% ²	[1]
			21/79	76/19/ 05 /00	72%	97%	
			36/64	72/18/ 10 /00	74%	98%	
			47/53	68/17/ 15 /00	78%	99%	

¹ rounded to integers; ² numbers read from graphs (not given in the text); ³ experiments performed at 2 bar; ⁴ experiments performed at 12.5 bar; ⁵ with Ar instead of N₂.

Table 5. Catalysts and reaction conditions for experiments on CH₄ influence on methanation over Ni/Al₂O₃ with Ru promoter [97].

Catalysts	Ni20/Al ₂ O ₃ Ni20-Ru0.5/Al ₂ O ₃
Activation conditions	600 °C, 6 h, H ₂ /N ₂
T	350 °C
p	1 bar
H ₂ /CO ₂	4
WHSV	56,000 mL g _{cat} ⁻¹ h ⁻¹
CH _{4,in}	0, 14, 29 vol%

As a second experiment, both catalysts were tested with 29 vol% CH₄ for 24 h [97]. No loss of CO₂ conversion was observed during this time. In general, CO₂ conversion in these experiments was slightly lower than in CO₂ methanation with pure H₂/CO₂ stream, but the difference is not significant. The same applies to the CH₄ selectivity, which remained above 99% in all cases (Table 4) [97]. Comparing the two studied catalysts, the Ru-promoted catalyst achieved higher CO₂ conversion (81%) than the non-promoted Ni20/Al₂O₃, with 70% CO₂ conversion in the 24 h experiment. As described in Section 4, the addition of Ru not only increases the number of active sites on the catalyst, but also promotes the

reducibility of the catalyst. This was supported by the reduction profile (H₂-TPR) for Ni₂₀-Ru_{0.5}/Al₂O₃ in that study [97].

These results show that the influence of 14 vol% and 29 vol% CH₄ on CO₂ methanation on Ni/Al₂O₃ is low, making both Ni catalysts on Al₂O₃ (with and without a Ru promoter) suitable for direct biogas methanation [97].

A second study investigated the influence of CH₄ using Mg-promoted Ni/Al₂O₃ catalysts prepared by precipitation [98]. The reaction conditions are given in Table 6. With an unspecified pressure, it is assumed that the experiments were performed at 1 bar.

Table 6. Catalyst and reaction conditions for experiments on CH₄ influence on methanation over Ni/Al₂O₃ with Mg promoter [98].

Catalyst	Ni ₂₀ -Mg ₃ /Al ₂ O ₃
Activation conditions	700 °C, 4 h, H ₂ /N ₂
T	400 °C
p	not specified
H ₂ /CO ₂	4
GHSV	30,000 h ⁻¹
CH _{4,in}	0, 12, 17, 27 vol%

CO₂ conversion decreased from 74% for the pure CO₂ methanation to 67%, 64%, and 54% as the CH₄ concentration increased (Table 4). Hence, compared to CO₂ conversion without CH₄ in the inlet gas, the highest tested CH₄ concentration in the reactant gas led to a 20% decrease of CO₂ conversion [98]. The CH₄ yield showed a similar trend. However, the CH₄ selectivity remained the same and thus appears to be independent of the CH₄ concentration in the input stream.

The results from the second study imply that a high CH₄ content leads to reduced CO₂ conversion for Ni₂₀-Mg₃/Al₂O₃ [98].

A third study investigated the influence of CH₄ in the inlet gas on two unpromoted Ni catalysts prepared by impregnation [99]. The reaction conditions for the first series of experiments in a fixed-bed reactor are given in Table 7.

Table 7. Catalyst and reaction conditions for fixed-bed reactor experiments on CH₄ influence on methanation over unpromoted Ni/Al₂O₃ [99].

Catalysts	Ni ₂₀ /Al ₂ O ₃ Ni ₄₀ /Al ₂ O ₃
Activation conditions	600 °C, 2 h, H ₂
T	350 °C, 600 °C
p	2 bar
H ₂ /CO ₂	4
WHSV	30 L g _{cat} ⁻¹ h ⁻¹
CH _{4,in}	0, 15.4 vol%

The experiments with CH₄ in the inlet gas were performed at 300 °C and 600 °C for 20 h respectively, while the reference experiment with no CH₄ in the inlet gas was performed at 350 °C for 20 h and then set to 600 °C for another 20 h [99]. The addition of CH₄ was compensated by the reduction of Ar concentration in the inlet gas (Table 4) to leave the inlet content of H₂ and CO₂ unaffected.

Both catalysts showed higher CO₂ conversion and higher CH₄ selectivity at 350 °C than at 600 °C. Compared to the reference experiment, the catalysts achieved a lower CO₂ conversion, which decreased to about the same value (81–82%) with CH₄ in the inlet

gas [99]. The CO₂ conversion decreased by about 6% for Ni20/Al₂O₃ and by about 10% for Ni40/Al₂O₃ at 350 °C (Table 4). For the CH₄ selectivity, even stronger decreases (21%) were observed. At 350 °C and no CH₄ present, both catalysts achieved 100% CH₄ selectivity. Over 20 h, conversion rate and selectivity remained constant in both cases [99].

In a second series of experiments with the same catalysts, the effect of CH₄ was tested for about 70 h in microchannel reactors (Table 8) [99].

Table 8. Catalyst and reaction conditions for microchannel reactor experiments on CH₄ influence on methanation with unpromoted Ni/Al₂O₃ [99].

Catalysts	Ni20/Al ₂ O ₃ Ni40/Al ₂ O ₃
Activation conditions	500 °C, 2 h, H ₂
T	350 °C
p	12.5 bar
H ₂ /CO ₂	4
WHSV	45 L g _{cat} ⁻¹ h ⁻¹
CH _{4,in}	15.4 vol%

The resulting CO₂ conversions in the microchannel reactor (12.5 bar) were higher than in the experiments with the fixed-bed reactor, which were performed at 2 bar (Table 4). This is consistent with the expectations of thermodynamic equilibrium (cf. Section 3). On average over 70 h on stream with CH₄ in the feed gas, Ni40/Al₂O₃ gave a higher CO₂ conversion (95.7%) compared to Ni20/Al₂O₃ (93.7%) [99]. Over the 70 h on stream, CH₄ selectivity remained around 100% and no deactivation (sintering, carbon depositions) was observed.

The results from that third study suggest that a biogas-like concentration of CH₄ with CH₄/CO₂ = 50/50 can lead to lower CO₂ conversion compared to pure CO₂ methanation. This was observed for both Ni/Al₂O₃ catalysts, with none standing out as performing significantly better. The study also shows that higher CO₂ conversions can be achieved by increasing the pressure in a direct biogas methanation.

6.2. Influence of CH₄ on Ni/CeO₂

In the third study discussed in Section 6.1, a catalyst supported on CeO₂ (Ni20/CeO₂) was also investigated [99]. The reaction conditions for the fixed-bed and microchannel reactor experiments were the same as given in Tables 7 and 8.

In the fixed-bed experiments, Ni20/CeO₂ showed higher CO₂ conversion and CH₄ selectivity at 350 °C compared to 600 °C. With CH₄ in the inlet gas, CO₂ conversion was lowered by around 10%, and CH₄ selectivity strongly decreased by 25% compared to the reference experiment without CH₄ addition (Table 4) [99]. These values remained constant over 20 h. It was suspected that the presence of CH₄ slows down processes at the surface of the CeO₂-supported catalyst [99].

In the microchannel reactor experiments with CH₄ in the inlet gas, Ni20/CeO₂ showed no significant difference over 70 h compared to the two Al₂O₃-supported catalysts described in Section 6.1 with no visible deactivation trends. Higher CO₂ conversion (94.6%) was reached in the microchannel reactor compared to the fixed-bed reactor experiment (Table 4).

6.3. Influence of CH₄ on Ni/CeO₂-ZrO₂

Among three catalysts for CO₂ methanation with 15 wt% Ni on CeO₂-ZrO₂ support (without promoter/3 wt% Co-promoter/3 wt% Mn promoter), the Co-promoted catalyst was selected, due to the best performance, for experiments on the influence of CH₄ [1]. The advantages of Co as promoter are explained in Section 4.3 (Table 2). The experiments were performed under reaction conditions given in Table 9.

Table 9. Catalyst and reaction conditions for experiments on CH₄ influence on methanation with Co-promoted Ni/CeO₂-ZrO₂ [1].

Catalyst	Ni15-Co3/CeO ₂ -ZrO ₂
Activation conditions	450 °C, 1 h, H ₂ /N ₂
T	200–450 °C
P	1 bar
H ₂ /CO ₂	4
WHSV	12,000 mL g ⁻¹ h ⁻¹
CH _{4,in}	0, 5, 10, 15 vol%

The experiments were run at 200–450 °C in 50 K intervals, each held for 30 min. A long-term test for 30 h at 300 °C was also performed with 15 vol% CH₄ in the feed gas [1].

In the range of 250–350 °C, a positive effect on CO₂ conversion was observed for all three initial CH₄ concentrations tested on Ni15-Co3/CeO₂-ZrO₂ [1]. Above 400 °C, only the experiment with 15 vol% CH₄ showed a higher conversion of CO₂ compared to pure CO₂ methanation. The highest CO₂ conversions were achieved at 350 °C, with the addition of 15% CH₄ yielding the best results (78% CO₂ conversion). Lower CH₄ content in the feed gas (10%, 5%) led to lower CO₂ conversions (74% and 72%, Table 4). For CO₂ methanation without CH₄ in the feed gas, the CO₂ conversion was about 71% [1]. The higher CO₂ conversion with increasing CH₄ content can be explained by secondary reactions of CO₂ with CH₄, such as reforming reactions, leading to higher CO₂ consumption. This effect was evident in experiments on the dry reforming of methane for the Co-promoted Ni catalyst at low temperatures [1]. CH₄ selectivity was also slightly improved by adding CH₄ to the feed gas, and reached its maximum (99%) with 15 vol% CH₄ at 300 °C. However, at the relevant methanation temperatures of 300–450 °C, the differences in CH₄ selectivity for the different gas compositions were not significant. Over the long-term experiment (38 h) with 15 vol% CH₄, the Co-promoted catalyst showed high stability and kept the high selectivity of 99% to CH₄ [1].

The tested Ni catalyst on CeO₂-ZrO₂ support with Co as promoter is suitable for further studies with real CH₄-containing gases such as flue gases, or methanation plants with recycling loops [1].

6.4. Further Studies

There is another experimental methanation study with a gas containing CH₄ using a wet-impregnated Ru0.5/Al₂O₃ catalyst [95]. Different parameters were varied to find the best reaction conditions (Table 10). The study was not considered in more detail above, because no reference information was provided on the behavior of the catalyst without CH₄ in the inlet gas.

Table 10. Parameters for experiments with Ru0.5/Al₂O₃ with H₂/CO₂ = 4 and CH₄/CO₂ = 50/50 [95].

Reduction T	400 °C, 600 °C
T	350–600 °C
P	1–3.8 bar
WHSV	90,000–420,000 mL g ⁻¹ h ⁻¹

The experiments were evaluated on the basis of CO₂ conversion and CH₄ selectivity [95]. The catalyst achieved its highest activity at 450 °C, high H₂/CO₂ ratios, and 90,000 mL g⁻¹ h⁻¹, as expected for pure CO₂ methanation without CH₄. In a long-term experiment (450 °C, 3 bar, GHSV = 90,000 mL g⁻¹ h⁻¹, and H₂/CO₂ = 4) the catalyst with

0.5 wt% Ru, as well as another catalyst with 0.05 wt% Ru, were able to maintain their activity over the entire time of the experiment (approximately 65–75 h) [95]. The catalyst with the higher Ru loading achieved almost 80% CO₂ conversion, and the catalyst with 0.05 wt% Ru reached 58% CO₂ conversion, which decreased to 54% during the experiment. The CH₄ selectivity remained constant at 98% for Ru0.5/Al₂O₃, while the 0.05 wt% Ru catalyst again showed a slight drop from 80% to 78% CH₄ selectivity [95]. These experiments show that with the Ru0.5/Al₂O₃ catalyst, even with CH₄ in the feed, conversions and yields predicted by thermodynamic equilibrium could be achieved.

There are two simulation studies in which the influence of CH₄ concentration on methanation was investigated.

In the first simulation study, a comprehensive thermodynamic analysis of both CO and CO₂ methanation was carried out [96]. The influence of CH₄ was investigated only for CO methanation (H₂/CO = 3, 200–800 °C, 1 and 30 bar), and CH₄/CO ratios of 1, 3, and 5 did not lead to large differences in CO conversion at the same reaction conditions. However, CH₄ cracking occurred above 400 °C, leading to carbon deposition [96]. This reaction may also take place during CO₂ methanation. The recycled fraction of the CH₄-containing product gas should therefore not be too high, suggesting a recycle ratio of product gas of 0.5–3.0 for the methanation process [96].

The second simulation study considered the influence of CH₄ from 1–10 bar [100]. The influence of the CH₄ concentration is only significant at low pressures, especially at atmospheric pressure. Above 8 bar, only a very small influence of the initial CH₄ concentration on the CO₂ conversion was observed. Based on the results, the separation of CO₂ from CH₄ is not necessary for methanation [100].

6.5. Discussion on the Effect of Methane in the Feed

The four studies in Sections 6.1–6.3 looked at CO₂ conversion and CH₄ selectivity to assess the influence of CH₄ on CO₂ methanation. While three studies show that the CH₄ selectivity in the experiments with CH₄ in the inlet gas did not change significantly in the temperature ranges studied, one study shows a decrease from 100% CH₄ selectivity to 75–79% for Ni catalysts on Al₂O₃ and on CeO₂ after the addition of CH₄ at the inlet [99]. This sharp decrease is surprising, since under similar conditions (similar catalyst mass, same catalyst composition Ni₂₀/Al₂O₃, CH₄/CO₂ = 50/50), CH₄ selectivity remained nearly 100% [97].

For better comparability of the data in the literature, a simulation of thermodynamic equilibrium was made. It shows that the maximum CO₂ conversion decreases with increasing CH₄ concentration (Table 11, see Appendix A for details on the calculation). At higher pressures, the maximum CO₂ conversion increases for a given CH₄ content in the feed.

Table 11. Calculated CO₂ conversion in equilibrium for methanation with 0, 14 or 20 vol% CH₄ in the feed, based on an Aspen Plus simulation with a Gibbs reactor at 350 °C, a feed with H₂/CO₂ = 4 and N₂ addition as described in [97].

	X(CO ₂), 0 vol% CH ₄	X(CO ₂), 14 vol% CH ₄	X(CO ₂), 29 vol% CH ₄
1 bar	85.0%	82.9%	81.5%
2 bar	88.3%	86.6%	85.6%
12.5 bar	94.0%	93.2%	92.7%

From the comparison of the CO₂ conversions achieved by the catalysts of the four studies, no clear conclusions can be drawn about the influence of CH₄ on the CO₂ methanation. One study shows a positive influence of CH₄ on the CO₂ conversion by the Co-promoted Ni/CeO₂-ZrO₂ catalyst [1]. The higher the CH₄ concentration at the inlet, the higher the CO₂ conversion [1]. With a concentration of 15 vol% CH₄ in the feed, a maximum increase in CO₂ conversion of 7% was achieved compared to CO₂ methanation without CH₄ [1]. This effect was attributed to the dry reforming of methane, which occurred at low tempera-

tures in an experiment with CO₂ and CH₄ as input gas [1]. In a second study, no significant effect of CH₄ on CO₂ conversion was observed for Ni catalysts supported on Al₂O₃ with and without Ru as a promoter [97]. When the CH₄ concentration was increased to 14 and 29 vol%, the CO₂ conversion decreased by only 1% compared to pure CO₂ methanation [97]. Based on Table 11, a stronger decline in conversion is expected compared to equilibrium. Therefore, mixing CH₄ into the feed gas had no significant negative effect. With 29 vol% CH₄ in the feed, the catalyst with Ru as promoter reached equilibrium conversion, while methanation without CH₄ did not. A third study shows the opposite result. There, the CO₂ conversion of Ni₂₀-Mg₃/Al₂O₃ decreased strongly by up to 20% for the experiment with the highest CH₄ content (27 vol%) compared to the experiment without CH₄ [98]. The equilibrium analysis suggests only a 3–4% drop in conversion rates and shows that the conversions achieved in that study are well below equilibrium. Similar results were obtained with unpromoted Ni catalysts on Al₂O₃ and on CeO₂, respectively [99]. At the tested methane concentration in the gas, which was adjusted to a CH₄/CO₂ ratio of 50/50, the CO₂ conversion decreased by up to 10% compared to pure CO₂ methanation.

In one study, Ni₂₀/CeO₂ and Ni₄₀/Al₂O₃ performed slightly better than Ni₂₀/Al₂O₃ [99]. This suggests that higher metal loading might be beneficial, and that CeO₂ could ease CO₂ activation compared to Al₂O₃. However, in the same study, it was suggested that CH₄ in the feed slowed down processes at the surface of the CeO₂ support [99].

From the comparison of the studies, it cannot be precisely concluded at which reaction conditions or catalyst compositions CH₄ is more readily tolerated in the inlet gas. However, the studies used different inert gas concentrations in the experiments, which affects the equilibrium at the end of the reaction, as the partial pressures of the products at equilibrium depend on the inert gas content.

Both a simulation [100] and an experimental study [99] indicate that at high pressures (10 and 12.5 bar, respectively), similar CO₂ conversions can be achieved with CH₄ in the feed gas compared to pure CO₂ methanation. The equilibrium analysis (Table 11) also shows a decreasing effect of methane admixture with increasing reaction pressure. A temperature effect was also observed experimentally. Comparing 350 °C and 600 °C, all tested catalysts were more active at the lower temperature [99].

7. Influence of H₂S in the Feed Gas

The origin of trace compounds in biogas can be traced back to the macromolecules of the biogas substrate, as described in Section 2. H₂S is a suitable test molecule for investigating the influence of sulfur-containing substances on the catalyst in the laboratory. It is therefore possible to examine how catalysts react to one of the most important catalyst poisons in biogas on a smaller scale. The toxicity of sulfur-containing molecules increases with the number of free electron pairs available for bonding and with lower shielding of the S atom, as well as with increasing electronegativity [63]. These factors make H₂S more toxic than oxidized sulfur-containing molecules such as SO₂ [33]. It has been observed that catalyst deactivation by H₂S proceeds in three prominent phases, which are visible, for example, in CO₂ conversion as depicted in Figure 4:

1. Phase 1 usually starts with a constant and high CO₂ conversion, which slightly decreases after a certain time on stream with H₂S in the feed gas. The decline in CO₂ conversion indicates that the catalyst can no longer reach equilibrium conversion due to H₂S poisoning [41]. During H₂S poisoning, deactivation of the catalyst particles proceeds along the catalyst bed with time on stream. CO₂ conversion is an integral parameter across the entire catalyst bed, which only begins to decrease as the poisoning approaches the rear end of the catalyst bed [41,50].
2. In phase 2, the CO₂ conversion decreases rapidly within a short time. This phase represents the poisoning of the remaining active catalyst particles at the rear end of the catalyst bed [41].

3. Finally, in phase 3, CO₂ conversion reaches a minimum, which remains constant over time on stream. The constant low CO₂ conversion indicates saturation of sulfur on the catalyst surface. Due to the formation of strong sulfur-metal bonds, the active sites are blocked and no longer available for CO₂ adsorption [87]. Hence, CO₂ adsorption is only possible on the catalyst support. Since the active metal is crucial to activate H₂ for CH₄ formation, CO₂ methanation activity is lost and only CO is formed as a product.

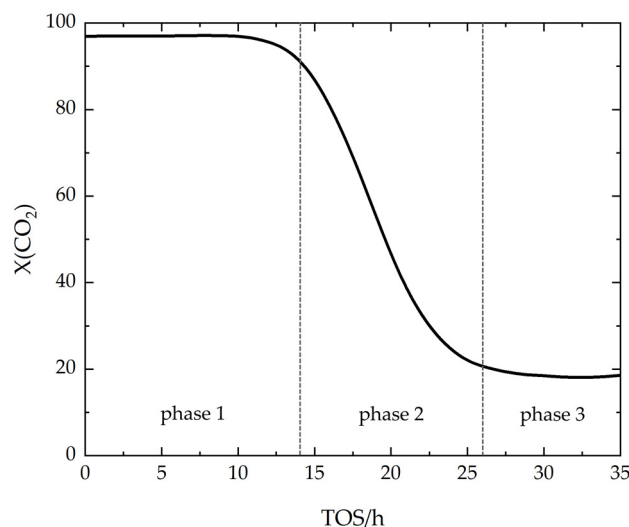


Figure 4. CO₂ conversion course during H₂S poisoning of arbitrary catalyst with division into three distinct phases.

The time to complete poisoning can vary depending on the amount of catalyst, the catalyst composition, and reaction conditions. The poisoning rate is, for example, influenced by the bed capacity, the temperature, and the H₂S concentration in the gas [63].

Since the effort for H₂S removal increases with decreasing target concentration, and complete removal upstream of CO₂ methanation units is not possible with current biogas-cleaning technologies, poisoning has to be either accepted in industrial applications, or sulfur-resistant catalysts have to be developed [50]. The latter was investigated in several studies, although most studies focus on the reforming of biogas or natural gas rather than CO₂ methanation with biogas [60]. Seven studies were found in recent literature which provide results from CO₂ methanation and are evaluated in the following.

7.1. Sulfur Tolerance of Unpromoted Ni Catalysts

The sulfur tolerance of three unpromoted Ni catalysts on Al₂O₃ and CeO₂, which were already discussed in Section 6.1, was studied in a fixed-bed reactor under the reaction conditions given in Table 12 [99]. H₂S was added after 2 h.

Table 12. Catalysts and reaction conditions for experiments on H₂S influence on methanation with unpromoted Ni catalysts in a fixed-bed reactor [99].

Catalysts	Ni20/CeO ₂ Ni20/Al ₂ O ₃ Ni40/Al ₂ O ₃
Activation conditions	600 °C, 2 h, H ₂
T	450 °C
p	2 bar
H ₂ /CO ₂	4
WHSV	not specified
H ₂ S _{in}	8 ppm

The influence of H₂S on the catalytic performance was discussed by CO₂ conversion (Figure 5a) and CH₄ selectivity [99]. At the same Ni loading, the catalyst on Al₂O₃ showed around a 10 h longer phase 1 (analogous to Figure 4) than the catalyst on CeO₂. Although the plateau of phase 3 was reached earliest by Ni/CeO₂, the CeO₂-supported catalyst kept 30% CO₂ conversion, which was around 10% higher than that of the Al₂O₃-supported catalysts in phase 3. With decreasing CO₂ conversion, a simultaneous decrease in CH₄ selectivity and an increase in CO selectivity was observed [99]. The change in selectivity was attributed to inhibited hydrogenation of carbon species on the surface, lower stability of intermediate carbonyl groups, and their desorption before methanation [99]. It was also shown that the catalyst with higher Ni loading resists sulfur poisoning over a longer time. The better sulfur tolerance at higher nickel loading can be attributed to the fact that sulfur adsorbs strongly on the active Ni sites, as described in Section 4.4. In STEM-EDX (scanning transmission electron microscope coupled with energy-dispersive X-ray spectroscopy) images, sulfur atoms were not only detected on Ni crystallites [99], but small amounts were also found on the support materials. This effect was more pronounced on CeO₂ [99].

The same catalysts were tested in a microchannel reactor under different conditions (Table 13), including the addition of CH₄ in the inlet gas. H₂S was added after 70 h.

Table 13. Catalysts and reaction conditions for experiments on H₂S influence on methanation with unpromoted Ni catalysts in a microchannel micro reactor [99].

Catalysts	Ni20/CeO ₂ Ni20/Al ₂ O ₃ Ni40/Al ₂ O ₃
Activation conditions	500 °C, 2 h, H ₂
T	350 °C
p	12.5 bar
H ₂ /CO ₂	4
WHSV	45 L g _{cat} ⁻¹ h ⁻¹
H ₂ S _{in}	1 ppm
CH ₄ ,in	15.4 vol%

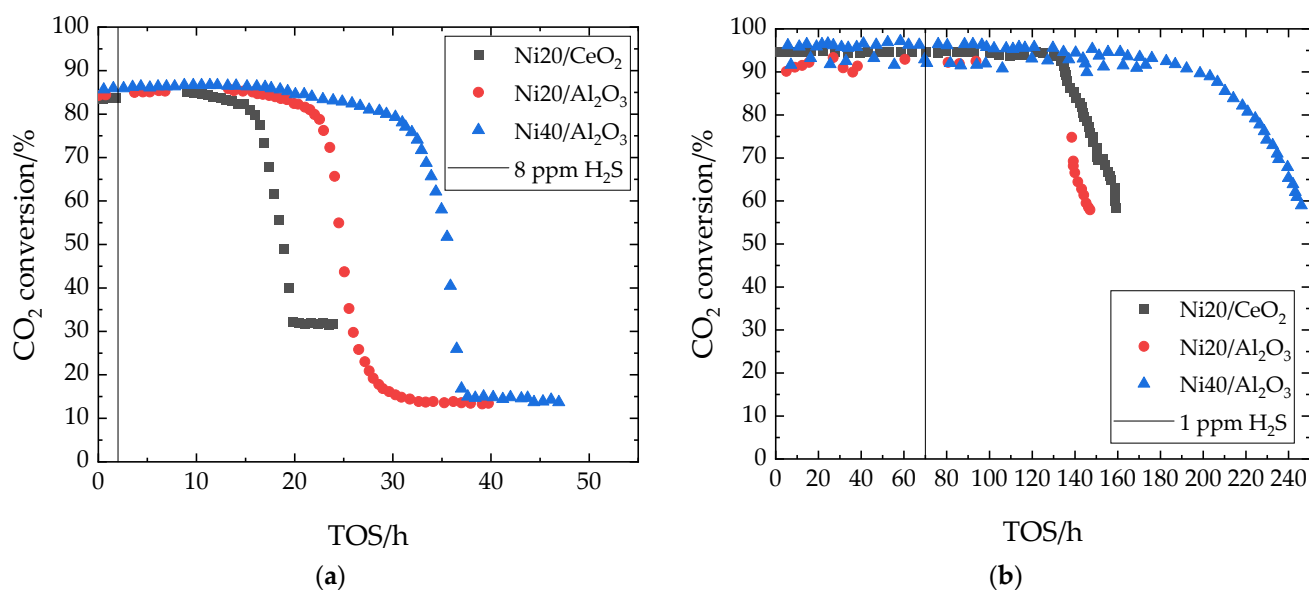


Figure 5. CO₂ conversion in H₂S poisoning experiments in CO₂ methanation with unpromoted Ni catalysts in (a) fixed-bed reactor and (b) microchannel reactor with CH₄ in the inlet gas [99].

In the microchannel reactor at higher pressure and lower H₂S concentration, similar deactivation phenomena (Figure 5b) were seen as described above. The stable runtime of the catalyst was increased by the lower amount of H₂S. Among the tested catalysts, Ni40/Al₂O₃ achieved a significantly longer phase 1 (by ~50 h) than the catalysts with lower Ni loading. STEM-EDX images of the H₂S poisoned catalysts showed a high dispersion of S atoms. Sulfur is present on the surface of the support, which was related to H₂S partial oxidation on lattice oxygen of CeO₂ or the formation of elemental sulfur on hydroxyl groups of Al₂O₃ [99]. Detailed mapping also indicated that sulfur atoms were located close to Ni in Ni20/CeO₂ [99]. The amounts of sulfur on the catalysts increased in the order Ni20/Al₂O₃ (0.1 wt%) < Ni20/CeO₂ (0.2 wt%) < Ni40/Al₂O₃ (0.7 wt%), and the high amount of sulfur on Ni40/Al₂O₃ can be attributed to the longer operation time [99]. Due to the lack of strong vibration bands associated with carbon materials in Raman spectra, deactivation due to carbon deposits is unlikely [99]. However, typical vibration bands ascribed to different sulfur species (sulfur, nickel sulfides, thiocarbonates, sulfur-containing organic compounds) were also not visible in Raman and FTIR (Fourier-transform infrared) spectra of the used catalysts [99]. This might indicate that deactivation occurs due to low amounts of sulfur, which is finely distributed on the catalyst surface as described in Section 4.4.

7.2. Sulfur Tolerance of Ni/Al₂O₃ with Ce Promoter

Two studies on the sulfur tolerance of CO₂ methanation catalysts were performed with Ce promoters on Ni/Al₂O₃ catalysts.

In the first study, long-term (70 h) experiments were carried out with impregnated catalysts under the reaction conditions given in Table 14. H₂S was added to the gas after 20 h [60].

Catalyst poisoning was evaluated by the CO₂ conversion curves (Figure 6a), CH₄ selectivity, and CO selectivity over time on stream, where complete loss of methanation activity occurred between 70–80 h. The graphs for CO₂ conversion and CH₄ selectivity can be divided very well into the three phases shown in Figure 4. The loss of CH₄ selectivity and CO₂ conversion occurred simultaneously for the respective catalysts. A change in selectivity to CO, as described in Section 7, became apparent at the same time, with CO selectivity reaching 100% in all cases after deactivation. Comparing Ni20/Al₂O₃ and Ni40/Al₂O₃, the Ni loading affected the course of the deactivation curve (Figure 6a), as already observed in Section 7.1. The higher Ni loading prolonged phase 1 by around 10 h, in which the activity of the catalyst remained high for the time being. The rate of deactivation and the final CO₂ conversion (around 14%) of the catalysts differ only slightly between Ni20/Al₂O₃ and Ni40/Al₂O₃.

Table 14. Catalysts and reaction conditions for experiments on H₂S influence on methanation with Ni/Al₂O₃ and Ce promoter [60].

Catalysts	Ni20/Al ₂ O ₃ Ni40/Al ₂ O ₃ Ni20-Ce5/Al ₂ O ₃ Ni40-Ce5/Al ₂ O ₃
Activation conditions	600 °C, 2 h, H ₂
T	475 °C
p	1.9 bar
H ₂ /CO ₂	4
WHSV	4.6 L _{CO2} h ⁻¹ g ⁻¹
H ₂ S _{in}	8 ppm

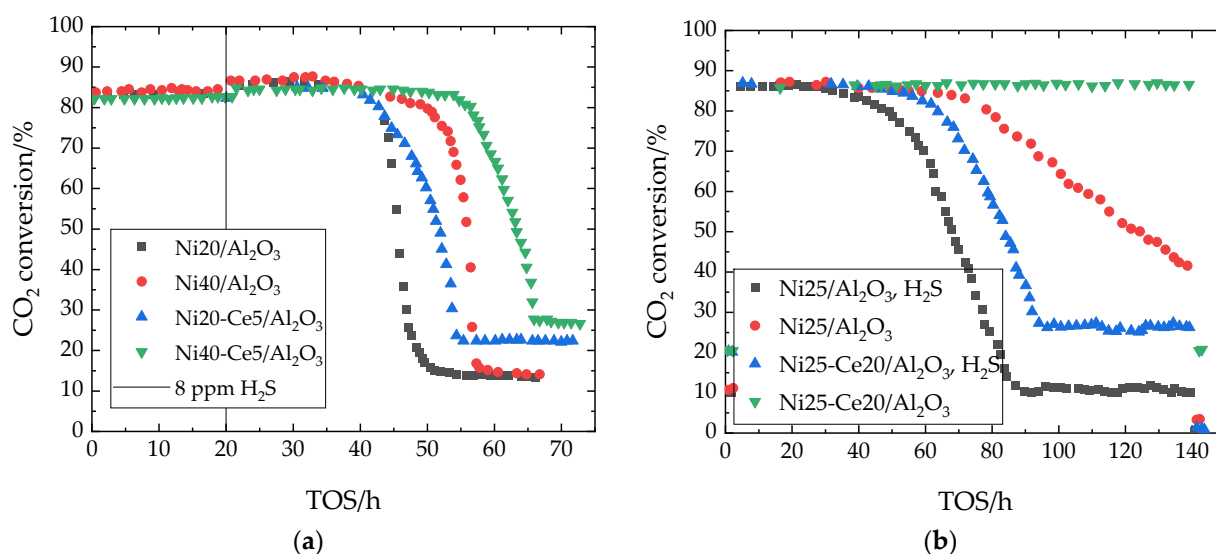


Figure 6. CO₂ conversion in H₂S poisoning experiments in CO₂ methanation with Ce-promoted Ni/Al₂O₃ catalysts with (a) 5 ppm H₂S addition after 20 h [60] and (b) 1 ppm H₂S addition compared to reference experiments [62].

No precise conclusions were made about the structure of the S species or their binding to the active sites. However, DRIFT (diffuse reflectance infrared Fourier transformed) spectra from the visible carbonate vibration bands indicated that thiocarbonates were formed from CO₂ and H₂S above 200 °C [60]. Since Raman spectra obtained of the spent catalysts do not show peaks for pure sulfur, nickel sulfides, or sulfur-containing organic compounds, it was assumed that the sulfur species were highly dispersed on the surface, as already described in Section 7.1. By DRIFT spectra it was shown that, in contrast to freshly prepared catalysts, no vibrational bands for carbonyl groups were found in the H₂S-deactivated catalysts [60]. This suggests that the first step of the carbide mechanism of methanation, CO₂ transformation to CO, is inhibited on the deactivated catalysts. Thus, H₂S adsorption results in deactivation.

The addition of Ce as a promoter changes the deactivation curve (Figure 6a). In both materials with Ce addition, the rate of deactivation in phase 2 was reduced, as indicated by a less severe drop in the curve. In addition, the final CO₂ conversions of the catalysts with Ce promoter were higher than for the analogous catalysts without Ce. DRIFT spectra showed that formate intermediates were formed on the Ce-promoted catalyst. This could explain the higher activity of the promoted catalysts [60]. For Ni40-Ce5/Al₂O₃, phase 1 lasts 5 h longer than for Ni40/Al₂O₃, making it the most stable one among the catalysts studied. It has been generally found that a larger active surface area available for reaction results in a longer catalyst life [60].

The second study looked at wet impregnated Ni catalysts with CeO₂ as promoter on Al₂O₃ in sulfur poisoning experiments [62]. The reaction was carried out with the conditions described in Table 15 at a temperature profile of 250 °C for 2 h, 500 °C for 138 h, and again 250 °C for 2 h. Reference experiments without H₂S addition were performed under the same conditions for the two catalysts.

CO₂ conversion was evaluated to determine the catalyst deactivation by H₂S. CH₄ selectivity was 100% in all cases. Only CH₄, H₂, CO, and CO₂ were detected with a gas micro-chromatograph [62]. In the reference experiment without H₂S, the unpromoted catalyst was deactivated during the experiment (Figure 6b), which was attributed to sintering. This indicates that Ce promotion stabilizes the Ni particles, and it was suggested that sintering occurs preferentially at CeO₂ [62]. In all experiments, the CO₂ conversion was higher at 500 °C compared to 250 °C.

Table 15. Catalysts and reaction conditions for experiments on H₂S influence on methanation with Ni/Al₂O₃ and Ce promoter [62].

Catalysts	Ni25/Al ₂ O ₃ Ni25-Ce20/Al ₂ O ₃
Activation conditions	500 °C, 3 h, H ₂
T	250 °C, 500 °C
P	5 bar
H ₂ /CO ₂	4
GHSV	40,000 mL g ⁻¹ h ⁻¹
H ₂ S _{in}	1–5 ppm

In the presence of 1 ppm H₂S, both catalysts deactivated within 80–100 h (Figure 6b) as described in Figure 4. The CeO₂-promoted catalyst showed both a higher stability due to a longer phase 1 and a higher final CO₂ conversion (~27%) in phase 3 compared to the unpromoted Ni25/Al₂O₃ catalyst (~11% CO₂ conversion) [62].

The better sulfur resistance of the CeO₂-promoted catalyst is due to adsorption of sulfur on the promoter. HRSTEM (high-resolution scanning transmission electron microscopy) showed the presence of cerium oxysulfide (Ce₂O₂S) species on the surface after poisoning [62]. The thermodynamically favored formation of Ce₂O₂S over NiS has already been described in Section 4.5.2. Accordingly, the poisoning of the active Ni phase is slowed down by the presence of CeO₂ [62]. An experiment with higher H₂S concentration (5 ppm) in the gas showed a faster deactivation of the Ce-promoted catalyst [62]. This is evident from a shortened phase 1 and a rapid drop in the curve in phase 2. In addition, the final CO₂ conversion in phase 3 dropped to 19%, which is slightly lower than with 1 ppm H₂S (~27% CO₂ conversion) [62]. The catalyst life is drastically shortened when higher H₂S concentrations are present in the reaction gas.

7.3. Sulfur Tolerance of Ni/Al₂O₃ with Transition Metal Promoters

Two studies were performed on screening different transition metal promoters for Ni/Al₂O₃.

The first study investigated sulfur poisoning of co-precipitated catalysts with Mn, Fe, Co, Cu, and Zn as promoters [41]. The catalysts and reaction conditions are given in Table 16. H₂S was added after an aging period of 24 h.

Table 16. Catalysts and reaction conditions for experiments on H₂S influence on methanation with Ni/Al₂O₃ and Mn, Fe, Co, Cu, and Zn promoter [41].

Catalysts	Ni41/Al ₂ O ₃ Ni37-Mn3.3/Al ₂ O ₃ Ni44-Fe4.4/Al ₂ O ₃ Ni41-Co4.4/Al ₂ O ₃ Ni39-Cu4.6/Al ₂ O ₃ Ni38-Zn4.3/Al ₂ O ₃
Activation conditions	450 °C, 4 h, H ₂ /Ar
T	400 °C
P	1 bar
H ₂ /CO ₂	4
GHSV	not specified
H ₂ S _{in}	5 ppm

The activity of the catalysts during the poisoning experiments was evaluated by CO₂ conversion [41]. All deactivation curves (Figure 7a) of the investigated catalysts, except for that of the Cu-promoted catalyst, follow the three phases shown in Figure 4. Already during aging without H₂S, the CO₂ conversion of the Ni-Cu catalyst showed a rapid decrease from 75% to 70% [41]. In Section 4.3 it was stated that Cu might not be a suitable promoter for a Ni-based CO₂ methanation catalyst, and it was shown that a Cu phase settles on the surface at the expense of active Ni centers [41]. The other catalysts showed no loss of activity prior to H₂S addition. Apart from Cu-promoted, all promoted catalysts revealed better sulfur resistance than the unpromoted catalyst, as shown by a longer phase 1 (Figure 7a). Results from CHNS analysis showed that sulfur uptake was increased by 10–20% for all promoted catalysts (to 658–722 $\mu\text{mol g}_{\text{cat}}^{-1}$) compared to the unpromoted Ni catalyst (608 $\mu\text{mol g}_{\text{cat}}^{-1}$). This proves that sulfur can accumulate not only on the Ni but also on the promoters, which can protect the active Ni centers. Among the deactivation curves of the Mn-, Fe-, Co- and Zn-promoted catalysts, the respective CO₂ conversions differ mainly in the steepness of the decline of phase 2 and the final activity in phase 3, which drops down to zero CO₂ conversion for NiFe and remains highest for NiCo (~3%) [41].

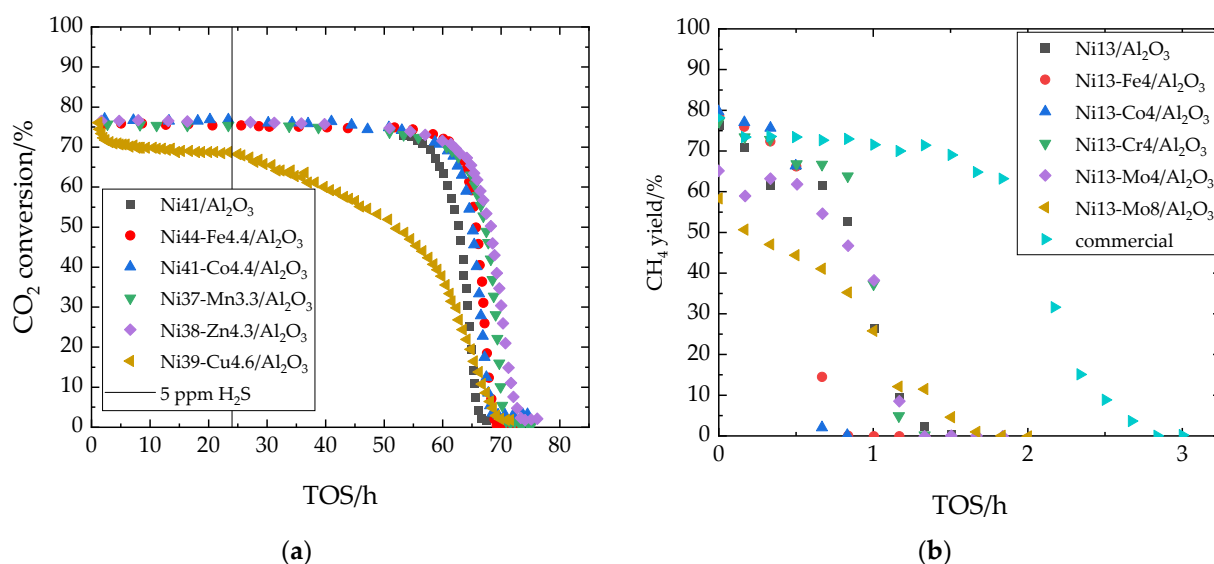


Figure 7. CO₂ conversion or CH₄ yield in H₂S poisoning experiments in methanation with Ni/Al₂O₃ catalysts and transition metal promoters with (a) 5 ppm H₂S addition after 24 h [41] and (b) 50 ppm H₂S addition [64].

The second study investigated sulfur poisoning on incipient wetness impregnated catalysts with Co, Cr, Fe, and Mo as promoters [64]. After activity tests at different temperatures (300–500 °C), methanation experiments were continued with the addition of H₂S under reaction conditions given in Table 17 until deactivation.

The evaluation of the poisoning experiments was based on the CH₄ yield [64]. After deactivation, the CH₄ yield decreased to zero in all cases (Figure 7b). Due to the rapid and complete deactivation of the catalysts within 50 to 170 min, most deactivation curves in Figure 7b cannot be divided into the three phases shown in Figure 4. The deactivation was attributed to the formation of both NiS and C deposits [64].

The first catalysts to show complete deactivation between 40 and 50 min were those promoted with Co and with Fe. Unlike the other catalysts investigated, these two catalysts kept high initial CH₄ yield above 73% for a longer time (20 min compared to ~10 min) but showed a very steep drop towards zero CH₄ yield. The catalyst with Cr promoter showed a similar deactivation curve, but with increased stability keeping a CH₄ yield above 64% for 50 min. After 80 min, the sample with Cr lost its activity, just as the 4 wt% Mo-promoted catalyst did. STEM-EDX images of spent catalysts showed that significant interactions

between promoter and Ni were only present in the catalysts with Cr and Mo [64]. These catalysts were referred to as bimetallic catalysts, while in the other two cases (Fe and Co) the promoter was distributed in the pore system alongside Ni [64].

Table 17. Catalysts and reaction conditions for experiments on H₂S influence with Ni/Al₂O₃ and Co, Cr, Fe, and Mo as promoter [64].

Catalysts	Ni13/Al ₂ O ₃ Ni13-Co4/Al ₂ O ₃ Ni13-Cr4/Al ₂ O ₃ Ni13-Fe4/Al ₂ O ₃ Ni13-Mo4/Al ₂ O ₃ Ni13-Mo8/Al ₂ O ₃
Activation conditions	400 °C, 4 h, H ₂ /N ₂
T	300–500 °C
p	10 bar
H ₂ /CO ₂	4
WHSV	33.5 g _{feed} g _{cat} ⁻¹ h ⁻¹
H ₂ S _{in}	50 ppm

Only the catalyst promoted with 8 wt% Mo can stabilize high methane yield for a longer time (100 min) than the unpromoted Ni catalyst (90 min until complete deactivation, Figure 7b). The higher S-resistance of the Mo-promoted catalyst was attributed to the inhibition of S²⁻ formation [64]. However, like the 4 wt% Mo-promoted catalyst, the initial CH₄ yield was 10–20% lower compared to the other catalysts. The advantages of Mo addition for improved sulfur resistance at the cost of a lower methanation activity have already been discussed in Sections 3 and 4. A commercial catalyst (no further details given) was also tested and showed a CH₄ yield drop to zero after 170 min.

After the poisoning experiments, regeneration experiments were carried out with 3% O₂ in N₂ for 4 h at 500 °C [64]. The catalyst activity could not be restored for any catalyst except for the Co-promoted with a much lower CH₄ yield of 13%.

7.4. Sulfur Tolerance of Unpromoted and Promoted Noble Metals on Different Supports

Two studies investigated the sulfur tolerance of noble metal-based CO₂ methanation catalysts.

The first study investigated the sulfur poisoning of co-impregnated Ru-based catalysts with Rh or Ni as promoters supported on CeO₂, SiO₂, or TiO₂ [69]. The reaction conditions for the experiments are listed in Table 18; H₂S was added immediately or after 118 min in the case of Ru5/CeO₂.

The stability of the catalysts after H₂S addition was evaluated based on CO₂ conversion and CH₄ selectivity [69]. The deactivation curves generally follow the three phases described in Figure 4, and are accompanied by decreasing CH₄ selectivity and an increase in CO selectivity.

The unpromoted Ru5/CeO₂ catalyst deactivated within 6 h after H₂S was introduced to the gas stream [69]. When Rh was added as a promoter, only the higher concentration (5 wt% Rh) contributed to improved sulfur resistance with a short (5 h) stable phase 1 (Figure 8a). By adding Ni (20 and 30 wt%) to the Ru catalyst on CeO₂, a longer stability of the CO₂ conversion and thus higher resistance to H₂S was achieved (Figure 8a). The EDX data of the deactivated catalysts showed a much lower concentration of sulfur (0.20 and 0.42 wt%) than of carbon (1.44 and 2.91 wt%) on the catalyst surfaces, with double the amount of sulfur and carbon found on the catalyst with 30 wt% Ni addition compared to Ru5-Ni20/CeO₂ [69]. The high affinity of sulfur to Ni is discussed in Section 2 and small amounts are shown to be sufficient for catalyst deactivation, as also described in the literature (Section 4.5.1). The Ru5-Ni20/CeO₂ has a stable phase 1 of around 20 h, and after

60 h the deactivation is nearly completed. Compared to 20 wt% Ni addition, the Ru catalyst with 30 wt% Ni is more sensitive to H₂S, and showed complete deactivation earlier (55 h, Figure 8a). It was assumed that due to the higher Ni loading, the more active Ru is less accessible to the gaseous reactants [69].

Table 18. Catalysts and reaction conditions for experiments on H₂S influence in methanation with bimetallic noble metal catalysts on different supports [69].

Catalysts	Ru5/CeO ₂ Ru5-Rh1/CeO ₂ Ru5-Rh5/CeO ₂ Ru5-Ni20/CeO ₂ Ru5-Ni30/CeO ₂ Ru5-Ni20/SiO ₂ Ru5-Ni20/TiO ₂
Activation conditions	500 °C, 2 h, H ₂
T	375 °C
p	12.5 bar
H ₂ /CO ₂	4
WHSV	40 L g _{cat} ⁻¹ h ⁻¹
H ₂ S _{in}	1 ppm

Comparing Ru5-Ni20 on three supports (CeO₂, SiO₂, TiO₂), the catalysts with CeO₂ and TiO₂ support both showed a typical stable phase 1 at the beginning of the poisoning tests. The longest stable phase 1 with 20 h was shown by the above described Ru5-Ni20/CeO₂. The SiO₂-supported catalyst showed a deviating behavior in the deactivation curve (Figure 8a) without clear differentiation into the phases shown in Figure 4. From the beginning, there was observed a continuous decline of the CO₂ conversion, but the full deactivation of the catalyst took the longest time (80 h) of all tested catalysts [69]. With the SiO₂ support, CH₄ was still formed with high selectivity (~78%) even after deactivation, while the CH₄ selectivity dropped to zero for the other catalysts [69]. TEM images with Ni mapping showed that Ni was well distributed on the support, which led to smaller particle sizes compared to the catalysts with different support materials. However, the specific surface area of Ru5-Ni20/SiO₂ (221 m² g⁻¹) was much higher than the surface area of the other catalysts (35–59 m² g⁻¹) [69].

The Ru5-Ni20/TiO₂ catalyst was used to test a regeneration procedure with 0.12% O₂ in N₂ (600 °C, 4 h) after poisoning [69]. The catalyst did not regain its initial activity, and deactivation started immediately after restarting the reaction.

In the second study, different unpromoted noble metals (Rh, Pd, and Ru) impregnated on TiO₂ were tested and the sulfur tolerance of Rh was further investigated on different supports [101]. The reaction conditions of the experiments are given in Table 19. Since no pressure during the reaction was specified, it is assumed that the experiments were performed at atmospheric pressure.

The catalyst activity during H₂S addition was evaluated based on CO₂ conversion and CH₄ formation rate [101].

For Rh/TiO₂, a promoting effect of 22 ppm H₂S was found when the freshly reduced catalyst was used (Figure 8b). However, with 116 ppm H₂S the catalyst deactivated rapidly within 130 min. For Ru and Pd on TiO₂, and for Rh/CeO₂, the addition of 22 ppm H₂S also resulted in an increased product formation rate compared to a reference experiment without H₂S addition. However, the main product of the reaction on Pd/TiO₂ was CO [101]. TPD (temperature-programmed desorption) measurements showed that sulfur was built into oxygen vacancies of the TiO₂ support and created new sites with catalytic activity at the metal-support interface. These sites prevented re-oxidation of the oxygen vacancies, and thus led to the observed higher stability of CO₂ methanation [101].

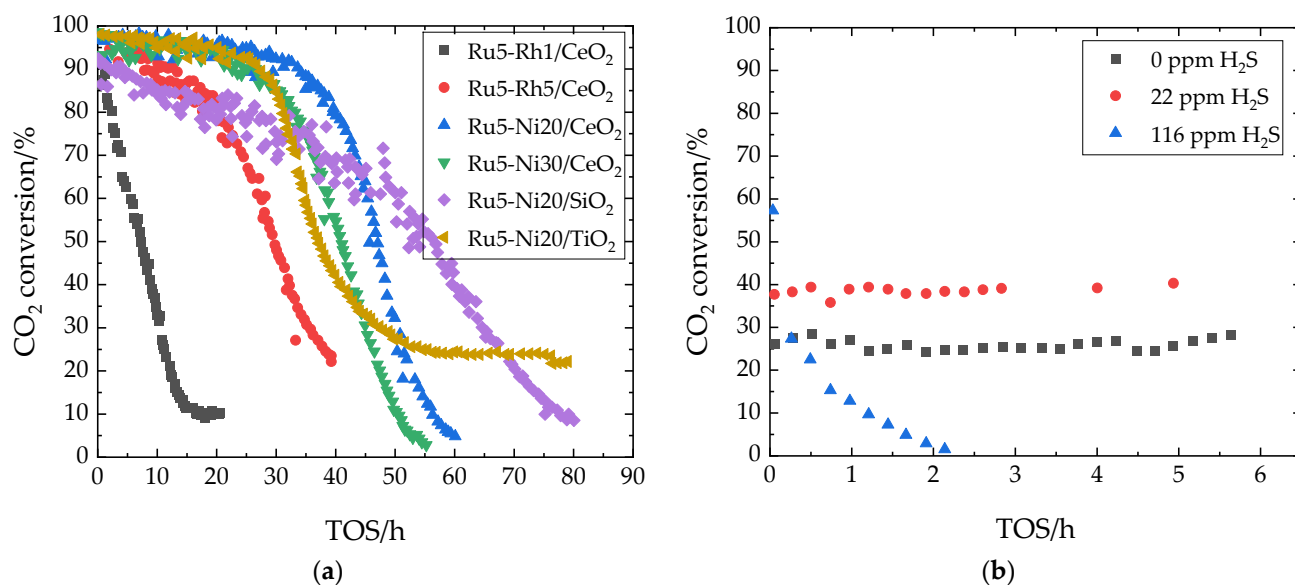


Figure 8. CO₂ conversion in H₂S poisoning experiments in methanation with (a) 1 ppm H₂S addition to bimetallic Ru catalysts [69] and (b) Rh/TiO₂ [101].

Table 19. Catalysts and reaction conditions for experiments on H₂S influence in methanation with noble metals on different supports [101].

Catalysts	Rh/TiO ₂ Ru/TiO ₂ Pd/TiO ₂ Rh/Al ₂ O ₃ Rh/SiO ₂ Rh/CeO ₂ Rh/ZrO ₂ Rh/MgO
Activation conditions	400 °C, 1 h
T	275 °C
p	not specified
H ₂ /CO ₂	4
GHSV	not specified
H ₂ S _{in}	22 ppm, 116 ppm

The promoting effect of 22 ppm H₂S was not observed for Rh/SiO₂ and Rh/Al₂O₃. Some of the catalysts (Rh/ZrO₂, Rh/MgO) initially showed CO₂ conversions below 1% in the absence of H₂S and no conversion when 22 ppm H₂S was added.

7.5. Discussion on the Effect of H₂S in the Feed

Characterization of the catalysts by Raman spectroscopy showed that sulfur species are strongly dispersed on the catalyst surface [60,99]. This means that even a small amount of sulfur can lead to deactivation, and explains the rapidly decreasing activity curves. Despite the use of different catalysts and reaction conditions, the studies considering the selectivity of CH₄ and CO have in common that deactivation is accompanied by a selectivity shift from CH₄ to CO as the main product [60,69,99]. This was seen for both Ni and noble metal catalysts.

It was also shown that the support material plays an important role. In the case of CeO₂, carbonates were formed more easily compared to Al₂O₃, which facilitates the subsequent hydrogenation to formate and leads to better CO₂ conversions [99]. In the case

of a Ru-Ni catalyst with SiO₂ as support, CH₄ could be formed even after severe catalyst deactivation with 80% selectivity due to the improved interaction with the catalytically active metal particles [69]. This performance was not seen with the other catalysts and requires a highly dispersed active phase.

Apart from the choice of a suitable support material, monometallic catalysts can be made more sulfur-resistant by increasing the concentration of the active metal (Figure 9) [60]. Comparing the amount of added H₂S up to complete deactivation (start of phase 3) for the unpromoted Ni catalysts, the tolerable amount of sulfur increases under-proportionally with increasing Ni loading. At twice the Ni loading (20 compared to 40 wt%), the sulfur content that passed over the catalyst increases only from 7.9 to 9.2 mg_{H₂S}/g_{cat} (Figure 9). This might be explained by geometrical features such as surface/volume ratio of the Ni particles, which depends on the dispersion.

Different transition metals (Mn, Fe, Co, Zn) were shown to adsorb H₂S [41]. The addition of promoters such as Ce [60,62] or Mo [64] seems especially promising (Figure 9) to protect the catalytically active sites. For Ce as a promoter, it was shown at the molecular level that Ce₂O₂S species form preferentially over Ni sulfides [62]. While Ce additionally led to an improved CO₂ methanation activity due to its structural properties, the activity of the tested Mo-promoted catalysts was lower. In the case of the catalysts studied in Section 7.3, this could also be due to the choice of support material. In the literature (cf. Section 4.5.3) it was described that Mo does not form a stable structure on Al₂O₃. The interaction of the promoter with the active metal also seems to play a major role. Among the promoters Co, Cr, Fe, and Mo, significant interactions with Ni were only seen with Cr and Mo. These were the catalysts that showed better sulfur resistances in the experiments [64].

In noble metal-based bimetallic catalysts, Ni can act as a sulfur trap. However, appropriate loading should be selected, as it has been shown that too high Ni concentrations can accelerate sulfur deposition and increase carbon formation [69]. The advantages of Ni as a sulfur trap are small in such cases, and the disadvantages in terms of C deposition outweigh the advantages.

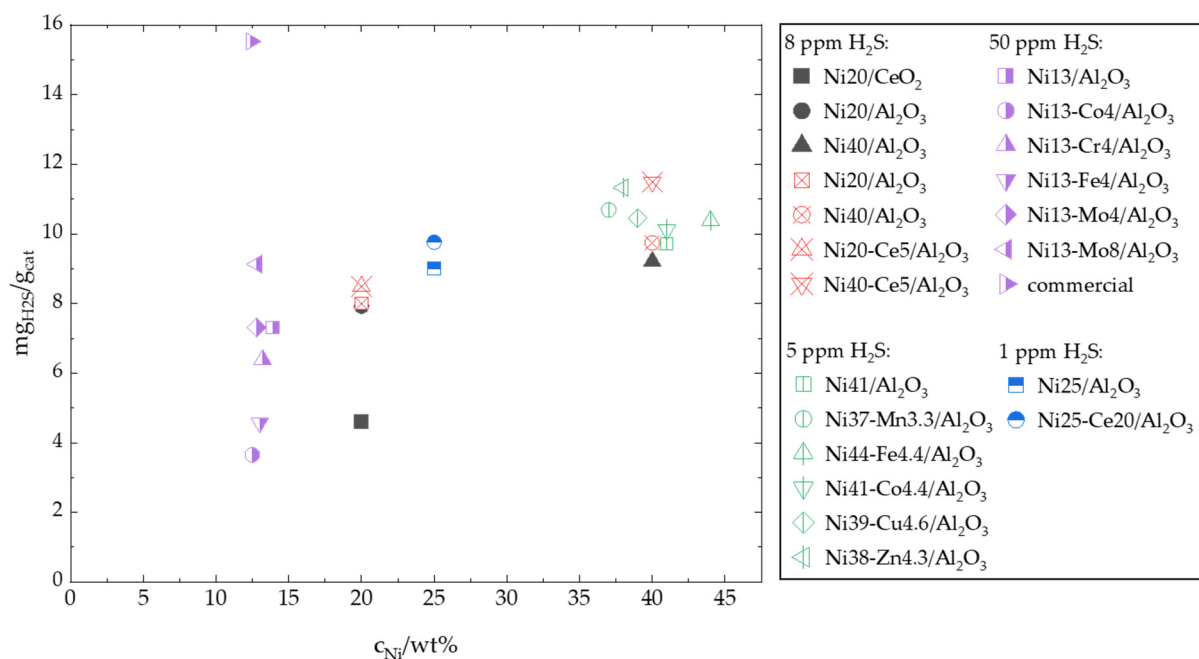


Figure 9. Correlation of total fed H₂S amount and metal content until complete deactivation (beginning of phase 3) for the catalysts from studies discussed in Section 7. Calculations are given in Appendix B.

In one study, a promoting effect of H₂S in the inlet gas on the CH₄ formation rate was described [101]. Since this effect was only observed at the lowest H₂S concentration within that study (22 ppm), and only on a fresh catalyst surface, the statement cannot be transferred to the real application. However, the study provides evidence that reducible support materials, e.g., with oxygen vacancies in the crystal lattice, are better suited for the application with H₂S in the feed gas than non-reducible supports such as MgO and Al₂O₃.

In the two studies in which reactivation with dilute O₂ was investigated after the poisoning experiments [64,69], the activity of the catalysts could not be restored.

8. Conclusions and Outlook

The presence of both CH₄ and H₂S affects the activity of methanation catalysts. No general conclusion can be drawn for CH₄ in the feed, whether it is beneficial for methanation or not. This seems to depend on the catalyst composition and reaction conditions. However, a high methane content in the feed can have a measurable effect on the synthesis process and thus on CO₂ conversion. Depending on the CH₄/CO₂ ratio, a product gas with a higher methane content can thus be obtained compared to reference experiments without CH₄. Since the results of the studies are inconclusive, this effect needs to be scrutinized.

It should also be investigated in detail which reactions take place, e.g., whether methane reforming is a side reaction in addition to methanation. Methane reforming would lead to an increased CO₂ conversion but not to a higher methane yield. This research could uncover suitable reaction conditions (e.g., T and p), at which the methanation reaction occurs predominantly. The reviewed studies on CH₄ influence were conducted at 1 bar or only slightly higher pressure. Investigating higher pressures would be a possible starting point for further studies on the influence of CH₄ on CO₂ methanation. Future experiments on CH₄ influence should also run over a longer time to clarify whether CH₄ favors deactivation processes by C-deposition or whether sintering is delayed due to a better temperature distribution.

H₂S in the feed resulted in deactivation for all tested catalysts within several hours. The addition of promoters to Ni or the addition of Ni to a noble metal-based catalyst has been shown to trap sulfur molecules, protecting the active phase. In addition, there is evidence that reducible supports such as CeO₂ or TiO₂, which have oxygen vacancies in the crystal lattice, lead to better sulfur resistance of the catalyst than non-reducible supports. During deactivation, selectivity shifted from CH₄ to CO for both Ni and noble metal-based catalysts. This seems to be characteristic for H₂S poisoning on methanation catalysts. For the unpromoted Ni catalysts with increasing Ni loading, the tolerable amount of sulfur increases under-proportionally. It could be a direction for further research to investigate higher volumes of catalysts with low Ni loading instead of lower volumes of highly loaded Ni catalysts.

Future experiments should also consider the influence of other catalyst poisons present in the biogas, such as NH₃ or siloxanes. The investigation of several biogas components together in the feed would also be an interesting research approach. This could help understanding the interaction of possibly simultaneously occurring deactivation processes such as poisoning and coking before scaling up to industrial applications.

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Appendix A

The thermodynamic equilibrium was simulated using a Gibbs reactor in Aspen Plus. Reaction conditions were 350 °C, 140 mL/min, H₂/CO₂ = 4, CH₄/CO₂ = 100/0, 50/50 and 67/33 respectively, according to the data in Table 4 from [97]. The CO₂ conversion ($X(\text{CO}_2)$) was calculated using the mole fractions of CO₂ at the inlet ($x_{\text{CO}_2, \text{in}}$) and CO₂ at the outlet ($x_{\text{CO}_2, \text{out}}$) as follows:

$$X(\text{CO}_2) = \frac{x_{\text{CO}_2, \text{in}} - x_{\text{CO}_2, \text{out}}}{x_{\text{CO}_2, \text{in}}} \quad (\text{A1})$$

Appendix B

The total mass of H₂S ($m_{\text{H}_2\text{S}}$) added until complete deactivation (t_{deact}) per catalyst mass (m_{cat}) was calculated using the mole flow of H₂S ($\dot{m}_{\text{H}_2\text{S}}$) as follows:

$$\frac{m_{\text{H}_2\text{S}}}{m_{\text{cat}}} = \frac{\dot{m}_{\text{H}_2\text{S}} * t_{\text{deact}}}{m_{\text{cat}}} \quad (\text{A2})$$

The time of complete deactivation was defined as the first data point of the plateau of phase 3 of the deactivation curves (Figures 5–8). For curves that do not follow the three deactivation phases, the last data point was used. If aging occurred prior to the poisoning experiments, this time was not considered, but only the time of H₂S addition.

The mass flow of H₂S was calculated by specifying temperature, pressure, total volume flow, and gas composition in Aspen Plus via a heater model. These reaction conditions and the catalyst mass were given in the corresponding publications.

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