

CO Methanation for Synthetic Natural Gas Production

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Abstract: Energy from woody biomass could supplement renewable energy production towards the replacement of fossil fuels. A multi-stage process involving gasification of wood and then catalytic transformation of the producer gas to synthetic natural gas (SNG) represents progress in this direction. SNG can be transported and distributed through the existing pipeline grid, which is advantageous from an economical point of view. Therefore, CO methanation is attracting a great deal of attention and much research effort is focusing on the understanding of the process steps and its further development. This short review summarizes recent efforts at Paul Scherrer Institute on the understanding of the reaction mechanism, the catalyst deactivation, and the development of catalytic materials with benign properties for CO methanation.

Keywords: Catalyst deactivation · CO methanation · Ni/Al₂O₃ · Reaction mechanism · SNG

1. Introduction

The energy demand has increased rapidly worldwide, especially in the emerging economies. However, petroleum sources continue to decrease, while there is an upward trend in price. Due to these issues, scientists face a unique challenge, and new opportunities arise for the development of technologies in order to meet current and future energy demands. These new technologies should minimize the environmental impact and mitigate the greenhouse phenomenon, which causes global warming and extreme weather situations. Strict emission legislation for the combustion of fuels requires the development of clean technologies, minimizing the environmental impact.^[1–3] Security concerns, resulting from the Fukushima nuclear disaster, also led to a reassessment of energy strategies worldwide. Especially after the decision to phase out nuclear energy in both Switzerland and Germany, the discussion about energy sustainability has intensified in academia, but even more so in industry. In order to satisfy the above-mentioned needs and concerns, new or less studied processes have attracted scientific interest and particularly catalysis will play an important role.

Non-fossil resources make up less than 20% of global energy use, while fossil resources still dominate the energy sector and chemical industry. Several issues are associated with the use of non-renewable resources. Fossil fuel reserves are finite and the high CO₂ emissions associated with their combustion is a great concern. Accordingly, renewable energy sources are needed for a future sustainable energy supply. Biomass has attracted increased interest lately because it can be converted to alternative energy using different pathways, depending on its source, type, developed conversion processes, infrastructure and economic issues.^[2,4–11]

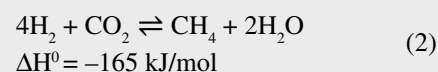
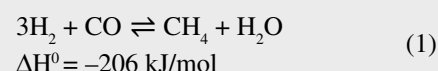
A particularly interesting energy carrier is natural gas due to its low carbon to hydrogen ratio, advantageous combustion properties, the existing pipeline grid for transportation and distribution and the well-established technologies, *e.g.* compressed natural gas cars, heating, *etc.*^[12] Today, the main starting material for the manufacture of synthetic methane is coal. Coal has an enormous potential to meet energy needs, especially in the United States and China, due to its abundant resources, since reserves are expected to last for more than 150 years. Recently, environmental concerns and the abundance of biomass have motivated researchers to shift their attention towards the conversion of biomass to methane, which is also called synthetic natural gas (SNG).^[12] Both wet biomass, such as manure, crops and sewage sludge, and dry biomass, such as wood, are advantageous starting materials for SNG. This short review will focus on the methanation activities from dry biomass developed at Paul Scherrer Institute, focusing on the process chemistry, the reaction mechanism and kinetics, sulfur poisoning, the carbon-

forming processes and recent attempts to develop novel catalytic materials.

2. CO Methanation Chemistry

The synthesis of SNG through thermochemical processes using dry biomass as feedstock follows several steps, as described in Fig. 1.^[12,13]

The initial step is the gasification of biomass (or coal) using steam or oxygen to so-called producer gas. This is a mixture containing H₂, H₂O, CO, CO₂, CH₄, saturated and unsaturated hydrocarbons, tars and impurities like ash, particles, chlorine, sulphur, *etc.* Its composition strongly depends on the biomass source and the gasification technology.^[12,14] In the next step, gas cleaning and conditioning follows to remove the impurities which may affect the process downstream. Then, SNG is synthesized by methanation according to the reaction equations (1) and (2), also known as the Sabatier reaction.^[15] Finally, fuel upgrading follows in order to remove remaining CO₂, H₂, H₂O, *etc.* and achieve the final product, methane (CH₄).



Depending on the gas mixture, the catalyst type and the reactor type, several of the above mentioned reactions occur simultaneously. If the stoichiometric ratio of H₂/CO and H₂/CO₂ is 3 and 4, respectively, reactions (1) and (2) result in the formation of the desired product. But, as seen in

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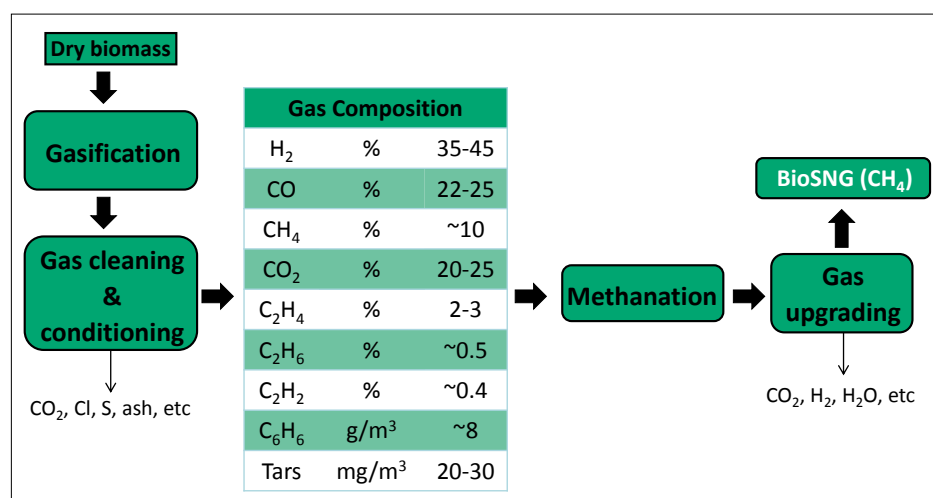
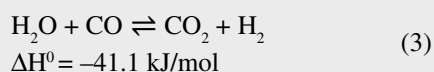
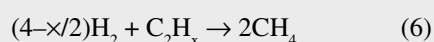
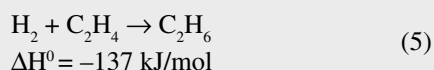
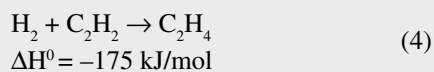


Fig. 1. General process chain from dry biomass to synthetic natural gas, applying dual fluidized-bed gasification.

Fig. 1, the H₂/CO ratio after biomass gasification is not the ideal one and may vary between 0.3 and 2. In this case, extra H₂ should be fed to the reactor. H₂/CO ratio can also be adjusted by the water gas shift reaction. The water gas shift reaction (3) accompanies the above-mentioned reactions, as it is initiated by the steam produced by them:

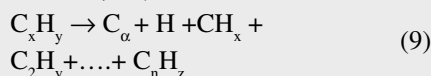
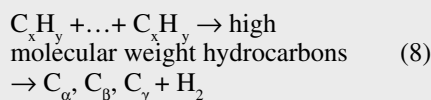


In addition to CO and CO₂, the producer gas from the gasification of biomass also contains methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), acetylene (C₂H₂), and aromatic and poly-aromatic compounds such as benzene (C₆H₆), naphthalene (C₁₀H₈), toluene (C₇H₈), *etc.*^[14,16] Due to this fact, several other reactions should be considered during the methanation step. For example C₂H₄ and C₂H₂ are hydrogenated either to C₂H₆ or CH₄, according to the reactions (4)–(6):^[17–19]

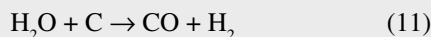
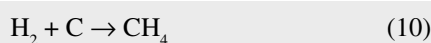


Fouling is one of the most important reasons for catalyst deactivation (others: poisoning, thermal degradation, mechanical deactivation and corrosion/leaching). The most important example of fouling and one of the major problems in many catalytic processes is the deposition of carbon or coke.^[20–22] Depending on the conditions (temperature, pressure, hydrogen, type of hydrocarbon, *etc.*) several reactions

may occur during CO methanation, leading to formation of carbonaceous deposits. Carbon-forming processes involve the chemisorption of different kind of carbons or condensed hydrocarbons, which then act as catalyst poisons. Carbon is usually formed by CO disproportionation (also known as the Boudouard reaction, (7)), unwanted polymerization and dehydrogenation of hydrocarbons (8) or dissociation of hydrocarbons (9).^[20,22]



The surface carbon may react with both H₂ and H₂O (gasification) again forming gaseous compounds:



All of the above-mentioned reactions are highly exothermic.

CH₄ synthesis is a heterogeneous catalyzed process and due to its exothermic nature, it brings several challenges for the catalyst itself and the process as a whole. Thermodynamically, methanation is favored at low temperatures and high pressures. These high pressures result in a large amount of heat per reactor volume. Under these conditions, the formation of hot spots on the catalyst is inevitable. High-temperature sites induce catalyst deactivation due to the promotion of sintering of metal sites and carbon deposition.^[12]

In the following sections, studies on a commercial Ni/Al₂O₃ catalyst for CO methanation will be presented, with a focus on the kinetics and mechanism of the process, the deactivation mechanism due to carbon deposition and sulphur poisoning, recent attempts to improve a Ni/Al₂O₃ catalyst against fouling and the application of unsupported nickel nanoparticles of different morphologies.

3. Reaction Mechanism and Kinetics for the Main Reactants during CO Methanation

Over the past 50 years, a variety of papers has been published with proposed kinetics and reaction mechanisms for CO methanation.^[15,23,24] Applying appropriate experimental conditions, the rate of reaction could be calculated. Due to the range of different catalysts tested, experimental conditions and reactor types, several propositions have been made. Recently, a study was published applying spatially resolved measurements in a catalytic plate reactor coated with a commercial Ni/Al₂O₃ catalyst aiming to investigate the influence of different reaction parameters on CO methanation.^[25,26] Two main models are proposed, shown in Table 1. Mechanism A proceeds on a nickel surface through the adsorption and dissociation of CO to adsorbed carbon. This adsorbed carbon is hydrogenated to CH₄ via a four-step process. This mechanism was initially proposed by Araki and Ponec^[27,28] and was confirmed by isotopic labelling experiments and also confirmed by Galuszka *et al.*^[29] using infrared spectroscopy. In mechanism B, hydrogenation of the adsorbed CO to COH_x* intermediates is necessary to facilitate the splitting of carbon–oxygen bond. The remaining steps are common in both mechanisms A and B.^[25,26,30,31]

Recent studies on temperature programmed desorption and hydrogenation applying modulation excitation infrared spectroscopy over a commercial Ni/Al₂O₃ catalyst demonstrated that the linear coordinated CO on Ni is weaker bonded and more reactive compared to the bridged CO.^[32] Isotopic labelling experiments, using ¹²CH₄, ¹³CO and D₂, demonstrated the formation of ¹³CD₄, ¹²CH₄, ¹³CHD₃ and ¹²CD₄. Thus, ¹²C- and ¹³C- species seem to compete for recombination with D₂ and for adsorption on Ni sites.

It is clear from Fig. 1 that high concentrations of CO₂ are also present in the gas feed after biomass gasification. The catalytic materials designed for CO methanation are in general active for CO₂ methanation as well.^[33] However, on all these catalysts CO preferentially reacts with H₂ due to the stronger adsorption of

Table 1. Reaction mechanisms A and B and possible rate determining steps. Adapted from refs [25] and [26]

Mechanism A	Mechanism B	Rate determining step
$H_2 + 2* \leftrightarrow 2H^*$		
$CO + * \leftrightarrow CO^*$		X
$CO^* + * \leftrightarrow C^* + O^*$		X
	$CO^* + \alpha H^* \leftrightarrow COH_v^* + \alpha^*$	X
	$COH^* + * \leftrightarrow CH^* + O^*$	X
	$COH^* + * \leftrightarrow C^* + OH^*$	X
	$COH_v^* + \alpha H^* \leftrightarrow COH_w^* + \alpha^*$	X
	$COH_x^* + \alpha H^* \leftrightarrow CH_y^* + H_zO^*$	X
$C^* + H^* \leftrightarrow CH^* + *$		X
$CH^* + H^* \leftrightarrow CH_2^* + *$		X
$CH_2^* + H^* \leftrightarrow CH_3^* + *$		X
$CH_3^* + H^* \leftrightarrow CH_4^* + *$		
$CH_4^* \leftrightarrow CH_4 + *$		
$CO^* + O^* \leftrightarrow CO_2^* + *$		
$CO_2^* \leftrightarrow CO_2 + *$		
$O^* + H^* \leftrightarrow OH^* + *$		
$OH^* + H^* \leftrightarrow H_2O^* + *$		
$H_2O^* \leftrightarrow H_2O + *$		
$CO^* + OH^* \leftrightarrow CO_2^* + H^*$		
$CO^* + H_2O^* \leftrightarrow CO_2^* + 2H^*$		

* empty active sites; CO* adsorbed species (e.g. adsorbed CO)

CO compared to CO₂.^[34,35] Methanation of CO₂ is completely suppressed until a high conversion of CO is achieved. It has also been reported that the rate of methanation during co-methanation of CO and CO₂ is higher than the individual reactions, despite the preferential reaction of CO during co-methanation.^[34]

4. Catalyst Deactivation (Sulphur Poisoning, Carbon Deposition)

Catalyst deactivation during CO methanation may be related with one of the following phenomena or a combination thereof:^[12]

- i) Loss of active surface, due to sintering of metal crystallites;
- ii) Loss of active phase, due to its separation (physically or chemically) from the main part of the catalyst;
- iii) Fouling, caused by carbon deposition;
- iv) Poisoning, due to inorganic compounds, where the nature of the active sites change.

Most of these processes can be limited or completely avoided at industrial scale, but understanding their impact and controlling their extent is a crucial step towards effective catalyst development and increased life-time. In the following sections, the phenomena leading to catalyst

deactivation caused by sulphur and carbon species will be further described.

4.1 Fouling by Carbon Deposition

As referred to in the section ‘Methanation Chemistry’, fouling is one of the main reasons for catalyst deactivation during CO methanation, due to the conversion of CO and hydrocarbons that are present in the gas stream. These carbon-containing compounds tend to react with each other or the active metal (e.g. Ni), forming various types of carbon deposits or coke and leading to deactivation. Several studies have been reported on this topic as it is one of the main reasons of catalyst deactivation not only in methanation but also on reforming processes (e.g. steam or dry reforming).^[20,22,36–38] The main problem of CO methanation from biomass-derived gas is the presence of C₂ species and aromatics.^[12,14] Most carbon species and coke stem from these compounds and strongly depend on the temperature, H₂ and CO concentrations, partial pressure of H₂O, nickel crystallite size and the type of support.^[23] An overview of the carbon types formed during CO methanation is given in Table 2.

CO and higher hydrocarbons (e.g. C₂ species, aromatics) dissociate on the surface of the catalyst to single carbon atoms, called adsorbed carbon atoms or C_α. These carbon atoms are the intermediate for the

synthesis of CH₄. When the carbon deposition rate is higher than that of the reaction with H₂, O₂ or H₂O and if temperatures are below 400 °C, these carbon atoms diffuse into the bulk nickel forming bulk nickel carbide or C_γ. With further increase of the temperature to 500 °C, the adsorbed carbon atoms polymerize forming an amorphous carbon film, called C_β. This film may cover the active metal sites, which are no longer accessible by the reactants. With time, the amorphous carbon transforms into graphitic carbon (C_ε), which is also referred to as encapsulating carbon (C_δ). Graphitic carbon may also be formed in the presence of C₂H₂ and C₂H₄ in the temperature range of 500–800 °C. In the same temperature region the formation of platelet carbon (C_e or C_c) is also favored. Finally, a whisker type of carbon or carbon fibers may be formed in a broad temperature range from 300 up to 1000 °C. This type of carbon is sometimes labelled as vermicular carbon (C_v) or filamentous carbon C₈. In this case, carbon diffuses into the bulk nickel (forming an intermediate nickel carbide) and lifts the nickel crystallite from the support. The catalyst is not deactivated, as the active nickel sites are still accessible to the reactants. But the continuous growth of the carbon whiskers leads to pore blockage or the loss of active phase during regeneration. Finally, pyrolytic or non-catalyst carbon (G) is formed at temperatures above

Table 2: Overview of the carbon types on nickel catalysts, including carbon source and formation temperature, based on refs. [13, 22, and 39]

Carbon type	Carbon source	Formation temperature
Adsorbed carbon atoms (C_α)	CO, H_2	
Pyrolytic or non-catalyst carbon (G)	CO, C_2H_2 , C_2H_4 , C_2H_6	>600 °C
Platelet (C_e or C_c)	C_2H_2 C_2H_4	500–800 °C 600–800 °C
Whiskers (C_v or C_δ)	CO	300–1000 °C
Graphitic or encapsulating (C_c or C_δ)	CO, C_2H_2 CO, C_2H_4 Amorphous carbon (C_β)	500–800 °C 600–800 °C 500–600 °C
Amorphous (C_β)	CO	250–500 °C
Bulk carbide (C_γ)	CO	<400 °C

600 °C in the presence of C_2 hydrocarbons. This type of carbon species is not connected with Ni crystallites, but leads to catalyst deactivation by blockage of the active metal sites.^[22,36,39]

4.2 Sulphur Poisoning

As discussed in more detail above, the gas mixture after biomass or coal gasification also contains hetero-atoms and inorganic compounds, such as nitrogen or sulphur species, chlorine, *etc.*^[12,40] Among them, sulphur-containing species are the most challenging to remove. Sulphur may be found in the form of hydrogen sulphide (H_2S), carbon disulphide (CS_2), carbonyl sulphide (COS), mercaptans and thiophenic species.^[41]

In large coal-to-SNG plants, sulphur compounds are removed with the use of Rectisol® scrubbing.^[41] This method is not economically feasible in small-scale units. For these units, two gas cleaning technologies have been proposed and used, based on catalytic processes and absorber columns. In the former, sulphur-containing organic compounds are converted to H_2S and hydrocarbons, typically on a transition metal catalyst. The same catalyst favors the conversion of high hydrocarbons, also present on the gas stream, to H_2 , CO and low hydrocarbons through hydrogenation or steam reforming.^[42] In the second method, the absorber columns filled with an absorbing liquid, such as polyethylene glycol, effectively remove the sulphur compounds. A disadvantage of this method is that the absorber columns have to be operated at low temperatures and high pressures. The absorbers are relatively expensive and may generate liquid waste.

Independent of the method used, sulphur compounds can be found even after the sulphur removal unit. For example, after long-term measurements in the FICFB gasifier in Güssing (Austria), catalyst deactivation was observed after 190 h.^[43] Post-treatment analyses of the catalyst by XPS revealed the presence of sulphur, in-

dicating that the removal of some species was not completely successful by ZnO. It is well-known that only a few ppm of sulphur species are sufficient to poison a nickel catalyst. H_2S has been reported to be the main compound in the gas stream, but thiophenic species are considered more important for catalyst deactivation (Fig. 2). Sulphur is considered as a very selective poison as it is adsorbed and dissociated on nickel surfaces specifically blocking the adsorption of both H_2 and CO. Due to its strong adsorption, its removal from a nickel catalyst can only be achieved by a complex redox cycle. Using high oxygen partial pressure, nickel sulphate may be formed, which can be further removed by oxidative treatment at $T > 800$ °C. The disadvantage of this method is the complete destruction of the catalyst, as it cannot be regenerated.^[44]

5. Catalyst Development

The performance of the methanation reactor usually is not limited by the cata-

lyst's activity, but mainly by mass transfer limitations, heat removal and the thermodynamic equilibrium. But the stability of the catalytic materials is always of great concern. Ni-based catalysts are considered to be active for CO methanation.^[2,16,45–48] Although noble metals can be even more active for this reaction, nickel is most attractive due to its lower price and abundance in nature. However, Ni-based catalysts are very sensitive to carbon formation. In the last decades, research efforts have been focused on the investigation of catalytic phenomena that occur on this material and their relation with its physicochemical properties. For this reason, several parameters, such as preparation and pretreatment conditions and catalysts composition have been extensively discussed and studied at the Paul Scherrer Institute. The aim is to introduce new catalytic systems with improved mechanical properties for fluidized-bed reactors,^[49] as well as benign properties with response to their long-term stability (sintering and coking resistance).^[50,51]

Recently, a novel catalytic material was

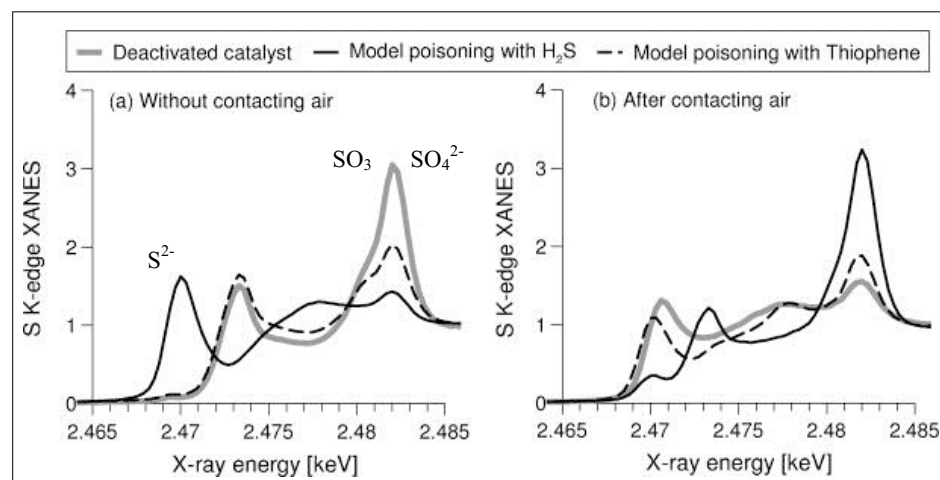


Fig. 2. (a) S K-edge XANES of the deactivated catalyst collected air-free from the methanation reactor in Güssing (Austria) and that of catalysts poisoned at $T = 400$ °C in model experiments with H_2S - and thiophene-doped carrier gas, respectively. (b) As with (a), but the samples was in contact with ambient air prior to analysis. Adapted from ref. [43].

proposed that showed remarkable stability during CO methanation in the presence of unsaturated hydrocarbons in the feed. A Ni/Al₂O₃ catalyst was synthesized by wet impregnation composed of 15 wt% of Ni, which is a much lower content compared to the commercial Ni/Al₂O₃ catalyst currently applied in the methanation processes.^[50] Boron was selected as promoter for this catalytic material, because it has been reported to improve the carbon resistance of Ni-based catalysts in steam and dry reforming reactions (high temperature processes).^[52–54] Because boron and carbon atoms have similar binding energies, boron has been proposed to block step and octahedral sites of Ni, which prevents carbon formation. As a result, carbon species remain on the surface, where they can be easily removed.^[55] In this work, boron was introduced as a promoter aiming at improved stability and carbon resistance of Ni/Al₂O₃ for the low temperature CO methanation in the presence of unsaturated hydrocarbons (C₂H₄) in the reaction feed. The catalysts were synthesized by wet impregnating nickel and boron precursors simultaneously or sequentially on a commercial γ -Al₂O₃ support. The stability tests were conducted at 593 K and GHSV = 120000 mLg⁻¹h⁻¹ under 25 vol% H₂, 5 vol.% CO, 2000 ppm C₂H₄ (bal. N₂). When C₂H₄ was not present in the reaction feed, Ni/Al₂O₃ remained stable during the 4 h catalytic test. In contrast, in the presence of C₂H₄, Ni/Al₂O₃ lost ~20% of its initial activity within 4 h. Co-addition of nickel and boron on Al₂O₃ resulted in a catalytic material stable with time on stream, as no deactivation was observed. The temperature programmed oxidation (TPO) results recorded after the stability tests exhibited significantly different CO₂ desorption peaks at the lower temperature region (450–700 K). The thermogram of the Ni/Al₂O₃ catalyst after exposure to ethylene was dominated by a strong CO₂ desorption peak centered at 560 K, which was attributed to nickel carbide and amorphous carbon species. This peak vanished in the presence of boron.^[50]

In order to elucidate this observation, the catalytic materials were characterized using transmission electron microscopy (HR-TEM, HAADF-STEM), X-ray diffraction (XRD), ¹¹B-MAS NMR, and Raman spectroscopy. The XRD results indicate that the NiO crystallite size was larger on the boron-containing catalyst. This result is also consistent with the HAADF-STEM results. Although literature predicts that boron may control the metal particle size, this effect was not observed. Boron seems to act as flux, similar to single crystal growth, increasing ion mobility and releasing strain. But in this case, the low amount of boron ions led to an increase of the average NiO particle size. The effect

of boron on the morphology of the materials was also evident in the HAADF-STEM images from the several dark areas on the NiO particles. These dark areas suggest that either these regions contain material with lower mass than Ni or the thickness is locally decreased. It was proposed that these dark regions correspond to non-interconnected pores of *ca.* 3 nm diameter formed on nickel particles in the presence of boron. EELS measurements on the B K-edge confirmed that these dark areas contain boron species. The close interaction of nickel and boron was confirmed by ¹¹B-MAS NMR and Raman spectroscopy. NMR indicated that boron atoms interact with the paramagnetic nickel species and only part of the magnetization is detected. Increased vibration in the Raman spectra at 800–900 cm⁻¹, assigned to symmetric and anti-symmetric vibrational modes of M-O-M bridges (M = Ni and/or B) also

confirms the above statements. In summary, it can be stated that a novel catalytic material was developed with enhanced stability against carbon deposition for the low temperature CO methanation reaction. This material is a potential candidate for both fixed-bed and fluidized-bed reactors.^[50]

Another approach for new types of CO methanation catalysts involved the development of modern engineered materials. Nickel nanoparticles were synthesized by means of a Segmented Flow Tubular reactor (SFTR), using the polyol method. Several synthesis parameters, like precursor, temperature, reaction time, were investigated to tune the particle surface morphology and size and study their influence on the catalytic properties.^[51] With the use of hydrazine (N₂H₄) the surface morphology was successfully controlled, which varied from raspberry-like to spiky nanoparticles

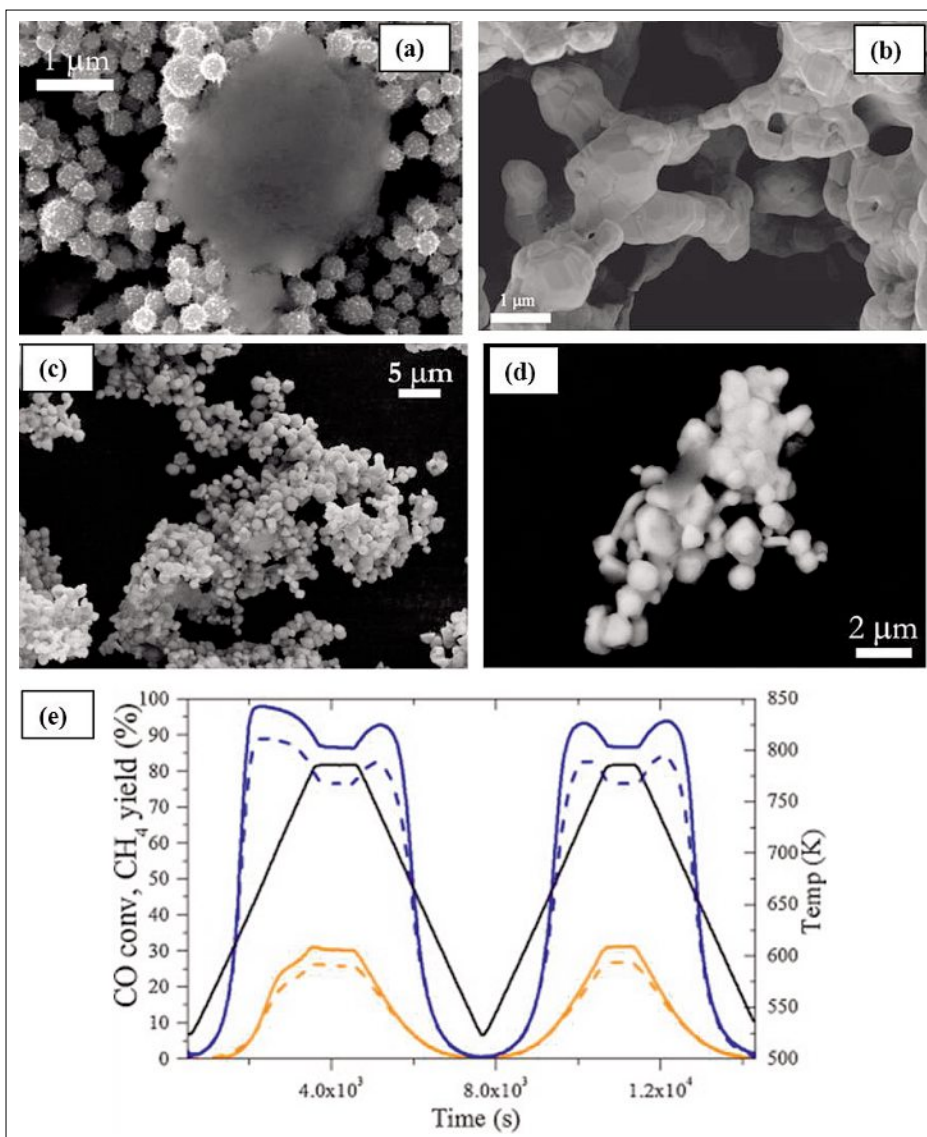


Fig. 3. SEM images of the catalyst before (a: spiky NPs, c: commercial particles) and after (b: spiky NPs, d: commercial particles) the catalytic tests. (e) Test of catalytic CO methanation with spiky NPs (blue line) and commercial particles (yellow line). The black line corresponds to the temperature in the catalyst bed. Adapted from ref. [51].

of ca. 160 nm size (Fig. 3a–d). In all cases a substructure of smaller primary particles of 8–16 nm size was detected.

The catalytic performance of all Ni NPs was evaluated for CO methanation in a fixed-bed reactor performing several heating ramps from 250 to 500 °C (Fig. 3e). The thermal treatment under operando conditions allowed the formation of catalyst, in a sponge-like morphology. This morphology can be developed only from nanoparticles and not from nickel particles in the micrometer range (reference commercial material). This sponge structure proved to be relatively active, stable and reproducible, but is still far from displaying the catalytic properties of the commercial Ni/Al₂O₃ catalyst. However, it is a first step towards the development of advanced engineered materials with tailored properties.

6. Conclusions and Outlook

Production of synthetic natural gas from biomass is considered to be an important process for a future sustainable energy system. In recent years, many research groups have focused on the further development of all process steps, from gasification of biomass to the SNG synthesis. In-depth study of the reaction mechanism and the deactivation pathways due to carbonaceous deposits and sulphur poisoning proved to be crucial for a further development of the catalysts with the aim to improve the process efficiency. Recent catalyst development strategies led to materials with benign properties for both fixed-bed and fluidized-bed reactors. These materials, based on nickel, show unique properties with respect to their long-term stability against sintering and coking.

The presence of unsaturated hydrocarbons is a challenge for the long-term catalyst stability and their conversion to less reactive species is of great importance. The understanding of their influence on the fundamental level is still lacking and further research efforts are needed for clarifying their impact on catalyst deactivation, which will allow the whole process to be further optimized. Additionally, since CO methanation technology is moving towards fluidized-bed reactors, the development of mechanically stable catalytic materials with improved attrition properties is a research direction of increasing significance.

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