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Coatings of active and heat-resistant cobalt-aluminium xerogel catalysts

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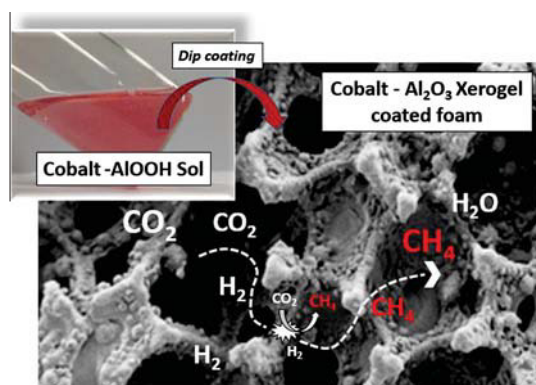
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GRAPHICAL ABSTRACT



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ABSTRACT

The application of catalytically coated metallic foams in catalytic processes has a high potential for exothermic catalytic reactions such as CO₂ methanation or Fischer-Tropsch synthesis due to good heat conductivity, improved turbulent flow properties and high catalyst efficiencies. But the preparation of homogenous catalyst coats without pore blocking is challenging with conventional wash coating techniques. Here, we report on a stable and additive free colloidal Co–AlOOH suspension (sol) for the preparation of catalytically active Co/Al₂O₃ xerogel catalysts and coatings. Powders with 18 wt% Co₃O₄ prepared from this additive free synthesis route show a catalytic activity in Fischer-Tropsch synthesis and CO₂ methanation which is similar to a catalyst prepared by incipient wetness impregnation (IWI) after activating the material under flowing hydrogen at 430 °C. Yet, the xerogel catalyst exhibits a much higher thermal stability as compared to the IWI catalyst, as demonstrated in catalytic tests after different heat agings between 430 °C and 580 °C. It was also found that the addition of polyethylene glycol (PEG) to the sol influences the catalytic properties of the formed xerogels negatively. Only non-reducible cobalt spinels were formed from a Co–AlOOH sol with 20 wt% PEG. Metallic foams with pores sizes between 450 and 1200 μm were coated with the additive free Co–AlOOH sol, which resulted in homogenous xerogel layers. First catalytic tests of the coated metal foams (1200 μm) showed good performance in CO₂ methanation.

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1. Introduction

Cobalt containing catalysts are well-known for their catalytic activity in Fischer-Tropsch synthesis (FTS) and CO₂-methanation [1–3]. To increase the specific metal surface area and the stability of the catalysts, cobalt is often supported on porous metal oxides, such as Al₂O₃ and SiO₂ [4].

In case of industrial fixed bed reactors, pellet catalysts are commonly used to reduce the pressure drop inside the reactor. Yet, problems with internal mass transport limitation often occur [5]. On a monolithic support, the catalyst is deposited in a channel in form of a thin layer. Monolithic catalysts are well established as mobile emission catalysts, where the layers are produced by a dip coating process using a viscose water-based suspension containing the catalytic active compounds and the support material. Layers of 10–300 μm thickness can be deposited on commercial honeycomb monoliths in this way [6]. These thin catalytic coatings provide a high effectiveness factor compared to pellet catalysts. Moreover, the pressure drop through a monolithic catalyst is considerably smaller than in a fixed bed filled with pellets [7].

Kapteijn et al. coated ceramic honeycomb monoliths with a Co–Al₂O₃ suspension and investigated the influence of the catalytic layer thickness in the range between 20 and 100 μm for the Fischer-Tropsch reaction [8]. They found that a layer thickness above 50 μm results in internal diffusion limitations. Although the amount of olefins decreases with increasing layer thickness, highest activity and selectivity were found for monoliths with catalytic coatings of 20 and 30 μm layer thickness. Almeida et al. reported increasing methane selectivity with increasing layer thickness for the Fischer-Tropsch reaction. They explained the effect by a different diffusivity of H₂ compared to CO in pores filled with liquid [9]. With increasing layer thickness the H₂/CO ratio increases within the pores and thus methane formation is favoured.

In contrast to ceramic substrates, metallic substrates exhibit better heat transfer properties. Due to the difference in the thermal expansion coefficient of the metallic substrate and the ceramic coatings, exfoliation may, however, occur after drying and calcination. Almeida et al. [9] coated different metallic supports (micro monolith, foam and a honeycomb monolith) with a suspension containing 20 wt% Co and 0.5 wt% Re and tested them for Fischer-Tropsch synthesis. The C₅₊ selectivity increased in the following order: micro monolith > foam > monolith > powder catalyst. Nevertheless, the application of finely structured foams for catalytic reaction offers the advantage of a high catalyst efficiency factors due to turbulent flow in comparison to honey-comb monoliths samples. Using foams with increasing ppi (pores per inch) and decreasing pores sizes can further increase the activity. But using conventional wash-coating techniques, the coating of foams with small pores can be difficult (pore blocking).

A different coating approach is achieved by using a colloidal suspension (sol), a strategy often employed in the field of membrane science for very homogenous and thin coatings. This chemistry involves the formation of three different phases. In a first step, a stable colloidal suspension is prepared, which can be coated on a substrate by a dip coating process. Subsequently, the solvent starts to evaporate and a hydrogel is formed on the substrate. The hydrogel can then be treated at high temperatures to get a (calcined) xerogel coating. With this technique, layers in a thickness range of 1–10 μm can be prepared [6]. In comparison to the suspension approach, the active phase is formed directly on the substrate, usually resulting in good adhesion properties [10]. The starting materials are metal-organic precursors such as aluminium-tri-sec-butoxide (ATB) or tetraethoxysilane (TEOS), which can be stabilized in a proper solvent [11–13]. Furthermore,

organic binders such as polyvinyl alcohol (PVA) or polyethylene glycol (PEG) are often added to the sol to increase the viscosity and improve the adhesion of the colloidal suspension on the substrate [10].

One challenge in terms of cobalt containing Al₂O₃ xerogel coatings for catalytic applications is the formation of a catalytically active xerogel material with good adhesion properties on the substrate. In addition, the sol properties have a huge influence on the layer formation by dip coating. On the one hand, the stability of the sol has to be ensured during the whole coating process without starting the gelation. On the other hand, the viscosity should be higher than water to realize good adhesion on the support. Eventually, the nature of the formed cobalt phase after pre-treatment determines the catalytic activity and selectivity. Too small Co₃O₄ particles exhibit limited reducibility and consequently low activity or the formation of CoAl₂O₄ results in inactive catalysts [14,15].

Zayat and Ayari et al. mixed a solution of ATB with a cobalt precursor solution and reported a fast gelation after adding the cobalt phase [16,17]. Lavrenčič et al. described a technique for the preparation of a stable Co–AlOOH based sol [18]. They used ATB in isopropanol and stabilized the solution with ethyl acetoacetate as chelating agent. The sol was stable over months, but, after calcination at 650 °C, a blue powder of CoAl₂O₄ crystals was obtained, which was neither active for Fischer-Tropsch reaction nor CO₂-methanation [19,20]. Many other authors as well reported the formation of CoAl₂O₄-spinel structures using sol-gel techniques [21–24].

In case spinel formation can be avoided, the cobalt particle size has a huge influence on the catalytic activity, stability and selectivity. Small and well-distributed particles offer a high specific surface area of the metal, but for FTS-reaction the selectivity to higher hydrocarbons is low on such small particles [14]. Furthermore, Co particles smaller than 5 nm show a high tendency towards reoxidation due to reaction with water formed as product [25,26]. In this context, a problem using sol-gel chemistry for the preparation of Co–Al₂O₃ catalysts is the encapsulation of Co₃O₄ particles into the support matrix or the formation of too small and Co₃O₄ crystallites, which are hard to reduce to metallic Co [15].

Some authors tested sol-gel prepared cobalt based xerogels for Fischer-Tropsch reaction. Most of the catalysts were not active for FT-reaction without using a reduction promoter [27–30]. The Co particles were too small and were embedded in the support matrix. Moreover, the reduction to the metal was very difficult.

In our earlier studies, Minnermann et al. tested Co–Al₂O₃ xerogels prepared by the so called-epoxide addition method - a sol-gel technique, where propylene oxide is added to a mixture of cobalt nitrate hexahydrate, aluminium nitrate monohydrate and ethanol - for Fischer-Tropsch reaction. These catalysts were not active after activation at 430 °C, while an incipient wetness prepared catalysts performed very well. But after activation at 800 °C the same activity was achieved as observed for the impregnated powders. In comparison to this, the activity of the reference catalysts drastically decreased after the high temperature treatment due to agglomeration of the cobalt particles. No sintering occurred for the xerogel catalysts, on the other hand, which is a prerequisite for a stable catalyst with long-term-stability. This phenomenon was explained by the very high metal support interaction of the sol gel catalysts [30].

In this paper, we describe the preparation of alumina-based Co catalysts based on a stable and additive free Co–AlOOH sol obtained from cobalt nitrate hexahydrate, aluminium-tri-sec-butoxide and water. Using this colloidal suspension, xerogel powders with different cobalt concentrations were prepared and characterised by XRD, BET and TPR. In one case also polyethylene

glycol (PEG) was added to the sol to investigate the influence of a binder. The systems were then compared to a reference catalyst prepared by incipient wetness impregnation (IWI). The most promising xerogel catalyst was then tested for Fischer-Tropsch reaction and CO₂ methanation. Furthermore, the influence of different heat agings before CO₂ methanation were investigated to get information about the thermal stability and reducibility of the xerogel catalyst compared to the IWI reference catalyst. Finally, we present SEM images and first catalytic results of a Co–Al₂O₃ xerogel coated metal foams prepared by our additive free synthesis route.

2. Experimental

2.1. Sol synthesis

First a 0.5-M aluminium based sol was prepared by hydrolysing aluminium-tri-sec-butoxide (97%, Sigma Aldrich) in deionized water at 80 °C. To stabilize the colloidal solution, nitric acid was added to achieve a pH = 3. Subsequently, the solution was stirred over night to produce a clear AlOOH sol. Co(NO₃)₂·6H₂O (98%, Sigma Aldrich) was dissolved in water and the precursor solution was added to the AlOOH sol at 80 °C and stirred for a few minutes. The concentration of the used precursor solution depends on the desired CoAl-ratio in the xerogel. With increasing cobalt content a higher amount of water was necessary to keep the stability of the AlOOH particles after precursor addition. If the H₂O content is too low, the gelation directly starts. In contrast, drastically increasing the water content results in a sol of low viscosity. Using the H₂O volumes given in Table 1 results in Co–AlOOH sols with a good stability and viscosity. If the sol was stored in a closed vessel, the prepared sols were stable for over a year.

Three different sols with Co/Al ratios of 0.1, 0.2 and 0.3 were prepared and named 10Co–AlOOH, 20Co–AlOOH, 30Co–AlOOH and 30Co–AlOOH + PEG, respectively. The sol with the highest Co content was also mixed with 20 wt% polyethylene glycol (PEG) (Molecular weight = 600) to investigate the influence of an binder additive. The amounts of reactants needed for the preparation of approx. 250 mg Co₃O₄–Al₂O₃ powder from each sol are summarized in Table 1.

2.2. Characterisation of the sol

The prepared Co–AlOOH sols were characterised by dynamic light scattering (DLS) using a Beckman Coulter-DelsaNano C instrument to determine the particle size distribution of the formed AlOOH-particles. The viscosity was analysed with a cone and plate rheometer Bohlin CVO 100 at shear rates between 1 and 25 1/s.

2.3. Preparation of Co₃O₄–Al₂O₃ powders

For catalytic tests and the characterisation of the material properties, xerogel powders were prepared from cobalt containing sols, as schematically described in Fig. 1.

For the preparation of Co₃O₄–Al₂O₃ xerogel catalysts with 7, 13 and 18 wt% Co₃O₄, sols with a Co–Al ratio of 0.1, 0.2 and 0.3 (calculation see Table 1) were dried in air at 120 °C for 3 h and calcined at 600 °C for 3 h. During the drying and calcination process, the temperature was slowly increased with a rate of 2 °C/min starting from room temperature. The catalyst are named 7CoXerogel, 13CoXerogel, 18CoXerogel and 18CoXerogelPEG. As a reference, a catalyst with 18 wt% Co₃O₄ was prepared by impregnating commercial γ-Al₂O₃ (Puralox, Sasol) with cobalt nitrate. The Co(NO₃)₂·6H₂O was dissolved in deionized water, which was additionally mixed with the Al₂O₃ powder. The impregnated Al₂O₃ powder was dried at 120 °C and calcined at 600 °C for 3 h in air. The heating rate was the same used for xerogels. The catalyst is referred to as 18CoIWI. All prepared catalysts and the corresponding weight percentages of Co₃O₄ are summarized in Table 2.

2.4. Characterisation of the powder catalysts

XRD data were collected using an X'pert diffractometer with Cu K_{α1} radiation from 5 to 85° 2θ. The data points were collected with a rate of 0.0423°/sec and a step wide of 0.0167° 2θ/step. The XRD-patterns of the freshly prepared catalysts were refined using Topas5.0 and the structural and microstructural parameters were extracted using Rietveld refinement. For the pattern refinement, the structural model for Al₂O₃ (ICSD- 66559) with space group (Fd-3mZ) [31] and Co₃O₄ (ICSD = 28158) [32] with space group (Fd-3mS) were used. Background, scale factor, unit cell parameters and peak widths parameters were simultaneously refined additionally to the Lorentzian crystallite size.

The specific surface area of the prepared powders was determined by a single-point-BET. The samples were measured with N₂/He gas at a relative N₂ pressure of 0.3 using a beta Scientific Instrument (Model 4200). Before starting the experiment, samples were outgassed at 120 °C for 2 h under He flow.

An adsorption-desorption isotherm was also obtained for the 18CoXerogel by nitrogen adsorption at –196 °C (Belsorp-Mini, Bel Japan Inc.). Before starting the measurement, the sample was dried at 120 °C for 3 h. The particle size was between 100 and 300 μm to diminish limitation of nitrogen diffusion within the timeframe of the experiment.

To characterise the reducibility of the prepared powders, inverse temperature reduction (iTPR) was used. The method iTPR has been patented by Roessner and Schoenen in 2011 [33]. In short, the apparatus consists of a quartz sample tube heated by an electrical furnace. The sample is held in position inside the sample tube by quartz wool. A continuous gas flow of 50 ml/min containing 5% H₂ is led through the tube during the whole measurement. To the gas stream leaving the sample tube, 2 ml/min CO₂ are added and the mixed stream is further led through a methanizer operating at 300 °C. The final gas mixture is monitored by a flame ionization detector (FID). If no reduction takes place in the sample tube, all of the hydrogen will react with the carbon dioxide to form methane resulting in a steady, high FID signal – the baseline. As soon as reduction takes place in the sample tube, a part of the hydrogen

Table 1
Composition of the prepared cobalt containing AlOOH sols and of the xerogel powders.

Sol names	Colloidal suspension				PEG (mg)	Co/Al ratio	Powders		
	0.5-M-Al Sol		Co-Precursor				Al ₂ O ₃ (mg)	Co ₃ O ₄ (mg)	Co ₃ O ₄ wt%
	Sol (ml)	Al (mg)	H ₂ O (ml)	Co (mg)					
10Co–AlOOH	10	134.9	0.5	13.49	–	0.1	254.9	18.4	7
20Co–AlOOH	10	134.9	2	26.98	–	0.2	254.9	36.7	13
30Co–AlOOH	10	134.9	3.3	40.47	–	0.3	254.9	55.1	18
30Co–AlOOH + PEG	10	134.9	3.3	40.47	26.7	0.3	254.9	55.1	18



Fig. 1. Preparation route of xerogel powders and xerogel coated foams.

Table 2

Name, concentration and preparation method of prepared $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ catalysts.

Catalyst name	Preparation	Co_3O_4 (wt%)
7CoXerogel	Sol-gel	7
13CoXerogel	Sol-gel	13
18CoXerogel	Sol-gel	18
18CoXerogelPEG	Sol-gel	18
18CoIWI	Incipient wetness	18

will be consumed prior to methanation leading to a lower formation of methane and thus a lower signal of the FID. The reduction profile was detected for 100 mg powder between 25 °C and 1200 °C with a constant heating rate of 2°/min.

2.5. Coatings and characterisation of coated metal foams

Metallic NiCrAl foam slices with different pore sizes were provided by Alantum Europe GmbH. For a better adhesion, slices were calcined before the coating process at 800 °C for 3 h to form an oxidic layer on the surface. After these pre-treatments, the foams were coated via dip coating with the 30%CoAlOOH sol. After dipping the metallic foams into the colloidal solution, excess suspension was blown out with compressed air. After one coating step, samples were dried at 120 °C and calcined at 600 °C to form the xerogel on the metallic support before taking images with a SEM (Zeiss; Model SUPRA 40). Foams with three different pore sizes were coated by this method. The density of the foams and the average pore diameters are listed in Table 3.

Table 3

Physical properties of metal foams used for coating tests.

Metal foam	Density (g/nm^3)	Porosity (%)	Average pore size (μm)	Pores per inch ppi
1	0.72	>92	450	130
2	0.60	>92	580	110
3	0.41	>92	1200	45

2.6. Catalytic testing of xerogel powders

Fischer-Tropsch synthesis was performed in a stainless steel 1/4" U-shaped fixed bed reactor after in-situ reduction of the catalysts with H_2 at 430 °C for 12 h (heating rate = 1 °C/min). A catalyst sample of 400 mg (sieve fraction of 200–315 μm) was diluted with 200 mg SiO_2 and exposed to synthesis gas at a 2:1 H_2 :CO ratio and a GHSV of 3500 h^{-1} . Reaction temperature was 230 °C and reaction pressure was 4 bar. The formed products were analysed by online gas chromatograph (GC)-FID (HP 6890 equipped with a Agilent Plot Q capillary column, 15 m, diameter = 0.32 μm) and GC-TCD (HP 5890 with Carbosieve S-II packed column, 3 m, diameter = 3.2 mm). As internal standard a mixture of cyclohexane and argon was fed into the stream after the reactor.

CO_2 methanation was performed in a quartz tube reactor with a diameter of 4 mm. The reactant gas was passed through the catalysts bed at 320 °C and 1 bar with a CO_2 : H_2 ratio of 1:4 (GHSV of 7165 h^{-1}). The steady state conversion was constant after a few minutes. 1 ml/min of argon was also feed to the product stream as internal standard. The product gases were separated on two columns, a molsieve 5 Å (15 m, diameter = 0.32 mm) and a parabond

column (15 m, diameter = 0.32 mm) and were detected with a compact gas chromatograph (Global Analyser Solution) equipped with two TCD detectors.

200 mg catalyst and 50 mg SiO₂ (sieve fraction of 100–200 μm) was activated under flowing hydrogen for 12 h (heating rate 1 °C/min), before starting the experiments. The activation temperature was varied between 430 and 575 °C to investigate the thermal stability of the catalyst.

Conversion and selectivity for the methanation process were calculated from Eqs. (1) and (2), where n_{CO_2} is the amount of CO₂ (mol) either before (in) or after (out) catalytic reaction and n_{CH_4} and n_{CO} are the amounts of CH₄ and CO detected in product gas stream (in a given time interval).

$$\text{Con}_{\text{CO}_2} (\%) = \frac{(n(\text{in})_{\text{CO}_2} - n(\text{out})_{\text{CO}_2})}{n(\text{in})_{\text{CO}_2}} \cdot 100 \quad (1)$$

$$\text{Sel}_{\text{CH}_4} (\%) = \frac{n_{\text{CH}_4}}{(n_{\text{CH}_4} + n_{\text{CO}})} \cdot 100 \quad (2)$$

2.7. Catalytic testing of xerogel coated metal foams

For catalytic testing of CO₂ methanation, 25 foams slices (diameter = 25 mm, thickness = 3.5 mm, pore size 1200 μm) were coated. After one coating step the samples were dried and calcined at the same conditions described for xerogels powders. After one coating step, a catalyst mass of 1.2 g was deposited, which gives a foam with a specific loading of 0.03 g/ml. All 25 slices were stacked into a stainless-steel lab-scale reactor to form a catalyst bed of approximately 90 mm and 25 mm diameter. Two flexible heating bands were used to heat the catalyst and the in- and outlet sections. Three thermocouples are placed in the front of the catalyst bed, after 10 mm and at the end of the catalysts bed to monitor the inlet gas temperature. A schematic set-up of the reactor is shown in Fig. 2.

After initial installation of the catalyst, the reactor was heated up in an H₂/N₂-mixture (each 0.5 l min⁻¹) to 400 °C with a rate of approx. 3 °C/min for activation. The pressure inside the reactor was set to 4 bar. After 120 min, the H₂-flow was increased to 2 l min⁻¹. After reaching the activation temperature the latter conditions were hold for another two hours to complete the activation.

To start the reaction, a 4:1 H₂/CO₂-mixture was feed into the hot reactor at 360 °C (inlet temperature); the total flow rate was 2.45 l min⁻¹ to obtain a GHSV of 3330 h⁻¹. Steady state was reached after 45–60 min. The product gas was cooled down to 5 °C in two sequential cooling stages to remove water, and analysed using a HP 6890 GC with a Carboxen™ 1010 PLOT column (30 m, 0.53 mm i.d.), and a single TCD.

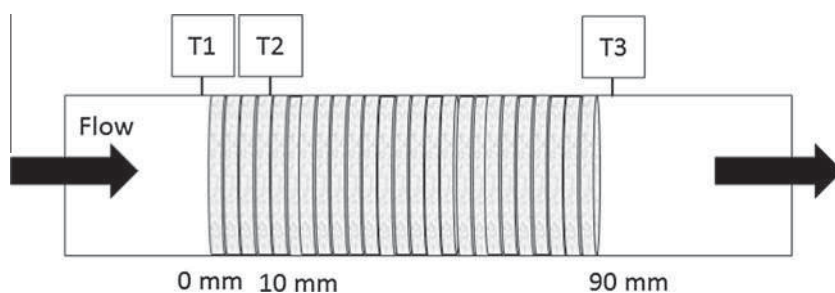


Fig. 2. Schematic drawing of the reactor set-up used for the testing of foams for CO₂-methanation.

3. Results and discussion

3.1. Characterisation of the sol

The viscosity and particles size of the sols were analysed before and after cobalt precursor addition to investigate the influence of the cobalt salts on the sol properties. Furthermore, also the sol with 20 wt% PEG was analysed.

3.1.1. Viscosity

The viscosities at a share rate of 1 s⁻¹ and 25 s⁻¹ for the pure AIOOH sol, additive free Co–AIOOH sols with Co/Al ratios of 0.1, 0.2 and 0.3 and Co–AIOOH sol with PEG are shown in Fig. 3. For all sols the viscosity decreased with increasing shear rate, demonstrating a thixotropic behaviour.

The pure sol had a very low viscosity around 15 mPa s at a shear rate of 1 s⁻¹. With increasing shear rate, the viscosity decreased to 10 mPa s. After Co-precursor addition, a high increase in viscosity was found, with a maximum for the 10%Co–AIOOH sol. Values between 180 and 260 mPa s at low shear rates and 95 and 140 at higher share rates were detected. An additional increase in viscosity was obtained with 20 wt% PEG.

The increases in viscosity after cobalt precursor addition indicate the growth of the sol particles. PEG is a viscose suspension, which explains the slightly higher values for the sol with 20 wt% PEG.

3.1.2. Colloidal particle size

The particle sizes of the formed AIOOH-particles were analysed by DLS as shown in Fig. 4. The pure AIOOH sol exhibits a bimodal particle size distribution with the main peak around 100 nm. These values agree with reported literature data [11]. With the addition of the H₂O/cobalt solution, the size distribution basically becomes monomodal with a maximum at 180 nm. After adding the PEG to the sol, no significant changes are observed except for a slight shift of about 20 nm towards higher values.

The results of the sol characterisation reveal a relation between viscosity and particle size. The particle size starts to increase after adding the Co-precursor to the sol, which results in an increasing viscosity.

The stability of aqueous suspensions can be influenced by different parameters. Each particle in an aqueous suspension is surrounded by an electrostatic double layer and the sol stability is directly related to the thickness of these layers. The electrostatic double layer can be influenced by added ions in the solution and the pH.

At pH = 3 (used in this study) the bohemite particles are positively charged and the negatively charged anions (NO₃⁻) stabilize the particles by forming a negatively charged layer around the AlO–(OH₂)⁺ particles. By further decreasing the pH more bohemite particles are dissolved and aluminium ions are released into the

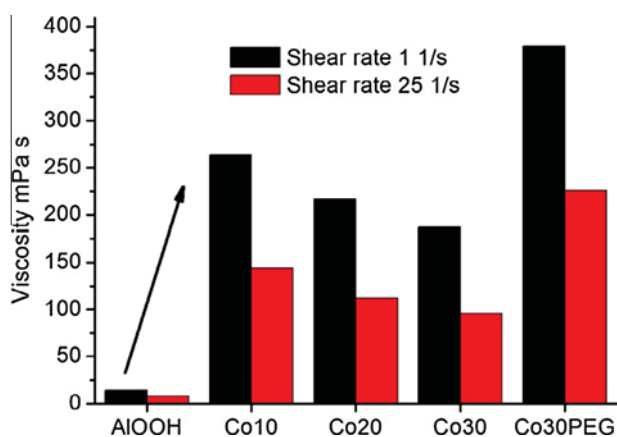


Fig. 3. Viscosity of Al and Co-AIOOH sols with different Co concentrations and with PEG at two different shear rates.

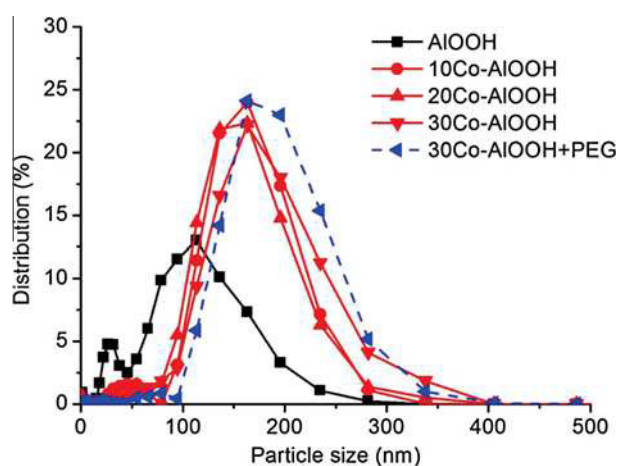


Fig. 4. Particle size distribution of the pure AIOOH sol and sols with different Co concentrations without and with PEG.

solution. Accordingly, the electrostatic double layer decreases and particles start to aggregate [34]. Another factor that influences the stability of the sol is the concentration of the aluminium precursor. With increasing AIOOH concentration particles size increases, which also increases the viscosity [35].

In our case, however, the pH was 3 for all samples, meaning that the increase in viscosity must be due to the addition of the cobalt salts. Gieselmann et al. described the influence of metal salts on boehmite sols. They concluded that adding metal salts to a colloidal suspension increases the ionic strength, which in turn decreases the repulsion between particles and favours aggregation [34]. Adding the H₂O/cobalt solution increases the ionic strength, which results in an increase in particles size and viscosity. Yet, the addition of water to the system reduces the sol concentration at the same time and thus, stabilizes the colloidal suspension by inhibiting further growth of the particles. Due to the right balance between the cobalt concentration and the amount of water it is possible to increase the viscosity without a loss of stability of the colloidal solution. The viscosity of the 30% Co-AIOOH sol with PEG as a binder was 70–120 Pa·s higher than for the additive free sols. The slightly different viscosities for the 10, 20 and 30%Co-AIOOH sols can be explained by different amounts of water which were used for stabilizing the particles.

3.2. Characterisation of the catalyst powders

3.2.1. XRD and Co₃O₄ particle size

After calcination black powders were obtained from incipient wetness impregnation and all PEG-free Co-AIOOH sols. From the Co-AIOOH sol with PEG a blue powder was formed, which points to the formation of cobalt spinel phases [21], known as Thénard's blue composed of CoAl₂O₄ crystals [19]. Images of the 18CoXerogel powders prepared from sol with and without PEG are shown in Table 4.

The XRD patterns of the prepared powders are depicted in Fig. 5. The intensity of the Co₃O₄ peaks increases with increasing cobalt content for the xerogel catalysts without PEG. The highest and sharpest diffraction peaks are found for the catalyst prepared by incipient wetness method, indicating the formation of the largest Co₃O₄ crystallites. The diffraction peaks of the xerogel catalysts show an increasing half width with decreasing Co content pointing to smaller particle sizes. For the 18Xerogel catalyst with PEG only small and broad reflexes are detected. Based on the observation that a blue coloured powder is formed, the formation of nano crystalline CoAl₂O₄-particles is likely [19]. Co₃O₄ and CoAl₂O₄ cannot be distinguished in XRD due to the formation of the same crystalline phase (Fd-3mS) with similar lattice parameters [32,36].


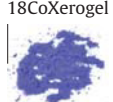
The Co₃O₄ crystallite sizes of the different samples were calculated with Topas 5.0, a software for Rietveld refinement, and are listed in Table 4. The largest particles are indeed formed in case of the 18CoIWI with 23 nm. For the 18CoXerogel a value of 12 nm is obtained and for the 13CoXerogel 6 nm. The particles of the 7CoXerogel and the 18CoXerogel + PEG are smaller than 1 nm.

Co/Al₂O₃ catalysts prepared by sol-gel techniques often result in very small Co₃O₄ particles, which are hard to reduce [27–30]. Apparently with increasing cobalt content the Co₃O₄ particle size increase, if no additives are added to the solution. Contrarily, the addition of PEG promotes the formation of CoAl₂O₄ crystals smaller than 1 nm. This effect is not clear, but it can be assumed that the PEG interacts in form of a ligand with the cobalt ions in solution, resulting in very small particles. The effect of additives on the size of Co₃O₄ crystals were described by Bamal et al. for Co-Al₂O₃ powders prepared by incipient wetness impregnation. They investigated the chelating properties of ethylenediaminetetraacetic acid (EDTA) and found that the addition of EDTA during impregnation leads to a decrease in Co₃O₄ particle size on the support and favours the formation of CoAl-spinels [37].

3.2.2. Specific surface area

The specific surface areas of the calcined catalysts from BET are summarized in Table 5.

Table 4
Particle size of formed Co₃O₄ crystallites, calculated with Topas 5.0 from XRD-pattern.

Catalyst	Co ₃ O ₄ crystallite size (nm)	Colour of powder	
18CoIWI	23	Black	
18CoXerogel	12	Black	
13CoXerogel	6	Black	
7CoXerogel	<1	Black	
18CoXerogel + PEG	<1	Blue	

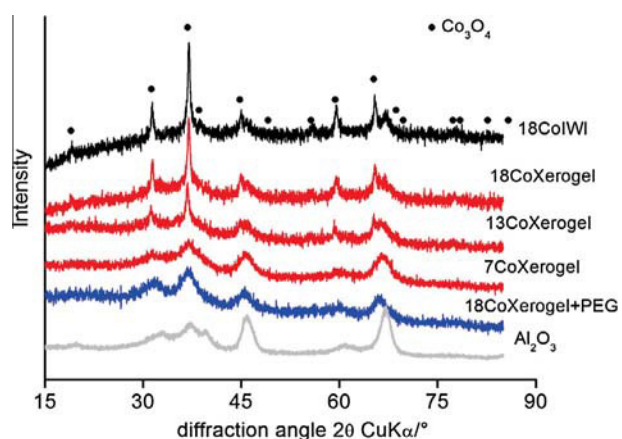


Fig. 5. XRD pattern of the Co–Al₂O₃ powders prepared by incipient wetness and our sol-gel approach using additive-free Co–AlOOH sols and the PEG containing Co–AlOOH sol.

Table 5

Specific surface area of the calcined Co-Catalysts prepared by incipient wetness (IWI) and our sol-gel approach using additive-free Co–AlOOH sols and the PEG containing sol.

Catalyst name	Surface area m ² per g Co–Al ₂ O ₃ catalyst	Surface area m ² per g Al ₂ O ₃
18CoIWI	120	157
Al ₂ O ₃ Xerogel	189	189
18CoXerogel	130	159
13CoXerogel	139	160
7CoXerogel	157	169
18CoXerogel + PEG	197	240

The drying and calcination process has a huge influence on the formation of the oxidic material and sintering of the particles, which decreases the surface area significantly. The values for the xerogel catalysts without PEG are between 130 and 157 m²/g and are slightly higher as compared to the incipient wetness catalyst (120 m²/g). The highest surface area was detected for 18CoXerogel + PEG (197 m²/g). This higher value might be attributed to the formation of additional pores by decomposition of PEG during the calcination process. The decrease of the specific surface area with increasing cobalt content is due to the decreasing amount of aluminium oxide per gram catalyst. Normalizing the surface area per gram aluminium oxide - as also listed in Table 5 - reveals

that the differences between the additive free xerogels is comparatively small.

To get information about the porous network, N₂ adsorption-desorption measurements were carried out for 18CoXerogel powder. The isotherms and the (meso)pore size distribution are depicted in Fig. 6.

A characteristic isotherm with hysteresis was found for the 18CoXerogel, which indicates the formation of a porous material consisting of micro and meso pores. Meso pores sizes were found to be in the range of 2–15 nm with a maximum around 5 nm. Mesoporous materials are very suitable for catalytic application due good mass transport inside the pores.

3.2.3. Temperature programmed reduction

The 18CoXerogel powders, prepared with and without PEG, and the 18CoIWI were characterised by TPR. The results are plotted in Fig. 7. In general, the reduction of Co₃O₄ is a two-step process. The first step is due to the reduction of Co₃O₄ to CoO and the second step results from the reduction to metallic Co. TPR profiles of supported cobalt catalysts can be more complex due interactions between Co₃O₄ particles and the oxidic support, resulting in differently reducible cobalt species [38–40].

The 18CoIWI shows a TPR-profile comparable to other supported Co–Al₂O₃ catalysts. A double peak between 400 and 600 °C is observed resulting from the two step reduction of cobalt oxide to metallic cobalt, while the small shoulder around 850 °C can be attributed to cobalt aluminates [39,40]. For the 18CoXerogel the reduction to metallic cobalt occurs between 300 °C and 700 °C with a maximum at 500 °C. Also a small amount of CoAl₂O₄ can be detected at 950 °C. In comparison to the CoIWI the reduction starts at lower temperatures but is completed at slightly higher temperatures, which can be explained by the existence of some CoO-particles with stronger metal-support interactions [39,40]. Furthermore, it is possible that CoO particles are embedded in the matrix, as described by Brambal et al. [37]. In comparison so that, the 18CoXerogel + PEG shows no reducible cobalt species below 900 °C. This supports the conclusion that only CoAl₂O₄ was formed when PEG is added to the sol.

In general, TPR profiles do not describe exactly the activation of the catalysts before catalysis. In comparison to the reduction process before catalytic tests, where the catalysts is activated with a very slow heating rate of 1 °C/min for 10 h, TPR profile were measured with a heating rate of 2 °C/min. Nevertheless, the data show on the one hand that metal support interactions are comparable or slightly higher for the 18CoXerogel compared to the 18CoIWI. On

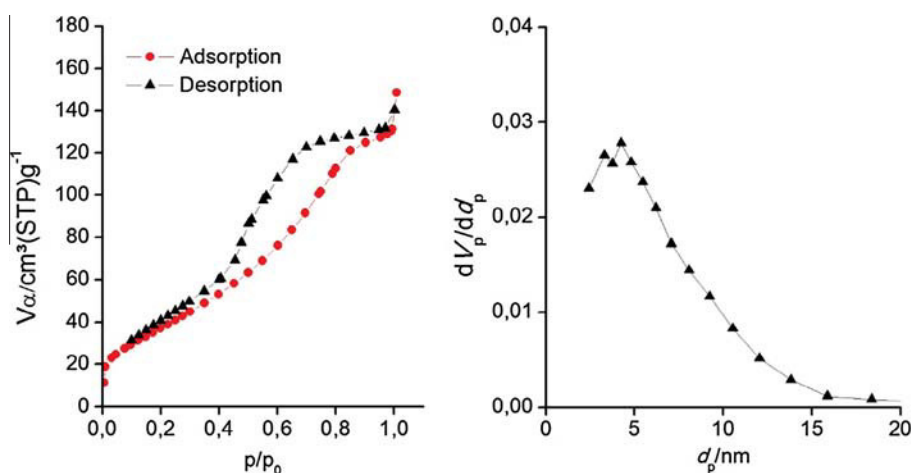


Fig. 6. N₂ adsorptions – desorption isotherms (left) and distribution of meso pores (right) for a 18CoXerogel powder.

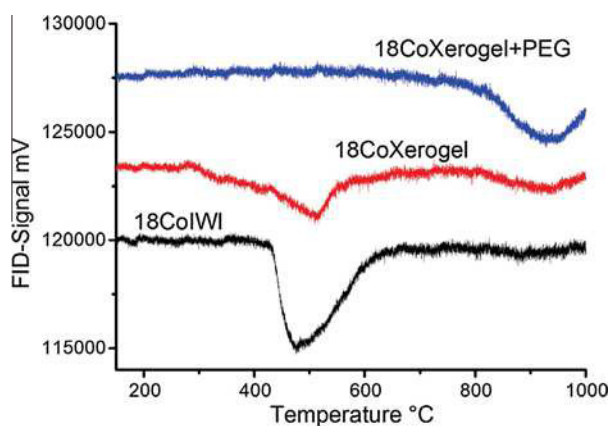


Fig. 7. Inverse TPR profiles for the incipient wetness Co–Al₂O₃ catalyst and 18 wt% Co-Xerogel prepared from additive free sol and with PEG.

the other hand, the 18Xerogel + PEG material shows no reducible species below 900 °C.

3.3. Characterisation of xerogel coated metal foams

After coating the metallic foam slices (Alantum) via dip coating with the 30%Co–AlOOH sol, the samples were dried at 120 °C and calcined at 600 °C to form a xerogel coat. SEM-images in Fig. 8 show an uncoated foam with the smallest pore size of 450 μm used (a1 and a2) as reference and the xerogel coated samples in Fig. 8b1 and b2. Fig. 8c and d shows coated foams with two other pore sizes (580 and 1200 μm). From the overview in Fig. 8b1, c, and d it can be concluded that only a few pores are blocked when using the sol coating. Furthermore, the coating appears to be smooth (Fig. 8b2) and the material homogeneously distributed on the metal foam.

Fig. 9 shows a foam window which was blocked by the coat and where the coat was quarried out afterwards (the dotted line indicates the border of the supporting foam strut; the thin layer pointing forward represents the broken coating layer). From the breaking edge, it is possible to estimate the layer thickness of the xerogel coat to be in the range of 4 μm. This value which may vary by a few μm along the sample, agrees well with other layers thickness obtained by sol gel techniques [7].

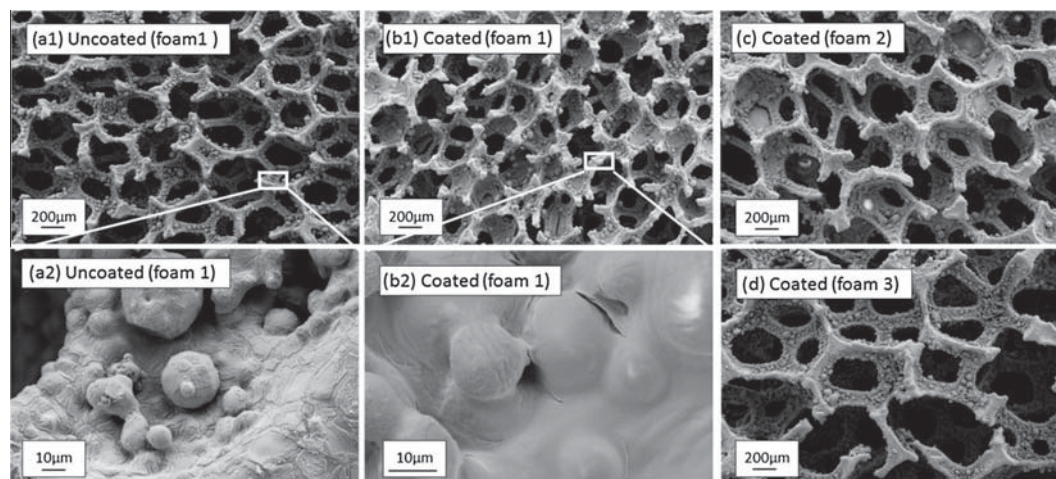


Fig. 8. (a1 and a2) uncoated foam as reference (130 ppi) and (b1 and b2) Co–Al₂O₃ coated foam from 30%Co–AlOOH sol after drying and calcination (130 ppi), (c) Co–Al₂O₃ coated foam (110 ppi), (d) Co–Al₂O₃ coated foam (45 ppi).

3.4. Catalytic testing

3.4.1. Catalytic testing the powder catalysts

The 18CoXerogel without PEG was tested for CO hydrogenation under Fischer-Tropsch like conditions at 4 bar and 230 °C for 24 h and, in addition, for CO₂ methanation at 1 bar at 320 °C for 30 min to reach the steady state. In comparison, the catalyst 18CoIWI prepared by incipient wetness impregnation was investigated in parallel.

The results of the Fischer-Tropsch experiment, i.e. the CO conversion and selectivities after 24 h to CH₄, C₂–C₄ and C₅₊ are summarized in Table 6.

Accordingly, the reference catalyst and the xerogel perform similarly in FTS, the latter showing only 13% lower CO conversion than the IWI catalyst. From TPR it was shown that reduction is easier for CoIWI, which explains the higher activity. Nevertheless, the selectivity to CH₄ and higher hydrocarbons is comparable; 15% C₂–C₄ and 12% C₅₊ products are detected for the IWI catalysts and 17% C₂–C₄ and 15% C₅₊ for the sol gel catalysts. Compared to other catalysts in the FT-literature, selectivities are far away from industrial standard as a consequence of the low pressures which were possible in our FT set-up. Nevertheless, the results suggest a first trend for the formation of higher hydrocarbons on our xerogel catalyst comparable to the reference catalyst and this is in contrast to some literature data, reporting inactive sol gel catalysts using similar activation conditions [27–30].

The incipient wetness and xerogel catalysts were also tested for CO₂ methanation at 320 °C at 1 bar. This reaction was used to demonstrate the high thermal stability of our xerogels catalysts. In a first step, catalysts were activated at 430 °C before catalytic testing. After testing the catalysts for 30 min, samples were aged in hydrogen at different temperatures between 475 and 575 °C for 10 h to gain information about the thermal stability of the catalysts. The resistance against thermal treatment is an important factor with respect to industrial applications, where hot spots can strongly stress the catalysts.

The conversion of CO₂ after exposing the catalysts to different aging temperatures are shown in Fig. 10 for both catalysts. It is obvious that after catalyst activation at 430 °C the Co-catalyst prepared by incipient wetness impregnation shows the highest activity. The conversion of the xerogel catalysts is by 7% lower. But when treating the catalysts at higher temperatures, a significant decrease of the conversion rate is detected for the CoIWI catalysts, while only a slight decrease is found for the xerogel. The IWI cata-

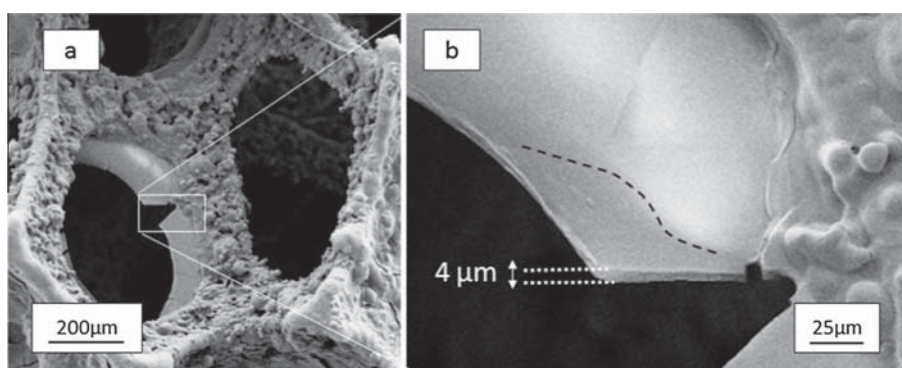


Fig. 9. Co-Xerogel coated foam (1200 μm pore size) at two magnifications to estimate layer thickness (see text).

Table 6

Fischer-Tropsch reaction at 4 bar and 230 $^{\circ}\text{C}$: CO conversion (%) and selectivity (%) for 18CoXerogel and 18CoIWI after 24 h.

Catalyst	Conv. CO (%)	Sel. CH_4 (%)	Sel. $\text{C}_2\text{--C}_4$ (%)	Sel. C_{5+} (%)
18CoIWI	57	72	15	13
18CoXerogel	44	68	17	15

lyst loses around 60% of the activity. In contrast, the activity of the xerogel catalyst decreases only by around 20%. The selectivity to CH_4 and CO was comparable for both catalysts. With increasing conversion, the selectivity to methane increased from 85 to 96%, while the selectivity to CO decreased from 15 to 4%.

3.4.2. Catalytic testing of xerogel coated metal foams

25 coated metal foams (pore size 1200 μm) with a catalyst mass of 1.2 g in total were placed in a reactor tube to get a packed foam of around 9 cm length and were tested for CO_2 -methanation. Before catalytic tests, the pressure drop was measured for uncoated and coated metal foams at different flow rates. With flow rates increasing from 1 to 5 l/min, the pressure drop increased for both samples from 1.18 to 2.25 bar. No difference was found for foams with and without catalysts coats, which clearly demonstrates the formation of a thin and homogenous catalysts coats without pore blocking.

The activation was carried out at 400 $^{\circ}\text{C}$ for 3 h before starting the reaction at 360 $^{\circ}\text{C}$. A typical H_2 : CO_2 ratio of 4:1 for methana-

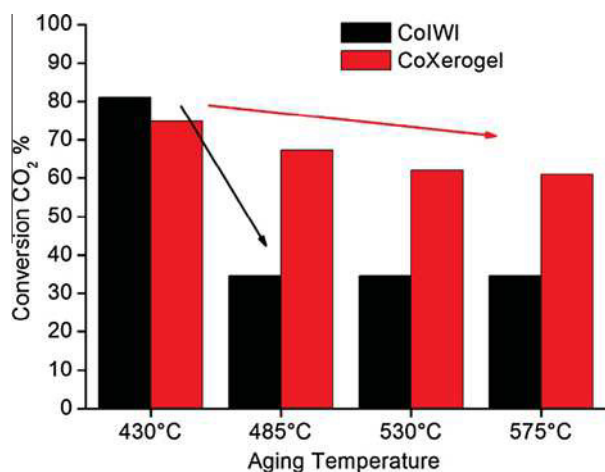


Fig. 10. CO_2 conversion at 320 $^{\circ}\text{C}$ achieved with the incipient wetness $\text{Co--Al}_2\text{O}_3$ catalyst (black) and the $\text{Co--Al}_2\text{O}_3$ xerogel catalyst (red/grey) after treating the catalysts at different aging temperatures.

Table 7

Temperature profile under CO_2 -methanation reaction condition for xerogels coated foams and CH_4 yield at the end of the catalyst bed.

Bed length	Temperature ($^{\circ}\text{C}$)	CH_4 yield (%)
Inlet	360	–
10 mm	450	–
90 mm	370	59%

tion was used with a final GHSV of 3330 1/h. Due to a much higher WHSV of 122,655 $\text{ml g}^{-1} \text{h}^{-1}$ compared to the catalytic experiments for the testing of the powders (WHSV = 9000 $\text{ml g}^{-1} \text{h}^{-1}$) a drastic increase of the inlet temperature was detected as a result of the exothermic reaction. The temperature inside the reactor and the achieved CH_4 yield at the end of the catalysts bed are listed in Table 7.

At this point, the CH_4 yield cannot be directly compared to the one obtained in the catalytic tests of the powders. On the one hand, the WHSV was 13 times higher for the foams, which results in lower conversion levels. On the other hand, the temperature inside the catalyst bed increased locally up to 450 $^{\circ}\text{C}$ due to the exothermic reaction. Higher temperatures results in a shift of the thermodynamic equilibrium towards lower yields [41].

Nevertheless, a methane yield of 59% could be obtained for the foams which shows that the supported catalysts are also reasonably active for CO_2 -methanation. We are confident that an improvement of the reactor concept, i.e., a longer catalyst bed, higher amounts of catalyst, and improved heat transport will increase the achievable CH_4 yield. The current study serves just as a first test of feasibility.

4. Conclusion

We developed a technique for the simple preparation of stable and additive-free Co--AlOOH sols based on water with a long term stability (when storing the sol). By adding the Co salt to the aluminium based sol, the sizes of the sol particles and accordingly the viscosity increased. The resulting sols exhibited properties, such as viscosities, which are excellent for the coating of foams with small pore sizes. In this way, additional additives are not required. Very homogenous catalyst coats could be formed on metallic foams with pore diameters between 450 and 1200 μm .

Catalytic testing of the 18CoXerogel catalysts powders showed a performance for CO_2 methanation and FTS which was comparable to a catalyst prepared by incipient wetness impregnation. Only approx. 10% higher activity was found for the IWI catalyst after activation at 430 $^{\circ}\text{C}$ under flowing hydrogen. The higher activity can be explained by easier reduction of the IWI catalysts due to lower metal support interactions, which was demonstrated by

TPR. But after thermal agings, the reference catalyst lost 60% of its activity. In contrast our 18CoXerogel showed a very good thermal resistance and also a high activity even after thermal treatments up to 575 °C. In contrast to this, inactive CoAl₂O₄ was formed during the calcination process if additives such as PEG were used for the stabilisation of the sol. PEG possibly acts as ligand resulting in very small crystallites with strong cobalt-support interaction.

The heat resistant xerogel coats on metallic foams with pores in the range of 1200 µm were also tested for CO₂ methanation. Here, CH₄ yields of 59% were obtained. This result clearly shows the great potential of this preparation technique for the manufacturing of coated metal foams with high ppi values for catalytic exothermic reaction.

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