

Nanostructured Encapsulated Catalysts for Combination of Fischer–Tropsch Synthesis and Hydroprocessing

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Controlling the selectivity of Fischer-Tropsch synthesis in a single reaction step is highly desirable, but is a major challenge in heterogeneous catalysis. One approach is the application of bifunctional catalysts. However, to control the catalytic properties the morphology of the catalyst needs to be controlled on the nanoscopic scale. Herein, an innovative synthetic approach that allows the bottom-up construction of nanostructured bifunctional catalysts in a step-wise manner is described. The resulting material, which exhibits cobalt nanoparticles encapsulated inside a zeolite matrix, was proven to be active in the combined Fischer-Tropsch and cracking reaction, evidenced by a shift from waxy to liquid products. Consequently, the use of this novel approach was demonstrated in terms of material synthesis and catalytic applications.

Introduction

Fischer-Tropsch (FT) synthesis is a 100 year old process, which allows the liquefaction of fossil (coal, natural gas) or regenerative (biomass, waste) carbon sources though XTL (X to liquids) technology to produce synthetic fuels.^[1] The reason for the renaissance of FT synthesis, and its future potential, is the high energy density and easy handling of the hydrocarbon products, as well as established distribution and utilization infrastructure.^[2] However, FT synthesis suffers from broad product distribution, owing to the polymerization-like reaction.^[3] The product spectrum consists of mainly linear olefins, paraffins, and oxygenates, which are distributed over a wide range of hydrocarbon fractions comprising methane, liquefied petroleum gas (LPG), fuels, and waxes.^[4]

Thus, to be used as liquid fuel, the crude FT product requires further workup by hydroprocessing (HP).^[5] This additional catalytic step can be performed by zeolite catalysts, which exhibit acidic catalytic functionalities. One approach is the combination of a FT and HP catalyst in a single reactor; this approach has been demonstrated on the reactor scale^[6] and the catalyst-particle scale.^[7] The results of these rather macroscopic approaches exhibit a significant shift in product distribution, leading to higher selectivity towards isoparaffins and shortchain hydrocarbons.

Although bifunctional catalysts for the FT and HP reaction have already been reported, as reviewed by Sartipi et al.,^[8] the

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on the nanoscopic scale has not been demonstrated to date.^[9] However, this approach is highly desirable because it offers several advantages and could have the potential to invoke a revolution in FT catalysis.^[10] The advantages of this system include: stabilization of small metal nanoparticles inside the encapsulating matrix,^[11] additional functionality of the tailored shell,^[9] as well as flexible application in various reactor geometries. One promising approach to manufacture nanostructured core-shell materials is a stepwise bottom-up synthesis strategy that offers a high degree of control of the material properties.[12]

encapsulation of cobalt nanoparticles inside a zeolitic matrix

For FT synthesis the control of the size, as well as the suppression of sintering, of the cobalt nanoparticles is highly desirable to improve the activity, selectivity, and stability of the catalyst.^[13] In this regard it has to be considered that cobaltbased catalysts undergo significant transformations under FT conditions.^[14] These transformations might be controlled or suppressed by the novel encapsulation approach. Additionally, the zeolite encapsulation of cobalt nanoparticles introduces two mechanisms to manipulate the selectivity, namely the shape selectivity and the acidic functionality.^[10] The shape selectivity will suppress the diffusion of long-chain hydrocarbons from the FT site to the bulk flow, whereas the acidic function is responsible for cracking and isomerization. Interestingly, the HP kinetics are faster,^[15] whereas the diffusion through the porous system is slower,^[16] for long-chain hydrocarbons. Furthermore, the catalytic functionalities of the FT and HP reaction are locally separated and serially arranged along the diffusion path of the reactants. These considerations illustrate the potential of the nanostructured, zeolite encapsulated FT catalysts to tailor the product distribution on the nanoscale by optimization of the diffusion and cracking rate of hydrocarbons within the zeolitic matrix.

Herein, we demonstrate the principle synthesis strategy of zeolite-encapsulated cobalt nanoparticles for combined FT and



HP catalysis, depicted in Figure 1. Firstly, colloidal cobalt oxide particles (material A) are prepared and subsequently covered by a mesoporous silica shell, according to a literature procedure, to obtain individual $Co_3O_4@mSiO_2$ particles (material B).^[17]



Figure 1. Strategy for stepwise bottom-up synthesis of zeolite-encapsulated cobalt oxide nanoparticles (material C) via colloidal cobalt oxide particles (material A) and Co_3O_4 @mSiO₂ particles (material B).

This material is subjected to a hydrothermal synthesis to transform the SiO_2 into a zeolite (ZSM-5), leading to Co_3O_4 @zeolite (material C). Furthermore, the materials were evaluated for combined FT and HP reaction in terms of activity, selectivity, and stability. Hence, the synthesis approach provides an excellent basis for the evaluation of the effect of the zeolite encapsulation by comparison of the catalytic properties of material B and C, since the HP activity is added to the same FT active cobalt core material in one single synthesis step.

The synthesis of nanostructured Co@SiO₂ and the effect of its morphology on catalytic properties during FT synthesis have already been studied.^[17, 18] The preparation of zeolite-encapsulated metal nanoparticles is essentially based on incipient wetness impregnation of the active-phase precursor into a porous substrate. Substrates that have already been reported are either mesoporous zeolites^[19] or silica, which is transformed into zeolite by hydrothermal synthesis.^[20] This impregnationbased procedure usually links the active particle size with the pore size of the substrate,^[21] hampering the independent control of both properties. An interesting alternative, given by Laursen et al.,^[22] is based on colloidal deposition of gold nanoparticles on silica subjected to hydrothermal synthesis of silicalite-1 zeolite in a subsequent step. Recently, a complex multistep approach was presented by Xing et al. for application in FT synthesis.^[23] The preparation strategy is based on the nanocasting of mesoporous carbon from SBA-15 as a hard template for hydrothermal zeolite synthesis. The active phase was introduced by impregnation of the cobalt precursor into the mesoporous carbon.

The strategy presented herein firstly demonstrates the rigorous, stepwise bottom-up synthesis of zeolite-encapsulated cobalt oxide nanoparticles. The combination of FT and HP reaction was chosen as interesting example for the validation of the catalytic activity of the manufactured bifunctional catalysts. Consequently, the novelty of the present work is the combination of the synthetic approach of nanostructured encapsulated catalysts with the demonstration of its bifunctional catalytic activity. This approach offers the possibility to be transferred to other catalyst systems because silica-encapsulated metal or metal oxide nanoparticles are extensively reported, for example, with Au, Ag, Ni, Pt, and Fe, among others.^[24]

Results and Discussion

Electron microscopic images (Figure 2) reveal that material B exhibits a rather uniform core-shell structure consisting of a Co_3O_4 core (diameter in the order of 40 nm) completely encapsulated inside a silica shell (overall diameter in the order of 180 nm). The X-ray diffraction (XRD) pattern (Figure 3) shows



Figure 2. Electron microscopic images (material B: SEM image, TEM image as inset; material C: TEM image).



Figure 3. XRD powder pattern of material B and C; characteristic reflections: Co_3O_4 (•) and ZSM-5 (•); the low angle powder pattern for material B is shown in Figure S4.

the presence of Co_3O_4 crystallites as well as amorphous SiO_2 (between $2\theta = 20$ and 30°). The low angle reflections confirm the presence of mesopores (Figure S4, see the Supporting Information). Physisorption experiments (Figure 4) confirm the



Figure 4. Pore-width distribution obtained from physisorption experiments at 77 K (adsorbate: N_2 for material B and Ar for material C); sorption isotherms are shown in Figure S3.

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porosity of the shell with a maximum in pore-width distribution at approximately 2.5 nm, which is in good agreement with the literature.^[17] The specific cobalt surface area of $2.8\ m^2g^{-1}$ was measured by H_2 chemisorption, which proves the accessibility of the active material by gaseous molecules through the porous silica shell of material B. Taking the cobalt content of approximately 7.5 wt% [by energy-dispersive X-ray spectroscopy (EDX) for calcined material; atomic Si/Co-ratio of 16.5 by EDX and 14 by inductively coupled plasma optical emission spectrometry (ICP-OES)] into account the size of the cobalt core can be calculated from the active surface area and amounts to about 18 nm, which in turn corresponds to a Co₃O₄ particle size of about 24 nm [$d(Co) = 0.75 d(Co_3O_4)^{[7b]}$]. The difference to the results from the electron microscopic images can be explained by the uncertainty of the cobalt-content measurements. Furthermore, TEM images of the as-synthesized material suggest that the core is present as an agglomerate of small Co₃O₄ nanoparticles of approximately 7 nm, rather than one single particle (Figure S1). Consequently, the cobalt mass of the porous agglomerate corresponds to a smaller single particle, which is formed during reduction prior to the chemisorption experiments.

During the transformation step of material B into C sulfuric acid was used to reduce the pH of the synthesis mixture, which in turn reduces the rate of dissolution of SiO₂. This allows a permanent separation of the individual Co_3O_4 cores by a SiO₂ or zeolite shell during the whole synthesis, by either partial dissolution of the SiO₂ shell or direct formation of zeolitic material around the core particles. However, the prevailing separation mechanism is a matter of ongoing research.

A characteristic TEM image of material C is shown in Figure 2. It is clear that the cobalt oxide nanoparticles are incorporated inside a zeolitic matrix (zeolite particle size 1-5 µm) and are, therefore, completely embedded inside a zeolite shell. The macroscopic observation of the supernatant after centrifugation shows a clear solution, indicating the absence of residual colloidal cobalt and complete immobilization of cobalt nanoparticles at the external surface or inside the zeolite crystal. The presence of ZSM-5 and Co₃O₄ crystallites was confirmed by XRD measurements. Physisorption experiments with Ar show a maximum in pore-width distribution of approximately 6 Å (Figure 4), which agrees well with the maximum included sphere diameter of MFI framework-type zeolites.^[25] Furthermore, the modal pore size of the precursor material B appears to be negligible. The elemental composition of the calcined material was measured by EDX, resulting in an atomic Si/ Co/Al-ratio of 93:6.3:1 and a cobalt content of 10.0 wt% (ICP-OES results: 8.1 wt% cobalt, Si/Co/Al-ratio of 119:11.5:1). The Si/Al-ratio corresponds well with the desired value in the synthesis mixture of 100. The atomic Si/Co-ratio decreases slightly from 16.5 to 14.8 (by EDX; from 14 to 10.3 by ICP-OES) during transformation of material B into C, suggesting that Si partially remains in solution. The cobalt content of material C is higher than for material B, as confirmed by a specific cobalt surface area of 3.9 m²g⁻¹ for material C obtained from chemisorption measurements. Hence, significant leaching of cobalt during zeolite synthesis can be ruled out. The corresponding size of the cobalt core for material C is approximately 17.3 nm (23 nm for Co_3O_4), which is similar to the results from material B and in agreement with the rough observation from the electron microscopic images. The comparable cobalt particle size offers a unique comparability of the catalytic properties of both materials.

A comparison of the FT activity of material B and C, with respect to selectivity and reaction rate, is show in Table 1. The

		Selec	tivity	Reaction rate ^[c]				
Т	$X_{\rm CO}^{\rm [b]}$	CH_4	CO ₂	m _{cat}	m _{Co}	S _{Co}		
[°C]				[mmol kg ⁻¹ s]	[mmol kg ⁻¹ s]	[µmol m ⁻² s]		
material B, 0.51 g catalyst								
210	0.022	0.211	0.029	2.66	3.55	0.95		
225	0.031	0.214	0.051	3.79	5.06	1.35		
240	0.057	0.212	0.075	6.97	9.29	2.49		
250	0.096	0.198	0.091	11.70	15.60	4.18		
material C, 0.55 g catalyst								
200	0.023	0.188	0.005	2.55	2.55	0.65		
225	0.084	0.163	0.004	9.42	9.42	2.42		
240	0.263	0.157	0.011	29.59	29.59	7.59		
250	0.374	0.180	0.022	42.00	42.00	10.77		
[a] Conditions: 2.1 MPa, $H_2/CO = 2$, 0.5 $L_{STP}h^{-1}$ CO feed flow rate. [b] X_{CO} : CO conversion. [c] Reaction rate of CO consumption is related to: m_{cat} (catalyst mass) and S _c (cobalt surface area)								

methane selectivity of material B and C is comparable and almost independent of temperature, with slightly higher values for material B. The rather high values (at approximately 20%) are comparable to literature data, in which 24% is reported for material $B^{[17]}$ and 19% for Co/zeolite^[7b] at 240 °C. The CO₂ selectivity appears to be unusual for Co catalysts and is higher for material B than for C. However, values in the same order of magnitude are also reported in literature.^[7b] The specific reaction rate observed for material C is higher than that for material B, which holds for catalyst mass, cobalt mass, as well as for cobalt surface area as a reference quantity. The order of magnitude agrees well with the literature, where a value of approximately 3.1 mmol_{CO}/kg_{cat} s can be derived for 10 wt% Co supported on zeolite at 240 °C and 1.5 MPa.^[7b] The analysis of the temperature dependency of the reaction rate reveals a higher apparent activation energy for material C (119 kJ mol⁻¹) than for material B (77 kJ mol⁻¹). A possible explanation could be the different product distribution, which is shifted to lighter hydrocarbons for material C (see below). Thus, the diffusion through the liquid-filled pores for material C is improved, leading to a higher reaction rate and activation energy. This finding is supported by the slightly higher methane selectivity for material B, which indicates more pronounced diffusion limitations. However, the different nature of the support material might also cause significant differences in reaction rate and selectivity. In addition, repeated temperature cycles between 200 and 260 °C during approximately 1100 h on stream revealed an exceptional catalytic stability of the FT component in material C regarding conversion and selectivity (Figure S5).

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The catalytic activity of the HP component was verified by comparing the composition of hydrocarbon products of material B and C in the wax samples at a reaction temperature of $250 \,^{\circ}$ C (Figure 5). The fraction of long chain *n*-alkanes is re-



Figure 5. Product distribution in the wax sample on carbon basis for material B and C [sampling at 250 °C during experiments shown in Table 1; material B=grey, material C=black; a) *n*-alkanes, b) non-*n*-alkanes, c) total].

duced (Figure 5 a), whereas the non-*n*-alkane fraction is increased (Figure 5 b) in the presence of a HP component in material C. This observation qualitatively agrees with literature reports.^[7b] In particular, according to Freitez et al.,^[6a] the highest non-*n*-alkane/*n*-alkane ratio is observed for the C₅₋₉ fraction. The explanation can be derived from the total carbon molar fraction in the C₅₋₉ fraction (Figure 5 c). The higher carbon content in this fraction for material C is caused by the cracking of long-chain hydrocarbons. Considering a symmetrical product distribution and a single C–C bond cleavage in each cracking event, one C₁₀ to C₁₈ molecule is cracked into two molecules of the C₅₋₉ fraction.^[26] Furthermore, C₁ and C₂ species are not formed by cracking and C₃ species only occur in small amounts.^[26] Consequently, the cracking and isomerization products accumulate within the C₅₋₉ fraction.

The Anderson–Schulz–Flory (ASF) plot (Figure 6) shows three distinct regions, regarding the slope of the curve, in carbon molar fraction with respect to the hydrocarbon chain length. In the short-chain region (below C_{11}) no clear slope is present, which can be explained by the sampling procedure^[27] consisting of both a wax and water separator at operating pressure. In the wax separator the hydrocarbon species are in gas–liquid equilibrium (at 150 °C, 2.1 MPa) and thus, significant amounts of species up to C_{10} are present in the gas phase. Furthermore, the sample pressure is reduced to atmospheric conditions during sampling, which causes partial evaporation of the liquid sample. Hence, the content of species up to C_{10} in the wax sample is falsified. In the mid-chain region (C_{11} to C_{16}) the re-

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Figure 6. ASF plot for the composition of the wax phase at a reaction temperature of 250 $^\circ\text{C}.$

sults are more reliable and a chain-growth probability of approximately 0.92 is achieved for both materials. The long-chain region is not affected by the sampling procedure and the chain-growth probability is observed to be significantly higher for material B (ca. 0.84) than for material C (ca. 0.76). Furthermore, the molar fraction of long-chain hydrocarbons in the wax sample of material C is one order of magnitude smaller than that of material B. The discussed results are also supported by the state of the wax samples at room temperature; a solid for material B and a liquid for material C (Figure S6).

The catalytic stability of the HP component in material C was not directly investigated because long-term tests at 250 °C were not conducted. However, the presented results were obtained after 1050 h TOS (time on stream) and thus, significant deactivation of the HP component is highly unlikely.

Conclusions

An innovative synthesis approach that allows the stepwise, bottom-up construction of nanostructured, bifunctional catalysts consisting of cobalt nanoparticles encapsulated inside a zeolite matrix has been presented. The material was proven to be active in the combined FT and HP reaction, evidenced by a shift from waxy to liquid products. Both, the FT and HP component show significant activity after approximately 1100 h TOS, which rules out significant deactivation of the cobalt nanoparticles during zeolite synthesis and underlines the exceptional high stability of the catalyst. Consequently, the principle of the novel approach was successfully demonstrated in terms of material synthesis and bifunctional catalytic application. Further steps are the control of cobalt particle size and composite morphology to optimize the material towards hydrocarbon distribution.



Experimental Section

Details of the material synthesis, catalytic characterization, and data evaluation are summarized in the Supporting Information. Key aspects of the material synthesis and catalytic characterization are briefly described below.

The synthesis procedure of material A and B was adapted from Xie et al.^[17] Material A was synthesized by solvothermal treatment of a mixture containing PVP (polyvinylpyrrolidone) and cobalt nitrate dissolved in ethanol at 180 °C in a Teflon-lined autoclave. To obtain material B by the Stöber process the as-synthesized colloidal solution of material A was added into a solution of CTAB (cetyltrimethylammonium bromide) and ammonia solution dissolved in a mixture of ethanol and water. Subsequently, TEOS (tetraethyl orthosilicate) was added under stirring and the mixture was allowed to react for 48 h, followed by collection of the solids by centrifugation. After calcination at 550 °C for 6 h material B was used as precursor for zeolite synthesis. For that purpose the solids were suspended in an aqueous mixture of sodium hydroxide and sodium aluminate. Next, TPAOH (tetrapropyl ammoniumhydroxide) was added as structure directing agent. Sulfuric acid was used to adjust The reaction mixture (1 SiO₂:0.005 Al₂O₃:0.27the pH. $Na_2O:0.49TPAOH:0.02H_2SO_4:67H_2O:0.4OH^-$) was transferred into a Teflon-lined autoclave and treated at 170°C for 24 h. The resulting material was calcined at 550 °C for 6 h followed by ammonia ion exchange and an additional calcination step at 600°C for 6 h under N₂.

Catalytic experiments were performed by using equipment described previously. $^{\scriptscriptstyle [28]}$ In the present work a slit-shaped micro reactor under isothermal conditions (slit width 1 mm) operated as a packed bed was used. The catalyst (500 mg) was applied after pelleting and crushing into a fraction of 90–180 $\mu m.$ The catalyst was reduced at 350 °C for 16 h under pure hydrogen at ambient pressure. The reaction was performed at 2.1 MPa, a H₂/CO ratio of 2 and a CO flow rate of 0.5 $L_{\text{STP}}\,h^{-1}$ (STP = standard temperature and pressure). Ar was used as internal standard for online gas analysis by GC. Liquid products were collected in a wax and water separator operated at 0 and 150 °C, respectively. The wax sample was analyzed by offline GC.

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FULL PAPERS

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Under control: Controlling the selectivity of Fischer–Tropsch (FT) synthesis in a single reaction step is a major challenge in heterogeneous catalysis. An innovative synthetic approach that allows the bottom-up construction of nanostructured bifunctional catalysts in a step-wise manner is described. The resulting material, which exhibits cobalt nanoparticles encapsulated inside a zeolite matrix, is proven to shift the FT selectivity from waxy to liquid products.