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On the role of cobalt carbidization in higher alcohol synthesis over hydrotalcite-based Co-Cu catalysts

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ABSTRACT

Co-Cu-based catalysts are widely applied in higher alcohol synthesis (HAS) from synthesis gas. Although the nature of the active sites is still not fully understood, the formation of Co₂C under HAS conditions seems to play a major role. A CO pretreatment procedure was developed allowing a systematic investigation of the influence of cobalt carbidization on the structural properties and catalytic performance of the catalysts. By exposing the catalyst to a CO-containing atmosphere prior to HAS, Co enrichment of the catalyst surface occurred followed by carbide formation. This surface modification decreased the formation of hydrocarbons and enhanced the formation of C₂+OH. The catalyst pretreated with CO at 20 bar achieved the highest selectivity to ethanol and the lowest hydrocarbon selectivity.

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1. Introduction

The catalytic conversion of synthesis gas to short-chain alcohols—usually referred to as higher alcohol synthesis (HAS)—provides a promising process for feedstock chemicals used for the production of lubricants, detergents and, plasticizers [1]. In order to establish an economically attractive industrial process different approaches are found in literature aiming at suitable catalyst systems [2–4]. For the formation of higher alcohols the catalysts need to provide active sites for dissociative as well as molecular adsorption of CO [5]. Catalysts based on Cu and Co, providing a dual site mechanism for molecular and dissociative CO adsorption, have already been extensively studied. A high metal dispersion and close vicinity of both metal species is claimed to improve the selectivity towards higher alcohols [6,7]. However, due to low solubility, the

formation of a Co-Cu alloy is not likely to occur for bulk catalysts [8–10]. In addition, the importance of Co-Co₂C sites in HAS was also discussed [8,11–16]. Similar to metallic Cu, Co₂C is assumed to provide active sites for molecular CO adsorption.

The formation of Co₂C occurs during the exposure of the catalyst to the CO-containing atmosphere under reaction conditions. The deposition of carbon on the catalyst surface is attributed to two main reactions:

Carbide formation is well-known for Fe- and Co-based catalysts applied in Fischer-Tropsch Synthesis (FTS) [19,20]. The so-called Hägg-Carbide (Fe₅C₂) is one of the main active carbide phases in FTS, while the cementite carbide (Fe₃C) exhibits lower FT activity [21]. In contrast, the formation of Co₂C during FTS is considered as the main reason for the deactivation of Co

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catalysts [22]. The formed carbide impairs dissociative CO adsorption limiting the chain growth of hydrocarbons. With respect to HAS, Spivey et al. [8] showed that Co-Co₂C sites improved the formation of alcohols. However, controlling the formation of Co₂C in order to adjust an optimal ratio between metallic Co and Co₂C remains challenging. Different promoters as well as pretreatment conditions were discussed, ranging from a few hours up to several weeks in CO atmosphere [23,24]. Cobalt carbidization was investigated by Hofer [25], who determined the temperature range for Co₂C formation over pure cobalt catalysts applied in FTS to be between 220 and 350 °C. Similar results were obtained by Volkova et al. [26] with a bimetallic Co-Cu system. Paterson et al. [14] investigated the influence of pressure and CO exposure time on monometallic Co catalyst used in FTS. They were able to show that both parameters have a similar influence on the formation of surface carbon species. Kruse and coworkers [27] derived a correlation between the composition of the gas phase and the surface and bulk composition of bimetallic core-shell Co-Cu catalysts. They observed a Cu-rich surface after reduction in H₂, followed by a Co enrichment of the surface when switching to CO-rich atmospheres. Tanaka et al. [28] showed that depending on the carbidization conditions, the initially formed carbide phase is covered by a passivating layer of graphitic carbon.

In summary, there is only a narrow temperature range that allows for the formation of a stable cobalt carbide phase, which is simultaneously suitable for HAS. Elevated pressure improves carbide formation, but also accelerates catalyst deactivation due to enhanced carbon deposition. However, there is no well-established standard CO pretreatment procedure leading to an optimal Co/Co₂C ratio without causing catalyst deactivation. Moreover, most of the catalysts tested in literature were monometallic or bimetallic systems based on Co-Co₂C and/or Cu.

The present contribution systematically investigates carbidization of a hydrotalcite-based Co-Cu/ZnO/Al₂O₃ catalyst applied in HAS. Previous studies of similar Na-modified malachite-based Co-modified Cu/ZnO/Al₂O₃ methanol synthesis catalysts revealed an improvement of C₂+OH formation due to Co₂C formation under reaction conditions [29]. Catalysts based on phase-pure hydrotalcite (HT) precursors showed improved metal dispersion and accelerated carbide formation under HAS conditions [30]. The HT-based precursors were activated in H₂ and then exposed to pure CO with varied exposure time and CO pressure. The pretreated catalysts were applied in HAS at 280 °C, 60 bar and a ratio of H₂/CO equal to 1. Characterization of the catalysts was performed after activation, after CO pretreatment and after 35 h under HAS conditions using X-ray diffraction (XRD), temperature-programmed reduction (TPR), thermogravimetry (TG), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation

The HT-based catalyst precursor was prepared by co-pre-

cipitation using metal nitrates leading to a molar composition of Co: Cu: Zn: Al = 20: 40: 15: 25. A detailed description of the preparation route can be found in Ref. [30].

2.2. Characterization

The actual metal composition as well as the absence of residual Na was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an UNICAM PU 7000. XRD patterns were recorded using a PANalytical Empyrean Bragg-Brentano diffractometer with Cu K α radiation (λ = 0.15406 nm, 45 kV, 40 mA) and a PIXcel detector. The measurements were performed at room temperature and atmospheric pressure with 2θ ranging from 5° to 80° with a step size of 0.013° and a fixed divergence slit of 0.38 mm. Powder diffraction files (PDFs) from the International Centre of Diffraction Data (ICDD) combined with the X'Pert Line software (PANalytical, Almelo) were used for qualitative analysis. Subsequent to transfer in air, the XPS measurements were performed in ultra-high vacuum with base pressure at 10⁻¹⁰ mbar using a Gammatdata-Scienta SES 2002 analyzer. The spectra were obtained with a pass energy of 200 eV in the high-pass energy mode. Monochromatic Al K α (1486.6 eV, 14.5 kV, 45 mA) radiation was used resulting in an overall resolution of 0.6 eV. By using a flood gun, charging effects were compensated. Since several carbon species were formed under HAS conditions, the Cu 2p binding energy of metallic copper at 932.8 eV was used as a reference. The deconvolution of the spectra was achieved using the CasaXPS software with Shirley-type background subtraction and asymmetric Gaussian-Lorentzian functions. Additionally, surface composition and atomic ratios were calculated by using the peak areas after background subtraction and the element-specific cross-sections. TPR experiments were carried out with 100 mg of the calcined catalyst in a quartz reactor using a flow in Ar of 5 vol% H₂ and a heating rate of 5 °C min⁻¹. Quantitative H₂ consumption was derived using a calibrated thermal conductivity detector. TG experiments were performed using a Rubotherm magnetic suspension balance coupled with a Pfeiffer ThermoStar online quadrupole mass spectrometer (QMS). For the TG experiments in H₂, 50 mg of the calcined sample was reduced at 350 °C with a heating rate of 5 °C min⁻¹ for 15 h in diluted H₂ (H₂/N₂ = 0.25). Afterwards, the sample was cooled to room temperature and the gas flow was switched to CO. TG experiments in CO were carried out with a heating rate of 5 °C min⁻¹ to 450 °C.

2.3. Catalytic tests

Catalytic tests were performed in a high-pressure flow set-up. The following gases were used: N₂ (99.9999%) as internal standard and purge gas, H₂ (99.9999%) for the reduction of the catalysts, and premixed synthesis gas with CO (99.997%), H₂ (99.9999%) and N₂ (99.9999%) with an overall feed gas composition of CO: H₂: N₂ = 40: 40: 20 (H₂/CO = 1). In a high pressure stainless-steel fixed-bed U-tube reactor, 250 mg of the calcined catalysts (particle sizes of 250–355 μ m) was fixed between quartz wool. The reduction was performed at

350 °C for 15 h in diluted H₂ (H₂/N₂ = 0.25). Activity measurements were performed at 280 °C, 60 bar with a volumetric feed rate of 40 ml min⁻¹ and a GHSV of 9600 ml h⁻¹ g_{cat}⁻¹. The U-tube reactor was positioned in a circulating air oven ensuring isothermal reaction conditions. Online gas chromatography was used for quantitative analysis [31].

Three catalysts were pretreated in pure CO at 280 °C after reduction in the same set-up prior to HAS testing. Two of them were pretreated in CO at atmospheric pressure for 24 and 50 h and denoted as 24 h and 50 h, respectively. A third sample, pretreated for 24 h at 20 bar, was denoted as 20 bar. A sample, that was not pretreated in CO and denoted as 0 h, was also studied as a reference.

3. Results and discussion

3.1. Catalyst activation in H₂ and CO

Reduction of the calcined catalyst precursor is mandatory in order to obtain the active metallic sites. The reduction temperature has to be chosen carefully, as it can significantly influence the performance of the catalyst. If the temperature is too low, incomplete reduction occurs, while high reduction temperatures can lead to thermal sintering and particle aggregation. Therefore, the reduction behavior of the HT-type precursor in diluted H₂ was investigated by TPR. The resulting profile up to 800 °C is shown in Fig. 1. It is known from previous studies that ZnO and Al₂O₃ are not reducible under the conditions applied and do not contribute to the detected H₂ consumption. The first sharp and narrow peak at around 250 °C is due to the reduction of Cu²⁺ to metallic Cu⁰. A shoulder at around 230 °C indicates the reduction of Cu²⁺ species in different chemical environments, i.e., copper oxide and copper oxycarbonate typical for HT-based structures [30,32,33]. The reduction of cobalt oxide to metallic Co⁰ requires higher temperatures resulting in a flat and broad peak in the range of 300–650 °C. Obviously, its reduction is favored in the presence of Cu⁰ due to hydrogen spillover [34–36]. A degree of reduction of about 96.4% derived from the overall H₂ consumption confirmed complete

Fig. 1. TPR profile of the calcined HT precursor.

reduction of both Co oxide and Cu oxide up to 650 °C.

The activation procedure for HT-based catalyst precursors consisted of an exposure to diluted H₂ only up to 350 °C, followed by a 15-h holding period in diluted H₂ at this temperature [31]. As revealed by TPR, complete cobalt oxide reduction was not likely to occur under these conditions. Therefore, the activation procedure was monitored in a thermobalance coupled with a QMS (Fig. 2). As expected, reduction of Cu²⁺ was observed at a temperature of about 250 °C resulting in a mass loss of about 20%. Reduction was accompanied by the simultaneous release of H₂O and CO₂ indicating the reduction of different Cu²⁺ species, such as CuO and Cu₂CO₃, respectively. After reaching 350 °C, no further reduction was detected after about 2 h as indicated by a constant H₂ signal and a constant sample mass.

The bulk structures of the samples reduced at 350 °C for 15 h (activation) and at 800 °C during TPR were characterized by XRD (Fig. 3). The reflections at $2\theta = 43.3^\circ$, 50.4° and 74.1° observed in the pattern of the sample reduced at 350 °C originate from metallic Cu. The mean Cu particle size was derived amounting to 5.6 nm by applying the Scherrer equation. In addition, the broad reflection at around 63.1° indicates the presence of CoO or spinel phases, whereas bulk metallic Co was not observed. In contrast, sharp and intense reflections in the pattern of the sample reduced at 800 °C indicate the presence of metallic Cu and metallic Co. Due to the high temperature the mean Cu particle size increased to 17.8 nm, and the mean Co crystallite size was derived amounting to 12.8 nm.

From investigations of spent Co-Cu-based catalysts applied in HAS, it is known that strong structural changes occur under reaction condition in synthesis gas. In order to investigate this effect in more detail, the activated catalyst was exposed to CO performing a TG experiment with a linear heating up to 450 °C (Fig. 4). At about 300 °C, the formation of CO₂ was observed. With increasing temperature CO₂ formation was strongly enhanced, accompanied by a roughly 30% increase in sample weight up to 450 °C. The results indicate the formation of surface carbon according to the Boudouard equilibrium (Eq. (2)). In order to avoid excess carbon deposition instead of carbide formation, a temperature of 280 °C was chosen for the CO pretreatment [37]. For this purpose, a second TG experiment in CO

Fig. 2. TG-QMS analysis of the calcined HT precursor during activation in diluted H₂.

Fig. 3. XRD patterns of the samples reduced at 350 for 15 h, 5% H₂ in N₂ (left) and after TPR at 800 °C, 5% H₂ in Ar (right).

was performed by applying a constant temperature of 280 °C for 50 h (Fig. 5). During the first initial heating period, CO₂ formation accompanied by a small weight loss is observed at 150 °C indicating the reduction of residual metal oxide phases, most likely CoO (not visible in Fig. 4 due to the scaling). The slight increase of the sample weight during further exposure at constant temperature without further formation of CO₂ may indicate the formation of Co₂C, whereas bulk carbon deposition can be excluded under the conditions applied.

3.2. Structural properties after the CO pretreatment

Lee and coworkers [23] investigated the behavior of monometallic Co catalysts under CO-rich atmospheres. The formation of cobalt carbide was found to be a function of exposure time and pressure. These findings were adopted for the pretreatment of the HT-based Co-Cu catalyst precursors, and the influence of the pretreatment conditions on the catalyst structure and performance was investigated in detail. Fig. 6 shows the diffraction patterns of the catalysts pretreated under different conditions and a non-pretreated sample. All patterns exhibit the intense reflections of metallic Cu at $2\theta = 43.3^\circ$ and

50.4° . The presence of cobalt oxide phases can be assumed for the 24 h pretreated sample ($2\theta = 42.4^\circ$) [37]. Formation of bulk Co₂C is excluded for both samples pretreated at ambient pressure. In contrast, small reflections at $2\theta = 42.7^\circ$ and 45.9° were observed for the sample pretreated at 20 bar, indicating the presence of Co₂C. In addition, metallic Co (fcc) is identified by the broadening of both Cu⁰ reflections at $2\theta = 43.3^\circ$ and 50.4° .

The XPS results comprising the Cu 2p, Co 2p and C 1s regions for the different samples are presented in Fig. 7. In the Cu 2p region Cu(0) and Cu(II) were observed for all samples at 932.8 and 933.9 eV, respectively. The presence of Cu(II) is accompanied by its satellite peaks in the range from 947 to 940 eV [38]. Although all samples contained Co(II) as indicated by the peak at 780.7 eV in the Co 2p region, the presence of metallic Co⁰ (778.6 eV) was only observed for CO-pretreated samples, demonstrating the reduction of Co(II) during the CO pretreatment. It is difficult to identify the carbide phase in this region due to its overlapping with other cobalt species. The Co 2p region for the sample pretreated at 20 bar was rather noisy compared with the samples pretreated at ambient pressure, pointing to the deposition of several carbon layers on Co during the pretreatment. The C 1s signal is composed of contributions

Fig. 4. TG-QMS of the reduced HT precursor in pure CO atmosphere.

Fig. 5. TG-QMS results obtained with the reduced HT precursor in pure CO.

Fig. 6. XRD patterns of the catalysts after different CO pretreatments.

from various carbon species, most of them originating from carbon-containing contaminants. The C 1s peak of surface carbide, which is usually located at 283.1–283.6 eV, can hardly be observed due to its overlapping with other carbon-containing species. The relative surface concentrations derived from the XP spectra are summarized in Table 1. The surface concentrations of Co and O increased for the samples pretreated at ambient pressure, whereas its concentrations decreased for the sample pretreated at 20 bar. In contrast, Cu, Al and Zn concentrations decreased for the two samples pretreated at ambient pressure. For the samples pretreated for 50 h and at 20 bar, a

Table 1

Relative XPS-derived surface concentrations of the CO-pretreated samples (transfer in air).

Sample	Surface concentration (mol%)					
	Co	Cu	Zn	Al	O	C
0h	1.9	3.5	5.6	22.2	39.1	27.7
24h	3.2	3.6	5.4	17.8	48.8	21.1
50h	3.7	2.6	3.7	12.6	54.4	23.1
20bar	2.3	1.7	5.7	15.8	45.6	28.9

Co/Cu ratio of about 1.4 was reached pointing to the formation of Co/Cu shell core particles.

3.3. HAS performance after the CO pretreatment

From recent studies it is known that Co-Cu-based catalysts often suffer from deactivation during the initial period under HAS conditions before reaching steady-state performance [29,30,39]. Fig. 8 shows the degree of CO conversion for differently pretreated catalysts during the first 10 h and after 35 h time on stream (TOS). Strong initial deactivation occurred for the non-pretreated catalyst (0 h). A quite similar behavior was found for the samples 24 h and 50 h, but at a lower degree of conversion. Compared with the other catalysts, only slight deactivation was observed for the catalyst pretreated at 20 bar, which showed the lowest degree of CO conversion in the initial period as well as after 35 h TOS.

The averaged selectivities for linear alcohols and hydrocarbons obtained after 10 and 35 h of TOS are shown in Fig. 9. A product distribution similar to ASF known from FTS was observed for alcohols as well as for hydrocarbons. After 10 h TOS, methane was the major product for all samples. However, the selectivity to C₂₊ hydrocarbons slightly decreased for the CO-pretreated catalysts. The highest alcohol selectivity was obtained for the catalyst pretreated at 20 bar. With increasing TOS the selectivity to hydrocarbons decreased significantly, while the selectivity to alcohols increased for all samples. The selectivities obtained after 35 h TOS are additionally summa-

Fig. 7. Cu 2p (left), Co 2p (middle), and C 1s (right) XPS regions of the catalysts after different CO pretreatments.

Fig. 8. CO conversion during the first 10 h and after 35 h TOS for the differently pretreated catalysts (280 °C, 60 bar, $H_2/CO = 1$).

ized in Table 2. Linear hydrocarbons were the main products for the catalyst 0 h. A significant decrease in hydrocarbon selectivity was observed for the CO-pretreated samples, whereas the selectivity towards the linear C_1 – C_3 alcohols increased.

Within the linear alcohols, methanol was the main product for all catalysts. The selectivity to other oxygenates (oxy) and ether decreased with increasing CO pretreatment time as well as with higher pressure.

3.4. Structural properties after CO pretreatment and HAS

The differently pretreated catalysts were further characterized after 35 h TOS under HAS conditions. Fig. 10 shows the XRD patterns of the spent catalysts. While only one reflection due to metallic Cu^0 was observed for sample 0 h, the presence of bulk cobalt carbide as indicated by the additional reflections at $2\theta = 42.7^\circ$ and 45.9° was also observed for the other samples. Moreover, metallic Co was identified indicated by the broadening of the Cu^0 reflection at $2\theta = 43.2^\circ$, which is most prominent for sample 20 bar.

The surface-near region of the spent catalysts was investigated by XPS (Fig. 11). The C 1s peak can be deconvoluted into various carbon species. Most of these peaks originate from carbon-containing contaminants remaining on the catalyst surface after reaction. For the non-pretreated, the 24 h and 20 bar pretreated catalysts the peak shapes and the ratios between the C–C (284.8 eV) and C–OR (286.0 eV) fraction are characteristic for adventitious surface carbon. The presence of remaining carbon species from HAS is also likely. An increased

Fig. 9. Product selectivities of linear alcohols (left) and hydrocarbons (right) after 10 h (top) and 35 h (bottom) TOS (280 °C, 60 bar, 9600 mL h^{-1} g_{cat}^{-1}).

Table 2

Averaged selectivities of the differently pretreated catalysts in HAS after 35 h TOS.

Sample	$X_{\text{Co}}/\%$	$S_i/\%$									
		CO ₂	MeOH	EtOH	PrOH	BuOH	PeOH	CH ₄	HC(C ₂ –C ₈) ^a	oxy ^b	ether ^c
0h	5.7	11.2	7.1	6.9	2.7	1.4	0.9	20.7	45.0	2.6	0.5
24h	4.0	17.4	10.5	7.8	2.7	1.3	1.3	25.4	31.8	1.4	0.4
50h	3.6	20.4	12.7	9.5	3.2	1.3	0.7	22.2	28.5	1.1	0.4
20bar	2.5	19.9	18.3	12.9	3.6	1.1	0.5	25.8	17.3	0.5	0.2

^alinear hydrocarbons, ^btert-butanol, 2-butanol ^cdimethylether, diethylether.

C-OR fraction was observed for the 50 h pretreated sample, indicating the presence of additional oxygen-containing surface carbon species as a result of HAS. Both metallic Cu⁰ (932.8 eV) and Cu(II) (933.9 eV), metallic Co⁰ (778.2 eV) and Co(II) (778.7 eV) were observed on all samples. The poor signal-to-noise ratio of the Co 2p region for the 50 h and 20 bar pretreated samples is presumable caused by carbon deposition during HAS. The relative surface concentrations are summarized in Table 3. The concentrations of Co and Al increased with increasing CO pretreatment time at ambient pressure.

3.5. Discussion

Different catalyst pretreatment procedures in CO were performed in order to evaluate the optimal activation conditions for the HT-based Co-Cu catalyst. As shown by TPR in H₂ (Fig. 1), an almost complete reduction (96.4%) of Cu and Co oxide was

achieved below 650 °C. Therefore, the formation of Cu and/or Co spinel phases (CuAl₂O₄, CoAl₂O₄) during calcination of the HT-based precursor can be excluded, because these phases exhibit high thermal stability and require higher reduction temperatures [30,32,40]. Reduction temperatures above 350 °C led to segregation and growth of the metallic Cu and Co nanoparticles, indicated by the intense reflections in the XRD pattern (Fig. 3(right)). In order to avoid thermal sintering and to achieve preferably small metallic particles, lower reduction temperatures are required [37]. Therefore, the reduction of the catalyst precursor was performed at 350 °C for 15 h. Copper oxide was completely reduced under those conditions, while significant amounts of CoO remained as revealed by TG in H₂ (Fig. 2), XRD (Fig. 3(left)), and XPS (Fig. 7). TG experiments in CO with the catalyst activated in hydrogen at 350 °C (Fig. 5) showed that the further reduction of CoO to Co⁰ occurred at relatively low temperature when exposed to a CO-containing atmosphere. Once metallic Co⁰ is formed, it has a strong tendency to bind carbon, e.g. by dissociative adsorption of CO [25,26,41,42]. At temperatures below 300 °C, the formation of Co₂C is likely to occur as indicated by a slight weight growth during the TG experiment in CO (Fig. 5). At higher temperatures a strong increase of the sample mass was observed accompanied by CO₂ formation (Fig. 4). Nakamura et al. [28] and Hofer et al. [25] related this strong mass growth to continuous formation of graphitic carbon following carbide formation due to dissociative CO adsorption (Eq. (1)) according to the Boudouard equilibrium (Eq. (2)). In order to avoid coking of the catalysts due to graphitic carbon deposition, a temperature of 280 °C was chosen for the CO pretreatment.

The activation of highly active catalysts in FTS and HAS is known to depend strongly on the right pretreatment conditions, especially with respect to temperature and pressure [14,27,43]. The major challenge is to achieve a metallic Co-rich surface mandatory for the formation of Co₂C. After activation in diluted H₂, mainly Cu⁰ and X-ray amorphous CoO were found to be present in the bulk of the catalyst (Fig. 3(left)). The Cu surface concentration was higher compared with Co as revealed by XPS (Table 1). Exposing the catalysts to CO at 280 °C for 24 h and for 50 h led to an increased surface concentration of Co and the formation of metallic Co⁰. These observations are in good agreement with the results obtained by Kruse and coworkers [27], who suggested a surface enrichment of metallic Co with increasing CO pretreatment time. Atomic carbon adsorbed on the surface reacts with Co⁰ forming Co₂C, as indicated by the XRD results (Fig. 6) [44–47]. Based on the obtained results, a surface modification towards a Co⁰/Co₂C-rich surface is as-

Fig. 10. XRD patterns in the 2θ range from 40° to 48° of the differently pretreated catalysts after 35 h TOS under HAS conditions.

Fig. 11. Cu 2p (left), Co 2p (middle), and C 1s (right) regions of the spent catalysts measured by XPS.

sumed during the CO pretreatment at ambient pressure for 24 and 50 h. For the catalyst pretreated under elevated CO pressure, an increased carbon surface concentration accompanied by a decreased Co concentration was observed indicating carbon deposition selectively on metallic Co (Table 1). The presence of several encapsulating graphitic layers is assumed to cause the noisy XP Co 2p spectrum and the decreased surface concentration. The presence of bulk and surface metallic Co was revealed by XRD (Fig. 6) and XPS (Fig. 7), respectively. A strong interaction of Cu⁰, ZnO or Al₂O₃ with carbon is excluded, as DFT calculations indicated only very low bond energies for Cu-, Zn- or Al-C bonds [41,48]. XRD indicated the presence of a bulk Co₂C phase only for the sample pretreated at 20 bar. However, XPS provided no clear indication for the presence of surface carbide in the C 1s region (283.0 eV). Obviously, bulk Co₂C was formed under the applied pretreatment conditions, but was covered by several layers of graphitic carbon.

The presence of bulk Co₂C was revealed by XRD for all pretreated samples (Fig. 10) after 35 h under HAS conditions. Further deposition of carbon occurred especially for the catalyst pretreated at 20 bar as indicated by the low signal-to-noise ratio of the XP Co 2p spectrum (Fig. 11). Niemantsverdriet and coworkers [42] characterized the different carbon species formed on the surface of a Co-based catalyst during exposure to CO and observed the formation of multiple layers of graphitic carbon. Therefore, in addition to some remaining carbon species produced by the reaction, the presence of graphitic carbon layers on top of Co carbide is highly likely.

Table 3

Relative XPS-derived surface concentrations of the spent catalysts (transfer in air).

Sample	Surface concentration/mol%					
	Co	Cu	Zn	Al	O	C
0h	2.5	4.5	5.0	13.9	47.0	27.1
24h	2.8	2.7	3.5	16.3	44.3	30.4
50h	4.5	3.2	5.9	20.3	44.7	21.5
20bar	2.1	3.0	4.7	12.5	45.1	29.8

The structural changes of the catalysts induced by the respective CO pretreatment procedure clearly influenced the catalytic performance in HAS. Nevertheless, all catalysts significantly deactivated during the initial 10 h TOS (Fig. 8). With regard to literature, initial deactivation is attributed to surface modifications, thermal sintering, or the formation of inactive carbon species under reaction conditions [27,37,49]. The strongest deactivation was observed for the non-pretreated sample. In contrast to the other samples, this catalyst was exposed to CO for the first time during HAS. Thus, similar surface modifications are assumed to occur in the initial period of the reaction as during the CO pretreatment, i.e., reduction of residual CoO and Co enrichment. Exposed metallic Co⁰ and Cu⁰ particles lead to the observed high selectivity to methane and CO₂, respectively, in the initial period of HAS (Fig. S1). With further progress of the reaction, the Cu surface concentration decreased, while Co⁰ was partly converted into Co₂C. As a result, CO₂ and methane selectivity decreased, and, in turn, higher selectivities to oxygenates and C₂₊-hydrocarbons were observed (Fig. 9). The catalyst pretreated at 20 bar exhibited a low Cu surface concentration and significant amounts of bulk Co₂C prior to HAS. Thus, the selectivities to CO₂ and methane were already lower in the initial period of the reaction (Fig. 9).

In summary, the pretreatment in CO led to an accelerated formation of the active state of the catalyst. The high selectivity towards linear C₂₊ alcohols indicates an intimate contact between metallic Co providing dissociative CO adsorption sites and predominantly Co₂C sites for molecular CO adsorption. The catalyst pretreated with CO at 20 bar features the highest selectivity to ethanol and the lowest hydrocarbon selectivity.

4. Conclusions

The influence of a CO pretreatment on the structural properties and catalytic performance of hydrotalcite-based Co-Cu catalysts applied in HAS was investigated. Exposure to CO prior to the reaction enhanced the formation of bulk and surface

carbide. With increasing exposure time as well as increasing pressure during the pretreatment, additional deposition of graphitic carbon occurred. Variation of the pretreatment conditions led to different surface compositions of the catalyst. For the non-pretreated catalyst a Cu⁰-rich surface and the presence of CoO after activation in H₂ were revealed, leading to high initial CO conversion with CO₂ and methane being the major products. Strong deactivation occurred during the first 10 h TOS indicating the modification of the catalyst surface in the CO-containing atmosphere during HAS, i.e., Co surface enrichment and carbide formation. With increasing exposure time to CO during the pretreatment, a Co⁰/Co₂C-rich surface was already obtained prior to HAS. As a result, improved selectivity towards linear C₂₊ alcohols accompanied by decreased selectivities to methane and CO₂ were observed, most likely due to an increased formation of Co₂C during the CO pretreatment. By the exposure to CO at elevated pressure additional coking occurred, i.e., deposition of graphitic carbon layers on Co⁰/Co₂C surfaces. This selective blocking of active sites during the pretreatment led to a lower degree of conversion due to less methane formation, but to the highest selectivities to methanol, ethanol and propanol. Thus, the pretreatment in CO prior to HAS seems to provide a promising method for the activation of catalysts containing significant amounts of FT-active Co⁰, leading to a catalyst state with improved overall alcohol selectivity and a lowered risk of wax formation.

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Graphical Abstract

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On the role of cobalt carbidization in higher alcohol synthesis over hydrotalcite-based Co-Cu catalysts

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CO pretreatment at elevated pressure enhances the selectivities to linear alcohols through surface cobalt enrichment and carbide formation.

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水滑石基钴铜催化剂中钴的碳化在高碳醇合成中的作用

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摘要: Co-Cu基催化剂广泛用于合成气制高碳醇反应(HAS)中。尽管很难从本质上完全理解催化剂的活性位, 但是在HAS条件下生成的Co₂C对反应的贡献是显而易见的。开发了CO预处理工艺, 系统地研究了钴的碳化对催化剂结构性能和催化性能的影响。通过在HAS反应之前将催化剂暴露在含CO的气氛中, 催化剂表面发生Co的富集, 然后形成碳化物。这种表面改性减少了烃类的形成, 促进了C₂+OH的形成。催化剂经20 bar下CO预处理后, 乙醇选择性最高, 烃类选择性最低。

关键词: 高碳醇合成; Co-Cu催化剂; 碳化钴; CO预处理

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