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Silver addition to a cobalt Fischer–Tropsch catalyst

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Silver is known to promote F–T catalysts as a reduction promoter, although it has also been observed to affect catalytic performance of, for instance, cobalt nanoparticles. In this work, a series of silica-supported cobalt catalysts with constant platinum content (0.04 wt%) and varying silver content were characterized and tested. Characterization shows that mainly coordinatively unsaturated cobalt atoms are substituted at low silver content (probed by N2 IR). Adding more silver results in replacement of both coordinatively unsaturated sites and planar sites (probed by H2 chemisorption and TEM-EDS). The presence of silver on the cobalt surface affects both structure-sensitive CO dissociation and structure-insensitive hydrogenation reactions. The Boudouard reaction shows that the CO dissociation rate decreases with increasing silver content. Hampered CO dissociation is also apparent from temperature-programmed CO IR spectroscopy. However, even at high silver content the surface still contains step-edge sites that can dissociate CO and a small amount of carbon is deposited (quantified by TPH). During the CO hydrogenation at 260 °C, CO conversion is reduced by less than 30% when 8.8 wt% silver is added. This does not correlate well with the loss in cobalt surface area measured by chemisorption (decreases by 93%) or CO dissociation rate probed by CO disproportionation (decreases by 90%). This mismatch is mainly because that the CO consumption rate under methanation condition is largely controlled by carbon and oxygen hydrogenation, rather than CO dissociation. On the other hand, transient experiments show that silver accelerates oxygen-removal steps. It turns out that CO conversion is only moderately affected by silver. The coverage of hydrogenation sites – mostly terrace sites – by silver causes slower CH4 formation. Longer residence of CH4 intermediates (determined by SSITKA) accordingly leads to an increase in chain-growth probability and therefore higher C2+ selectivity. SSITKA also confirms the decrease in steady-state CO/CHx distribution in a similar manner as graphitic carbon deposited on terrace sites as we reported earlier.

1. Introduction

One of the approaches to improve the performance of Fischer–Tropsch (F–T) catalysts is addition of small amounts of other elements, known as promoters. Silver, which does not exhibit measurable F–T activity itself, was initially proposed as a reduction promoter for iron-based F–T catalysts. Early work by Wachs et al. [1] showed that silver helps iron oxide reduction but less effectively than copper does, because reduced silver poorly disperses on the iron oxide surface. Recent investigations on silver as a promoter for iron-based F–T catalysts showed that silver facilitates the reduction of Fe3+ into magnetite during the pretreatment via either CO or H2, which was attributed to the ability of silver to spillover hydrogen to iron oxide [2]. The iron-silver catalyst also shows enhanced F–T activity and increased chain growth, but at the expense of an increased CO2 selectivity [2]. Chuang and Pien studied the effect of silver on a silica-supported rhodium catalyst [3]. The increased activity and selectivity of C2 and C3 oxygenates was attributed to a higher ratio of linear CO to bridged CO on the silver-promoted sample compared to the un-promoted one. On a ruthenium F–T catalyst, a decreased turnover frequency (TOF) after silver addition was reported by Kelzenberg and King [4], who attributed the decline in TOF to occupation of coordinatively unsaturated sites by silver atoms. Later, this hypothesis was described in more detail by the same group [5]. They proposed that...
low-coordinated edge and corner sites on the catalyst surface act as reservoirs for highly mobile surface H atoms. Silver atoms preferentially occupy these coordinatively unsaturated sites, slowing down the supply of atomic hydrogen. Silver addition consequently results in a decreased CO hydrogenation rate due to the lack of surface hydrogen. Jacobs et al. provided detailed characterization and testing of silver-promoted cobalt catalysts [6]. They showed that the silver promoter enhances cobalt reducibility and therefore increases the number of active sites, leading to enhanced CO conversion. In parallel with the increase in F–T activity, a decrease in CH₄ selectivity and an increase in Cₛ selectivity were also observed. EXAFS characterization showed increased Ag–Ag coordination numbers with increasing Ag content, indicating the formation of a segregated metallic silver phase [7].

In spite of these investigations, fundamental understanding about the role of Ag promoter in cobalt–catalyzed F–T synthesis is still lacking. In this contribution, silica-supported cobalt catalysts with a constant platinum content (0.04 wt% based on catalyst weight) and varying silver content were prepared by a step-wise impregnation procedure (first cobalt and platinum, then silver). The effect of silver promotion was studied by means of temperature programmed reduction (TPR), chemisorption, CO exposure followed by temperature programmed hydrogenation (TPH), transmission electron microscopy (TEM), infrared spectroscopy (IR), steady state isotopic transient kinetic analysis (SSITKA) and F–T performance tests.

2. Experimental

2.1. Preparation

The silver-promoted cobalt catalysts were prepared by step-wise incipient wetness impregnation (IWI). Firstly, the parent catalyst, CoPt/SiO₂, was prepared by IWI of silica support (X080, provided by Shell, 120–250 μm) with an aqueous solution of Co(NO₃)₂·6H₂O (Merck, 99.99%) and Pt(NH₃)₄(NO₃)₂ (Alfa Aesar, 99.99%) as precursor. Typically, 2 g of dried silica support is impregnated with a solution consisting of 2.47 g Co(NO₃)₂·6H₂O, 0.45 g deionized water, and 0.5 g Pt(NH₃)₄(NO₃)₂ aqueous solution (containing 0.2 wt% Pt). The catalyst was sequentially dried in static air at 110 °C for 12 h, calcined in static air at 350 °C for 2 h with a ramp of 1 °C min⁻¹, reduced in dilute H₂ flow (20% H₂ in He) at 450 °C for 6 h with a ramp rate of 5 °C min⁻¹, and passivated in dilute O₂ flow (2% O₂ in He) at 35 °C for 12 h [8]. As-prepared CoPt/SiO₂ catalyst was then impregnated with an aqueous solution containing different amount of AgNO₃ (Alfa Aesar, 99.99%). Following the impregnation step, the catalysts were dried in static air at 110 °C overnight and subsequently calcined at 350 °C for 2 h using a heating rate of 1 °C min⁻¹. Notably, the silver-free catalyst was impregnated with an equal amount of water, and treated by the same drying and calcination procedure as the silver-promoted ones. The metal content was determined by ICP–OES (Spectroblue, AMETEK Inc.). The cobalt and platinum content are 17 wt% and 0.04 wt%, respectively. The samples are coded by silver weight content, e.g., 4.3AgCo stands for a catalyst containing 4.3 wt% Ag, 17 wt% cobalt, and 0.04 wt% platinum on a silica support. The silver free sample is denoted as 0AgCo.

2.2. Characterization

Infrared (IR) spectra were recorded by Bruker Vertex V70v FTIR spectrometer. Typically, 18–20 mg of ground catalyst was pressed into a self-supporting wafer and placed in a controlled-environment infrared transmission cell, which is capable of heating and cooling, gas dosing and evacuation. Prior to the measurement, the catalyst wafer was in situ reduced by heating to 450 °C at a rate of 5 °C min⁻¹ in a H₂ flow (100 mL min⁻¹) and kept at this temperature for 2 h. Then, the cell was evacuated at 450 °C for 1 h, and was cooled to 35 °C in vacuum. The IR spectrum recorded at this condition was used as the background for subsequent measurements. Spectra were acquired at a resolution of 2 cm⁻¹ and 16 spectra were averaged. In CO adsorption experiments, the cell was pressurized to 10 mbar at 35 °C by carefully adjusting a needle valve connecting to gas reservoir. The cell was then heated to 300 °C at a rate of 5 °C min⁻¹. IR spectra were recorded every 5 °C during the heating. IR spectra of adsorbed N₂ were taken after reduction in H₂ for 2 h followed by cooling in a dynamic vacuum to −175 °C using liquid nitrogen. Small doses of N₂ were admitted to the cell until the IR bands were saturated.

Transmission electron microscopy (TEM) images and energy dispersive spectroscopy (EDS) mapping were recorded on a FEI Tecnai 20 transmission electron microscope at an acceleration voltage of 200 kV using a LaB₆ filament. Statistical analysis of the TEM images shows a volume-averaged cobalt particle size [9] at 15 nm.

H₂-chemisorption measurements were performed on Micromeritics ASAP 2010. Typically, 200 mg sample was in situ reduced at 450 °C and measured at 110 °C. The total H₂ uptake was determined by extrapolating the straight-line portion of adsorption isotherm to zero pressure. It was assumed that one H atom adsorbs per surface Co atom. The result for the unpromoted cobalt catalyst, which is 116.7 μmol g⁻¹, was employed to calculate the coverage of surface species.

Temperature-programmed reduction (TPR) experiments were carried out on ASAP 2920 II (Micromeritics). Typically, 10 mg sample was reduced in diluted H₂ flow (10% H₂ in Ar) using a heating rate of 10 °C min⁻¹. A Cu/SiO₂ reference sample was used to calibrate the H₂ consumption.

Temperature-programmed hydrogenation (TPH) following carbon deposition were performed in a tubular reactor. Typically, 200 mg in situ reduced (20% H₂ in Ar, 450 °C, 16 h) catalyst was exposed to a diluted CO flow (10% CO in Ar) for 30 min and then cooled to room temperature in Ar flow. The subsequent TPH experiments were conducted by heating the reactor to 650 °C at a rate of 5 °C/min in an dilute H₂ flow (10% H₂ in Ar). The signal of the main hydrogenation product, which is CH₄, was quantified by a calibrated online mass spectrometer (ESS, GeneSys Evolution). The amount of deposited carbon was obtained by integrating the CH₄ flow with time on stream.

2.3. Steady-state and transient experiments

Catalytic activity measurements and transient experiments were performed in a setup capable of switching gas feeding. After reduction in a dilute H₂ flow (20% H₂ in Ar, 50 mL min⁻¹ in total) at 450 °C for 16 h, the reactor was cooled to 260 °C in an Ar flow and pressurized to 2 bar. The Ar flow was subsequently switched to a synthesis gas mixture (CO/H₂/Ar = 5/5/40 mL min⁻¹). The responses after the switch are monitored by online spectrometry (ESS, GeneSys Evolution). The activity and selectivity were measured on a gas chromatograph (VARIAN CP–3800) equipped with TCD and FID detectors. Reported catalytic data were obtained after 21 h of steady state operation.

Steady-state isotopic transient kinetic analysis (SSITKA) was performed by switching from a mixture of ¹³CO/H₂/Ar (5/5/1 mL min⁻¹) to a mixture of ¹³CO/H₂/Ne (5/5/1 mL min⁻¹) when steady state conversion was reached. In addition, a 39 mL min⁻¹ Ar flow was used to keep the total flow rate at 50 mL min⁻¹. The Ne gas was used as a tracer to determine the gas-phase hold-up time. The transient responses of H₂ (m/z = 2), ¹²CH₄ (m/z = 15), ¹³CH₄ (m/z = 17), H₂O (m/z = 18), Ne (m/z = 22), ¹²CO (m/z = 28), ¹³CO (m/z = 29) and CO (m/z = 44) were acquired with a mass spectrometer (RMS, MassAnalyzer).
(m/z = 29) were monitored by online mass spectrometry. Procedures to determine the residence time and coverages of CO and CH₄ (intermediates of CH₄) are provided in our earlier work [10,11].

3. Results and discussion

3.1. Cobalt reducibility

Temperature-programed reduction (TPR) was performed to trace the influence of silver promotion on the cobalt reducibility. Fig. 1 shows that as little as 0.3 wt% silver reduces the temperature of CoO to Co reduction by 40 °C, qualitatively keeping in line with earlier studies [6,7]. However, increasing the silver content further does not decrease the reduction temperature of CoO. It is known that silver alone is not able to dissociate H₂ molecules at room temperature, showing negligible dissociative hydrogen adsorption [12,13]. This promotion effect is probably due to the change of electron density induced by the presence of silver [14]. Quantification of H₂-consumption during the TPR indicates that the presence of 0.04 wt% platinum enhances the cobalt reduction degree from 64% to 93%. Differing from earlier studies of Ag-Co catalysts [6,7], adding silver to our platinum-containing catalysts increases the cobalt reduction degree only marginally. For instance, the cobalt reduction degree of 8.8AgCo is 96%, slightly higher than that of the parent CoPt/SiO₂ catalyst (93%). We accordingly speculate that all the samples can achieve a similar reduction degree after the reduction at 450 °C for 16 h. EXAFS study of carbon nanofiber supported cobalt catalysts under F–T condition shows that neither bulk oxidation nor substantial surface oxidation occurs on cobalt [15], implying that the degree of reduction of cobalt does not change during the F–T reaction. Therefore, we can rule out an effect of silver promotion on the reducibility of the cobalt catalysts containing platinum. In addition, the effect of silver promotion upon platinum is absent for two reasons. (1) The CoPt/SiO₂ catalyst, i.e., the parent catalyst of silver promoted ones, is prepared by co-impregnation method. Cobalt and platinum precursors were well mixed in aqueous solution, guaranteeing the good dispersion of platinum in cobalt particles. Therefore, the molar ratio of Pt/Co on surface is close to its value in bulk, which is merely 1/1652. (2) Platinum signal is not visible in either TEM-EDS (detection limit ~2%) or XPS (detection limit ~0.1%) (not shown here), suggesting a very low platinum surface content and in any case much lower than the silver content.

3.2. CO exposure followed by TPH

CO disproportionation, known as the Boudouard reaction [16–18], was employed to probe the activity of silver-promoted cobalt catalysts towards CO bond scission [19]. ¹²C¹⁶O/¹³C¹₈O isotopic scrambling experiments reported earlier have demonstrated that (reversible) CO dissociation in the absence of H₂ occurs on a small fraction of the cobalt surface [20]. As previously discussed, the C–O bond can only be broken on step-edge sites, because the barrier of CO dissociation on terrace sites without the assistance of hydrogen is very high [21,22]. Therefore, we attribute the CO dissociation activity to these step-edge sites on cobalt nanoparticles. As determined by TEM, the silver-free cobalt catalyst contains on average 15 nm particles [20], whose surface is dominated by terrace sites with about 20% coordinately unsaturated cobalt atoms such as corner, edges and step-edges among which the latter dominate at the given size [23,24]. Give the silver is introduced by impregnation of pre-reduced and passivated CoPt/SiO₂ catalyst, we do not expect significant changes in the cobalt particle size caused by silver promotion.

Fig. 2 illustrates the response of the in situ reduced catalysts to an Ar → CO switch at 260 °C. As for the cobalt catalyst [20], CO₂ appears immediately after the switch for the AgCo catalysts, followed by a rapid decrease due to the deposition of C atoms, which block the active sites for CO dissociation in the absence of hydrogen. These data clearly show that addition of silver strongly decreases the CO₂ formation rate. For instance, addition of 0.3 wt% Ag results in a two times lower initial activity compared to the 0AgCo catalyst. This difference suggests that silver atoms modify the active sites for CO bond dissociation. A rough estimation shows that 0.3 wt% Ag could occupy a maximum of about 15% of the 15 nm nanoparticle surface (6.7% dispersion) [20]. The decrease in CO dissociation rate observed for silver-promoted cobalt is consistent with the report that adding a small amount of silver to ruthenium (Ag/Ru = 0.03) suppresses the rate of CO hydrogenation by more than 80% [5]. Increasing the silver content to 8.8 wt% results in a further decrease of the CO dissociation activity. For 8.8AgCo, the CO₂ formation rate is suppressed by 90%. However, the observation that 8.8AgCo still shows considerable CO₂ formation implies that not all the cobalt step-edge sites are covered. These findings indicate that addition of silver to the cobalt catalyst preferentially blocks sites involved in CO bond dissociation. Not all of these sites are blocked, even if the silver content becomes very high. With increasing silver content, the silver atoms segregate from the cobalt surface [25] and result in separate silver particles [7], which can be observed in TEM/EDS of reduced 4.3AgCo in Fig. 3. The amount of carbon deposited by CO disproportionation was determined by subsequent TPH experiments. The TPH profiles together with the carbon to surface cobalt ratio (based on silver-free catalyst) are presented in Fig. 4. It was possible to remove

![Fig. 1. TPR profiles of the xAgCo catalysts.](image1)

![Fig. 2. CO₂ responses following the switch from Ar to CO (10% CO in Ar) over reduced xAgCo catalysts at 260 °C. The sharp CO₂ increasing occurs simultaneously with CO breaking in. The curves are shifted in time for the clarity.](image2)
all the carbon by TPH up to a temperature of 650 °C. For the silver-free sample, a carbon-to-surface-cobalt ratio of 0.79 was determined, illustrating that nearly the complete surface was covered after CO-exposure for 30 min. The total amount of carbon is too large to be accommodated only on coordinatively unsaturated cobalt sites of the surface [23,24]. As reported earlier, the C atoms derived from CO dissociation will migrate from step-edge sites to terrace sites [26,27] and aggregate in the form of graphitic carbon [27,28]. The rate of carbon formation on cobalt surface may be limited by C migration from step-edge to terrace, since CO dissociation on step-edge sites is intrinsically very fast [20]. One can see that the carbon-to-surface-cobalt ratio decreases from 0.79 to 0.32 as the Ag content increases from 0 to 8.8 wt%. The decrease in carbon deposits is therefore likely not only due to inhibited CO dissociation on step-edge sites, but also to partial blocking of the terraces, which can accommodate graphitic carbon.

We also measured H₂-chemisorption on the xAgCo samples (shown in Fig. 5) and found that the cobalt surface area is decreased by 93% upon addition of 8.8 wt% silver. Clearly, the large decrease in the chemisorption of H₂ on the cobalt catalysts is not only due to coverage of step-edge sites but also due to blocking of terrace sites.

3.3. N₂ and CO infrared spectroscopy

Identifying step-edge sites in nanoparticle catalysts has remained a challenging task. Van Hardeveld and Van Montfoort attributed an unusual adsorption feature of N₂ on Pt, Ni and other transition metal nanoparticles to strong adsorption of N₂ in the step-edges [29,30]. Ligthart et al. demonstrated a strong correlation between the intensity of a similar IR band of adsorbed N₂ at 2205 cm⁻¹ and the CO bond dissociation activity for zirconia-supported rhodium particle [31]. Complementary DFT calculations show that the unusual N₂ stretching feature is not due to direct adsorption of N₂ in a step-edge site but, instead, due to top adsorption of N₂ on coordinatively unsaturated sites such as corner, edge and step-edge atoms of nanoparticles [31]. The intensity increases with higher coordinative unsaturation of the surface metal atom to which N₂ binds. We employed here a similar approach to follow the impact of silver on step-edge sites of cobalt nanoparticles. The corresponding N₂ IR spectra recorded at liquid nitrogen temperature on a series of silver-promoted cobalt catalysts and the un-promoted one are presented in Fig. 6. The band observed at 2200 cm⁻¹ is close to perturbed N₂ bands observed on nanoparticles of Ni, Pt, Pd [29,30], and Rh [31]. A small shoulder peak around 2230 cm⁻¹ was assigned to the N₂ chemisorption at defect/step on Pt(1 1 1) [32]. A recent study of Dillinger et al. assigned IR frequencies in the 2180–2290 cm⁻¹ range for size-selected cobalt clusters to coordinatively unsaturated sites [33]. Given the N₂ IR spectra were obtained on cobalt nano-particles, the broadening/ asymmetry of observed N₂ adsorption peak is more likely due to the heterogeneity of the cobalt surface. Fig. 6 illustrates that silver substantially suppresses the intensity of the N₂ band at 2200 cm⁻¹. Addition of 0.3 wt% silver results in a decrease of the intensity by 75%. This band is not present anymore when the silver content is
raised to 1.7 wt%. This observation is qualitatively in keeping with the strong decrease in the rate of CO₂ formation during the Boudouard reaction. It is also in line with results of DFT calculations [4,34] that group IB group metal atoms preferentially occupy coordinatively unsaturated sites on metal surfaces. Experimental data confirm this as well [35]. Vang et al. observed by STM that silver atoms selectively block step-edge sites of the Ni(1 1 1) surface [36]. The results attest that silver on cobalt nanoparticles preferentially blocks coordinatively unsaturated sites. Although this is qualitatively reflected in a strong decline of the CO dissociation rate, the Boudouard reaction activity data show that some step-edge sites are still available. We emphasize that the N₂ binding probability increases from 0.44 to 0.62 with increasing silver content.

In earlier work, we attributed a blue-shift in the CO IR adsorption band observed above 150 °C to lateral interactions with co-adsorbed carbon and oxygen atoms derived from CO dissociation [20]. Here, we employ the same approach to determine the influence of silver on CO bond dissociation. Fig. 7 presents the evolution of the CO IR spectrum as a function temperature for 0AgCo, 0.3AgCo and 1.7AgCo catalysts. The dashed lines guide the eye to the center of the main CO adsorption feature. We use the inflection point of the dashed line as an indication for the temperature at which appreciable CO dissociation occurs. Clearly, the addition of silver to the cobalt catalyst increases this temperature of CO dissociation from 180 °C to 230 °C. Additional support for this difference is derived from temperature-programmed reaction experiments in a dilute CO flow. Fig. 8 shows that the temperature at which CO consumption (by the Boudouard reaction) starts is higher for 0.3AgCo (200 °C) than for 0AgCo (160 °C). Together with the N₂ IR data, we infer that a small amount of silver blocks step-edge sites, thereby decreasing the rate of CO dissociation. For 1.7AgCo, the evolution of the IR spectra is different. Interestingly, increasing the silver content to 1.7 wt% does not raise the CO dissociation temperature further. Although the blue-shift of the CO IR band is still observed at nearly the same temperature as in 0.3AgCo, the intensity of this feature is much lower. We attribute this to a substantial coverage of terrace sites by silver atoms. Accordingly, the terrace sites cannot accommodate large amounts of C atoms and the strongly perturbed CO adsorption state observed for 0AgCo is not observed pronouncedly anymore.

3.4. Influence of silver on catalytic performance

We evaluated the catalytic performance of the various catalysts in a model F-T reaction using a H₂/CO ratio of 1 and a temperature of 260 °C. We verified that the silver-only catalyst does not show measurable activity. Fig. 9a shows CO conversion, CH₄ selectivity, C₂⁺ selectivity and CO₂ selectivity as a function of the silver content. While CO conversion and CH₄ selectivity decrease from 6.2% to 4.4% and from 50% to 26%, respectively, the C₂⁺ selectivity increases substantially from 40% to 67% with increasing silver content. Fig. 9b illustrates the decreasing CH₄ yield and increasing C₂⁺ yield. CO₂ yield also decreases. Concomitantly, the chain-growth probability increases from 0.44 to 0.62 with increasing silver content.

The decrease in CO conversion can be attributed in part to the coverage of step-edge sites by silver atoms. In contrast to the observation that the rate of the Boudouard reaction is suppressed by nearly 90% for the catalyst with the highest silver content, the CO conversion only decreases by 29% (i.e., 0AgCo vs. 8.8AgCo). This difference can be explained by the notion that CO methanation at 260 °C is not limited by CO dissociation but by carbon and oxygen hydrogenation [10]. This observation also confirms that only a small fraction of the active sites for CO dissociation are directly involved in the CO hydrogenation reaction [20]. It underpins our standpoint, i.e., CO dissociation is intrinsically fast as compared to carbon/oxygen hydrogenation.

To understand this aspect better, we report residence times of CH₄ derived from SSITKA measurements at 260 °C as a function of the silver content. Fig. 10a shows that the residence time of...
CH increases as a function of silver content. This trend means that the carbon hydrogenation rate is decreased when a larger part of the surface is occupied by silver. The longer CH residence time can also be correlated to a higher probability of C–C coupling reactions, explaining the higher chain-growth probability. It would be noted here that the conversion and selectivity changes impacted by silver are similar with the impact of graphitic carbon on CO hydrogenation reaction as discussed earlier [8]: graphitic carbon on terraces significantly suppresses CH production and increases the chain-growth probability. Fig. 10b shows the surface coverages derived from the SSITKA data. Comparing with the accessible cobalt surface measured by H2-chemisorption (Fig. 5), the CH coverage is only slightly affected at low silver content and decreases more pronouncedly with increasing silver content. The CO coverage decreases more gradually, but still its trend is less pronounced than the total accessible cobalt surface area with silver content. This is understandable as the silver atoms preferentially occupy the step-edge sites when silver content is high, whereas reversible CO adsorption and CH hydrogenation mainly occur on terraces sites [8]. It means the SSITKA mainly probes the coverages on terraces, even though the step-edge sites are not blocked by silver. However, the SSITKA-determined coverages can still qualitatively reflect to the influence of silver on the total accessible cobalt surface area.

Fig. 11 shows that the ethylene-to-ethane and propylene-to-propane ratios also strongly increase with silver content. It is well understood from experiment [37–40] and theory [41] that olefins are the primary products of the F–T reaction. Paraffins are mainly formed by olefin re-adsorption and hydrogenation. Similar to CH hydrogenation, olefin hydrogenation is expected to be largely insensitive to active site structure. Therefore, we argue that the decrease in olefin hydrogenation is well in line with the loss of cobalt surface. It can therefore also be linked to a decreased H coverage. Notably, the increase in the olefin-to-paraffin ratio is relatively minor up to a silver content of 0.9 wt% but increases steeply when more silver is added. This further underpins the conclusion that low amounts of silver more significantly affect step-edge sites than terrace sites.

Fig. 9. Catalytic performance of F–T reaction over Ag promoted cobalt catalysts as a function of silver content. Conditions: pH2 = pCO = 200 mbar, T = 260 °C.

Fig. 10. SSITKA-determined residence times (a) and coverage (b) as a function of silver content. Steady state conditions: pH2 = pCO = 200 mbar, T = 260 °C. The SSITKA measurements were performed after 21 h time on stream.

Fig. 11. Ethylene-to-ethane and propylene-to-propane ratios over silver-promoted cobalt catalysts as a function of silver content. Steady state conditions: pH2 = pCO = 200 mbar, 260 °C. The data were obtained after 21 h time-on-stream.
Fig. 12. Normalized (to the steady state flow rate) H$_2$O responses after a switch from Ar to CO/H$_2$ over in situ reduced xAgCo catalysts. Steady state conditions: $p_{\text{H}_2} = p_{\text{CO}} = 200$ mbar, $T = 260$ °C.

As reported earlier, the presence of silver can increase the reducibility of supported cobalt catalysts [6,7]. It is probably due to the facilitated oxygen removal from the cobalt. This step is one of the rate-controlling steps in CO hydrogenation under F–T conditions [10,41,42]. Fig. 12 presents the normalized water response after an $\text{Ar} \rightarrow \text{CO/H}_2$ switch on in situ reduced xAgCo catalysts. Adding as little as 0.3 wt% silver significantly reduces the water delay time. Further increasing the silver content, however, prolongs the water delay again. This is not surprising, since the systematic delay time caused by adsorption/desorption (the chromatographic effect, $\Delta t$) correlates with the flow rate and the amount of surface sites via

$$\Delta t_{\text{H}_2\text{O}} = \frac{A}{F_{\text{H}_2\text{O}}}$$

where $A$ is the total surface area of the system and $F_{\text{H}_2\text{O}}$ the molar flow rate of water, which can be correlated to CO conversion. Because the CO conversion decreases by 30% when 8.8 wt% silver is added, the systematic delay time of water accordingly increases. The un-promoted cobalt catalyst showing the highest CO conversion, however, bears the longest systematic delay time, implying a slow oxygen removal as compared with silver-promoted catalysts. Consequently, the decrease in water delay time reflects the enhancement of the oxygen removal step. This effect compensates the decrease of the available cobalt surface. Thus, we speculate that, despite the decrease in CO dissociation rate due to partial deactivation of step-edges, the faster oxygen removal will facilitate the reaction, resulting in a less pronounced decrease in CO conversion.

4. General discussion

Promoters are widely employed in F–T catalysts to increase the reduction degree of the active transition metal or to improve the intrinsic catalytic performance. We investigated the role of silver as a promoter for cobalt-catalyzed F–T synthesis. All of the catalysts contained small amount of platinum, which is effective in facilitating the reduction of cobalt oxide. Silver was added to reduced cobalt catalysts followed by calcination and reduction with the purpose of investigating the influence of a low-reactive transition metal on the cobalt-catalyzed F–T reaction. Considering the fact that silver alone shows negligible F–T activity, the impact of silver as a promoter will mainly be due to its influence on the topology of cobalt surface, where elementary reaction steps occur. The surface of the reduced catalysts was investigated by $N_2$ and CO IR spectroscopy. Steady state and transient experiments under model F–T conditions are then conducted to determine CO conversion and the product distribution.

The addition of silver to the cobalt catalyst results in a decrease of the cobalt surface area, suggesting that part of the added silver covers the surface. In line with surface science models [36] and other studies on supported nanoparticle catalysts [5], the low-reactive promoter atoms will preferentially replace or cover coordinatively unsaturated cobalt atoms. Only at higher silver content, an appreciable part of the terrace surfaces will be covered by silver atoms. The selective coverage of step-edge sites is evident from a strongly decreased intensity of the $N_2$ IR band, which is characteristic for low-coordinated cobalt atoms. The Boudouard reaction involving CO dissociation, which is the main structure-sensitive reaction in F–T catalysis, was used to establish that a large fraction of the step-edge sites are deactivated by silver. Nevertheless, even at the highest silver content, CO dissociation remains possible at an appreciable rate. Temperature-programmed CO IR spectroscopy shows that CO dissociation is shifted to higher temperature, reflecting the lower amount of active sites for CO dissociation. Combining the data of CO IR spectroscopy, $H_2$–chemisorption and steady-state CO/$CH_4$ coverage values derived from SSITKA, we infer that an appreciable part terrace sites on the cobalt nanoparticles is occupied by silver atoms when silver content is high. As the CO conversion is reduced by less than 30% when 8.8 wt% silver is added, we speculate that there are still cobalt atoms at the surface of the terraces, but the decrease in cobalt ensembles will strongly affect the ability of the surface to dissociate $H_2$, thus resulting in decreased hydrogenation performance.

The interpretation presented in this section is mainly based on the structure sensitivity of CO dissociation [22,43–45] and chain-growth and chain-decoupling [46] reactions and the structure insensitivity of $CH_4$ hydrogenation reactions. It also involves the migration of C species generated by direct CO bond dissociation on step-edge sites to terrace sites [41]. The presence of silver only moderately decreases CO conversion at methanation conditions (260 °C) in spite of a substantial blockage of step-edge sites. On one hand, small amount of silver addition effectively reduces the sites for CO dissociation as we discussed earlier. To be more specific, CO dissociation is sufficiently fast to supply the $CH_4$ intermediates that lead to the dominant $CH_4$ formation occurring on terrace sites, even if a large fraction of step-edge sites is blocked by silver. On the other hand, transient data show that the water delay is considerably shorter upon addition of silver, proving that the weaker O adsorption on a surface in which silver replaces cobalt atoms leads to easier water formation. The combination of these two opposite effects therefore causes only moderately effect on CO conversion. This can be understood by taking into account that the CO methanation is mainly controlled by carbon and oxygen hydrogenation, which occurs on terraces [8]. Moreover, blocking an increasing fraction of terrace sites results in lower $CH_4$ and higher $C_2+$.selectivity. The lower $CH_4$ selectivity is due to the slower $CH_4$ hydrogenation caused by a decrease in hydrogenation sites. The increased $C_2$ selectivity and chain-growth probability correlate well with the resulting long $CH_4$ residence time as revealed by SSITKA. Finally, hydrogenation of the primary olefin products is also delayed by silver, in line with the notion that also hydrogenation of olefins is a structure-insensitive reaction. All of these results are qualitatively in line with the earlier observed impact of graphitic carbon deposited on terrace sites on F–T performance [8].

5. Conclusions

In this work, we studied the influence of silver on a cobalt-based F–T catalyst. As platinum is used as a reduction promoter,
addition of silver does not further enhance cobalt reduction. Given that the particle size of the promoted catalysts does not strongly vary with silver content, silver mainly impacts catalytic performance through changing the topology of the cobalt surface. H₂ chemisorption shows that silver atoms are covering a large part of the surface. At low silver content, mainly coordinatively unsaturated surface cobalt atoms are substituted by silver as follows from low-temperature N₂ IR spectroscopy. This results in a strong decrease of the CO dissociation rate as confirmed by a transient switch from Ar to CO leading to CO disproportionation and temperature-programmed CO IR spectroscopy, showing a shift of CO dissociation to higher temperatures as compared to the silver-free catalyst. With increasing silver content, a substantial fraction of the cobalt atoms is replaced by silver. The combined characterization and catalytic data suggest some step-edge sites remain active in CO dissociation and the terrace surfaces contain mainly silver when silver content is high. During CO hydrogenation at 260 °C, the CO conversion is only decreased by less than 30% due to the presence of silver, in contrast to more than 90% decreases in CO dissociation rate as probed by CO disproportionation. Because the CO consumption rate under methanation conditions is largely controlled by carbon and oxygen hydrogenation. Transient experiments reveal that silver accelerates oxygen-removal steps, likely because silver binds oxygen weaker than cobalt. Therefore, the opposite effects of silver on these two reactions explain why CO conversion is not significantly affected by silver. As silver poisons sites for the structure-insensitive CH₄ hydrogenation – mostly terrace sites –, the CH₄ formation rate is suppressed. SSITKA reveals that CH₄ residence time increases with silver content, resulting in higher C₄⁺-selectivity, thus higher chain-growth probability. SSITKA also confirms a qualitative correlation between the steady-state CO/CH₄ coverages and accessible cobalt surface area. Another effect of slower hydrogenation is that the olefins-to-paraffins ratios are strongly increased when silver is added to the catalyst. Importantly, covering the cobalt surface by silver affects the F-T product distribution in a similar manner as graphitic carbon catalyst. Importantly, covering the cobalt surface by silver affects the F-T product distribution in a similar manner as graphitic carbon deposited on terrace sites. A difference is that the silver also affects step-edge sites, while C atoms on step-edge sites are removed in the form of hydrocarbon products as we earlier reported in Ref. [8].

References