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Silver addition to a cobalt Fischer–Tropsch catalyst

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ABSTRACT

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 a 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 N_2 IR). Adding more silver results in replacement of both coordinatively unsaturated sites and planar sites (probed by H_2-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 CH_4 formation. Longer residence of CH_x intermediates (determined by SSITKA) accordingly leads to an increase in chain-growth probability and therefore higher C_{2+} selectivity. SSITKA also confirms that the decrease in steady-state CO/CH_x coverage qualitatively correlates to the loss in cobalt surface area. Another consequence of slower hydrogenation is that the olefins-to-paraffins ratios are higher when silver is added to the catalyst. Importantly, covering the cobalt surface with silver affects the F–T product distribution in a similar manner as graphitic carbon deposited on terrace sites as we reported earlier.

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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 promoter for iron-based F–T catalysts showed that silver facilitates the reduction of Fe^{3+} into magnetite during the pretreatment via either CO or H_2, 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 CO_2 selectivity [2]. Chuang and Pien studied the effect of silver on a silica-supported rhodium catalyst [3]. The increased activity and selectivity of C_2 and C_3 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

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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 CH_4 selectivity and an increase in C_{5+} 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 programed reduction (TPR), chemisorption, CO exposure followed by temperature programed 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, $CoPt/SiO_2$, was prepared by IWI of silica support (X080, provided by Shell, 120–250 μm) with an aqueous solution of Co $(NO_3)_2{\cdot}6H_2O$ (Merck, 99.99%) and $Pt(NH_3)_4{\cdot}(NO_3)_2$ (Alfa Aesar, 99.995%) as precursor. Typically, 2 g of dried silica support is impregnated with a solution consisting of 2.47 g $Co(NO_3)_2{\cdot}6H_2O$, 0.45 g deionized water, and 0.5 g $Pt(NH_3)_4{\cdot}(NO_3)_2$ 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 H_2 flow (20% H_2 in He) at 450 °C for 6 h with a ramp rate of 5 °C min^{-1}, and passivated in dilute O_2 flow (2% O_2 in He) at 35 °C for 12 h [8]. As-prepared $CoPt/SiO_2$ catalyst was then impregnated with an aqueous solution containing different amount of $AgNO_3$ (Alfa Aesar, 99.995%). 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 H_2 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 N_2 were taken after reduction in H_2 for 2 h followed by cooling in a dynamic vacuum to −175 °C using liquid nitrogen. Small doses of N_2 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.

H_2-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 H_2 uptake was determined by extrapolating the straight-line portion of adsorption isotherm to zero pressure. It was assumed that one H atoms adsorbs per surface Co atom. The result for the unpromoted cobalt catalyst, which is 116.7 μmol g_{cat}^{-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 H_2 flow (10% H_2 in Ar) using a heating rate of 10 °C min^{-1}. A Cu/SiO_2 reference sample was used to calibrate the H_2 consumption.

Temperature-programmed hydrogenation (TPH) following carbon deposition were performed in a tubular reactor. Typically, 200 mg *in situ* reduced (20% H_2 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 H_2 flow (10% H_2 in Ar). The signal of the main hydrogenation product, which is CH_4, was quantified by a calibrated online mass spectrometer (ESS, GeneSys Evolution). The amount of deposited carbon was obtained by integrating the CH_4 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 H_2 flow (20% H_2 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 ($CO/H_2/Ar$ = 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 $^{12}CO/H_2/Ar$ (5/5/1 mL min^{-1}) to a mixture of $^{13}CO/H_2/Ne$ (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 H_2 (m/z = 2), $^{12}CH_4$ (m/z = 15), $^{13}CH_4$ (m/z = 17), H_2O (m/z = 18), Ne (m/z = 22), ^{12}CO (m/z = 28), ^{13}CO

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