Impact of the synthesis route of supported copper catalysts on the performance in the methanol synthesis reaction

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ABSTRACT

Two Cu/SiO_2 methanol synthesis catalysts were synthesized, one via precipitation and one via impregnation. The copper particle size distribution and local copper weight loading were similar for both catalysts. Electron tomography revealed for the precipitated catalyst a plate-like silica structure with copper particles partially entrapped, whereas for the impregnated catalyst the copper particles were located in the pores between the primary particles of a silica gel. The precipitated catalyst displayed a lower initial copper weight normalized activity and a higher stability in the methanol synthesis reaction (40 bar, 260 °C). Copper particle growth during reaction, as determined by transmission electron microscopy, was more limited for the precipitated catalyst, in line with the higher catalyst stability, possibly due to the partial entrapment of the copper particles. In addition to copper particle growth, deactivation of both catalysts was ascribed to restructuring of the silica resulting in partial coverage of the copper surface.

1. Introduction

Supported metal catalysts are the workhorses of the chemical and petrochemical industry [1,2]. In general, catalysis takes place at the surface of the metal. Small particles and hence a high dispersion are therefore a prerequisite for a high activity. The role of the support is to facilitate the formation of small particles and to improve their thermal stability [3]. In some cases the support is also a chemical promoter, which increases the activity due to strong metal support interactions [4,5]. Despite the stabilizing effect of the support, metal particle growth is still one of the main causes for deactivation of cobalt and iron catalysts in the Fischer–Tropsch reaction [6,7], platinum and palladium in three-way catalysts [8,9], nickel catalysts in the methanation reaction [10], and copper catalysts in the water-gas shift and methanol synthesis reactions [11].

Particle growth can occur via particle diffusion and coalescence and via Ostwald ripening [12,13]. In the former mechanism, entire particles diffuse over the support surface until they meet each other and coalesce. In the latter, larger particles grow at the expense of smaller particles due to a net flux of metal-containing species from thermodynamically less stable smaller particles to more

stable larger particles. Irrespective of the mechanism, particle growth is generally considered to depend on the reaction conditions [14], the metal-support interaction [15–17], the particle size (distribution) [18,19] and the interparticle spacing [20–22], and also on the geometry of the support [9,15,16,23,24]. It has for instance been shown that particle migration can be restricted by encagement or entrapment [23–27]. The geometry of the support can also affect the thermodynamic stability of a supported nanoparticle since the chemical potential of a supported nanoparticle depends on the contribution of the metal-support interfacial energy [3,28]. As a result, particles whose dimensions and volumes are commensurate with concavities in the support and hence have a large metal–support interface area tend to be more stable than particles on a flat support [28]. An increased metal–support interface area of the nanoparticle also leads to a decreased metal surface area accessible to the reactants and, hence, a lower activity. The optimal metal–support interface area is thus the one that provides a balance between nanoparticle activity and nanoparticle stability.

In industry two main routes are used to prepare supported metal catalysts, i.e. precipitation and impregnation [29]. In precipitation, a metal precursor is deposited on a preformed support (deposition–precipitation) or precipitated together with a support precursor (co-precipitation). Subsequent drying, calcination and reduction result in the formation of metallic particles and in the case of a co-precipitate also in the formation of the support

[30,31]. In impregnation, a support is contacted with a metal solution and metallic particles are formed upon drying, calcination and reduction [32]. The interface area between the metal particles and the support is dependent on the preparation route [33]. It might be larger in case of precipitation due to incomplete segregation [34–36]. During reaction the interface area might change due to a change in particle size, particle shape or support structure [28,37].

To study the effect of the synthesis method on the metal–support interaction and hence on metal nanoparticle activity and stability, we selected Cu/SiO_2 methanol synthesis catalysts as a model system. In such catalysts, the activity for CO/CO_2 hydrogenation scales with the copper surface area, and the loss of activity during reaction is often mainly due to copper particle growth [11,38,39]. Moreover, recent developments in the synthesis of well-defined copper on silica catalysts allow careful tuning of the size and distribution of the copper particles [40,41]. In this work Cu/SiO_2 catalysts with similar copper particle sizes and local copper weight loadings were synthesized via impregnation and via precipitation. Electron tomography was used to characterize the SiO_2 support structure and the location of the Cu particles within the support. The performance in the methanol synthesis reaction of both catalysts was investigated at 40 bar at 260 °C for a period of 10 days. The catalysts were retrieved after reaction to determine the extent of copper particle growth and change in support structure.

2. Material and methods

2.1. Synthesis of Cu/SiO$_2$ via precipitation

Precipitated Cu/SiO_2 was synthesized via a modified method of van der Grift et al. [42]. 20.1 g LUDOX-AS 30 (Sigma–Aldrich, 30 wt% SiO_2), 16.1 g $Cu(NO_3)_2 \cdot 3H_2O$ (Acros Organics, 99% for analysis) and 12.1 g Urea (Acros Organics, 99.5% for analysis) were added to 1.7 l of demineralized water in a 2 l reaction vessel. The pH was adjusted to 2–3 with a few drops of HNO_3 (Merck, 65% for analysis) to prevent premature hydrolysis of copper nitrate. The suspension was then heated to 90 °C over 1 h under stirring. At 90 °C the hydrolysis of urea led to an increase in pH resulting in precipitation of $Cu_2(NO_3)(OH)_3$. The well-stirred reaction vessel was kept at 90 °C for 7 days to allow recrystallization of precipitated copper and silica, which resulted in the formation of copper phyllosilicate [43,44]. The precipitate was obtained by hot filtration of the suspension and washed three times with demineralized water, filtered and dried overnight at 60 °C. The yield was 10 g. Part of the as-prepared copper phyllosilicate was used for catalytic reaction (with in situ reduction to obtain metallic Cu on SiO_2) as described below. Another part (2 g) intended for characterization was reduced at 250 °C (2 °C/min) in a flow of 100 ml/min of 20% H_2 in Ar for 2½ h. After the reduction treatment the resulting Cu/SiO_2 was passivated for 15 min by slowly exposing the sample to diluted air/N_2 at room temperature. The sample was stored in a glove box under argon atmosphere.

2.2. Synthesis of Cu/SiO$_2$ via impregnation

Copper was deposited on a commercial silica gel (Davicat 1454, Grace-Davison, pore volume $p/p_0 < 0.95 = 0.81 \, cm^3/g$, pore diameter 9 nm) via incipient wetness impregnation with an aqueous solution of 2 M $Cu(NO_3)_2 \cdot 3H_2O$ (Acros Organics, 99% for analysis) and 0.1 M HNO_3 (Merck, 65% for analysis), followed by drying overnight under vacuum at room temperature and calcination in 375 ml/min (GHSV = 15,000 h^{-1}) of 2% NO/N_2 at 350 °C (2 °C/min) for 1 h. Part of the as-prepared sample was used for catalytic reaction (with in situ reduction to obtain metallic Cu on SiO_2) as described below and a portion (2 g) intended for characterization

that underwent reduction in a flow of 100 ml/min of 20% H_2 in Ar at 250 °C (2 °C/min) for 2½ h. After the reduction treatment, the resulting Cu/SiO_2 was passivated for 15 min by slowly exposing the sample to diluted air/N_2 at room temperature. The sample was stored in a glove box under argon atmosphere.

2.3. Characterization

N_2-physisorption measurements were performed at −196 °C using a Micromeritics Tristar 3000 apparatus. The BET method was used to calculate the specific surface areas. The pore volumes were determined at $p/p_0 = 0.983$. Pore size distributions were determined from the adsorption branch by the BJH method [45]. X-ray diffraction (XRD) was performed with a Bruker-Nonius D8 Advance X-ray diffractiometer using Co-$K_{\alpha 12}$ ($\lambda = 1.79026$ Å) radiation. Diffractograms were collected at room temperature from 20° to 70° (2θ). The specimen holder was loaded in the glove box with the catalysts either after reduction and passivation or catalysis and passivation and was subsequently sealed. Copper crystallite sizes were estimated by applying the Debye–Scherrer equation to the (1 1 1) diffraction of Cu ($2\theta = 50.5°$, $k = 0.9$) [46]. H_2-TPD was performed on the catalysts before and after methanol synthesis [47,48]. Measurements were carried out in a fixed-bed flow setup and online gas analysis was performed by a quadrupole mass spectrometer (Balzers GAM 445). The copper phyllosilicate was reduced in situ at 250 °C (2 °C/min) in 100 ml/min of 1% H_2/He. At 250 °C the gas flow was changed to 100 ml/min of 100% H_2 for 2½ h. The calcined copper on silicagel and the samples after catalysis and passivation were reduced in situ at 220 °C (2 °C/min) in a flow 100 ml/min of 1% H_2/He for 7 h. Then the samples were flushed for ½ h in 100 ml/min of He to remove any adsorbed hydrogen and subsequently cooled down to 0 °C. At this temperature the reactor was pressurized to 1.6 MPa of H_2, before it was cooled down further to −33 °C. After ½ h, the catalyst was rapidly cooled to −196 °C and depressurized. The gas flow was changed to 100 ml/min of He to flush out the excessive hydrogen. After 1 h the temperature was increased up to 210 °C (6 °C/min) and the H_2 desorption profile was recorded. Copper surface areas (SA_{Cu, H_2}) were calculated from the amount of desorbed hydrogen assuming a H/Cu ratio of 0.5 and 1.47×10^{19} copper surface atoms per m^2. Temperature programmed reduction (TPR) was performed using an Autochem II ASAP 2910 from micromeritics. The H_2 concentration during the experiment was measured with a thermal conductivity detector. About 0.05 g of sample was put on top of a quartz wool bed in a glass reactor tube and subsequently heated to 500 °C (5 °C/min) under a (50 ml/min) flow of 5% H_2/Ar. The copper loading was estimated from the H_2 consumption by assuming the following reduction stoichiometry: $CuO + H_2 \rightarrow Cu + H_2O$. Transmission electron microscopy (TEM) images were acquired with a Tecnai 12 (FEI) microscope operated at 120 kV with a pixel size of 0.45 nm. Precipitated Cu/SiO_2 samples before and after catalytic tests were prepared by grinding followed by sonication in ethanol. A droplet of the ethanol suspension was deposited on a carbon coated copper TEM grid (Agar S162 200 Mesh Cu). The resolution and contrast were sufficient to detect particles larger than 2 nm (4 × 4 pixels). The impregnated Cu/SiO_2 was ground, embedded in a two component epoxy resin (Epofix, EMS) and cured at 60 °C overnight, and cut into thin sections (50–100 nm) using a Diatome Ultra 35° diamond knife mounted on an Ultracut E microtome (Reichert-Jung). Sections were deposited on a TEM grid. The resolution and contrast were sufficient to detect and measure particles larger than 3 nm (6 × 6 pixels). Copper surface areas ($SA_{Cu, TEM}$) were calculated from the particle size distributions obtained via TEM, and assuming spherical particles. Energy dispersive X-ray (EDX) spectroscopy was performed on a Technai 20FEG (FEI) electron microscope equipped with a field emission gun and an EDAX Super Ultra Thin Window EDX detector and