



Impact of heterogeneities in silica-supported copper catalysts on their stability for methanol synthesis



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ABSTRACT

Precipitation and impregnation are two common methods to synthesize heterogeneous catalysts. In this paper we compare the stability and activity of silica-supported catalysts prepared by precipitation or by impregnation, having comparable support morphology and copper weight loading. To obtain catalysts with comparable support morphology, plate-like silica was prepared from the precipitated catalyst. This porous, high surface area plate-like silica was subsequently impregnated with an aqueous copper solution and reduced in hydrogen. Catalysts characterization revealed that catalysts prepared by impregnation contained heterogeneities, present as particles significantly larger than the vast majority, whereas catalysts prepared by precipitation displayed a narrow particle size distribution. In particular the catalyst prepared by impregnation with a copper weight loading of 34 wt% displayed heterogeneities in the form of large particles, which were detrimental for both activity and stability in methanol synthesis from synthesis gas.

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1. Introduction

Heterogeneous catalysts, consisting of supported metal nanoparticles, are important for the production of many bulk chemicals. These catalysts are intended for prolonged usage, however, often catalysts deactivate over time and need to be replaced at a certain point in time. Replacement is expensive and time consuming and therefore more stable catalysts are highly desirable [1,2].

Almost all catalysts contain heterogeneities in for example the metal particle size distribution and the distribution of the particles over the support. Usually these heterogeneities are undesired, but in some cases it is beneficial for the activity or selectivity of the catalyst, e.g., with Pt-zeolite-alumina catalyst for hydrocracking the location of the Pt particles on the zeolite or on the alumina binder affects the efficiency of the catalyst [3]. It is important to understand the origin of these heterogeneities, as well as their location and appearance within a catalyst material. Thereby the effect on the performance and the lifetime is key to understand and to improve catalysts [4].

The metal particle size distribution of a catalyst can affect the rate of deactivation; a monodisperse system may lower the rate of Ostwald ripening, where a polydisperse particle size distribution

may increase this rate [5,6]. Usually heterogeneities result in a less stable, active or selective catalyst and therefore a uniform catalyst is required. Hence, the control over the position, size and monodispersity of the active metal particles in heterogeneous catalysts is key to improve the characteristics and the stability of the particular catalyst [7].

In industry methanol is produced from synthesis gas (syngas), derived from natural gas, by use of a Cu/ZnO/Al₂O₃ catalyst at a scale of 65 million tons per year. This catalyst is usually produced by precipitation and contains a Cu loading of up to 70 wt% [1,8,9]. The methanol is used as fuel additive, as reactant in the methanol-to-olefins (MTO) process to produce olefins for plastics and to produce many other chemicals [10]. The catalyst mainly deactivates by particle growth of the active Cu nanoparticles and in some extent by loss of the promoter effect of Zn [1,7,11,12].

There are two main methods for the preparation of supported catalysts, i.e. precipitation and impregnation [13,14]. For the first method the support or support precursor and metal precursor are mixed in an aqueous solution and the precursors are precipitated together. This precipitation is usually achieved by a change in pH. For the second method a concentrated metal salt solution is added to a previously synthesized support. Both methods require an activation step at elevated temperatures to obtain an active catalyst [15]. A high weight loading of metal is often desirable to obtain a high productivity per gram of catalyst and is mostly obtained by precipitation. More challenging is to obtain catalysts

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with a high metal weight loading and homogeneous distribution of the metal nanoparticles by impregnation [7,14,16].

The influence on the stability of using precipitation and impregnation as preparation methods for Cu/SiO₂ catalysts in methanol synthesis has been studied before in our group [17]. In that case a commercial silica gel was used as the support material for the catalyst prepared by impregnation. After the impregnation the material was heated in an NO/N₂ flow, obtaining an inhomogeneous distribution of copper nanoparticles with an overall loading of 9 wt% [7,16,17]. In this paper we show that using plate-like silica, obtained from the precipitated catalyst, resulted in a homogeneous distribution of the copper particles after impregnation and reduction and allowed to use high metal loadings.

In this study, Cu/SiO₂ was used in the methanol synthesis from syngas as a model system to investigate the difference in activity and stability caused by heterogeneities of the copper phase, using catalysts with the same weight loading of metal, metal particle size and support morphology. The absence of zinc as promoter prevents deactivation by loss of the promoter effect and allows to study only particle growth (coalescence and Ostwald ripening) as deactivation mechanism [18,19]. To achieve the use of the same support morphology in both preparation methods, plate-like silica was prepared from the precipitated and reduced catalyst by removal of the copper, and subsequent impregnation was performed. The high weight loading of the impregnated catalyst was obtained by a double impregnation with a concentrated copper nitrate solution, since the required concentration is above the solubility limit [20]. A second catalyst prepared by impregnation with a lower weight loading was used as reference.

Silica is a very versatile material and can be synthesized in all kinds of shapes and sizes, from colloidal particles with various sizes and shapes to porous 3D structures with a broad range of pore sizes [21–26]. However, to our knowledge plate-like silica with a high surface area has not been synthesized before. The plate-like silica we describe here is very suitable as a support for metal nanoparticle catalysts because of its high specific surface area and porosity.

In this paper we show the advantages of a more uniform catalyst obtained by precipitation over a less uniform catalyst obtained by impregnation. We synthesized catalysts with the same plate-like silica as support, the same metallic particle size and weight loading of the metallic nanoparticles over the support by two different methods: impregnation and precipitation. The catalyst synthesized by a double impregnation exhibited a broad nanoparticle size-distribution. The stability and activity of the catalysts were tested under high-pressure methanol synthesis conditions and the results are discussed in this paper. Fast coalescence of particles located in clusters and the presence of heterogeneities, in the form of large particles, in the double-impregnated sample led to fast deactivation compared to the precipitated catalyst that displayed a narrower particle size distribution.

2. Experimental

2.1. Synthesis precipitated catalyst

Copper phyllosilicate was synthesized by co-precipitation and recrystallization of copper nitrate and Ludox AS-30 silica spheres in the presence of urea (CO(NH₂)₂) [17,27]. 16.42 g Cu(NO₃)₂·3 H₂O (Sigma Aldrich), 12.30 g urea (Acros Organics, 99.5% for analysis) and 20.50 g Ludox AS-30 (Sigma Aldrich, 30 wt% SiO₂) were dissolved in 1.7 L demi-water, in a 2 L double walled vessel. A few drops of 65% HNO₃ were added to bring the pH to 2–3 to maintain soluble Cu²⁺ at the start of the synthesis. The mixture was heated to 90 °C, resulting in the hydrolysis of urea to form

ammonia (NH₃) and carbon dioxide (CO₂). Ammonia is a base and therefore its formation leads to an increase in pH and subsequently to the precipitation of copper hydroxide (Cu(OH)₂) and basic copper nitrate (Cu₂(NO₃)(OH)₃) [28]. The mixture was stirred for 7 days to complete the formation of copper phyllosilicate from the silica source and Cu²⁺ [17,29,30]. The copper phyllosilicate was recovered from the suspension by hot filtration and three washing steps. For each washing step the solid was redispersed in 800 mL demi-water and stirred for 5 min after which it was filtrated. After the washing steps the material was dried at 120 °C. The obtained blue copper silicate was crushed and sieved to obtain a sieve fraction of 425–630 μm.

This precursor was split into two batches and reduced under different conditions; one part resulting in the precipitated catalyst and the other part was used to obtain bare plate-like silica. For the synthesis of the precipitated catalyst part of the precursor was reduced in 5% H₂ in N₂ and heated to 250 °C with 5 °C/min, for 2 h. The sample was not exposed to air and was transferred to an Ar-glovebox. This sample will be denoted as PREC from now on and contained 36 wt% of copper. The particle size was determined by TEM and XRD and the stability was measured under methanol synthesis conditions.

2.2. Synthesis plate-like silica and impregnated catalyst

For the synthesis of the bare plate-like silica and subsequently the impregnated catalyst, another part of the same precursor (copper phyllosilicate) as for PREC was reduced in 20% H₂ in N₂ at 250 °C (heating rate of 2 °C/min) for two hours and passivated at 100 °C in 5% O₂. The copper in this material was removed by dissolution in concentrated (65%) HNO₃. Therefore 1.13 g of the reduced and passivated material was placed in a 250 mL round bottom flask. The flask was cooled by an ice bath to prevent heating of the sample during the removal. The dissolution and oxidation of copper in HNO₃ is exothermic and an increase in temperature increases the solubility of silica in water, which is undesirable in this case [31,32]. 31 mL concentrated HNO₃ was added to the solid and subsequently the suspension turned green, and brown NO₂ gas escaped from the solution, due to oxidation of metallic copper. The formed gasses were removed to the exhaust by a tube, connected to the cooler on the flask.

The suspension was stirred by a magnetic stirrer during the addition of HNO₃ and the ice bath was removed shortly after the acid addition. The extraction was performed at room temperature for 20 min. The suspension was diluted with approximately 100 mL demi-water after the 20 min to stop the reaction. The color of the solution turned blue upon dilution.

The silica was washed by filtration with in total 4 L of demi-water, to remove the excess of copper and acid. The first liter was acidified with HNO₃ to a pH of 2–3 to prevent (re-)adsorption of removed Cu²⁺, or adsorption in the precipitated form as Cu(OH)₂ onto the silica. After washing, the silica was dried at 60 °C. The etching procedure, including washing, was performed two times in total, to increase the extent of copper removal. UV-Vis spectroscopy after both etching steps showed the importance of a second removal step. X-ray diffraction (XRD), transmission electron microscopy (TEM) and N₂-physisorption were performed as well to check the extent of copper removal and the conservation of the plate-like silica structure.

The plate-like silica support was dried under dynamic vacuum at approximately 170 °C for at least two hours. After cooling down to room temperature the solid was impregnated with an aqueous 4.06 M Cu(NO₃)₂ solution, acidified with 0.1 M HNO₃, by incipient wetness impregnation (IWI), using 1 mL/g support. During the addition the solid was mixed using a magnetic stirring bar. After the impregnation the material was dried for 20 h under dynamic

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