



# 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/Al<sub>2</sub>O<sub>3</sub> 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/SiO<sub>2</sub> 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/N<sub>2</sub> 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/SiO<sub>2</sub> 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(NH<sub>2</sub>)<sub>2</sub>) [17,27]. 16.42 g Cu(NO<sub>3</sub>)<sub>2</sub>·3 H<sub>2</sub>O (Sigma Aldrich), 12.30 g urea (Acros Organics, 99.5% for analysis) and 20.50 g Ludox AS-30 (Sigma Aldrich, 30 wt% SiO<sub>2</sub>) were dissolved in 1.7 L demi-water, in a 2 L double walled vessel. A few drops of 65% HNO<sub>3</sub> were added to bring the pH to 2–3 to maintain soluble Cu<sup>2+</sup> at the start of the synthesis. The mixture was heated to 90 °C, resulting in the hydrolysis of urea to form

ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>). Ammonia is a base and therefore its formation leads to an increase in pH and subsequently to the precipitation of copper hydroxide (Cu(OH)<sub>2</sub>) and basic copper nitrate (Cu<sub>2</sub>(NO<sub>3</sub>)(OH)<sub>3</sub>) [28]. The mixture was stirred for 7 days to complete the formation of copper phyllosilicate from the silica source and Cu<sup>2+</sup> [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% H<sub>2</sub> in N<sub>2</sub> 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% H<sub>2</sub> in N<sub>2</sub> at 250 °C (heating rate of 2 °C/min) for two hours and passivated at 100 °C in 5% O<sub>2</sub>. The copper in this material was removed by dissolution in concentrated (65%) HNO<sub>3</sub>. 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 HNO<sub>3</sub> 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 HNO<sub>3</sub> was added to the solid and subsequently the suspension turned green, and brown NO<sub>2</sub> 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 HNO<sub>3</sub> 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 HNO<sub>3</sub> to a pH of 2–3 to prevent (re-)adsorption of removed Cu<sup>2+</sup>, or adsorption in the precipitated form as Cu(OH)<sub>2</sub> 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 N<sub>2</sub>-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(NO<sub>3</sub>)<sub>2</sub> solution, acidified with 0.1 M HNO<sub>3</sub>, 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

vacuum at room temperature. The once impregnated sample was reduced in 20% H<sub>2</sub> in N<sub>2</sub> at 230 °C after this drying step [33]. After drying the impregnated sample was impregnated again with the same amount and concentration Cu(NO<sub>3</sub>)<sub>2</sub> solution after which it was dried for 20 h under dynamic vacuum. We further refer to this sample as 'twice impregnated'. The sample with the low loading contained 20.7 wt% and the sample with the high loading contained 34.1 wt% of copper.

Reduction of both samples was performed in 20% H<sub>2</sub> in N<sub>2</sub> at 230 °C for 1.5 h, using a heating rate of 2 °C/min [33]. Subsequently, the samples were transported in the sealed reactor, further handled in a glovebox and subsequently analyzed using XRD and TEM. From now on, the once and twice impregnated samples after reduction will be denoted as IMP1 and IMP2, respectively. Sieve fractions of the reduced catalyst of 450–625 μm were made in air and tested under methanol synthesis conditions.

### 2.3. Characterization

X-ray diffraction (XRD) patterns of non-air sensitive and/or passivated samples were obtained with a Bruker D2 phaser, using a 1.0 mm fixed slit. Reduced samples, containing solely Cu<sup>0</sup> as Cu phase, were placed in an air-tight sample holder and patterns were recorded on a Bruker D8 advance, equipped with a variable slit. Both machines were equipped with Co K<sub>α</sub> radiation (λ = 1.78897 Å). The patterns were compared with the PDF-4+ database. Transmission electron microscopy (TEM) was performed using a Tecnai 12 or Tecnai 20 microscope, operating at 120 kV and 200 kV respectively. Both were equipped with a CCD camera, and particle size distributions were determined from the micrographs. An ultra-sonicated suspension of the samples in ethanol was drop cast on carbon/formvar 300 mesh copper grids, and after drying they were imaged in the microscope. Powder diffuse reflectance ultraviolet–visible (DRUV–Vis) spectra of the copper phyllosilicate and the silica materials after copper removal were obtained with a Varian Cary 500 UV/Vis/NIR spectrometer. The PbS detector was located in a 110 mm diameter integrating sphere. The powder sample was placed in a holder containing a 20 mm quartz window. N<sub>2</sub>-physisorption was performed using a Micromeritics TriStar instrument at –196 °C. The samples were dried before the measurement under a N<sub>2</sub>-flow at 300 °C to remove water from the pores. The copper phyllosilicate was dried under vacuum at 100 °C to prevent the formation of CuO particles. The total pore volume was determined at p/p<sub>0</sub> = 0.995. Temperature programmed reduction (TPR) and thermogravimetric analysis (TGA) were performed to determine the copper weight loading in the copper phyllosilicate and in the precipitated catalyst after reduction (data not shown). TPR was performed using a Micromeritics Autochem II, with 35 mg sample under a flow of 50 mL/min 5% H<sub>2</sub>. Prior to the measurement the sample was dried at 100 °C *in situ* under an inert gas. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA under 20% H<sub>2</sub> using approximately 5 mg of sample. The sample was heated to 250 °C using a heating rate of 5 °C/min, and held at this temperature for 2 h. The amount of residual copper after the etching procedure was determined by inductively coupled plasma-mass spectrometry by the Mikroanalytisches Laboratorium Kolbe, Germany.

### 2.4. Catalytic stability

The stability and activity of the three catalysts (PREC, IMP1, IMP2) were tested under methanol synthesis conditions for 250 h in a two-parallel reactor set-up of Autoclave Engineers. 200–400 mg of the catalyst, diluted with 1 mL SiC, was loaded into the reactor and was supported in the middle of the reactor tube by a hollow steel tube and quartz wool. Prior to the methanol

synthesis the Cu/SiO<sub>2</sub> was reduced *in situ* at 250 °C (heating rate of 2 °C/min) for 2.5 h using a flow of 110 mL/min 20% H<sub>2</sub> in Ar. After the reduction the reactor was cooled down before syngas was introduced. The reactor was flushed with syngas for 30 min and subsequently pressurized to 40 bar. A premixed syngas was used with the composition: 23% CO, 7% CO<sub>2</sub>, 60% H<sub>2</sub> and 10% Ar. The Ar in the syngas feed acted as internal standard for the GC. This mixture was purified from carbonyls by a carbonyl trap placed before the reactor inlet, which contained zeolite-Y and activated carbon. The carbonyl trap was heated to 50 °C. After pressurization three blank chromatograms were recorded to determine the CO/Ar and CO<sub>2</sub>/Ar signal of the feed stream and subsequently the reactor was heated from 100 °C to 260 °C with a rate of 2 °C/min. The equilibrium conversion of CO + CO<sub>2</sub> at these conditions is 28%.

All three samples were tested using the same copper-based weight hourly space velocity syngas (WHSV) of 7.6 g<sub>syngas</sub>/(g<sub>Cu</sub> \* h), to be able to compare the activities of the catalysts, as they all contained different copper weight loadings. The products were analyzed by an on-line Varian 450 GC. This GC was equipped with two parallel channels; the first channel consisted of two series-connected HAYESEP Q (0.5 M × 1/8") packed columns and a MOL-SIEVE 13 × (1.5 M × 1/8") molecular sieve column connected to a TCD to determine the activity from the relative decrease in CO/Ar and CO<sub>2</sub>/Ar signal. Since the selectivity towards methanol was close to 100%, the yield will be expressed as mol<sub>MeOH</sub>/(g<sub>Cu</sub> \* s). The second channel consisted of a CP-SIL 8CB FS capillary column connected to an FID to determine the selectivity. The normalized methanol yield was determined by the relative decrease in the MeOH/Ar signal from the TCD, relative to the highest observed activity close to t = 0.

The spent catalysts were exposed to air in a controlled manner following removal from the methanol synthesis reactor. The catalysts were re-reduced in a glass reactor under 20% H<sub>2</sub> at 230 °C and subsequently transferred to an Ar-glovebox and XRD patterns were recorded using an air-tight sample holder.

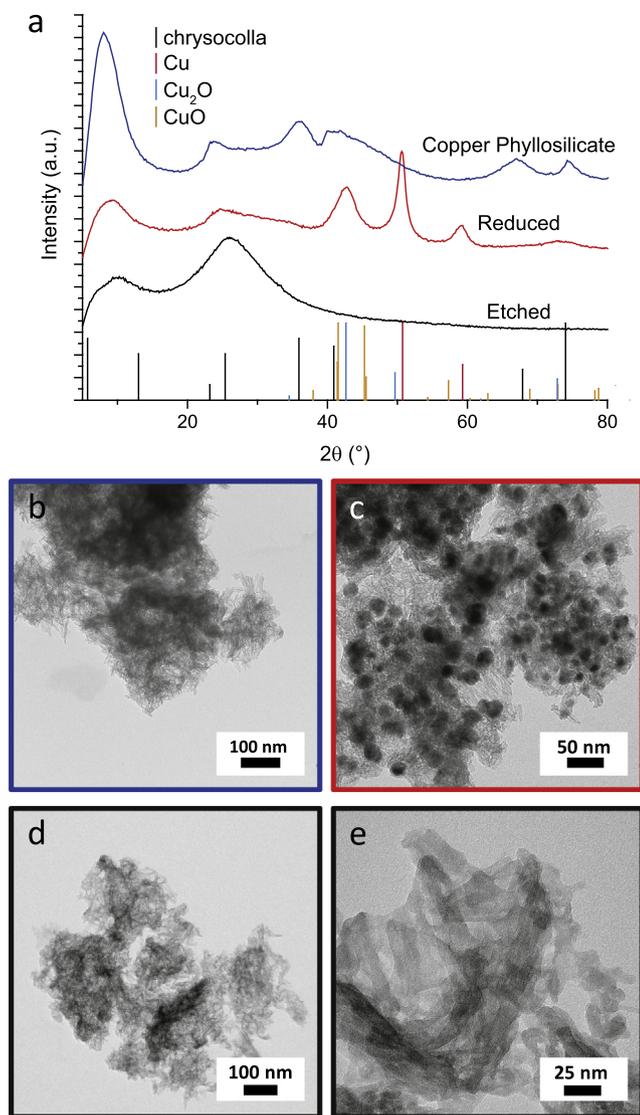
## 3. Results

### 3.1. Efficiency copper removal

In this section the efficiency of the copper removal and the preservation of the plate-like structure of the silica is reported, based on XRD, TEM, N<sub>2</sub>-physisorption and DRUV–Vis analysis. The XRD pattern of the as prepared copper phyllosilicate (blue line), the reduced and passivated copper phyllosilicate (red line) and the obtained silica after copper removal (black line) are shown in Fig. 1a. The pattern of copper phyllosilicate matches the pattern of chrysocolla ((Cu<sub>8</sub>(OH)<sub>12</sub>)(Si<sub>4</sub>O<sub>10</sub>)<sub>2</sub>·8H<sub>2</sub>O) [28,34].

After reduction and mild oxidation of this copper phyllosilicate, one broad peak around 25° 2θ was observed, as well as peaks at 42.6°, 50.7°, 59.3° and 72.8° 2θ. The broad band at 25° 2θ was due to the presence of amorphous silica, where the other four peaks are ascribed to the presence of crystalline metallic copper and monovalent copper oxide (Cu<sub>2</sub>O). After the etching this silica peak was still present and no other peaks were observed above 30° 2θ, excluding the presence of crystalline copper. Furthermore, in all three patterns a peak was present at 8° 2θ which is caused by a regular spacing of the structure, likely related to the plate-like structure of the material [34].

Fig. 1b shows a bright-field TEM image of the as-prepared copper phyllosilicate, and Fig. 1c shows the material after reduction in 20% H<sub>2</sub>. Fig. 1d and e show the silica material after removal of the copper. All images show a plate-like structure, whereby the reduced material in Fig. 1c displays dark features, which indicates the nanoparticles on the support formed during reduction. The

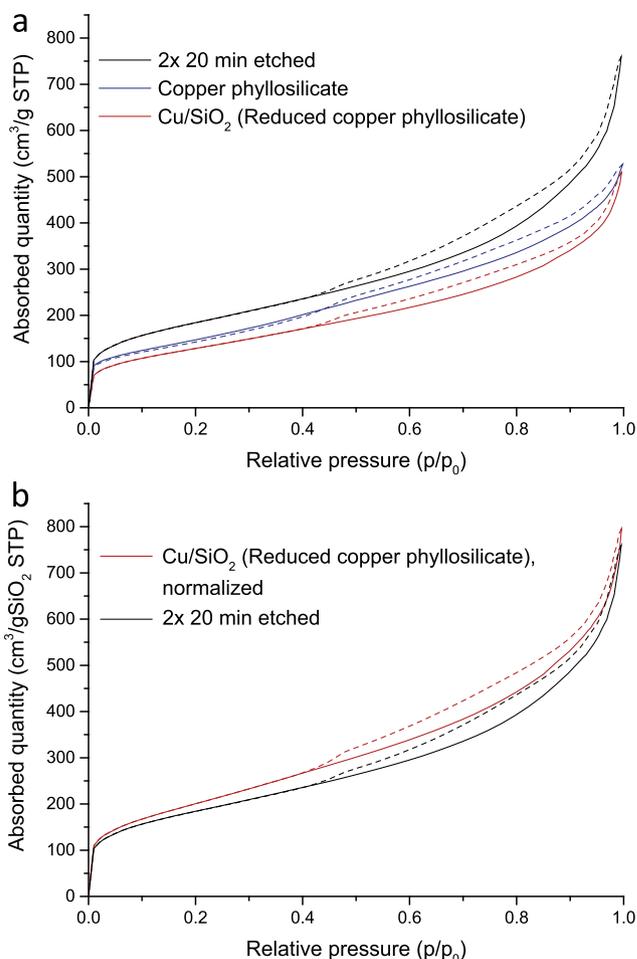


**Fig. 1.** (a) XRD patterns of as prepared copper phyllosilicate (blue line), the phyllosilicate after reduction in 20% H<sub>2</sub> (red line) and the silica after the two etching steps (black line) in concentrated nitric acid. The copper phyllosilicate matches the chrysocolla pattern, and no amorphous silica or crystalline CuO was observed. The reduced material shows an amorphous silica band and Cu and Cu<sub>2</sub>O peaks, showing that the copper phyllosilicate was transformed into Cu and SiO<sub>2</sub>. After etching, only the amorphous silica band was preserved and no crystalline Cu(O) was observed. All patterns show a peak around 8° 2θ, likely to arise from the ordered plates. (b) Image of the as-prepared copper phyllosilicate, showing the plate-like structure of the material and (c) shows the material after reduction in 20% H<sub>2</sub> at 250 °C, which contained 17 nm nanoparticles. (d) and (e) show images of the silica after removal of the copper. The shape of the plates is preserved and no differently shaped silica was observed; no copper particles were seen either.

as-prepared copper phyllosilicate has been characterized extensively by high-resolution electron microscopy before, showing that the thickness of the platelets is in the range of 5–20 nm and are up to 100 nm in length [15].

After copper removal by the acid treatment no dark features were observed anymore and the plate-like structure was still present. This indicates that copper removal was efficient and did not affect the silica structure.

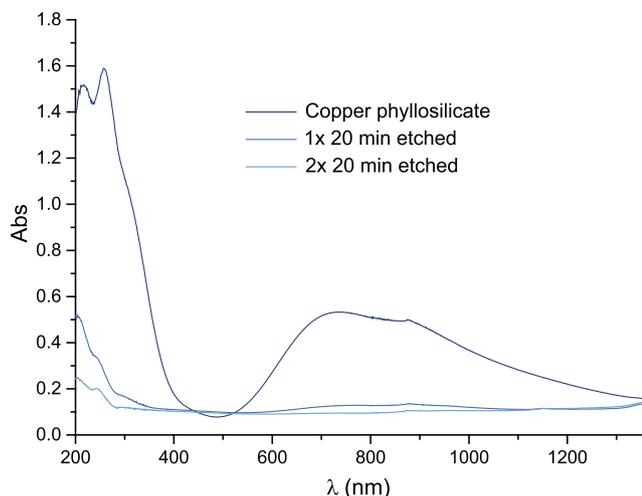
In Fig. 2a the N<sub>2</sub>-physorption isotherms are shown for the copper phyllosilicate (blue line), the copper phyllosilicate after reduction (red line) and the silica after copper removal (black line). The shape of all three isotherms is similar and indicated a slit-like pore



**Fig. 2.** N<sub>2</sub>-physorption isotherms of (a) the copper phyllosilicate (black line), the copper phyllosilicate after reduction (Cu/SiO<sub>2</sub>, red line) and the silica after removal of the copper (blue line) and, (b) the silica after removal of the copper (blue line) and the reduced copper phyllosilicate normalized for the amount of silica (red line). The absorption branches are indicated by the solid and the desorption branches by the dashed lines. After removal of the copper by the acid treatment the silica-normalized surface area and porosity were not affected.

structure, as well as mesoporosity [35]. The BET-surface area was determined from the isotherm and after removal of the copper the silica displayed a higher surface area and porosity per gram of material, going from 468 m<sup>2</sup>/g (Cu/SiO<sub>2</sub>) to 666 m<sup>2</sup>/g (silica after etching). This increase was due to the removal of the large amount of copper. Fig. 2b shows therefore the isotherm for the copper phyllosilicate after reduction (Cu/SiO<sub>2</sub>), normalized to the weight of the silica. The specific surface area for the Cu/SiO<sub>2</sub> was 731 m<sup>2</sup>/g silica, in contrast to 666 m<sup>2</sup>/g for the silica after copper removal. The total pore volume was similar for both samples as well namely: 1.23 cm<sup>3</sup>/g SiO<sub>2</sub> for the Cu/SiO<sub>2</sub> and 1.17 cm<sup>3</sup>/g for the silica. This shows that the surface area and porosity per gram of silica did not change upon reduction and the acid treatment.

DRUV-Vis spectroscopy was performed on the as-prepared copper phyllosilicate (a blue powder) before reduction, and the silica after both copper removal steps. The spectra are shown in Fig. 3 and two bands are present; a band between 200 and 300 nm, due to charge transfer from O<sup>2-</sup> from the silica to Cu<sup>2+</sup> and a broad band between 500 and 1200 nm, arising from d-d transitions in Cu<sup>2+</sup> [33,36]. Both bands decreased upon the first etching step. The silica had a light grey color after this first step, observed by eye. After the second etching step the bands decreased even



**Fig. 3.** DRUV-Vis of as prepared copper phyllosilicate, the silica after one etching step and the silica after two etching steps. After the first etching step the intensity of both bands showed a major decrease. After the second etching step the intensity of the two bands decreased even further.

further and the silica appeared white. The decrease of the two bands indicated the removal of copper and the necessity of the second step to remove residual copper. Inductively coupled plasma-mass spectrometry (ICP-MS) showed that the residual amount of copper was as low as 0.1 wt%.

DRUV-Vis showed that the two etching steps successfully removed copper and the residual amount of copper was determined to be 0.1 wt% by ICP-MS. XRD and TEM showed that the copper particles had disappeared from the material. Furthermore XRD, TEM and  $N_2$ -physisorption showed that the plate-like structure of the copper phyllosilicate was not affected by the acid treatment and the porosity was preserved.

### 3.2. Particle size analysis by electron microscopy and XRD

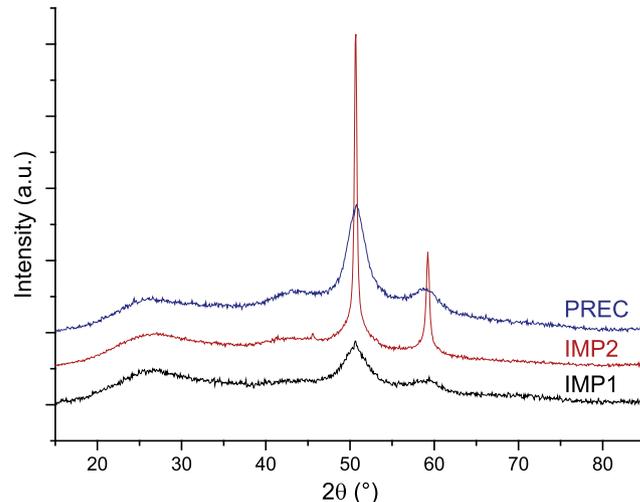
TEM images of the fresh and spent catalysts were recorded and are shown in Figs. 4 and 8 respectively. 150–300 particles were counted for each sample to determine the average particle size. For all three fresh catalysts, as can be seen in Fig. 4, a homogeneous distribution of the copper particles over the support was observed. For catalysts prepared by precipitation this is always the case, because the copper is already homogeneously distributed within

the crystal structure of the precursor. For catalysts prepared by impregnation it is more challenging to obtain a homogeneous distribution of copper particles as shown in our group before [7,16].

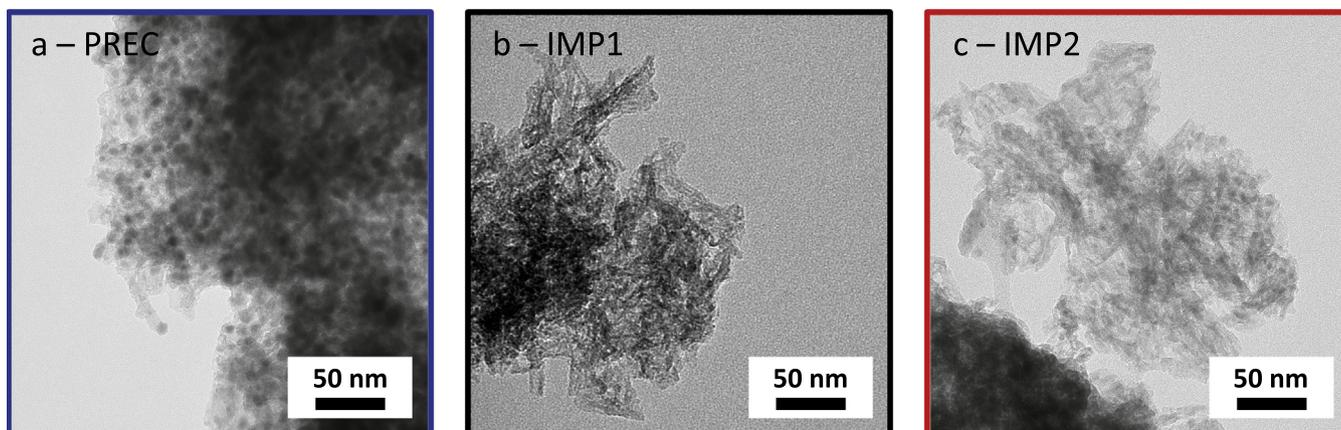
For the three fresh samples particles between 2 and 12 nm were observed and the average particle size obtained from the TEM images for PREC (frame a), IMP1 (frame b) and IMP2 (frame c) were  $6.2 \pm 1.5$  nm,  $5.3 \pm 1.9$  nm, and  $5.8 \pm 1.5$  nm, respectively. The histogram, based on the TEM micrographs, comparing the three catalysts is shown in Fig. S1. In addition, the particle size of the precipitated catalyst can be tuned by changing the reduction conditions.

Fig. 5 displays XRD patterns of the reduced fresh catalysts, obtained in inert atmosphere. All three patterns contained a broad peak at  $25^\circ 2\theta$ , and two peaks at  $50.7^\circ$  and  $59.3^\circ 2\theta$ . The broad band at  $25^\circ 2\theta$  originated from the amorphous silica present in all samples as previously discussed, the other two peaks are diffractions from crystalline metallic copper.

In the pattern of PREC (blue line) both diffraction lines corresponding to copper showed a broad peak. In the case of IMP2 (red line) these two peaks consisted of a broad peak base and a



**Fig. 5.** X-ray diffractograms of PREC (blue), IMP1 (black) and IMP2 (red). PREC contained exclusively small copper crystallites concluding from the broad copper reflections at  $50.7^\circ$  and  $59.3^\circ 2\theta$ . IMP1 shows a broad peak, with a sharp top. IMP2 shows a broad peak base and a narrowing of the copper diffraction lines. Both IMP1 and IMP2 contained a fraction of large crystallites, but IMP2 to a much larger extent.



**Fig. 4.** TEM images of (a) PREC (36.0 wt% Cu), (b) IMP1 (20.7 wt% Cu) and (c) IMP2 (34.1 wt% Cu) after reduction. All three catalysts contained small copper particles around 6 nm and the particles were homogeneously distributed over the support surface in all cases.

narrow high peak. This indicated that PREC exclusively contained small crystallites, where IMP2 contained a mixture of small and large crystallites. The copper peaks for IMP1 (black line) showed a broad and a narrow peak as well, however the intensity of the narrow peak is very low. Therefore it contained only a small number of large crystallites. For both IMP1 and IMP2 these large particles were not observed in the TEM images, meaning that they were indeed low in number.

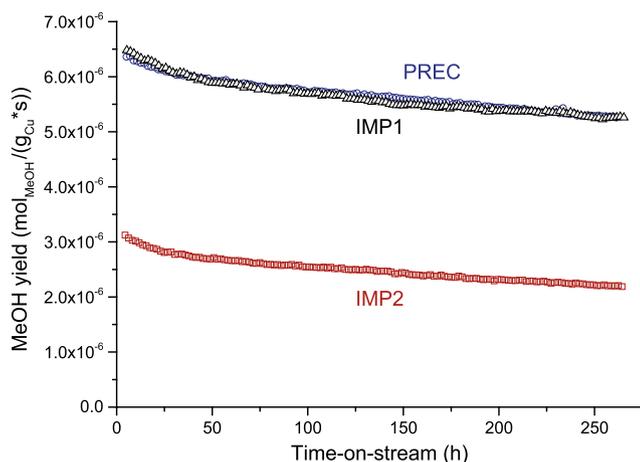
The copper crystallite sizes were determined from these two peaks by the Scherrer equation [37], therefore the peaks for the impregnated samples were deconvoluted, to determine the size of the small and of the large crystallites [38]. The deconvolutions are shown in Figs. S2 and S3 for IMP1 and IMP2, respectively. Table S1 lists the crystallite sizes obtained for the fresh and spent catalysts, determined from the  $\text{Cu}^0$  diffraction lines in the XRD patterns. The determined size for the small crystallites was 3–4 nm, in all three samples. The large crystallites present on the IMP1 and IMP2 were larger than 30 nm. By comparing the areas of the deconvoluted peaks, approximately 50% of the copper in IMP2 is located in the large crystallites. For IMP1 this is only a few percent of the copper.

A possible explanation for the formation of the large crystallites in IMP2 is that part of the  $\text{Cu}(\text{NO}_3)_2$  is not present inside the pores during the second impregnation step and precipitates upon drying outside the pores since the pores are partially filled with  $\text{Cu}(\text{NO}_3)_2$  from the first impregnation step. Consequently, the formed copper particles during reduction are much larger than the pore diameter. Approximately all copper introduced in the second step is incorporated into these large crystallites.

### 3.3. Catalyst activity and stability

The performance of the three catalysts was tested under methanol synthesis conditions at the same copper-based WHSV, as explained in the experimental section, for 250 h. The methanol yield per gram of copper in  $\text{mol}_{\text{MeOH}}/(\text{g}_{\text{Cu}} \cdot \text{s})$  is given in Fig. 6. All three catalysts displayed a stable and high selectivity  $\geq 98\%$  towards methanol during the run.

The methanol yield per gram of copper of the PERC and IMP1 catalyst were the same, namely  $6.3 \cdot 10^{-6} \text{ mol}_{\text{MeOH}}/(\text{g}_{\text{Cu}} \cdot \text{s})$ , at the start of the reaction, and showed a similar loss in activity over the 250 h. The activity of IMP2 was two-fold lower namely



**Fig. 6.** Activity evolution, expressed as the methanol yield in  $\text{mol}_{\text{MeOH}}/(\text{g}_{\text{Cu}} \cdot \text{s})$ , for PREC (blue circles), IMP1 (black triangles) and IMP2 (red squares). Reaction conditions: WHSV of  $7.6 \text{ g}_{\text{syngas}}/(\text{g}_{\text{Cu}} \cdot \text{h})$ ,  $260^\circ\text{C}$  and 40 bar (23%  $\text{CO}$ , 7%  $\text{CO}_2$ , 60%  $\text{H}_2$ , 10% Ar). PREC and IMP1 displayed a high activity, IMP2 showed a low copper based activity due to the presence of large copper particles, which hardly contribute to the activity.

$3.1 \cdot 10^{-6} \text{ mol}_{\text{MeOH}}/(\text{g}_{\text{Cu}} \cdot \text{s})$  at the start of the run. The activity, conversion levels and particle size for the three catalysts (at the start and the end of the run) are listed in Table 1. It was difficult to determine the turn-over-frequency for IMP1 and IMP2 due to the presence of an unknown amount of large particles. The turn-over-frequency for the PREC was  $2.3 \cdot 10^{-3} \text{ s}^{-1}$  at the start and the end of the run, which is the expected value for copper catalysts in methanol synthesis under these conditions [39].

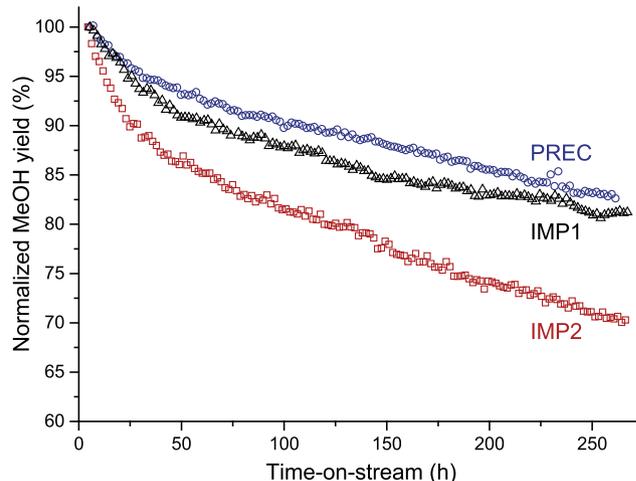
The copper particles in IMP1 were slightly smaller than in PREC at the start of the reaction. Therefore a higher methanol yield per gram of copper for the IMP1 would be expected than measured. However IMP1 contained a small amount of large particles, as illustrated by XRD in Fig. 5, which might explain the difference. This resulted in an equal methanol yield per gram of copper for PREC and IMP1. The much lower activity for IMP2 can be ascribed to the presence of large copper particles. These large particles expose a small specific surface area and therefore hardly contributed to the copper-weight-based catalytic performance. It is concluded from the measured activity that approximately half of the copper was situated in the large particles, which is in agreement with the XRD results.

To compare the relative rate of deactivation, the normalized methanol yield of the catalysts were plotted, since this is a direct measure for the relative loss in surface area (Fig. 7). The PREC

**Table 1**

Properties and catalytic performances of the three used catalysts. The methanol yield per gram of copper was equal for PREC and IMP1, where the methanol yield of IMP2 was two-fold lower. The number averaged particle size was calculated by:  $d_N = \frac{1}{N} \sum_{i=1}^N d_i$  and the surface averaged particle size by:  $d_S = \sqrt{\frac{1}{N} \sum_{i=1}^N d_i^2}$ . Particle diameters were determined from TEM micrographs.

	PREC	IMP1	IMP2
Copper loading (wt%)	36.0	20.7	34.1
Activity t = 0 h ( $\text{mol}_{\text{MeOH}}/(\text{kg}_{\text{cat}} \cdot \text{h})$ )	8.0	4.5	3.5
Activity t = 250 h ( $\text{mol}_{\text{MeOH}}/(\text{kg}_{\text{cat}} \cdot \text{h})$ )	6.6	3.4	2.7
MeOH-yield t = 0 h ( $\text{mol}_{\text{MeOH}}/(\text{g}_{\text{Cu}} \cdot \text{s})$ )	$6.3 \cdot 10^{-6}$	$6.3 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$
Conversion $\text{CO} + \text{CO}_2$ t = 0 h (%)	14.7	14.6	7.1
Conversion $\text{CO} + \text{CO}_2$ t = 250 h (%)	12.0	11.3	5.3
$d_N$ t = 0 h (nm)	$6.2 \pm 1.5$	$5.3 \pm 1.9$	$5.8 \pm 1.5$
$d_S$ t = 0 h (nm)	$6.4 \pm 1.5$	$5.6 \pm 1.9$	$6.0 \pm 1.5$
$d_N$ t = 250 h (nm)	$7.2 \pm 2.2$	$5.8 \pm 1.4$	$9.0 \pm 11$
$d_S$ t = 250 h (nm)	$7.5 \pm 2.2$	$6.0 \pm 1.4$	$14 \pm 12$



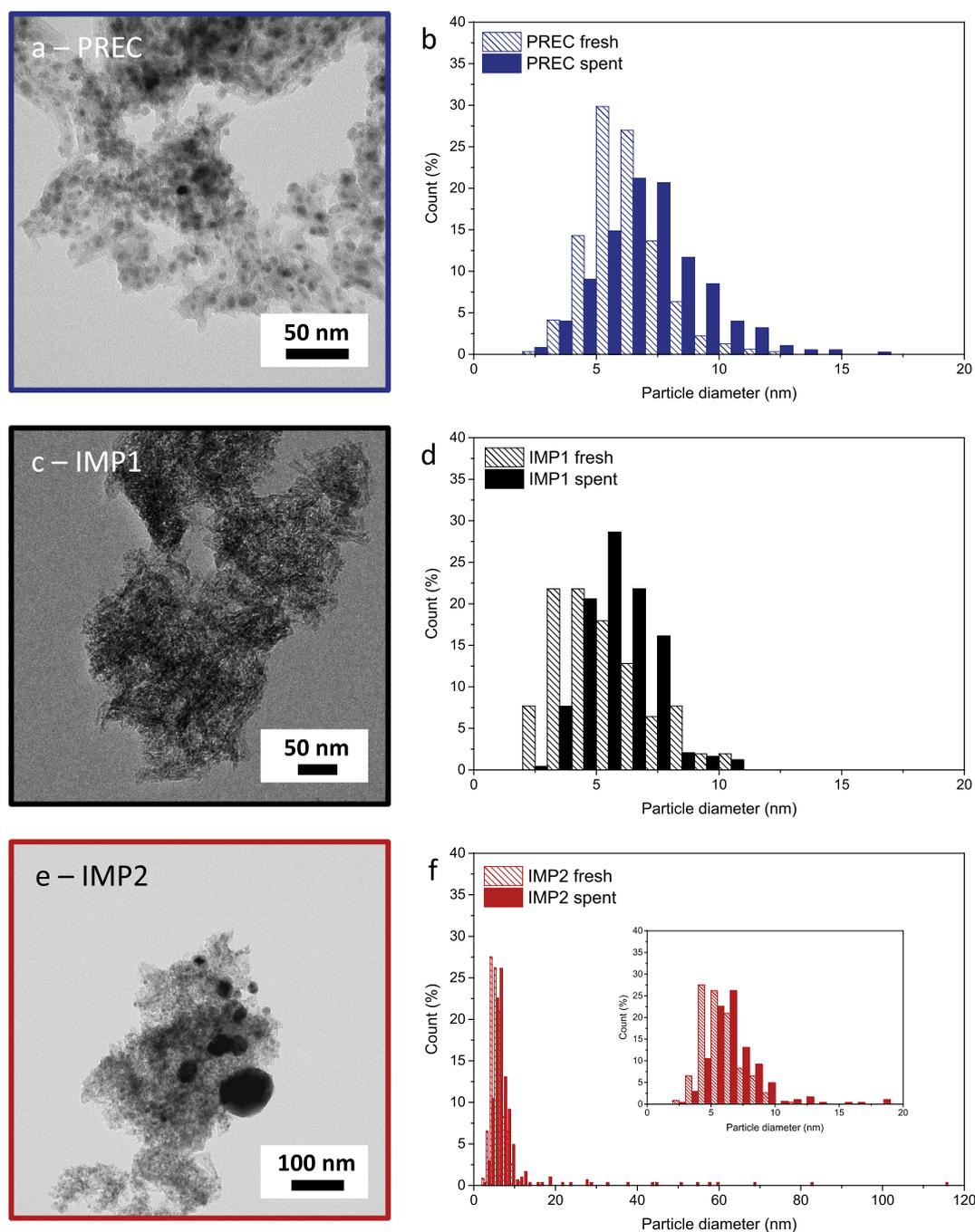
**Fig. 7.** Normalized methanol yield for PREC (blue circles), IMP1 (black triangles) and IMP2 (red squares). Reaction conditions: WHSV of  $7.6 \text{ g}_{\text{syngas}}/(\text{g}_{\text{Cu}} \cdot \text{h})$ ,  $260^\circ\text{C}$  and 40 bar (23%  $\text{CO}$ , 7%  $\text{CO}_2$ , 60%  $\text{H}_2$ , 10% Ar). The PREC and IMP1 catalyst displayed a high, almost similar, stability. IMP2 was less stable, due to the presence of large particles, causing a higher rate of Ostwald ripening.

and IMP1 catalyst displayed a higher stability than IMP2. The largest difference was observed in the first 50 h, where IMP2 deactivated much faster than the other two. Moreover, on the longer time scale there was a difference in the deactivation rate as well; the slope for the straight part of the curve was steeper for IMP2 than for PREC and IMP1. The inter-particle distance for the IMP2 was similar to that of the PREC catalyst, due to the similar weight loading. Therefore the difference in the slope was likely caused by a higher rate of Ostwald ripening in IMP2, since this sample contained a broader distribution of particle sizes.

A possible explanation for the difference during the start of the curves could be coalescence of particles in IMP2. Possibly the heterogeneities in this samples did not only consist as large

particles but also as clusters of particles which could have coalesced fast at the start of the syngas exposure. IMP1 showed a slightly faster loss of normalized activity than PREC as well during the first 50 h of the reaction. This difference might be attributed to the same phenomenon.

The spent catalysts were analyzed by TEM and XRD to determine the particle size after 250 h of methanol synthesis. The TEM images, together with the histograms comparing the particle size of the fresh and spent catalyst are shown in Fig. 8. The values for the particle sizes are also listed in Table 1. The XRD patterns and the determined crystallite sizes are displayed in Fig. S4 and Table S1, respectively. As for the fresh catalysts, the peaks in the XRD were deconvoluted. Approximately the same amount of



**Fig. 8.** TEM images of the spent catalysts, on the left, and histograms comparing the fresh and spent particle size distributions (on the right), for PREC (frame a and b), IMP1 (frame c and d) and IMP2 (frame e and f).

copper was present in the large crystallites for the spent catalysts as for the fresh catalysts.

Fig. 8a shows a TEM image of the spent PREC catalyst and frame b the histogram of the fresh and spent material. The average particle size increased slightly over time to from 6.2 to 7.2 nm. Also a slight peak narrowing was observed in the XRD pattern. Frame c and d in Fig. 8 show the TEM image and the histogram for the IMP1. For this sample a slight increase in particle size was also observed, and the final particle size was 5.8 nm after 250 h of catalysis. Large crystallites were identified also by XRD, however these were not observed in TEM.

In Fig. 8e can be seen that for the spent catalyst IMP2 large particles were observed, which were not seen in the TEM images for the fresh catalyst. The obtained average particle size determined from TEM increased therefore to 9.0 nm with a standard deviation of 11 nm after catalysis. The small particles present on the sample did not change much in size. Large crystallites were observed for the fresh and spent sample in XRD, as can be seen in Figs. 5 and S5. These large particles influenced the activity, as can be seen in Fig. 7, and the stability (Fig. 8) to great extent.

#### 4. Conclusions

We synthesized catalysts by impregnation and precipitation with the same support morphology. Synthesis of plate-like silica, starting from the precipitated and reduced precursor was successfully performed by removal of the copper in nitric acid. The morphology, porosity and surface area of the silica were not affected by the reduction and acid treatment. To obtain a catalyst by impregnation with the same high weight loading as the precipitated catalyst, the plate-like silica was impregnated twice with a high concentration copper (IMP2). For comparison a catalyst using one impregnation step was synthesized as well (IMP1).

IMP2 contained heterogeneities in the form of large (>30 nm) particles that approximately contained half the amount of copper. These large particles affected detrimentally the activity and stability during methanol synthesis, compared to the more homogeneous catalysts PREC and IMP1. The lower stability of IMP2 is attributed to an increased rate of Ostwald ripening, due to the broader particle size distribution and consequent coalescence of less homogeneously dispersed clusters of copper particles.

PREC was very uniform in the sense of particle size, resulting in a high activity and long-term stability during methanol synthesis. Impregnation led to the presence of heterogeneities in the form of large particles, being not only detrimental for activity but also for stability.

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#### References

- [1] H.H. Kung, Deactivation of methanol synthesis catalysts - a review, *Catal. Today* 11 (1992) 443–453, [https://doi.org/10.1016/0920-5861\(92\)80037-N](https://doi.org/10.1016/0920-5861(92)80037-N).
- [2] C.H. Bartholomew, Sintering kinetics of supported metals: new perspectives from a unifying GPLE treatment, *Appl. Catal. A Gen.* 107 (1993) 1–57, [https://doi.org/10.1016/0926-860X\(93\)85114-5](https://doi.org/10.1016/0926-860X(93)85114-5).
- [3] J. Zečević, G. Vanbutsele, K.P. de Jong, J.A. Martens, Nanoscale intimacy in bifunctional catalysts for selective conversion of hydrocarbons, *Nature* 528 (2015) 245–248, <https://doi.org/10.1038/nature16173>.
- [4] B.M. Weckhuysen, Chemical imaging of spatial heterogeneities in catalytic solids at different length and time scales, *Angew. Chemie - Int. Ed.* 48 (2009) 4910–4943, <https://doi.org/10.1002/anie.200900339>.
- [5] K. Wettergren, F.F. Schweinberger, D. Deiana, C.J. Ridge, A.S. Crampton, M.D. Rötzer, T.W. Hansen, V.P. Zhdanov, U. Heiz, C. Langhammer, High sintering resistance of size-selected platinum cluster catalysts by suppressed ostwald ripening, *Nano Lett.* 14 (2014) 5803–5809, <https://doi.org/10.1021/nl502686u>.
- [6] R. Ouyang, J.X. Liu, W.X. Li, Atomistic theory of ostwald ripening and disintegration of supported metal particles under reaction conditions, *J. Am. Chem. Soc.* 135 (2013) 1760–1771, <https://doi.org/10.1021/ja3087054>.
- [7] G. Prieto, J. Zečević, H. Friedrich, K.P. de Jong, P.E. de Jongh, Towards stable catalysts by controlling collective properties of supported metal nanoparticles, *Nat. Mater.* 12 (2013) 34–39, <https://doi.org/10.1038/nmat3471>.
- [8] M. Behrens, Coprecipitation: an excellent tool for the synthesis of supported metal catalysts - from the understanding of the well known recipes to new materials, *Catal. Today* 246 (2015) 46–54, <https://doi.org/10.1016/j.cattod.2014.07.050>.
- [9] K.C. Waugh, *Methanol synthesis*, *Catal. Today* 15 (1992) 51–75.
- [10] G.A. Olah, A. Goepfert, G.K.S. Prakash, Beyond oil and gas: the methanol economy, *Angew. Chemie Int. Ed.* 44 (2005) 2636–2639, <https://doi.org/10.1002/9783527627806>.
- [11] S. Kuld, M. Thorhauge, H. Falsig, C.F. Elkjaer, S. Helveg, I. Chorkendorff, J. Sehested, Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis, *Science* 352 (2016) 969–974, <https://doi.org/10.1126/science.aaf0718>.
- [12] M.B. Fichtl, D. Schlereth, N. Jacobsen, I. Kasatkin, J. Schumann, M. Behrens, R. Schlögl, O. Hinrichsen, Kinetics of deactivation on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalysts, *Appl. Catal. A Gen.* 502 (2015) 262–270, <https://doi.org/10.1016/j.apcata.2015.06.014>.
- [13] K.P. de Jong, *Synthesis of Solid Catalysts*, Wiley-VCH Verlag, Weinheim, 2009, doi: 10.1002/9783527626854.ch6.
- [14] P. Munnik, P.E. de Jongh, K.P. de Jong, Recent developments in the synthesis of supported catalysts, *Chem. Rev.* 115 (2015) 6687–6718, <https://doi.org/10.1021/cr500486u>.
- [15] R. van den Berg, C.F. Elkjaer, C.J. Gommers, I. Chorkendorff, J. Sehested, P.E. de Jongh, K.P. de Jong, S. Helveg, Revealing the formation of copper nanoparticles from a homogeneous solid precursor by electron microscopy, *J. Am. Chem. Soc.* 138 (2016) 3433–3442, <https://doi.org/10.1021/jacs.5b12800>.
- [16] P. Munnik, M. Wolters, A. Gabriëlsson, S.D. Pollington, G. Headdock, J.H. Bitter, P.E. de Jongh, K.P. de Jong, Copper nitrate redispersion to arrive at highly active silica-supported copper catalysts, *J. Phys. Chem. C* 115 (2011) 14698–14706, <https://doi.org/10.1021/jp111778g>.
- [17] R. van den Berg, J. Zečević, J. Sehested, S. Helveg, P.E. de Jongh, K.P. de Jong, Impact of the synthesis route of supported copper catalysts on the performance in the methanol synthesis reaction, *Catal. Today* 272 (2016) 87–93, <https://doi.org/10.1016/j.cattod.2015.08.052>.
- [18] P. Wynblatt, N.A. Gjostein, Supported metal crystallites, *Prog. Solid State Chem.* 9 (1975) 21–58.
- [19] P.J.F. Harris, Growth and structure of supported metal catalyst particles, *Int. Mater. Rev.* 40 (1995) 97–115, <https://doi.org/10.1179/095066095790326102>.
- [20] J.R. Rumble (Ed.), *Handbook of Chemistry and Physics*, 98th ed., CRC Press, Taylor & Francis Group, 2018.
- [21] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science* 279 (1998) 548–552.
- [22] L. Rossi, S. Sacanna, W.T.M. Irvine, P.M. Chaikin, D.J. Pine, A.P. Philipse, Cubic crystals from cubic colloids, *Soft Matter* 7 (2011) 4139–4142, <https://doi.org/10.1039/c0sm01246g>.
- [23] P. Schmidt-Winkel, W.W. Lukens Jr., D. Zhao, P. Yang, B.F. Chmelka, G.D. Stucky, Mesocellular siliceous foams with uniformly sized cells and windows, *J. Am. Chem. Soc.* 121 (1999) 254–255, <https://doi.org/10.1021/ja983218i>.
- [24] D. Nagao, C.M. van Kats, K. Hayasaka, M. Sugimoto, M. Konno, A. Imhof, A. van Blaaderen, Synthesis of hollow asymmetrical silica dumbbells with a movable inner core, *Langmuir* 26 (2010) 5208–5212, <https://doi.org/10.1021/la903673j>.
- [25] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interface Sci.* 26 (1968) 62–69, [https://doi.org/10.1016/0021-9797\(68\)90272-5](https://doi.org/10.1016/0021-9797(68)90272-5).
- [26] F. Hagemans, W. Vlug, C. Raffaelli, A. Van Blaaderen, A. Imhof, Sculpting silica colloids by etching particles with nonuniform compositions, *Chem. Mater.* 29 (2017) 3304–3313, <https://doi.org/10.1021/acs.chemmater.7b00687>.
- [27] C.J.G. van der Grift, A. Mulder, J.W. Geus, Characterization of silica-supported copper catalysts by means of temperature-programmed reduction, *Appl. Catal.* 60 (1990) 181–192, [https://doi.org/10.1016/S0166-9834\(00\)82181-8](https://doi.org/10.1016/S0166-9834(00)82181-8).
- [28] C.J.G. van der Grift, P.A. Elberse, A. Mulder, J.W. Geus, Preparation of silica-supported copper catalysts by means of deposition-precipitation, *Appl. Catal.* 59 (1990) 275–289, [https://doi.org/10.1016/S0166-9834\(00\)82204-6](https://doi.org/10.1016/S0166-9834(00)82204-6).
- [29] T. Toupance, M. Kermarec, J.-F. Lambert, C. Louis, Conditions of formation of copper phyllosilicates in silica-supported copper catalysts prepared by selective adsorption, *J. Phys. Chem. B* 106 (2002) 2277–2286, <https://doi.org/10.1021/jp013153x>.
- [30] L.F. Chen, P.J. Guo, M.H. Qiao, S.R. Yan, H.X. Li, W. Shen, H.L. Xu, K.N. Fan, Cu/SiO<sub>2</sub> catalysts prepared by the ammonia-evaporation method: texture, structure, and catalytic performance in hydrogenation of dimethyl oxalate to ethylene glycol, *J. Catal.* 257 (2008) 172–180, <https://doi.org/10.1016/j.jcat.2008.04.021>.

- [31] A. Ayrál, A. Julbe, S. Roualdes, V. Rouessac, Silica membranes - basic principles, *Period. Polytech. Ser. Chem. Eng.* 50 (2006) 67–79.
- [32] G. Alexander, W. Heston, R. Iler, The solubility of amorphous silica in water, *J. Phys. Chem.* 58 (1954) 453–455, <https://doi.org/10.1021/j150516a002>.
- [33] T. Toupance, M. Kermarec, C. Louis, Metal particle size in silica-supported copper catalysts. Influence of the conditions of preparation and of thermal pretreatments, *J. Phys. Chem. B.* 104 (2000) 965–972, <https://doi.org/10.1021/jp993399q>.
- [34] M.-C. Van Oosterwyck-Gastuche, La structure de chrysocolle, *C. R. Seances Acad. Sci. D.* 271 (1970) 1837–1840.
- [35] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* 87 (2015) 1051–1069, <https://doi.org/10.1515/pac-2014-1117>.
- [36] R.S. Da Cruz, J.M. De, U. Arnold, M.S. Sercheli, U. Schuchardt, Copper containing silicates as catalysts for liquid phase cyclohexane oxidation, *J. Braz. Chem. Soc.* 13 (2002) 170–176, <https://doi.org/10.1590/S0103-50532002000200007>.
- [37] A.L. Patterson, The Scherrer formula for X-ray particle size determination, *Phys. Rev.* 56 (1939) 978–982, <https://doi.org/10.1103/PhysRev.56.978>.
- [38] M. Wojdyr, Fityk: a general-purpose peak fitting program, *J. Appl. Crystallogr.* 43 (2010) 1126–1128, <https://doi.org/10.1107/S0021889810030499>.
- [39] R. van den Berg, G. Prieto, G. Korpershoek, L.I. van der Wal, A.J. van Bunningen, S. Lægsgaard-Jørgensen, P.E. de Jongh, K.P. de Jong, Structure sensitivity of Cu and CuZn catalysts relevant to industrial methanol synthesis, *Nat. Commun.* 7 (2016) 20457–20465, <https://doi.org/10.1038/ncomms13057>.