Interplay between pore size and nanoparticle spatial distribution: consequences for the stability of CuZn/SiO₂ methanol synthesis catalysts

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Abstract

Particle growth is a major deactivation mechanism for supported metal catalysts. This study reveals that the impact of pore size on catalyst stability is very sensitive to the nanoscale metal distribution. A set of *ex-nitrate* CuZn/SiO₂ catalysts was synthesised using SiO₂-gel supports (pore size 5-23 nm). The catalyst compositions were adjusted to attain series of catalysts with either constant pore volumetric (1.6 Cu nm⁻³) or surface (2.0 Cu nm⁻²) overall metal loading. The procedures of thermal decomposition of the metal nitrate precursors were adjusted to achieve < 10 nm Cu particles displaying markedly different nanospatial distributions, *i.e* either gathered in *high-metal-density domains* with small interparticle spacings or evenly distributed over the support with maximum interparticle spacings. Under industrially relevant methanol synthesis conditions, a strong increase of the deactivation rate with the support pore size is observed for catalysts with high-density domains of Cu particles. For these samples the local, nanoscale Cu surface loading is determined by pore size rather than by the *overall* metal content, as ascertained by HAADF-STEM/EDX. Conversely, Cu nanoparticles evenly spaced on the surface of the SiO₂ carrier show improved stability, being the deactivation rate chiefly independent of the support pore size. The differences in catalyst stability are ascribed to the dominance of different particle growth mechanisms. Our study highlights the significance of local, nanoscale properties for rationalizing the relevance of structural parameters such as pore size for catalyst stability.

Keywords:

Pore size; particle size; particle distribution; clustering; microtomy; sintering; migration-coalescence; Ostwald ripening; synthesis gas; methanol synthesis.

1. Introduction

Supported metal catalysts are crucial for the production of clean and renewable fuels and chemicals. Processes ranging from synthesis gas ($\text{H}_2+\text{CO}+\text{CO}_2$) production and conversion [1,2,3] to the transformation of biomass into liquid fuels [4,5,6] require the use of supported metal catalysts. Catalyst synthesis and activation procedures are designed to achieve small metal nanoparticles exposing large catalytic metal surface areas [7,8]. However under realistic operation conditions, metal nanoparticles are inherently prone to grow into larger crystals, which results in catalyst deactivation owing to the reduction of the available metal surface [9,10,11]. Usually, particle growth also translates into additional undesired effects on activity and selectivity since frequently these properties are sensitive to the metal particle size [12,13,14,15,16]. Therefore, particle growth limits catalyst functionality and lifetime.

Metal particle growth can proceed via the migration of nanoparticles on the surface of the support, followed by collision and coalescence, or via the exchange of atomic or molecular species between individual nanoparticles (Ostwald ripening) [17]. Owing to an enhanced atom mobility, low melting point metals such as Cu, Au or Ag are particularly prone to grow. Cu-based catalysts, typically promoted by ZnO, are employed in industrial processes such as the water-gas shift reaction [18,19] and the synthesis of methanol from synthesis gas [20,21], for which Cu particle growth is a prominent deactivation mechanism [22,23,24].

The design and synthesis of catalysts with enhanced stability requires a fundamental understanding of the factors governing metal particle growth [25,26,27,28]. The influence of catalyst composition and structure on metal particle growth has been previously studied for several systems [29,30,31,32]. The size of the metal particles is an important parameter. Higher surface diffusion coefficients have been proposed for smaller nanoparticles, increasing the probability of particle collision events [17,33]. In addition, particle size distributions play a significant role in Ostwald ripening, since differences in size determine the net driving force for the exchange of metal atoms

between nanoparticles, as demonstrated mainly for 2D model systems [34,35,36].

The support material is a key component in stabilizing the metal nanoparticles. The choice of the chemical nature of the support is often subject to considerations such as chemical and mechanical stability under process conditions [37,38]. Textural properties like pore size and surface area are also very relevant in determining the size and stability of the supported metal nanoparticles. Especially the support pore size has been classically considered an important variable, in particular when migration-coalescence contributed significantly to particle growth. Earlier theoretical studies modelled the effect of support pore size on the kinetics of metal particle migration and coalescence [39]. In addition, the impact of pore size on the growth-stability of Ni/Al₂O₃ [40], Au/SiO₂ [41] and Ag/SiO₂ [42] catalysts has been experimentally assessed. Generally, narrow pores were found to enhance metal particle stability, which was ascribed to partial confinement of the metal particles by the pore walls leading to impeded particle mobility.

The pore size might also indirectly influence the particle growth. Pore diameter is typically correlated to the specific surface area of the support. It is common practice to apply constant weight metal loadings on support materials with varying pore size and surface area. Hence, in practice, catalysts with notably different metal surface loadings (metal atoms per unit surface area) and particle surface densities were often compared in previous investigations. However, metal particle surface density, i.e. number of metal nanoparticles per unit surface area of support, might be very relevant for particle growth since it relates directly to interparticle spacing. Decoupling the diverse structural parameters is desirable in order to understand their relevance for catalyst stability.

Spatial heterogeneities in the metal distribution at the nanoscale are often found in supported catalysts, which translate into significant deviations between local and overall (*bulk*) metal loading. For example, clustering of Co nanoparticles in high-metal-density domains, typically tens-to-hundreds of nanometers in size, has been reported for Co/SiO₂ and commercial Pt-Co/Al₂O₃ Fischer-Tropsch catalysts [43,44,45,46,47]. Similar non-uniform spatial distributions of metal nanoparticles have been revealed for Ni-Mo/Al₂O₃ [48], Pd/SBA-15 [49] and NiO/SBA-15 catalysts [50]. Such uneven metal distributions result both in an inefficient use of the support surface area and in interparticle spacings notably shorter than those estimated from macroscopic measurements under the assumption of

uniform metal distribution. Thus, assessment of local, nanoscale heterogeneities seems essential for fundamental studies on catalyst stability.

Recent mechanistic insights into the synthesis of supported catalysts provide means to control the nanospatial distribution of metal particles on porous carriers [51,52]. We have previously reported on the impact of the gas composition and hydrodynamics during the calcination of *ex*-nitrate Cu/SiO₂ catalysts on the resulting size and spatial distribution of the metal particles [52]. Addition of small amounts of NO to the gas phase promotes low-temperature hydrolysis of the hydrate nitrate precursor into Cu₂(OH)₃NO₃. This species shows reduced mobility minimizing metal re-distribution and eventually decomposes into small CuO nanoparticles in close proximity. In contrast, nitrate decomposition under moderate-to-high N₂ flow rates proceeds via an anhydrous and volatile Cu(NO₃)₂ intermediate which re-disperses on the SiO₂ surface, resulting in near-maximum interparticle distances [53]. The spatial distribution of the Cu nanoparticles has important implications for catalyst stability under methanol synthesis conditions [53].

In this work, previous mechanistic information on the decomposition pathways of supported metal nitrate precursors was exploited to synthesize CuZn/SiO₂ 3D model methanol synthesis catalysts. Industrial Cu/ZnO/Al₂O₃ methanol synthesis catalysts are synthesized by highly optimized co-precipitation routes, which lead to small (<10 nm) Cu nanoparticles homogeneously distributed within a matrix of ZnO and Al₂O₃ nanocrystallites at remarkably high copper loadings (>50 wt%) [54,55,56]. The CuZn/SiO₂ catalysts employed here are models for catalysts with lower metal loadings (generally <20wt%) prepared by routes such as impregnation on porous carriers (frequently SiO₂ or Al₂O₃), which are widely applied in catalytic processes. Synthesis and activation procedures were tuned to achieve materials displaying notably different nanospatial distribution of the catalytic Cu particles on silica supports with varying pore sizes. The interplay between these two parameters in determining the catalytic stability under industrially relevant conditions was studied. In order to decouple structural factors and enable interpretation at a fundamental level, the composition of the catalysts was systematically adjusted to obtain materials with equal overall (*bulk*) surface or pore volumetric metal loadings, rather than fixed weight loadings. Using ultrathin catalyst sections, the size and spatial distribution of the metal particles was studied by means of scanning-transmission electron

microscopy. Local metal surface loadings and particle surface densities were quantified by energy dispersive X-ray spectroscopy, which enabled the assessment of nanoscale deviations from the overall metal loading. This approach provides the fundamental basis to interpret the dependence of catalyst stability on support pore size.

2. Experimental

2.1. Catalyst synthesis

High-purity silica gel materials with pore sizes varying from 5 to 23 nm were used as supports (see Supplementary methods for purity specifications). These supports are labelled as SG x , where x denotes the mean pore diameter in nm. To synthesize the CuZn/SiO₂ catalysts, the silica supports were sieved to select particles of 38-90 μ m and dried at 523K under dynamic vacuum for 2 hours prior to the incorporation of the metal species. Then the supports were impregnated to incipient wetness using an aqueous solution of Cu and Zn nitrates (atomic ratio Cu/Zn=65/35) in 0.1 M HNO₃ (pH<1). For a first set of catalysts, the total concentration of the metal nitrate solution was adjusted in the range of 1.0 to 5.0 M in order to achieve a constant *bulk* Cu *surface* loading ($\delta_{\text{Cu,S}}$), i.e. Cu atoms per unit surface area, of ca. 2 Cu nm⁻². For another series of catalysts the concentration of the metal nitrate solution was set invariably to 4.0 M, resulting in a constant *bulk* pore volumetric Cu loading ($\delta_{\text{Cu,V}}$), i.e. metal atoms per unit pore volume, of ca. 1.6 Cu nm⁻³. As the ratio of pore volume to surface area of the support materials increases with increasing pore size, the latter catalysts display $\delta_{\text{Cu,S}}$ varying from 3 to 8 Cu nm⁻². After impregnation, the powders were dried for 12 h at room temperature (RT) under dynamic vacuum. Finally, the supported metal nitrate precursors were decomposed by submitting the samples to a thermal treatment at 723 K for 1 hour under a flow of either pure N₂ or 2%NO/N₂(v/v), hereafter denoted N₂-calcined and NO-calcined catalysts, respectively. A heating rate of 2 K min⁻¹ and a gas hourly space velocity (GHSV) of 1.0·10⁴ h⁻¹ were applied. As discussed in the results (*vide infra*), these thermal treatments lead to different spatial distributions of the Cu nanoparticles on the support. Catalysts are denoted CuZn/SG x ($\delta_{\text{Cu,S}}$)- z , where x refers to the support pore size (nm), $\delta_{\text{Cu,S}}$ is the *bulk* Cu surface loading (Cu atoms nm⁻²) and z is either NO or N₂ for catalysts calcined in a flow of 2%NO/N₂ or N₂, respectively. A reference Cu/ZnO/Al₂O₃ catalyst was prepared following a synthesis route representative for commercial methanol synthesis

catalysts (Supplementary methods).

2.2. Characterization

N₂ physisorption isotherms were measured at 77 K using a Micromeritics TriStar 3000 apparatus. Prior to analysis, the samples were treated in N₂ flow at 523K for 12 h. Surface areas were derived using the BET method and the total pore volumes were based on the amount of N₂ adsorbed at a relative pressure $p/p_0=0.95$. Pore size distributions were calculated from the desorption branch using the BJH theory with the Harkins-Jura thickness equation. The pore size was defined as the size corresponding to the peak maximum in the pore size distribution.

Hydrogen temperature programmed reduction (H₂-TPR) was employed to determine the Cu loading in the catalysts in an Autochem 2910 from Micromeritics. 30-80 mg of catalyst (0.42-0.63 mm sieve fraction) was loaded into a quartz tube reactor and flushed with He at 353K for 1 h. To reduce the samples, a flow of 5 vol% H₂/Ar was applied (50 STP mL min⁻¹) and the temperature was increased to 773 K at a heating rate of 10 K min⁻¹. A N₂(liq)/2-propanol trap was placed downstream of the reactor in order to retain the water produced during the reduction, and the H₂-consumption rate was monitored using a thermal conductivity detector (TCD), which was calibrated using different known amounts of CuO. The single reduction peak at 493-533 K was integrated and the determined H₂ consumption was ascribed to CuO species (reduction of Zn species was neglected in the examined temperature range since it requires higher temperatures). The Cu loading was estimated by assuming the following reduction stoichiometry: $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$.

X-ray diffractograms of the calcined catalysts were acquired at RT in the 2 θ range from 10° to 80° (step size of 0.043°, scan speed 356 s/step) using Co-K $\alpha_{1,2}$ radiation ($\lambda=1.79026$ Å). The copper oxide crystallite size was estimated by applying the Scherrer equation ($k=0.9$) to the (1 1 1) diffraction of CuO (2 $\theta=45.5$). Corundum ($\alpha\text{-Al}_2\text{O}_3$) was used to determine the experimental line broadening.

N₂O reactive frontal chromatography (RFC) was used to estimate the exposed Cu area in selected as-reduced catalysts. Experimentally, the catalyst (ca. 0.3 g) was reduced in situ at 503 K for 3 hours under a flow of 5% H₂/He. After reduction, the catalyst sample was cooled down to 341 K

under He flow. Then, N₂O RFC was carried out at 341 K flushing the sample with a 2.5% N₂O/He gas stream. The exposed Cu surface area was calculated assuming a surface stoichiometry of N₂O:Cu_s=0.5 and a surface density of 10 Cu atoms nm⁻².

High-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) and *energy dispersive X-ray spectroscopy* (EDX) were performed in a Tecnai 20FEG microscope (FEI company) operated at 200 kV, which was equipped with an EDAX EDX spectrometer and a Fischione HAADF detector. After H₂-reduction or catalysis, the catalysts were passivated by controlled exposure to oxygen at RT and stored in a glove-box (<1 ppm O₂) until sample preparation for microscopy. Next, catalysts were embedded in an epoxy resin (Epofix, EMS) and cured at RT for 72 hours. The embedded specimens were then cut into ultrathin sections (nominal thickness of 50 nm) using a Diatome 35° knife mounted on a Reichert-Jung Ultracut microtome, and the sections were collected on carbon-coated Ni TEM grids (200 mesh, Agar Scientific). For microscopy observation and EDX analysis, TEM grids were mounted on a low-background sample holder (Philips) with a 0.1 mm thick Be specimen support film and a Be ring to clamp the grid. Cu particle size histograms were generated by counting at least 200 particles.

2.3. Catalysis

Methanol synthesis tests were performed in a fixed-bed stainless steel reactor. The catalyst (0.2-0.5 g, particle size of 0.42-0.63 mm) was diluted with SiC granules (0.25-0.42 mm) in a ca. 1:1 volume ratio, in order to achieve plug-flow isothermal conditions. Prior to catalysis, the catalyst was reduced in situ at 523 K for 150 min (heating ramp of 2 K min⁻¹) under a flow of 20 vol% H₂/Ar. After reduction, the reactor was cooled down to 373 K and flushed with a synthesis gas mixture (Ar:CO₂:CO:H₂=10:7:23:60, vol.) for 30 minutes. The synthesis gas mixture was fed from a pressurized gas-mixture cylinder (Linde) and purified using a metal carbonyl trap containing H-USY zeolite (CBV-780 from Zeolyst Int., 0.5-1.5 mm) situated upstream of the reactor. The pressure was gradually increased to 40 bar and then the reactor was heated up to the reaction temperature of 533 K (2 K min⁻¹). The gas space velocity was adjusted to achieve initial (CO+CO₂) conversions of 15-20%. The gas flow leaving the reactor was decompressed and periodically injected into a Varian 450 gas

chromatograph (GC) connected online. All lines connecting the reactor with the GC were kept at 423 K to avoid product condensation. The GC was equipped with two channels: the first channel consisted of two series-connected Haysep Q (0.5Mx1/8") packed columns and a Molsieve 13x (1.5Mx1/8") molecular sieve column connected to a TCD detector, while the second channel consisted of a CP-SIL 8CB FS capillary column connected to an FID detector. Product flow rates were quantified using Ar as internal standard.

3. Results and discussion

3.1. Structural characterization

3.1.1. Texture, metal content and metal particle size

The textural properties of the SiO₂ supports determined by N₂-physisorption are given in Table 1. The corresponding pore size distributions are depicted in Fig. 1. The specific surface area continuously decreases and the total pore volume increases on increasing the pore diameter from 5 to 23 nm. All silica gels show mono-modal pore size distributions with slightly increasing broadening with increasing average pore diameter. No micropores were detected. The sharp peak observed at ca. 4.3 nm in the pore size distribution for the silica with the narrowest pores, i.e. SG5, is an artefact arising from the steep closure of the desorption branch due to *cavitation* of N₂ condensed in pores (ca. 26% of total pore volume) constrained by pore entrances narrower than ca. 4.7 nm [57,58,59].

Table 2 gives an overview of the Cu content and metal crystallite/particle size in the CuZn/SiO₂ catalysts. Decomposition of the metal nitrates in N₂ flow resulted in slightly lower Cu contents in the calcined materials than for the NO-calcined counterparts. This is ascribed to a (limited) loss of Cu species with the gas stream during calcination, owing to the volatility of the anhydrous Cu(NO₃)₂ species formed during the decomposition of the nitrate precursor in N₂ flow [52]. The experimental Cu surface loading was 2.1-2.4 Cu nm⁻² for those catalysts for which a constant bulk surface loading was targeted. Impregnation with a fixed nitrate solution concentration (4 M) led to a constant overall Cu pore volumetric loading of 1.6±0.2 Cu nm⁻³, corresponding to a Cu surface loading increasing from ca. 3 to 8 Cu nm⁻² on increasing the support pore size from 7 to 23 nm.

XRD was used to analyze the crystalline phases present in the catalysts after calcination (Supplementary Fig. S1). No crystalline Zn species were detected, indicating very high Zn dispersions

irrespective of the textural properties of the support and the calcination protocol applied. Previous X-ray absorption (XAS) characterization results for CuZn/SBA-15 catalysts obtained through the same synthesis procedures revealed the formation of highly-dispersed surface Zn (hydro)silicate species [53]. CuO was the only crystalline copper-containing phase observed.

Average CuO crystallite sizes were derived from the line broadening of the X-ray diffractograms (Table 2). For catalysts calcined in 2%NO/N₂, crystallite sizes increase from 2.4 to 6.7 nm for samples with constant surface loading on increasing the pore size from 5 to 23 nm. The increase in CuO crystallite size is from 4.8 nm to 9.9 nm for samples with constant metal volumetric loading on increasing the pore size from 7 to 23 nm. This relationship between metal oxide crystallite size and support pore diameter is in agreement with previous results reported for *ex-nitrate* NiO/SiO₂ and Co₃O₄/SiO₂ catalysts obtained by calcination in NO-containing atmospheres [60]. For selected samples, Cu particle sizes were assessed by HAADF-STEM after H₂-reduction (Table 2 and Supplementary Fig. S2). The results are in agreement with the XRD analysis, indicating that the average Cu particle size increases with increasing pore diameter and *bulk* metal surface loading. However, the increase in particle size with pore diameter tends to level off for the widest pores, i.e. >11 nm (Supplementary Fig. S3). Thus, the difference in size between silica pores and Cu nanoparticles is smallest for the narrowest pores, for which hence the most severe confinement upon particle growth is expected.

N₂-calcined catalysts showed no CuO diffractions for *bulk* surface loadings $\leq 3 \text{ Cu nm}^{-2}$, indicating highly dispersed species. After H₂-reduction, 2-5 nm Cu nanoparticles were observed by HAADF-STEM for these catalysts (*vide infra*). For higher Cu surface loadings, CuO diffractions were detected in the calcined materials. The line broadenings correspond to crystallite sizes of 10-12.5 nm. In all cases the peak intensities of the CuO diffraction lines were lower for N₂-calcined catalysts than for their NO-calcined counterparts. This indicates that after N₂ calcination not all CuO species are crystalline. To compare the CuO crystallinities in these two series of materials, the X-ray diffractograms were normalized to the intensity of the amorphous SiO₂ scattering band (Fig. S1). The integrated CuO peak areas were corrected for the Cu loading. In the N₂-calcined catalysts with *bulk* surface loadings of 4, 6 and 8 Cu nm⁻² the amount of crystalline CuO was only 14, 40 and 88%,

respectively, of that in the NO-calcined counterparts. Therefore, the relatively large CuO crystallites in N₂-calcined catalysts coexist with a fraction of highly dispersed copper species which lack long-range crystallinity, and hence cannot be detected by XRD. These results indicate that calcination in N₂ flow provides an efficient dispersion of the Cu species on the available SiO₂ surface for metal surface loadings up to ca. 3 Cu nm⁻². At higher Cu surface contents, the surplus metal results in larger CuO crystallites.

N₂O RFC was employed to measure the Cu surface areas for selected as-reduced catalysts with 2 Cu nm⁻² (Table 2). In line with XRD results, calcination in N₂ flow results in catalysts with the highest metal surface areas, i.e. 90-130 m² g_{Cu}⁻¹ versus 75-78 m² g_{Cu}⁻¹ for NO-calcination. For samples with the smallest pore size, 5 nm, at first sight unexpected results were found. N₂O RFC revealed a lower active surface area for CuZn/SG5(2)-NO than for a catalyst prepared on a wider pore support, i.e. CuZn/SG11(2)-NO, in apparent contradiction to XRD and STEM analysis. Also, CuZn/SG5(2)-N₂ showed 19-29% lower surface area than N₂-calcined catalysts supported on wider-pore silicas SG11 and SG15. The lower than expected areas for catalysts supported on SG5 might relate to the blockage of a larger fraction of the metal surface area by direct contact with the silica pore walls, due to the similar dimensions of the Cu nanoparticles and the silica mesopores [61].

Concluding, small Cu nanoparticles, predominantly <10 nm, are obtained with both catalyst calcination protocols. Average Cu particle size increases with increasing support pore size for catalysts calcined in 2%NO/N₂. When N₂ flow is applied during the calcination, Cu nanoparticles smaller than ca. 5 nm are obtained for *bulk* Cu surface loadings below 3 Cu nm⁻², irrespective of the support pore size, which co-exist with larger metal crystallites (>10 nm) at higher Cu surface loadings.

3.1.2. Spatial distribution of the Cu nanoparticles

Bulk characterization methods offer average information on metal particle size, loading, and exposed Cu surface area, but fall short to provide insight into deviations from the overall properties at the nanoscale. Therefore, ultrathin sections of the CuZn/SiO₂ catalysts were obtained by microtomy and characterized by HAADF-STEM and EDX. HAADF-STEM is particularly suitable to image

nanosized metal crystallites supported on SiO₂ since contrast scales strongly with the atomic number (Z) [62]. EDX provides local, quantitative chemical analysis at the micron and nanoscales. Besides, the use of microtomed specimens allows for visualization of extended regions of the samples while minimizing variations in the resolution due to differences in sample thickness.

Fig. 2 shows HAADF-STEM micrographs for selected N₂-calcined catalysts after H₂-reduction. Uniform Z-contrast levels within the micron-sized regions indicate a homogeneous distribution of the metal species, irrespective of whether wide or narrow pore silica is used as support (Figs. 2a and 2b). In addition, high magnification observation allowed imaging the small (ca. 2-5 nm) Cu nanoparticles evenly distributed throughout the SiO₂ support.

In contrast, for NO-calcined catalysts after H₂-reduction, bright patches distributed throughout the silica support are observed at low magnifications (Fig. 3a), corresponding to regions with high local metal content. The size of these *high-metal-density domains* (HMDD) ranges from ca. 20 nm to a few microns (Fig. 3b), and their average size increases with increasing the overall Cu pore volumetric loading. Higher magnification imaging revealed that these domains consist of individual Cu nanoparticles in very close proximity (Fig. 3c). EDX showed insignificant Cu concentrations on the SiO₂ support outside the HMDD. Remarkably, the present series of NO-calcined materials constitutes a relevant case, as similar non-uniform distributions of metal particles are found in other technically relevant catalysts [43,46,48].

It is clear that such an inhomogeneous spatial distribution of the Cu nanoparticles corresponds to local Cu loadings deviating markedly from the *bulk* Cu content. EDX was employed to quantify the local Cu/Si atomic ratio in the metal domains.

The EDX spectra were collected from regions of typically 100 x 100 nm². These regions were randomly selected along the catalyst section in the case of N₂-calcined materials, which show homogeneous distribution of the metal species. For NO-calcined catalysts, the EDX spectra were acquired from several HMDD with cross-sections larger than 1·10⁴ nm². In this way we ensured that the metal ensembles occupied the entire volume of the sampled microtomed section (nominal thickness of 50 nm). The experimental Cu/Si ratio was used to derive the local Cu surface and pore volumetric loading (Supplementary equations S1 and S2).

Fig. 4 summarizes the results from the EDX study. Given the uniform distribution of metal species in N₂-calcined catalysts, a good correspondence is expected between local and overall metal loading. Therefore, CuZn/SG5(2)-N₂ was used as an internal reference for the EDX analysis. Fig 4a shows the histograms of the local Cu surface loading for selected catalysts calcined in flow of N₂ with an overall Cu surface loading of ca. 2 Cu nm⁻². A spatially homogeneous Cu content was found for catalysts supported on silicas with markedly different pore diameter, which confirm the uniform Cu distribution afforded by the redispersion mechanism operating during calcination in N₂ flow. For N₂-calcined catalysts having overall Cu surface loadings in excess to 3 Cu nm⁻², HAADF-STEM confirmed bimodal size distribution of Cu particles (Supplementary Figure S4). Most regions studied showed well distributed 2-5 nm-sized Cu nanoparticles like those revealed as sole species at lower Cu metal loadings. EDX evidenced a local Cu surface coverage of 3-3.4 Cu nm⁻² in those micron-sized regions. In addition, large Cu aggregates (>20 nm) were sparsely found, which confirmed that Cu content in surplus of 3 Cu nm⁻² formed large Cu particles. Given their size, these additional population of larger Cu particles is not expected to have contributed significantly to the Cu surface area and catalytic activity.

For all NO-calcined catalysts, a rather constant Cu pore volumetric loading of 10.1±2.0 Cu nm⁻³ was locally found in the HMDD (not shown). This result suggests that these domains originate from a common phase, which has locally filled the silica pores during an intermediate stage of the metal precursor decomposition, after which no further Cu redistribution has occurred. Such precursor phase is likely to be a Cu hydroxy-nitrate, i.e. Cu₂(OH)₃NO₃, which was previously identified as an intermediate species during the decomposition of silica-supported Cu nitrate hydrate in NO-bearing atmospheres [52]. Fig. 4b shows the histograms for the local Cu surface loading at the HMDD for several NO-calcined materials with varying pore diameters. The average local metal surface loading exceeds the bulk loading (Table 2) by a factor of 4-7 and increases with increasing the support pore size (Fig. 4c).

For a given pore size, catalysts with different bulk metal loadings were also studied (not included in Fig. 4). For catalysts with low metal content (<8 Cu wt%), i.e. those with overall Cu surface loading of 2 Cu nm⁻² on wide-pore, low-surface silica supports, the cross-section of the

HMDD was generally comparable in size or smaller than the thickness of the microtomed slice. This fact often hampered an accurate determination of the local Cu/Si ratio without contribution from extra-HMDD silica. However, for CuZn/SG11(2)-NO, EDX analysis of few metal domains reaching the minimum required size revealed the same local Cu surface loading, within standard error, as in CuZn/SG11(4)-NO, despite the latter has double the overall Cu loading (results not included in Fig. 4). This provides a further confirmation of the common origin of the HMDD and remarks that, for such non-uniform spatial distribution of the metal species, local Cu surface loading is mainly determined by the support pore size regardless of the bulk metal loading.

In addition, EDX showed a rather uniform distribution of Zn species on the SiO₂ surface regardless of the pore size and calcination protocol, consistent with the formation of surface Zn (hydro)-silicate species by reaction with the silica support [63,64].

The Cu nanoparticle surface density is another relevant parameter for particle growth, as it relates to interparticle spacing. For N₂-calcined catalysts, the spatially uniform Cu surface loading implies that the metal nanoparticles are, on average, maximally spaced. This was previously proven quantitatively by means of electron tomography on similar CuZn/SBA-15 catalysts [53]. The metal nanoparticle surface density was calculated from the EDX-derived local Cu surface loading and the volume-averaged Cu particle diameter determined by HAADF-STEM, assuming spherical particle morphology (Supplementary equation S3). For the evenly distributed Cu nanoparticles found in the N₂-calcined catalysts, an average Cu particle size of ca. 4-5 nm was inferred from high magnification HAADF-STEM micrographs (eg. Fig. 2c). The particle surface density in these catalysts was determined to be 350-700 particles μm^{-2} .

For NO-calcined catalysts, local nanoparticle surface densities in the range of 400-2000 particles μm^{-2} were obtained. As a result of the relationship between pore size and average particle size, the local surface density of Cu nanoparticles in the HMDD decreases with increasing support pore size, in spite of the concomitant increase in Cu surface loading (Fig. 4c). Results for catalysts supported on SG11 with bulk Cu surface loadings of 2 and 4 Cu nm⁻² indicate that the change in bulk metal loading causes minor (<30%) variations in the local Cu nanoparticle surface density at the HMDD.

An important inference is that using bulk loadings to calculate the local metal particle densities, or simply considering both parameters proportional, might result in erroneous conclusions if the spatial distribution of metal species is not uniform at the nanoscale.

3.2. Methanol synthesis

The performance of the CuZn/SiO₂ catalysts was evaluated for methanol synthesis under industrially-relevant conditions. Since the focus of our study is on catalyst stability, the catalytic tests were run at a reaction temperature of 533K, at the high end of the range of industrially-applied temperatures, in order to achieve significant catalyst deactivation within laboratory time-scales.

3.2.1. Initial catalytic performance

The initial methanol yield, normalized to the mass of Cu, ranges from 0.06 to 0.13 mol g_{Cu}⁻¹ h⁻¹ for all the studied catalysts (see Supplementary Fig. S5). This is comparable to the initial activity of the Cu/ZnO/Al₂O₃ reference catalyst (51.4 wt% Cu) under the same reaction conditions (0.13 mol g_{Cu}⁻¹ h⁻¹).

For selected CuZn/SiO₂ catalysts with varying pore sizes and obtained by the two different calcination procedures, for which the exposed metal surface area was determined (Table 2), the initial catalytic activity was normalized per surface Cu atom. All catalysts showed a constant initial surface-specific activity of $(1.8 \pm 0.3) \cdot 10^{-2} \text{ s}^{-1}$. Therefore, differences in Cu mass-specific initial yield seem to be due exclusively to variations in the exposed Cu surface area, rather than to differences in the intrinsic site-activity. We use a substoichiometric amount of H₂ in the syngas feedstock ($\text{H}_2\text{-CO}_2/(\text{CO}+\text{CO}_2) < 2$) [20] and CO+CO₂ conversion levels >10%, the presence of ZnO_x species in close intimacy with the Cu nanoparticles has been previously shown essential to achieve a high catalytic activity. The origin of this effect, generally referred to as Zn promotion or Cu-ZnO_x synergism, is under debate. Possible explanations include the provision of activated hydrogen to the Cu surface from neighbouring ZnO_x species [65], electron transfer effects at the Cu-ZnO_x boundary [66], formation of surface alloys, and stabilization of surface-terminated Cu lattice defects by ZnO_x species [67]. Under our experimental conditions, Cu/SiO₂ catalysts without ZnO_x species gave notably

lower initial catalytic activities (Cu particle sizes in the range of 3-7 nm, TOF of $4.5 \cdot 10^{-3} \text{ s}^{-1}$). This confirms the relevance of Zn promotion under the applied reaction conditions. As similar surface specific activities were determined for the different ZnO_x promoted catalysts, the required intimacy between the Cu nanoparticles and highly dispersed Zn species was in all cases attained after catalyst reduction.

3.2.2. Catalyst stability

The evolution of the normalized methanol yield with time-on-stream during the exposure of the CuZn/SiO₂ catalysts to methanol synthesis conditions is given in Fig. 5. For the sake of clarity, only catalysts with $\delta_{\text{Cu,S}}$ of 2 Cu nm⁻² are included, while similar deactivation curves were obtained for catalysts with higher metal surface loadings. Under the applied reaction conditions, the catalytic activity dropped with 50% - 80% in the first 240 hours on-stream. Pore blockage did not contribute to the measured catalyst deactivation since N₂-physisorption revealed negligible loss of pore volume on prolonged exposure to catalysis (Supplementary Table S1). Our previous investigations on similar CuZn/SBA-15 catalysts exposed to the same reaction conditions [53] revealed that Cu particle growth correlates with catalyst deactivation, although it does not fully account for the observed activity decay. Similar results were obtained for the present CuZn/SiO₂ catalysts (Supplementary Fig. S6). This suggests that particle growth brings about additional secondary effects on the catalytic activity, which might be explained by a deterioration of the interaction with the Zn promoter species.

Significant differences in the deactivation rates were observed for catalysts calcined in 2%NO/N₂ flow as a function of the pore diameter of the SiO₂ support (Fig. 5a). In contrast, N₂-calcined counterparts showed minor differences in the deactivation curves for different pore sizes (Fig. 5b).

Power-law equations of the type

$$da/dt = -k_d \cdot a^n \quad (1)$$

have been extensively used to describe experimental catalyst deactivation by metal particle growth [68,69,70,71]. In equation (1), a typically denotes the exposed metallic surface area or the catalytic activity, t is the time-on-stream, k_d the deactivation rate constant at a given temperature and n

an exponent usually ranging from 2 to 10. Equation (1) was used to fit the experimental deactivation curves for our CuZn/SiO₂ catalysts. In all cases the best fit was found for exponents of 2 ± 0.3 . Although the exponent n is assumingly related to the growth mechanism, no consensus exists on its interpretation. In particular, an exponent n of 2 has been previously ascribed to fundamentally different growth mechanisms such as Ostwald ripening mediated by gas-phase atom transport [72] and particle migration-coalescence for which the particle coalescence events are rate-limiting [73]. For CuZn/SBA-15 catalysts similar to those reported in this study, we recently found that particle coalescence events likely contribute to Cu particle growth when metal particles are in close proximity [53] as those present in the HMDD of the NO-calcined catalysts. In order to consistently compare the deactivation rates for different catalysts, all the deactivation curves were fitted to the linear integrated form of a second-order law, i.e. $n=2$, and the corresponding deactivation rate constants ($k_{d,2}$) were determined (Supplementary Fig. S7). The dependence of the second-order deactivation rate constant with the support pore size is shown in Fig. 6.

For NO-calcined catalysts with constant pore volumetric Cu loading, the deactivation rate constant steeply increases (more than fivefold) on increasing the support pore size from 5 to 23 nm. For a given pore diameter in the range of 5-11 nm, the deactivation rate constant for NO-calcined catalysts with up to twofold difference in overall Cu surface loading is virtually the same. This is in agreement with the fact that key structural properties such as Cu particle size and local nanoparticle surface density are largely determined by the support pore size and depend only weakly on the applied overall metal loading, as shown by HAADF-STEM/EDX. The general trend of increasing deactivation rates with increasing pore diameter also applies for the series of NO-calcined catalysts with a $\delta_{\text{Cu,S}}$ of 2 Cu nm⁻². In this case, however, the trend tends to level off for pores wider than 11 nm. The reason underlying this specific trend is not certain yet, and requires further investigation. Given that low-concentration nitrate solutions (< 2M) are required to attain surface Cu loadings of 2 Cu nm⁻² on silica supports displaying large pore sizes and low specific surface areas, it is speculated that strong electrostatic adsorption of the metal cations [74] may play a role.

Lower deactivation rate constants are observed for the N₂-calcined catalysts, which are ascribed to the maximal interparticle spacings afforded by the Cu redispersion during catalyst

calcination [53]. For a given pore size, the deactivation rate constant is virtually insensitive to the bulk Cu surface loading. This observation can be rationalized considering that the amount of highly dispersed Cu species is practically the same in all catalysts ($2\text{-}3\text{ Cu nm}^{-2}$), regardless of the overall metal loading, as ascertained by XRD and HAADF-STEM (*vide supra*). The associated small Cu nanoparticles are seemingly the main contribution to catalysis and, given their similar sizes ($2\text{-}5\text{ nm}$) and surface density, comparable rates of particle growth and catalyst deactivation are expected. Remarkably, in contrast to the behaviour observed for NO-calcined catalysts, $k_{d,2}$ remains largely unchanged in the pore size range of $5\text{ to }23\text{ nm}$.

According to these findings, the dependence of catalyst deactivation on pore size is very sensitive to the spatial distribution of the Cu nanoparticles. This observation might relate to differences in the dominant growth mechanism.

3.2.3. Particle growth mechanisms

For NO-calcined catalysts, the increment in the deactivation rate with pore size coincides with an increase in the (initial) average Cu particle size and a decrease in the local nanoparticle surface density. Notably, the opposite dependence on these parameters would be expected for a growth mechanism based on particle migration and coalescence with unrestricted particle mobility, as on flat surfaces [17,72]. When metal nanoparticles are hosted in mesopores, however, additional effects of pore size and corrugation on particle mobility must be considered [39]. It is reasonable to assume that when the diameter of the metal nanoparticles reaches the size of the pores, the surface diffusion becomes impeded. Indeed, our results point to a direct influence of pore confinement on Cu particle mobility. The deactivation becomes progressively slower upon decreasing support pore size. Given that for catalysts with small pores the initial Cu particle size is very similar to the pore diameter (e.g. $6.4\text{ or }6.8\text{ nm}$ Cu particles in SG7 possessing 6.9 nm pores) in the course of Cu particle growth, an increasingly larger fraction of Cu nanoparticles are expected to reach the size of the silica pores and become less mobile (or immobile). For gradually wider pores, the difference between initial particle size and pore diameter becomes larger (e.g. 8.6 nm Cu particles in SG15 having 15.2 nm pores). Hence, the larger pores literally leave the metal particles more room to move around, collide and

coalesce into larger particles, which would explain the increase in catalyst deactivation rates with increasing pore size. Hence the effect of pore size on catalyst stability for Cu nanoparticles grouped in HMDD with very short interparticle distances is coherent with an impeded mobility of the Cu nanoparticles when their size approaches that of the silica pores. However, the contribution of Ostwald ripening to particle growth cannot be ruled out. Indeed, a higher driving force for ripening would be expected on increasing support pore size, as the Cu particle size distribution also broadens for progressively wider pores in this series of NO-calcined catalysts (see Supplementary Fig. S2).

Remarkably, catalysts with the narrowest pores (5 nm) show the same deactivation behaviour irrespective of the calcination procedure, i.e. regardless of the spatial distribution of the Cu nanoparticles. Catalysts prepared on SiO₂ with even narrower pores of 3.5 nm (not shown) exhibited the same behaviour. For such narrow pore sizes, confinement of Cu nanoparticles by the pore walls is likely and already occurs in the reduced state, as judged from the discrepancies between Cu particle size and available Cu surface area (*vide supra*). Hence particle migration is expected to be hindered.

Interestingly, virtually the same deactivation rate constants as for catalysts supported on SG5, i.e. the lowest found for all the studied catalysts, are observed for all N₂-calcined catalysts regardless of pore size. Since for this series of catalysts the Cu nanoparticles are evenly spaced on the support, and hence the interparticle distances are larger, the likelihood of particle collision events is also expected to be lower. We hypothesize that in those catalysts showing the highest stability, as particle migration and coalescence is expected to have a lower contribution, Ostwald ripening remains as the dominant particle growth mechanism, giving a rather constant, low, intrinsic deactivation rate.

Conclusions

The relevance of support pore size for the stability of CuZn/SiO₂ model methanol synthesis catalysts depends strongly on the distribution of the Cu particles at the nanoscale. For catalysts displaying Cu nanoparticles grouped in high-metal-density domains, with small interparticle spacings, the deactivation rate is strongly sensitive to the support pore size. Conversely, deactivation rates are virtually independent of pore size in the range of 5-23 nm when the Cu nanoparticles are evenly distributed on the support surface. Quantification of Cu particle size and local surface density by HAADF/STEM-EDX enables rationalization of the interplay between these different structural

properties and is essential for a plausible mechanistic interpretation of the different dependences of particle growth rates on pore size. Overall, our results illustrate that local, nanoscale rather than overall properties of supported catalysts must be considered to rationalize the relevance of structural parameters, such as metal content and pore size, for catalyst stability.

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Table 1: Textural properties of the silica gel supports as determined by N₂-physisorption.

Support	A _{B.E.T.} ^a (m ² /g)	V _p ^b (cm ³ /g)	d ^c (nm)
SG5	573	0.63	5.0
SG7	522	0.82	6.9
SG11	354	1.03	10.9
SG15	328	1.20	15.2
SG23	299	1.43	22.8

^a B.E.T. specific surface area; ^b Total pore volume; ^c Pore diameter.

Table 2: Copper content, particle size and surface area in the CuZn/SiO₂ catalysts.

Catalyst	Conc. ^a (M)	Cu ^b (wt%)	δ _{Cu,S} ^c (Cu nm ⁻²)	d(CuO) _{XRD} ^d (nm)	d(Cu) _{STEM} ^e (nm)	S _{Cu} ^f (m ² g _{Cu} ⁻¹)
CuZn/SG5(2)-NO	5.0	10.8	2.3	2.4	4.6	77.7
CuZn/SG5(2)-N ₂	5.0	10.2	2.1	n.d. ^g	---	92.3
CuZn/SG7(2)-NO	3.4	10.0	2.3	3.2	6.4	---
CuZn/SG7(2)-N ₂	3.4	9.3	2.1	n.d.	---	---
CuZn/SG7(3)-NO	4.0	10.8	2.8	4.8	6.8	---
CuZn/SG7(3)-N ₂	4.0	11.3	2.6	n.d.	---	---
CuZn/SG11(2)-NO	2.0	7.6	2.4	5.4	7.8	75.3
CuZn/SG11(2)-N ₂	2.0	6.8	2.1	n.d.	---	113.4
CuZn/SG11(4)-NO	4.0	11.8	4.1	6.4	9.7	---
CuZn/SG11(4)-N ₂	4.0	10.7	3.6	10.0	---	---
CuZn/SG15(2)-NO	1.6	6.9	2.3	6.8	8.6	---
CuZn/SG15(2)-N ₂	1.6	6.5	2.2	n.d.	---	129.2
CuZn/SG15(6)-NO	4.0	16.0	6.7	9.5	10.5	---
CuZn/SG15(6)-N ₂	4.0	14.6	5.9	12.5	---	---
CuZn/SG23(2)-NO	1.0	4.6 ^h	1.8	6.7	11.3	---
CuZn/SG23(2)-N ₂	1.0	4.6 ^h	1.8	n.d.	---	---
CuZn/SG23(8)-NO	4.0	17.0 ^h	8.0	9.9	13.1	---
CuZn/SG23(8)-N ₂	4.0	17.0 ^h	8.0	11.8	---	---

^a Total concentration (Cu+Zn) of the aqueous solution of nitrate precursors used to impregnate the SiO₂ support. Cu/Zn atomic ratio was always fixed to 65/35.

^b Copper weight-loading as determined by H₂-TPR.

^c Overall (bulk) copper surface loading, i.e. number of Cu atoms per nm² of SiO₂ support.

^d CuO crystallite size as determined by X-ray diffraction.

^e Surface-averaged Cu particle size as determined by HAADF-STEM after H₂-reduction.

^f Specific copper surface area as measured by N₂O RFC after in situ reduction.

^g n.d.: not detected.

^h Nominal metal loading.

Figure captions

Fig. 1: Pore size distributions for the SiO₂ gel supports as determined by N₂-physisorption.

Fig. 2: HAADF-STEM micrographs for **a)** CuZn/SG11(4)-N₂, **b)** CuZn/SG5(2)-N₂, and **c)** CuZn/SG5(2)-N₂ (high magnification detail of homogeneously distributed Cu nanoparticles, visible as small bright dots) after reduction.

Fig. 3: HAADF-STEM micrographs for **a)** CuZn/SG11(4)-NO, **b)** CuZn/SG15(6)-NO, **c)** CuZn/SG7(2)-NO after reduction, showing high Z-contrast (bright) patches corresponding to *high-metal-density domains*. Panel **c** shows a high magnification view of the Cu nanoparticles in one of the metal domains.

Fig. 4: Histograms of the local Cu surface loading as determined by EDX for **a)** selected N₂-calcined catalysts with an overall Cu surface loading of 2 Cu nm⁻² and **b)** the high-metal-density domains in selected NO-calcined catalysts with a bulk Cu surface loading of 2-8 Cu nm⁻². The histograms were generated from 20-25 measurements. Lines correspond to the Gaussian fits. The catalyst CuZn/SG5(2)-N₂ (included in panel a) was used as internal standard for the EDX analysis. The identity of the silica support has been included in the figures. **c)** evolution of the local Cu surface loading and nanoparticle surface density in the high-metal-density domains with the support pore size for the series of NO-calcined catalysts. Lines are a guide to the eyes.

Fig. 5: Evolution of the normalized methanol yield *versus* the time-on-stream for CuZn/SiO₂ catalysts having an overall Cu surface loading of ca. 2 Cu nm⁻², calcined in a flow of 2%NO/N₂ (**a**) or a flow of N₂ (**b**). Each panel includes catalysts supported on SiO₂ gel with a pore size of (i) 5 nm, (ii) 7 nm, (iii) 11 nm and (iv) 23 nm. Reaction conditions: T=533 K, P=40 bar, synthesis gas feedstock Ar:CO₂:CO:H₂=10:7:23:60 (vol), initial (CO+CO₂) conversion of 15-20%.

Fig. 6: Evolution of the second-order deactivation rate constant ($k_{d,2}$) with the pore size of the SiO₂ support for CuZn/SiO₂ catalysts. Stars and circles represent catalysts calcined in flow of 2%NO/N₂ and flow of N₂, respectively. Open symbols correspond to catalysts with a Cu surface coverage of 2 Cu nm⁻². Closed symbols represent catalysts with a Cu pore volumetric loading of 1.6 Cu nm⁻³, which corresponds to Cu surface loadings of 3-8 Cu nm⁻². Lines are guide to the eye.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Electronic Supplementary Information

Interplay between pore size and nanoparticle spatial distribution: consequences for the stability of CuZn/SiO₂ methanol synthesis catalysts

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Supplementary methods.

Purity specifications for the SiO₂-gel supports.

Typical maximum levels of the most common impurities in the employed silica gel supports, according to certificate of analysis provided by the manufacturer, are the following. SG5 (Merck): Fe₂O₃<0.05%, SO₄²⁻<0.1%, heavy metals<5·10⁻⁴%; SG7, SG11, SG15 and SG23 (Davisil grades from Grace): Fe₂O₃<0.014%, Na₂O<0.15%, SO₄²⁻<0.1%, heavy metals<5·10⁻⁴%.

Synthesis of reference Cu/ZnO/Al₂O₃ catalyst.

The reference catalyst was synthesized by a standard co-precipitation procedure at constant temperature and pH. Aqueous solutions of Cu, Zn and Al nitrates (1M, atomic ratio 55:30:15) and Na₂CO₃ (1.5 M) were added dropwise to deionized water at 338 K keeping the pH constant at 7.0±0.1. The obtained precipitate was aged for 2 h at 338 K in the mother liquor, filtrated, extensively washed with water, dried at 343K and calcined at 673K in a muffle oven.

Supplementary figures.

Fig. S1: X-ray diffractograms of the CuZn/SiO₂ catalysts calcined in a flow of 2%NO/N₂ (a) and in a flow of N₂ (b). All diffractograms have been normalized to the intensity of the scattering band of the amorphous silica support ($2\theta \approx 26^\circ$).

Fig. S2: HAADF-STEM micrographs and the corresponding Cu particle size histograms for selected CuZn/SiO₂ catalysts with a bulk Cu surface loading of 2 Cu nm⁻² supported on **a)** SG5, **b)** SG7, **c)** SG11, **d)** SG15 and **e)** SG23 after calcination in 2%NO/N₂ and reduction.

Fig. S3: Dependence of the Cu particle size on support pore diameter for catalysts calcined in a 2%NO/N₂ flow. The plot represents the surface-averaged Cu particle as derived from the HAADF-STEM analysis on the as-reduced catalysts *versus* the support pore diameter as determined by N₂-physisorption. Closed symbols represent catalysts with constant bulk Cu surface loading (ca. 2 Cu nm⁻²), whereas open symbols represent catalysts with constant Cu volumetric loading (ca. 1.6 Cu nm⁻³).

Fig. S4: HAADF-STEM micrographs of ultrathin (50 nm) sections of CuZn/SG11(4)-N₂ (a-c) and CuZn/SG15(6)-N₂ catalysts after H₂-reduction. Some of the shown micrographs correspond to higher-magnification details of the red-framed regions in the low-magnification overview micrographs. Cu nanoparticles are perceived as bright objects (higher Z-contrast). Large Cu aggregates appear contrast-saturated in order to make it possible the observation of the neighboring smaller Cu nanoparticles.

For N₂-calcined catalysts with bulk Cu surface loading $>3 \text{ Cu nm}^{-2}$, HAADF-STEM confirms the existence of two populations of Cu particles. Small (2-5 nm) Cu nanoparticles appear uniformly distributed within micron-sized regions of the silica support. In these regions, EDX evidenced a local Cu surface coverage of 3 Cu nm^{-2} for the catalyst supported on SG11 (panels a-c) and 3.4 Cu nm^{-2} for the catalyst supported on SG15 (panels d-f). In addition, large Cu aggregates ($>20 \text{ nm}$) were also found. These Cu aggregates are generally located in the pores of the silica support. For CuZn/SG15(6)-N₂, with larger bulk Cu surface loading, the Cu aggregates constitute a larger fraction of the metal in the catalyst and are, on average, larger in size. The Cu aggregates reach sizes of even $>100 \text{ nm}$ when they are located on the external surface of the SiO₂ particles (see panel e).

Fig. S5: Copper-normalized initial methanol yield as a function of support pore size for CuZn/SiO₂ catalysts calcined in 2%NO/N₂ flow (a), and N₂ flow (b). Reaction conditions: T=533 K, P=40 bar, synthesis gas feedstock Ar:CO₂:CO:H₂=10:7:23:60 (vol), initial (CO+CO₂) conversion of 15-20%.

Fig. S6: HAADF-STEM micrographs after reduction and after 240 hours on-stream under methanol synthesis conditions, and the corresponding Cu particle size histograms for CuZn/SG5(2)-NO (**a-c**) and CuZn/SG15(6)-NO (**d-f**).

For selected catalysts showing different deactivation behaviors, HAADF-STEM was employed to investigate Cu particle growth by comparing the Cu particle size in the as-reduced state (prior to catalysis) and after the extended catalytic tests. Extensive metal sintering was observed for the wide-pore CuZn/SG15(6)-NO catalyst, for which large Cu aggregates (>30 nm) were observed after catalysis. Besides, worm-like Cu shapes were suggestive of particle coalescence constricted by the support porosity (inset to Fig. S5e). More limited Cu particle growth was evident for CuZn/SG5(2)-NO, in agreement with the lower deactivation observed. An intermediate behavior was observed for CuZn/SG11(4)-NO (not shown). Analysis of the size histograms translated into a decrease in the Cu surface area of 29% and 62% for CuZn/SG5(2)-NO and CuZn/SG15(6)-NO, respectively. Hence, the measured particle growth correlated with deactivation, but did not fully account for the observed activity decay. The discrepancies suggest that metal particle growth brings about additional undesired effects on the catalytic activity, possibly deterioration in the interaction with the Zn promoter species.

Fig. S7: Linear fits of the inverse of the normalized methanol yield (a^{-1}) versus time-on-stream for CuZn/SiO₂ catalysts with δ_{Cu} of 2 Cu nm⁻² calcined in a flow of 2%NO/N₂ (a) or a flow of N₂ (b). The slope of the linear fit corresponds to the deactivation rate constant for a second order deactivation law of the type $da/dt = -k_{d,2} \cdot a^2$, where a denotes the normalized catalytic activity (methanol yield), t is the time-on-stream and $k_{d,2}$ is the deactivation rate constant. Dots represent the experimental points and the red line depicts the linear fit. Data have been fitted for times-on-stream (TOS) > 25 hours, since in all cases a slightly faster deactivation was observed during the first 20 hours on-stream, followed by a “terminal” deactivation kinetics which better represents the deactivation behavior of the catalysts.

Table S1: Assessment of pore blockage by N₂-physisorption for selected catalysts in their calcined state (as-synthesized) and after exposure to methanol synthesis conditions for 240 hours.

Support/Catalyst	B.E.T. ^a (m ² /gSiO ₂)	PV ^b (cm ³ /gSiO ₂)	PV loss ^c (%)
CuZn/SG5(2)-NO	509	0.57	---
CuZn/SG5(2)-NO (after catalysis)	486	0.56	2
CuZn/SG5(2)-N ₂	512	0.57	---
CuZn/SG5(2)-N ₂ (after catalysis)	492	0.56	2
CuZn/SG15(2)-NO	316	0.96	---
CuZn/SG15(2)-NO (after catalysis)	298	0.96	0
CuZn/SG15(6)-NO	306	0.96	---
CuZn/SG15(6)-NO (after catalysis)	288	0.94	2

^a B.E.T. specific surface area.

^b Total pore volume determined by the amount of N₂ adsorbed at P/P₀=0.95.

^c Loss of total pore volume (per SiO₂ mass).

No significant decrease in pore volume was observed for catalysts after exposure to methanol synthesis for 240 hours, regardless of the pore size and metal loading. This result discarded any remarkable pore blockage and therefore ruled it out as a contribution to catalyst deactivation.

Supplementary equations.

Equation S1

$$\delta_{Cu,S}^L = \frac{(Cu/Si) \cdot N_A}{60 \cdot BET \cdot 10^{18}} \text{ (Cu nm}^{-2}\text{)}$$

where $\delta_{Cu,S}^L$ denotes the local Cu surface loading, (Cu/Si) is the atomic ratio determined by EDX, BET is the support specific surface area (m²/g) and N_A denotes Avogadro's number. The macroscopic specific B.E.T. surface area of the silica support is assumed spatially homogenous and therefore representative also locally, at the nanoscale.

Equation S2

$$\delta_{Cu,V}^L = \frac{(Cu/Si) \cdot N_A}{60 \cdot PV \cdot 10^{21}} \text{ (Cu nm}^{-3}\text{)}$$

where $\delta_{Cu,V}^L$ denotes the local Cu pore volumetric loading, (Cu/Si) is the atomic ratio determined by EDX, PV is the support total pore volume (cm³/g) and N_A denotes Avogadro's number. The macroscopic specific pore volume of the silica support is assumed spatially homogenous and therefore representative also locally, at the nanoscale.

Equation S3

$$\delta_{Cu,NP}^L = \frac{\delta_{Cu}^L \cdot AW}{(1/6) \cdot \pi \cdot (d_{Cu})^3 \cdot \rho \cdot N_A} \cdot 10^6 \text{ (NP } \mu\text{m}^{-2}\text{)}$$

where $\delta_{Cu,NP}^L$ denotes the local Cu nanoparticle surface density, expressed per unit surface area of the silica support, AW is the atomic weight of copper, ρ is the density of metallic copper, N_A denotes Avogadro's number, and d_{Cu} is the volume-averaged Cu particle diameter as determined by HAADF-STEM. Metal nanoparticles are approximated by spheres with a volume equivalent to the volume of the average particle size determined by microscopy.