

 Open access • Journal Article • DOI:10.1021/JP201839S

Dynamic Cu/Zn Interaction in SiO₂ Supported Methanol Synthesis Catalysts Unraveled by in Situ XAFS — [Source link](#)

Didier Grandjean, Didier Grandjean, V. Pelipenko, E. D. Batyrev ...+4 more authors

Institutions: Utrecht University, Laboratory of Solid State Physics, University of Amsterdam

Published on: 28 Sep 2011 - Journal of Physical Chemistry C (American Chemical Society)

Topics: X-ray absorption fine structure and Bimetallic strip

Related papers:

- [In Situ Investigations of Structural Changes in Cu/ZnO Catalysts](#)
- [The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts](#)
- [On the issue of the active site and the role of ZnO in Cu/ZnO methanol synthesis catalysts](#)
- [The influence of La doping on the catalytic behavior of Cu/ZrO₂ for methanol synthesis from CO₂ hydrogenation](#)
- [Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/dynamic-cu-zn-interaction-in-sio2-supported-methanol-259cp2abpi>

Dynamic Cu/Zn Interaction in SiO₂ Supported Methanol Synthesis Catalysts Unraveled by in Situ XAFS

Didier Grandjean,^{*,†,‡} Vladimir Pelipenko,[§] Erdni D. Batyrev,^{||} Johannes C. van den Heuvel,^{||} Alexander A. Khassin,[§] Tamara M. Yurieva,[§] and Bert M. Weckhuysen[‡]

[†]Laboratory of Solid State Physics and Magnetism & INPAC, K. U. Leuven, Celestijnenlaan 200D, B-3001, Leuven, Belgium

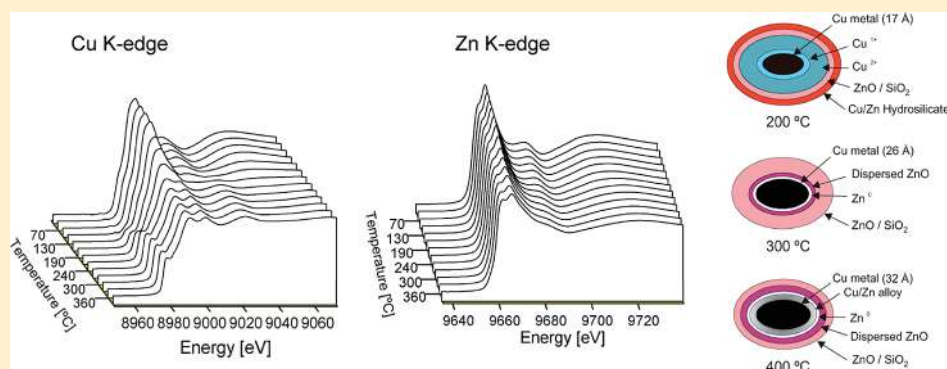
[‡]Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

[§]Boreskov Institute of Catalysis, Ak. Lavrentieva 5, Novosibirsk 630090, Russia

^{||}van't Hoff Institute for Molecular Sciences, University of Amsterdam, PO Box 94157, 1090 GD Amsterdam, The Netherlands.

S Supporting Information

ABSTRACT:



In situ X-ray absorption spectroscopy XAFS at the Cu and Zn K-edge has been used to unravel the Cu/Zn interaction and identify the possible active site of Cu-based methanol synthesis catalysts in the Cu/ZnO/SiO₂ ternary system. These highly dispersed silica supported catalysts, whose activity increases sharply as a function of the reduction temperature, were studied calcined, reduced at 200, 300, and 400 °C, and for each reduction temperature under passivation/rereduction and methanol synthesis conditions. Results showed that the calcined form consists mainly of a mixed Cu/Zn hydrosilicate that is progressively transformed as the reduction temperature increases into (i) Cu metal particles, (ii) increasingly dispersed ZnO species on SiO₂, and (iii) finally a Zn metallic phase forming segregated bimetallic Cu–Zn α -brass alloy particles. These different structures and Cu/Zn interfaces may correspond to different active phases and activities in methanol synthesis. After reduction at 200 and 300 °C, Cu⁰ is likely composing most of the active phase, whereas above 300 °C, the sharp increase in the number Zn⁰-based sites formed as a function of the reduction temperature could explain the major role played by this parameter in controlling the activity of these catalysts. The dynamic Cu/Zn interaction as a function of the temperature and gas environment pointed out in this ternary system may be at the origin of the existence of different and sometimes contradictory models to account for the mechanisms of the methanol synthesis.

1. INTRODUCTION

Cu/ZnO based catalysts are highly selective and active for the low pressure synthesis of methanol,¹ which is a principal feedstock for the production of many organic compounds and an important power supplier in fuel cells.² Although these copper catalysts have been investigated for some decades, the nature of the active sites as well as the role of promoters is still debated. As a consequence, catalyst design and optimization are rather empirical.

Three main theories may be distinguished concerning the active state of copper in catalysts for methanol synthesis, viz., Cu⁰, Cu¹⁺, and a Cu–Zn alloy.^{3–5} Depending on the gas phase

and temperature, dynamic behavior of the structure has been observed for which various models⁶ have been developed: wetting/nonwetting phenomena of ZnO by metallic Cu particles,^{7,8} flat epitaxial Cu particles on top of ZnO balanced by dissolved protons,⁹ and coverage of Cu particles or mixed oxide by ZnO_x species.¹⁰

A major factor that is influencing the nature of the active site and the catalytic activity of these Cu/Zn catalysts is the reduction

Received: February 24, 2011

Revised: August 30, 2011

Published: August 30, 2011

temperature.^{11–13} Indeed, after reduction at 400 °C, SiO₂-supported Cu/Zn catalysts feature a sharp increase in the rate of methanol synthesis corresponding to a large dispersion of the Cu/ZnO phase on the support.¹⁴ This enables tuning of the catalyst activity by varying the reduction temperature, and allows systematic investigations on the nature and formation of the active site. Another factor that will significantly influence the active phase concerns the nature of the calcined state before reduction. However, this aspect has received less attention so far. Fujitani et al.¹⁵ already observed that formation of an intimately mixed Cu/Zn/carbonate aurichalcite phase during the preparation stage enhanced the creation of a Cu–Zn alloy, which they identified as the main active site in methanol synthesis after calcination and reduction. Similarly, under nonhydrothermal conditions the formation of a copper–zinc hydrosilicate phase of the zincsilite-type was demonstrated in the Cu/ZnO/SiO₂ (CZS) system by Yurieva et al.^{16,17} using XRD, HRTEM, and IR. The occurrence of this phase was further confirmed in a more recent investigation of the CZS system that pointed out a linear increase of the activity in the methanol synthesis with the Zn content, indicating the active site may also be closely related to the Zn phase.¹⁸

In order to get a better understanding of the structure as well as the nature and formation of the active surface in these ternary CZS catalysts, an extensive characterization under various gas and temperature treatments was performed using in situ XRD, N₂O chemisorption, HRTEM, ICP-AES¹⁹ and LEIS.^{10,20} An important result of these investigations was that they showed that the surface of the most active catalyst reduced at 400 °C was strongly enriched with ZnO_x species (0 < x < 0.8). However due to the complex and disordered nature of these CZS materials, a clear picture of the real structure could not be unambiguously drawn from the previous characterization methods.

To complete these techniques, we present here a systematic in situ X-ray absorption fine structure (XAFS) study at the Cu and Zn K-edge in the CZS system. XAFS is element specific and enables extensive structural characterization of materials that lack detectable long-range order and is particularly well suited to study the active phase of bimetallic catalysts.²¹ For these reasons, XAFS was applied successfully to characterize several types of binary Cu/ZnO systems.^{8,22–29} If a large variety of this catalyst was investigated at the Cu K-edge, few measurements at the Zn K-edge^{26,28,30,31} have been reported due to the bulk nature of the ZnO phase when used as a support. In a recent study, XAFS carried out at both the Cu and Zn K-edge on ball-milled Cu/ZnO catalysts allowed us to identify new highly mixed phases in the Cu/ZnO system.^{30,32} However, no XAS studies have been reported on Zn promoted silica supported Cu catalysts.

The metals oxidation state and coordination in the ternary CZS system have been studied ex situ after calcination, and in situ during reduction at 200, 300, and 400 °C corresponding to increasing catalytic activity.^{6,14} The reduction treatment was followed by a passivation/reduction cycle to probe the nature of the active site located on the surface, and a subsequent methanol synthesis to monitor in situ the changes occurring to the active phase under working conditions. This sequence was shown to fully preserve the enhanced catalyst activity, rendering it relevant to practical applications.⁶ To evaluate the role of the different constituents 2 additional binary systems have been included in this study: a nonpromoted Cu/SiO₂ (CS) and a copper free Zn/SiO₂ (ZS) material. Similarly, to study the influence of the reduction temperature, a CZS material reduced

ex situ at 627 °C and subsequently passivated was investigated. This detailed investigation is essential to address the central question concerning the nature and the formation of the active surface in Cu/ZnO/SiO₂ catalysts and the crucial role played by the Cu–ZnO interface.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Catalysts. Cu/SiO₂, Cu/ZnO/SiO₂, and ZnO/SiO₂ catalysts were prepared by homogeneous deposition precipitation of copper nitrate trihydrate (Merck, > 99.5% pure) and/or zinc nitrate hexahydrate (Janssen, > 98% pure) onto Aerosil 200 silica (Degussa) according to Van der Griff et al.³³ During precipitation the pH was raised by decomposition of urea (Aldrich, >98% pure) at 90 °C; three equivalents urea were used per equivalent of metal. The required amounts of metal nitrates, urea and 10 g silica were added to 1 L of doubly distilled water and adjusted to pH 3.0 using a 0.1 M nitric acid solution. Subsequently, the temperature was raised to 90 °C and kept for 24 h while vigorously stirring. The precipitate was washed twice with doubly distilled water and dried at 90 °C overnight. Subsequently, the precipitate was crushed and sieved to obtain the required size of the silica particles of 125–212 μm. The metal loading of the prepared catalysts determined by inductively coupled plasma atomic emission spectroscopy amounted to Cu/SiO₂ (12.9 ± 0.5 wt % Cu), Cu/ZnO/SiO₂ (12.9 ± 0.5 wt % Cu, 4.8 ± 0.2 wt % Zn, Cu/Zn = 2.8, (Cu+Zn)/Si = 0.09), and ZnO/SiO₂ (9.2 ± 0.4 wt % Zn). Catalysts were calcined in a Setaram TG-85 thermobalance by heating 200 mg of as-prepared material in a porous basket in a flow of 2 cm³/s dry air at 477 °C for 12 h.¹⁹

2.2. X-ray Absorption Spectroscopy. X-ray absorption data were collected on beamline DUBBLE (BM26A) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), operating under beam conditions of 6 GeV, 200 mA, 2 × 1/3 filling mode. It is equipped with a Si (111) double-crystal monochromator and a vertically focusing Si mirror that suppresses higher harmonics. XAS signals were measured in transmission mode both at the Cu K-edge (8978.9 eV) and the Zn K-edge (9658.6 eV). Cu₂O, CuO, and ZnO powder (Aldrich 99.999%) and zincsilite (Zn₃Si₄O₁₀(OH)₂·4(H₂O) prepared at the Boreskov Institute of Catalysis¹⁶ were used as reference samples. The ionization chambers were filled with Ar/He gas mixtures. For each treatment, EXAFS spectra were measured at the beginning and at the end of each treatment, whereas shorter XANES spectra were recorded continuously throughout the treatment. Both Cu and Zn K-edges were collected in the same data set with acquisition times of less than 30 min for the XANES measurements and up to 90 min for the EXAFS measurement (5 to 25 s/point). Energy resolution was better than 0.5 eV in the XANES regions of Cu and Zn K-edges. Exact calibration of the X-ray energy for detailed comparison of the XANES features was achieved by simultaneously recording a Cu foil spectrum in the monitor position with a third ionization chamber.

Data reduction of experimental X-ray absorption spectra was performed with the program EXBROOK.³⁴ Pre-edge background subtraction and normalization was carried out by fitting a linear polynomial to the pre-edge region and cubic splines to the postedge region of the absorption spectrum. A smooth atomic background was then obtained. EXAFS refinements were performed with the EXCURV98 package.³⁴ phase shifts and backscattering factors were calculated ab initio using

Hedin-Lundqvist potentials. Refinements were carried out using k^3 weighting typically in the range 3.5 to 12 \AA^{-1} . As anharmonic motion at high temperatures of the surface atoms of small metal particles can lead to a reduction of the EXAFS amplitude, materials containing a metallic phase were analyzed with the cumulant expansion approach implemented in EXCURV98³⁴ using the coefficient of linear expansion of Cu metal (17.1×10^{-6} m/m/°C) and a weighted Zn metal coefficient of 10×10^{-6} m/m/°C. Metallic shells consisting both of Cu and Zn that possess similar scattering properties were fitted with a mixed site³⁴ (Cu/Zn) corresponding to a 0.5Cu:0.5Zn occupancy to improve the quality of the fit and the accuracy of the bond distance. The AFAC factors (amplitude reduction due to many-electron processes) calibrated from the fit of the Cu metal foil and Zn metal foil were respectively fixed at 0.9 at the Cu K-edge and 1.0 at the Zn K-edge. Due to the amorphous character of the Cu phases, the oscillations of the Cu K-edge EXAFS continuing beyond the Zn K-edge are significantly damped at $k > 13\text{--}14 \text{\AA}^{-1}$, and did not affect the EXAFS analysis at the Zn edge.

All XAS measurements were carried out in our in-house controlled atmosphere cell³⁵ operating at 1 bar. Appropriate amounts of sample were finely ground with boron nitride and pressed (2 bar) into 0.7 cm² rectangular pellets in a sample holder producing a suitable edge jump. The calcined CZS catalyst was reduced in three different experiments corresponding to three temperatures, i.e., 200 (CZS-R200), 300 (CZS-R300), and 400 °C (CZS-R400), whereas the monometallic samples CS and ZS were only reduced at the highest temperature of 400 °C (CS-R400 and ZS-R400). In each case the reduction was carried out in a flow of 67% H₂ in argon (120 mL/min) with a temperature ramp of 72 °C/h. The sample remained 1 h at the final temperature and after measurement was slowly cooled in the reducing flowing gas. Reduced samples were then passivated by flushing the cell with a gas mixture consisting of 1% N₂O in argon (120 mL/min) at 90 °C during 1 h. After measurements, passivated samples were then rereduced in a flow of 67% H₂ in argon (120 mL/min) at a ramp of 15 °C/min with a reduction temperature 23 °C lower than the corresponding first reduction temperature and measured again in these conditions. Finally CZS catalysts reduced at 200, 300, and 400 °C as well as Zn free CZ rereduced at 377 °C were measured in reaction conditions (methanol synthesis) by flushing them with a syngas mixture of 75% H₂/25% CO₂ (7.5 mL/min) during 3 h at 200 °C.

3. RESULTS AND DISCUSSION

3.1. Calcined CZS Sample. *3.1.1. Cu K-Edge.* The calcined CZS XANES spectrum (Figure 1a) is clearly related to the CuO reference in terms of edge position but features a different profile, as suggested by the higher intensity of the white line. This difference is more obvious when one compares the first derivative of these spectra along with CuO, Cu₂O, and Cu metal references presented in Figure 1b. The absence of the ~8981 eV feature corresponding to the strong pre-edge dipole-allowed 1s–4p transition characteristic of Cu¹⁺ in Cu₂O indicates that copper in CZS consists entirely of Cu²⁺.^{36,37} The weak peak at ~8977.5 eV in CuO that is generally present in all Cu²⁺ compounds corresponds to a 1s–3d quadrupole allowed pre-edge transition that gains intensity in a noncentrosymmetric environment.^{36,38} In CZS the energy of this pre-edge is shifted down by 0.5 eV and its intensity increases 25% relative to CuO reference, suggesting a stronger ligand donor set and a slightly less centro-symmetric Cu

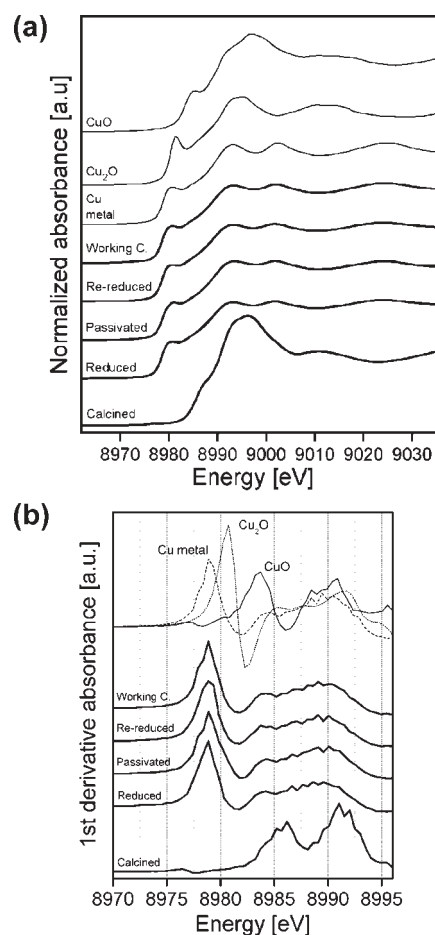


Figure 1. (a) Cu K-edge background subtracted and normalized XANES spectra and (b) first derivatives of the Cu/Zn/SiO₂ material, calcined (CZS), reduced at 400 °C (CZS-R400), passivated in N₂O, rereduced at 377 °C, and under working conditions at 200 °C along with reference bulk samples Cu metal, CuO, and Cu₂O.

environment.³⁶ The peak at ca. 8983.5 eV in CuO attributed to a 1s–4p transition with shakedown contributions,^{38,39} characteristic of tetragonal Cu²⁺ compounds, is shifted up in energy by 2 eV to ~8985.5 eV in CZS suggesting a different ligand charge transfer between the two materials. Finally the second peak at ~8991 eV in CuO assigned to a normal 1s–4p transition³⁸ is located at the same energy both in CuO and CZS. The shoulder at ~8992 eV in CZS corresponding to the edge absorption maximum due to multiple scattering effects, indicates a slightly altered Cu local geometric structure in CZS compared to CuO.⁴⁰ The XANES analysis suggests that, although copper in this material has an oxidation state of 2+, it is forming a phase distinct from CuO.

The main peak around 1.9 Å of the CZS phase corrected Fourier transforms (FTs; Figure 2a) corresponds to an O shell, while the smaller peak around 3.1 Å corresponds to a Cu/Zn shell.

The low intensity of the latter peak and the absence of peaks at higher distances indicate that this material is significantly amorphous or disordered on a nanometer scale. This is in line with the XRD measurements that showed the absence of detectable Bragg peaks.¹⁹ Compared to bulk CuO, the main Cu–O peak is slightly shifted toward higher R, whereas the second peak is

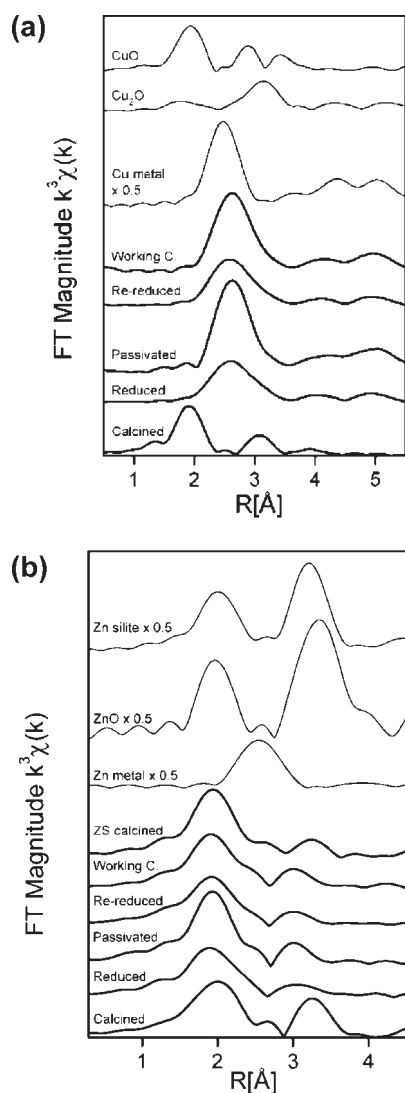


Figure 2. (a) phase-corrected FTs of the Cu K-edge k^3 -weighted EXAFS of the Cu/Zn/SiO₂ material, calcined (CZS), reduced at 400 °C (CZS-R400), passivated in N₂O, rereduced at 377 °C and under working conditions at 200 °C along with reference bulk samples Cu metal, CuO, and Cu₂O; (b) phase-corrected FTs of the Zn K-edge k^3 -weighted EXAFS of the Cu/Zn/SiO₂ material, calcined (CZS), reduced at 400 °C (CZS-R400), passivated in N₂O, rereduced at 377 °C and under working conditions at 200 °C along with calcined binary Zn/SiO₂ (ZS) material and reference bulk samples Zn metal, ZnO, and zincsilite.

located between the peaks that correspond to the typical first and second Cu–Cu shell of the CuO tenorite structure.

The EXAFS analysis (Table 1) shows that Cu is 4-fold coordinated to O with a Cu–O bond distance of 1.951 Å, similar to the typical Cu–O bond distance of 1.956 Å in bulk CuO,⁴¹ whereas the second shell consisting of 2.2 Cu/Zn atoms at 2.965 Å does not correspond to the typical Cu–Cu bond distances of 2.90 or 3.083 Å⁴¹ in tenorite. Due to the strong Jahn–Teller effect that characterizes Cu²⁺ (d⁹ configuration), the copper coordination in the CuO tenorite structure actually consists of highly elongated octahedra with two extra oxygen located at 2.78 Å. Since the contribution of the latter O-shell is very weak (long distance, low coordination and high disorder) and did not improve the fit of the CuO reference it was not

considered in the EXAFS analysis. Consequently, the geometry of Cu cations in CZS material more likely corresponds to highly tetragonally distorted octahedrons. In agreement with the XANES analysis, these results confirm that the Cu atoms do not form a CuO-type phase in CZS.

3.1.2. Zn K-Edge. CZS XANES (Figure 3a) also exhibits a significantly different profile from the ZnO reference compound. On the other hand, a clear resemblance with the profile of zincsilite is observed with a similar wiggle at ~9686 eV. Edge positions measured at half the normalized jump are ~9662.3, ~9662.7, and ~9663 eV for ZnO, CZS, and zincsilite. An edge position similar to the one in zincsilite (9663 eV) is also observed in ZnCO₃ in which Zn adopts a 6-fold coordination.⁴²

The ZnO spectrum shows a main peak located at ~9669 eV with a shoulder at ~9663 eV, corresponding in the first derivative (Figure 3b) to two peaks located at ~9667.5 and ~9661.5 eV, respectively. These features can be assigned to the Zn²⁺ dipole allowed electron transitions relative to the crystallographic axis of wurtzite ZnO 1s – 4p_{a,b} and 1s – 4p_c respectively.^{43,44} No s–d transitions are expected due to the full occupancy of the d-orbital in Zn²⁺ (d¹⁰). The broader white line observed in zincsilite seems mostly due to the intensity increase of the 1s – 4p_c shoulder accompanied with a shift toward higher energies (~9663.4 eV) clearly seen in the first derivative. The general pattern of the first oscillations around 9680 eV, due to multiple scattering effects differs substantially from that of bulk ZnO. The increase in the white line and the first resonance peak (9680 eV) intensities accompanied by a shift to higher energies of the edge (2 eV) have been interpreted as the indicators of the transformation of Zn²⁺ from a tetrahedral to an octahedral coordination^{45,46} and correspond here to the phase transition from zincsilite (octahedral Zn²⁺) to ZnO (tetrahedral Zn²⁺).⁴⁷ CZS, whose first derivative main peak is located halfway between those of ZnO and zincsilite, likely consists of an intermediate phase between these two compounds.

For comparison, Figure 3, panels a and b, also present the XANES spectrum of the Cu-free ZS material. The CZS spectrum profile exhibits a more intense white line and marked oscillations compared to the ZS spectrum, indicating that the Zn environment in ZS is structurally more disordered than in CZS. Comparison of the ZS edge position (~9661.6 eV) as well as the 1s – 4p_c shoulder position (~9662 eV) shows that these values correspond to an intermediate value between those of CZS and ZnO. The ZS XANES profile demonstrates a very close resemblance to those obtained for highly dispersed Zn oxide species on silica at the highest Zn content (30 mol % Zn) in reference⁴⁸ suggesting the formation in ZS of highly dispersed ZnO species on SiO₂.

The FT's of CZS and ZS (Figure 2b) exhibit two peaks, the first at ca. 1.9 Å corresponds to the oxygen contribution and the second at ca. 3.2 Å to a metal shell. The first peak in CZS is shifted toward higher distances compared to that of ZS whereas the position of the second peak in both materials is closer to that of zincsilite than the one of ZnO. In line with the XANES analysis, the lower intensity of the second peak in ZS shows that the Zn phase in this material has a more disordered structure than in CZS. The EXAFS analysis (Table 2) shows that the first shell corresponds to ca. 5.3 O at 2.024 Å in CZS and 4.3 O at 1.973 Å in ZS. In CZS the coordination number corresponding to the first O shell is intermediate between the tetrahedral coordination in ZnO and the octahedral coordination found in zincsilite (6.1), whereas the Zn–O bond distance lies halfway between that of

Table 1. Summary of the Structural Results of Cu K-Edge EXAFS Refinements of Cu/ZnO/SiO₂ and Cu/SiO₂ Materials under Different Treatments^a

sample	treatment	T (°C)	R (%)	E _f (eV)	N atoms	R (Å)	2σ ² (Å ²)	metal particle size (Å)	Cu ^{0/1+/2+} fraction	
bulk Cu	n.a.	RT	21.8	−11.6 (9)	12 ^b Cu	2.560 (2)	0.017 (1)	n.a.	Cu ⁰ -100%	
					6 ^b Cu	3.620 (3)	0.029 (6)			
					24 ^b Cu	4.433 (1)	0.025 (2)			
bulk Cu ₂ O	n.a.	RT	12.4	−9.5 (3)	2 ^b O	1.846 (3)	0.007 (1)	n.a.	Cu ¹⁺ -100%	
					12 ^b Cu	3.014 (5)	0.014 (3)			
bulk CuO	n.a.	RT	29.6	1.1 (9)	4 ^b O	1.953 (7)	0.014 (2)	n.a.	Cu ²⁺ -100%	
					2 ^b Cu	2.745 (9)	0.022 (8)			
					4 ^b Cu	2.89 (3)	0.012 (8)			
					4 ^b Cu	3.08 (3)	0.019 (9)			
Cu/ZnO/SiO ₂ (CZS)	calcined	RT	19.4	3.1(7)	3.7 (2) O	1.951 (5)	0.0011(1)	n.a.	Cu ²⁺ -100%	
					2.2(6) Cu/Zn	2.965(8)	0.0020(4)			
CZS-R400	CZS reduced (CZS-R400) passivated/N ₂ O rereduced working Cond.	400	29	−10.9 (9)	9.9 (9) Cu	2.578(8)	0.0381(2)	32	Cu ⁰ -100%	
		90	30.7	−9.6 (9)	9.6 (9) Cu	2.563 (9)	0.0240 (2)	28	Cu ⁰ -100%	
		377	27.4	−9.5(9)	9.8 (9) Cu	2.574(9)	0.0369(3)	30	Cu ⁰ -100%	
		200	29.5	−9.7(9)	11.1 (9) Cu	2.571(9)	0.0292 (3)	85	Cu ⁰ -100%	
CZS-R300	CZS reduced (CZS-R300) passivated/air	300	24.9	−8.9 (9)	9.3 (9) Cu	2.558(7)	0.034 (1)	26	Cu ⁰ -100%	
		RT	20.2	−10.7 (9)	2.1 (1) O	1.904(7)	0.013 (2)	7	Cu ¹⁺ -31%	
			2.3 (9) Cu	2.57(2)	0.026 (6)		Cu ²⁺ -37%			
	rereduced	277	−9.7 (9)	9.3(9) Cu	2.556 (9)	0.032 (2)	26	Cu ⁰ -100%		
			200	26.8	−10.2(9)	10.3(9) Cu	2.563 (8)	0.0300 (2)	38	Cu ⁰ -100%
		200	30.2	−9.2(9)	7.3 (9) Cu	2.556(9)	0.0292 (2)	17	Cu ¹⁺ -8%	
CZS-R200	passivated/N ₂ O	90	26.7	−10.0 (9)	6.5 (9) Cu	2.553 (9)	0.025 (2)	15	Cu ⁰ -72%	
					1.0 (3) O	1.91 (2)	0.010 (7)		Cu ¹⁺ -22%	
	rereduced	177	29.6	−10.5 (9)	8.1(9) Cu	2.558 (9)	0.028 (2)	19	Cu ²⁺ -13%	
					0.7 (3) O	1.95 (2)	0.011 (9)		Cu ⁰ -65%	
					8.6 (9) Cu	2.560 (9)	0.029 (2)		21	Cu ¹⁺ -3%
	working cond.	200	27.3	−9.9 (9)	0.5 (3) O	1.94 (3)	0.006 (9)	21	Cu ²⁺ -12%	
					8.6 (9) Cu	2.560 (9)	0.029 (2)		21	Cu ⁰ -85%
	CZS-R627	passivated/N ₂ O+O ₂	RT	29.1	−0.1 (9)	1.4 (4) O	1.92(2)	0.011 (7)	12	Cu ¹⁺ -24%
						5.2 (8) Cu	2.572 (9)	0.020 (2)		Cu ²⁺ -22%
	Cu/SiO ₂ (CS)	CS-R400 passivated/N ₂ O+O ₂	RT	18.9	4.3 (7)	2.2 (9) O	1.891(5)	0.002	n.a.	Cu ⁰ -54%
1.4 (5) Cu						2.93 (9)	0.003	Cu ¹⁺ -93%		
CS-R400 rereduced		377	33.7	−9.6 (9)	10.5 (9) Cu	2.572 (9)	0.041(3)	42	Cu ²⁺ -7%	
CS-R400 working cond.		200	30.3	−9.2 (9)	10.1(9) Cu	2.554(9)	0.029(2)	34	Cu ⁰ -100%	

^a T = temperature of measurement. RT = room temperature. R = fit agreement factor. E_f = contribution of the wave vector of the zero photoelectron relative to the origin of k. N = number of atom in the different coordination shells. R = radial distance of atoms. 2σ² = Debye-Waller term (with σ² = Debye-Waller factor). Cu/Zn = mixed Cu/Zn site corresponding to 0.5 Cu: 0.5 Zn occupancy. ^b These parameters were kept fixed during the refinement.

ZnO (1.972 Å) and zincsilitite (2.083 Å). This is in line with the results of a systematic EXAFS investigation of the correlation between Zn–O bond distance and coordination in Zn²⁺ compounds that showed that a Zn–O distance of 2.024 Å in general corresponds to an O coordination number of 5.⁴⁶ The higher R-region in CZS could be fitted with two shells of 5.1 Zn at 2.92 Å and 2.9 Zn at 3.059 Å which differ significantly from the Zn–Zn distance in bulk ZnO (3.19 Å) but are very similar to those of

2.88 and 3.07 Å found in the zincsilitite reference compound (Table 2). These results indicate that in CZS Zn does not form a ZnO bulk phase but rather a hydrosilicate-type phase as proposed by Yurieva et al.^{16–18}

Indeed, their studies on ternary Cu/Zn/SiO₂ systems with different Cu/Zn stoichiometries have already pointed out the formation under nonhydrothermal conditions of Zn, Cu, and mixed Cu/Zn hydrosilicates that were stable up to calcination

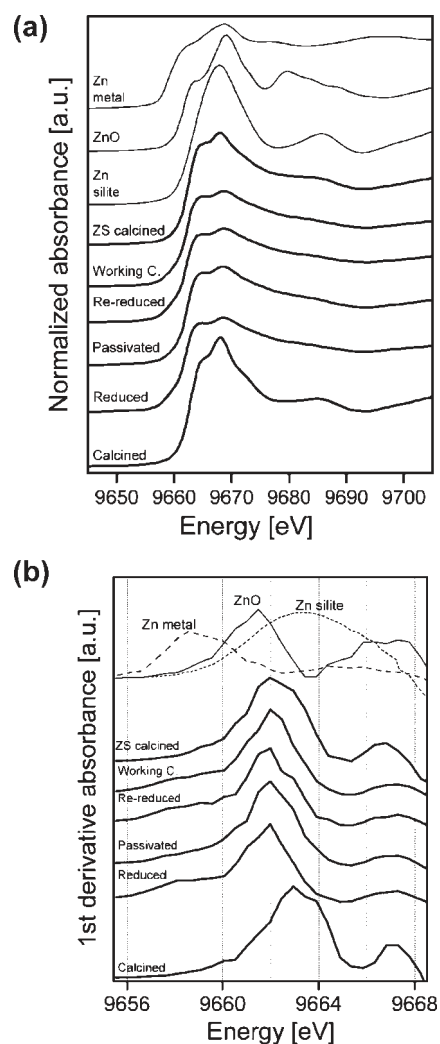


Figure 3. (a) Zn K-edge background subtracted and normalized XANES spectra and (b) first derivatives of the Cu/Zn/SiO₂ material, calcined (CZS), reduced at 400 °C (CZS-R400), passivated in N₂O, rereduced at 377 °C, and under working conditions at 200 °C along with calcined binary Zn/SiO₂ (ZS) material and reference bulk samples Zn metal, ZnO, and zincsilite.

temperatures of 650 °C. More specifically, in Zn/SiO₂ systems with a Zn/Si ratio <0.75, such as in our system, formation of a zincsilite-type structure was reported.¹⁶ This layered silicate belonging to the trioctahedral smectite group consists of ternary layers of tetrahedral and octahedral sheets (TOT), separated by an interlayer of water molecules, in which Zn is expected to fill the octahedral positions.^{16,49} In Cu/Zn/SiO₂ systems, the formation of a mixed copper–zinc hydrosilicate of the zincsilite-type was reported with Cu atoms substituting Zn in octahedral positions.¹⁷

The formation of a Cu–Zn mixed phase is confirmed by the finding that in a similarly treated copper-free ZS material the Zn environment is markedly different from that in CZS. The Zn–O bond distance (1.973 Å) is significantly shorter than that found in CZS (2.024 Å), whereas the coordination number of the metal shell at 2.86–2.92 Å has decreased from 5.1 to 3.2 (Table 2). These results indicate that a hydrosilicate-type phase does not occur in significant amount in its pure Zn counterpart, pointing out the crucial role Cu plays regarding the nature of the formed

phase. As suggested by the XANES analysis, ZS rather consists mainly of ZnO species dispersed on SiO₂.

Although the two Zn–Zn distances found in CZS are in very good agreement with those of zincsilite, the O coordination and Zn–O distances correspond to intermediate values between ZnO and zincsilite phases. This discrepancy may originate from disorder in the zincsilite structure caused by the presence of Cu substituting a significant amount of Zn in the octahedral layer. Indeed, the largely distorted octahedral-like environment of Cu²⁺ with the presence of two long distances that may correspond to a CuO₄(OH)₂ species typical for bivalent cations in a trioctahedral phyllosilicate, is certainly introducing a disorder in this layer that also affects the Zn environment. The presence of Cu atoms in this Zn hydrosilicate-type phase is evidenced by the XANES analysis, and by the short Cu–Cu bond distance that does not belong to a pure CuO-type phase found at the Cu K-edge. Another explanation to this discrepancy in the O coordination is the presence of a limited amount of dispersed ZnO species as observed in Cu-free ZS.

Our results show that in CZS calcination is transforming most of the initial bulk CuO and ZnO phases into a Cu/Zn mixed hydrosilicate-type phase related to the zincsilite-type Zn₃–[Si₄O₁₀](OH)₂·nH₂O. This is supported by the TEM micrograph of the CZS material (Figure 4) that exhibits randomly stacked thin (<3 nm) plates extended from 20 to 100 nm that are typical of many layered silicates, e.g., montmorillonite,⁵⁰ nontronite,⁵¹ smectite⁵², and zincsilite.¹⁷ Although the XRD pattern of CZS did not exhibit any sharp reflections indicating that this material was mostly amorphous and/or that the size of the randomly stacked crystallites was under the detection limit of the XRD technique,¹⁹ a recent XRD study of a similar Cu/Zn/SiO₂ system showed the occurrence of two broad and weak reflections corresponding to a zincsilite-type phase.¹⁸

Regardless of the exact type of its structure, the presence of a hydrosilicate-type phase in the calcined material in which Cu and Zn have a close intimacy is likely at the origin of the formation of a large number of homogeneously dispersed mixed Cu/Zn active sites in the reduced catalyst that could explain the excellent catalytic performance of the reduced material.

3.2. Reduction and Passivation of the Calcined Samples. **3.2.1. Reduction of CZS at 200, 300, and 400 °C.** **3.2.1.1. Cu K-Edge.** Figure S1a shows the stacked background subtracted and normalized XANES spectra measured in situ during the reduction of CZS from room temperature up to 400 °C. Reduction of the copper oxide into copper metal starts at a temperature close to 160 °C and is almost completed at 270 °C as the progressive transformation of the Cu²⁺ XANES spectra into Cu metal shows.

Indeed the XANES profile of the materials reduced at 300 and 400 °C (Figure 5a) closely resemble the profile of the copper foil, indicating that the reduction has proceeded to the apparent full reduction of Cu²⁺ into Cu metal. The damped oscillations compared to the metal foil point out the amorphous character of this metallic phase, or more likely, the presence of nanosized crystallites in these two materials. The slight shift of the maximum from ~8979 eV in the Cu foil to ~8979.5 eV in CZS-R400, -R300 and -R200 suggests that traces of Cu¹⁺ (1s-4p pre-edge transition at 8981 eV) are present in all the CZS reduced materials. The profile (Figure 5a) and first derivative (Figure 5b) of CZS-R200 XANES consist of a combination of the Cu oxide and copper metal spectra showing that in this catalyst only a fraction of the copper atoms have been reduced into metal.

Table 2. Summary of the Structural Results of Zn K-Edge EXAFS Refinements of Cu/ZnO/SiO₂ and ZnO/SiO₂ Materials under Different Treatments^a

sample	treatment	T (°C)	R (%)	E _f	N atoms	R (Å)	2σ ² (Å ²)
bulk ZnO	n.a.	RT	26.1	−4.3 (7)	4 ^b O	1.968 (4)	0.012 (2)
					12 ^b Zn	3.215 (6)	0.019 (1)
					8 ^b O	3.73 (2)	0.016 (6)
					6 ^b Zn	4.60 (2)	0.012 (4)
bulk zincsilite	n.a.	RT	22.1	−0.2 (7)	6.1 (7) O	2.083 (8)	0.022 (3)
					4.6 (9) Zn	2.88 (9)	0.04 (6)
					7.4 (9) Zn	3.07 (2)	0.02 (1)
					2.8 (9) Si	3.30 (6)	0.010 (6)
Cu/ZnO/SiO ₂ (CZS)	calcined	RT	16.7	1.1(9)	5.3 (4) O	2.024 (6)	0.031 (2)
					5.1 (9) Zn	2.92 (9)	0.05 (4)
					2.9 (7) Zn	3.059 (6)	0.02 (1)
					5.5 (9) Zn	4.66 (2)	0.04 (2)
CZS-R400	CZS reduced (CZS-R400)	400	17.2	1.8(9)	3.2 (2) O	1.945 (8)	0.025(2)
					2.4 (8) Cu/Zn	2.58(9)	0.04(9)
					1.7(9) Zn	2.85(4)	0.042(4)
	passivated/N ₂ O	90	18.8	−2.5(8)	3.7(2) O	1.957 (6)	0.018(2)
					1.2 (8) Cu/Zn	2.62 (4)	0.03 (2)
					2.5 (9) Zn	2.87 (2)	0.033(1)
	rereduced	377	20.9	0.9(9)	3.3 (2) O	1.940(9)	0.025(2)
					3.3 (9) CZ	2.59 (5)	0.05 (2)
					3.4 (9) Zn	2.86 (3)	0.04(1)
	working cond.	200	20.8	−1.4(9)	3.5 (2) O	1.945 (8)	0.022 (2)
					3.1 (9) Cu/Zn	2.60 (5)	0.04 (2)
					2.4 (9) Zn	2.86 (3)	0.04 (1)
CZS-R300	CZS reduced (CZS-R300)	300	24.7	0.5(9)	3.8 (3) O	1.945 (8)	0.024 (2)
					1.2 (9) Cu/Zn	2.61(9)	0.04 (4)
					3.3 (9) Zn	2.87 (9)	0.04 (4)
	passivated/air	RT	24.3	−1.7(8)	4.2 (3) O	1.981 (7)	0.022 (2)
					2.5 (9) Zn	2.90 (9)	0.03 (4)
					0.7 (9) Zn	3.07 (6)	0.01 (2)
	rereduced	277	24.5	−1.0 (9)	3.6 (2) O	1.962 (8)	0.024 (2)
					1.1 (9) Zn	2.83 (2)	0.02 (5)
					0.4 (8) Zn	3.0 (1)	0.01 (3)
	working cond.	200	23.0	−1.2(8)	3.9 (2) O	1.963 (7)	0.023 (2)
					1.0 (9) Zn	2.88 (9)	0.02 (5)
					0.3 (8) Zn	3.04 (9)	0.01 (4)
CZS-R200	CZS reduced (CZS-R200)	200	17.0	3.1 (5)	4.6 (3) O	1.985 (5)	0.030 (2)
					3.7 (9) Zn	2.89 (9)	0.05 (4)
					1.0 (8) Zn	3.02 (1)	0.02 (2)
	passivated/N ₂ O	90	17.6	2.7 (5)	4.8 (3) O	1.989 (5)	0.030 (2)
					3.8 (9) Zn	2.91(9)	0.05(5)
					1.1(8) Zn	3.03 (1)	0.02 (2)
	rereduced	177	18.2	2.1 (6)	4.6 (3) O	1.983 (6)	0.029 (2)
					3.8 (9) Zn	2.91 (9)	0.05 (5)
					1.0 (8) Zn	3.02 (1)	0.02 (2)
	working cond.	200	16.5	1.8 (5)	4.5 (2) O	1.985 (6)	0.028 (2)
					3.6 (9) Zn	2.88 (1)	0.04 (4)
					1.1 (2) Zn	3.02 (4)	0.03 (1)
CZS-R627	passivated/N ₂ O/O ₂	RT	21.6	3.3 (9)	3.3 (3) O	1.938 (8)	0.017 (2)
					4.2 (9) CZ	2.57 (2)	0.04 (1)
					2.2 (9) Zn	2.90 (2)	0.03 (1)

Table 2. Continued

sample	treatment	T (°C)	R (%)	E_f	N atoms	R (Å)	$2\sigma^2$ (Å ²)
ZnO/SiO ₂ (ZS)	calcined	RT	16.6	2.1 (5)	4.3 (2) O	1.973(5)	0.022 (1)
					3.2 (9) Zn	2.86 (8)	0.05 (6)
					0.6 (5) Zn	3.03 (1)	0.01 (1)
ZS reduced (ZS-R400)	400	13.7	4.6 (5)	4.6 (5)	3.6 (1) O	1.947 (4)	0.026 (1)
					0.5 (5) Si	3.03(4)	0.001(5)
					0.2 (2) Zn	3.00(4)	0.001(1)

^a T = temperature of measurement. RT = room temperature. R = fit agreement factor. E_f = contribution of the wave vector of the zero photoelectron relative to the origin of k . N = number of atom in the different coordination shells. R = radial distance of atoms. $2\sigma^2$ = Debye-Waller term (with σ^2 = Debye-Waller factor). Cu/Zn = mixed Cu/Zn site corresponding to 0.5 Cu:0.5 Zn occupancy. ^b These parameters were kept fixed during the refinement.

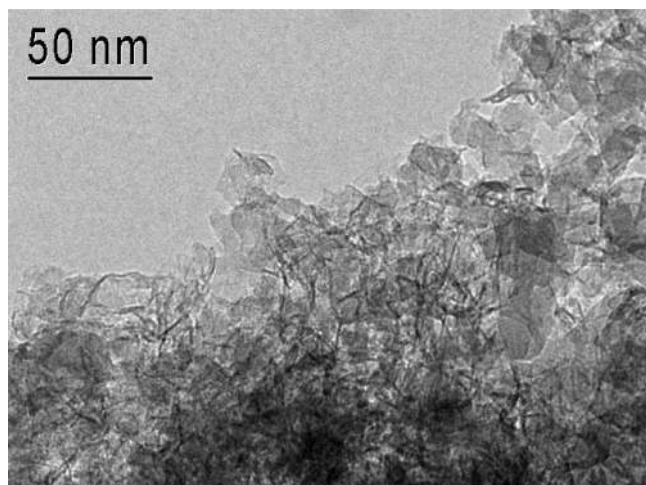


Figure 4. TEM micrograph of calcined CZS; experimental details are described in ref 16.

In particular the peak at ~ 8991 eV (Cu^{2+} 1s-4p transition) has a significant intensity indicating that a large part of the copper atoms have not been reduced and may still be part of the hydrosilicate phase. FT's of the CZS reduced at 200, 300, and 400 °C (Figure 6a) all feature a main peak at 2.5 Å and 2 or 3 low intensity broad peaks located respectively at ca. 4.1, 4.9, and 5.9 Å corresponding all to Cu metallic shell distances. In addition, CZS-R200 shows an extra contribution at ca. 2 Å corresponding to an oxygen shell.

EXAFS analysis (Table 1) using the cumulant expansion approach gives coordination numbers in very good agreement with the corrected values determined by Clausen et al.^{7,53,54} The main peak of the FT corresponds to 9.9 Cu atoms at 2.578 Å in CZS-R400 and 9.3 Cu atoms at 2.558 Å in CZS-R300. These distances are very close to the typical Cu–Cu distance in bulk metallic copper (2.563 Å)⁴¹ and together with the absence of any oxygen shell, show the full reduction of the Cu oxide phase into Cu metal. The second and third copper metal Cu–Cu shells featuring low coordination and large structural disorder were not included in the EXAFS model since they did not improve the quality of the fit.

The relatively low coordination number as compared to the value of a bulk fcc structure (12) indicates that the Cu phase is forming nanosized Cu metallic particles. In CZS-R200 the first peak can be fitted with ca. 1 O at 1.94 Å and the main peak with 7.3 Cu at 2.556 Å. In line with the XANES analysis these results demonstrate that the reduction at 200 °C is incomplete with both Cu oxide and Cu metal present in the material.

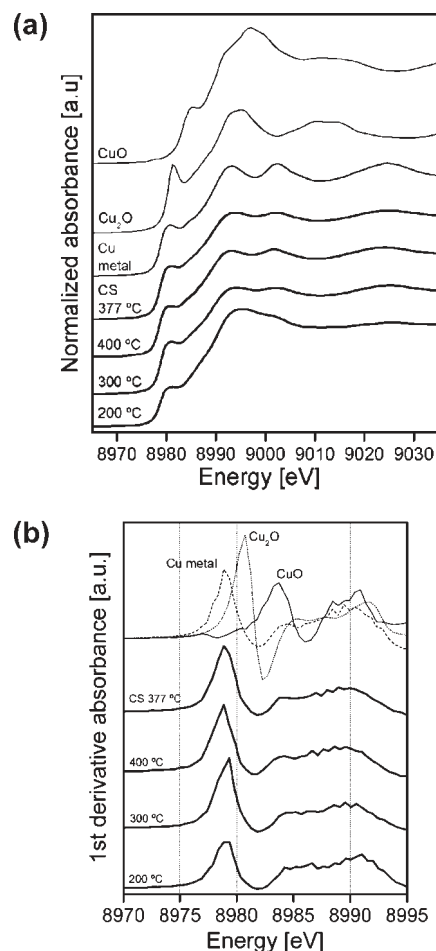


Figure 5. (a) Cu K-edge background subtracted and normalized XANES spectra and (b) first derivatives of the Cu/Zn/SiO₂ material (CZS) reduced at 200, 300, and 400 °C along with binary Cu/SiO₂ (CS) rereduced at 377 °C and reference bulk samples Cu metal, CuO, and Cu₂O.

Because EXAFS can determine distances in a very reliable way (± 0.02 Å), the Cu–O distance can be used as a guide to evaluate the extent of oxidation as well as the relative amount of different phases in a multiphase material.^{55,56} If we consider that copper is coordinated to 4 O located at ca. 1.96 Å in bulk tenorite CuO as well as in the hydrosilicate phase and to 2 O at 1.85 Å in bulk cuprite Cu₂O,⁴¹ the relative amount δ_{CuO} and $\delta_{\text{Cu}_2\text{O}}$ of the Cu^{2+} and Cu^{1+} phases in the incompletely reduced CZS-R200 material can be roughly estimated using the Cu–O bond distance $R_{\text{Cu–O}}$

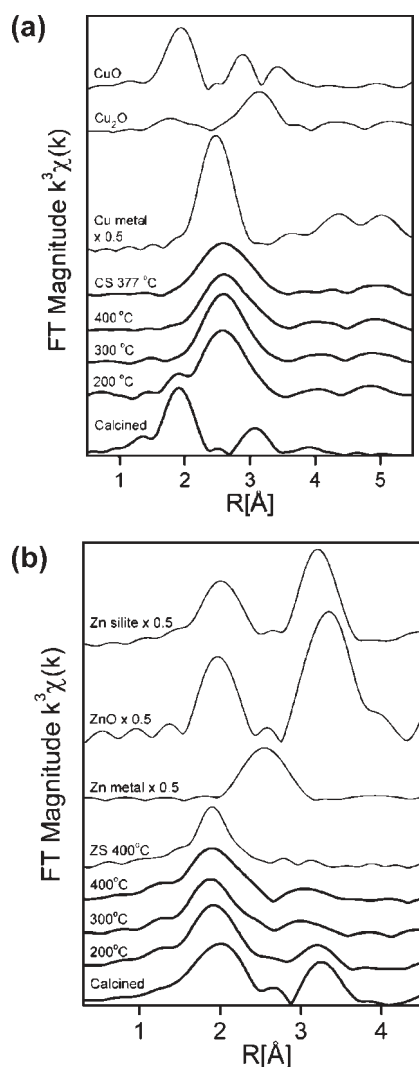


Figure 6. (a) Phase-corrected FTs of the Cu K-edge k^3 -weighted EXAFS of the calcined Cu/Zn/SiO₂ material (CZS) reduced at 200, 300, and 400 °C along with binary Cu/SiO₂ (CS-R400) rereduced at 377 °C and reference bulk samples Cu metal, CuO, and Cu₂O; (b) phase-corrected FTs of the Zn K-edge k^3 -weighted EXAFS of the calcined Cu/Zn/SiO₂ material (CZS) reduced at 200, 300, and 400 °C along with binary Zn/SiO₂ (ZS) reduced at 400 °C and reference bulk samples Zn metal, ZnO, and zincsilite.

determined from EXAFS and weighted by the respective coordination number of the two Cu oxide phases. Solving the equations $R_{\text{Cu-O}} = 4 \times 1.96\delta_{\text{CuO}} + 2 \times 1.85\delta_{\text{Cu}_2\text{O}}/4\delta_{\text{CuO}} + 2\delta_{\text{Cu}_2\text{O}}$ and $\delta_{\text{CuO}} + \delta_{\text{Cu}_2\text{O}} = 1$ gives the respective Cu²⁺ ratio relative to the total Cu oxide phase that is $\delta_{\text{CuO}}100 = 69\%$. Although coordination numbers in EXAFS are generally determined with much less accuracy ($\pm 20\%$) than the distances, the amount of copper metal in CZS reduced at 200 °C can be estimated by comparing the total oxygen coordination number corresponding to the Cu¹⁺/Cu²⁺ ratio derived from $R_{\text{Cu-O}}$ bond distance $N_{\text{Oxy}} = 4\delta_{\text{CuO}} + 2\delta_{\text{Cu}_2\text{O}} = 3.4$ and the coordination number of ca. 1 found in the fitting process giving a ratio of $\delta_{\text{CuOx}}100 \approx 28\%$ of Cu atoms belonging to the oxide phase and 72% of Cu atoms to the metallic phase. The relative atomic ratio of the Cu⁰, Cu¹⁺, and Cu²⁺ species present in CZS-R200 amounts then to 72, 20, and 8% as shown in Table 1.

Conversely, important information such as the size of the metal nanoparticles can be derived from the coordination number. Evaluation of the particle size has been made using an interpolation of the rigorous analytical formulas derived by Benfield⁵⁷ assuming that the metal particles adopt a geometry close to the cuboctahedron. The size of the copper metal particles in CZS reduced at 200, 300, and 400 °C obtained from the coordination numbers that amount to 17, 26, and 32 Å, respectively, are in good agreement with the corresponding sizes determined by XRD (28 Å for CZS reduced at 227 °C and 40 Å for CZS reduced at 327 and 400 °C).¹⁹ The smaller sizes obtained from EXAFS likely originate from the fact that XRD is only sensitive to long-range order whereas EXAFS is additionally sensitive to nanoscale or amorphous regions presenting a large fraction of low coordinated atoms.⁵⁸

Like the structures found in a previous study of Cu/ZnO ball-milled materials,³⁰ the metallic particle size found in CZS-R200 likely corresponds to the core of a core–shell particle consisting of a Cu⁰ core surrounded by an unreduced Cu²⁺ phase with some Cu¹⁺ species at the interface while the metal particle in CZS-R300 corresponds to a pure copper phase with a small amount of Cu¹⁺ species at Cu⁰/ZnO interface. The relatively large size of the metallic particle in CZS-R400 combined with the enlarged Cu–Cu metal bond distance (2.578 Å) indicate that the metallic core, which consists of almost pure Cu (Zn⁰-depleted) is surrounded by an outer layer of a Zn⁰-enriched Cu–Zn alloy.

For comparison the Zn-free CS-R400 material rereduced in situ (Table 1) presents fully reduced copper metallic particles that are slightly larger (42 Å) than in CZS-R400 (32 Å). This indicates that the presence of Zn in the material is apparently increasing the dispersion of the copper metallic phase. However, the absence of a ZnO layer around the particle that is normally expected to flatten the metal particle⁸ (see sections 3.3 and 3.4) may also explain this apparent limited size increase.

3.2.1.2. Zn K-Edge. Figure S1b shows the stacked background subtracted and normalized XANES spectra of the in situ reduction of CZS from room temperature up to 400 °C. Reduction starts producing significant structural changes on the Zn hydro-silicate phase only above 190 °C. Contrarily to the Cu K-edge XANES measurements, the evolution of the XANES profile at the Zn K-edge as a function of the temperature is very smooth and regular during the whole heating process. The reduction of the copper phase that occurs at a temperature ranging from 160 to 270 °C does not strongly affect the Zn K-edge XANES profile, showing that the segregation and reduction of the Cu²⁺ into Cu metal particles is a smooth phenomenon. The building up of the ~ 9658 eV feature, typical of Zn metal, in the zoomed view (Figure S1c) is a clear indication of the formation of Zn⁰. This feature appears at 190 °C and slowly increases to become significant at temperatures above 300 °C. Although Zn reduction starts at 190 °C, Zn⁰ is probably only present in the form of traces at this temperature. It can be clearly detected at 300 °C as shown by the small bump at ~ 9658.5 eV in the first derivative of CZS-R300 and becomes significant at 400 °C as a larger bump in CSZ-R400 shows.

During reduction the white line intensity and edge energy is monotonously decreasing whereas the first resonance peak is progressively damped indicating a change of Zn²⁺ coordination from octahedral to tetrahedral.^{45,46} This is clearly seen in the comparison of the XANES spectra (Figure 7a) of the CZS material reduced at 200, 300, and 400 °C. These effects are more evident in the corresponding first derivatives (Figure 7b)

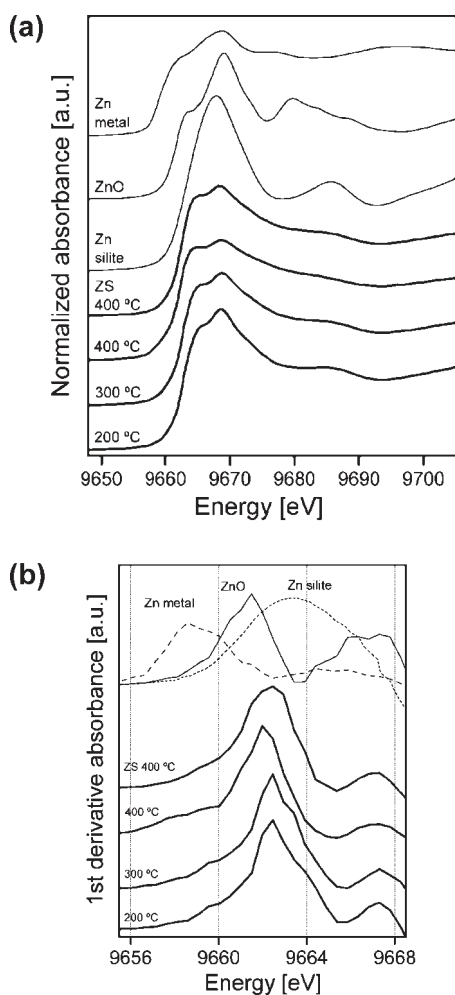


Figure 7. (a) Zn K-edge background subtracted and normalized XANES spectra and (b) first derivatives of the calcined Cu/Zn/SiO₂ material (CZS) reduced at 200, 300, and 400 °C along with binary Zn/SiO₂ (ZS) reduced at 400 °C and reference bulk samples Zn metal, ZnO, and zincsilite.

that shows a regular shift in energy and decrease in intensity of the Zn²⁺ 1s–4p peak from ~9663 eV in the calcined material to ~9662.5 eV in CZS-R200 and CZS-R300, ~9662.0 eV in CZS-R400, and finally down to ~9661.5 eV in the ZnO reference compound. XANES of CZS-R400 closely resembles that of ZS and likely also corresponds to the formation of highly dispersed ZnO species on SiO₂.⁴⁸ This indicates that, as the reduction temperature increases, the Zn-based phase is undergoing a regular transformation from the mixed hydrosilicate-type in which Zn possesses an octahedral geometry to a highly dispersed and amorphous ZnO phase with Zn in tetrahedral coordination. As the XANES analysis of the calcined state showed, the energy shift of the Zn²⁺ 1s–4p peak is a direct measure of the reduction in the O coordination number and the level of dispersion of the ZnO phase in the catalyst during reduction.

In order to elucidate the influence of Cu on the reduction of Zn, the XANES first derivative of CZS-R400 has been compared to that of a Cu free ZS material measured after reduction at the same temperature (Figure 7b). It is clear that the formation of a Zn metallic phase at 400 °C can only occur in the presence of Cu as shown by the absence of any Zn⁰ feature in the first derivative

of the ZS material around ~9658.5 eV. In the meantime, the Zn²⁺ 1s–4p peak in the first derivative of ZS-R400 has retained the same shape and position (~9662.5 eV) as in the calcined state (Figure 3b). This means that highly dispersed ZnO/SiO₂ in ZS undergoes only limited changes during the reduction process.

Comparison of FT's of the reduced CZS materials (Figure 6b) and ZS-R400, show that the main broad peak at ca. 2 Å corresponding to oxygen atoms is gradually shifted toward shorter distances as the reduction temperature increases, whereas in the meantime a shoulder on the main peak at ca. 2.5 Å is building up in CZS-R400. As the reduction temperature increases to 300 and 400 °C, the intensity of the second peak at ca. 3.2 Å (metal shell) decreases and its position shifts to lower R-values indicating that in addition to the dispersion, a phase transformation is taking place. Copper-free ZS-R400 features a much thinner main oxygen peak with very weak higher R peaks supporting the presence of a highly dispersed and amorphous phase. EXAFS fitting (Table 2) confirms these observations with a Zn–O bond distance varying from 2.024 Å in the CZS calcined material to 1.985, 1.947, and 1.945 Å in the same material reduced at 200, 300, and 400 °C, respectively. In the meantime, the oxygen coordination number is decreasing from 5.3 in the calcined material to 4.6 in CZS-R200, 3.8 in CZS-R300, and 3.2 in CZS-R400. The first Zn–Zn bond distance decreases from 2.92 in the calcined material to 2.85 Å in CZS-R400, whereas the second Zn shell at 3.06 Å, still present in CZS-R200 but with a shorter value of 3.02 Å, is absent in the two other reduced materials. These results, in line with the XANES analysis, are pointing out the regular transformation of the Cu/Zn hydrosilicate phase into a dispersed ZnO/SiO₂ phase as a function of the reduction temperature.

In Cu-free ZS-R400, reduction produces a phase in which Zn is surrounded by 3.6 O at 1.947 Å, 0.2 Zn at 3.00 Å, and 0.5 Si at 3.03 Å. This is significantly different from the Zn environment in CZS reduced at the same temperature. The Zn coordination of 0.2 in ZS-R400 compared to a typical value of 1.7 in CZS-R400, shows that phases in ZS calcined and reduced materials are more dispersed and amorphous when no Cu is present. In line with XANES analysis this confirms that reduction has a limited effect on ZS since it only increases the dispersion of the ZnO/SiO₂ phase already present in this material.

The metal shell located at 2.58–2.62 Å in the CZS-R400 and CZS-R300 series does not belong to a Zn oxide phase but to a Cu–Zn alloy, as these distances lie between the typical Cu–Cu (2.56 Å) and Zn–Zn (2.66 Å) distances in pure Cu and Zn metallic phases. This is in good agreement with the results at the Cu K-edge that showed a Cu–Cu first neighbor distance (2.58 Å) slightly larger than the expected bulk value (2.56 Å). The coordination number of this mixed Cu/Zn shell varies from 1.2 in the CZS-R300 to 2.4 in CZS-R400, pointing out quantitatively the amount of Zn effectively reduced as a function of the reduction temperature. The formation of a Cu–Zn alloy during reduction of the same system has already been reported by Nakamura et al.⁵⁹ Moreover, these results are in good agreement with our previous LEIS measurements that clearly pointed out a surface enrichment in Zn metal as a function of the reduction temperature from a ratio of 0.02 Zn⁰ at 200 °C up to 0.19 Zn⁰ at 400 °C.¹⁰ The presence of a Zn rich Zn–Cu alloy at the surface of the particles could also explain the results of chemisorption measurements that pointed out a surprising difference in oxygen uptake of 47% between Zn promoted and unpromoted catalysts.¹⁹ Indeed, the oxidation of Zn⁰ into Zn²⁺ requires twice

as much oxygen as the oxidation of Cu^0 into Cu^{1+} . More recently the formation of a Cu–Zn α -brass with 24% Zn was clearly evidenced by XRD on a similar Cu–Zn– SiO_2 system with a lower Cu/Zn ratio of 0.41 (Cu 18.6 wt % and Zn 44.8 wt %), prepared with the same method and reduced above 600 °C.¹⁸

This indicates that, as the reduction temperature increases, the Cu/Zn hydrosilicate phase in CZS is progressively transformed into (i) Cu^0 , (ii) increasingly dispersed ZnO species on SiO_2 , and (iii) finally into a Zn metallic phase forming Cu–Zn α -brass alloy particles. This is in line with LEIS results showing that dispersed ZnO is covering the Cu particles but also the SiO_2 support with a significantly more pronounced effect in CZS-R400 than in CZS-R300.⁶ This is probably resulting from ZnO having a substantially lower surface energy than Cu and SiO_2 .⁶⁰ In order to minimize the surface energy, ZnO tends to segregate to the surface and spread over Cu and the silica support.

A strong evidence of this transformation is clearly visible in CZS-R200 in which Zn has an intermediate coordination between 4 and 5 of 4.6, and an intermediate Zn–O bond distance between 2.024 and 1.945 Å of 1.985 Å. Together with the results obtained at the Cu K-edge, this shows that a large amount of copper has not been reduced into copper metal and that the Cu/Zn hydrosilicate and the dispersed ZnO/ SiO_2 phase still coexist in CZS-R200 because the low reduction temperature has stopped the transformation process halfway.

In summary, the reduction of calcined CZS in a narrow range of temperatures (160 to 270 °C) induces the segregation of Cu^{2+} ions from the mixed Cu/Zn hydrosilicate structure into possibly Cu^{1+} in a first quick stage, and finally into Cu^0 particles. According to the reduction temperature, copper is either fully reduced into metal particles with sizes of 26 and 32 Å for reduction temperatures of 300 and 400 °C, respectively, or partially reduced into core–shell particles consisting of a small metallic core (72%) of 17 Å covered by an amorphous interface layer of Cu^{1+} (8%) surrounded by a shell of Cu^{2+} when the reduction temperature is lower (200 °C). In the meantime this segregation provokes in a first stage a smooth transformation of the Cu/Zn mixed hydrosilicate phase into a dispersed ZnO phase on SiO_2 , whose level of dispersion increases with the temperature. In CZS-R200, the Cu/Zn mixed hydrosilicate and the dispersed ZnO/ SiO_2 phases still coexist. Dispersed ZnO species are likely to concentrate around the Cu metal particles as confirmed by the reduction of Zn^{2+} into Zn^0 and the formation of a Cu–Zn alloy. Increasing further the reduction temperature up to 627 °C (see section 3.2.2.4) not only provokes the reduction of a larger number of Zn atoms at the Cu metal surface, but also their diffusion toward the very core of the metal particle.

3.2.2. Passivation and Rereduction of the Reduced Samples. **3.2.2.1. CZS-R200 Passivated in N_2O .** As discussed in the previous section, the copper phase in CZS-R200 has not been fully reduced and consists of a mixture of Cu^0 , Cu^{1+} , and Cu^{2+} species. Passivation of CZS-R200 in N_2O slightly decreases the amount of Cu^0 , as evidenced by the slight intensity reduction of the XANES (Cu K-edge) first derivative metal peak (~ 8979 eV) in Figure S4a. In the meantime a shoulder building up at ca. ~ 8981.5 eV (Cu^{1+} 1s-4p) indicates the formation mainly of Cu^{1+} and to a lesser extent of Cu^{2+} during the process. After rereduction at 177 °C the amount of Cu^0 returns to a slightly larger value than in the reduced material as the higher intensity of the metal peak and the disappearance of the Cu^{1+} shoulder shows.

In agreement with the XANES analysis, Cu K-edge FT's in Figure S5a shows that except for changes in intensity and shape of the peaks due mainly to the different measurement temperature, only limited effects of the passivation-rereduction cycle are observed in CZS-R200. EXAFS analysis (Table 1) indicates that the copper metal particle size first decreases from 17 to 15 Å during the passivation, and subsequently increases to 19 Å during rereduction, i.e., a value larger than the particle size in the reduced material. In the meantime the Cu–O distance and O coordination number in the fraction of copper belonging to the different phases show that passivation is transforming surface Cu^0 into Cu^{1+} . This Cu^{1+} fraction increases from ca. 8% in the reduced material up to 22% in the passivated sample, and decreases back to 3% in the rereduced material, whereas the Cu^{2+} fraction is undergoing less significant changes (13 to 20%). After a full passivation-rereduction cycle, the fraction of Cu^0 in the catalyst (81%) is larger than in the initially reduced material (72%).

At the Zn–K-edge the effect of passivation and rereduction in CZS-R200 is almost nonexistent as shown by the absence of any changes in the XANES derivative (Figure S4b) as in the FT's (Figure S5b). This is confirmed by the stability of the EXAFS fitting results (Table 2) showing that the Zn oxide phase is relatively stable toward N_2O passivation.

3.2.2.2. CZS-R400 Passivated in N_2O . Similarly to CZS-R200, passivation of CZS-R400 has a very limited effect on the copper phase since the metal peak (~ 8979 eV) in the Cu K-edge XANES derivative (Figure 1b) has almost the same intensity in the passivated and the reduced material. However, a little shoulder that appears on the right-hand side of the metal peak indicates that traces of Cu^{1+} are also formed. As expected the rereduction at 377 °C removes the shoulder on the metal peak corresponding to Cu^{1+} and transforms the Cu oxide phase back into a metallic state. As passivation is probing the nature of the reactive phases present at a material surface, the relative insensitivity of the copper phase due to this treatment suggests that copper atoms in CZS-R400, contrarily to CZS-R200, may not be located directly at the surface of the particles but rather are protected by an outer layer of a Zn-based phase.

No noticeable changes are affecting the FTs at Cu K-edge either (Figures 2a), and EXAFS analysis shows that during the passivation-rereduction treatment copper in CZS-R400 remains always metallic and only slight changes affecting the coordination numbers can be detected. These changes translated into particle size indicate that the passivation only slightly reduces the apparent size of the copper particles from 32 Å in the reduced material to 28 Å in the passivated sample, and back to 30 Å in the rereduced material. This effect has to be taken with caution due to the relative large errors associated with these figures, since it might be due to an enlargement of the metallic particles by the reduction of a significant amount of Zn atoms (see section 3.2.2.4).

In order to assess the role of Zn in this binary catalyst, zinc free CS-R400, passivated in N_2O and further exposed to air has been investigated. EXAFS results indicate that in this material Cu^0 metal has been entirely converted into Cu^{1+} (93%) and Cu^{2+} (7%) whereas in all passivated CZS materials a metallic core could be detected. This demonstrates that Cu metal oxidation is never complete in the presence of Zn suggesting that dispersed ZnO present around the metallic particles is protecting them from oxidation.

At the Zn K-edge, passivation provokes a significant decrease of the Zn metal feature at ~ 9658 eV and a proportional increase

of the main Zn oxide peak ($\text{Zn}^{2+} 1s-4p$ at ~ 9662.0 eV) of the XANES derivative as shown in Figure 3b. Rereduction at 377°C has a reverse effect almost transforming the material back into its original reduced state. The fact that a passivation - rereduction cycle is reversibly oxidizing part of the Zn metallic phase back into Zn oxide without affecting the Cu phase, is further supporting the coverage of the Cu metal particles by a Zn metallic phase that protects them from reactive atmospheres.

Except a peak magnitude change due to different measurement temperatures the FTs at Zn K-edge (Figures 2b) before and after passivation are very similar. This is confirmed by the EXAFS analysis (Table 2) showing that, except for a slight increase of the Zn–O bond distance from 1.945 to 1.957 Å that probably originates from some back transformation of dispersed ZnO phase into hydrosilicate, the Zn oxide phase is relatively stable toward N_2O passivation.

Contrarily, passivation induces significant changes to the second metal shell at ca. 2.6 Å. The coordination number decreases from 2.4 in the reduced material down to 1.2 in the passivated sample, whereas in the meantime the bond distance increases from 2.58 to 2.62 Å. This effect is partially reversed by the rereduction process that increases the coordination number back to 3.5 Cu/Zn, but leaves the bond distance unchanged at ca. 2.59 Å. This corresponds to the nearly reversible changes of the Zn metal features observed in the first derivative of the XANES spectra. The Zn–Cu/Zn bond distance can be used as a direct evaluation of the relative concentration of the Zn atoms in the Cu/Zn metallic phase. If a Zn–Cu/Zn distance of 2.58 Å, found in reduced CZS-R400 that is close to the Cu–Cu bond distance in pure Cu metal, corresponds to a situation in which Zn atoms are very diluted in the copper matrix, a Zn–Cu/Zn distance of 2.62 Å, closer to the Zn–Zn bond distance in the pure Zn metallic phase found in passivated CZS-R400, would correspond to a low concentration of Cu in a Zn matrix. These results show that during the treatment, Zn atoms are undergoing a large rearrangement by migration inside the metallic particles. A possible interpretation is that the reduction process transforms ZnO/SiO₂ at the metallic particle surface into Zn⁰ that is migrating toward the core of the particle, yielding a dispersed distribution of Zn atoms among the Cu metallic matrix. Contrarily, when the external atmosphere becomes more oxidizing Zn atoms segregate back toward the surface of the particles to get oxidized into ZnO/SiO₂ and tend to form a highly concentrated outer layer of Zn metal at the surface of the particle.

3.2.2.3. CZS-R300 Passivated in Air. To test the role of N_2O in the passivation process, CZS-R300 was passivated directly in air. As expected, the oxidation has proceeded to a deeper oxidation of the copper phase into similar amounts of Cu^{1+} and Cu^{2+} , and a relative small amount of Cu^0 remains in the material as shown by the presence of three peaks in the Cu K-edge XANES first derivative (Figure S2a), corresponding to Cu^0 , CuO, and Cu_2O phases, respectively. This oxidation process is entirely reversed by the rereduction treatment which transforms the whole Cu phase back into a metallic phase as in the first reduction process.

EXAFS fitting at Cu K-edge (Table 1) indicates that the Cu phase is roughly divided in three equal parts: 37% Cu^{2+} , 31% Cu^{1+} , and 32% Cu^0 , confirming the XANES analysis. The structural model corresponding to these results is probably a $\text{Cu}^0/\text{Cu}^{1+}/\text{Cu}^{2+}$ core shell structure with a copper metal core of less than 10 Å. Compared to CZS-R400 passivated in N_2O the relative amount of Cu^0 oxidized has doubled, illustrating the stronger

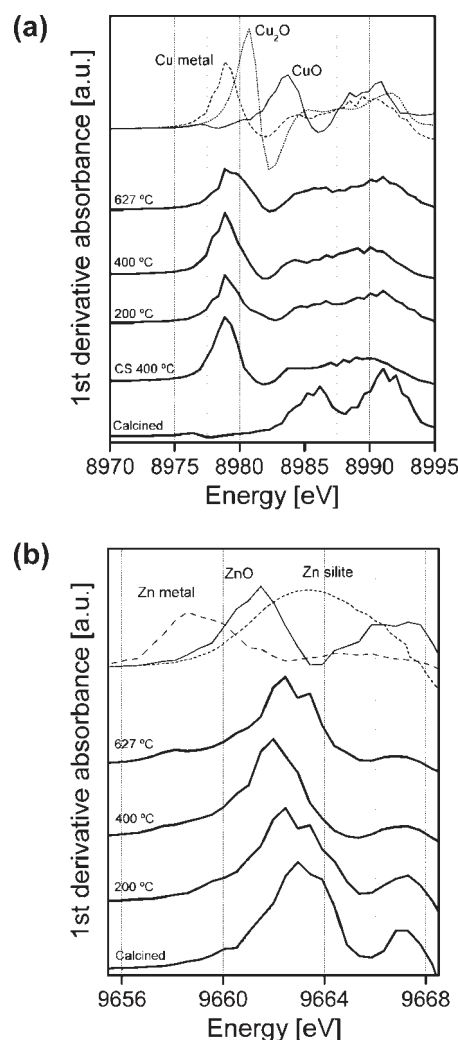


Figure 8. (a) First derivative of the Cu K-edge background subtracted and normalized XANES spectra of calcined Cu/Zn/SiO₂ (CZS), CZS-R200 and CZS-R400 passivated in N_2O , CZS-R627 (reduced ex situ) passivated in $\text{N}_2\text{O} + \text{O}_2$ and exposed to air along with binary Cu/SiO₂ material (CS-R400), rereduced at 377°C , and passivated in N_2O and reference bulk samples Cu metal, CuO, and Cu_2O . (b) First derivative of the Zn K-edge background subtracted and normalized XANES spectra of calcined CZS, CZS-R200 and CZS-R400 passivated in N_2O , CZS-R627 (reduced ex situ) passivated in $\text{N}_2\text{O} + \text{O}_2$ and exposed to air along with reference bulk samples Zn metal, ZnO, and zincsilite.

oxidizing potential of air compared to N_2O . However, passivation in air is not lowering the potential catalytic properties of this material since the rereduction transforms the copper phase entirely back into a metallic phase having the same size as in the material treated in the first reduction process.

EXAFS results at Zn K-edge (Table 2) shows clearly the transformation of the Zn phase back into the Zn hydrosilicate with a large Zn–O distance of 1.981 Å and the presence of a low magnitude Zn shell at 3.07 Å corresponding to a typical Zn–Zn distance as in the calcined material.

3.2.2.4. CZS-R627 Passivated in N_2O and Air ex Situ. In order to evaluate the effect of a higher reduction temperature on the structure of these materials, a CZS material was reduced ex situ at a high temperature of 627°C , passivated in N_2O , and then exposed to air. The first derivative (Figure 8a) shows clearly

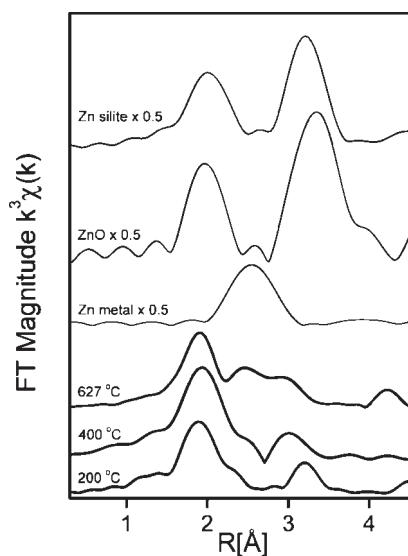


Figure 9. Phase-corrected FTs of the Zn K-edge k^3 -weighted EXAFS of CZS-R200 and CZS-R400 passivated in N_2O and CZS-R627 (reduced ex situ) passivated in $N_2O + O_2$ and exposed to air along with reference bulk samples Zn metal, ZnO, and zincsilite.

the presence of a high amount of Cu^{1+} as the maximum of the derivative at ~ 8980.5 eV coincides with the Cu^{1+} 1s–4p peak. However, the shoulder at the left side of this peak corresponding to the maximum of the Cu metal derivative indicates that Cu metal is still present in the material. Similarly, the small feature at ~ 8986.5 and ~ 8991 eV shows that to a lesser extent Cu^{2+} can also be found in the material, probably in a silicate phase.

This is confirmed by the EXAFS analysis that shows the presence of an oxygen shell at 1.92 Å corresponding to two different Cu oxide phases and a metal shell at 2.57 Å corresponding to a Cu metallic phase. The relative ratio of the different phases derived from the Cu–O distance and the O shell coordination number show that nearly half of the Cu atoms are in a metallic phase corresponding to an average particle size of 12 Å. The second half of the Cu atoms contains equal amounts of Cu^{1+} and Cu^{2+} phases. These results support the formation of a core shell structure after passivation, as in passivated CZS-R300, with a small Cu^0 core surrounded by a Cu^{1+} shell that is in turn covered up with a Cu^{2+} phase. Cu oxide phases are mostly amorphous and the XANES analysis shows that most of Cu^{2+} probably consists of dispersed CuO species on SiO_2 .

The first derivative of XANES spectrum at the Zn K-edge (Figure 8b) is very similar to the corresponding derivative of passivated CZS-R300 and CZS-R200, except for the presence of a small feature at 9658.1 eV close to the Zn^0 peak that indicates the presence of a significant amount of Zn metal in this passivated material.

This is confirmed by the FT at the Zn K-edge (Figure 9) that shows that, in addition to the expected Zn oxide phase, the Zn metal is surprisingly present in significant amounts in this fairly oxidized material. The presence of a dispersed ZnO/ SiO_2 phase with short Zn–O bond distance (1.938 Å) indicates that contrarily to CZS-R300 passivated in air, this phase has not been transformed back into hydrosilicate. A plausible explanation would be that at this high reduction temperature, the ZnO dispersed layer surrounding the copper particles is of sufficient thickness to resist oxidation. The EXAFS analysis also indicates

the presence of a Zn metal shell containing a relatively high number of 4.2 Cu/Zn atoms at 2.57 Å. This bond distance corresponds to a Cu–Zn alloy in which Zn is present in a relatively low concentration in the Cu matrix. The fact that a significant amount of Zn^0 is not oxidized during passivation and air exposure indicates that these atoms are likely intimately mixed with Cu^0 atoms up to the very core of the metallic particle since only a small part of the reduced metallic particle remains after passivation. The presence of Zn metal in a passivated material has also been observed in CZR-R400, be it in a relatively small amount. This would imply that as the reduction temperature increases, the amount of metallic Zn increases and that Zn atoms migrate toward the very core of the bimetallic particle. This increase in the amount of Zn^0 atoms may be accompanied with the increase in ZnO dispersion and the coverage of the metallic particles.

In summary, passivation in N_2O softly oxidized the outer shell of the Cu metal particles mostly into Cu^{1+} . Further exposure to air after passivation increases the amount of Cu^{1+} and Cu^{2+} and can, when no Zn is present as in CS-R400, almost entirely transform the Cu phase into Cu^{1+} . On the contrary, passivation of CZS-R400 that surprisingly induces the formation of only a limited amount of Cu^{1+} suggests that copper may not be located directly at the surface of the metal particles. In the meantime, the fact that passivation is oxidizing a significant part of the Zn^0 atoms present in the material into dispersed ZnO would imply that the copper metal particle is coated by a superficial Zn metal layer. This metallic layer is in turn covered up by a layer of dispersed ZnO whose thickness increases with the reduction temperature. Passivation in CZS-R400 seems to induce a dynamic migration or segregation of the Zn atoms dispersed in the Cu metallic matrix toward the surface of the particles suggesting that the nature of the surface of the copper metallic particles is changing from pure Cu metal phase into a Zn-rich Cu–Zn alloy according to the reduction temperature. Reduction and passivation are fully reversible and cycles of these processes can even accentuate the original level of reduction by producing a larger fraction of metallic Cu and Zn. As passivation principally affects the surface of the particles, the XAFS study of the passivated and rereduced materials has allowed for an indirect characterization of the phase present at the surface of the metallic particles.

3.3. Rereduced Catalysts under Methanol Synthesis Conditions. The first derivatives of the Cu K-edge XANES spectra of the 3 rereduced samples CZS-R400, CZS-R300, and CZS-R200 (Figures 1b, S2a, and S4a, respectively) does not show any visible change in either of the two materials compared to the original rereduced state. Under working conditions at 200 °C, Cu remains in a pure metallic phase in CZS-R400 and CZS-R300, and a mixture of Cu^0 , Cu^{1+} , and Cu^{2+} in CZS-R200. This is corroborated by the FTs of CZS-R300 and CZS-R200 (Figures S3a and S5a) that present no visible differences with those of the corresponding rereduced materials.

However in CZS-R400, the FT (Figure 2a) exhibits a sharp increase in the main peak magnitude. Although EXAFS analysis (Table 1) confirms that no major changes are occurring in the composition of the three materials under working conditions, the coordination number of the first Cu shell in CZS-R400 increases from 9.8 in the rereduced sample up to 11.1 . Translation of these coordination numbers into apparent copper particle sizes points out a large increase in the particle size from 30 Å in the rereduced material up to 85 Å. Even if the accuracy of the particle size determined from the EXAFS coordination number diminishes

sharply as the coordination number gets closer to its bulk value of 12, the significant difference between the coordination numbers suggests that this effect is real. This apparent enlargement is observed to a lesser extent in CZS-R300, in which the metal particle size increases from 27 Å in the rereduced sample up to 38 Å in the material under working conditions.

As for the Cu K-edge data, comparison of the XANES derivatives of CZS-R400, CZS-R300, and CZS-R200 at the Zn K-edge (Figures 3b, S2b, and S4b) reveals no obvious differences between the rereduced state and that under the working conditions. Similarly the FT's of the three rereduced samples (Figures 2b, S3b, and S5b) and the EXAFS fitting results at the Zn K-edge (Table 2) seem almost identical before and during working conditions.

However, a careful inspection of Zn K-edge XANES derivatives (Figure 3b) shows that in CZS-R400 the main peak at ~ 9662 eV ($\text{Zn}^{2+} 1s-4p$) of the material under working conditions is almost overlapping the corresponding peak in the passivated material. In the meantime the intensity of the ~ 9658 eV feature (Zn^0) is close to the one in the rereduced material. A plausible interpretation is that, unlike the passivation process, the loss of a significant amount of dispersed ZnO around the metal particle in CZS-R400 transformed back into a hydrosilicate-type phase and probably is not compensated by the oxidation of the Zn metal present in the alloyed bimetallic particles.

A possible explanation of an actual enlargement of the metallic particle size could be sintering, or alternatively the reduction into Zn^0 of a large number of Zn ions from the surrounding Zn oxide phase. However, a sintering effect should be excluded since no indications were found in a previous in situ XRD study¹⁹ where no visible increase in the amount of metallic Zn atoms was observed either in the XANES nor in the EXAFS analysis at the Zn K-edge. A more plausible interpretation of this phenomenon could be a change in the shape of the particles from flat into a more rounded shape. Indeed, such a shape change would be associated with a sharp diminution in the number of low coordinated surface atoms that in turn would sharply increase the mean coordination number determined by EXAFS analysis. This change in the particle shape has already been observed in the literature upon changing the oxidation potential of the synthesis gas and was interpreted in terms of change in the particle dispersion due to a wetting/non wetting phenomenon of small Cu particles on the ZnO support.⁸ An increase in the oxidation potential (wet conditions) generates nonwetting of the support, i.e., the Cu particles become more spherical giving relatively higher coordination numbers. A subsequent decrease in the oxidation potential (dry conditions) results in wetting of the support, i.e., the particles become more disk-like resulting in low coordination numbers. Calculation of the relative surface and interface free energies of a particle based on the Wulff⁶¹ construction showed that the change in contact free energy could be related to the changes in the number of oxygen vacancies at the interface between the Cu particle and the ZnO support. This change may be in line with the observed decrease in the amount of dispersed ZnO at the surface of the particles that is generally expected to flatten the particles.⁸ The role of the Zn phase in this phenomenon is evident when one compares to the Zn free material CS-R400 that in contrast exhibits a diminution of the metallic particle size from 42 Å in the rereduced material to 34 Å under working conditions (Table 1).

3.4. Proposed Catalyst Structure and Nature of the Active Interface. The catalytic activity and the Cu/Zn interaction in the

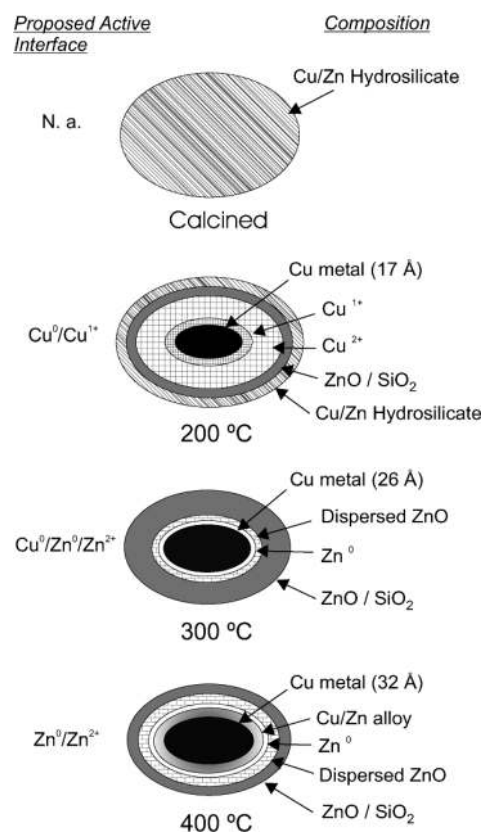


Figure 10. Schematic cross sections representing an average view of the zones of different composition centered on a copper metallic particle of the Cu/Zn/SiO₂ catalyst calcined, and reduced at 200, 300, and 400 °C.

CZS system have been shown to vary significantly according to the catalyst treatment and more specifically as a function of the reduction temperature employed. Depending on the feed mixture, a reduction temperature of 400 °C produces a catalyst featuring a huge 3 to 10-fold increase in methanol synthesis activity ($50 \text{ nmol s}^{-1} \text{ g}^{-1} \text{ cat}$) compared to the same materials reduced at 300 °C.^{6,10} This suggests that a significant change in the very nature of the active site in the ternary CZS catalyst could be at the origin of the enhanced catalyst performance.

A summary of the proposed structures and catalytically active interface/phases formed in Cu/ZnO/SiO₂ system reduced at different temperatures (200, 300, and 400 °C) is illustrated in Figure 10. This schematic representation corresponds only to an average view centered on a copper metallic particle of the cross sections of the catalysts. Different metallic particle sizes associated with different fractions of Cu and Zn species probably coexist in the materials. It is noteworthy that the concentric zones in these schemes do not correspond to phases but represent zones that differ by chemical composition. Thus, the zone denoted as Cu⁺ represents the Cu⁺ species lying at the interface between the metallic core and the CuO shell. The three zones denoted as Cu⁰, Cu–Zn alloy and Zn⁰ represent the same Cu–Zn α -brass alloy phase, which segregates to form the Zn-depleted core, Zn-enriched surface and Cu–Zn alloy subsurface layer. On the other hand, the zone denoted as ZnO/SiO₂ corresponds to the two-phase polycrystalline shell of the particle.

In CZS-R200, the metal interface likely consists of a core of a pure metallic copper of 17 Å surrounded by a Cu⁺ outer layer

that is in turn covered up by a Cu^{2+} layer. At this temperature no significant dispersion of ZnO was observed. No direct Cu/ZnO interaction is expected to occur in this material except in a marginal CuO/ZnO solid solution located around the metal particle as depicted in the Yurieva model.⁶² The active interface within this material could consist of Cu^0 in contact with Cu^{1+} . This catalyst features a very low activity,^{6,14} possibly because the metal interface consisting of a $\text{Cu}^0/\text{Cu}^{1+}$ transition is covered by an additional shell of Cu^{3+} oxide.

In CZS-R300, the Cu phase is entirely reduced into Cu metal particles of 26 Å with a small amount of superficial Zn⁰, in turn covered with a significant layer of dispersed ZnO. A very thin coverage of the Cu metal particles by dispersed ZnO species as envisaged in the previous investigations¹⁰ may also exist. In this case the active phase could consist of Cu^0 in contact with ZnO/SiO₂.

Finally, in CZS-R400 the result of the passivation to rereduction cycle shows clearly Cu–Zn alloyed bimetallic particles of 32 Å consisting of a rather pure copper, i.e., Zn-depleted metal core and a Zn-enriched Cu–Zn alloy shell. This layer is probably forming a progressive interface from the copper metal core to a rather pure Zn metal surface and gradually to a highly dispersed ZnO phase on the outer layer of the particle. Only very small amounts of Cu^{1+} are formed during the passivation whereas under reaction conditions no visible trace of Cu^{1+} could be observed. The concomitant presence of Cu^{1+} and a significant amount of Zn metal is unlikely in an intimately mixed Zn/Cu bimetallic phase since Zn metal has a higher affinity for oxygen than Cu metal and would be oxidized before Cu in the material. This much higher activity may be at the origin of the dramatic change in the particle morphology observed in this catalyst under working conditions since no change in the coordination number under the same working conditions is observed in the Zn-free material. In this ternary system Zn is forming a α -brass Zn–Cu alloy that segregates with Zn⁰ active sites at the surface of the Cu metal particles that are in contact with a dispersed ZnO layer enhancing dramatically the activity of the Cu catalyst for methanol synthesis. The number of these sites as well as the thickness of the ZnO layer increase as a function of the reduction temperature. Further increase in the reduction temperature favors the Cu/Zn brass formation with Zn present at the core of the metal particles provoking a decrease in the methanol activity.¹³ This general interpretation is in line with the more recent results obtained on a similar Cu–Zn–SiO₂ catalysts with a different Cu/Zn ratio that demonstrated a sharp increase of the activity in the methanol synthesis as a function of the Zn content as well as the reduction temperature employed.¹⁸ On a comparable Cu/Zn/SiO₂ catalyst (39 wt % Cu, 13 wt % Zn, Cu/Zn = 3), the activity k varied from 7.8×10^{-5} for the material reduced at 220 °C to 2.3×10^{-4} reduced at 250 °C. Similarly, when the Zn content increased to 44.8 wt % the k value increases sharply to 3.07×10^{-4} when reduced at 220 °C up to 1×10^{-3} for the material reduced at 250 °C.¹⁸

Formation of Zn⁰ active sites on the surface of copper particles in Cu/Zn catalysts would be in very good agreement with the work of Fujitani et al.^{15,59} These authors that combined methanol synthesis activity measurements on Cu/SiO₂ and ZnO/SiO₂ mixtures with the study of Zn-deposited Cu(111) surface by techniques clearly showed that the metallic Cu–Zn surface alloy is catalytically active for the conversion of methanol. They suggested that methanol synthesis could be divided in two parts, the formation of formate species from CO₂ and H₂ and its

hydrogenation into methanol. Zn metal in the reaction mechanism would promote formate hydrogenation into methoxy species as the Cu–Zn site was found to remain basically metallic during the methanol synthesis. Similarly, the ZnO phase may adsorb and stabilize the formate species up to 873 °C. This could be in line with our observations that indicate that if Cu and Zn remain metallic under working conditions, the dispersed ZnO/SiO₂ phase is undergoing a slight oxidation.

This model would also be in line with the wetting to nonwetting mechanism⁸ since we observed the covering of the copper metal particles by dispersed ZnO species during the reduction process. Furthermore, we also reported a large change in the coordination number under working conditions in CZS-R400 and to a lesser extent in CZS-R300, which may be due to a change in the particle morphology under more oxidizing syngas conditions.⁸ However, the moving species should not be restricted to Zn metal since we observed that even when the particle appears to take a round-like shape, a significant amount of Zn metal is still present in the particle.

The Yurieva model⁶² proposed for binary Cu/ZnO solid solutions with low Cu/Zn ratio consists of three different states. The initial state is a solid solution of Cu^{2+} in a ZnO matrix that is transformed in the presence of H₂ into a reduced state in which a portion of the Cu^{2+} ions are substituted for protons. In the meantime the corresponding amount of Cu^0 is forming an epitaxially bonded phase over the surface. Finally, an activated state is formed during methanol synthesis from CO₂ and H₂, consisting of $\text{Cu}^{1+}\text{--O--Cu}^{1+}$ sites on the metal particle surface. The presence of visible amounts of Cu^{1+} or Cu^{2+} could not be evidenced in CZS-R400 from our measurements. Moreover the concomitant presence of a large amount of Zn metal and Cu oxide is more likely to be associated to the structural state of the catalysts at a reduction temperature lower than 400 °C. However, an epitaxial copper metal layer formed on top of ZnO is probably not occurring in our ternary system with a high Cu/Zn ratio. Indeed, this Cu layer would be extremely sensitive to any passivation process that would oxidize this metal phase entirely. This was not the case in this study since in our CZS catalyst we always retain more than 60% of Cu^0 whereas only traces of Cu^{1+} in the CZS catalysts reduced at 200 and 300 °C could be suspected.

4. CONCLUSION

This in situ XAFS study has allowed for a detailed and exhaustive structural characterization of ternary silica supported copper/zinc (CZS) catalysts. This investigation is bringing valuable new insight on the complex and dynamic Cu/Zn interaction that is occurring in these materials at all stages of their treatment. According to the reduction temperature very different structures and Cu/Zn interfaces are formed explaining why this parameter is playing such a major role in designing the properties and controlling the overall activity of these catalysts. This variety of Cu/Zn interactions may also partly explain the existence of different and apparently contradictory theories to account for the mechanism of the methanol synthesis. In good agreement with our previous investigations, this study pointed out the formation of a Cu–Zn α -brass alloy highly concentrated in Zn at the surface of the metal particles that might be a major active site in the highly active silica supported Cu/ZnO catalyst reduced at 400 °C. This investigation should lead to a better control of the structure and therefore the catalytic properties of the Cu/Zn system.

■ ASSOCIATED CONTENT

S Supporting Information. Figures S1, S2, S3, S4, and S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +32 16327205. Fax: + 32 16327983. E-mail: didier.grandjean@fys.kuleuven.be.

■ ACKNOWLEDGMENT

The Netherlands Organization for Scientific Research NWO (Project Numbers 047.015.004 and 047.005.03.96) is gratefully acknowledged for financial support. Access to the synchrotron at ESRF (DUBBLE-experiment 26-01-192) was arranged through the general support of NWO for the use of central facilities. We wish to acknowledge the assistance and advice of Dr. Jurriaan Beckers (UvA) and Dr. Sergey Nikitenko (DUBBLE beamline) during the measurements, the use of the EPSRC Chemical Database Service at Daresbury, and Dr. Vladimir Zaikovskii (BIC) for the TEM micrograph.

■ REFERENCES

- Gusi, S.; Trifiro, F.; Vaccari, A.; Del Piero, G. *J. Catal.* **1985**, *94*, 120–127.
- Shukla, A. K.; Christensen, P. A.; Dickinson, A. J.; Hamnett, A. *J. Power Sources* **1998**, *76*, 54–59.
- Chinchen, G. C.; Waugh, K. C.; Whan, D. A. *Appl. Catal.* **1986**, *25*, 101–107.
- Klier, K. *Adv. Catal.* **1982**, *31*, 243–313.
- Nakamura, J.; Choi, Y.; Fujitani, T. *Top. Catal.* **2003**, *22*, 277–285.
- Poels, E.; Brands, D. *Appl. Catal. A-Gen.* **2000**, *191*, 83–96.
- Clausen, B. S.; Topsøe, H.; Hansen, L. B.; Stoltze, P.; Nørskov, J. K. *Catal. Today* **1994**, *21*, 49–55.
- Grunwaldt, J. D.; Molenbroek, A. M.; Topsøe, N. Y.; Topsøe, H.; Clausen, B. S. *J. Catal.* **2000**, *194*, 452–460.
- Yurieva, T. M.; Plyasova, L. M.; Makarova, O. V.; Krieger, T. A. *J. Mol. Catal. A-Chem.* **1996**, *113*, 455–468.
- Jansen, W. P. A.; Beckers, J.; van den Heuvel, J. C.; van der Gon, A. W. D.; Blik, A.; Brongersma, H. H. *J. Catal.* **2002**, *210*, 229–236.
- Makarova, O. V.; Harlamov, G. V.; Litvak, G. S.; Ketchik, S. V.; Yurieva, T. M.; Plyasova, L. M. *Izv. Sib. Otd. AN Khim.* **1990**, *3*, 67–73.
- Plyasova, L. M.; Solovyeva, L. P.; Krieger, T. A.; Makarova, O. V.; Yurieva, T. M. *J. Mol. Catal. A-Chem.* **1996**, *105*, 61–66.
- van de Scheur, F. T.; Brands, D. S.; van der Linden, B.; Luttkhuis, C. O.; Poels, E. K.; Staal, L. H. *Appl. Catal. A-Gen.* **1994**, *116*, 237–257.
- Brands, D. S.; Poels, E. K.; Krieger, T. A.; Makarova, O. V.; Weber, C.; Veer, S.; Blik, A. *Catal. Lett.* **1996**, *36*, 175–182.
- Fujitani, T.; Nakamura, J. *Catal. Lett.* **1998**, *56*, 119–124.
- Yurieva, T. M.; Kustova, G. N.; Minyukova, T. P.; Poels, E. K.; Blik, A.; Demeshkina, M. P.; Plyasova, L. M.; Krieger, T. A.; Zaikovskii, V. I. *Mater. Res. Innov.* **2001**, *5*, 3–11.
- Yurieva, T. M.; Minyukova, T. P.; Kustova, G. N.; Plyasova, L. M.; Krieger, T. A.; Demeshkina, M. P.; Zaikovskii, V. I.; Malakhov, V. V.; Dovlitova, L. S. *Mater. Res. Innov.* **2001**, *5*, 74–80.
- Minyukova, T. P.; Shtertser, N. V.; Khassin, A. A.; Plyasova, L. M.; Kustova, G. N.; Zaikovskii, V. I.; Shvedenkov, Y. G.; Baronskaya, N. A.; van den Heuvel, J. C.; Kuznetsova, A. V.; Davydova, L. P.; Yurieva, T. M. *Kinet. Catal.* **2008**, *49*, 821–830.
- Batyrev, E. D.; van den Heuvel, J. C.; Beckers, J.; Jansen, W. P. A.; Castricum, H. L. *J. Catal.* **2005**, *229*, 136–143.
- Viitanen, M. M.; Jansen, W. P. A.; van Welzenis, R. G.; Brongersma, H. H.; Brands, D. S.; Poels, E. K.; Blik, A. *J. Phys. Chem. B* **1999**, *103*, 6025–6029.
- Skårman, B.; Grandjean, D.; Benfield, R. E.; Hinz, A.; Andersson, A.; Wallenberg, L. R. *J. Catal.* **2002**, *211*, 119–133.
- Clausen, B. S. *Catal. Today* **1998**, *39*, 293–300.
- Clausen, B. S.; Gråbæk, L.; Steffensen, G.; Hansen, P. L.; Topsøe, H. *Catal. Lett.* **1993**, *20*, 23–36.
- Clausen, B. S.; Topsøe, H. *Catal. Today* **1991**, *9*, 189–196.
- Grunwaldt, J. D.; Clausen, B. S. *Top. Catal.* **2002**, *18*, 37–43.
- Günter, M. M.; Ressler, T.; Jentoft, R. E.; Bems, B. *J. Catal.* **2001**, *203*, 133–149.
- Kulkarni, G. U.; Rao, C. N. R. *Top. Catal.* **2003**, *22*, 183–189.
- Günter, M. M.; Ressler, T.; Bems, B.; Büscher, C.; Genger, T.; Hinrichsen, O.; Muhler, M.; Schlögl, R. *Catal. Lett.* **2001**, *71*, 37–44.
- Meitzner, G.; Iglesia, E. *Catal. Today* **1999**, *53*, 433–441.
- Grandjean, D.; Castricum, H. L.; van den Heuvel, J. C.; Weckhuysen, B. M. *J. Phys. Chem. B* **2006**, *110*, 16892–16901.
- van den Berg, M. W. E.; Polanz, S.; Tkachenko, O.; Kahler, K.; Muhler, M.; Grunert, W. *Catal. Lett.* **2009**, *128*, 49–56.
- Grandjean, D.; Castricum, H. L.; van den Heuvel, J. C.; Weckhuysen, B. M. *Am. Inst. Phys.* **2007**, *CP 882*, 636–638.
- van der Grift, C. J. G.; Elberse, P. A.; Mulder, A.; Geus, J. W. *Appl. Catal.* **1990**, *59*, 275–289.
- Binsted, N.; Campbell, J. W.; Gurman, S. J.; Stephenson, P. C. *EXAFS Analysis Programs; Daresbury Laboratory; Warrington, U.K.*, 1991.
- Vaarkamp, M.; Mojet, B. L.; Kappers, M. J.; Miller, J. T.; Koningsberger, D. C. *J. Phys. Chem.* **1995**, *99*, 16067–16075.
- Kau, L. S.; Spirasolomon, D. J.; Pennerhahn, J. E.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 6433–6442.
- Moen, A.; Nicholson, D. G.; Ronning, M. *J. Chem. Soc.-Faraday Trans.* **1995**, *91*, 3189–3194.
- DuBois, J. L.; Mukherjee, P.; Stack, T. D. P.; Hedman, B.; Solomon, E. I.; Hodgson, K. O. *J. Am. Chem. Soc.* **2000**, *122*, 5775–5787.
- Bair, R. A.; Goddard, W. A. *Phys. Rev. B* **1980**, *22*, 2767–2776.
- Lytle, F. W.; Gregor, R. B. *Phys. Rev. B* **1988**, *37*, 1550–1562.
- Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749.
- Veiga, J. P.; Figueiredo, M. O. *X-Ray Spectrom.* **2008**, *37*, 458–461.
- Chiou, J. W.; Kumar, K. P. K.; Jan, J. C.; Tsai, H. M.; Bao, C. W.; Pong, W. F.; Chien, F. Z.; Tsai, M. H.; Hong, I. H.; Klauser, R.; Lee, J. F.; Wu, J. J.; Liu, S. C. *Appl. Phys. Lett.* **2004**, *85*, 3220–3222.
- Lee, E. Y. M.; Tran, N.; Russell, J.; Lamb, R. N. *J. Appl. Phys.* **2002**, *92*, 2996–2999.
- Galoisy, L.; Cormier, L.; Calas, G.; Brioso, V. *J. Non-Cryst. Solids* **2001**, *293*, 105–111.
- Waychunas, G. A.; Fuller, C. C.; Davis, J. A. *Geochim. Cosmochim. Acta* **2002**, *66*, 1119–1137.
- Gaines, R. V.; Skinner, H. C. W.; Foord, E. E.; Rosenzweig, A. *Dana's New Mineralogy*, 8th ed.; John Wiley & Sons: New York, 1997.
- Yoshida, H.; Shimizu, T.; Murata, C.; Hattori, T. *J. Catal.* **2003**, *220*, 226–232.
- Lhommédé, F.; Le Dred, R.; Saehr, D.; Baron, J. *C.R. Acad. Sci. Paris* **1996**, *322*, 827–830.
- Beermann, T.; Brockamp, O. *Clay Miner.* **2005**, *40*, 1–13.
- Kim, J. W.; Furukawa, Y.; Dong, H. L.; Newell, S. W. *Clays Clay Miner.* **2005**, *53*, 572–579.
- Giorgetti, G.; Monecke, T.; Kleeberg, R.; Hannington, M. D. *Clays Clay Miner.* **2009**, *57*, 725–741.
- Clausen, B.; Topsøe, H.; Hansen, L.; Stoltze, P.; Nørskov, J. *Jpn. J. Appl. Phys.* **1993**, *32*, 95–97.
- Clausen, B. S.; Nørskov, J. K. *Top. Catal.* **2000**, *10*, 221–230.
- Barrett, P. A.; Sankar, G.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem.* **1996**, *100*, 8977–8985.

- (56) Grandjean, D.; Benfield, R. E.; Nayral, C.; Maisonnat, A.; Chaudret, B. *J. Phys. Chem. B* **2004**, *108*, 8876–8887.
- (57) Benfield, R. E. *J. Chem. Soc.-Faraday Trans.* **1992**, *88*, 1107–1110.
- (58) Frenkel, A. I.; Hills, C. W.; Nuzzo, R. G. *J. Phys. Chem. B* **2001**, *105*, 12689–12703.
- (59) Fujitani, T.; Saito, M.; Kanai, Y.; Kakumoto, T.; Watanabe, T.; Nakamura, J.; Uchijima, T. *Catal. Lett.* **1994**, *25*, 271–276.
- (60) Overbury, S. H.; Bertrand, P. A.; Somorjai, G. A. *Chem. Rev.* **1975**, *75*, 547–560.
- (61) Ovesen, C. V.; Clausen, B. S.; Schiøtz, J.; Stoltze, P.; Topsøe, H.; Nørskov, J. K. *J. Catal.* **1997**, *168*, 133–142.
- (62) Yurieva, T. M. *Catal. Today* **1999**, *51*, 457–467.