Synthesis of highly loaded Cu/Ce mesoporous silica. Active catalyst for the simultaneous reduction of SO$_2$ and NO with CO

Constantinos C. Pantazis* and Philippos J. Pomonis

We report the synthesis of a thermally stable, highly loaded (15 wt.%) Cu/Ce bimetallic mesoporous silica with high surface area and metal dispersion, which was the first template assisted mesoporous network successfully tested for the simultaneous reduction of SO$_2$ and NO with CO, achieving complete conversion of the reactants to elemental sulfur and N$_2$ at high space velocity 32 000 h^{-1}.

The synthesis of thermally stable template-assisted mesoporous silica is highly desirable as such inorganic frameworks are very promising supports for heterogeneous catalysts on which a high amount of catalytically active sites can be dispersed. However, in most cases incorporation of various metal species at amounts exceeding 6–7 wt.%[1–10] leads to dramatic loss of mesoporosity and surface area as a result of sintering effects.

Copper and ceria containing mesoporous silica have not been widely studied probably due to the deterioration of the mesoporous framework caused by the large size of cerium cations especially at a high degree of incorporation.

By applying the ion exchange method Long *et al.*,[11] synthesized Al-MCM-41 that contained <2% mol Ce with respect to silica and specific surface area 904 m^2 g^{-1}. They also developed a silicate system containing Cu/Ce at 4/0.5% mol and specific surface area 870 m^2 g^{-1}.

Moreover, ceria containing MSU-X alumina has been synthesized by direct incorporation of the Ce source in the reactant mixture that resulted in a 5% mol Ce/MSU alumina possessing specific surface area 357 m^2 g^{-1} after calcination at 600 °C.[12] Also MCM-41 type mesoporous silica containing 2% mol Ce has been developed with a wormlike structure and specific surface area 845 m^2 g^{-1} after calcination at 550 °C.[13]

The reaction 2NO + SO$_2$ + 4CO → 4CO$_2$ + S + N$_2$ has attracted considerable interest as it results in the simultaneous elimination of all three major air pollutants, *i.e.* NO, SO$_2$ and CO. The difficulty of this process is that a suitable catalyst has to overcome the deactivation of NO reduction due to strong SO$_2$ adsorption on its surface.

This fact excludes noble metal based materials from potential catalysts for the above reaction as they adsorb strongly SO$_2$ and suffer early deactivation.

Copper and cerium on various substrates are among the metals of choice for deNO$_x$[14–18] and deSO$_x$[19,20] catalytic operations and for the demanding operation of the simultaneous reduction of SO$_2$ and NO.[21]

University of Ioannina, Department of Chemistry, 45110, Ioannina, Greece. E-mail: me00596@cc.uoi.gr; Fax: +32651098795; Tel: +32651098703

So far template assisted mesoporous inorganic frameworks have not yet been employed in deSO$_x$ operations and especially in the simultaneous reduction of SO$_2$ and NO with CO. This could be due to the lack of suitable surface properties, induced by the particular metal cations, necessary to activate both SO$_2$ and NO molecules, which compete for adsorption sites on the catalyst surface. Moreover, high metal load and dispersion are also important in order for high reaction rates to be achieved.

Recently, as a follow up of previous work with pure hexagonal and P$m3n$ cubic mesoporous silica,[22,23] we reported the synthesis of highly loaded copper containing hexagonal mesoporous silica using poly(acrylic acid) (Pac)–CTAB complexes as templates, where Pac acts also as a carrier of the metal species on the framework through complexation,[24] providing materials with high metal load and dispersion. The material exhibited excellent performance for the catalytic reduction of NO by CO. However, it proved unable to catalyze the simultaneous reduction of SO$_2$ and NO by CO.

Thus, based on the relevant literature, this work aims first at the synthesis of a thermally stable and highly loaded Cu and Ce containing mesoporous silica. The synthesis protocol is mentioned in detail elsewhere.[24] In the present case we have added 1.6 mmol Cu(NO$_3$)$_2$·3H$_2$O and 0.7 mmol Ce(NO$_3$)$_2$·6H$_2$O (Merck) in the reactant mixture so as Si/(Cu + Ce) = 8.7 (10.3 mol% Cu+Ce). The total molar composition of the mixture was TEOS/C$_{16}$TAB/Pac2(2000 a.u.)/(Ce + Cu) = 1/0.35/0.013/0.12. The material designated as Pac2C$_{16}$CuCe was calcined in air at 600 °C for 5 h.

Then, a preliminary test on the simultaneous reduction of SO$_2$ and NO with CO was conducted in order to assess the catalytic activity of the material in the specific reaction.

Nitrogen adsorption measurements were performed at 77 K on a Sorptomatic 9000 Fisons instrument after outgassing for 12 h at 473 K. X-ray diffraction measurements were acquired on a Bruker Advance D8 system using Cu-K$_\alpha$ radiation (λ = 1.5418 Å) and a step of 0.01°. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometric analysis (EDS) was performed on a Jeol JSM 5600 at 20 kV equipped with an Oxford EDS X-ray microanalysis apparatus.

In Fig. 1 the X-ray diffractograms of the calcined (b) and uncalcined (a) Pac2C$_{16}$CuCe samples both at the low and the higher angle ranges are shown. A single strong reflection in the range $1.5 < 2\theta < 4°$ is observed for the uncalcined (a) sample with a *d*-spacing d_{100} = 4.58 nm. This mesophase is probably hexagonal as this is the parent phase of the Pac2C$_{16}$ system.[22–24] The rest of the higher order reflections of low intensity appear quite broad indicating a disordered mesophase. Calcination at 600 °C for 5 h results in a wormlike mesoporous network with a d_{100}-spacing
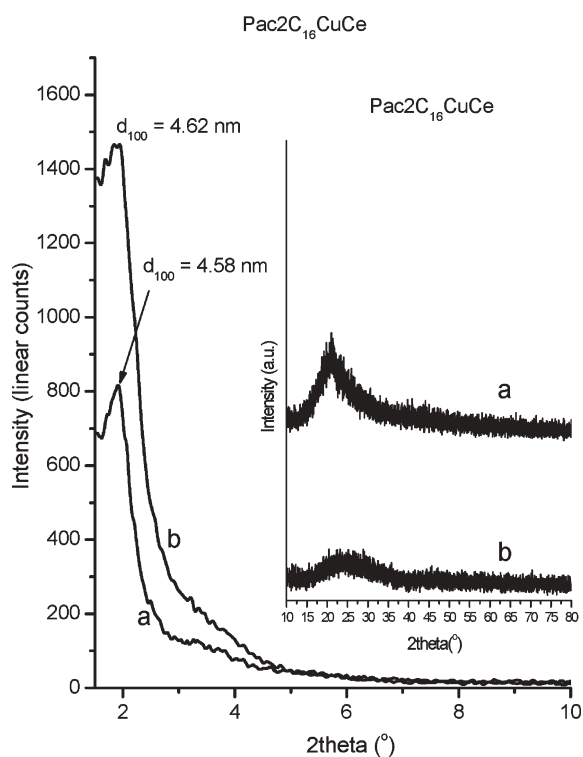
Fig. 1 X-ray diffractograms of Pac2C$_{16}$CuCe sample (a) uncalcined and (b) calcined at 600 °C for 5 h both at low and high angle range (inset). The stability of the wormlike mesoporous network is evidenced by the appearance of the d_{100} reflection of the calcined sample at the same value as the corresponding one of the uncalcined. The high dispersion of the metal species is indicated by the lack of characteristic metal oxide reflections at the high angle diffractogram (inset b).

value at 4.62 nm, which surprisingly remains practically unaffected by the thermal treatment up to 600 °C. This result indicates no shrinkage of the mesoporous network upon calcination and implies the high thermal stability of the latter. We should note that the pure silica material undergoes a shrinkage of about 7 Å upon calcination (from d_{100} = 3.9 nm to d_{100} = 3.2 nm). Addition of the metal species, although it degrades ordering and periodicity, seems to lead to pore expansion and strengthening of the network, a fact which indicates a favorable interaction with the latter.

In Fig. 2 a typical EDS microanalysis spectra of the calcined sample is shown. The analysis indicates at an exceptionally high concentration of the metal species that reaches the total of 11.6 mol% and specifically 8.1 mol% for Cu and 3.5 mol% for Ce with respect to Si atoms or 15 wt.% total metal load if calculated by considering formation of SiO$_2$, CuO and CeO$_2$ upon calcination. We should note that analysis were performed in several regions and magnifications of the material with practically similar results, indicating the homogeneity of the latter.

Moreover, in spite of the high metal content, the dispersion of the metal species into the inorganic framework remains high after calcination, as indicated by the high angle diffractogram of the calcined sample (Fig. 1, inset b), which shows no characteristic reflections of the corresponding metal oxides even at this elevated metal content. This result also implies a strong interaction of the metal species with the matrix that should inhibit the formation of large crystallites of the metal oxides maintaining the high dispersion of the latter after calcination.
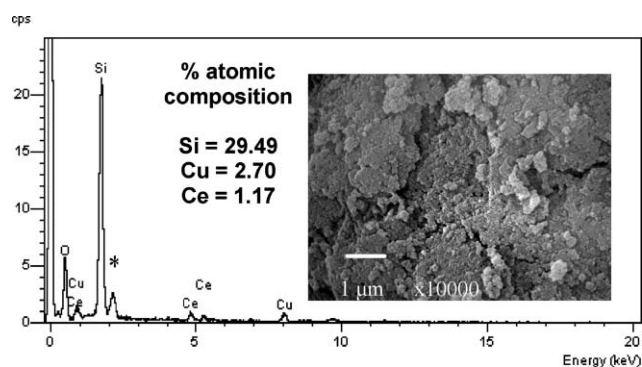

Fig. 2 Typical EDS spectra of the sample microanalysis along with a SEM image of the analyzed region. (The star (*) corresponds to Au used for the sample coating).

In Fig. 3, the N$_2$ adsorption–desorption isotherms at 77 K for the calcined sample are shown. The material exhibits a large BET specific surface area 829 m^2 g^{-1}. The characteristic condensation step at P/P_o 0.3–0.4 indicates a mesoporous material, with a pore diameter of 3.4 nm as calculated by the Horvath–Kawazoe method. However, the low height of the condensation step indicates at a relevantly low mesopore volume and mesopore population, while the initial, high adsorption step could imply the presence of microporosity. A parallel hysteris loop is observed at the desorption step, which ends before the condensation step at the mesopores. This should be attributed to a secondary intraparticle porosity formed by the sintering of the particles.[25]

Finally, in Fig. 4, the conversion profiles of a preliminary test on the simultaneous catalytic reduction of SO$_2$ and NO by CO are shown. The catalytic test was performed in a lab scale plug flow reactor similar to that described elsewhere[26] at a steady state mode. In the present experiment 200 mg of the solid Pac2C$_{16}$CuCe catalyst was used. The total flow rate of the reactant mixture (CO/NO/SO$_2$/He, 1.04%/0.22%/0.25%/98.49) was 200 ml min^{-1}, which corresponded to a GHSV of 32 000 h^{-1}. The effluents were analysed on a Carlo Erba GC using a combination of Porapac Q and Molecular Sieve 13X columns.
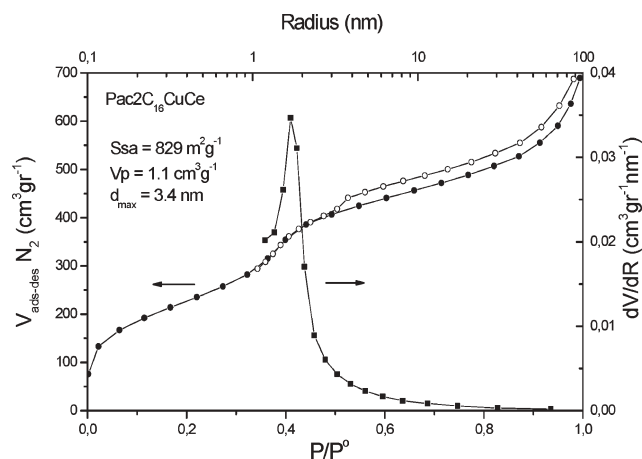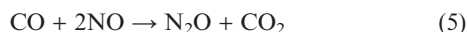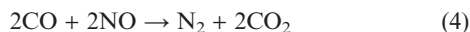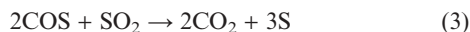

Fig. 3 N$_2$ adsorption–desorption isotherms at 77 K and the corresponding pore size distribution calculated according to the Horvath–Kawazoe method for the calcined at 600 °C Pac2C$_{16}$CuCe sample.
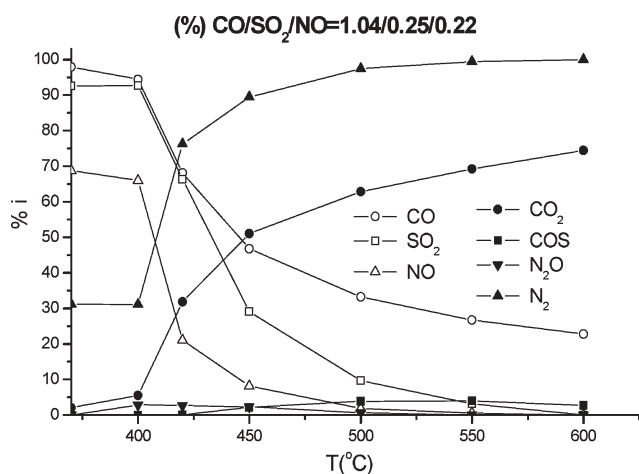
Fig. 4 Percent remaining SO_2, NO and CO in the products and % yields of CO_2, COS, N_2 and N_2O for the reaction indicated. Catalyst mass 200 mg at 32 000 h^{-1}.

The CO is in excess with respect to the stoichiometry of the following reactions, that are believed to take place[20] and cannot be totally consumed.

$$2CO + SO_2 \rightarrow S + 2CO_2 \qquad (1)$$

$$2CO + 2S \rightarrow 2COS \qquad (2)$$

$$2COS + SO_2 \rightarrow 2CO_2 + 3S \qquad (3)$$

$$2CO + 2NO \rightarrow N_2 + 2CO_2 \qquad (4)$$

$$CO + 2NO \rightarrow N_2O + CO_2 \qquad (5)$$

However, since we observe formation of negligible amounts of byproducts COS and N_2O along the whole tested temperature range, the predominant reactions should be (1) and (4). Reactions (2) and (3) may occur, but reaction (3) should be much faster than (2) in order that COS is not to be detected in large amounts. Activity starts around 350 °C and 100% conversion of NO to N_2 is achieved at 500 °C. Complete conversion of SO_2 to elemental sulfur takes place between 550–600 °C.

The catalytic testing lasted about 8 h indicating no signs of deactivation. We should note that the material was active at high space velocity 32 000 h^{-1} contrary to some relevant reports,[27] which apply an SV in the range 2 500–10 000 h^{-1} for the same reaction.

In conclusion, we report the synthesis of copper and cerium bimetallic mesoporous silica, where the metal species are favorably embodied in the network reinforcing it at the same time. The material exhibits exceptionally high metal load, surface area, thermal stability and metal dispersion compared to similar systems. This material was the first template assisted bimetallic mesoporous catalytic system to have been successfully tested for the simultaneous reduction of SO_2 and NO by CO towards elemental sulfur and N_2 respectively. Further investigation towards a more complete view of the catalytic properties of the material in the subject reaction is being undertaken.

Notes and references

1 K. Schumacher, M. Grun and K. K. Unger, *Microporous Mesoporous Mater.*, 1999, **27**, 201.
2 M. Hartmann, S. Racouchot and C. Bischof, *Microporous Mesoporous Mater.*, 1999, **27**, 309.
3 M. Hartmann, S. Racouchot and C. Bischof, *Chem. Commun.*, 1997, 2367.
4 H. Kosslick, G. Lschke, H. Landmesser, B. Parlitz, W. Storek and R. Fricke, *J. Catal.*, 1998, **176**, 102.
5 S. Kawi and M. Te, *Catal. Today*, 1998, **44**, 101.
6 M. A. Karakassides, A. Bourlinos, D. Petridis, L. Coche-Guerente and P. Labbe, *J. Mater. Chem.*, 2000, **10**, 403.
7 R. S. Mulukutla, T. Shido, K. Asakura, T. Kogure and Y. Iwasawa, *Appl. Catal., A*, 2002, **228**, 305.
8 L. X. Dai, Y. H. Teng, K. Tabata, E. Suzuki and T. Tatsumi, *Microporous Mesoporous Mater.*, 2001, **44**, 573.
9 S. Che, Y. Sakamoto, H. Yoshitake, O. Terasaki and T. Tatsumi, *J. Phys. Chem. B*, 2001, **105**, 10565.
10 D. Ji, T. Ren, L. Yan and J. Suo, *Mater. Lett.*, 2003, **1–4**, 4545.
11 R. Q. Long and R. T. Yang, *Ind. Eng. Chem. Res.*, 1999, **38**, 873.
12 W. Zhang and T. J. Pinnavaia, *Chem. Commun.*, 1998, 1185.
13 V. Antochshuk, A. S. Araujo and M. Jaroniec, *J. Phys. Chem. B*, 2000, **104**, 9713.
14 D. Panayotov, l. Dimitrov, M. Kristova, L. Petrov and D. Mehandjiev, *Appl. Catal., B*, 1995, **6**, 61.
15 J. Xiaoyuan, L. Liping, C. Yinghu and Z. Xiaoming, *J. Mol. Catal. A: Chem.*, 2003, **197**, 193.
16 P. Carniti, A. Gervasini, V. H. Modica and N. Ravasio, *Appl. Catal., B*, 2000, **28**, 175.
17 P. Bera, S. T. Aruna, K. C. Patil and M. S. Hedge, *J. Catal.*, 1999, **186**, 36.
18 P. G. Harrison, I. K. Ball, W. Azelee, W. Daniell and D. Goldfarb, *Chem. Mater.*, 2000, **12**, 3715.
19 C.-H. Wang, S. S. Lin, W. U. Hwang and H. S. Weng, *Ind. Eng. Chem. Res.*, 2002, **41**, 666.
20 M. F. Stephanopoulos, T. Zhu and Y. Li, *Catal. Today*, 2000, **62**, 145.
21 B. Wien and M. He, *Appl. Catal., B*, 2002, **37**, 75.
22 C. C. Pantazis and P. J. Pomonis, *Chem. Mater.*, 2003, **15**, 2299.
23 C. C. Pantazis, P. N. Trikalitis, P. J. Pomonis and M. J. Hudson, *Microporous Mesoporous Mater.*, 2003, **66**, 37.
24 C. C. Pantazis, P. N. Trikalitis and P. J. Pomonis, *J. Phys. Chem. B*, 2005, **109**, 12574.
25 M. Kruk and M. Jaroniec, *Chem. Mater.*, 2001, **13**, 3169.
26 (*a*) A. A. Leontiou, A. K. Ladavos and P. J. Pomonis, *Appl. Catal., A*, 2003, **241**, 133; (*b*) V. C. Belessi, T. V. Bakas, C. N. Costa, A. M. Efstathiou and P. J. Pomonis, *Appl. Catal., B*, 2000, **28**, 13; (*c*) V. C. Belessi, P. N. Trikalitis, A. K. Ladavos, T. V. Bakas and P. J. Pomonis, *Appl. Catal., A*, 1999, **177**, 53.
27 (*a*) Z. Zhaoliang, M. Jun and Y. Xiyao, *Chem. Eng. J.*, 2003, **95**, 15; (*b*) S. X. Zhuang, M. Yamazaki, K. Omata, Y. Takahashi and M. Yamada, *Appl. Catal., B*, 2001, **31**, 133; (*c*) H. M. Lee and J. D. Han, *Ind. Eng. Chem. Res.*, 2002, **41**, 2623.