

Supporting Information

Copper-containing monodisperse mesoporous silica nanospheres by a smart one-step approach

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1. X-ray diffraction analysis

X-Ray diffraction measurements¹ of copper-containing monodisperse mesoporous silica spheres were carried out in the low angle range in order to characterise the long-range pore ordering of the material, and in the high angle range to probe the structure of the copper oxide particles. The X-ray powder diffraction pattern in the low angle region of copper-containing mesoporous silica spheres (MSS) is shown in Fig.1. The sample exhibits a main diffraction peak at low 2θ value (about $2.7^\circ 2\theta$), characteristic of the (100) plane for pores in a hexagonal array. The presence of higher order diffraction peaks at 2θ values around 5 and $5.7^\circ 2\theta$ shows the ordered hexagonal regularity of the material. These results clearly indicate that the long-range pore ordering of copper-containing MSS is not affected by the *in situ* metal functionalisation.

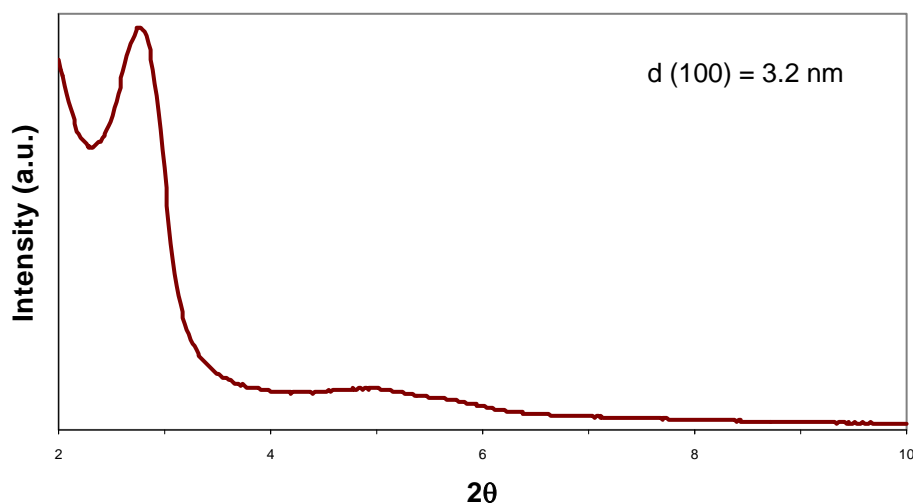


Fig. 1. Low angle range X-ray powder diffraction pattern of copper-containing MSS

The X-Ray diffraction analysis at larger 2θ values has been considered to study the nature and location of Cu species, in particular the hypothetical presence of extra-framework crystalline metal oxide aggregates in the material. The X-ray powder diffraction pattern of the copper-containing MSS shown in Fig. 2 exhibits no peak in the whole range, thereby suggesting that the metal species are very well dispersed in the material.² The location of copper species has been further examined with the aid of UV-vis spectroscopy.

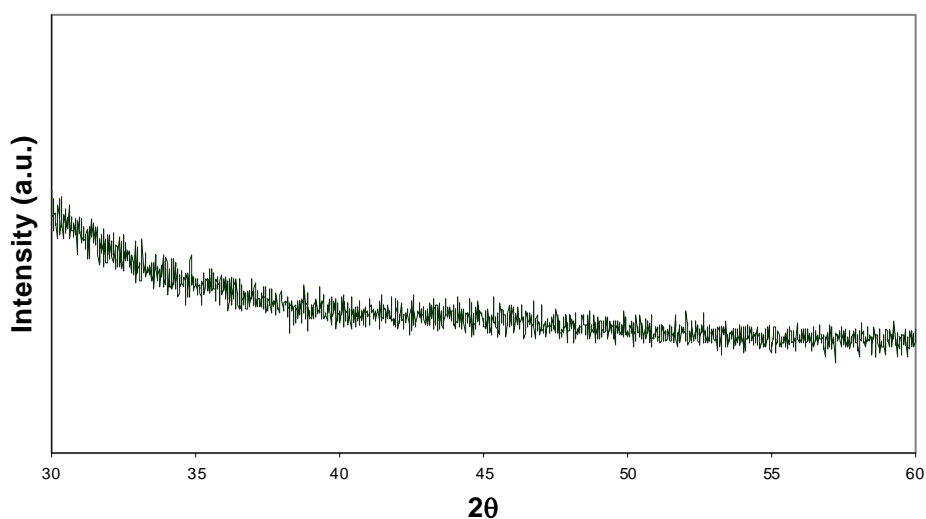


Fig. 2. High angle range X-ray powder diffraction pattern of copper-containing MSS

2. UV-visible DR spectroscopy

The UV-vis DR spectroscopy of copper-containing MSS has been performed¹ in order to provide information on the location of the copper species, *i.e.* are they dispersed on the internal surface or partially mixed in the silica framework? Electronic spectroscopy in the UV-vis region is a useful tool for investigations of the local coordination environment and electronic state of the transition metal species.³ The UV-vis spectrum of Cu-MSS shown in Fig. 3 displays features comparable to those observed by Vansant and co-workers⁴ in the spectra of copper-modified mesoporous materials prepared by infiltration and calcination of the same copper precursor $\text{Cu}(\text{acac})_2$ in the pores of various structures.

The spectrum of Cu-MSS exhibits a main band with maximum at about 235 nm attributed to the ligand to metal charge transfer (LMCT) transition between Cu^{2+} ion and oxygen in mononuclear species located at the surface.⁴ A slight shoulder can be observed around 300 nm indicating the limited presence of oligomeric cluster-like moieties through the charge-transfer between Cu^{2+} and oxygen in the $(\text{Cu-O-Cu})_n$ surface species.⁴ This sample spectrum also exhibits a weak and broad band around 800 nm, which is assigned to the ${}^2E_g \rightarrow {}^2T_{2g}$ spin-allowed transition of Cu in an octahedral coordination with oxygen in CuO .⁵ These results show that the copper is located at the internal surface of the mesoporous silica spheres, mainly as mononuclear oxide species very well dispersed at the surface of the pores. This conclusion is in agreement with the results of H_2 -TPR analysis.

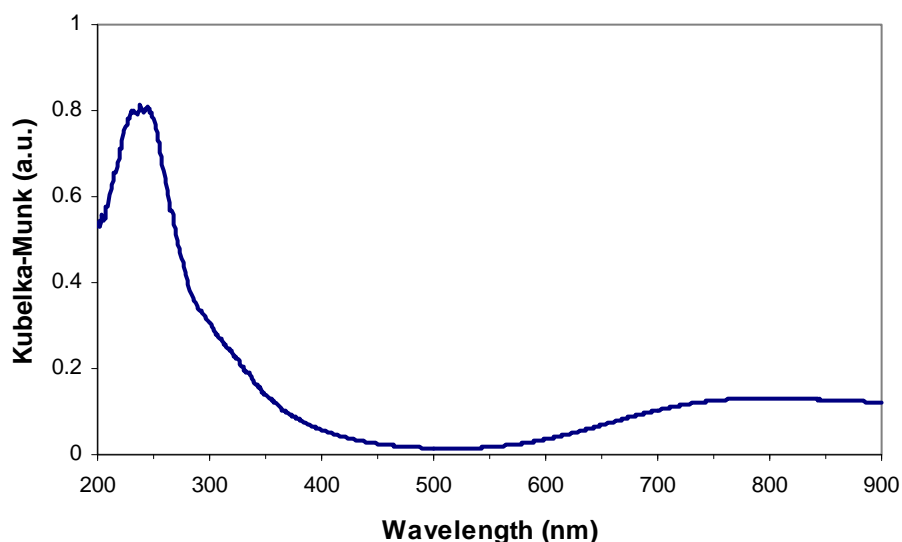


Fig. 3. DR UV-vis spectrum of copper-containing MSS

3. Complementary characterisation of the porosity using α_S method

Since the nitrogen adsorption-desorption isotherm of the sample displays a significant nitrogen adsorption at low relative pressures pointing out the presence of micropores, the adsorption data have been processed further to better characterise the porosity, mainly by means of α_S -method.⁶ The α_S -curve is plotted in the Fig. 4 together with two linear regression segments commonly used to determine the volume of micro and mesopores. The microporous volume (V_{mic}) calculated from the ordinate of the intersection point between the first linear segment and the adsorption axis from the Y-intercept is equal to $0.07 \text{ cm}^3 \cdot \text{g}^{-1}$. This relatively low value compared to the mesoporous volume ($V_{mes} = 0.63 \text{ cm}^3 \cdot \text{g}^{-1}$), indicates that the porosity of the synthesized silica nanospheres is essentially in the mesopore range.

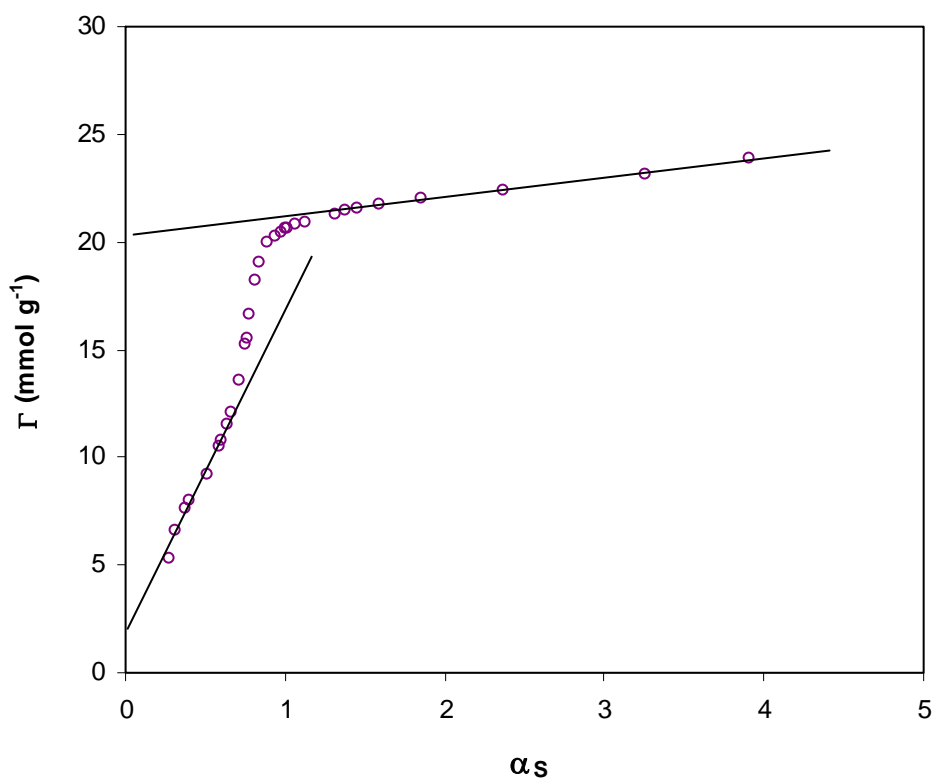


Fig. 4. N₂ α_S -plot for copper-containing porous silica spheres

4. Thermogravimetric analysis

The thermogravimetric analysis (TGA) of copper-containing monodisperse mesoporous silica spheres provides evidence for complete template removal, even at the relatively low calcination temperature, *i.e.* 623 K (instead of 823 K for pure MSS).⁷

The TGA profile of the calcined Cu-MSS, shown in Fig. 5, displays no weight loss that could be ascribed to the decomposition of remaining surfactant. The weight loss that occurs at temperatures below 373 K can be assigned to the release of physisorbed water. The TGA profile of copper-containing sample exhibits an additional weight loss of <0.5 wt % which is regular over the temperature range studied. This insignificant weight variation is attributed to the base-line drift. These conclusions are corroborated by the high specific area of the calcined sample, as inferred from the nitrogen adsorption study.

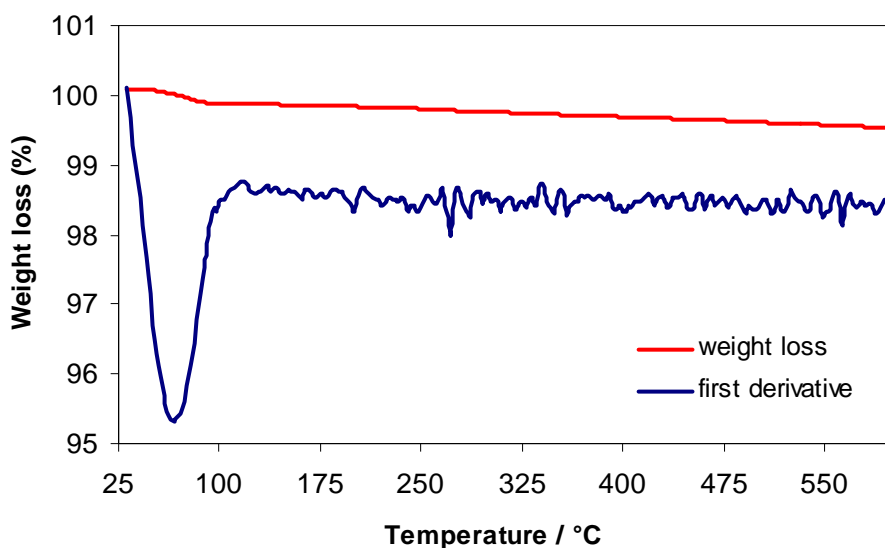


Fig. 5. TGA profile of copper-containing porous silica spheres calcined at 623 K

References

- 1 XRD measurements were performed with an X-PERT PRO II Philips goniometer. The Diffuse Reflectance UV-vis spectrum was measured on a Perkin-Elmer Lambda 14 spectrometer equipped with an integrating sphere (Labsphere, North Sutton, USA). The spectrum is displayed as its Kubelka-Munk $F_{(R)}$ transform: $F_{(R)} = (1-R^2) / 2R$; in which R is the measured reflectance.
- 2 M. Trejda, A. Tuel, J. Kujawa, B. Kilos and M. Ziolk, *Microporous Mesoporous Mater.*, 2008, **110**, 271.
- 3 S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola and G. Vlaic, *J. Catal.*, 1996, **158**, 486.
- 4 L. Chmielarz, P. Kustrowski, R. Dziembaj, P. Cool and E.F. Vansant, *App. Catal. B: Environmental*, 2006, **62**, 369.
- 5 M. Shimokawabe, H. Asakawa and N. Takezawa, *Appl. Catal.*, 1990, **59**, 45; G. Centi, S. Perathoner, D. Biglino and E. Giamello, *J. Catal.*, 1995, **151**, 75.
- 6 S. J. Gregg and K. S. W. Sing, in Adsorption, Surface Area and Porosity, Academic Press, London, 2nd edn., 1982, pp. 195-245.
- 7 Y. Yamada and K. Yano, *Microporous Mesoporous Mater.*, 2006, **93**, 190.