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Gold-assisted E' centres formation on the silica surface of Au/SBA-15 catalysts for low temperature CO oxidation

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Electronic Supplementary Information

Solid state NMR spectroscopy of ^{29}Si and ^{13}C was used (in addition to CHS analysis) to check the effective incorporation of MPTMS onto the walls of SBA-15, as well as to investigate the interactions between gold and the mercaptopropyl groups. The pertinent results are reported in Fig. S1. Besides the three partially overlapping signals in the region from -80 to -120 ppm, ascribable to Q^2 (-92 ppm), Q^3 (-100 ppm), and Q^4 (-110 ppm) silicon atoms,[S1] the SBA-15-SH functionalized support (Fig. S1a) shows the two low-field signals T^2 (-56 ppm) and T^3 (-66 ppm) typical of the silane organic moieties incorporated as a part of the

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silica walls structure.[S2,S3] The successful incorporation of the mercaptopropyl groups onto the mesopore surface is also confirmed by the ^{13}C CPMAS NMR analysis. In the SBA-15-SH spectrum (Fig. S1b) the peak at 10.7 ppm can be attributed to the methylene carbon atom directly bonded to the silicon atom (C1); the other two methylene carbon atoms (C2 and C3) are responsible for the strong signal at 27.0 ppm. Although the ratio between the intensities of the T and the Q signals does not change significantly after addition of gold, the ^{29}Si MAS spectrum of the Au/SBA-15-SH sample shows some rearrangement in the distribution of the Si atoms within the Q and T sites, which seems to depend on the reducing treatment rather than on the gold presence itself.[S4] A more complicated pattern is obtained for the Au/SBA-15-SH catalyst when submitted to the ^{13}C CPMAS NMR analysis. New signals (at 17.5 ppm, 22.1 ppm, 28.9 ppm, and a very broad asymmetric one at *ca.* 40 ppm) are observed, which might be originated by the C3 and C2 methylene carbon atoms of the propylic chains:[S4] (i), in the presence of S–Au interactions (*ca.* 40 ppm); (ii), in the presence of disulfide species (22.1 ppm); and (iii), as a consequence of some perturbation of the $-(CH_2)_3-SH$ groups (17.5 ppm and 28.9 ppm), induced by the presence of gold.

The Raman spectrum of the as-made Au/SBA-15-SH catalyst (not shown) exhibited the stretching (2800-2900 cm^{-1}) and bending vibrations (1250-1500 cm^{-1}) of the $-CH_2$ methylene groups as well as the stretching frequency of the C–S bond (650 cm^{-1}).[S5] This result further confirms the successful functionalization of SBA-15 by MPTMS. The stretching bands of both S–Au[S6] and S–H[S7] bonds were also observed at 300 cm^{-1} and 2580 cm^{-1}, respectively, indicating that only a fraction of the –SH groups are involved in the formation of S–Au bonding. In agreement with the ^{13}C NMR results, an additional band at *ca.* 500 cm^{-1}, ascribable to the S–S stretching mode, was detected as well, revealing the presence of disulfide species formed by reaction between adjacent thiol groups.[S6]

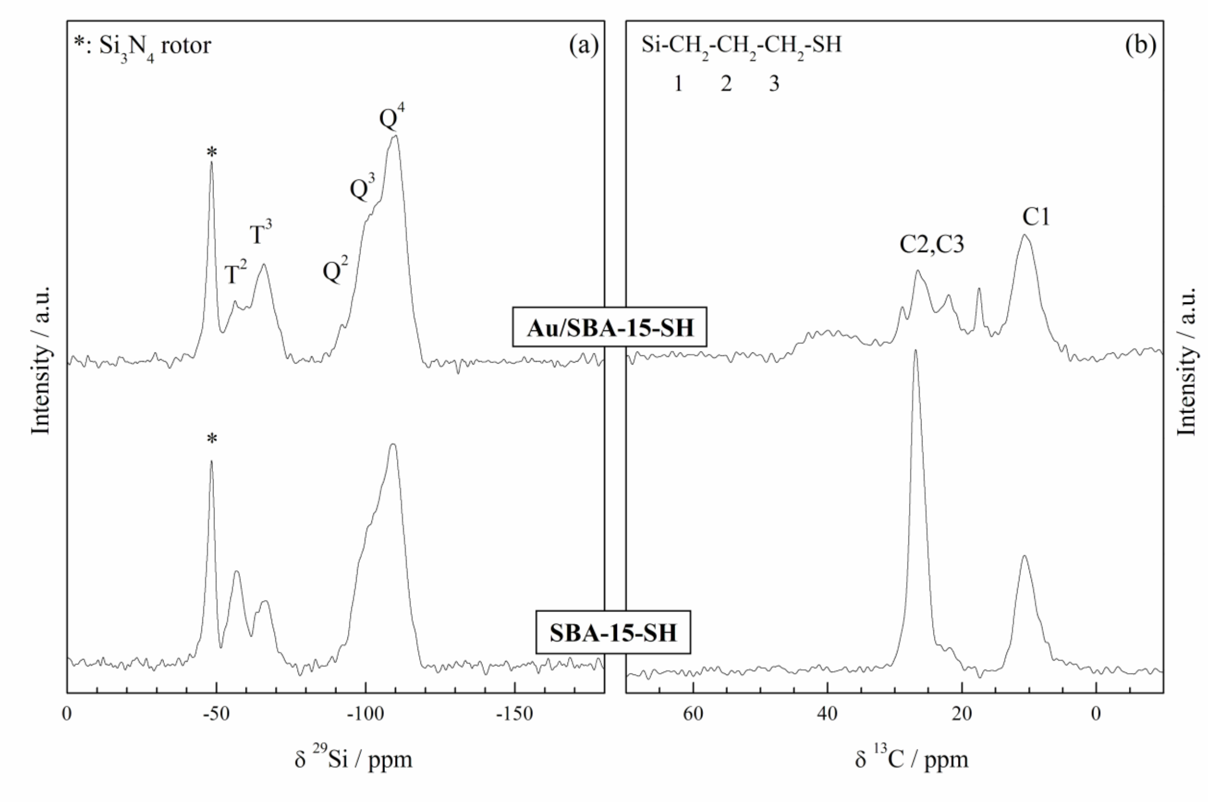

Figure S1. Solid state ^{29}Si MAS (a) and ^{13}C CPMAS (b) NMR spectra.

The low-angle X-ray diffraction (LA-XRD) patterns of both the bare and the functionalized supports as well as of the as-made catalyst are reported in Fig. S2. The SBA-15 sample shows the well-resolved (100), (110), and (200) diffraction peaks typical of the 2-D hexagonal mesostructure (P6mm space group) of the pore system. The LA-XRD pattern of the SBA-15-SH sample is similar to that of the parent SBA-15, though the weak (110) and (200) diffraction peaks are less intense, indicating a less ordered system. A slight shift of the reflections towards lower angles is observed, in agreement with previous results on similar systems.[S8] The corresponding slight increase in the lattice constant (of *ca.* 0.15 nm) indicates that changes in the pore size and/or the wall thickness have occurred as a consequence of the functionalization process. No changes in the LA-XRD pattern of the gold-containing sample are observed.

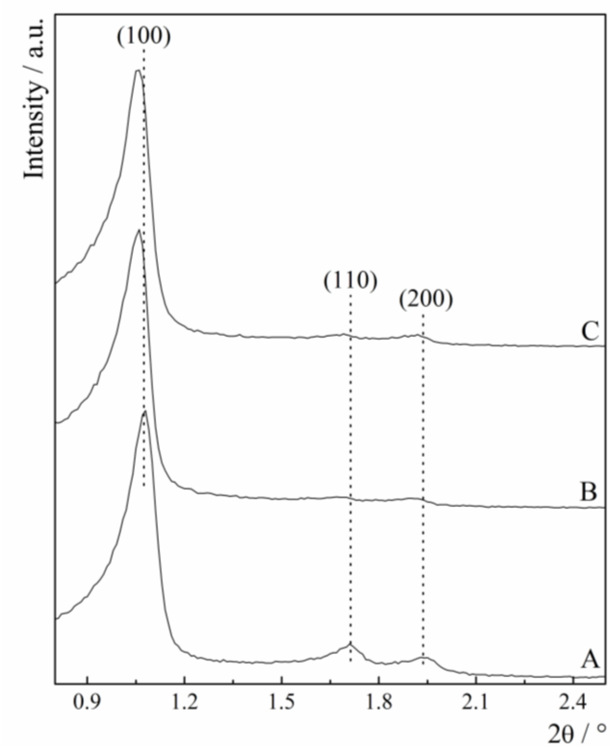

Figure S2. Low-angle X-ray Diffraction patterns of SBA-15 (A), SBA-15-SH (B), and Au/SBA-15-SH (C).

References

S1. E. Lipmaa, M. Magi, A. Samson, G. Engelhardt, A. R. Grimmer, *J. Am. Chem. Soc.*, 1980, 102, 4889-4893.

S2. M. Llusar, G. Monros, C. Roux, J. L. Pozzo, C. Sanchez, *J. Mater. Chem.*, 2003, 13, 2505-2514.

S3. Y. Q. Wang, C. M. Yang, B. Zibrowius, B. Spliethoff, M. Linden, F. Schüth, *Chem. Mater.*, 2003, 15, 5029-5035.

S4. M. G. Cutrufello, E. Rombi, C. Cannas, M. Casu, B. Onida, S. Fiorilli, I. Ferino, in *Topics in Chemistry and Material Science*, ed. K. Hadjiivanov, V. Valtchev, S. Mintova and G. Vayssilov, Heron Press, Sofia, 2010, vol. 4, pp. 222-232.

S5. G. Socrates, in *Infrared and Raman Characteristic Group Frequencies – Tables and Charts*, John Wiley & Sons, Chichester, 3rd edn., 2001.

S6. G. J. Kluth, C. Carraro, and R. Maboudian, *Phys. Rev. B*, 1999, 59, R10449-R10452.

S7. S. W. Raso, P. L. Clark, C. Haase-Pettingell, J. King, and G. J. Thomas, Jr., *J. Mol. Biol.*, 2001, 307, 899-911.

S8. M. G. Cutrufello, E. Rombi, C. Cannas, M. Casu, A. Virga, S. Fiorilli, B. Onida, I. Ferino, *J. Mater. Sci.*, 2009, **44**, 6644-6653.