

Oxidation of alkenes to 1,2-diols: FT-IR and UV studies of silica-supported sulfonic acid catalysts and their interaction with H₂O and H₂O₂

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Supporting Information

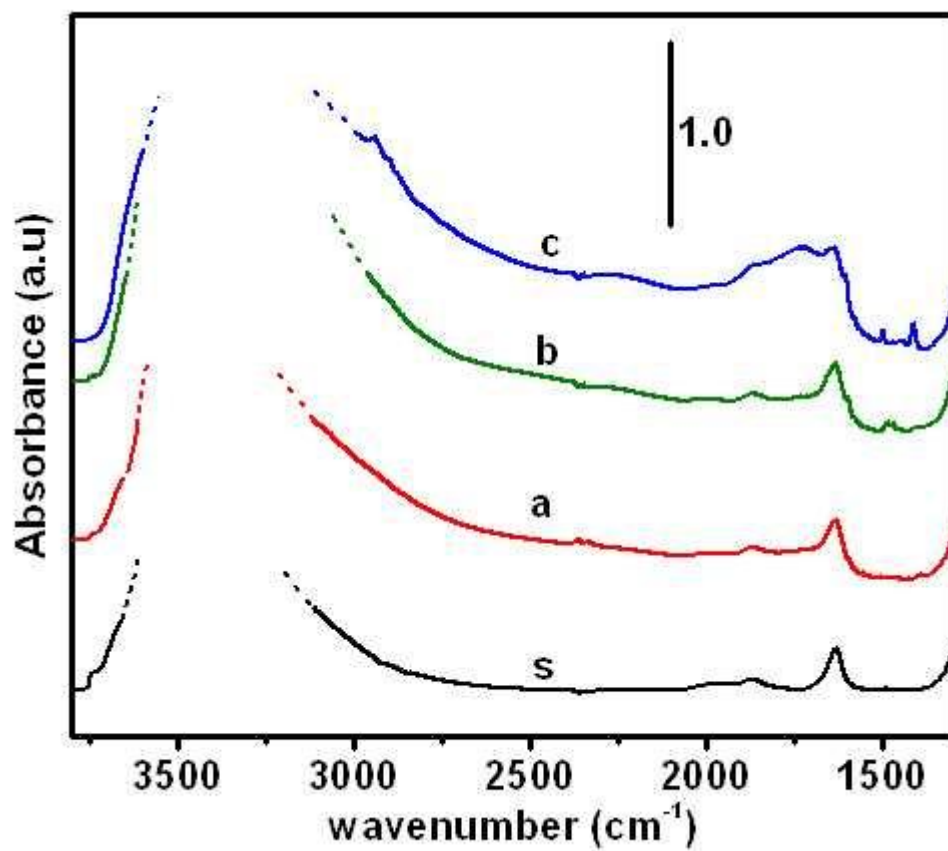


Figure SI-1. IR spectra of the samples in contact with air: s bare SiO₂; a) catalyst A; b) catalyst B; c) catalyst C. The maximum of the main absorption in the high frequency region was out of scale

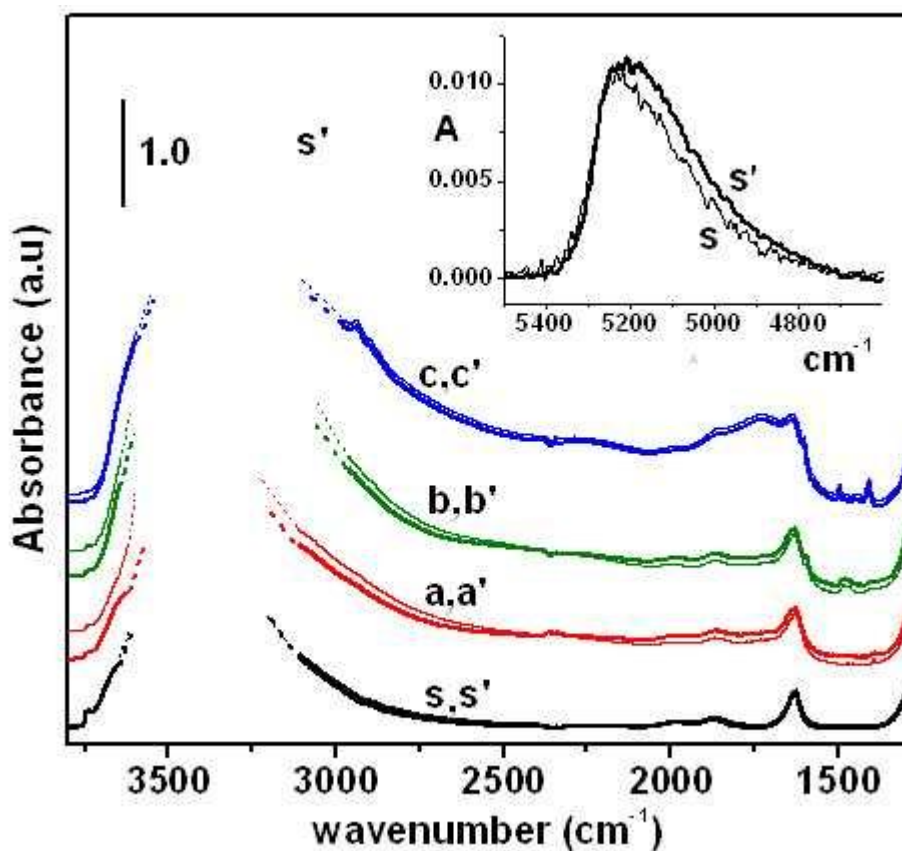


Figure SI-2. IR spectra of the samples in contact with 20 mbar of H₂O vapour (curves x) or of H₂O₂/H₂O (30% vol H₂O₂) (curves x'): s, s') bare SiO₂; a, a') catalyst A; b, b') catalyst B; c, c') catalyst C. The maximum of the main absorption in the high frequency region was out of scale. Inset: spectra, in the NIR region, of the bare SiO₂ in contact with 20 mbar of: s) H₂O; s') H₂O₂/H₂O (30% vol H₂O₂), as in the main frame. Similar data were obtained for the other samples.

Comment to Figure SI-2. No significant changes were observed between the spectra collected after admission on the samples of H₂O or H₂O₂/H₂O vapour. However, the presence of H₂O₂ in the liquid-like molecular layers formed on the sample surface was witnessed by the broadening towards the low frequency side of the $\nu_{\text{OH}} + \delta_{\text{OH}}$ band of water at 5230 cm⁻¹ (NIR region), likely due to the presence of an additional component due to the same combination mode of H₂O₂ [1] (see inset).

[1] L.G.Weyer, S.-C. Lo, Handbook of Vibrational Spectroscopy, J.M. Chalmers, P.R. Griffiths (Eds), Wiley, Chichester 2003, Volume 3, p. 1832

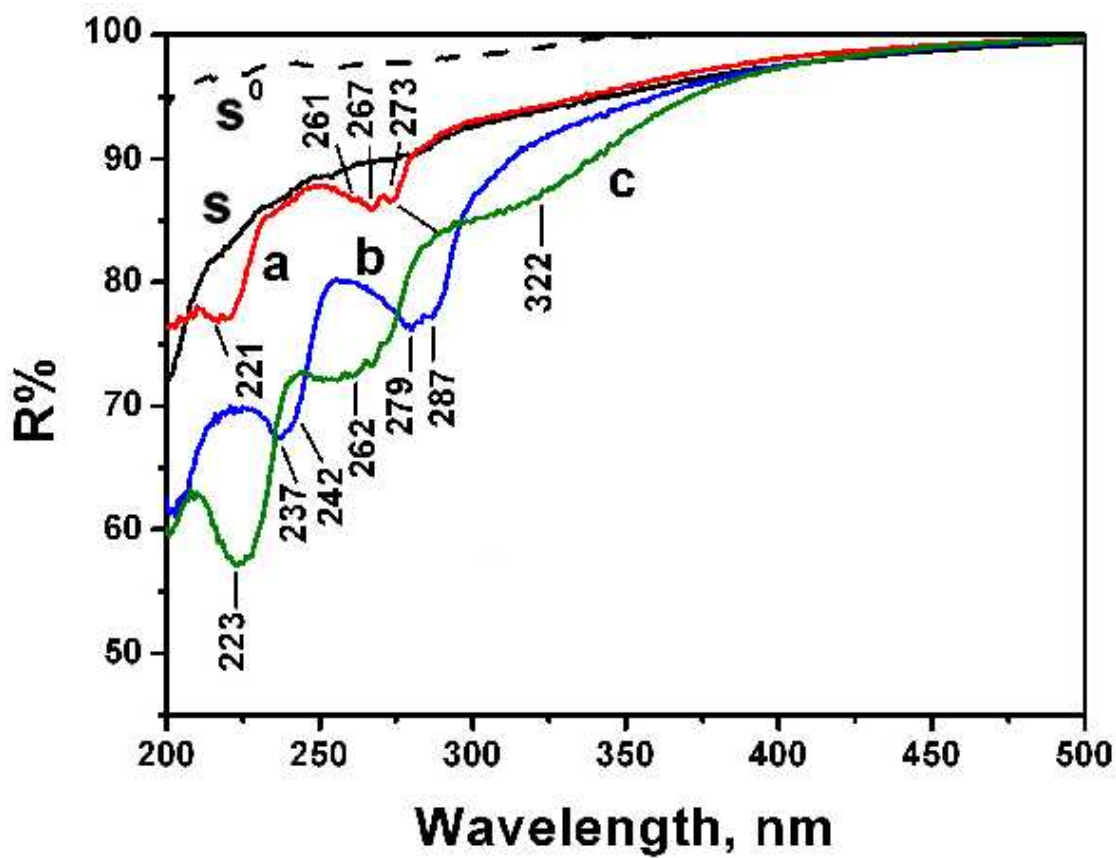


Figure SI-3. DR UV-Vis of samples in air: s⁰) pyrogenic silica used as diluents; s) bare silica support; a) catalyst A; b) catalyst B; c) catalyst C.

Reaction catalysed by *p*-toluenesulfonic acid: a 10-mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser was charged with *p*-toluenesulfonic acid (14.5 mg, 0.08 mmol), 30% aqueous H₂O₂ (0.86 mL, 8.4 mmol) and 1-methylcyclohexene (0.50 mL, 4.2 mmol). The mixture was heated at 70 °C under stirring for 22 h and then cooled to rt. Then MnO₂ (ca. 100 mg) was added to the solution to destroy any hydrogen peroxide excess. Subsequently, bromobenzene was added as external standard, the mixture was diluted with methanol and analysed by GC: 1-methylcyclohexene conversion 99%; 1-methyl-1,2-cyclohexanediol yield 61%.

Reaction carried out in the presence of 1-methyl-1,2-cyclohexanediol: a 10-mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser was charged with 30% aqueous H₂O₂ (0.86 mL, 8.4 mmol), 1-methylcyclohexene (0.50 mL, 4.2 mmol), 1-methyl-1,2-cyclohexanediol (0.027 g, 0.21 mmol) and catalyst A (2% mol with respect to 1-methylcyclohexene, 140 mg). The mixture was heated at 70 °C under stirring for 8 h and then cooled to rt. Then MnO₂ (ca. 100 mg) was added to the solution to destroy any hydrogen peroxide excess. Subsequently, bromobenzene was added as external standard, the mixture was diluted with methanol and analysed by GC. The results are reported in Figure SI-4.

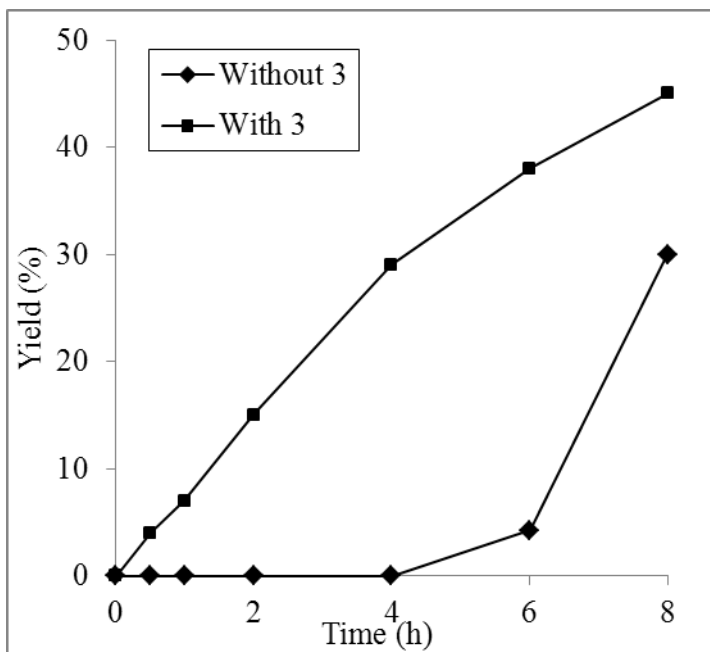


Figure SI-4. Yield versus time of the model reaction carried out with catalyst A in the absence (♦) and in the presence (■) of 1-methyl-1,2-cyclohexanediol.