

Electronic Supplementary Information

Ordered Mesoporous V₂O₅–WO₃ Composite Catalysts for Efficient Oxidation of Aryl Alcohols

Euaggelia Skliri^a, Ioannis N. Lykakis^b and Gerasimos S. Armatas^{*a}

^a *Department of Materials Science and Technology, University of Crete, Voutes GR-71003, Heraklion, Greece.*

^b *Department of Chemistry, Aristotle University of Thessaloniki, University Campus GR-54124, Thessaloniki, Greece.*

*E-mail: garmatas@materials.uoc.gr.

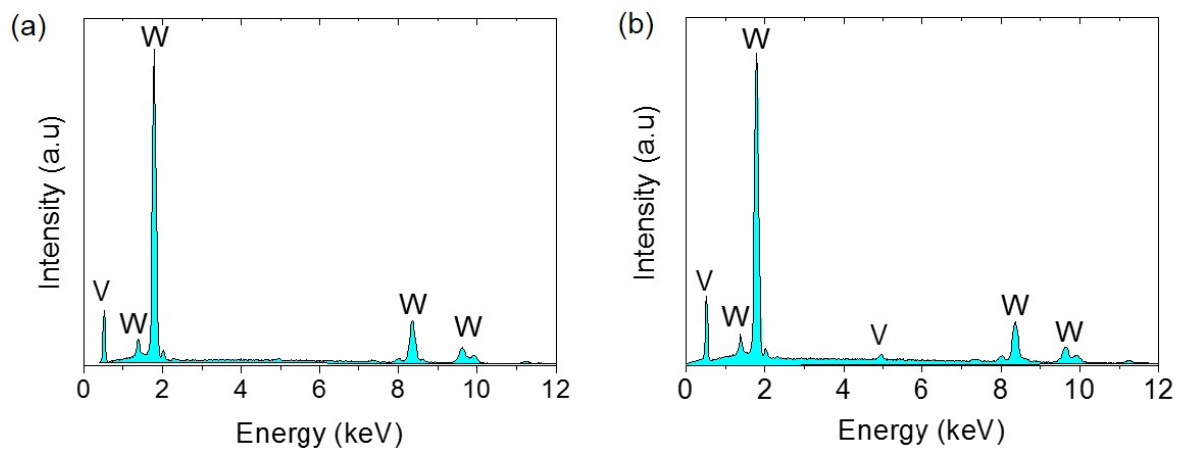


Fig. S1 Typical EDS spectra of mesoporous WO_3 materials containing (a) 1% and (b) 4% V_2O_5 . The EDS spectra show an average atomic ratio W/V of $\sim 97.5:2.5$ and $\sim 90.9:9.1$ that corresponds to a ~ 1 wt % and ~ 3.8 wt % V_2O_5 loading for 1% $\text{V}_2\text{O}_5/\text{WO}_3$ and 4% $\text{V}_2\text{O}_5/\text{WO}_3$ composites, respectively.

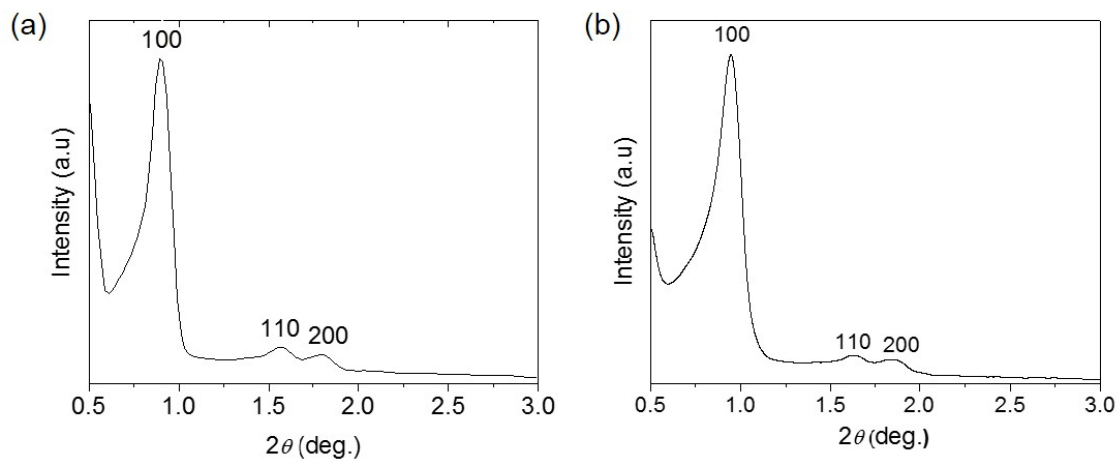


Fig. S2 Low-angle XRD patterns of mesoporous (a) SBA-15 and (b) APS/SBA-15 materials. The indexing of the Bragg diffractions is consisted with a hexagonal $p6mm$ unit cell with lattice parameter $a_0 \sim 11.1$ nm for SBA-15 and ~ 10.7 nm for APS/SBA-15.

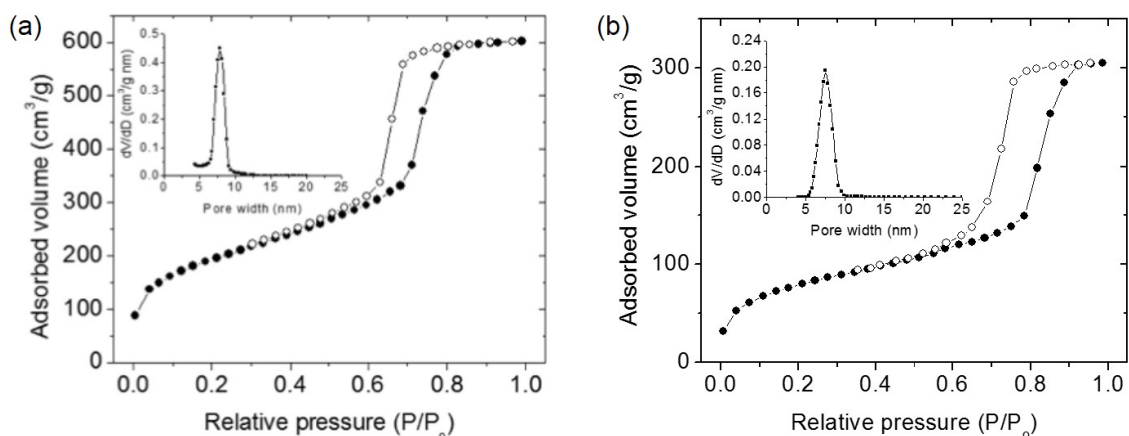


Fig. S3 Nitrogen adsorption–desorption isotherms and the corresponding NLDFT pore size distribution (inset) for mesoporous (a) SBA-15 and (b) NH₂-functionalized SBA-15 (APS/SBA-15) materials. The SBA-15 shows specific surface area of 676 m²g⁻¹, total pore volume of 0.96 cm³g⁻¹ and narrow pore size distribution with pore width of 7.8 nm. The APS/SBA-15 shows specific surface area of 286 m²g⁻¹, total pore volume of 0.96 cm³g⁻¹ and narrow distribution of pore size with pore width of 7.4 nm. The pore wall thickness of modified silica (APS/SBA-15), estimated by the equation $WT = a_0 - D_p$, is about 3.3 nm.

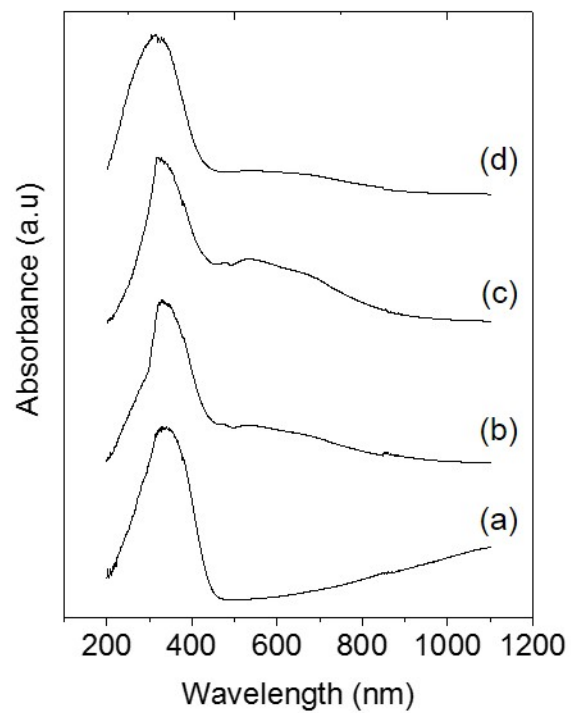


Fig. S4 Diffuse reflectance ultraviolet-visible (UV-vis) spectra of mesoporous (a) *meso*-WO₃ and (b) 1% V₂O₅/WO₃, (c) 4% V₂O₅/WO₃ and (d) 6% V₂O₅/WO₃ composite materials.

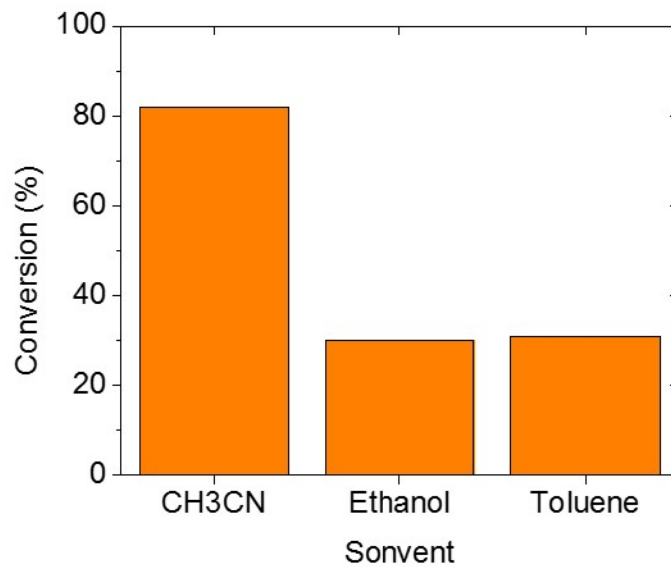


Fig. S5 Oxidation of 1-phenylethanol with 4% V_2O_5/WO_3 catalyst in different solvents. *Reaction conditions:* 0.1 mmol 1-phenylethanol, 50 mg catalyst, 40 equiv. *t*-BuOOH, 2 mL solvent, 50 °C, 4 h.

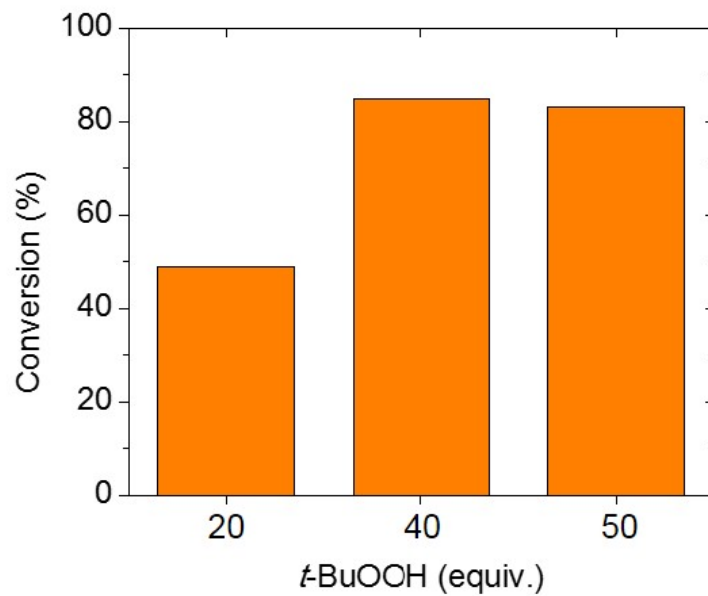


Fig. S6 Oxidation of 1-phenylethanol with 4% V_2O_5/WO_3 catalyst, using various equivalents of *t*-BuOOH oxidant. *Reaction conditions:* 0.1 mmol 1-phenylethanol, 50 mg catalyst, 2 mL CH_3CN , 50 °C, 2 h.

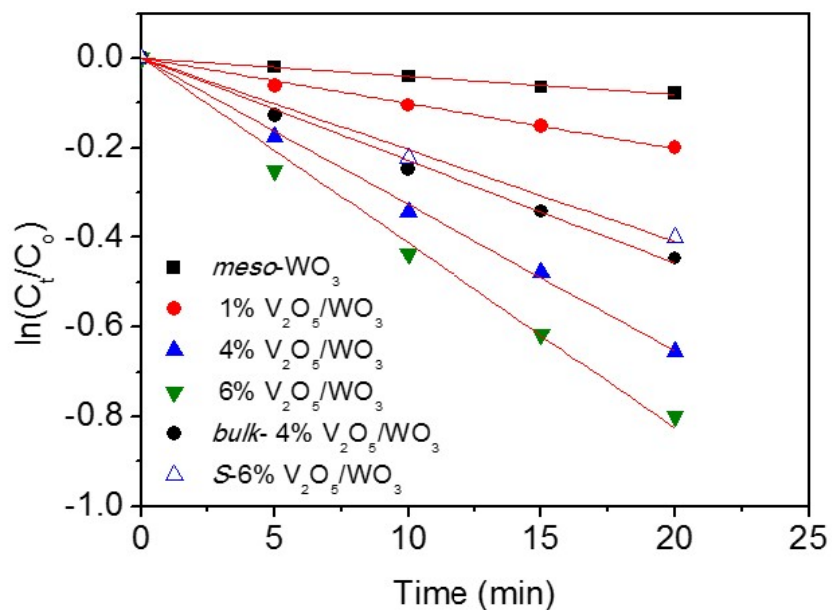


Fig. S7 Kinetic profiles (where C_0 and C_t are the concentrations of 1-phenylethanol at the initial state of reaction and at the time t , respectively) of the oxidation of 1-phenylethanol catalyzed by mesoporous $meso-WO_3$, $x\% V_2O_5/WO_3$ ($x= 1, 4$ and 6) and S- $4\% V_2O_5/WO_3$ materials and macroscopic *bulk*- $4\% V_2O_5/WO_3$ solid.

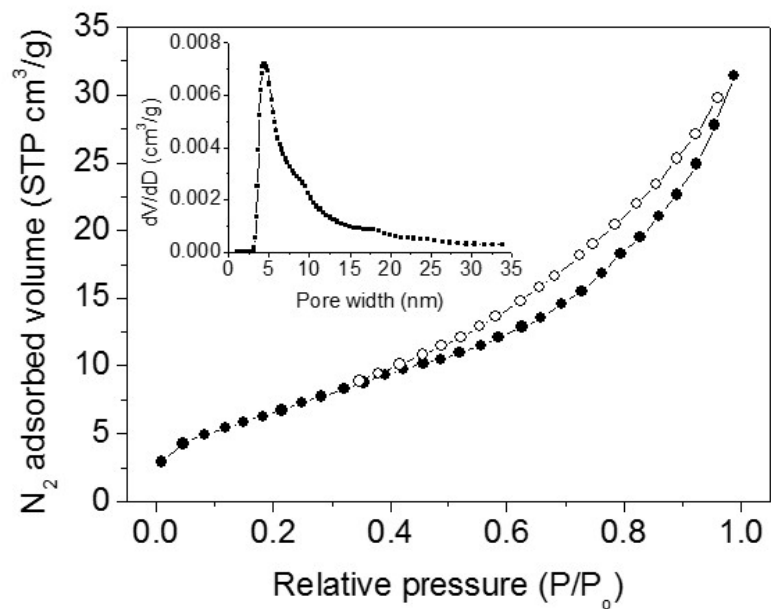


Fig. S8 Nitrogen adsorption–desorption isotherms at 77K of reused 4% V₂O₅/WO₃ catalyst. Analysis of the adsorption data with the BET method gives surface area of 26 m²g⁻¹ and total pore volume of 0.05 cm³g⁻¹. Inset: the corresponding NLDFT pore size distribution, indicating pore size of ~4.5 nm

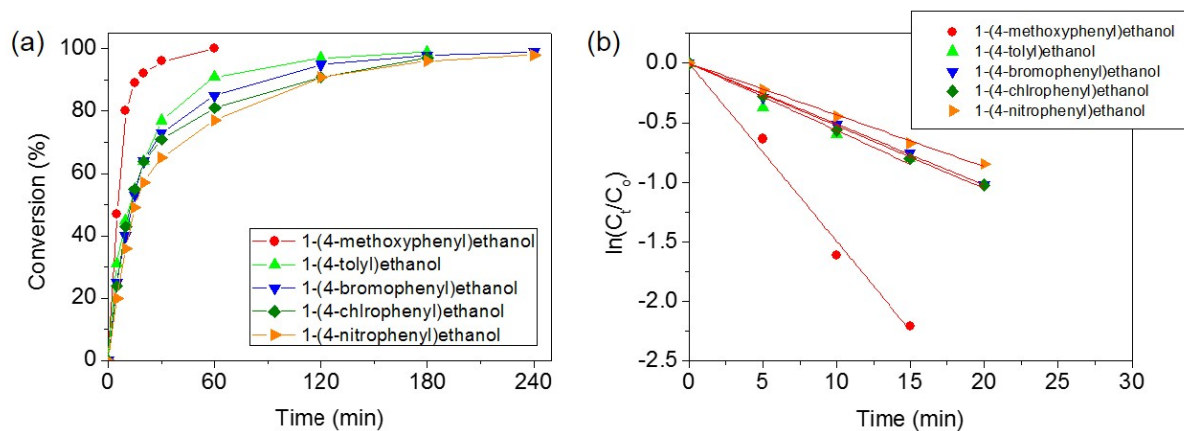


Fig. S9 (a) Time evolution and (b) kinetic profiles (where C_0 and C_t are the concentrations of substrate at the initial state of reaction and at the time t , respective) of the oxidation of various *para*-substituted benzyl alcohols catalyzed by mesoporous 4% V₂O₅/WO₃ catalyst. In panel b the corresponding red lines are fit to the data. *Reaction conditions*: 0.1 mmol substrate, 50 mg catalyst, 40 equiv. *t*-BuOOH, 2 mL CH₃CN, 50 °C.