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Supporting information for article:

**Zirconia-supported 11-molybdovanadophosphoric acid catalysts:
effect of the preparation method on their catalytic activity and
selectivity**

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Reinoso**

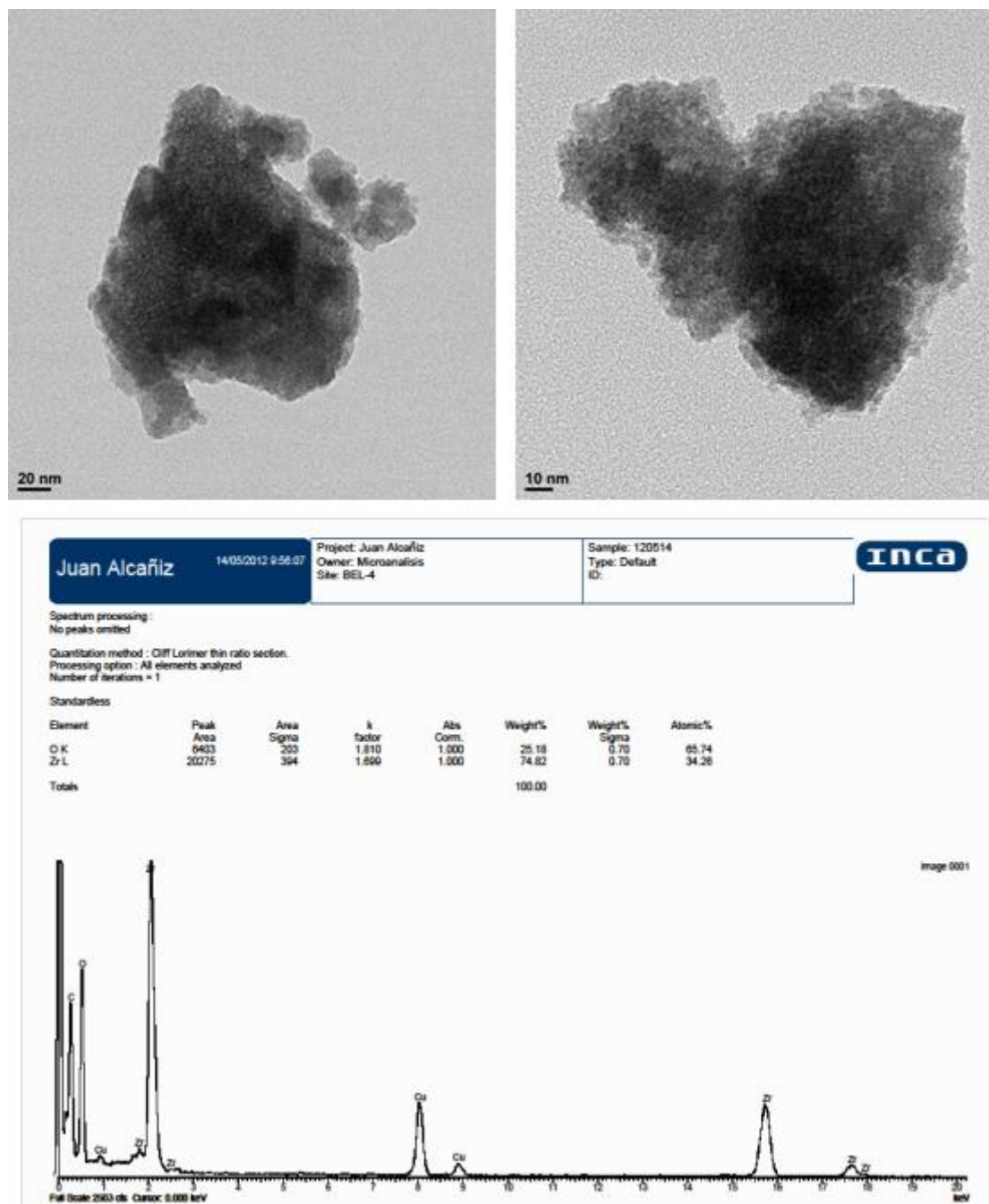


Figure S1 TEM micrographs and EDX analysis of the Z support.

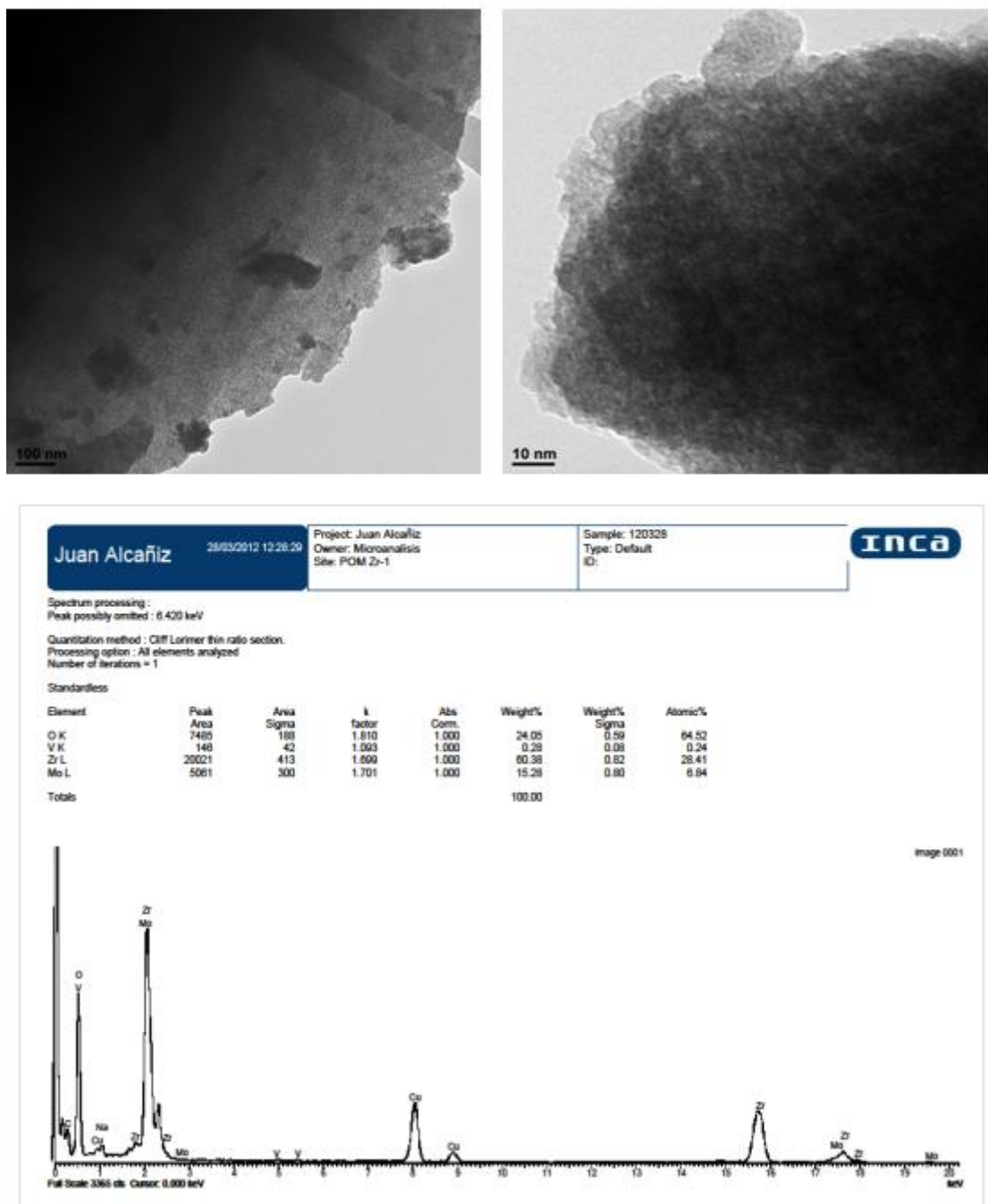


Figure S2 TEM micrographs and EDX analysis of the fresh 50VPMo/Z100 catalyst.

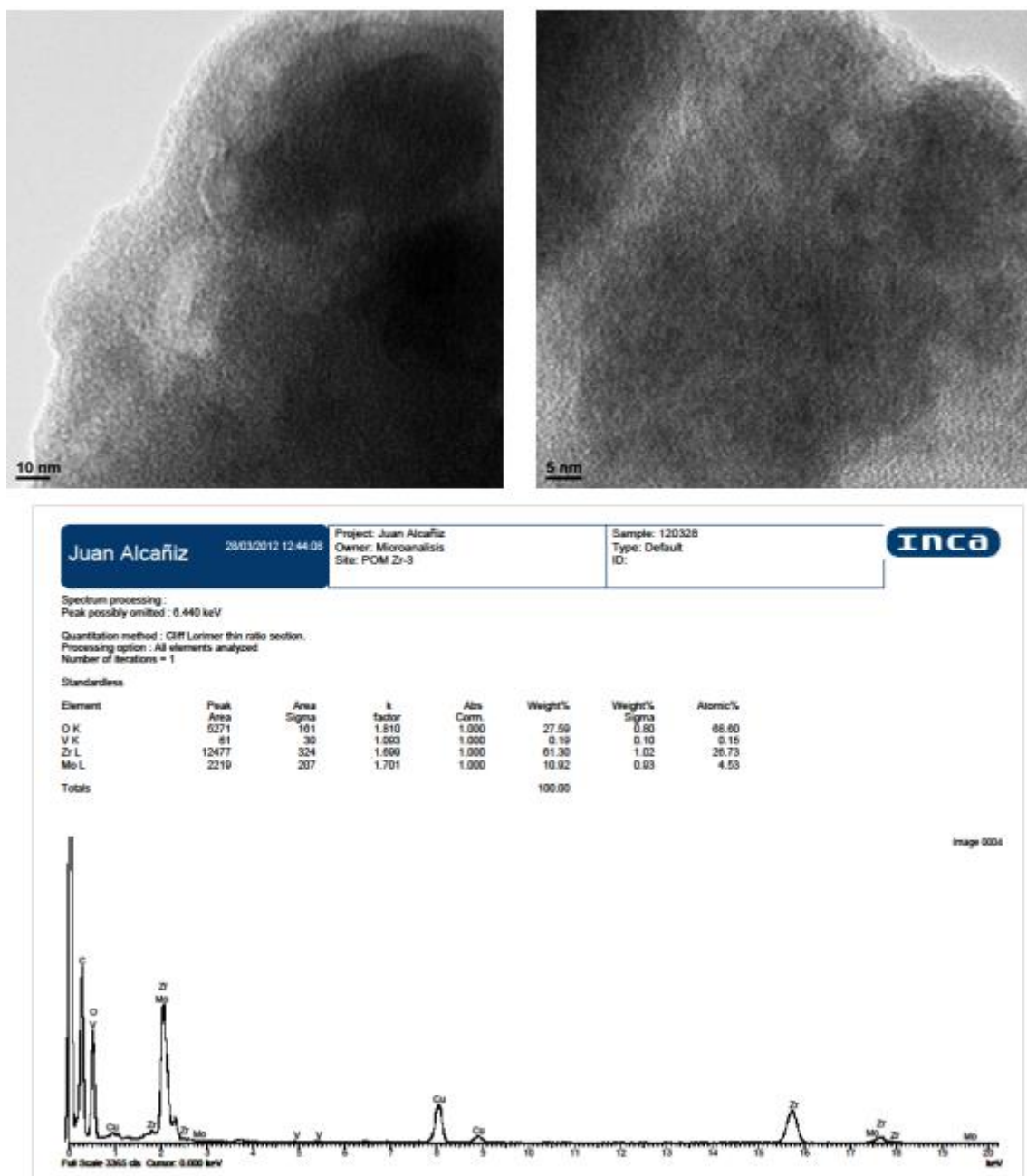


Figure S3 TEM micrographs and EDX analysis of the 50VPMo/Z100 catalyst recovered after performing the catalytic cycle C1.

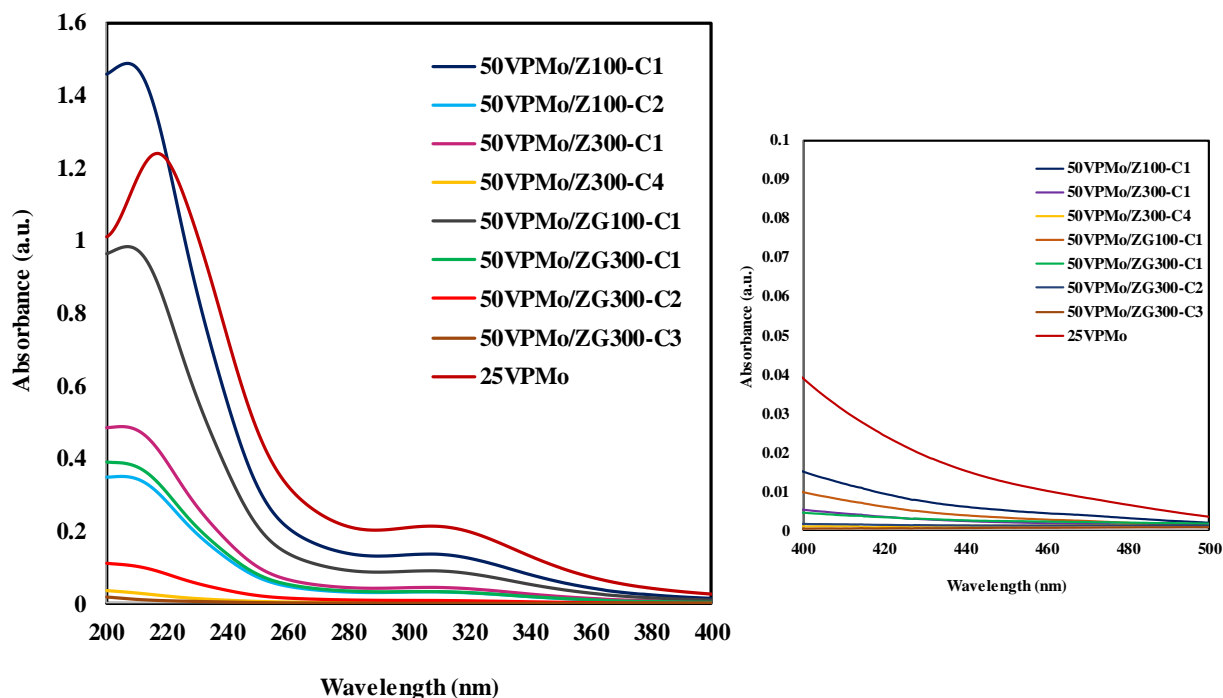


Figure S4 UV-Vis spectra of the filtrates obtained upon separation of several different 50VPMo/Z catalysts (synthesized by either impregnation or sol-gel methods, and calcined at 100 or 300 °C) from the reaction mixture of the adamantane oxidation at different catalytic cycles. Reaction conditions: 0.1 g of catalyst; 30 mmol of H₂O₂; 0.184 mmol of adamantane; 10 mL of acetonitrile; 75 °C, 6 h.

Figure S4 shows the solution UV–Vis spectra of the H₄PVMO₁₁O₄₀ heteropolyacid (**VPMo**) compared to those of the filtrates obtained upon separation of several different 50VPMo/Z samples from the reaction mixture of the adamantane oxidation at different catalytic cycles. The spectra of the filtrates are all similar to that of **VPMo** heteropolyacid and this fact is indicative of the **VPMo** leaching process taking place to some extent from the supported catalyst materials. Thus, all spectra show a band at 308 nm with a long tail at lower wavelength, which is associated with the ligand–to-metal charge-transfer (LMCT) transitions characteristic of the PVMO₁₁O₄₀⁴⁻ cluster. It should be noted that a distortion in the LMCT band takes place at the lower wavelength region after the reaction in the presence of H₂O₂ is completed, and this fact indicates changes in the environment around the PVMO₁₁O₄₀⁴⁻ anion that could be related with the formation of peroxyanions. However, the band assigned to the peroxyvanadate species located at 447 nm is absent in the spectra of the filtrates, and what is more, the intensity of the region at 400–500 nm decreases with respect to that of the pristine H₄PVMO₁₁O₄₀. Identical results have been published by Kala et al. [N.K. Kala Raj, A.V. Ramaswamy, P. Manikandan; Journal of Molecular Catalysis A: Chemical 227 (2005) 37–45], who indicated that not much information could be obtained from UV–Vis studies about the vanadium–peroxide interaction.

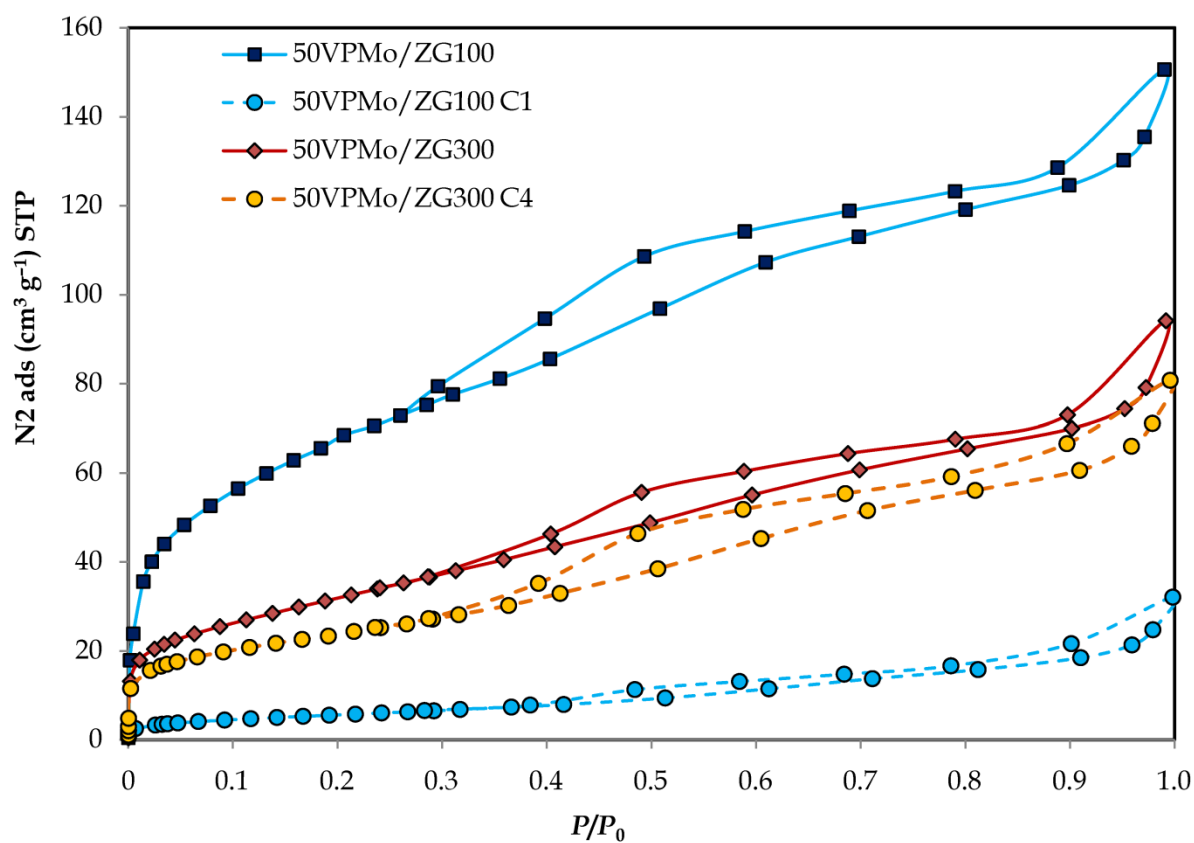


Figure S5 N₂ adsorption-desorption isotherms at -196 °C of the fresh 50VPMo/ZG100 and 50VPMo/ZG300 catalysts compared with those corresponding to the same catalysts after being recovered from the first (C1) and fourth (C4) catalytic cycles, respectively.

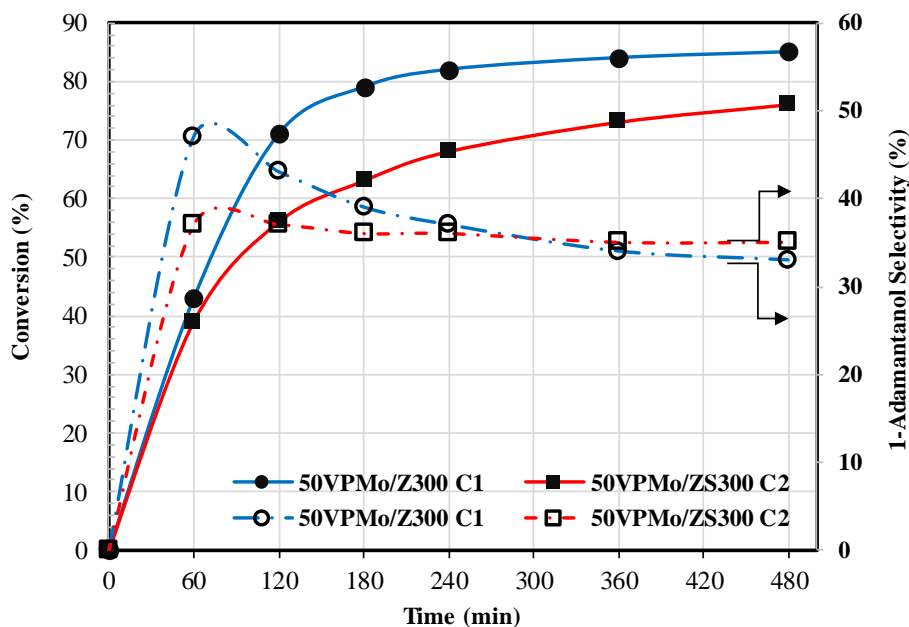


Figure S6 Conversion of adamantane (continuous line) and selectivity toward 1-adamantanol (broken line) as a function of time for the 50VPMo/Z300 catalyst run throughout the first catalytic cycle (C1, blue) and the second reaction run (C2, red). Reaction conditions: 0.1 g catalyst; 30 mmol H₂O₂; 1.84 10⁻¹ mmol adamantane; 10 mL acetonitrile; 75 °C.

Figure S6 shows the evolution of the selectivity toward 1-adamantanol as the conversion of adamantane progresses for the 50VPMo/Z300 catalyst throughout two consecutive reaction runs. In the case of fresh catalyst (C1), the selectivity toward 1-adamantanol gradually decreases after 1 hour of reaction as the conversion of adamantane increases, whereas for the reused catalyst (C2), the selectivity toward 1-adamantanol is maintained at nearly similar values during the whole adamantane conversion process. These results show that, once the product 1-adamantanol is formed, it progresses to overoxidation for the fresh catalyst and remains nearly intact for the reused sample.

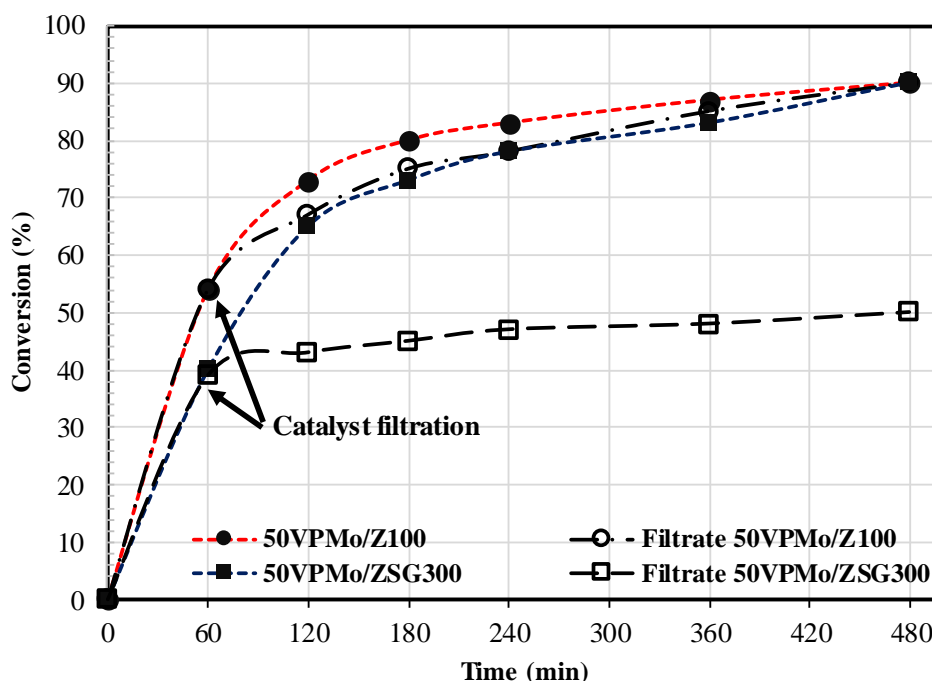


Figure S7 Monitoring of the conversion of adamantane as a function of time for the catalytic tests run with the fresh 50VPMo/Z100 and 50VPMo/ZG300 samples compared to that of the same catalytic tests for which the catalyst is separated by filtration after just 1h of reaction. Reaction conditions: 0.1 g of catalyst; 30 mmol of H₂O₂; 0.184 mmol of adamantane; 10 mL of acetonitrile; 75 °C.

The kinetics of the adamantane conversion catalysed by the 50VPMo/Z100 and 50VPMo/ZG300 samples are shown in Figure S7. Both catalysts afford a fast adamantane conversion for the first 2 h of reaction, the impregnation catalyst showing a higher initial activity. This difference could be related with a homogeneous catalytic contribution due to its higher VPMo leaching into the reaction medium. For the impregnation catalyst, the filtration test shows that the homogeneous catalysis contributes significantly to the adamantane oxidation process due to VPMo leaching as the reaction continues with little affection upon removing the solid catalyst by filtration after just 1 h. In contrast, the conversion remains nearly constant upon filtering the sol-gel synthesized catalyst, and thus, the oxidation of adamantane must be mainly catalysed by the immobilized VPMo species in this case.