Composite β-$AgVO_3$@$V_{1.6}^{5+}V_{0.4}^{4+}O_{4.8}$ hydrogels and xerogels for catalytic applications

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Silver vanadium oxides and vanadium oxides, and concretely β-$AgVO_3$ phase, have received considerable attention in the last decade due to their unique physical and chemical properties, including electrochemical[1] and photo-catalytic activities,[2] sensing, optical, magnetic, electrical properties,[3] and antibacterial activity.[4]

A series of 36 β-$AgVO_3$@$V_{1.6}^{5+}V_{0.4}^{4+}O_{4.8}$ composite hydrogels were synthesized using a mixture of two solutions of $NaVO_3$ and $AgNO_3$.[5] Adding different amounts of HNO_3, hydrogels with different β-$AgVO_3$/$V_{1.6}^{5+}V_{0.4}^{4+}O_{4.8}$ ratio and gelification degree were obtained. The morphological analysis reveals that the hydrogels are composed by cross linked three dimensional network of silver vanadium oxide and vanadium oxide nano-ribbons which traps water. Xerogels of the selected materials were produced by drying the hydrogels at 70 ºC. These xerogels maintain the hydrogel porosity in some degree, with BET surface areas from 44.8 to 73.6 m^2g^{-1} and average pore diameter from 190 to 97 Å.

Three hydrogels and their dehydrated xerogels were selected to test them as heterogeneous catalysts for the oxidation of alcohols with tert-butyl hydroperoxide (TBHP) as oxidizing agent. The selected hydrogels were: H1A10, H3A7 and H4A6, which compositions are $0.92(Ag_{0.92}V_{0.92}O_{2.76})$@$0.08(V_{1.38}^{5+}V_{0.62}^{4+}O_{4.69})$, $0.75(AgVO_3)$@$0.25(V_{1.63}^{5+}V_{0.37}^{4+}O_{4.815})$ and $0.65(AgVO_3)$@$0.35(V_{1.64}^{5+}V_{0.36}^{4+}O_{4.820})$, respectively. The reactions were carried out at 70 ºC in acetonitrile, using 2 eq. of TBHP, with a ratio catalyst/substrate of 5 %, based on the vanadium content. The powdered dried xerogels, H1A10-X, H3A7-X and H4A6-X, showed conversions of about 70 % when benzyl alcohol was used as substrate. When using the hydrogels, a pre-activation stage was carried out, letting them under stirring during 12 hours in acetonitrile, in order to exchange the water trapped into them for the reaction solvent. In this case, the reaction yields differ a lot between one hydrogel to another, with conversions of 92 % for H1A10, 66 % for H4A6 and 25 % for H3A7, after 6 hours of reaction. The study was completed with other related substrates and the catalysts were characterized after the reactions by powder X-ray diffration, IR spectroscopy and scanning electron microscopy.

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[1] H. Zeng, Q. Wang and Y. Rao, *RSC Adv.*, 2015, **5**, 3011–3015.

[2] X. Yang, F. Ma, K. Li, Y. Guo, J. Hu, W. Li, M. Huo and Y. Guo, *J. Hazard. Mater.*, 2010, **175**, 429–438.

[3] J. Dexmer, C. M. Leroy, L. Binet, V. Heresanu, P. Launois, N. Steunou, C. Coulon, J. Maquet, N. Brun, J. Livaje and R. Backov, *Chem. Mater.*, 2008, **20**, 5541–5549.

[4] J. Rena, W. Wang, M. Shang, S. Sun, L. Zhang and J. Chang, *J. Hazard. Mater.*, 2010, **183**, 950–953.

[5] R. Fernández de Luis, A. Martínez-Amesti, E.S. Larrea, L. Lezama, A. Tomás Aguayo and M. I. Arriortua, *J. Mater. Chem. A*, 2015, **3**, 19996-20012.