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

Edurne S. Larrea[a], Roberto Fernández de Luis[b], Marta Iglesias[c] and María I. Arriortua[a,b]

[a]Dpto. Mineralogía y Petrología, University of the Basque Country, UPV/EHU, Sarriena s/n, 48940 Leioa, Spain; [b]BCMaterials-Basque Center for Materials, Applications & Nanostructures, Building 500 - 1st. Floor, Bizkaia Science and Technology Park, 48160 Derio, Spain; [c]Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, Sor Juana Ines de la Cruz 3, Cantoblanco, 28049 Madrid, Spain.

Introduction

Silver vanadium oxides (SVO) and vanadium oxides have received considerable attention in the last decade due to their unique physical and chemical properties. [1-4]

The particle size, morphology and surface properties are directly related with the synthetic method and conditions, and influence drastically the phisico-chemical properties os the SVO materials. Several authors have crystallized this materials from hydrothermal conditions (120 - 180 ºC) as highly crystalline micrometric ribbons with nanometric withs (20-50 nm). [5-6] Our research group has obtained similar β-$AgVO_3$ ribbons with a very fast synthesis procedure at room temperature [7]

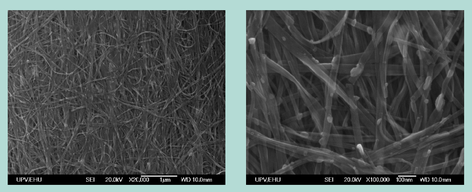
1. H. Zeng, Q. Wang and Y. Rao, *RSC Adv.*, **2015**, 5, 3011-3015.
2. X. Yang, F. Ma, K. Li, Y. Guo, J. Hu, W. Li, M. Huo and Y. Guo, *J. Hazard. Mater.*, **2010**, 175, 429-438.
3. J. Dexmer, C. M. Leroy, L. Binet, V. Heresanu, P. Launois, N. Steunou, C. Coulon, J. Maquet, N. Brun, J. Livaje and R. 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. N. D. Leifer, A. Colom, M. Martocci, S. G. Greenbaum, F. M. Alamgir, T. B. Reddy, N. R.Gleason, R.A. Leising, E. S. Takeuchi, J. *Electrochem. Soc.*, **2007**, 154, A500.
6. Y. Xu, X. Han, L. Zheng, W. Yan, Y. Xie, *J. Mater. Chem.*, **2011**, 21, 14466.
7. R. Fernández de Luis, A. Martínez-Amesti, E.S. Larrea, L. Lezama, A. T. Aguayo and M. I. Arriortua, *J. Mater. Chem. A*, **2015**, 3, 19996-20012.

Synthesis and Characterization

SVO hydrogel were easily synthesized at room temperature by mixing aqueous solutions of sodium vanadate with different HNO_3 content and silver nitrate. Immediately after the mixing, the gelation process starts, taking from 1 hour to several days. A series of 36 β-$AgVO_3$@$V_{1.6}^{5+}V_{0.4}^{4+}O_{4.8}$ composite hydrogels were obtained. The morphological analysis reveals that the hydrogels are composed by cross linked three dimensional network of SVO and vanadium oxide nanoribbons which traps water. Xerogels were produced by drying the hydrogels at 70 ºC. These xerogels maintain the hydrogel porosity in some degree, with BET surface areas ranging from 44.8 to 73.6 m^2g^{-1} and average pore diameter from 190 to 97 Å.

Three hydrogels and their corresponding xerogels were selected to be studied as heterogeneous catalysts:

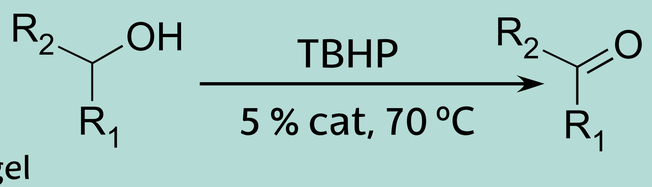
	Chemical Composition
H1A10	$0.92(AgVO_3)@0.08(V_{1.38}^{5+}V_{0.62}^{4+}O_{4.69})$
H3A7	$0.75(AgVO_3)@0.25(V_{1.63}^{5+}V_{0.37}^{4+}O_{4.815})$
H4A6	$0.65(AgVO_3)@0.35(V_{1.64}^{5+}V_{0.36}^{4+}O_{4.820})$



SEM micrographies of H1A10-xerogels before grinding

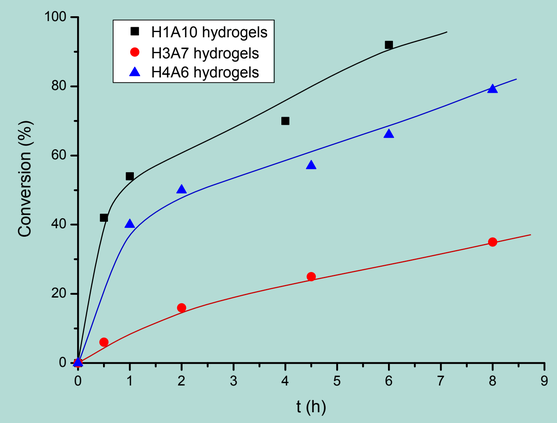
Catalytic activity tests

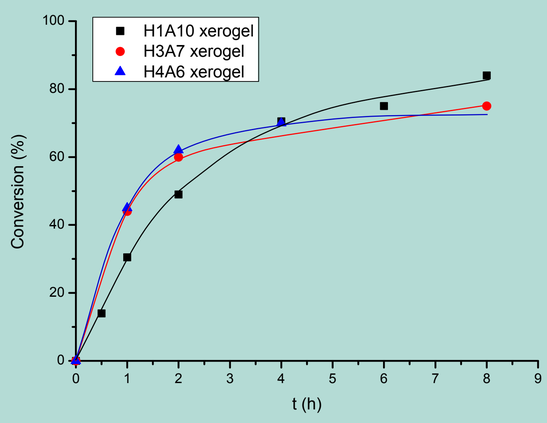
The selected materials were proved as catalysts for the oxidation of alcohols with tert-butyl hydroperoxide (TBHP) as oxidizing agent. The reactions were carried out at 70 ºC in CH_3CN, using 2 eq. of TBHP, with a ratio catalyst/substrate of 5 %.



Comparing hydrogels and xerogels

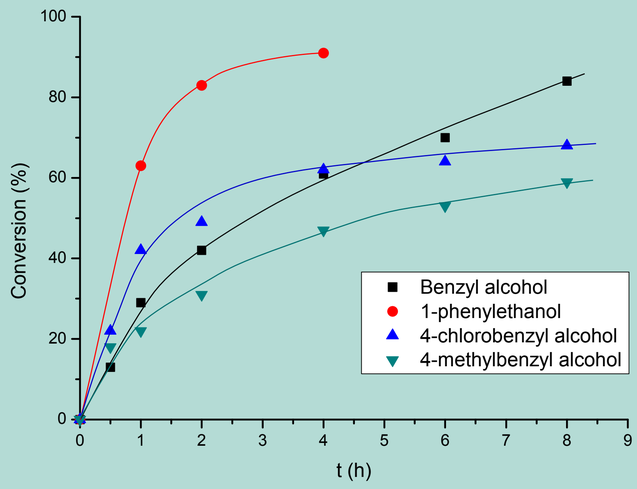
The reaction with benzyl alcohol was made over the six catalysts. All of them were preactivated with TBHP. The kinetic profiles are quite different for hydrogels and xerogels, due to their different physical properties. However, in both cases, the highest conversion rates is obtained with the H1A10 composition. For this reason further studies were made over the powdered H1A10 xerogel



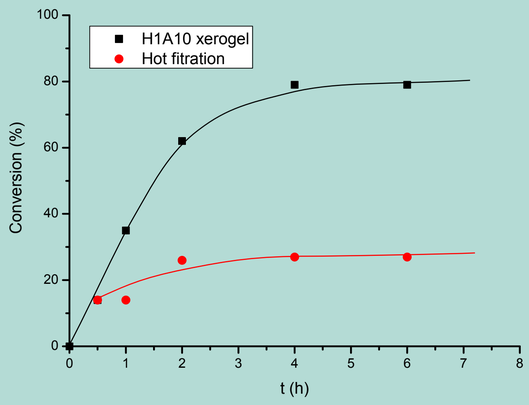


Scope of reaction with H1A10 xerogel

The scope of the reaction was studied for H1A10 xerogel with various substracts. The most activated one is the 1-phenylethanol.



Substrate	C (4h)	TOF (h^{-1})
Benzyl alcohol	62	26
1-phenylethanol	91	62
4-chlorobenzyl alcohol	62	44
4-methylbenzyl alcohol	47	22

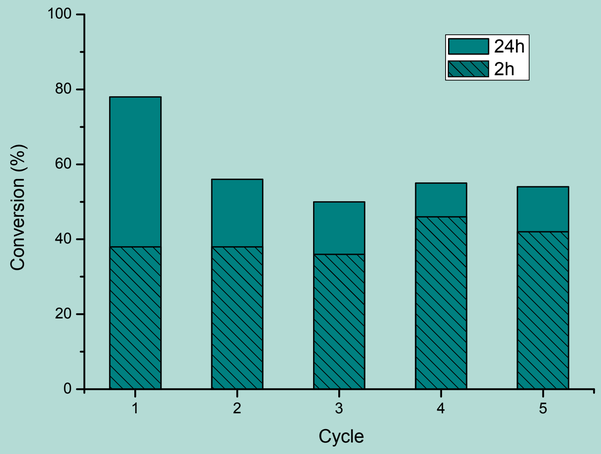


Hot filtration

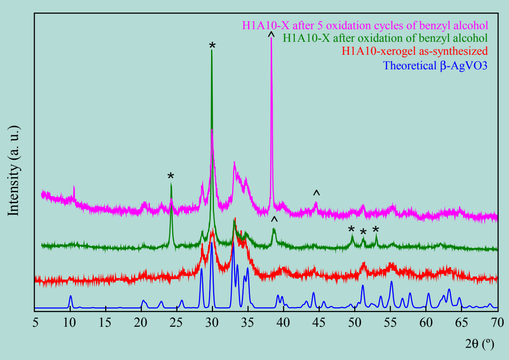
Hot filtration of the catalyst was carried out to verify its hetereogenity. The conversion reached by the filtered solution showed a slight increase, but much lower than those obtained for the reaction with catalyst.

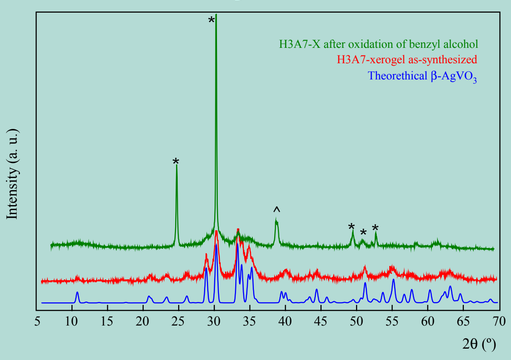
Reutilisation tests

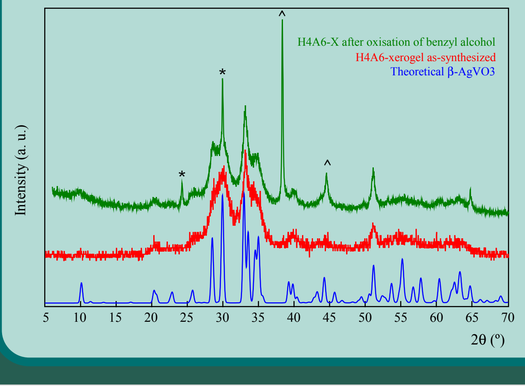
The reutilisation tests were made over H1A10 xerogel for the oxidation of benzyl alcohol. The conversion after 2 hours is very similar for all the cycles, while the values of conversion reached after 24 hours vary between one cycle and the next one, decreasing in the first three cycles, increasing in the fourth and decreasing a little in the fifth.



Characterization of the recovered catalysts

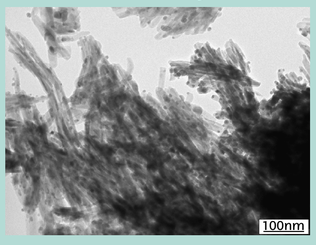




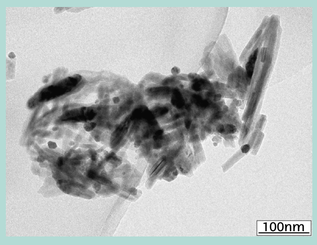


The diffractograms show diferences between the as-synthesized xerogels and the recovered catalysts. Firstly, an unidentified crystallyne phase is formed (*) followed by the reduction of the Ag^+ to Ag^0 (^). In the case of H4A6, both Ag^0 and the unknown phase are present, while for the recycled catalyst H1A10, this phase dissapeared and Ag^0 maxima are clearly observed.

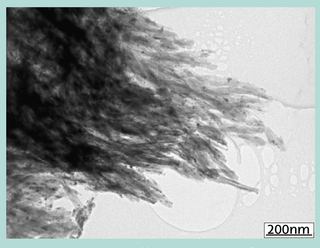
Scanning electron microscopy images of the recovered catalysts confirmed the occurrence of Ag^0 as particles adhered to the ribons of catalysts. The fibrous nanostructure is maintained while the length of the ribbons is notably shorter.



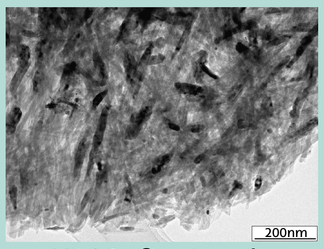
H1A10 after 1 cycle



H1A10 after 5 cycles



H3A7 after 1 cycle



H4A6 after 1 cycle

Conclusions

β-$AgVO_3$@$V_{1.6}^{5+}V_{0.4}^{4+}O_{4.8}$ composite materials have been proved as heterogeneous catalysts with good results for the oxidation of alcohols to aldehydes an ketones. They are reusable, at least for 5 cycles with lower loss of activity after 2 hours. The catalysts experienced chemical and structural change, during the catalytic process, giving rise to an unknown crystalline phase and to metallic silver.

Acknowledgements

This work has been financially supported by the "Ministerio de Economia y Competitividad" (MAT2013-42092-R), the "Gobierno Vasco" (Basque University Research System Group, IT-630-13) and UPV/EHU (UFI 11/15) which we gratefully acknowledge. The authors thank for technical and human support provided by SGIker of UPV/EHU and European funding (ERDF and ESF). Edurne S. Larrea thanks the "Ministerio de Enonomía y Competitividad" for her contract.

eman ta zabal zazu

Universidad del País Vasco

Euskal Herriko Unibertsitatea

BCMATERIALS

BASQUE CENTER FOR MATERIALS, APPLICATIONS & NANOSTRUCTURES

ehu group

icmm