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Elucidating the effect of hydrophobicity of methyl-functionalized mesoporous titanosilicate in the epoxidation of olefins

L.E. Manangon-Perugachi,[a,c] V. Smeets,[a] A. Vivian,[b] C. Aprile,[b] D.P. Debecker[a] and E.M. Gaigneaux*[a]

a) Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCLouvain), Place Louis Pasteur 1, box L4.01.09, 1348 Louvain-la-Neuve, Belgium.
b) Unit of Nanomaterial Chemistry, Department of Chemistry, University of Namur, Namur, Belgium.
c) Department of Extractive Metallurgy, Escuela Politecnica Nacional, Quito, Ecuador.
* eric.gaigneaux@uclouvain.be

Introduction

Titanosilicates (Ti-SiO_2) are well-known catalysts for the epoxidation of olefins which is an important reaction in the fine and bulk chemical industry. Isolated Ti inserted in the silica framework in tetrahedral coordination are the active species for epoxidation.[1] Recently, tuning the hydrophobic/hydrophilic balance of such catalyst surface has appeared as a promising tool to further boost their performance,[2-5] leading to greener epoxidation processes. However, tuning the hydrophobic/hydrophilic balance via a one-pot sol-gel generally led to a decrease of Ti dispersion and/or collapse of the pore network. To tackle this limitation, hydrophobic mesoporous Ti-SiO_2 were here prepared by aerosol-assisted one-pot sol-gel, which allowed the simultaneous control of Ti dispersion, degree of methyl-functionalization, and textural properties.

Outline

Methyl-functionalization was achieved by a partial substitution of tetraethoxy silane (TEOS) by methyltriethoxy silane (MTES) in different ratios. Titanium butoxide (TiBut) was used as Ti precursor to reach nominal Ti molar ratios (Ti/(Si+Ti)) of 0.020 and 0.025. The precursor solution was atomized, and the collected powder was aged and calcined at 623 K. Solid-State ^{29}Si-NMR, FTIR, TGA and vapor-phase water adsorption showed that methyl moieties were effectively incorporated, conferring a hydrophobic character to the Ti-SiO_2 catalysts. Our Ti-SiO_2 catalysts exhibited three effective degrees of methyl-functionalization: 3%, 9%, and 14%, which were compared to a pristine Ti-SiO_2 as a reference. ICP-AES, DRUV, XPS, and N_2 physisorption demonstrated that Ti dispersion and textural properties were both successfully preserved upon the incorporation of the methyl moieties. Hydrophobic Ti-SiO_2 showed higher catalytic performance in the epoxidation of cyclooctene with tert-butyl hydroperoxide than the pristine analogous prepared without MTES. In addition to isolating the positive effect of hydrophobization of Ti-SiO_2 on their catalytic performance, this work demonstrates that the aerosol route is more advantageous than the conventional sol-gel route to prepare functionalized mesoporous Ti-SiO_2 catalysts with highly dispersed active sites.

References

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