Heterogeneous Zirconium oxocluster-based hybrid catalysts: a composition-catalytic activity and stability correlation study

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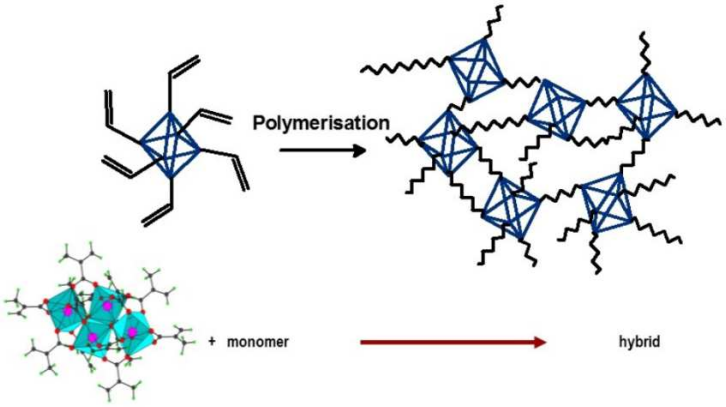
Hybrid materials based on a polymeric matrix covalently reinforced by zirconium oxocluster have already proven to be effective heterogeneous catalysts for the oxidation of organic sulphides by hydrogen peroxide, with potential industrial applications for the oxydesulfurisation of fuels [1]. In this work, in order to study the correlation between composition and catalytic activity, polymeric matrixes with different compositions were prepared and examined. The aims of the study were to improve the affinity of the hybrid catalyst for the substrate, to increase the hydrolytic stability of the oxocluster under reaction conditions and to enhance the stability of the matrix, while varying its polarity by changing the composition. New hybrid materials were synthetised by thermal radical polymerisation using methyl methacrylate, an additional monomer (2,2,2-trifluoroethyl methacrylate or poly(ethylene glycol) methyl ether methacrylate) and $Zr_4O_2(OMc)_{12}$ oxocluster (Mc=Methacrylate) as starting reagents [2].



The composition, microstructure and thermal stability of the obtained materials were analysed trought different methods, including FT-IR, Raman

Spectroscopies and Thermogravimetric Analysis (TGA). The catalytic performance of the hybrids as oxidation catalysts was assessed through a kinetic study, monitoring the oxidation of methyl *p*-tolyl sulphide with hydrogen peroxide to the corresponding sulfoxide and sulfone, by means of gas-chromatography. At 50°C, the reaction occurs in less than 12 h, with > 95% selectivity for the sulfone. Following this study, the stability of the hybrid materials under catalytic conditions was investigated through FT-IR after the recovery and washing of the catalysts, while activity retention was assessed by recharging of the reaction mixture after the first catalytic run.

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[1] M. Vigolo, M. Carraro, S. Gross *et al., Applied Catalysis B: Environmental*, **2016**, 182, 636-644
[2] M. Carraro, S. Gross, *Materials*, **2014**, 7(5), 3956-3989