

**Title:** Copper(II) aza-bis(oxazoline) complex immobilized onto ITQ-2 and MCM-22 based materials as heterogeneous catalysts for the cyclopropanation of styrene

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**Abstract:** A copper(II) chiral aza-bis(oxazoline) homogeneous catalyst (CuazaBox) was anchored onto the external surface of MCM-22 and ITQ-2 structures, as well as encapsulated into hierarchical MCM-22. The transition metal complex loading onto the porous solids was determined by ICP-AES and the materials were also characterized by elemental analysis (C, N, H, S), FTIR, XPS, TG and low temperature N<sub>2</sub> adsorption isotherms. The materials were tested as heterogeneous catalysts in the benchmark reaction of cyclopropanation of styrene to check the effect of the immobilization procedure on the catalytic parameters, as well as on their reutilization in several catalytic cycles.

Catalyst CuazaBox anchored onto the external surface of MCM-22 and ITQ-2 materials were more active and enantioselective in the cyclopropanation of styrene than the corresponding homogeneous phase reaction run under similar experimental conditions. This is due to the propylation of the acidic aza-Box nitrogen. HMCM-22 was nevertheless the best heterogeneous catalyst. Encapsulation of CuazaBox on post-synthesis modified MCM-22 materials led to low activities and enantioselectivities. But reversal on the stereochemical course of the reaction was observed, probably due to confinement effect. (C) 2013 Elsevier Inc. All rights reserved.

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