

## Abstract

The main objective of this work was to evidence versatile applications of ordered siliceous mesoporous materials, especially in adsorption and catalysis. For these reasons four mesoporous molecular sieves (SBA-15, SBA-16, MCM-41, and MCM-48) with different structures and textural properties have been chosen.

To show the possible application of mesoporous molecular sieves as a CO<sub>2</sub> adsorbent, magnesium oxide, and potassium carbonate were incorporated into SBA-15, SBA-16, and MCM-48 silicas. In order to avoid destruction of silica supports, a novel procedure based on the precipitation of magnesium acetate on the silica surface was developed. Subsequent *in situ* chemical conversion of magnesium acetate provided magnesium oxalate, while magnesium oxide was formed by calcination. To introduce potassium carbonate, silica modified with MgO was impregnated with potassium oxalate followed by its conversion to carbonate. All prepared mesoporous adsorbents preserved characteristic features of mesoporous molecular sieve (large surface areas, narrow pore size distributions). The comparison of carbon dioxide isotherms obtained on prepared samples revealed that their adsorption properties are influenced by the type of mesoporous structure. The SBA-15 silica containing magnesium oxide and promoted by potassium carbonate exhibited the steepest adsorption isotherm. The CO<sub>2</sub> adsorption capacity of this sample was higher than those of analogous samples prepared from SBA-16, and MCM-48. The amount adsorbed at 100 kPa and 20 °C increased in the order Mg/K-SBA-16 (10.3 cm<sup>3</sup>/g) < Mg/K-MCM-48 (12.7 cm<sup>3</sup>/g) < Mg/K-SBA-15 (18.8 cm<sup>3</sup>/g).

Mesoporous molecular sieves were used as supports for the preparation of new heterogeneous metathesis catalysts by immobilization of Ru alkylidenes (homogeneous catalysts highly active and tolerant towards a variety of functional groups in substrates). New heterogeneous catalysts for metathesis reactions were prepared either by immobilization *via* phosphine linkers or *via* non-covalent interactions. New catalysts were prepared by immobilization of the Hoveyda-Grubbs 1<sup>st</sup> generation-type catalyst (**RC-304**), and the Grubbs 2<sup>nd</sup> generation catalyst (**G-II**) onto the surface of mesoporous molecular sieves bearing dicyclohexylphosphine groups (PCy<sub>2</sub>). The Hoveyda-Grubbs 2<sup>nd</sup> generation-type catalysts bearing a polar quaternary ammonium group in *N*-heterocyclic ligand were immobilized *via* non-covalent interaction onto the surface of mesoporous molecular sieves. The catalysts are bound to the silica surface by adsorption probably with a participation of surface silanol bonds.

UV-Vis spectroscopy, solid state NMR, X-ray powder diffraction and elemental analysis were used to determine structures of prepared heterogeneous catalysts. For textural characterization of the catalysts, nitrogen adsorption measurement was used. In all cases, the

mesoporous structure and morphology of the support remained unaffected by the immobilization process.

The activity of prepared catalysts was tested in various metathesis reactions. They were highly active in ring-closing metathesis (RCM) of 1,7-octadiene, diethyl diallylmalonate, *N,N*-diallyl-2,2,2-trifluoroacetamide, *tert*-butyl *N,N*-diallylcarbamate, (-)- $\beta$ -citronellene, and allyl ether, self-metathesis and cross-metathesis (CM) of 5-hexenyl acetate, methyl 10-undecenoate, 1-decene, methyl oleate; allylbenzene with *cis*-1,4-diacetoxy-2-butene, and in ring-opening metathesis polymerization (ROMP) of cyclooctene. In many cases, high TONs (up to 16 000) at nearly 100 % selectivity were achieved. Depending on the support used, the catalyst activity was found to increase with increasing pore size of mesoporous molecular sieves.

All catalysts were easily separable from reaction mixtures, and in some cases they exhibited very low Ru leaching, enabling easy preparation of products with Ru content below 10 ppm (which is an acceptable level for pharmaceutical use). Successful catalyst reusing was achieved in most cases. These catalysts proved to have those properties: (i) preservation of high activity and selectivity of the parent homogeneous catalysts; (ii) easy catalyst separation; (iii) (multiple) catalyst reusing; and (iv) catalyst residue-free products.