

Abstract

The main emphasis of the dissertation focuses on the preparation of new heterogeneous metathesis catalysts, their characterization, and testing their activity and selectivity in different metathesis reactions. This work has been completed at the Department of Synthesis and Catalysis, J. Heyrovský Institute of Physical Chemistry, AS CR.

Hoveyda-Grubbs type catalyst **ZC** (Zhan catalyst 1-B) was immobilized on mesoporous molecular sieves of different architecture and pore diameter, d , (hexagonal: MCM-41, $d = 4.0$ nm; SBA-15, $d = 6.8$ nm; SBA-15 large pore (LP), $d = 11.1$ nm and cubic: MCM-48, $d = 6.0$ nm) and conventional silica (Merck) for comparison. The immobilization was done by simple mixing of **ZC** solution with appropriate support at room temperature. Ru loading in all immobilized catalyst was 0.93 wt%. The catalysts and supports were characterized by X-ray diffraction and nitrogen adsorption measurement. XPS and UV-Vis spectroscopic studies of **ZC** immobilized on SBA-15 (**ZC/SBA-15**) indicated the attachment of **ZC** on mesoporous sieve surface by non-covalent interactions. The immobilized catalysts exhibited high activity and 100% selectivity in ring-closing metathesis of diethyl diallylmalonate and 1,7-octadiene, in metathesis of methyl oleate and methyl 10-undecenoate, and in the ring-opening metathesis polymerization of cyclooctene. Ru leaching was dependent on the solvent and substrate used for the reaction. In non-polar system Ru leaching was negligible (0.04% of starting Ru amount for ring-closing metathesis of 1,7-octadiene in cyclohexane), however, the highest Ru leaching was observed in polar system (14% for ring-closing metathesis of diethyl diallylmalonate in dichloromethane). The filtration experiment carried out for ring-closing metathesis of 1,7-octadiene and citronellene proved that the catalytic active species were completely bound to the solid phase in non-polar solvent. A positive effect of the pore size of the supports on catalyst activity was observed for ring-closing metathesis of β -citronellene, metathesis of 1-decene, acyclic metathesis polymerization of 1,9-decadiene, and ring-opening metathesis polymerization (ROMP) of cyclooctene. In all cases, the initial reaction rate increased with increasing pore size of the catalyst support; however, support architecture did not play any important role.

The activity of Grubbs second generation catalyst immobilized on SBA-15 via phosphine linker (**G.II/SBA-15**), and **ZC/SBA-15** was tested in metathesis and cross-metathesis of cardanol (the main component of Cashew Nut Shell Liquid). Both heterogeneous catalysts proved to be highly active and selective in cardanol metathesis and cross-metathesis with ethene and cis-1,4-diacetoxy-2-butene. Easy separation of both catalysts from products and low Ru leaching (0.5% for **G.II/SBA-15** and 2.5% for **ZC/SBA-15**) ensure the delivery of products of low contents of Ru residues.