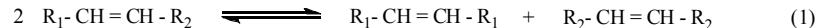


## Mesoporous Molecular Sieves Based Catalysts for Olefin Metathesis

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### Introduction

Olefin metathesis (eq.1, where  $R_1, R_2 = \text{alkyl, H}$ ) is a powerful method in organic synthesis having numerous important applications in petrochemistry, polymer chemistry and fine chemical synthesis [1]. Various compounds of W, Mo, Re and Ru are used as catalysts in this reaction. In spite of development of “well defined” Mo and Ru homogeneous catalysts, heterogeneous Mo and Re oxide based catalysts are still important, especially in industrial applications, and further improvement of their activity is desirable.



Mesoporous molecular sieves with their regular nanostructure, large surface area, large void volume and narrow pore size distribution in mesopore range [2] represent novel supports for many advanced catalysts. The aim of this contribution is to report on new heterogeneous catalysts for olefin metathesis based on mesoporous molecular sieves as supports and molybdenum and rhenium oxides as active phase.

### Materials and Methods

Siliceous hexagonal mesoporous sieves MCM-41 (pore diameter  $d = 3.1 \text{ nm}$ ) and SBA-15 ( $d = 6.1 \text{ nm}$ ) were prepared by homogeneous precipitation method using sodium silicate or tetraethylorthosilicate as silicon sources and hexadecyltrimethylammonium bromide (MCM-41) and Pluronic PE 9400 (SBA-15) as structure directing agents. Details are given in ref. [3]. Wormhole-like mesoporous organized alumina (OMA) samples of different pore size (from 3.5 nm to 6.5 nm) were prepared from aluminum sec.butoxide using lauric acid or PE 10400 as structure directing agents, respectively [4].  $\text{MoO}_3$ , (Lachema, Czech Rep.), molybdenum dioxide bis(acetylacetonate)  $\text{MoO}_2(\text{acac})_2$  (Strem), molybdenum dioxide bis(glycolate)  $\text{MoO}_2(\text{gly})_2$  [5] and  $\text{NH}_4\text{ReO}_4$  (Fluka) were used as a source of Mo and Re oxide species. Thermal spreading method (TS) was used for oxide species deposition on the support surface. Supports and catalysts were characterized by XRD (Bruker AXS D8 diffractometer), nitrogen adsorption at  $-193^\circ\text{C}$  (Micromeritics ASAP 2020), scanning electron microscope JEOL JSM-5500LV and Laser Raman spectroscopy (Bruker FRA 106/S spectrometer with Nd-YAG-laser). Catalyst loading was determined by ICP AES. Metathesis reactions were carried out in stirred batch reactors under inert atmosphere. Products were analyzed by GC/MS.

### Results and Discussion

Thermal spreading method was found to be a suitable method for the preparation of oxide-based catalysts. During this process, the structure of mesoporous sieves was preserved (even to the 16 wt. % of metal) and pore size distribution did not change essentially. Fig. 1 shows initial TOFs for 1-octene metathesis with different Mo oxide catalysts. It is seen that

$\text{MoO}_3$  on MCM-41 (6 wt.% of Mo) exhibited higher activity at  $40^\circ\text{C}$  in comparison with similar catalyst using conventional support (Silica gel 40, Merck). The low activity of catalyst on SBA-15 was explained by imperfect spreading of  $\text{MoO}_3$  on the surface in this case [3].

However, using acetylacetonato and glycolato complexes, which loose their organic ligands during TS under delivery of well dispersed surface molybdate species, SBA-15 based catalysts of enhanced activity was also prepared.

Re(VII) oxide on OMA, SMA and LMA (9 wt. % of Re) exhibited high activity and nearly 100% selectivity in metathesis of higher linear alkenes (from  $\text{C}_5$  to  $\text{C}_{18}$ ) and high activity in

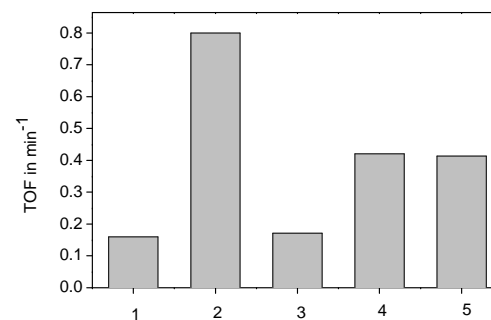
metathesis of  $\alpha,\omega$ -dienes ( $\text{C}_6, \text{C}_8, \text{C}_{10}$ ) at room or slightly elevated temperature [4]. Initial TOFs are about 1 order of magnitude higher in comparison with catalysts based on conventional  $\gamma$ -alumina. When combined with  $\text{Me}_4\text{Sn}$ , Re(VII) oxide on OMA, SMA and LMA is also highly active in metathesis of unsaturated esters and ethers [6].

### Significance

New highly active heterogeneous Mo and Re oxide catalysts were developed potentially applicable both in industry and laboratory.

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**Figure 1.** Activity of  $\text{MoO}_3/\text{Silica}$  (1),  $\text{MoO}_3/\text{MCM-41}$  (2),  $\text{MoO}_3/\text{SBA-15}$  (3),  $\text{MoO}_2(\text{acac})_2/\text{SBA-15}$  (4), and  $\text{MoO}_2(\text{gly})_2/\text{SBA-15}$  (5). Neat 1-octene, 6 wt % of Mo,  $40^\circ\text{C}$ .