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Mesoporous Molecular Sieves as Advanced Supports for Olefin Metathesis Catalysts

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Summary: Siliceous mesoporous molecular sieves MCM-41, MCM-48 and SBA-15 and organised mesoporous alumina represent progressive supports for new heterogeneous catalysts for olefin metathesis and metathesis polymerization. In combination with Mo and Re oxides they provide catalysts of considerably higher activity in comparison with those based on conventional silica and alumina. Immobilization of Mo and Ru alkylidenes on these materials led to the highly active and selective catalysts with negligible leaching of transition metal.

Keywords: heterogeneous catalysts; mesoporous molecular sieves; olefin metathesis; ring-opening metathesis polymerization; transition metal catalysts

Introduction

Siliceous mesoporous molecular sieves (MMS)[1] and organised mesoporous alumina (OMA)[2] are new materials with regular structures, high surface areas (even more than 1000 m^2/g), high void volumes (up to 1 cm^3/g), and pores in mesoporous region (diameter from 2 nm to 30 nm) with narrow pore size distribution. Because of these unique properties they are used frequently as supports for advanced heterogeneous catalysts[3,4] including metathesis ones.[5–7] This communication summarizes our results concerning the application of mesoporous materials in preparation of new heterogeneous catalysts for olefin metathesis and metathesis polymerization.

MMS of different architectures and pore sizes (hexagonal MCM-41 and SBA-15, cubic MCM-48) and OMA of wormhole-like architecture and different pore size were prepared and used as supports for (i) Mo and Re oxides or their precursors, and (ii) Mo alkylidenes (Schrock type) and Ru alkylidenes (Grubbs type). Table 1 gives a survey of used supports together with their characteristics (BET surface area S_{BET}, void volume V and average pore diameter D).

Oxide Catalysts

Re and Mo oxide catalysts were prepared from NH_4ReO_4, MoO_3 or $MoO_2(glycolate)_2$ combined with supports by thermal spreading method (heating of physical mixture of support and transition metal source at 500 °C for 3 h). Re and Mo compounds reacted with surface OH groups under formation of Re and Mo oxide species covalently bound to the surface. The support architecture and pore size did not change substantially up to the relatively high loading (16 wt. % of Mo). In general, the activity of this type of catalyst depends on the quality of spreading of transition metal oxide species along the surface, their oxidation state and their accessibility by substrate molecules during reaction. The results obtained indicate that MMS and OMA can ensure these requirements better than conventional supports.

In metathesis of neat liquid 1-alkenes, catalysts based on MMS or OMA exhibited considerably higher activity than catalysts based on conventional silica or alumina supports. For example, in 1-octene metathesis, the initial TOF of MoO_3/MCM-41 (8

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Table 1.
Mesoporous support used.

	S_{BET} (m^2/g)	V (cm^3/g)	D (nm)	Ref.
MCM-41	1070	0.871	3.1	[8]
MCM-48	1334	0.927	2.8	[8]
SBA-15	777	1.258	6.1	[8]
OMA3	332	0.250	3.5	[9]
OMA5	267	0.529	4.9	[9]
OMA6	314	0.745	6.5	[10]

wt. % of Mo) under mild condition (batch reactor, 40 °C, argon atmosphere) was 0.45 min^{-1}, which was 8 times higher in comparison with MoO_3 on conventional silica (Merck, $S_{BET} = 559$ m^2/g, broad pore size distribution).[8] The selectivity to 7-tetradecene was 80%. Using MoO_2(glycolate)$_2$ as precursor of Mo oxide species, even better dispersion of Mo oxide species was achieved than using MoO_3. In metathesis of 1-dodecene (catalyst loading 6 wt. % of Mo, 40 °C), TOF values found for catalysts based on conventional silica, MCM-41 and SBA-15 were 0.03, 0.10, and 0.26 min^{-1}, respectively.[11]

In 1-decene metathesis, Re oxide on OMA supports exhibited specific activity more than 1 order of magnitude higher than Re oxide on conventional alumina Alcoa ($S_{BET} = 342$ m^2/g, broad pore size distribution, large micropore fraction), moreover, the activity increased with increasing pore diameter of OMA (optimum catalyst loading 9 wt. % of Re, 60 °C, argon atmosphere).[10] Selectivity to 9-octadecene was about 95% in all cases. Similar effect of the pore size on catalyst activity was found for α,ω-diene metathesis (Figure 1).

Not only catalyst activity but also selectivity was influenced by catalyst pore size.[12] In metathesis of 1,7-octadiene over ReO_x/OMA6, the amount of acyclic diene metathesis (ADMET) dimer accompanying the main reaction product, cyclohexene, was about 5%. Over ReO_x/OMA6, however, this dimer formed in the early stage of the reaction was able to re-enter the reaction and its amount in final mixture decreased to zero. Similarly, in metathesis of 1,9-decadiene, the populations of individual ADMET oligomers differed according to the catalyst pore size. Over ReO_x/OMA3 the most populated oligomer was dimer, over ReO_x/OMA6 it was tetramer.[12]

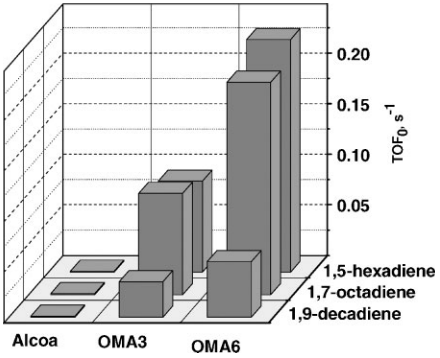


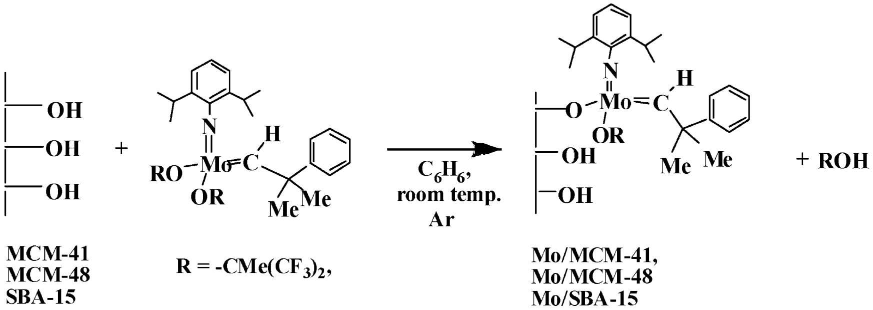
Figure 1.
Initial TOF of ReO_x heterogeneous catalysts in metathesis of α,ω-dienes in dodecane; 25 °C (1,7-octadiene 40 °C).

Immobilized Schrock and Grubbs Alkylidenes

Immobilization of Mo and Ru alkylidenes on solid supports attracts attention because it opens the possibility of obtaining highly active and selective catalysts, easily separable from reaction mixture and reusable. Both polymer and silica supports have been used for this purpose and several strategies of immobilization have been developed.[13–16]

On MMS, Schrock type alkylidenes were immobilized by direct reaction of alkoxy ligand with surface OH group (Scheme 1). Reaction proceeded quantitatively; catalysts of 1 wt. % of Mo were prepared and stored under inert conditions. In metathesis of neat 1-heptene, they exhibited high activity and near 100% selectivity to 6-dodecene.[17] The activity slightly increased in the order MCM-48 < MCM-41 < SBA-15 (Figure 2).

Metathesis of unsaturated ether and esters (4-allylanisole, 5-hexenyl acetate, diethyl diallylmalonate) proceeded smoothly with these catalysts but only low TONs were achieved (about 20). Filtration experiments proved that catalytic activity was bound to the solid phase during



Scheme 1.
Immobilization of Schrock alkylidene on MMS.

the reaction. No metal leaching was found. Reaction products could be easily separated from catalysts and Mo content in products was <0.004 ppm.

Grubbs type alkylidene **1** (Zhan catalyst-1B) was immobilized on SBA-15 via fluorocarboxylate linker according to the published procedure[18] (Scheme 2).

In ring-closing metathesis (RCM) of 1,7-octadiene and diethyl diallylmalonate, the reaction rates over **1**/SBA-15 catalyst were lower in comparison with those of reactions catalysed with **1** in homogeneous phase (effect of linker and diffusion), see Figure 3. The selectivity was near 100% for both homogeneous and heterogeneous conditions. Heterogeneous catalyst could be separated from products by centrifugation and reused with minimal lost of activity.[19]

Applications in Metathesis Polymerization

Catalysts based on MMS and OMA were successfully used in ring-opening metathesis polymerization (ROMP).[12,17,19] Large pores in these cases enabled easy release of polymer molecules from catalysts and ensured high yields of polymers in contrast to the conventional silica and alumina supports. With ReO_x/OMA6 (toluene, 40 °C) ROMP of cyclooctene (COE) gave high-molecular weight polymer ($M_w = 850\,000$) in 65% yield. Mo/SBA-15 delivered polymer of COE ($M_w = 210\,000$) in 87% yield and polymer of norbornene ($M_w = 1\,800\,000$) in 60% yield. With **1**/SBA-15 polymer of norbornene of $M_w = 2\,200\,000$ was prepared in 60% yield

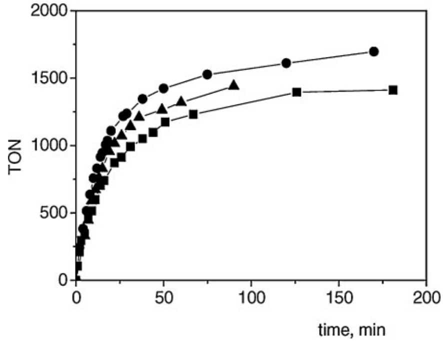


Figure 2.
Metathesis of neat 1-heptene with Mo/MCM-41 (▲), Mo/MCM-48 (■), and Mo/SBA-15 (•); 1-heptene/Mo = 2000, 1ml of 1-heptene, room temperature, Ar.

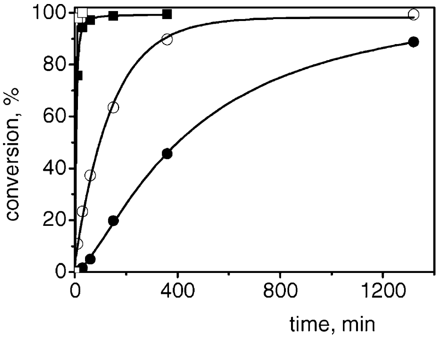
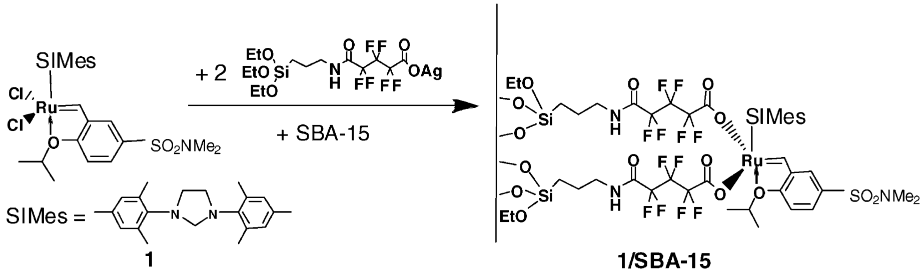


Figure 3.
RCM of 1,7-octadiene (open symbols) and diethyl diallylmalonate (solid symbols) with 1 (square) and 1/SBA-15 (circle); reaction conditions: t = 30 °C, Ru/substrate = 1: 2000, $c°_{substrate} = 0.21$ mol/l.



Scheme 2.
Immobilization of Grubbs alkylidene on SBA-15.

(toluene, 40 °C). However, molecular weight distribution was very broad ($M_w/M_n > 2$), even multimodal in some cases, probably as a result of slow initiation and chain transfer on the catalyst surface. Metathesis polymerization of 1-alkynes were accomplished with Mo oxide catalysts.[20] For 1-hexyne, the yield and polymer molecular weight (M_w) increased with increasing catalyst pore size in the order MoO_3/MCM-48 (22%, 9 000) < MoO_3/MCM-41 (38%, 23 000) < MoO_3/SBA-15 (64%, 30 000). The advantage of these heterogeneous catalysts consists in their easy separation from polymer solutions and delivery of polymers free of catalyst residue.

Conclusions

MMS and OMA are suitable supports for new advanced heterogeneous olefin metathesis catalysts. Mo and Re oxides on MMS and OMA, respectively, exhibit higher activity in neat alkene and diene metathesis than the corresponding catalysts based on conventional supports. Schrock and Grubbs type alkylidenes immobilized on MMS allow to perform metathesis reaction smoothly with expected high selectivity, to separate catalysts from reaction mixture easily, and to get products of minimal content of catalyst residues. Due to their large pores MMS and OMA allow to prepare effective heterogeneous catalysts for ROMP and metathesis polymerization of acetylenes. The most challenging feature of catalysts on MMS and OMA is a possibility to affect catalyst selectivity by pore size of support.

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