A remarkable Mo catalyst for olefin metathesis: hexagonal mesoporous silica-supported molybdenum oxide (MoO_3/HMS)

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Hexagonal mesoporous silica-supported molybdenum oxide exhibits much higher catalytic activity for the metathesis of oct-1-ene in the liquid phase, compared with MoO_3 on normal porous silica and MoO_3 on γ-alumina.

The application of mesoporous materials for various catalysts in organic reactions has been intensively investigated since a Japanese research group[1] and researchers at Mobil Oil[2] independently discovered mesoporous molecular sieves such as FSM-16 and MCM-41 with uniform pore openings in the range 2.0–10.0 nm as well as a tunnel pore structure. For example, acidic FSM-16 containing Al_2O_3 is an effective and recyclable solid acid promoter for *meso*-tetraarylporphyrin synthesis from the corresponding aromatic aldehydes and pyrrole.[3] It has also been shown that titanocene-derived MCM-41 shows high efficiency in the epoxidation of cyclohexene and more bulky cyclic olefins,[4] while *rac*-ethenebis(indenyl)zirconium dichloride-grafted MCM-41 provides highly isotactic polypropenes with a unique spherulite morphology.[5]

Supported molybdenum oxides have received much attention as solid metathesis catalysts because they can be practically used in industrial petrochemical processes such as the Shell higher olefin process for producing detergent-range olefins.[6] Their surface properties and catalytic activity are critically influenced by the oxide support, the surface molybdenum oxide content, the activation conditions, and the oxidation state of the molybdenum species. Supported molybdenum catalysts have generally been prepared in the following ways: (i) by impregnation of the support with molybdate solution;[7] (ii) by treatment of the support with $Mo(CO)_6$;[8] and (iii) by reaction of the support with π-allylmolybdenum compounds.[9]

This paper focuses on hexagonal mesoporous silica (HMS) in terms of developing a new silica support for molybdenum-based olefin metathesis catalysts, and demonstrates that HMS impregnated with molybdenum oxide (MoO_3/HMS) is an efficient catalyst for oct-1-ene metathesis [eqn. (1)].

$$2\ CH_2{=}CH(CH_2)_5CH_3 \xrightarrow{\text{Mo/HMS}} \begin{array}{c} CH_3(CH_2)_5CH{=}CH(CH_2)_5CH_3 \\ + \\ CH_2{=}CH_2 \end{array} \qquad (1)$$

HMS was first prepared from tetraethylorthosilicate (TEOS) and primary amine as a templating agent.[10] The preparation of HMS has several advantages over that of MCM-41: (i) the use of more commercially available primary alkylamines as templating agents in place of expensive alkyltrimethylammonium halides; (ii) the applicability of shorter alkylamines as templating agents; and (iii) easier procedures for sol–gel processing than those for hydrothermal preparations for MCM-41. In work, three HMSs were synthesized by the use of three alkylamines with different alkyl chain lengths (C8, C12, C16).† HMS(C*n*) shall hereafter stand for the HMS obtained using C*n*-alkylamine.

MoO_3-supporting catalysts were prepared by impregnation of the HMSs with molybdate solution.‡ The HMS(C*n*) supports and MoO_3/HMS catalysts were characterized using powder X-ray diffraction and N_2 adsorption. As shown in Table 1, all MoO_3/HMS samples exhibited a single diffraction peak corresponding to a d_{100} spacing of > 3.0 nm,[10] and high BET surface areas of > 800 $m^2\ g^{-1}$, proving that the MoO_3/HMSs were mainly composed of mesopores. No diffraction peaks intrinsic to MoO_3 crystallites were observed, indicating that MoO_3 was finely dispersed on the interior surface of mesoporous HMS.

As a control, MoO_3 was supported on commercially available silica, CARIACT Q-3 (Fuji Silysia Chemical), which has a narrow mesopore-size distribution centered at 3 nm, a specific surface area of 619 $m^2\ g^{-1}$, a pore volume of 0.45 ml g^{-1}, and 75–500 μm particle sizes. The 3.5 and 7 wt% MoO_3/SiO_2 were applied to the metathesis of oct-1-ene in a similar way to MoO_3/HMS.

By the use of 7 wt% MoO_3/SiO_2 (0.15 g) and 3.5 wt% MoO_3/SiO_2 (0.3 g), the metathesis products were scarcely obtained at 323 K, as shown in Fig. 1. Surprisingly, MoO_3-supporting HMS catalysts could induce metathesis of oct-1-ene.§ The catalytic activity is critically dependent on the kind of alkylamine which functioned as templating agent in the formation of HMSs. In particular, MoO_3-supporting HMS(C8) prepared with the aid of octylamine had the highest activity. At the early stage of the metathesis, 7 wt% MoO_3/HMS(C12) and 7 wt% MoO_3/HMS(C16) converted oct-1-ene more rapidly than 7 wt% MoO_3/HMS(C8). However, after this stage on 7 wt% MoO_3/HMS(C12) and 7 wt% MoO_3/HMS(C16), the conversion

Table 1 Structural properties of HMS, MoO_3/HMS, and MoO_3/SiO_2

Mesoporous silica or Mo-supported catalyst	d_{100} Spacing/nm	Surface area/$m^2\ g^{-1}$
HMS(C8)	3.0	1350
7 wt% MoO_3/HMS(C8)	3.0	854
HMS(C12)	3.5	1450
7 wt% MoO_3/HMS(C12)	3.4	1060
HMS(C16)	4.0	1230
7 wt% MoO_3/HMS(C16)	3.5	844
SiO_2[a]	—	619
7 wt% MoO_3/SiO_2[a]	—	514
3.5 wt% MoO_3/SiO_2[a]	—	563

[a] CARIACT Q-3.

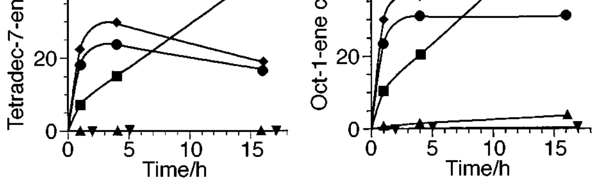

Fig. 1 Metathesis of oct-1-ene on MoO_3/mesoporous silica: ■ 7 wt% MoO_3/HMS(C8). ● 7 wt % MoO_3/HMS(C12), ◆ 7 wt% MoO_3/HMS(C16), ▲ 7 wt% MoO_3/SiO_2 (CARIACT Q-3), ▼ 3.5 wt% MoO_3/SiO_2 (CARIACT Q-3).

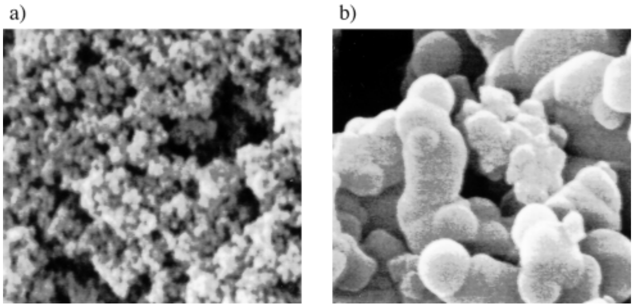

Fig. 2 SEM micrographs of (a) HMS(C8) and (b) HMS(C12) (scale: 30 mm = 1.5 μm).

reached the highest limit owing to the deactivation of the catalysts, and the yield of tetradec-7-ene and the selectivity to tetradec-7-ene decreased [7 wt% MoO_3/HMS(C12), yield: 23% (at 4 h), 17% (at 16 h), selectivity: 75% (at 4 h), 55% (at 16 h); 7 wt% MoO_3/HMS(C16), yield: 29% (at 4 h), 19% (at 16 h), selectivity: 81% (at 4 h), 52% (at 16 h)] due to the fact that the olefinic products gradually decomposed when in contact with the catalysts. In contrast, on 7 wt% MoO_3/HMS(C8), the yield of tetradec-7-ene steadily increased from 14% (at 4 h) to 44% (at 16 h) while maintaining high tetradec-7-ene selectivity [74% (4 h), 77% (at 16 h)], indicating that the metathesis product, tetradec-7-ene,¶ did not undergo further metathesis, polymerization, isomerization, or degradation on the catalyst. In this case, the products other than tetradec-7-ene are mainly highly polymerized products from oct-1-ene.

The SEMs in Fig. 2 of HMS(C8) and HMS(C12) indicate that HMS(C8) is made up of small silica particles of <50 nm in diameter, while HMS(C12) is spherical silica of 200–700 nm. The shape and size of HMS(C16) (not shown in Fig. 2) are almost the same as those of HMS(C12). Based on the powder X-ray and SEM analysis, HMS(8) has not only smaller pore diameter, but also shorter pore length than HMS(12) and HMS(16). Therefore, it is supposed that at the initial stage of the metathesis (in Fig. 1), MoO_3/HMS(12) and MoO_3/HMS(16) showed higher conversions of oct-1-ene owing to easier passage of the olefin in the wider pores, but MoO_3/HMS(8) was suffering from less deactivation of the Mo sites or less blockage of the pores by polymeric side-products owing to the shorter channel structure, leading to retention of the high yield and high selectivity of the metathesis product.

There are also distinct differences in the catalytic activities on olefin metathesis between MoO_3-supporting HMS and normal silica. Although the reasons why the MoO_3/HMS shows much higher catalytic performance have yet to be elucidated, it is likely that silica with hexagonal channel-type pores is adequate for fixing finely dispersed molybdenum oxides and for stabilizing the molybdenum species in the oxidation state which is essential to the metathesis catalysis. Disordered normal silica could not play such a role.

Silica-supported molybdenum catalysts are normally activated by cocatalysts such as tetraalkyltin[11] or by photoreduction.[12] Neither the presence of such volatile and poisonous cocatalysts nor the photoactivation process is necessary for the MoO_3/HMS system to show high catalytic performance.

MoO_3/HMS(C8) was also compared not only with traditional Al_2O_3-supported[13] molybdenum catalyst (MoO_3/Al_2O_3)[14] but also with MoO_3/Al_2O_3 modified with CoO[14] or K_2O[15] in the metathesis of oct-1-ene at 323 K.[16] In the light of the yield of tetradec-7-ene as well as the selectivity to tetradec-7-ene, 7 wt% MoO_3/HMS(C8) is much superior to 7 wt% MoO_3/Al_2O_3 [yield: 3.8% (at 4 h), 12.5% (at 16 h), selectivity: 35% (at 4 h), 35% (at 16 h)], 7 wt% MoO_3/2 wt% CoO/Al_2O_3 [yield: 4.9% (at 3 h), 3.4% (at 16 h), selectivity: 52% (at 3 h), 27% (at 16 h)], and 7 wt% MoO_3/0.3 wt% K_2O/Al_2O_3 [yield: 3.6% (at 3 h), 4.5% (at 16 h), selectivity: 51% (at 3 h), 51% (at 16 h)].

In conclusion, MoO_3-supporting hexagonal mesoporous silica which was prepared in the sol–gel reaction directed by relatively short alkylamine shows remarkable catalysis in oct-1-ene metathesis in the liquid phase under mild conditions. The interior properties of hexagonal mesoporous silica are quite different from those of normal porous silica and γ-alumina, hence HMSs can be expected to work as effective, new supports for heterogeneous metal-catalyzed reactions.

Notes and references

† Under vigorous stirring, TEOS (100 mmol) was added to a mixture of ethanol (650 mmol), deionized water (3000 mmol) and *n*-octylamine (25 mmol). The resulting mixture was aged by stirring for 48 h at room temperature. Then, the resulting gel was filtered, washed with ethanol, dried *in vacuo* at 393 K, and calcined at 873 K for 4 h in dry air. When *n*-dodecylamine and *n*-hexadecylamine were used as templating agents, the molar compositions of TEOS : amine : EtOH : H_2O were 1.0 : 0.25 : 8.5 : 28.4 and 1.0 : 0.3 : 14 : 23, respectively.

‡ A representative preparation procedure for the 7 wt% MoO_3/HMS catalyst is given: HMS (1.0 g) was kept in contact with saturated steam in a desiccator for 12 h. To the wet HMS was added an aqueous solution (5 ml) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.0923 g). The mixture was stirred gently for 10 min, and dried to almost complete dryness at room temperature under a stream of dry N_2. Five ml of deionized water was added to the supported HMS. The mixture was stirred for 10 min, and exposed again to a N_2 stream reaching almost complete dryness. Then, the catalyst was dried further at 393 K for 2 h under reduced pressure of 1 mmHg.

§ A representative metathesis reaction was performed as follows: the MoO_3/HMS catalyst (0.15 g), which had been predried at 873 K for 2 h in dry air, was weighed and placed in a 20 ml round-bottomed Pyrex flask. The Mo catalyst contained in the flask was again treated at 773 K under reduced pressure of 0.6 mmHg in a tubular electric furnace. After cooling, to the catalyst was added oct-1-ene (3.5 mmol) in dry *n*-heptane (5 ml), and the mixture was stirred at 323 K under a dry N_2 stream. After a specified time, the solid catalyst was filtered off, and the organic products were collected and analyzed by GC using an internal standard of *n*-decane. Tetradec-7-ene was isolated from the organic products through distillation on a Kugelrohr apparatus at 373 K bath temperature under 3 mmHg.

¶ When the distilled products from the metathesis of oct-1-ene on 7 wt% MoO_3/HMS(C8) were oxidatively cleaved upon treatment with $RuCl_3$ and $NaIO_4$, no aldehydes other than heptanal were detected. This result indicates that during the metathesis, no isomerization of the C=C bonds in the olefinic substrates or products took place.

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