Olefin Metathesis over Mesoporous Alumina-supported Rhenium Oxide Catalyst

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Rhenium oxide finely dispersed on mesoporous alumina with uniform pore size was found to be a more active and selective catalyst for liquid-phase metathesis reactions of terminal and inner olefins than rhenium oxide on normal γ-alumina with random pore shape.

Olefin metathesis is an intriguing reaction in terms of not only the reaction mechanism but also its practical application to chemicals synthesis in chemical industry. Since the discovery of olefin metathesis, a variety of homogeneous and heterogeneous catalyst systems for metathesis have been developed.[1] Especially for the last seven years, ruthenium carbene complexes have been focused on as powerful homogeneous catalysts for elaborate syntheses of pharmaceuticals and polymers with various functional groups.[2] By contrast to such marvelous development of homogeneous catalysts, finding new efficient heterogeneous catalysts for metathesis has been stagnant.

The discovery of FSM-16[3] and the M41S family[4] of mesoporous molecular sieves with uniform nanometer-sized pores has stimulated interest in the potential use of these materials as catalyst and catalyst support. In our previous study, we found that MoO_3 supported on mesoporous HMS silica[5] with a narrow pore-size distribution centered at 2 nm showed much higher catalytic activity for metathesis of 1-octene in a liquid phase than MoO_3 on commercial SiO_2.[6] In our continuous efforts to develop more effective heterogeneous catalysts for liquid-phase olefin metathesis than MoO_3 on mesoporous silica, we next focused on mesoporous alumina-supported rhenium oxide, because rhenium oxide has been known as a more active species for metathesis than molybdenum oxide, and mesoporous aluminas with homogeneous pores and high surface area have just been developed by Davis[7] and Pinnavaia.[8] As compared with mesoporous silica, mesoporous alumina has not been put to practical use in catalytic organic reactions. In this communication we report how rhenium oxide fixed on the surface of mesoporous alumina is different in liquid-phase olefin metathesis from rhenium oxide on conventional γ-alumina.

$$R^1HC{=}CHR^2 \rightleftharpoons R^1HC{=}CHR^1 + R^2HC{=}CHR^2$$

1a ($R^1{=}C_6H_{13}$, $R^2{=}C_8H_{17}$; cis/trans=2.9) **2a**, **2b** **3a**, **3b**
1b ($R^1{=}H$, $R^2{=}C_6H_{13}$)

Mesoporous alumina (designated as meso-Al_2O_3) was prepared according to Davis' procedure.[9] The prepared meso-Al_2O_3 had specific surface area of 564 m^2/g, a narrow pore-size distribution centered at 3 nm, and pore volume of 0.485 ml/g. Re_2O_7-supporting meso-Al_2O_3 was prepared by impregnation of the meso-Al_2O_3 with an ammonium perrhenate solution.[10] As a control catalyst, Re_2O_7 was also supported on typical γ-alumina provided by the Catalysis Society of Japan: JRC-ALO-7 (specific surface area = 166 m^2/g; pore diameters ranging from 1 to 20 nm; pore volume = 0.426 ml/g).

Metathesis of alkenes (7-hexadecene (cis/trans = 2.9) and 1-octene) was performed in a batch reactor at 50 or −1 °C.[11]

Figure 1 shows changes in the conversion of 7-hexadecene in the metathesis at 50 °C. On 7 wt% Re_2O_7/meso-Al_2O_3, the conversion of **1a** (cis/trans = 2.9) smoothly reached the statistical equilibrium value of 50% after 4 h to produce equal amounts of 7-tetradecene (**2a**) and 9-octadecene (**3a**) with 95–98% selectivity and cis/trans ratio of 0.23. In contrast, on a control catalyst of 7 wt% Re_2O_7/ALO-7 the metathesis stopped at the conversion of ~30% (selectivity of **2a** and **3a** = 93–95%; cis/trans ratio = 0.22) after 10 h due to the deactivation of the catalyst. It is worth noting that 1) 7 wt% Re_2O_7/meso-Al_2O_3 revealed high metathesis activity without reductive pretreatment on the catalyst; 2) a long inner olefin underwent metathesis on 7 wt% Re_2O_7/meso-Al_2O_3 under mild conditions (at 50 °C) to reach its chemical equilibrium without the formation of any side products such as olefinic isomers and polymers of 7-hexadecene.

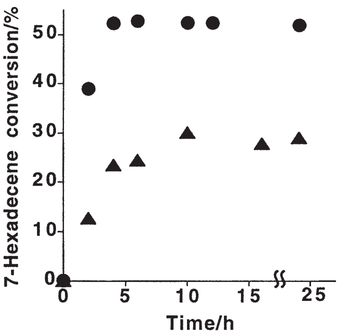

Figure 1. Metathesis of 7-hexadecene to 7-tetradecene and 9-octadecene catalyzed by rhenium oxide supported on mesoporous alumina and γ-alumina. (●): 7 wt% Re_2O_7/meso-Al_2O_3, (▲): 7 wt% Re_2O_7/ALO-7.

Figure 2 shows the metathesis of more reactive terminal olefin, 1-octene (**1b**) at a lower temperature of −1 °C by use of 7 wt% Re_2O_7/meso-Al_2O_3 and two control catalysts of 2.1 and 7 wt% Re_2O_7/ALO-7. In the metathesis of 1-octene, 7 wt% Re_2O_7/meso-Al_2O_3 revealed better performance in the reaction rate and the selectivity to 7-tetradecene than the control catalysts.[12] It was reported that rhenium oxide supported on alumina was present as monomeric surface ReO_4^- species, independent of the rhenium loading.[13] Interestingly, a comparison of the metathesis activity among 3.5, 7, and 15 wt% Re_2O_7/meso-Al_2O_3 disclosed that the highest activity was attained at 7 wt% Re loading, which was inconsistent with the previous report in which the activity increased with the loading amount of Re_2O_7 up to ~18 wt%.[14] 2.1 wt% Re_2O_7/ALO-7, which has the same rhenium oxide density on the alumina surface as 7 wt% Re_2O_7/meso-Al_2O_3, showed almost the same catalytic activity as

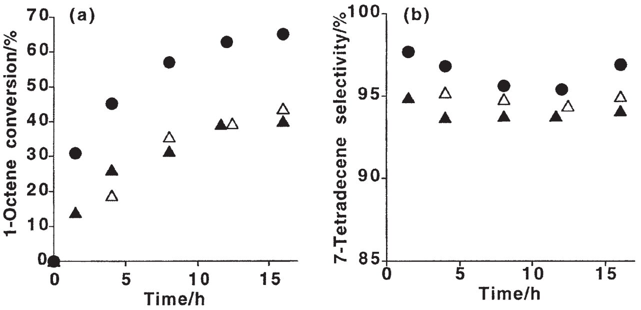

Figure 2. Metathesis of 1-octene to 7-tetradecene and ethylene catalyzed by rhenium oxide supported on mesoporous alumina and γ-alumina. (●): 7 wt% Re_2O_7/meso-Al_2O_3, (▲): 7 wt% Re_2O_7/ALO-7, (△): 2.1 wt% Re_2O_7/ALO-7. (a) Changes in the conversion of 1-octene, (b) the selectivity to 7-tetradecene.

7 wt% Re_2O_7/ALO-7 with a little improvement in selectivity to 7-tetradecene. The solvent also affected the rate of the metathesis of 1-octene catalyzed by Re_2O_7/meso-Al_2O_3: the reaction in heptane was 1.5 times faster than that in benzene.

The scanning electron micrographs (SEM) indicated that the meso-Al_2O_3 was made up of small alumina particles of 100–300 nm in diameter, while ALO-7 showed the form of agglomerates.

On both the transmission electron micrographs (TEM) of 7 wt% Re_2O_7/meso-Al_2O_3 and 7 wt% Re_2O_7/ALO-7 we could not observe any rhenium oxide particles on the surface of the alumina supports. In addition, no diffraction patterns specific to Re_2O_7 crystals were found in both the catalysts by powder X-ray diffractometry. Combined, these analytical results imply that the rhenium oxide was finely dispersed on the surface of meso-Al_2O_3 and ALO-7.

Then, the structures of dispersed rhenium oxide on meso-Al_2O_3 and γ-alumina (ALO-7) were compared by extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy.[15] Unfortunately, no difference in Re–O distances between the two catalysts was observed from the data of EXAFS. Both the rhenium ions on meso-Al_2O_3 and ALO-7 were identified as tetra-coordinated ReO_4^- ions based on XANES.

Although the structural uniqueness of Re_2O_7/meso-Al_2O_3 has not been fully elucidated, we speculate that the intermediate oxidation state of rhenium species, which is necessary for the propagation of the metathesis reaction,[1] could be more stabilized and maintained by the framework of mesoporous alumina than that of γ-alumina, and so that the rate and selectivity of the metathesis reactions could be enhanced.[16]

In summary, rhenium oxide finely dispersed on mesoporous alumina with uniform pore size of 3 nm was a more active and selective catalyst for metathesis of terminal and inner olefins in a liquid phase than rhenium oxide on normal γ-alumina. Rhenium oxide on meso-Al_2O_3 was found more efficient in metathesis than that on γ-alumina when ReO_4^- was fixed on the alumina surface with the same Re ion density.

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References and Notes

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9 A solution of dodecanoic acid (53.9 mmol) in 1-propanol (195 ml) was added to a solution of Al(O-*s*-Bu)$_3$ (178 mmol) in 1-propanol (30 ml) and deionized water (10 ml), and the mixture was vigorously stirred for 24 h at room temperature. Then, the mixture was transferred into a 300 ml-autoclave, and aged at 110 °C for 48 h. The resulting gel was filtered, washed with EtOH (300 ml), and dried in N_2 for 12 h. The gel (2.0 g) was set in an electric furnace, gradually heated to 600 °C at a ramping rate of 9.6 °C/min in N_2, and finally calcined at 600 °C for 4 h in dry air to give mesoporous alumina.

10 The preparation of 7 wt% Re_2O_7 supporting meso-Al_2O_3 (designated as 7 wt% Re_2O_7/meso-Al_2O_3) was as follows: The meso-Al_2O_3 (1.0 g) was immersed in a solution of NH_4ReO_4 (0.31 mmol) in deionized water (5 ml), and the suspension was gradually dried up at room temperature for 12 h in N_2. After complete evaporation of the water, deionized water (5 ml) was added to the solid sample, and the drying procedure was repeated. The supported sample was then set in an electric furnace and heated in dry air to 600 °C at a ramping rate of 6.9 °C/min, and finally calcined at 600 °C for 4 h to give 7 wt% Re_2O_7/meso-Al_2O_3.

11 As activation of the Re catalyst, Re_2O_7/meso-Al_2O_3 (0.6 g ($C_{16}H_{32}$), 0.3 g (C_8H_{16})) put in a 30 ml flask was heated to 500 °C at a ramping rate of 7.9 °C/min, and finally at 500 °C under 0.6 Torr (1 Torr $\approx$ 133.322 Pa) for 2 h. After cooling to room temperature under evacuation, the flask was filled with N_2. After the addition of *n*-heptane solvent (5 ml) to the catalyst, the metathesis was run at 50 °C ($C_{16}H_{32}$) or -1 °C (C_8H_{16}) by introducing alkene (5.0 mmol ($C_{16}H_{32}$), 7.9 mmol (C_8H_{16})) into the flask in N_2. After a specified time, the solid catalyst was filtered and washed with hexane (15 ml). The combined filtrate was analyzed with a gas chromatograph using an internal standard (*n*-decane). The geometrical isomer ratios of olefin products isolated through fractional distillation were determined by NMR.

12 The amount of rhenium oxide included in each catalyst was adjusted to be the same. Cis/trans ratios of 7-tetradecene produced were 0.22 on 7 wt% Re_2O_7/meso-Al_2O_3, 0.23 on 7 wt% Re_2O_7/ALO-7, and 0.23 on 2.1 wt% Re_2O_7/ALO-7.

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16 When Re_2O_7 was supported on mesoporous silica, the catalyst showed no metathesis of 1-octene. This is due to the sublimation of Re_2O_7 from SiO_2 during the calcination at 600 °C in preparation of the catalyst. With mesoporous aluminosilicate (Al-HMS)-doped Re_2O_7 the metathesis of 1-octene took place. However, the isomerization of olefin competed against the metathesis owing to the acidic character of Al-HMS, and the selectivity to 7-teteradecene drastically fell to 3.5%.