

Lewis acid-modified mesoporous alumina: A new catalyst carrier for methyltrioxorhenium in metathesis of olefins bearing functional groups

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Abstract

Lewis acid-modified mesoporous alumina was found to be an efficient carrier as well as an activator for methyltrioxorhenium (MeReO₃) in olefin metathesis reactions. Especially, MeReO₃ doped on zinc chloride-modified mesoporous alumina catalyzed the metathesis of olefins with functional groups such as acetoxy, alkoxyacetyl, acyl, chlorine, and bromine groups under mild conditions. The novel heterogeneous catalytic system promoted the metathesis of not only such functionalized olefins but also simple olefins without double bond migration that was often encountered on strong solid acids. We here present a new methodology for activation of a metal complex with Lewis acidic mesoporous materials in the metathesis reactions. This novel heterogeneous catalyst would be advantageous over conventional one from the viewpoint of environmental and economical organic synthesis.

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1. Introduction

Olefin metathesis reactions have been performed by transition metal complexes or oxides of molybdenum and tungsten [1]. Especially, ruthenium–carbene complexes have attracted much attention because of their tolerance to various polar functional groups in olefin substrates and easy handling [2]. Among heterogeneous catalysts for metathesis, it is well known that rhenium-based catalysts are powerful ones. For example, supported Re₂O₇ shows higher activity for liquid-phase metathesis reactions of simple olefins than MoO₃ and WO₃ catalysts [1a,3]. Although rhenium-based catalysts have high potential for olefin metathesis, they have serious drawbacks of little activity toward functionalized olefins without help of additives such as R₄Sn and R₄Pb [1a]. In 1991, organometallic methyltrioxorhenium (MTO) was reported to be very effective

for metathesis and epoxidation of olefins by Herrmann's group [4]. Metathesis with MTO was particularly attractive to us because the complex smoothly induced the metathesis of functionalized olefin only on the surface of a solid acid, SiO₂–Al₂O₃ [4a]. However, the nature of the rhenium species and the role of the catalyst carrier, SiO₂–Al₂O₃, have not been fully illuminated. Although the substantial interaction of MTO with Lewis acidic sites on SiO₂–Al₂O₃ could be responsible for the effectiveness in metathesis, few investigations have followed Herrmann's report on the MTO catalysis for functionalized olefins except for studies on MTO with niobium oxide [5].

Mesoporous materials have gained attention because of their high potential as catalysts, adsorbents, electronic devices, and so on [6,7]. In terms of catalysis chemistry, the mesoporous materials can provide us not only highly arranged catalyst sites on the surface where reactants are activated, but also the nano-sized space where the motion and conformation of the reactants should suffer strict constraints. In our previous study, we revealed that Re₂O₇

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dispersed on mesoporous alumina (abbreviated as *meso*-Al₂O₃) with a narrow pore-size distribution centered at 3 nm showed much higher catalytic activity in the metathesis of internal as well as terminal olefins without functional groups than Re₂O₇ on normal γ -Al₂O₃ in a liquid phase [8]. Recently, various attempts to functionalize solid surfaces of mesoporous materials have been made through chemical modification mostly in two ways: (i) incorporating hetero atoms into the framework of the materials during the hydrothermal process (referred to as *direct synthesis*), and (ii) modifying the material using various reagents after the synthesis of the mesoporous material (referred to as *post synthesis*).

In the molybdenum and tungsten-catalyzed metathesis of functionalized olefins there have been some difficulties to overcome, which are caused by the interference of functional groups in the olefin with the catalyst metal centers: (i) the need of high catalyst concentration, (ii) indispensable use of poisonous additives such as tetraalkyl tin and tetraalkyl lead for high catalytic achievements, and (iii) catalyst deactivation [1].

In this paper, we report that a zinc chloride-modified mesoporous alumina, ZnCl₂//*meso*-Al₂O₃, with a high surface area, relatively uniform mesopores, and Lewis acidic character is developed, and that MTO doped on the alumina, MTO/ZnCl₂//*meso*-Al₂O₃, demonstrates higher catalytic performance for the metathesis of *functionalized* olefins than Herrmann's system of MTO on SiO₂-Al₂O₃ (MTO/SiO₂-Al₂O₃). In our catalytic system, ZnCl₂//*meso*-Al₂O₃ not only immobilizes MTO on its solid surface, but also activates MTO enough to accelerate the metathesis of functionalized olefins. Porous carriers such as silica and γ -alumina have been modified with various Lewis acids, and employed as a solid acid in organic reactions, e.g. the Friedel-Crafts alkylation. This paper deals with the first application of Lewis acidic carriers for the activation of organotransition metal catalysts.

2. Results and discussion

2.1. Catalytic activity of MTO on various solid carriers in metathesis of methyl 10-undecenoate

Since a combination of MTO and a solid acid, SiO₂-Al₂O₃, was reported to show excellent catalysis for the metathesis of functionalized olefins such as unsaturated esters and brominated olefins [4a], we surveyed potential of other typical solid acids as an activator for MTO in order to discover a more efficient catalyst system for the metathesis. We selected the following solid acids: *meso*-

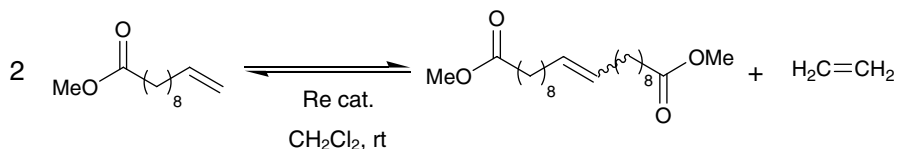
Al₂O₃ with regular mesopores [9], γ -Al₂O₃ consisting of irregular pores, sulfated γ -Al₂O₃, MCM-41 (pure silica) [6c], SBA-15 (pure silica) [10], HMS (pure silica) [11], Al-HMS (aluminum-incorporated HMS) [11,12], K10 (acid-treated clay montmorillonite), NaX zeolite, ZnCl₂, and ZnO.

meso-Al₂O₃ was readily prepared from Al(O-*s*-Bu)₃ through a sol-gel process using lauric acid as a template surfactant [9]. The *meso*-Al₂O₃ had a specific surface area of 560 m²/g and a pore diameter of 3.0 nm. As γ -Al₂O₃ and SiO₂-Al₂O₃, we used the reference catalysts of alumina (JRC-ALO-7) and two types of silica-aluminas (JRC-SAH-1 (Si/Al = 2.3) and JRC-SAL-2 (Si/Al = 5.4)), which were provided by the Catalysis Society of Japan. Sulfated γ -Al₂O₃ was prepared by rinsing γ -Al₂O₃ with concentrated H₂SO₄ [13]. Other mesoporous materials, MCM-41, SBA-15, HMS, and Al-HMS, were prepared according to standard procedures. Commercially available NaX, ZnCl₂, and ZnO were used without modification.

As a model reaction we chose the metathesis of methyl 10-undecenoate in a *liquid* phase (Scheme 1): a catalytic amount of colorless MTO was added to a suspended CH₂Cl₂ solution including a solid acid. The solid surface immediately turned dark brown, indicating that MTO was adsorbed on the solid. Then, methyl 10-undecenoate was added, and the metathesis reaction was run in CH₂Cl₂ at room temperature for a specified time.

The results shown in Table 1 suggest properties of solid carriers necessary for activating MTO:

- (1) Lewis acidity of the solid is mainly responsible for the catalytic activity of MTO in the metathesis. With aluminum isomorphically substituted HMS, Al-HMS, the yield of the metathesis product was influenced by the content of Al ions in the silicate framework: the more aluminum atoms included, the higher the yields obtained (entries 7–9). This indicates that the Lewis acidity of Al-HMS is closely related to the metathesis activity of MTO. On the contrary, Br ϕ -nsted acidic solids like K10 and sulfated γ -Al₂O₃, which contain abundant acidic protons, did not activate MTO (entries 10 and 11).
- (2) Regarding pure Al₂O₃, *meso*-Al₂O₃ with regular pores showed better activity than conventional γ -Al₂O₃ with irregular pores (entries 12 and 13), although the activity was far less than that of SiO₂-Al₂O₃. This suggests that *meso*-Al₂O₃ is a promising carrier for MTO. Interestingly, mesoporous pure silicas had no ability to activate MTO even though those silicas had regular mesopores (entries 12 vs. 14–16).



Scheme 1. Metathesis reaction of methyl 10-undecenoate.

Table 1
Metathesis reaction of methyl 10-undecenoate catalyzed by MTO on various solid carriers^a

Entry	Carrier ^b	Time (h)	Yield (%) ^c
1	ZnCl ₂ // <i>meso</i> -Al ₂ O ₃ (Al/Zn = 16)	6	79
2	ZnCl ₂ // γ -Al ₂ O ₃ (Al/Zn = 17)	24	32
3	ZnCl ₂ //HMS (Si/Zn = 15.2)	24	N.R.
4	ZnCl ₂ //HMS (Si/Zn = 21.0)	24	N.R.
5	SiO ₂ -Al ₂ O ₃ (Si/Al = 5.4)	24	40
6	SiO ₂ -Al ₂ O ₃ (Si/Al = 2.3)	24	41
7	Al-HMS (Al/Si = 4.6) ^d	24	16
8	Al-HMS (Al/Si = 6.8) ^d	24	10
9	Al-HMS (Al/Si = 118) ^d	24	N.R.
10	K10 ^e	24	N.R.
11	Sulfated γ -Al ₂ O ₃ ^f	24	N.R.
12	<i>meso</i> -Al ₂ O ₃	24	11
13	γ -Al ₂ O ₃	24	3
14	HMS	24	N.R.
15	MCM-41	24	N.R.
16	SBA-15	24	N.R.
17	NaX	24	N.R.
18	ZnCl ₂	24	N.R.
19	ZnO	24	N.R.
20	No carrier ^g	24	N.R.

^a Methyl 10-undecenoate (2.5 mmol) was treated with MTO (3.0 wt%, 9 mg, 0.036 mmol) doped on porous carrier (300 mg) in CH₂Cl₂ (5 mL) at 25 °C for 24 h under N₂ atmosphere.

^b All carriers were activated at 500 °C and 0.6 Torr for 2 h just before the addition of MTO. Specific data of the carriers are shown in Section 3. Al/Zn ratios were determined by ICP-AES analysis.

^c Isolated yields are shown after purification by silica gel chromatography. Yields were calculated based on the following definition: "Yield (%)" = 2 × "Mol of a product isolated, dimethyl 10-eicosenedioate" / "Mol of a reactant, methyl 10-undecenoate" × 100.

^d Al-HMS was prepared according to Ref. [7].

^e K10 is commercially available acid-treated montmorillonite clay.

^f Sulfated γ -Al₂O₃ was prepared according to Ref. [12].

^g MTO (0.036 mmol) was used as a homogeneous catalyst.

- (3) On the surface of NaX, ZnCl₂, and ZnO, MTO was not activated (entries 17–19).
- (4) As a control, MTO in the absence of a solid carrier did not promote the metathesis (entry 20).

Based on the above facts, it is easily deduced that enhancing the Lewis acidic character of *meso*-Al₂O₃ should result in significant improvements in catalysis of MTO.

2.2. Catalytic activity of MTO on modified mesoporous alumina and other carriers in metathesis of methyl 10-undecenoate

In order to increase the Lewis acidity of the alumina carrier, we chemically modified the surface of the *meso*-Al₂O₃ with Lewis acidic zinc salts such as ZnCl₂, ZnBr₂, and Zn(NO₃)₂ in the following way: (1) *meso*-Al₂O₃ was impregnated with a solution of ZnCl₂ in EtOH; (2) the suspended mixture was gently dried; and (3) ZnCl₂-treated *meso*-Al₂O₃ was calcined in air at 400 °C to give ZnCl₂-modified *meso*-Al₂O₃ (designated as ZnCl₂//*meso*-Al₂O₃) as a white powder. Modification with other zinc salts like ZnBr₂ and Zn(NO₃)₂ was also made similarly.

Fixation of MTO on ZnX₂//*meso*-Al₂O₃ (X = Cl, Br, NO₃) was straightforward: A colorless solution of MTO in CH₂Cl₂ was added at rt with stirring to a suspension of ZnX₂//*meso*-Al₂O₃ in CH₂Cl₂. The white surface of ZnX₂//*meso*-Al₂O₃ readily turned dark brown, suggesting that the MTO in solution was transferred to the surface of ZnX₂//*meso*-Al₂O₃. The fixed MTO is designated as MTO/ZnX₂//*meso*-Al₂O₃. MTO was likewise fixed on *meso*-Al₂O₃ and γ -Al₂O₃.

To a suspension of MTO-loading catalyst in CH₂Cl₂ was added methyl 10-undecenoate (2.5 mmol), and the metathesis reaction was run at rt. The MTO/ZnCl₂//*meso*-Al₂O₃ system showed higher catalytic performance with a large increase in the rate for the metathesis of methyl 10-undecenoate than MTO/*meso*-Al₂O₃ as shown in Fig. 1: the reaction with MTO (3 wt%) on ZnCl₂-modified *meso*-Al₂O₃ (300 mg) proceeded with an excellent yield (79%) of dimethyl 10-eicosenedioate and a high product selectivity of >97% after 6 h, while MTO (3 wt%) on unmodified *meso*-Al₂O₃ (300 mg) gave only 5% yield.

Compared with Herrmann's catalyst system, MTO/SiO₂-Al₂O₃ [4a], MTO/ZnCl₂//*meso*-Al₂O₃ showed much higher catalytic activity (Fig. 1 and Table 1, entries 1, 5 and 6). ZnCl₂// γ -Al₂O₃ was a less effective carrier than ZnCl₂//*meso*-Al₂O₃ (entries 1 and 2). Interestingly, when MTO was doped on ZnCl₂-modified mesoporous silica, ZnCl₂//HMS, no metathesis proceeded, implying that the use of an alumina-based carrier is indispensable for activation of MTO (entries 1 vs. 3–4).

Table 2 shows that ZnBr₂ was almost as efficient a modifier as ZnCl₂, but MTO on Zn(NO₃)₂ or ZnO-modified *meso*-Al₂O₃ showed no metathesis (entries 10–12). These observations suggest that zinc salt modifiers bearing halide ions are essential to activate MTO for metathesis of functionalized olefins.

To create the optimal Lewis-acidic environment on the *meso*-Al₂O₃ for activating MTO, surface modifications were made using different amounts of ZnCl₂ on the alumina (Table 2 entries 1–7). It was revealed that the optimum atomic ratio of Al/Zn in the ZnCl₂-modified *meso*-Al₂O₃

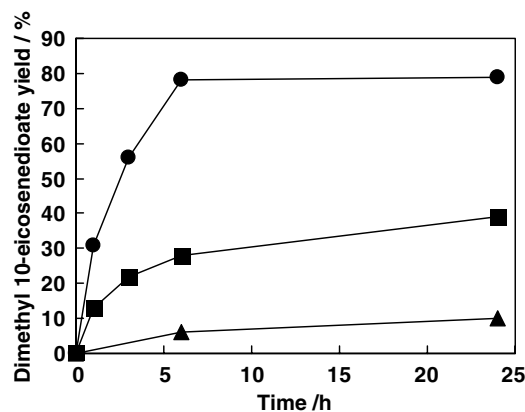


Fig. 1. Yields of the metathesis reaction of methyl 10-undecenoate as a function of reaction time; ●: MTO/ZnCl₂//*meso*-Al₂O₃ (Al/Zn = 16), ■: MTO/SiO₂-Al₂O₃, ▲: MTO/*meso*-Al₂O₃.

Table 2
Effects of modifiers on mesoporous alumina upon catalytic activity of MTO for metathesis of methyl 10-undecenoate^a

Entry	Modifier	Al/Zn ^b	Yield (%) ^c
1	ZnCl ₂	5.5	27
2	ZnCl ₂	9.6	32
3	ZnCl ₂	16	54
4	ZnCl ₂	24	43
5	ZnCl ₂	30	45
6	ZnCl ₂	43	33
7	ZnCl ₂	70	22
8	ZnBr ₂	10.5	44
9	ZnBr ₂	14.6	37
10	Zn(NO ₃) ₂	8.5	N.R.
11	Zn(NO ₃) ₂	16.2	N.R.
12	ZnO ^d	16	N.R.

^a Methyl 10-undecenoate (2.5 mmol) was treated with MTO (3.0 wt%, 9 mg, 0.036 mmol) doped on porous carrier (300 mg) in CH₂Cl₂ (5 mL) at 25 °C for 3 h under N₂ atmosphere.

^b Al/Zn ratio was determined by ICP-AES analysis.

^c Isolated yields are shown after purification by silica gel chromatography. Yields were calculated based on the following definition: "Yield (%)" = 2 × "Mol of a product isolated, dimethyl 10-eicosenedioate" / "Mol of a reactant, methyl 10-undecenoate" × 100.

^d ZnO was mechanically mixed with *meso*-Al₂O₃ at rt, and calcined for 4 h at 400 °C in air. The Al/Zn ratio shows an atomic ratio in the mixture.

was 16 over the range of 5.5–70 to show the highest metathesis activity for methyl 10-undecenoate (entry 3).

It is also important to point out that the modified carrier maintains the mesoporous structure upon treatment with ZnCl₂. As shown in Table 3 and Fig. 2, all the modified aluminas had regular mesopores with a relatively narrow pore-size distribution and high specific surface areas, suggesting that they should have potential to function as effective reaction media where rhenium species are coordinated to be activated, and reactant and product olefins are smoothly adsorbed, desorbed, and transferred.

In order to examine the effect of the pore size of the catalyst on the metathesis, we prepared three *meso*-Al₂O₃ with different pore sizes, 3.1, 3.3, and 4.1 nm by changing the amount of added water in preparation of *meso*-Al₂O₃, and modified the aluminas with ZnCl₂ in the same Al/Zn ratio of 16 to obtain ZnCl₂-modified *meso*-Al₂O₃ carriers. Then, MTO was fixed on the carriers (100 mg), and applied to the metathesis of methyl 10-undecenoate (2.5 mmol) at rt for 12 h. As shown in Table 4, the larger the pore size and the pore volume of *meso*-Al₂O₃ were, the higher yields of the self-metathesis product were obtained. We suppose that the diffusivity of the reactant and product in the mesopores should be critical to the reaction rate because 10-undecenoate and 10-eicosenedioate are relatively large molecules to pass through the pores.

From XRD analysis of MTO/ZnCl₂/*meso*-Al₂O₃, no bulk rhenium metals, Re₂O₇ and ZnO were observed on the surface. The IR spectrum of MTO/ZnCl₂/*meso*-Al₂O₃ showed two weak absorption bands at 2922 and 2856 cm⁻¹ that were not observed in the spectrum of the carrier, ZnCl₂/*meso*-Al₂O₃. Since two absorption bands at 2984 and 2899 cm⁻¹ appear for free MTO[14], the two

Table 3
Textural characteristics of carriers based on N₂ isotherms at -196 °C

Entry	Carrier ^a	S _{BET} (m ² g ⁻¹) ^b	D _p (nm) ^c
1	<i>meso</i> -Al ₂ O ₃	560	3.1
2	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 5.5)	410	3.0
3	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 9.6)	410	3.0
4	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 16)	450	3.1
5	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 24)	410	3.1
6	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 30)	460	3.1
7	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 43)	490	3.1
8	ZnCl ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 70)	510	3.1
9	ZnBr ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 14.6)	410	3.0
10	Zn(NO ₃) ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 8.5)	380	2.9
11	Zn(NO ₃) ₂ / <i>meso</i> -Al ₂ O ₃ (Al/Zn = 16.2)	410	3.0
12	γ-Al ₂ O ₃	170	–
13	ZnCl ₂ /γ-Al ₂ O ₃ (Al/Zn = 17)	160	–
14	SiO ₂ -Al ₂ O ₃ (Si/Al = 5.4)	560	–
15	SiO ₂ -Al ₂ O ₃ (Si/Al = 2.3)	510	–
16	HMS	1450	2.7
17	ZnCl ₂ /HMS (Si/Zn = 15.2)	400	2.6
18	Al-HMS (Al/Si = 4.6)	1340	2.4
19	Al-HMS (Al/Si = 6.8)	1450	2.7
20	Al-HMS (Al/Si = 118)	1070	2.9
21	MCM-41	1170	2.7
22	SBA-15	1120	2.0
23	NaX	790	–
24	K10	220	–
25	ZnO	60	–

^a Al/Zn ratios were determined by ICP-AES analysis.

^b Specific surface areas were determined by the BET method.

^c Pore diameters were determined by the DH method.

observed bands are assigned to asymmetric and symmetric C–H stretching vibrations of MTO anchored on the modified carrier without decomposition.

It was confirmed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) that the rhenium content in the MTO/ZnCl₂/*meso*-Al₂O₃ catalyst did not change after the reaction, demonstrating that free MTO could not be separated from the surface of the ZnCl₂/*meso*-Al₂O₃ carrier during the metathesis.

It was also interesting to note that MTO in the presence of 1.0–10 equiv. of typical Lewis acids such as ZnCl₂, Me₃Al, Me₂AlCl, and MeAlCl₂ gave no desired self-coupling products in the metathesis of methyl 10-undecenoate, indicating that homogeneous Lewis acids are inadequate for the activation of MTO toward metathesis promotion of functionalized olefins.

Herrmann assumed that MTO is fixed by condensation reactions with Al–OH or Si–OH groups on SiO₂-Al₂O₃ and that the rhenium ions undergo electronic influences from the acidic carrier to show catalysis for metathesis [4a]. Similarly, we suppose that ZnCl₂/*meso*-Al₂O₃ has much stronger acidity than original *meso*-Al₂O₃, and that upon contact of MTO with the ZnCl₂/*meso*-Al₂O₃ the rhenium species form steady Re–O–Al bonds spontaneously. The rhenium ions then experience electron-withdrawing influences from the acidic carrier enough to develop the catalysis for metathesis not only of simple olefins, but also of functionalized olefins.

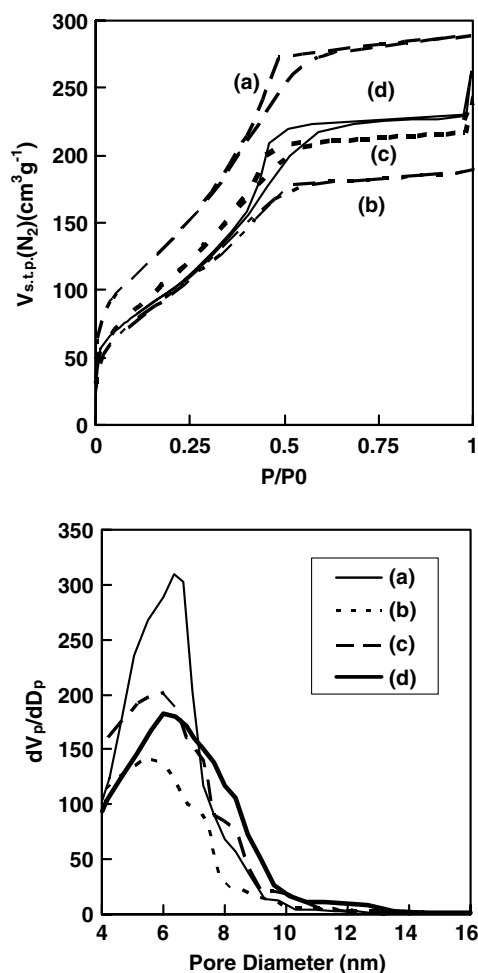


Fig. 2. (A) N_2 adsorption and desorption isotherms at $-196\text{ }^\circ\text{C}$; (B) Pore-size distribution profiles for (a) pristine $meso\text{-Al}_2\text{O}_3$, (b) $ZnCl_2/meso\text{-Al}_2\text{O}_3$ ($Al/Zn = 5.5$), (c) $ZnCl_2/meso\text{-Al}_2\text{O}_3$ ($Al/Zn = 9.6$), (d) $ZnCl_2/meso\text{-Al}_2\text{O}_3$ ($Al/Zn = 16$).

Table 4
Effects of pore sizes of mesoporous alumina upon the catalytic activity of doped MTO for the metathesis of methyl 10-undecenoate^a

Entry	D_p (nm) ^b	S_{BET} ($m^2 g^{-1}$) ^c	V_p ($mm^3 g^{-1}$) ^d	TON ^e
1	3.1	560	485	26
2	3.3	560	530	42
3	4.1	440	550	44

^a Methyl 10-undecenoate (2.5 mmol) was treated with MTO (3.0 wt%, 3 mg, 0.013 mmol) doped on $ZnCl_2/meso\text{-Al}_2\text{O}_3$ (100 mg) in CH_2Cl_2 (5 mL) at $25\text{ }^\circ\text{C}$ for 12 h under N_2 atmosphere.

^b Pore diameters were determined by the DH method.

^c Specific surface areas were determined by the BET method.

^d Pore volumes.

^e Turnover numbers per rhenium atom.

2.3. Comparison of catalytic activity in metathesis of various functionalized and simple olefins between MTO on zinc chloride-modified $meso\text{-Al}_2\text{O}_3$ and MTO on $SiO_2\text{-Al}_2\text{O}_3$

To disclose the usefulness of $MTO/ZnCl_2/meso\text{-Al}_2\text{O}_3$ system, metathesis reactions were performed under mild

conditions with various functionalized and simple olefins in Table 5. The results of control reactions catalyzed by $MTO/SiO_2\text{-Al}_2\text{O}_3$ are also shown in Table 5 and Fig. 1. In all the experiments, $MTO/ZnCl_2/meso\text{-Al}_2\text{O}_3$ converts olefins to products in better yields and higher product selectivities. The unsaturated esters except for allyl acetate can be coupled into the corresponding unsaturated diesters without migration of a double bond. Although it was reported that allyl acetate was also a good reactant for metathesis by $MTO/SiO_2\text{-Al}_2\text{O}_3$ [4a], we were not able to obtain good results by both catalyst systems (entry 3).

Metathesis reactions of unsaturated ketone, bromide, and chloride also proceeded more smoothly on $MTO/ZnCl_2/meso\text{-Al}_2\text{O}_3$ than $MTO/SiO_2\text{-Al}_2\text{O}_3$ (entries 6–8).

In addition, this novel catalyst system catalyzes not only functionalized olefins but also simple olefins without double bond migration, which was often encountered on strong solid acids (entries 9 and 10). For example, the metathesis of 7-hexadecene catalyzed by $MTO/ZnCl_2/meso\text{-Al}_2\text{O}_3$ only afforded desired olefins, 7-tetradecene and 9-octadecene with >99% selectivity, while $MTO/SiO_2\text{-Al}_2\text{O}_3$ gave complex isomeric olefin products including cross-metathesis products and oligomers, which were confirmed by GC analysis, and the selectivity of desired olefins dropped to 53% at 8 h: $SiO_2\text{-Al}_2\text{O}_3$ is such a strong acidic carrier that double bonds in a reactant and product easily migrate to lead to the formation of various metathesis products. Such olefinic substrates are also promoted to oligomerize on $SiO_2\text{-Al}_2\text{O}_3$ [15].

3. Experimental

3.1. Preparation of $meso\text{-Al}_2\text{O}_3$

Mesoporous alumina ($meso\text{-Al}_2\text{O}_3$) was synthesized according to Davis' method [9]: Into a 300-mL polypropylene vessel containing a stirring bar was added $Al(O\text{-}i\text{-}Bu)_3$ (21.9 g, 89 mmol), 1-propanol (138 g, 2.29 mol). After 10 min vigorous stirring at room temperature (rt), deionized water (5.2 g, 286 mmol) was added, followed by stirring at rt. After 1 h, a solution of lauric acid (5.4 g, 27.0 mmol) in 1-propanol (18 g, 290 mmol) was added under vigorous stirring, and the mixture was further stirred vigorously at rt for 24 h. The resulting white liquid was placed in a 300-mL autoclave, and heated at $110\text{ }^\circ\text{C}$ for 48 h without stirring to afford a white precipitate. The precipitate was washed on a filter paper with a large amount of ethanol, and dried at rt under an N_2 flow. The white solid thus obtained was heated from rt to $600\text{ }^\circ\text{C}$ at a ramping rate of $9.6\text{ }^\circ\text{C min}^{-1}$ under an N_2 flow, and then calcined under an air flow at $600\text{ }^\circ\text{C}$ for 4 h to burn out the organic species to give pure $meso\text{-Al}_2\text{O}_3$.

In order to prepare $meso\text{-Al}_2\text{O}_3$ with different pore sizes, we used different amounts of deionized water added, 5.2 g, 7.8 g, and 10.4 g, respectively, in the above procedure.

Table 5
Metathesis of various functionalized and simple olefins catalyzed by MTO/ZnCl₂//*meso*-Al₂O₃ and MTO/SiO₂-Al₂O₃^a

Entry	Olefin	Product	Time [h] ^b	Yield (%) ^c
1			24 [24]	79 (41)
2			8 [12]	53 (37)
3			12 [23]	11 (7)
4			5 [5]	54 (18)
5			12 [16]	62 (27)
6			3 [3]	31 (8)
7			4 [4]	71 (59)
8			2 [2]	93 (54)
9 ^d			0.5 [0.5]	75 (32)
10 ^d			8 [8]	50 (18)

^a Olefin (2.5 mmol) was treated with MTO (3.0 wt%, 9 mg, 0.036 mmol) doped on ZnCl₂//*meso*-Al₂O₃ or SiO₂-Al₂O₃ (300 mg) in CH₂Cl₂ (5 mL) at 25 °C for a specified time under N₂ atmosphere.

^b Figures in square brackets show reaction times of the metathesis using MTO/SiO₂-Al₂O₃.

^c Yields were calculated based on the following definition: “Yield (%)” = 2 × “Mol of a product olefin isolated”/“Mol of a reactant olefin” × 100. Yields in entries 1–8 are shown after purification by silica gel chromatography. Yields in entries 9 and 10 were determined by gas chromatography using an internal standard. Figures in brackets show yields of the metathesis using the MTO/SiO₂-Al₂O₃ catalyst.

^d The metathesis was run at 0 °C.

3.2. Preparation of ZnCl₂//*meso*-Al₂O₃

A specified amount of ZnCl₂ (for example, 0.334 g, 2.45 mmol) was dissolved in ethanol (5 mL) under sonication and was added dropwise to *meso*-Al₂O₃ (2.0 g) in a 100-mL glass beaker. The slurry was mildly stirred with a glass rod and dried under an N₂ flow. Ethanol (5 mL) was added to the dried material, followed by being stirred and dried. This procedure was repeated twice. The dried sample obtained was heated under an air flow from rt to at 400 °C at a ramping rate of 9.6 °C min⁻¹ and then calcined at 400 °C at for 4 h to give ZnCl₂-modified *meso*-Al₂O₃ (ZnCl₂//*meso*-Al₂O₃ (Al/Zn = 16)). Other chemically modified mesoporous aluminas were similarly prepared using ZnBr₂ and Zn(NO₃)₂.

3.3. The other mesoporous carriers

Aluminum-incorporated HMS (Al-HMS), MCM-41 (pure silica), and SBA-15 (pure silica) were synthesized according to Refs. [12,6c,10], respectively.

3.4. Measurement of surface area and pore diameter

N₂ adsorption–desorption measurements were performed at –196 °C with a BELSORP 28SA (Bel Japan) using static adsorption procedures. The samples were pre-treated at 400 °C and 10⁻³ Torr for 12 h prior to analysis. Adsorption data were analyzed by the Brunauer–Emmett–Teller (BET) method [16] for surface areas, and Dollimore–Heal (DH) method [16] to obtain pore-size distribution curves. The representative data of *meso*-Al₂O₃, ZnCl₂//*meso*-Al₂O₃ and other carriers are summarized in Tables 3 and 4.

3.5. X-ray diffraction and ICP analysis

X-ray powder diffraction measurement was performed with a MultiFlex (Rigaku) under ambient atmosphere. The sample was mounted on an XRD sample cell as fine powder under ambient atmosphere, and analyzed at a current of 40 mA and a voltage of 40 kV in the 2θ range 1–60° with a scanning rate of 1.0° min⁻¹.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was carried out with a CIROS-CCD (Rigaku). Each sample (ca. 20 mg) was added to 1 mL of 10 wt% aqueous NaOH in the case of silicate or 1 mL of 10 wt% aqueous H₂SO₄ in the case of alumina, and completely dissolved under sonication. The solution was diluted 100 times and applied to the measurement.

3.6. Reaction procedures

The metathesis reaction was carried out in solution under a dry N₂ flow. A carrier (300 or 100 mg) was placed in a 30-mL flask and activated at 500 °C in an electric furnace under a reduced pressure of 0.6 Torr for 2 h. After the carrier was cooled to rt and N₂ gas was introduced in the flask, a solution of MTO (9.3 or 3.1 mg, 0.037 or 0.012 mmol) in CH₂Cl₂ (3 mL) was added and the white surface of the carrier instantly turned dark brown. The suspended mixture was stirred at rt for 10 min.

To the mixture was added methyl 10-undecenoate (or other olefin reactants) (2.5 mmol) in CH₂Cl₂ (2 mL) and the mixture was stirred at rt for a specified reaction time. After adding methanol (1 mL) to the reaction mixture to stop the metathesis, the mixture was filtered, concentrated, and purified by silica gel chromatography to give dimethyl 10-eicosenedioate.

Yields were calculated based on the definition: “Yield (%)” = 2 × “Mol of an olefin product”/“Mol of an olefin reactant” × 100. Product selectivities were calculated based on the definition: “Selectivity (%)” = “an observed yield of an olefin product”/“A theoretical yield of an olefin product based on conversion of a reactant” × 100.

3.6.1. Dimethyl 10-eicosenedioate (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.35 (2H, m), 3.65 (6H, s), 2.30 (4H, t, *J* = 6.2 Hz), 1.93 (4H, m), 1.50 (4H, m), 1.35 (20H, m). ¹³C NMR (125 MHz, CDCl₃) δ 174.6, 130.7, 51.7, 34.5, 32.9, 30.0, 29.6, 29.5, 29.4, 25.3. IR (CCl₄) 2930, 2869, 1740, 1442, 1153, 963, 794 cm⁻¹. MS (EI) *m/z* 368 (M⁺).

3.6.2. 1,8-Dibromo-4-octene (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.4 (2H, m), 3.4 (4H, t, *J* = 6.48 Hz), 2.16 (4H, q, *J* = 7.29 Hz), 1.91 (4H, m). ¹³C NMR (125 MHz, CDCl₃) δ 129, 33.3, 32.2, 30.6. IR (CCl₄) 2938, 2846, 1438, 947, 786 cm⁻¹. MS (EI) *m/z* 268 (M⁺).

3.6.3. 1,8-Diacetoxy-4-octene (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.43 (2H, m), 4.05 (4H, t, *J* = 6.48 Hz), 2.08 (4H, m), 2.06 (6H, s), 1.66 (4H, m). ¹³C NMR (125 MHz, CDCl₃) δ 171.2, 129.8, 129.3, 63.9, 28.7, 28.4, 28.27, 23.4, 20.9. IR (CCl₄) 2925, 2850, 1743, 1369, 965, 784 cm⁻¹. MS (EI) *m/z* 228 (M⁺).

3.6.4. 1,20-Diacetoxy-10-eicosene (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.38 (2H, m), 4.05 (4H, t, *J* = 6.75 Hz), 2.04 (4H, m), 1.97 (4H, m), 1.61 (4H, m),

1.28 (24H, m). ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 130.1, 129.6, 64.5, 32.56, 29.72, 29.59, 29.45, 29.39, 29.22, 29.09, 28.57, 27.17, 25.88, 20.98. IR (CCl₄) 2927, 2850, 1743, 1457, 1369, 968, 790 cm⁻¹. MS (EI) *m/z* 396 (M⁺).

3.6.5. 5-Decene-2,9-dione (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.43 (2H, m), 2.48 (4H, t, *J* = 7.3 Hz), 2.25 (4H, m), 2.14 (6H, s). ¹³C NMR (125 MHz, CDCl₃) δ 207.5, 129.8, 43.7, 31.4, 27.0. IR (CCl₄) 2921, 1708, 1436, 1257, 1164, 964, 780 cm⁻¹. MS (EI) *m/z* 168 (M⁺).

3.6.6. 1,4-Acetoxy-2-butene (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.82 (2H, m), 4.76 (4H, t, *J* = 6.46 Hz), 2.03 (6H, s). ¹³C NMR (125 MHz, CDCl₃) δ 171.1, 129.8, 129.4, 70.4, 69.1, 17.4. IR (CCl₄) 1740, 1670, 1370, 970, 776 cm⁻¹. MS (EI) *m/z* 172 (M⁺).

3.6.7. 1,20-Diacetoxy-10-eicosene (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.38 (2H, m), 4.05 (4H, t, *J* = 6.75 Hz), 2.04 (4H, m), 1.97 (4H, m), 1.61 (4H, m), 1.28 (24H, m). ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 130.1, 129.6, 64.5, 32.56, 29.72, 29.59, 29.45, 29.39, 29.22, 29.09, 28.57, 27.17, 25.88, 20.98. IR (CCl₄) 2927, 2850, 1743, 1457, 1369, 968, 790 cm⁻¹. MS (EI) *m/z* 396 (M⁺).

3.6.8. Dioctyl 10-eicosenedioate (a *cis/trans* mixture)

¹H NMR (500 MHz, CDCl₃) δ 5.37 (2H, m), 4.05 (4H, t, *J* = 6.75 Hz), 2.29 (4H, m), 1.62 (8H, m), 1.28 (40H, s). ¹³C NMR (125 MHz, CDCl₃) δ 172.0, 131.6, 66.7, 33.6, 33.3, 30.4, 30.3, 29.9, 29.7, 28.3, 26.5, 25.4, 14.0. IR (CCl₄) 2927, 2857, 1731, 790 cm⁻¹. HRMS Calcd for C₃₆H₆₈O₄: M, 564.5117; Found: *m/z* 564.5115.

3.6.9. 1,20-Diacetoxy-10-eicosene

¹H NMR (500 MHz, CDCl₃) δ 5.78 (2H, m), 3.48 (4H, t, *J* = 6.85 Hz), 2.03 (4H, m), 1.74 (4H, m), 1.39 (4H, m), 1.29 (20H, m). ¹³C NMR (125 MHz, CDCl₃) δ 131.7, 45.0, 33.1, 30.4, 30.3, 29.5, 27.4, 27.3. IR (CCl₄) 2936, 2845, 1440, 947, 786, 651 cm⁻¹. HRMS Calcd for C₂₀H₃₈Cl₂: M, 348.2351; Found: *m/z* 348.2350.

3.6.10. 7-Tetradecene (a mixture of *cis/trans* = 0.22)

¹H NMR (500 MHz, CDCl₃) δ 5.38 (2H, m), 1.96 (4H, m), 1.27 (16H, m), 0.88 (6H, t, *J* = 6.5 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 130.3, 129.8, 31.9, 31.7, 29.8, 29.7, 29.1, 28.9, 27.3, 22.8, 14.2. IR (CCl₄) 2995, 2957, 2926, 2871, 2854, 1459 cm⁻¹.

3.6.11. 9-Octadecene (a mixture of *cis/trans* = 0.22)

¹H NMR (500 MHz, CDCl₃) δ 5.37 (2H, m), 2.00 (4H, m), 1.27 (24H, m), 0.88 (6H, t, *J* = 6.5 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 130.2, 129.8, 32.0, 29.8, 29.6, 29.4, 29.2, 27.3, 22.7, 14.2. IR (CCl₄) 3007, 2956, 2927, 2855, 1466 cm⁻¹.

4. Conclusion

We have developed a novel catalyst system of methyltrioxorhenium doped on zinc chloride-modified mesoporous alumina (MTO/ZnCl₂//*meso*-Al₂O₃). The solid system can work as an efficient heterogeneous catalyst for metathesis reactions not only of functionalized olefins but of simple olefins without double bond migration and oligomerization, and the activity is the most prominent among rhenium-based catalyst systems that have been developed so far. The newly devised catalyst carrier, ZnCl₂//*meso*-Al₂O₃, is a much more efficient activator for organometallic MTO compared with other “homogeneous” Lewis acidic modifiers. To our knowledge, this methodology is the first report on outstanding activation of organometallic complexes with an acidic carrier composed of mesoporous alumina and immobilized Lewis acidic zinc chloride.

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