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Activation of Encapsulation System MoO_3/SnO_2 for Olefin Metathesis by $SnMe_4$

Katsumi Tanaka,* Masaki Sasaki, and Isamu Toyoshima

Research Institute for Catalysis, Hokkaido University, Kika-ku, Sapporo 060, Japan

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Inactive MoO_3/SnO_2 was changed to a metathesis catalyst by treating the surface with tetramethyltin ($SnMe_4$) at room temperature. On the catalyst olefin metathesis proceeded selectively without accompanying side reactions such as hydrogen scrambling. During the treatment of MoO_3/SnO_2 with $SnMe_4$, a small amount of methane formed concurrent with decomposition of $SnMe_4$. Decomposition of tetraethyltin ($SnEt_4$) also occurred on MoO_3/SnO_2; however, the surface showed no metathesis activity. From these results, it was concluded that the cause for activation of MoO_3/SnO_2 by $SnMe_4$ is attributed not to reduction of Mo species or the presence of Sn but to the formation of CH_2 species pivotal to the catalytic olefin metathesis cycle. When MoO_3/SnO_2 was reduced with H_2 or CO at 500 °C, Mo species migrated into reduced SnO_2 and no metathesis activity was observed even after treating the surface with $SnMe_4$. However, when the reduced sample was reoxidized with O_2 at 500 °C for 1 h followed by being treated with $SnMe_4$, the surface was changed to metathesis active.

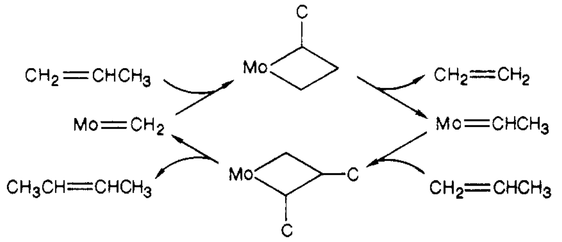
Introduction

It is assumed that olefin metathesis on solid catalysts proceeds through metal alkylidene and metallacyclobutane intermediates, which are accepted species in homogeneous catalytic systems.[1] In fact, the stereoselectivities in olefin metathesis observed on $SnMe_4$ treated molybdena-titania catalysts[2] are quite similar to those in homogeneous systems,[3] which supports a validity for the reaction mechanism on solid metathesis catalysts. In this sense, whether or not a surface shows metathesis activity may depend on the initiation step, a metal alkylidene formation process by a contact with olefin, and if a metal alkylidene species is formed on the surface, it may be able to participate in the propagation step, the chain carrying process involving metallacyclobutane intermediates:[4]

initiation step of propene metathesis:

$$\text{Mo cation} + \text{propene} \rightarrow \text{Mo}{=}\text{CH}_2 \text{ or } \text{Mo}{=}\text{CHCH}_3$$

propagation step:



Consequently, it is interesting to elucidate the behavior of grafted CH_2 species on solid surfaces. So far MoO_3 supported on various kinds of metal oxide supports that are completely metathesis-inactive materials have been treated with $SnMe_4$ to convert them to metathesis catalysts. For instance, MoO_3/TiO_2 treated with $SnMe_4$ (hereafter denoted as MoO_3/TiO_2–$SnMe_4$),[4,5] MoO_3/SiO_2–$SnMe_4$,[6] MoO_3/Al_2O_3–$SnMe_4$, and MoO_3/ZrO_2 changed into super-active olefin metathesis catalysts.[7] While their reduced catalysts were less active for metathesis, however, their metathesis activities were also drastically enhanced more than by a factor of 10^3 by treating with $SnMe_4$. Consequently these metathesis activities are not induced by reduction of Mo species on their surfaces but are interpreted by grafting CH_2 on Mo species formed as a result of CH_4 evolution during the treatment with $SnMe_4$. Contrary to these, MoO_3 supported on ZnO, MgO, and GeO_2 did not have any metathesis activity irrespective of the oxidized and reduced forms even after being treated with $SnMe_4$. These results clearly induce an effect of support on grafting CH_2 species on Mo cations formed by decomposition of $SnMe_4$. Compared to these supported molybdenum oxide catalysts, the MoO_3/SnO_2 system showed an unexpected behavior. That is, metathesis-inactive MoO_3/SnO_2 changed to an olefin metathesis-active catalyst by treating it with $SnMe_4$; however, the H_2-reduced surface showed no activity following treatment with $SnMe_4$.[7] In this paper, first the cause of metathesis activity generation on MoO_3/SnO_2 treated with $SnMe_4$ is elucidated, and second the cause of metathesis inhibition on reduced MoO_x/SnO_{2-y} treated with $SnMe_4$ is studied.

Experimental Section

Molybdenum trioxide supported on SnO_2 was obtained by immersing SnO_2 powder into an aqueous solution of ammonium paramolybdate salt; water was then removed by heating the solution at 120 °C. The starting material was oxidized with O_2 at 500 °C to obtain 6.7 wt % MoO_3/SnO_2. Here SnO_2 was obtained by oxidation of $Sn(OH)_4$ under O_2 flow at 700 °C for 12 h, and oxide formation was ascertained by the oxygen 1s X-ray photo-

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TABLE I: Composition and Deuterium Distribution of Products Formed in the Metathesis Reaction of a 1:1 Mixture of Propene-d_0 and -d_6 on MoO_3/SnO_2-$SnMe_4$ at Room Temperature[a]

			deuterium distribution, %								
product	time, min	comp, %	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
propene	0	100.0	48.1	0	0	0	0	1.5	50.4		
	20	91.8	36.1	0	12.5	0.2	12.4	0.9	37.9		
	160	78.3	26.0	0.3	22.5	0.6	22.1	0.8	27.8		
ethylene	20	4.7	27.2	1.5	49.7	0.1	22.6				
	160	11.9	26.5	0	49.2	1.5	22.8				
2-butene	20	3.5	24.5	0.8	0.3	1.3	46.4	0	1.2	1.2	24.4
	160	9.8	23.7	0	0.4	1.5	48.8	0	0.5	1.3	23.9

[a] Total propene, 18.4 Torr; MoO_3/SnO_2, 0.3 g; $SnMe_4$ used, 5 Torr.

electron spectrum (XPS). The partially reduced catalyst (denoted as MoO_{3-x}) was obtained by reoxidizing a fully reduced catalyst (MoO_x) with a 1:1 mixture of N_2O and H_2 of total pressure of about 200 Torr (1 Torr = 133.3 Pa); here the fully reduced catalyst was obtained by reducing MoO_3/SnO_2 with H_2 at 500 °C for 1 h. The same procedure was performed to obtain partially reduced MoO_{3-x}/TiO_2 ($0.1 > x > 0.7$).[8] The catalyst treatment changing the extent of reduction was carried out in a conventional glass circulation system with volume of ca. 260 mL. Each catalyst was evacuated at 500 °C for 1 h and was supplied to reactions with olefins, $SnMe_4$, and $SnEt_4$. Tetramethyltin or $SnEt_4$ (both are commercially available) vapor (generally 5 Torr) was diluted with He (about 60 Torr), and the mixed gas was exposed to molybdena–stannic oxide catalysts at room temperature for 30 min; the catalyst was then followed by evacuation at room temperature for 30 min.

Catalytic reactions were carried out in the glass circulation system at room temperature, and analysis of produced gases was performed by using a Shimadzu GC-4C gas chromatograph with thermal conductivity detector and flame ionization detector, in which a 6-m long and 3-mm i.d. stainless steel column involving a VZ-7 was equipped, and deuterium distributions of products were measured by using a Hitachi RMU-6 mass spectrometer with ionization voltage between 10 and 12 eV. Commercially available propene-d_6, 1,3-butadiene-d_6, unlabeled propene, 1-butene, and 1,3-butadiene were used after purification.

XPS spectra were recorded with a Vacuum Generators ESCA 3 MKII photoelectron spectrometer employing Mg Kα radiation ($h\nu$ = 1253.6 eV). The background pressure was below 5×10^{-9} Torr. Analyzer energy used was 20 eV. Binding energy (BE) values on XPS were corrected with reference to the peak at 530 eV for O 1s, which is roughly common in the spectra of metal oxides.[9] A fully reduced sample was prepared in the glass circulation system and was transferred to the preparation chamber of the ESCA machine, in which the sample was reduced again with 1×10^{-4} Torr of H_2 at 500 °C for 1 h. Depth profile analysis of fully oxidized MoO_3/SnO_2 and the fully reduced sample was performed by taking spectra following Ar^+ ion sputtering with 2-kV acceleration voltage at room temperature.

Results and Discussion

Molybdenum trioxide supported on SnO_2 was completely inactive to propene metathesis reaction at room temperature. However, when MoO_3/SnO_2 was treated with $SnMe_4$ at room temperature, a small amount of methane formed and the surface was changed to a metathesis catalyst. Table I shows the deuterium distribution of products formed in the metathesis reaction of a 1:1 mixture of propene-d_0 and -d_6 on MoO_3/SnO_2–$SnMe_4$:

productive metathesis:

$$CH_2{=}CHCH_3 + CD_2{=}CDCD_3 \rightarrow \text{ethylene} + \text{2-butene}$$

degenerate metathesis:

$$CH_2{=}CHCH_3 + CD_2{=}CDCD_3 \rightarrow CD_2{=}CHCH_3 + CH_2{=}CDCD_3$$

TABLE II: Product Distribution and Deuterium Distribution of Products Formed in the Decomposition Reaction of $SnMe_4$ on MoO_3/SnO_2 at Room Temperature, on Which Hydrogen Was 97.4% Exchanged by Deuterium Atom[a]

		deuterium distribution, %			
product	amt, Torr	d_0	d_1	d_2	d_3
methane	0.49	92.0	8.0	0	~0
ethane	0.51	100.0	0	0	~0
ethylene	0.08	95.4	4.6	0	~0

[a] For catalyst preparation, see text. MoO_3/SnO_2, 3.5 g, pressure and reaction time of $SnMe_4$, 14.4 Torr, 30 min.

As shown in the table, ethylene and 2-butenes were formed in the productive fashion, and these were composed of d_0, d_2, and d_4 isomers for ethylene and d_0, d_4, and d_8 isomers for 2-butenes. On the other hand, propene-d_2 and -d_4 isomers were produced in the degenerate fashion. From these results, it is concluded that this surface catalyzes propene metathesis selectively and does not show any activity to side reactions such as hydrogen scrambling of olefins or double bond shift reaction. It is noted that the turnover frequency of the productive metathesis of propene was 8.7×10^{-5} (ethylene molecules (Mo cations)$^{-1}$ s^{-1}), assuming all Mo cations in the catalyst participate in the reaction. The number of active $Mo{=}CH_2$ species should be much less than that of the total number of Mo cations included in the catalyst, so that the real turnover frequency is expected to be much higher than the reported value.

To elucidate the cause of the generation of metathesis activity on MoO_3/SnO_2–$SnMe_4$, we studied products formed in the treatment of MoO_3/SnO_2 with $SnMe_4$ and their deuterium distributions. Here hydrogen in MoO_3/SnO_2 was 97.4% converted into deuterium by the following reactions:

$$MoO_3/SnO_2 \text{ (with H)} \xrightarrow[\text{1 h}]{D_2,\ 500\ °C} MoO_x/SnO_{2-y} \text{ (97.4\% D)} \xrightarrow{O_2,\ 500\ °C,\ 3\ h} MoO_3/SnO_2 \text{ (97.4\% D)}$$

The results are shown in Table II. Methane, ethane, and ethylene formed in the treatment with $SnMe_4$ on MoO_3/SnO_2 at room temperature for 30 min. It is significant to note that methane was composed of almost all d_0 isomers and ethane was a completely d_0 species. The former result might be significant only if the catalyst contained considerably more moles of D than was present in methane. These results imply that ethane is formed by recombination of two methyls in $SnMe_4$ and that methane is formed by the reaction $2CH_3 \rightarrow CH_4 + CH_2$, that is, grafting of a CH_2 species, which is pivotal to the propagation step in the propene methathesis reaction. The fact that ethylene was formed also supports the CH_2 formation on the surface since it is interpreted that ethylene is formed by either coupling of two CH_2 species or β-hydrogen abstraction of the ethyl group formed as a result of CH_2 insertion into the metal (Sn or Mo)–methyl bond. This assumption may be supported by the fact that ethylene is significantly composed of d_0 species.

It is generally considered that the treatment of MoO_3/SnO_2 with $SnMe_4$ may reduce Mo cations on the surface, and the reduction of their species may be the reason for generation of

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TABLE III: Products Formed in the Decomposition of $SnMe_4$ and Metathesis Reaction of Propene on the $SnMe_4$-Treated Surfaces at Room Temperature

	products formed,[a] Torr			metathesis of propene	
catalyst	CH_4	C_2H_6	C_2H_4	TF[b]	cis/trans 2-butene
MoO_3/SnO_2	0.043	0.061	0.010	8.7×10^{-5}	0.69
MoO_{3-x}/SnO_{2-y}	7×10^{-4}	0	0	0	
MoO_x/SnO_{2-y}	5×10^{-4}	0	0	0	
MoO_3/SnO_2 (reoxidized)	0.045	0.076	0.005	2.2×10^{-5}	0.93
SnO_2	0.015	0	0	0	
SnO_{2-y}	8×10^{-4}	0	0	0	

[a] Reaction with $SnMe_4$; 5 Torr; 30 min at room temperature on 0.5 g of catalyst. [b] Turnover frequency (ethylene (molybdenum cations)$^{-1}$ s^{-1}), assuming all Mo cation participate in the metathesis reaction of propene (20–30 Torr).

methathesis activity. In fact, Xu et al. reported that SnR_4 (R = Me, Et, and Bu) reduces the Re species on γ-Al_2O_3 at room temperature.[10] To verify such a possibility, we treated MoO_3/SnO_2 with $SnEt_4$ at room temperature. During the treatment, decomposition of $SnEt_4$ occurred and small amounts of ethylene and ethane were formed. However, the surface did not show activity for the metathesis of propene at all. Consequently, an effect of Sn derived from $SnMe_4$ as well as of reduction of Mo species can be neglected for the metathesis activity generation by $SnMe_4$, and it is concluded that grafting of CH_2 species is the reason for the metathesis activity on MoO_3/SnO_2–$SnMe_4$. It is noted that reduction of Mo species on MoO_3/SnO_2 was not made clear by Mo 3d XPS spectra, which may be due to the amount of reduced Mo species.

Molybdenum trioxide supported on SnO_2 reduced with H_2 or CO at 500 °C and then reoxidized with a 1:1 mixture of N_2O and H_2 at 200 °C was inactive for propene metathesis even after $SnMe_4$ treatment. This was an unexpected result, because metathesis activities on partially reduced MoO_{3-x} supported on TiO_2, SiO_2, Al_2O_3, and ZrO_2 were drastically enhanced.[7] It is significant to point out that SnO_2 as well as MoO_3 support was reduced on MoO_3/SnO_2 with H_2 or CO at 500 °C, which was ascertained by the amount of H_2O or CO_2 formed in the reduction. It is pointed out that SnO_2 is an easily reducible oxide and is completely reduced to SnO above 260 °C,[11] and it is reported that reduction of SnO_2 to metallic Sn occurs on Rh/SnO_2 by hydrogen spillover.[12] Accordingly, hereafter partially reduced and fully reduced catalyst are denoted as MoO_{3-x}/SnO_{2-y} and MoO_x/SnO_{2-y}, respectively. To verify why activation of MoO_{3-x}/SnO_{2-y} and MoO_x/SnO_{2-y} was unsuccessful, we compared products formed in the decomposition of $SnMe_4$ on these surfaces with reduced SnO_{2-y}. As shown in Table III, 5×10^{-4} Torr of methane formed on MoO_x/SnO_{2-y} (0.5 g of catalyst for 30 min of reaction with $SnMe_4$), and 7×10^{-4} Torr of methane formed on MoO_{3-x}/SnO_{2-y}, which were quite similar to results for SnO_{2-y} following the same treatments. It is also an important result that no formation of ethane and ethylene was observed on SnO_{2-y}-supported MoO_{3-x} and MoO_x catalysts. These results imply that the surface is covered with reduced SnO_2 if MoO_3/SnO_2 is reduced with H_2 or CO, and no Mo species seems to be present on the surface.

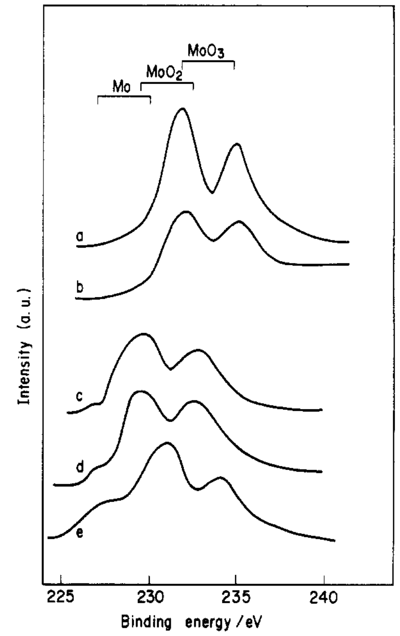

Figure 1. Mo 3d spectra of MoO_3/SnO_2 (a), MoO_x/SnO_{2-y} (c), and following Ar^+ ion sputtering for 0.5 min on a (b), for 0.5 min (d) and 370 min on c (e).

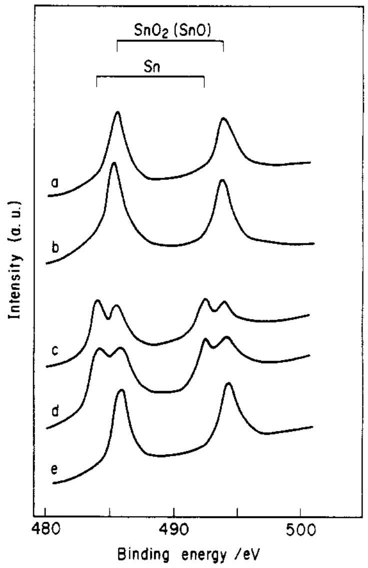

Figure 2. Sn 3d spectra of MoO_3/SnO_2 and MoO_x/SnO_{2-y}. Notations are the same as in Figure 1.

For elucidation of whether or not Mo species are present on the surface, (a) hydrogenation of 1,3-butadiene, (b) hydrogen-exchange reaction between 1,3-butadiene-d_0 and -d_6, (c) isomerization of 1-butene, and (d) hydrogen-exchange reaction between propene-d_0 and -d_6 were studied on MoO_x/SnO_{2-y}. It is reported that these reactions proceed quite rapidly on a fully reduced MoO_x/TiO_2 catalyst at room temperature.[13] As Mo species are reduced (Figure 1c, mentioned later), these reactions should proceed as long as Mo species are present on the surface. However, these reactions did not take place at all. Consequently we would like to interpret that no metathesis activity on $SnMe_4$ treated MoO_x/SnO_{2-y} and MoO_{3-x}/SnO_{2-y} is attributed to such migration of Mo species from the surface to the bulk of reduced SnO_2.

X-ray photoelectron spectra of Mo 3d and Sn 3d regions were studied on fully oxidized MoO_3/SnO_2 and fully reduced MoO_x/SnO_{2-y}. As shown in Figure 1a, Mo 3d doublets ($3d_{5/2,3/2}$) of Mo^{6+} are observed at 232.0 and 235.4 eV on MoO_3/SnO_2. After Ar^+ ion bombardment for 0.5 min, the intensity of these bands decreased and Mo^{5+} species were partially produced (Figure 1b). Tin 3d spectra of corresponding samples are shown in Figure 2, parts a and b, in which Sn 3d doublets ($3d_{5/2,3/2}$) were observed at 485.7 and 494.0 eV. Binding energy values of the Sn 3d doublet observed here are close to those reported on SnO_2, in which the O 1s peak was detected at 530.1 eV.[14] However, BE values of Sn^{4+} and Sn^{2+} are so close that it is crucial to classify these two

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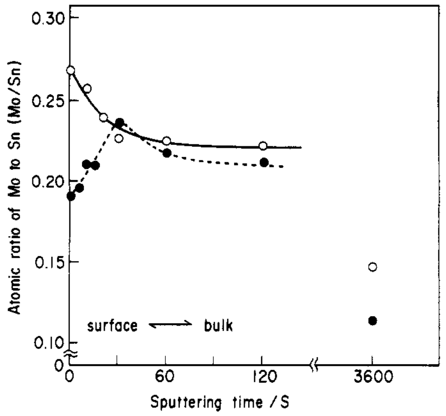

Figure 3. Depth profiles with respect to Mo/Sn atomic ratios on MoO_3/SnO_2 (○) and MoO_x/SnO_{2-y} (●). Sputtering conditions are 2-kV acceleration voltage and room temperature.

species.[15] Two sets of 3d doublets were newly observed at 229.5 and 232.7 eV and at 227.1 and 230.3 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively (Figure 1c). These BE values correspond to those reported on MoO_2 and metallic Mo.[16] After Ar^+ ion sputtering for 0.5 min, the intensity of these Mo species did not change appreciably (Figure 1d). Corresponding Sn 3d spectra are shown in Figure 2, parts c and d. The peaks at 484.5 and 491.6 eV newly appeared in addition to the Sn 3d doublet for Sn^{4+} (Sn^{2+}). These BE values of newly appearing peaks are almost the same as reported for Sn^0.[14,17] After Ar^+ sputtering for 370 min, Mo^{6+} (Figure 1e) and Sn^{4+} species (Figure 2e) were detected definitely. These results clearly indicate that SnO_2 is reduced on the surface and Mo species migrate into the bulk of SnO_{2-y} in MoO_x/SnO_{2-y}.

In Figure 3, depth profiles of MoO_3/SnO_2 and MoO_x/SnO_{2-y} are shown. Here the atomic ratio of Mo/Sn should have rigid information concerning chemical composition if a plate sample was used. However, the powder materials are used in our experiments so that the atomic ratios of Mo/Sn in bulk have less quantitative sense than that on the surface in Figure 3. The atomic ratio of Mo/Sn decreased sharply from the surface to bulk of MoO_3/SnO_2; however, the ratio of MoO_x/SnO_{2-y} was lower than on MoO_3/SnO_2 at the surface, reached a maximum, and then decreased. From this result it can be concluded that migration of Mo species occurs when support SnO_2 is reduced on MoO_x/SnO_{2-y}.

Migration of Pt-group metals into reduced oxide support, which is often mentioned in terms of encapsulation,[18] has been studied in relation to strong metal–support interaction (SMSI).[19] The same behavior was observed in MoO_x/SnO_{2-y}; however, it should be emphasized that migration of reduced Mo cations occurs in our system. It is an established behavior in an encapsulation system that metal atoms show the usual behavior after being reoxidized at 500 °C. Accordingly, MoO_x/SnO_{2-y} was reoxidized at 500 °C for 1 h and then was supplied to the treatment with $SnMe_4$ at room temperature. Interestingly, methane, ethane, and ethylene were formed in almost the same amount as fresh MoO_3/SnO_2 during the $SnMe_4$ treatment as shown in Table III, and the surface showed a catalytic propene metathesis activity with a turnover frequency of 2.2×10^{-5} at room temperature.

In conclusion, (a) MoO_3/SnO_2, for which the conventional reduction procedure cannot be applied due to encapsulation by reduced SnO_2, is activated by treating the surface with $SnMe_4$ at room temperature, and (b) the treatment with $SnMe_4$ is essential not to reduce the surface mildly but to graft CH_2 species, which can participate in catalytic olefin metathesis cycle.

Registry No. MoO_3, 1313-27-5; SnO_2, 18282-10-5; $SnMe_4$, 594-27-4; propene, 115-07-1; 1-butene, 106-98-9; 1,3-butadiene, 106-99-0.

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