SYNTHESIS OF ACTIVE SITES FOR ALKENE METATHESIS REACTION ON MOLYBDENUM OXIDE FILMS BY THE REACTION WITH ALKYLIDENE RADICALS

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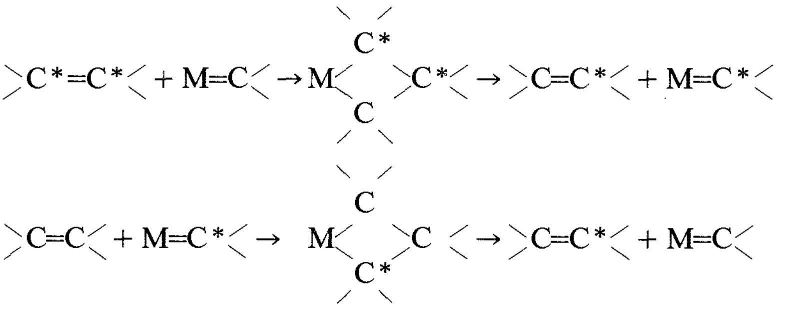
A super active catalyst (T.F. = 0.2 ~ 0.3) for alkene metathesis reaction was prepared by coordinating CH_2 radicals onto sublimed molybdenum oxide films, where the radicals were prepared by the reaction of CH_2I_2 with Al or Mg metals deposited near the oxide film.

So far, alkene metathesis reaction, $>C{=}C< + >C^*{=}C^*< \rightarrow 2>C{=}C^*<$, in homogeneous catalysis has been described by metal alkylidene and metallacyclobutane mechanism such as shown below.



$$>C^*{=}C^*< + M{=}C< \rightarrow M\underset{C}{\overset{C^*}{<}}\;>C^*< \rightarrow >C{=}C^*< + M{=}C^*<$$

$$>C{=}C< + M{=}C^*< \rightarrow M\underset{C^*}{\overset{C}{<}}\;>C< \rightarrow >C{=}C^*< + M{=}C<$$

If the alkene metathesis reaction on heterogeneous catalyst is caused by the same mechanism, alkylidene species should be produced in the initial stage of the reaction when the catalyst surface contacts the alkenes. Accordingly, if the surface is defective in the ability to form alkylidenes from alkene, no metathesis reaction will be promoted on it. The formation of alkylidene species from alkenes, however, is still a matter of debate not only in heterogeneous catalysis but also in homogeneous catalysis.

In this brief paper, we intended to synthesize the active sites on catalytically less active molybdenum oxide films by furnishing alkylidene species. The molybdenum oxide films were sublimed on a Pyrex glass tube wall of an UHV system by flashing molybdenum wire in a small amount of oxygen. The oxide

Table 1
Catalytic activities of MoO_x films after various treatments

Activation treatment [a]	T.F. (s^{-1}) [f]	Activity for alkene isomerization [h]
(1) No treatment	2×10^{-4}	–
(2) Evaporation of Al (or Mg) aside	1×10^{-2} [g] (2.5×10^{-3}) [g]	– (+ [i])
(3) CH_2I_2/Al treatment	0.3	–
(4) CH_2I_2/Mg treatment	0.2	–
(5) CH_2I_2 treatment (without Al and Mg)	2×10^{-4}	–
(6) CH_3I/Al treatment	3×10^{-2}	–
(7) CH_3I/Mg treatment	6×10^{-3}	–
(8) $Sn(CH_3)_4$ treatment [b]	9×10^{-4}	–
(9) Treatment with hydrogen atoms at liq. N_2 temperature [c]	3×10^{-3}	+
(10) Treatment with alkene and hydrogen atoms at liq. N_2 temperature [c]	0.6	+ [j]
(11) O_2 [d] (or N_2O [e]) treatment following (3)	0.2 (0.5)	–

[a] Every film was sintered at 450 ° C before the activation treatment.

[b] Treatment with 1 Torr of He containing 2% of $Sn(CH_3)_4$ at room temperature.

[c] The films were reduced with hydrogen atoms in advance to prevent H_2O production during these treatments [2].

[d] 0.01 Torr, 1 min.

[e] 1 Torr, 10 min.

[f] Turnover frequencies of the propylene metathesis reaction per surface Mo atom. (Initial propylene pressure: 3 Torr, r.t.).

[g] The slight activations were probably caused from reduction of oxide films by a small amount of metal vapor deposited on the films.

[h] Double bond isomerization of n-butene.

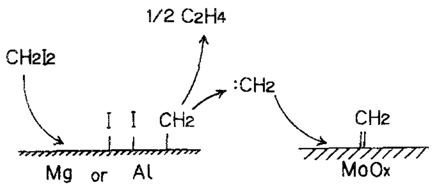
[i] The value of cis/trans ~ 4 in the isomerization of but-1-ene suggests that this activity is caused from MgO.

[j] Activity for hydrogen scrambling was also confirmed with 1 : 1 mixture of C_2H_4 and C_2D_4.

films prepared by this way were inactive for the metathesis reaction as well as for the double bond isomerization reaction of alkenes as shown in table 1 (run 1). If the low activity of the molybdenum oxide films for the alkene metathesis reaction derives from the inability to form alkylidene species from alkene, the oxide films could be activated by furnishing alkylidene species onto the surface.

Based on this concept, we tried to synthesize the active sites for alkene metathesis reaction by grafting methylidene radicals onto the molybdenum oxide films (scheme 1). Methylidene radicals were produced by the reaction of CH_2I_2 with Al or Mg metal film deposited near the oxide film, because the CH_2 radicals are evolved in gas phase when CH_2I_2 condensed on an aluminum plate at liquid nitrogen temperature was warmed to 170 K [1].

A molybdenum oxide film sublimed on a Pyrex glass tube wall was sintered in vacuum at 450 ° C. After that, Al or Mg metal was vaporized on a different part



Scheme 1. Grafting of alkylidene.

of the glass tube being apart from the molybdenum oxide film (see scheme 1). It was confirmed that the molybdenum oxide film was not appreciably activated by vaporizing Al or Mg metal (table 1, run 2). However, if 1 Torr of He containing 1.5–2.0 percent of CH_2I_2 was contacted for 30 minutes at room temperature, the oxide film changed to a very active catalyst for the metathesis reaction as shown in fig. 1 and table 1 (run 3 and 4). It is worthy of note that the oxide films activated by CH_2 radicals are not active for the isomerization and for the hydrogen scrambling reactions of alkenes.

As was reported in our preceding paper, the molybdenum oxide films activated by the reaction of adsorbed alkene with atomic hydrogen at liquid nitrogen temperature catalyzed both the metathesis reaction and the isomerization reaction of alkenes (table 1, run 10). If the surface was treated with a trace amount of oxygen or nitrous oxide at room temperature, however, the activity for the isomerization reaction was selectively diminished as shown in table 1 (run 11). From this fact we speculate that the hydrogen atoms trapped on the molybdenum oxide film in a form of monohydride site [3] are responsible for the activity for the isomerization reaction. In fact, the thermal desorption experiments proved that the amount of desorbed hydrogen decreased to a quarter of its original value when the oxide surface was treated with O_2.

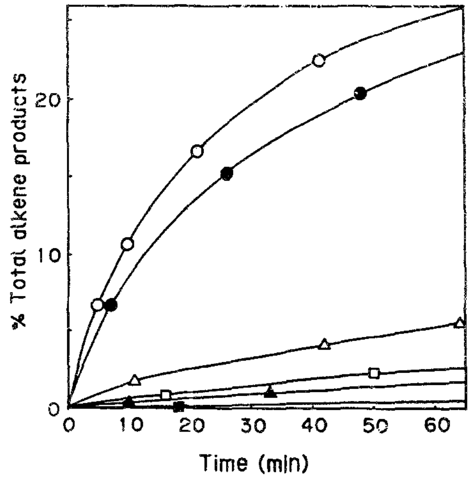


Fig. 1. Propene metathesis reaction at room temperature (initial propene pressure, 3 Torr) on various MoO_x films; ○ treated with CH_2I_2/Al; ● treated with CH_2I_2/Mg; △ treated with CH_3I/Al; ▲ treated with CH_3I/Mg; □ with Al aside; ■ with Mg aside

As proved in our previous paper [2], the molybdenum oxide treated with hydrogen atoms without adsorbed alkenes showed no activity for the alkene metathesis reaction (table 1, run 9).

From these results, we can speculate that the isomerization reaction proceeds via alkyl intermediates but these alkyls do not convert to alkylidene intermediates for the alkene metathesis reaction.

To confirm this speculation, we adopted a reaction of CH_3I with Al or Mg metals as a source of CH_3 radicals. Recently the adsorption and/or reaction of alkyl halides on aluminium and magnesium metals were studied in relation to the Grignard reagent, and it was found that the adsorption of CH_3I on clean Al(111) surface is dissociative at 150 K, but CH_3Cl and CH_3Br are inactive on the surface [4]. Contrary to this, CH_3Br undergoes dissociation on Mg(0001) surface at 123 K, but no alkyl adsorption was observed on the surface [5].

Some He gas containing CH_3I was introduced into the reactor where Al or Mg metal had been vaporized near the molybdenum oxide film [6]. As shown in fig. 1 and in table 1 (run 6 and 7), neither the metathesis activity nor the isomerization activity was enhanced by this treatment [7]. From these results we could conclude that methyls furnished onto the molybdenum oxide do not convert into methylidenes on the molybdenum oxide surface. It might be also an interesting fact that the molybdenum oxide film was not activated by $Sn(CH_3)_4$ (table 1, run 8) although it is quite effective for the activation of supported molybdenum oxides [8].

From these result, we concluded that the formation of alkylidene species from adsorbed alkenes is realized only on some specific sites on the surface of molybdenum oxide, but alkylidene radicals coordinate to the molybdenum ions on the surface to yield active sites. As a result, we succeeded in developing a superactive alkene metathesis catalyst by synthesizing active sites on inactive molybdenum oxide films.

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References and notes

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[6] Generation of ethane was observed on CH_3I/Mg, but not on CH_3I/Al, that is, Mg is preferable to Al for the formation of CH_3 radical.

[7] A slight activation after the treatment with CH_3I in fig. 1 and table 1 is comparable to the activation observed on the blank test by Al or Mg metal deposition (run 2).

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