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Synthesis of Active Sites for Alkene Metathesis Reaction on Molybdenum and Tungsten Oxide Films

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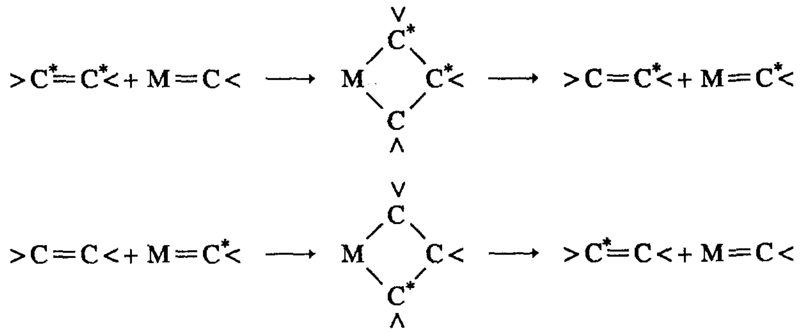
Two methods were developed for the synthesis of active sites for the alkene metathesis reaction on sublimed oxide films (MoO_x and WO_x). One method involves the reaction of the oxide films with alkyl radicals which are themselves produced by reacting condensed alkenes on the films at liquid nitrogen temperature with atomic hydrogen. The other method is the reaction of the oxide films with CH_2 radicals which are produced by the reaction of CH_2I_2 on Al or Mg metals. Both methods were effective for activation of the MoO_x films, yielding catalysts with turnover frequencies as large as 0.6 s^{-1} (3 Torr propene at room temperature). However, the first method was less effective for the activation of WO_x film. The isomerization and the hydrogen scrambling reactions of alkenes were also studied.

INTRODUCTION

A mechanism involving metal alkylidene and metallacyclobutane, such as shown in the following scheme, is generally accepted in the homogeneous alkene metathesis reaction, $\rangle C^*{=}C^*\langle \; + \; \rangle C{=}C\langle \; \rightarrow \; \rangle {}^*C{=}C\langle \; + \; \rangle C{=}C^*\langle$ (*1*).



If the alkene metathesis reaction on heterogeneous catalysts follows a comparable mechanism, then alkylidene species which are the key intermediates should be produced from alkenes on the surface in the initial stage of the reaction. This initiation process is, however, still a matter of debate. Since the activity of a catalyst depends in general on the number of active sites, the number of alkylidene sites produced by reaction with alkenes determines the activity of the traditional catalyst.

The role of supporting oxides is also an interesting problem which should be solved, because the activity of MoO_x for the metathesis reaction depends strongly on the support (*2*).

In this paper, we propose a new idea of

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synthesis of active sites, in which the sublimed oxide films were subjected to the reaction with alkyl or alkylidene radicals. By means of this newly developed method, new, extraordinarily active catalysts for alkene metathesis reaction were prepared.

EXPERIMENTAL

The apparatus used in our experiment is shown in Fig. 1. The volume of a Pyrex glass reactor was about 1000 ml and a base pressure of 10^{-8}–10^{-9} Torr was achieved. The oxide film (MoO_x or WO_x, $x \simeq 3$) was sublimed on the Pyrex reactor wall by flashing a Mo or a W filament (99.95%) in 0.2 Torr of oxygen (99.99%). The thickness of the film was estimated to be about 50 monolayers. After the sublimation of the oxide film, the wall was annealed at 450°C for 30 min *in vacuo,* and then the oxide film was subjected to the synthesis of active sites by the following two methods.

Formation of Active Sites on Oxide Films by Reacting Alkene with Atomic Hydrogen

The oxide film sublimated on the glass wall was partially reduced by treatment with atomic hydrogen at liquid N_2 temperature. That is, the glass tube with the oxide film was dipped in liquid nitrogen and was treated with atomic hydrogen for 5 min by flashing a Mo or a W filament in 0.3 Torr of hydrogen which had been purified by passage through a Palladium thimble. This treatment is denoted hereafter as "atomic H-treatment." The oxide film was then evacuated for 30 min at 450°C after atomic H-treatment. At this stage we call it a "pre-reduced" film.

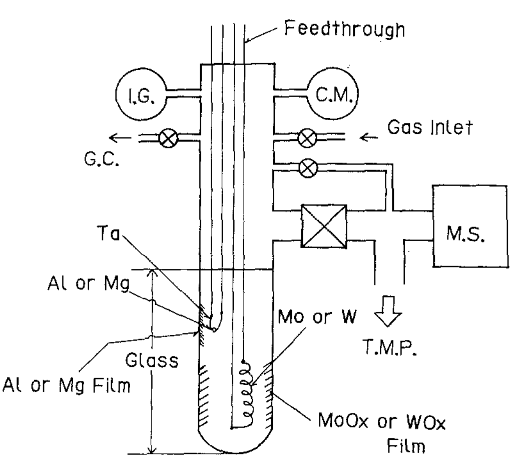


FIG. 1. Deposition and reaction chamber.

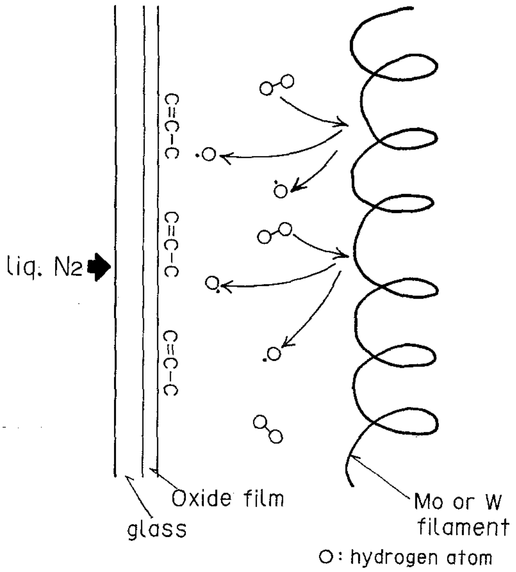


FIG. 2. Reaction of alkene with atomic hydrogen at liquid N_2 temperature.

After the pre-reduction, 0.01 Torr of alkene (ca. 10^3 ml) was condensed on the oxide film by dipping in liquid nitrogen, and then the oxide film with condensed alkene was treated with atomic hydrogen for 3 min (Fig. 2). After the treatment with H atoms, the reactor was evacuated at room temperature for 10 min. Ethene (99.9%), propene (99.8%), *cis*-2-butene, *trans*-2-butene, and isobutene (99.0%) were adopted as the condensed alkene on the MoO_x film, but the activation of WO_x films was performed only by propene.

Synthesis of Active Sites on Oxide Films by Using CH_2 Radicals

Al (99.99%) or Mg (99.9%) metal was vaporized onto the glass wall adjacent to the oxide film by heating the metal with a Ta

TABLE 1

Activities of the Oxide Films after Various Treatments

Activation treatment	N^a (s^{-1}) for alkene metathesis		Activity for isomerization[b]
	MoO_x	WO_x	
(A) No treatment	2×10^{-4}	1.7×10^{-4}	–
(B) "Pre-reduction"	3×10^{-3}	2.4×10^{-4}	–
(C) Reaction of alkene with atomic H at liquid N_2 temp			
(i) Propene as alkene	6×10^{-1}	8×10^{-4}	+
(ii) Ethene as alkene	5×10^{-1}		+
(D) O_2 treatment[c] after (C)	2×10^{-1}		–
N_2O treatment[d] after (C)	5×10^{-1}		–
(E) Atomic H-treatment	3×10^{-3}		+
(F) Evaporation of Al	1×10^{-2}	1.8×10^{-3}	–
Evaporation of Mg	2.5×10^{-3}		+[e]
(G) CH_2I_2/Al treatment	3×10^{-1}	2.6×10^{-2}	–
CH_2I_2/Mg treatment	2×10^{-1}		–
(H) CH_2I_2 treatment (without Al and Mg)	2×10^{-4}	3×10^{-5}	–
(I) CH_3I/Al treatment	3×10^{-2}		–
CH_3I/Mg treatment	6×10^{-3}		–
(J) $Sn(CH_3)_4$ treatment	9×10^{-4}		–

[a] Turnover frequencies per surface Mo or W atom. Initial propene pressure, 3 Torr; reaction temp, rt

[b] Double bond isomerization of *n*-butene measured on the MoO_x films. +, Active; –, inactive.

[c] 0.01 Torr for 1 min at rt.

[d] 1 Torr for 10 min at rt.

[e] A *cis*/*trans* ≈4 in the isomerization of but-1-ene suggests that this activity is caused by MgO.

wire (Fig. 1). Then, 1 Torr of He containing 1.5–2.0% of CH_2I_2 was introduced in the reactor at room temperature and maintained for 30 min. The reactor was then evacuated for 10 min at that temperature.

The CH_2I_2 (GR, Kanto Chem.) was purified by several freeze–pump–thaw cycles and was mixed with He purified through 3-Å molecular sieves at liquid nitrogen temperature.

The catalytic activity of the oxide films for alkene metathesis reaction was evaluated by the formation of ethene and butene when 3 Torr of propene was added at room temperature. That is, the metathesis reaction of propene yielded ethene and but-2-ene, which were quantitatively analyzed by a quadrupole mass spectrometer and a gas chromatograph. The double bond isomerization reaction of but-1-ene and the hydrogen scrambling reaction of C_2H_4 and C_2D_4 were also carried out on the MoO_x films at room temperature.

RESULTS AND DISCUSSION

Synthesis of Active Sites for Metathesis Reaction on MoO_x Film by Reaction of Alkene with Atomic Hydrogen at Liquid N_2 Temperature

We found that the reaction of condensed alkenes with atomic hydrogen on MoO_x film yields a highly active alkene metathesis catalyst (*3*). The alkenes used for the activation of MoO_x films (see Experimental) were almost equally effective for the activation of the MoO_x film. In Table 1-C and Fig. 3 the surfaces activated using ethene and propene are compared. It can be seen that the activity of MoO_x films was about 200 times that of the pre-reduced MoO_x film. In the

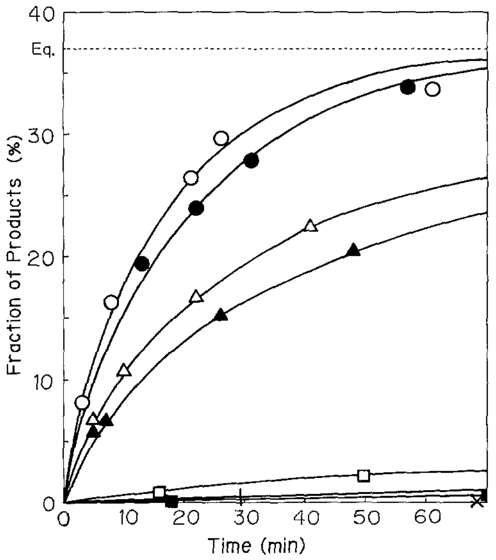


FIG. 3. Propene metathesis reaction at room temperature (initial propene pressure, 3 Torr) on various MoO_x films. ○, Treated with propene and atomic H at liquid N_2 temperature; ●, treated with ethene and atomic H at liquid N_2 temperature; △, treated with CH_2I_2/Al; ▲, treated with CH_2I_2/Mg; □, with adjacent Al; ■, with adjacent Mg; +, "pre-reduced"; ×, with no treatment.

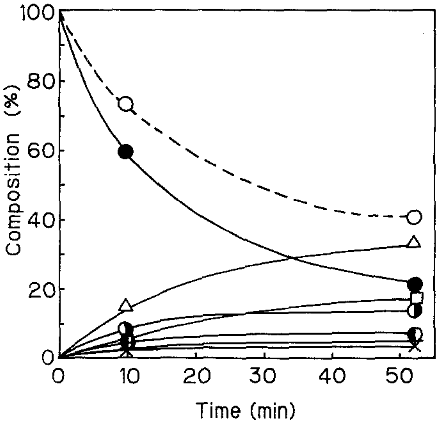


FIG. 4. Reaction of alkene at room temperature (initial, 3 Torr of but-1-ene) on MoO$_x$ film treated with propene and atomic hydrogen at liquid N_2 temp. ○, Total butene; ●, but-1-ene; ◑, *trans*-but-2-ene; ◐, *cis*-but-2-ene; △, propene; □, pentene; +, hexene; ×, ethene.

case of the MoO$_x$ film activated with propene, the turnover frequency (N = number of C_3H_6 molecules converted/Mo atom · second), evaluated by assuming that all the Mo atoms deposited on the glass contribute, is 0.01 s^{-1}. If only the surface Mo atoms are assumed to be effective, N is estimated to be 0.6 s^{-1} (Table 1-C-i). Consequently, our catalyst is about 100 times more active than a catalyst prepared by anchoring Mo(π–C_3H_5)$_4$ with acidic OH groups on Al_2O_3 (5.0×10^{-3} s^{-1}) (*4*) and about 60 times more active than one of the most active MoO$_x$/Al_2O_3 catalysts obtained by treatment with Sn$(CH_3)_4$ (1×10^{-2} s^{-1}) (*2*). Kazansky and co-workers prepared a very active catalyst (N = 0.42 s^{-1}) by photoreduction of MoO_3–SiO_2 in CO (*5*). Our catalyst (N = 0.01–0.6) is comparable to this catalyst in activity. If we repeat the condensation of alkene and the reaction with atomic hydrogen on the same oxide film at liquid N_2 temperature, we obtain even more active catalysts.

The MoO$_x$ films activated by alkene and atomic hydrogen were very active also for the isomerization (double bond migration) and hydrogen scrambling reaction of alkenes (Figs. 4 and 5a). However, these catalytic activities are selectively diminished by treatment with a trace amount of oxygen or nitrous oxide (N_2O) at room temperature, as shown in Table 1-D and Figs. 6 and

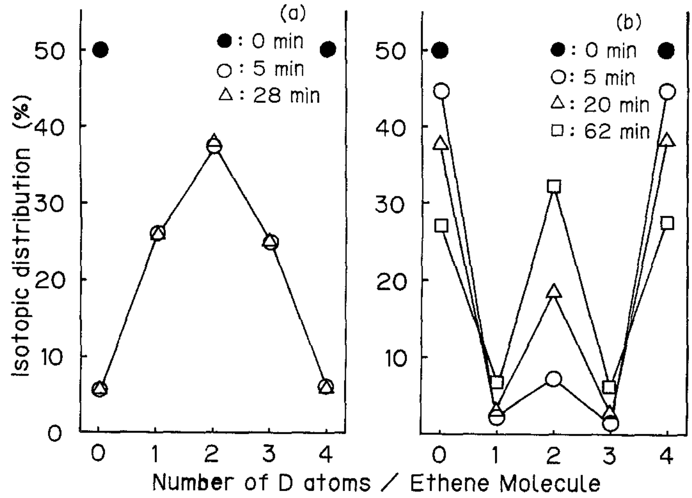


FIG. 5. Effect of O_2 treatment on hydrogen scrambling reaction of ethene (rt, total ethene pressure: 1 Torr) on MoO$_x$ film treated with propene and atomic hydrogen; the reaction on the film before (a) and after (b) O_2 treatment (0.01 Torr, 1 min, room temperature).

5b. This fact suggests that the alkyl intermediates for these reactions are formed by reacting alkenes with hydrogen atoms remaining on the surface (Scheme 1), but they will be removed by the reaction with O_2 or N_2O. In fact, the amount of hydrogen desorbed by heating up to 450°C decreased by $\frac{3}{4}$ after the treatment with O_2. It was confirmed that the treatment of the MoO_x film only with hydrogen atoms, i.e., without condensed alkenes, did not increase activity for the metathesis reaction, although the activity for the isomerization reaction was markedly enhanced (Fig. 7 and Table 1-E—compare with Table 1-B). It is noteworthy that the alkyl intermediates for the isomerization do not convert into the alkylidene intermediates for the alkene metathesis reaction. When we used a Ta filament for the dissociation of H_2, we observed the same promoting effects on the isomerization and the isotope scrambling of alkenes. Thus, we can exclude the possibility of catalysis by Mo metal evaporated on the oxide films.

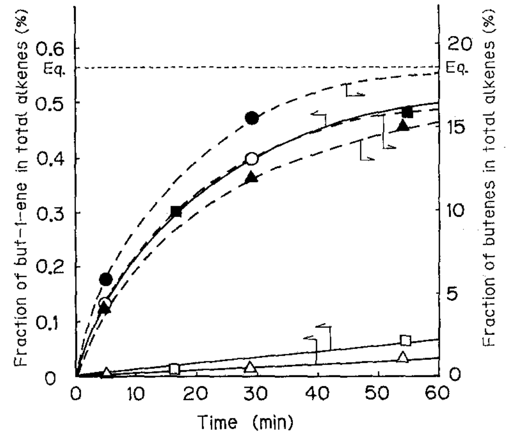
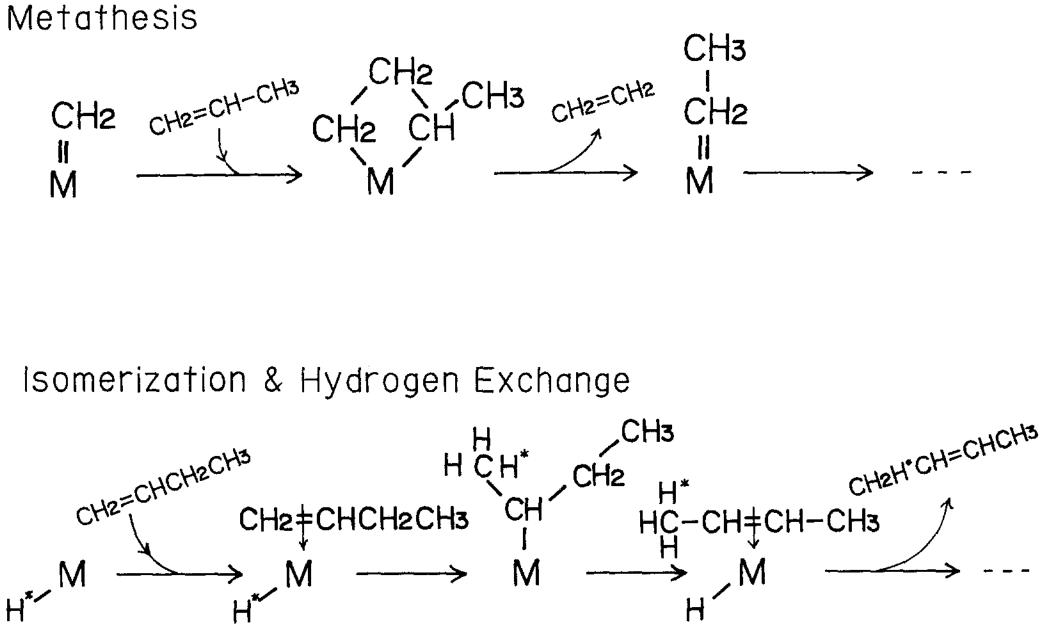


FIG. 6. Effect of O_2 or N_2O treatment on the metathesis and isomerization reactions of alkene on MoO_x films at room temperature (initial, 3 Torr of propene); production of butene on the film treated with propene and atomic hydrogen without additional treatment (○, ●), after O_2 treatment (△, ▲), after N_2O treatment (□, ■). The production of total butenes (solid symbols and dashed lines) shows the activity for the propene metathesis reaction, and the production of 1-butene (open symbols and solid lines) shows that for the double bond isomerization of the butenes.



SCHEME 1

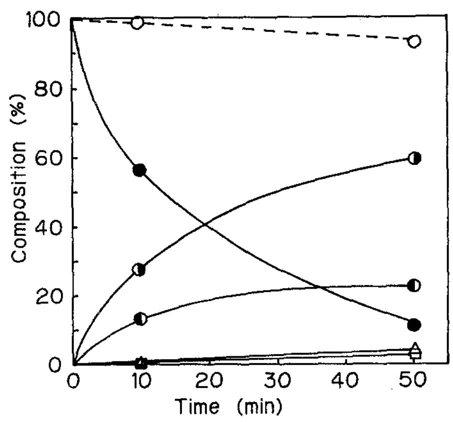


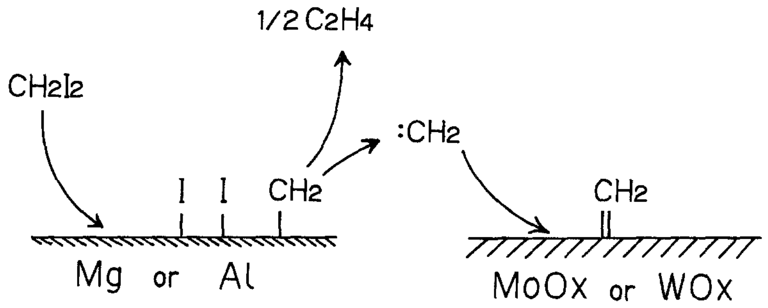
FIG. 7. Reaction of alkene at room temperature on MoO_x film treated with atomic hydrogen at liquid N_2 temperature. ○, Total butene; ●, but-1-ene; ◑, *trans*-but-2-ene; ◐, *cis*-but-2-ene; △, propene; □, pentene; (initial, 3 Torr of but-1-ene).

Synthesis of Active Sites for Metathesis Reaction on MoO_x Film by Reaction of CH_2I_2 or CH_3I with Al or Mg (6)

MoO_x film was markedly activated by treatment with CH_2I_2 when Al or Mg was deposited adjacent to the MoO_x film (Table 1-G and Fig. 3). As shown in Table 1-F, the oxide film was slightly activated by the evaporation of Al or Mg metal. It is difficult to comment on the reasons for this behavior at the present time, but the Al and Mg metals evaporated on the oxide film might reduce the oxide films of Mo or W. On the other hand, treatment of the MoO_x films with CH_2I_2 in the absence of Al or Mg caused no activation, as shown in Table 1-H. Consequently, the remarkable activation shown in Table 1-G is caused by the CH_2 radicals which are generated by reacting CH_2I_2 with Al or Mg (Scheme 2). In fact, a CH_2 radical is detected in the gas phase when CH_2I_2 is condensed on a clean Al plate at liquid nitrogen temperature and is warmed to 170 K (7). In our study, CH_2I_2 was also condensed on the deposited Al at liquid nitrogen temperature and was warmed to room temperature. However, the activity of the oxide surface obtained by this activation procedure was the same as that following treatment at room temperature. After the admission of CH_2I_2, ethene was detected in the gas phase. It may be a product of the coupling reaction of CH_2 radicals formed on Al or Mg. It is noteworthy that the oxide films activated by CH_2I_2/Al or Mg show no activity for double bond isomerization or for hydrogen scrambling in alkenes.

In order to detect alkylidenes on molybdenum oxide film by using the IR spectroscopic method, molybdenum oxide was sublimed on a Si wafer and was treated with CH_2I_2 in the presence of aluminum evaporated on the wall of the glass cell, but no CH_2 could be detected.

It should be an interesting question as to whether or not the alkyl species convert to alkylidene intermediates on MoO_x film. The adsorption and/or reaction of alkyl halides on Al and Mg metals has been studied in



SCHEME 2

relation to the Grignard reagent, and CH_3I is known to dissociate on a clean Al(111) surface at 150 K, even though CH_3Cl and CH_3Br do not (*8*). In contrast, CH_3Br produces Br on a Mg(0001) surface at 123 K, but no adsorption of CH_3 was observed on the surface (*9*). Taking account of these facts, CH_3I was reacted with Al or Mg metal vaporized adjacent to the MoO_x film in the same manner as CH_2I_2 reacted with Al or Mg. In the case of CH_3I/Mg, ethane was detected in the gas phase, but in the case of CH_3I/Al no ethane was detected. This fact may indicate that CH_3 radicals are formed on Mg but not on Al. However, no appreciable activation of the MoO_x film for the metathesis reaction was observed for either Al or Mg. It is also an interesting fact that the treatment with CH_3I does not enhance the activity for the alkene isomerization reaction (Table 1I). From these results we can conclude that the CH_3 radicals furnished from CH_3I produce neither active $Mo{=}CH_2$ sites for the metathesis reaction nor Mo—H sites for the isomerization reaction on MoO_x, although the alkyl radicals formed by reaction of condensed alkenes with atomic hydrogen undergo the synthesis of the active sites for metathesis reaction.

Therefore, the activation mechanism of the MoO_x film by reaction of condensed alkenes with atomic hydrogen at liquid N_2 temperature can be explained by the following reactions:

$$CH_3{-}\dot{C}H_2 + CH_3{-}\dot{C}H_2 \rightarrow Mo{=}CH{-}CH_3 + CH_3{-}CH_3 \quad (1)$$

$$CH_3{-}\dot{C}H_2 + H\cdot \rightarrow Mo{=}CH{-}CH_3 + H_2 \quad (2)$$

Since the activities for the metathesis reaction of MoO_x supported on Al_2O_3, SiO_2, and TiO_2 are markedly enhanced by treatment with $Sn(CH_3)_4$ (*10*), we also exposed the MoO_x film to $Sn(CH_3)_4$ (1 Torr of He containing 2% of $Sn(CH_3)_4$ for 30 min at room temperature). As shown in Table 1J, this treatment did not activate the oxide film. This result suggests that the support oxides may play important roles in the decomposition of $Sn(CH_3)_4$ and/or the formation of CH_2 species by reaction with $Sn(CH_3)_4$.

Activation of WO_x Film by Reaction of Alkene with Atomic Hydrogen or by a Reaction of CH_2I_2 with Al

The two activation reactions were performed on WO_x film: the reaction of condensed alkenes with atomic hydrogen at liquid nitrogen temperature, and the reaction of CH_2I_2 with evaporated Al metal. The results are summarized in Table 1 and Fig. 8. These two reactions markedly activate the MoO_x film as discussed above, but are less efficient for the activation of WO_x film. It was found that the reaction of CH_2I_2 with Al activates the WoO_x film more efficiently than the reaction of propene with atomic hydrogen on the WO_x film. This is opposite from the behavior of the MoO_x film. This fact suggests that the appropriate methods for the synthesis of active alkylidene sites depend on the kind of oxide.

The temperature dependence of the propene metathesis reaction was measured at 100°C and at room temperature on the MoO_x and WO_x films activated by treatment

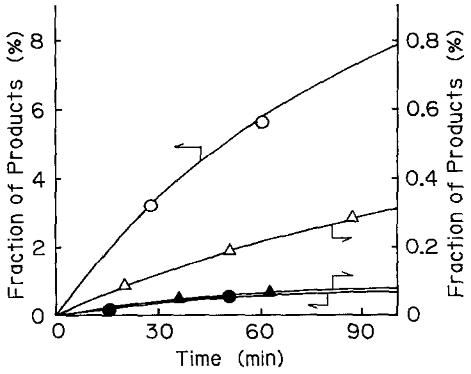
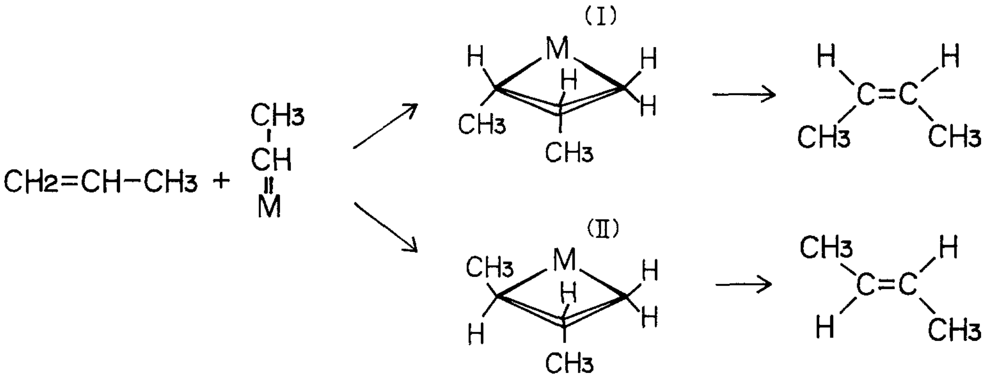


FIG. 8. Propene metathesis reaction at room temperature (initial propene pressure, 3 Torr) on various WO_x films. ○, Treated with CH_2I_2/Al; ●, with adjacent Al; △, treated with propene and atomic H at liquid N_2 temperature; ▲, "pre-reduced."



SCHEME 3

with CH_2I_2/Al. When the reaction temperature was raised from room temperature to 100°C, the reaction rate on the WO_x film increased five times, but that on the MoO_x film did not change appreciably. The temperature dependence of the reaction rate on the WO_x film was reversible; that is, when the temperature was lowered from 100°C to room temperature, the reaction rate decreased to the initial value. This fact suggests that the temperature enhancement is not caused by an increase in the number of active sites at 100°C but is caused by the activation energy of the reaction; that is, the metathesis reaction on the WO_x film has an activation energy higher than that on the MoO_x film.

The *cis*/*trans* ratio of the but-2-ene produced by the propene metathesis reaction on the oxide films activated with CH_2I_2/Al or Mg was about 0.7 at room temperature on both the MoO_x and WO_x films (Fig. 9). The configuration of the metallacyclobutane intermediates (Scheme 3) is responsible for the *cis*/*trans* ratio, and configuration **II** is preferred to **I** (*11*). It is interesting that the *cis*/*trans* ratio was almost the same on the two oxide films, although their activation energies are different. Another noteworthy fact is that the *cis*/*trans* ratio is close to 1, which is larger than that on the supported catalyst (<0.2) (*12*). This fact indicates that the two configurations of metallacyclobutanes (Scheme 3, **I** and **II**) contribute almost equally to the reaction regardless of the activation energy; that is, temperature may not appreciably affect the ratio.

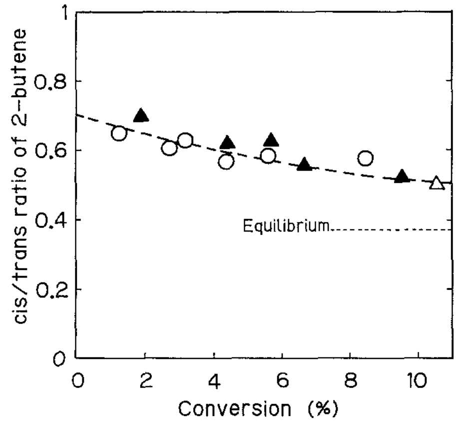


FIG. 9. The *cis*/*trans* ratio of but-2-ene produced by propene metathesis reaction at room temperature. ○, WO_x films treated with CH_2I_2/Al; △, ▲, MoO_x films treated with CH_2I_2/Mg (△) or with CH_2I_2/Mg (▲).

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