Preparation of very Active Molybdenum Oxide Films for Use in the Alkene Metathesis Reaction

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Molybdenum oxide films prepared by sublimation *in vacuo* are converted into super active alkene metathesis catalysts by functionalization of the surface with alkene and atomic hydrogen at liquid nitrogen temperature.

Metal alkylidenes and metallacyclobutanes have been accepted as key intermediates in the alkene metathesis reaction.[1] However the mechanism of the initiation process from alkenes alone is still unsolved in homogeneous as well as in heterogeneous catalysis. The role of supporting oxides in heterogeneous catalysts is also a problem, because the activity of the molybdenum oxide catalyst depends strongly on the support.[2] support.[2]

Taking account of these facts, we attempted to prepare molybdenum oxide films which are active in the alkene metathesis reaction, and now report a specific functionalization procedure for obtaining very active molybdenum oxide films.

Molybdenum oxide (MoOx) films were prepared in a high-vacuum system (10^{-8}—10^{-9} Torr) on a Pyrex glass reactor wall by heating an Mo-filament in 0.2 Torr of oxygen pressure. MoOx ($x \simeq 3$) film sublimed on the glass wall was sintered by heating at 450 °C for 30 min *in vacuo*. The glass tube reactor with the oxide film was then cooled by dipping in liquid nitrogen and was treated with atomic hydrogen for 5 min. The hydrogen atoms were produced by thermal dissociation of hydrogen molecule[5] on a hot Mo-filament at a pressure of 0.3 Torr of hydrogen.[3] After the reduction with atomic hydrogen, the film was evacuated at 450 °C for 30 min. It should be emphasized that this partly reduced molybdenum oxide film was inactive not only for the alkene metathesis reaction (Table 1, entry 2) but also for the alkene isomerization reaction.

This inert oxide film was functionalized using the following procedure. 0.01 Torr of alkene (ethylene, propene, but-1-ene, but-2-ene, and isobutene were tested) was introduced in the

Table 1. Turnover frequencies (T.F.) of the propene metathesis reaction at room temperature on various MoOx catalyts.

Entry	Catalyst	Activation pretreatment	Initial C_3H_6 pressure/ Torr	T.F./s^{-1}	Reference
(1)	Sublimed	No pretreatment	3	0.0006[a]	This work
(2)	MoOx films	Reduction with atomic hydrogen	3	0.003[a]	This work
(3)		Atomic hydrogen treatment at liq. N_2 temperature after reduction	3	0.003[a]	This work
(4)		Functionalization			This work
		with propene	3	0.6[a]	
		with ethylene	3	0.5[a]	
(5)	MoO_3–SiO_2	Photoreduction at 300 K in CO	85	0.42	4
(6)	Mo(η-C_3H_5)-SiO_2	No pretreatment	120	0.09	5

[a] T.F. for a surface Mo atom.

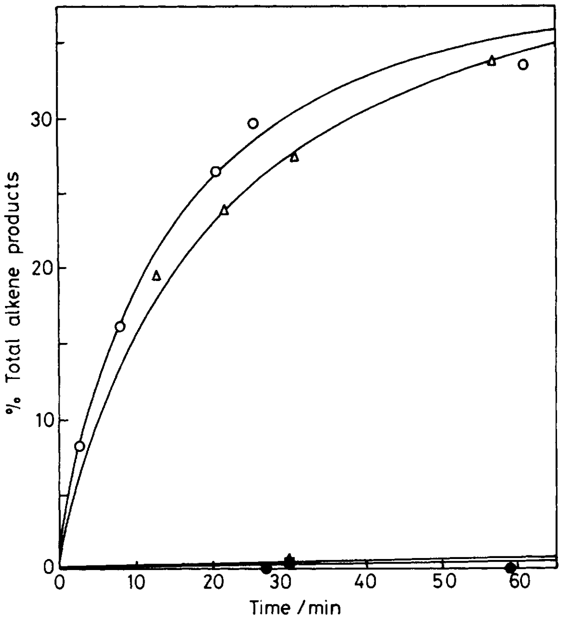

Figure 1. Propene metathesis reaction at room temperature (initial propene pressure, 3 Torr) on various MoOx films; functionalized with propene (○), and ethylene (△) at liquid N_2 temperature, after the reduction with hydrogen atoms; ● unreduced; ▲ reduced; ■ treated with atomic hydrogen at liquid N_2 temperature after the reduction.

reactor (*ca.* 900 ml) and was condensed on the MoOx film by cooling with liquid nitrogen. The film containing alkene was then exposed to atomic hydrogen for 3 min while kept at liquid nitrogen temperature. The liquid nitrogen Dewar was then removed and the gas phase evacuated for 10 min at room temperature.

This functionalization procedure changed the film into a very active catalyst for the alkene metathesis reaction. The catalytic activities of a series of molybdenum oxide films are summarized in Figure 1 and Table 1. The functionalized films were 200 times more active than the films obtained by the simple reduction with hydrogen atoms (Table 1, entries 2, 4). The turnover frequency (number of C_3H_6 molecules converted per one Mo atom per second) of the functionalized films is evaluated to be 0.01 s^{-1} if all the Mo atoms on the reactor wall participate in the reaction, and is 0.6 s^{-1} if only the surface Mo atoms participate in the reaction (Table 1, entry 4). Recently, Kazansky and coworkers prepared a very active catalyst (0.42 s^{-1}) by photoreduction of MoO_3–SiO_2 in CO.[4] Our catalysts might surpass this catalyst for activity. Moreover, further enhancement of the activity was observed by repeating the functionalization of the film surface.

Goddard's criterion suggests that the alkene metathesis reaction requires covalently bonded alkylidene intermediates.[6] Accordingly we speculate that a covalently bonded alkylidene species might be produced at liquid nitrogen temperature by the reaction of alkene with hydrogen atoms on specific sites *via* α-hydrogen elimination from the alkyl groups.

The reduced oxide film treated with atomic hydrogen without preadsorbed alkene at liquid nitrogen temperature was inactive in the alkene metathesis reaction (Table 1, entry 3). It is worthy of note that the isomerization reaction of alkenes is catalysed on this film *via* alkyl intermediates.† This fact indicates that the alkyl intermediates produced on the isomerization sites are not converted into alkylidene species in the alkene metathesis reaction.

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† The functionalized film, as well as the film treated with atomic hydrogen at liquid nitrogen temperature, shows activity in the isomerization reaction, but the isomerization activity of the functionalized oxide film was selectively killed on contact with a trace amount of O_2 or N_2O.