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Mo/Al$_2$O$_3$ Catalysts Prepared via Metal Complex Precursors

1. Synthesis of Catalysts and Their Activity in Propene Metathesis

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Propene metathesis catalysts were obtained by the anchoring of the complexes $MoO_2(C_5H_7O_2)_2$, $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$, and $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ to γ-Al_2O_3, followed by the treatment of the surface metal complexes with H_2 or CO at elevated temperature. The activity of these catalysts was higher than that of those obtained by impregnation and of those prepared using $Mo(C_3H_5)_4$. The activity in propene metathesis of the Mo/Al$_2$O$_3$ catalysts obtained from mono-, bi-, and trinuclear complexes are shown to be practically identical. The catalysts are characterized by a longer lifetime (more than 100 h) at room temperature. © 1993 Academic Press, Inc.

INTRODUCTION

One of the efficient catalytic systems for olefin metathesis is that based on molybdenum. Propene metathesis was in fact discovered over these catalysts (*1*). Nevertheless, later it was found that W- and Re-based heterogeneous catalysts were more active in high- and low-temperature metathesis, respectively (*2, 3*). However, this refers only to catalysts obtained by an impregnation method. Studies on homogeneous systems have shown that all three metals have comparable activities under mild conditions (*4–6*). Moreover, photoreduced silica-supported molybdena catalysts are evidently the most active catalytic system of olefin metathesis (*7*).

Organometallic molybdenum complexes anchored to the surface of an oxide support rank separately among the metathesis catalysts (*8–13*). These catalysts are active even at temperatures below 0°C, but they are quickly deactivated by reaction media; the deactivation is reversible at low temperatures, but at temperatures above 20°C the changes of catalyst activity are irreversible. The synthesis of catalysts via allyl and diene molybdenum complexes requires special equipment, water-free solvents, and an inert atmosphere, which makes the synthesis and investigation of such catalysts difficult.

The present paper is the first in a series on the study of Mo/Al$_2$O$_3$ catalysts prepared by anchoring to the surface of γ-Al$_2$O$_3$ molybdenum complexes with various nuclearities containing Mo^{6+}, Mo^{5+}, and Mo^{4+}. The properties of these catalysts of metal complex origin (MCO) are compared with those of catalysts prepared by a conventional impregnation method (standard catalysts, ST), on the one hand, and with those of catalysts obtained by anchoring the organometallic Mo complexes to the same support (organometallic origin, OMO), on the other hand. The subject of the first paper in this series is the synthesis of the catalysts and their properties in propene metathesis.

EXPERIMENTAL

Preparation of Catalysts

γ-Al$_2$O$_3$ (S_{BET} = 220 m^2/g, pore volume 0.7 cm^3/g, particle size 0.5–0.25 mm) was utilized in the synthesis of catalysts. The support was calcined at 500°C in air for 4 h.

Mononuclear complexes were anchored to a support surface in a way similar to that described in Ref. (*14*), i.e., by treating γ-

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Al_2O_3 for 8 h with a solution of Mo(VI) acetylacetonate, $MoO_2(C_5H_7O_2)_2$, in dry benzene, decanting the excess solution, and washing the catalyst several times with pure solvent. The catalyst was then dried under vacuum at 80°C (catalyst designation $\{Mo_1\}/Al_2O_3$).

$MoO_2(C_5H_7O_2)_2$ was synthesized according to Ref. (*15*) by dissolving $Na_2MoO_4 \cdot 2H_2O$ in HCl followed by addition of acetylacetone and separation of the precipitate formed on a filter.

Binuclear complexes were attached to the surface according to the procedure described in Ref. (*16*) by the treatment of γ-Al_2O_3 with an aqueous solution of Mo(V) oxalate, $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$, for 8 h. The excess of solution was decanted and the catalyst was washed with water followed by drying under vacuum (catalyst designation $\{Mo_2\}/Al_2O_3\}$.

The initial Mo(V) oxalate $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ was synthesized by the treatment of $(NH_4)_7Mo_6O_{24} \cdot 4H_2O$ with a 50% solution of hydrazine–hydrate and dissolution of the precipitate formed in an aqueous solution of oxalic acid. The structure and properties of both solid and water-dissolved complex were studied by EXAFS, NMR, IR, and UV–VIS spectroscopy (*17*).

Trinuclear complexes were anchored to the support surface by treatment of γ-Al_2O_3 for 8 h by an aqueous solution of Mo(IV) oxalate, $(NH_4)_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$, after which the catalyst was washed with water several times and dried in vacuum at 100°C. The catalyst preparation method is described in Ref. (*18*) (catalyst designation $\{Mo_3\}/Al_2O_3$). The starting Mo(IV) oxalate was synthesized according to Ref. (*19*) by electrochemical reduction of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in a solution of oxalic acid, followed by oxidation with air.

$Mo(C_3H_5)_4$ was anchored to γ-Al_2O_3 from a pentane solution for 4 h, washed with pure pentane, and dried under vacuum at 100°C. All the catalyst preparation operations were carried out under dry oxygen-free argon. Before use, the Al_2O_3 was evacuated at 500°C until the pressure was 10^{-3} Torr. The catalyst synthesis is described elsewhere (*13*) (designation {Mo(all)}/Al_2O_3 catalyst). The starting $Mo(C_3H_5)_4$ was synthesized according to Ref. (*20*).

The standard catalysts (MoO_3/Al_2O_3) were prepared by impregnation of γ-Al_2O_3 with an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ for 8 h; the catalysts were then dried under a IR lamp and calcined in air for 4 h at 550°C.

Catalyst Activation and Testing

Prior to reaction all the catalysts (except for {Mo(all)}/Al_2O_3) were treated at elevated temperature in a circulating system in a flow of CO or H_2 (pressure 350 Torr, temperature 300–500°C, duration 1 h). The reaction products were frozen out in a trap cooled with liquid nitrogen. After reduction the catalyst was evacuated at activation temperature until the residual pressure was 10^{-3} Torr.

The activity of the catalysts in propene metathesis was determined in a circulating system of 600 ml vol at 120 Torr pressure in the temperature range 20–200°C. The catalyst loading was 0.01–0.05 g. The reaction products were analyzed by gas chromatography. The catalyst activities were compared according to the initial rate of propene conversion. Polymerization grade pure propene was employed as a reagent.

RESULTS

$\{Mo_1\}/Al_2O_3$ catalysts. Upon treatment of γ-Al_2O_3 with $MoO_2(acac)_2$ benzene solution decolorization of the latter is observed with the support turning yellow. The surface reaction proceeds with elimination of the acetylacetonate ligand as reported previously (*14, 21*). The maximal quantity of molybdenum that can be fixed on this type of γ-Al_2O_3 is ca. 10 wt%, which corresponds to the monolayer coverage.

The initial form of the catalyst shows no activity in propene metathesis. The catalyst activity appears only after treatment with H_2 or CO at 400°C and higher temperatures

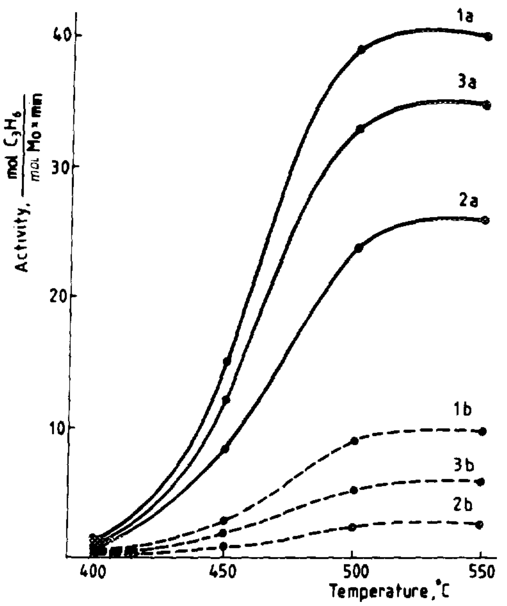

FIG. 1. Dependence of {Mo_1}–{Mo_3} catalyst (5 wt% Mo) activity on the reductive treatment temperature under (a) — CO, (b) --- H_2. The curve number corresponds to the number of Mo atoms in the initial complexes used for catalyst preparation. Reaction temperature is 100°C.

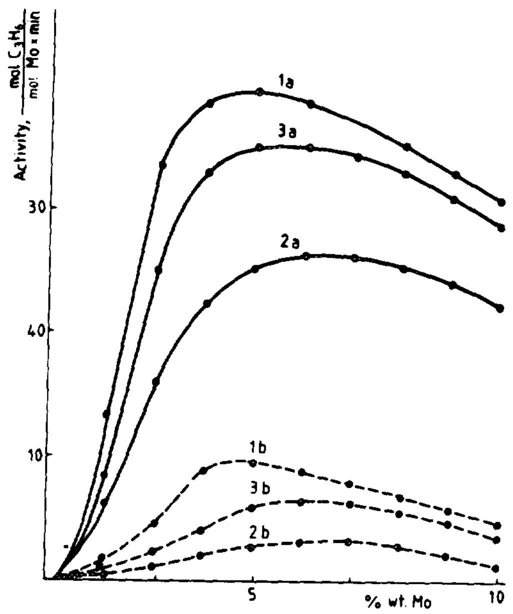

FIG. 2. Dependence of activity on the Mo content in the catalyst. Catalysts were treated at 500°C under (a) — CO, (b) --- H_2. The curve number corresponds to the number of Mo atoms in the surface species.

(Fig. 1). The samples treated in CO are more active than those reduced with H_2. The highest activity is observed with catalysts reduced at 500–550°C.

The activity depends strongly on the Mo content in a sample. Catalysts that contain less then 1% Mo are not active in this reaction. Samples with 4 wt% Mo content have the highest activity (Fig. 2).

Reduced catalysts are active for propene metathesis even at room temperature (Fig. 3). The initial reaction rate increases with increasing temperature followed by a decrease after the maximum at 150°C. The characteristic feature of these catalysts is their relatively long operation period at low temperatures. Indeed, the catalyst activities show some increase at room temperature (Fig. 4), reach a maximum after 0.5–1.0 h of operation, and then decrease, reaching the initial value in 50 h (Fig. 5).

The completely deactivated catalyst can

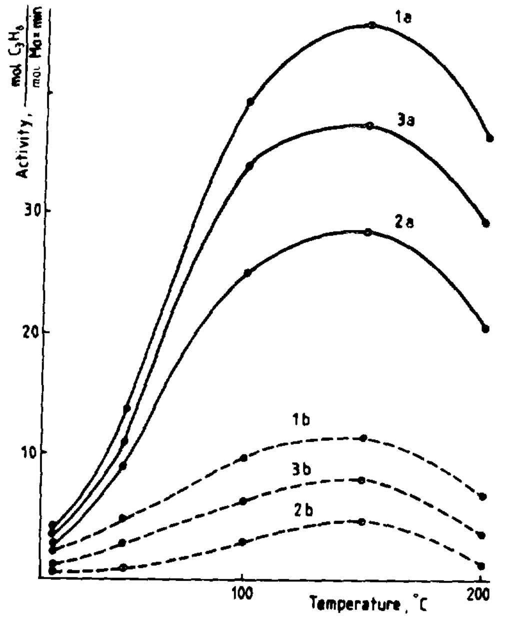

FIG. 3. Temperature dependence of propene metathesis over {Mo_1}–{Mo_3} catalysts. Designations as in Figs. 1, 2.

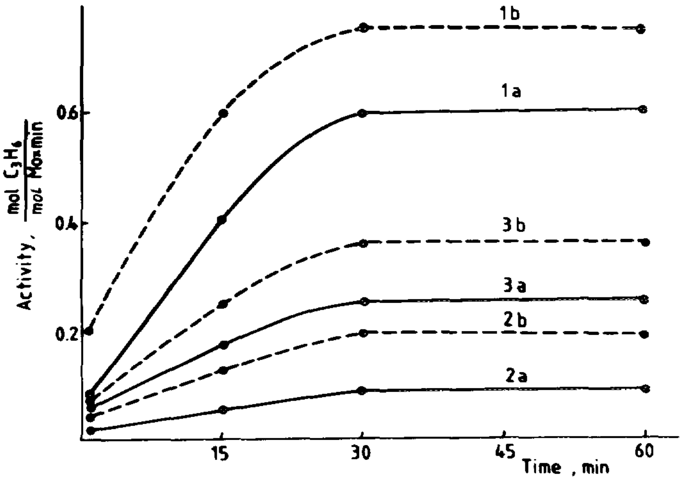

FIG. 4. Time dependence of propene metathesis over {Mo_1}–{Mo_3} catalysts. Temperature, 20°C. The curve number corresponds to the number of Mo atoms in a surface species. (a) — catalyst activated with H_2 at 500°C. (b) --- deactivated catalyst from (a) was evacuated at 500°C to 10^{-3} Torr.

be regenerated by repeated reduction in H_2 or CO at 500°C. However, catalyst regeneration by evacuating until 10^{-3} Torr at 500°C leads to a marked increase of activity (Figs. 4, 5).

The initial activity of the regenerated catalyst first increases and then decreases after a maximum at 0.5–1.0 h. In this case the initial activity value is reached only after 100 h of catalyst operation.

The rate of catalyst deactivation increases with increasing temperature faster than the rate of the propene metathesis; at 150°C the catalyst becomes deactivated in ca. 1.0 h of operation.

{Mo_2}/Al_2O_3. Upon treatment of γ-Al_2O_3 with $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ aqueous solution, decolorization of the latter is observed with the support turning brown.

The initial form of the catalyst does not show any activity in propene metathesis. Similarly to the previous case, activity ap-

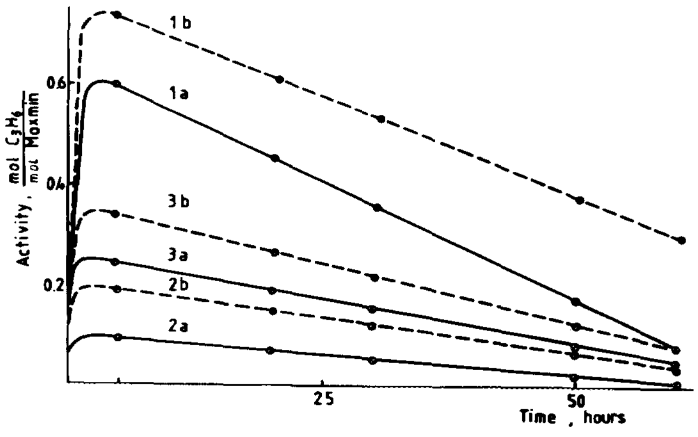

FIG. 5. Long-term time dependence of propene metathesis. Designations as in Fig. 4.

TABLE 1

Propene Metathesis over Mo/Al_2O_3 Catalysts

Catalyst	Mo content (wt%)	Activation[a]	Reaction temperature			
			100°C		20°C	
			Activity[b]	Operation period[c]	Activity[b]	Operation period[c]
$\{Mo_1\}/Al_2O_3$	4.0	H_2	12.0	3.5	0.60[d]	70
					0.75[e]	110
		CO	42.0	1.5	1.00	12
$\{Mo_2\}/Al_2O_3$	8.0	H_2	2.8	3.0	0.10[d]	50
					0.20[e]	100
		CO	24.0	1.0	0.50	10
$\{Mo_3\}/Al_2O_3$	6.0	H_2	5.9	3.3	0.25[d]	50
		CO	35.3	1.2	—	—
$\{Mo(all)\}/Al_2O_3$	5.0	Without activation	10.0	0.6	0.30	2.9
$\{MoO_3\}/Al_2O_3$	8.0	H_2	0.7	0.8	0.03[d]	2.5
		CO	10.0	0.5	—	—

[a] Catalyst was activated at 500°C under CO or H_2.

[b] Reaction rate in 1 h after beginning of the reaction was taken as a measure of activity mol C_3H_6/mol Mo · min.

[c] Time to decrease the activity by 90% was taken as the measure of the operation period (h).

[d] Activity in 1 h after beginning of the reaction.

[e] Deactivated catalyst from the previous example was evacuated at 500°C until 10^{-3} Torr.

pears only after treatment with CO or H_2 at 400°C and higher temperatures. The activities of these catalysts show the same behavior as those of $\{Mo_1\}/Al_2O_3$ samples, but the activity values of the former are markedly lower (Figs. 1–5). Moreover, maximum activity for these catalysts is reached at higher molybdenum content, ca. 7 wt% (Fig. 2).

$\{Mo_3\}/Al_2O_3$ catalysts. These catalysts show the same behavior in propene metathesis as the two previous cases. With all other conditions the same, the general level of activities of these catalysts lies between those of $\{Mo_1\}/Al_2O_3$ and $\{Mo_2\}/Al_2O_3$ (Figs. 1–5).

$\{Mo(all)\}/Al_2O_3$ catalysts. In contrast to the previous cases, the initial form of these catalysts shows high activities in propene metathesis (Table 1). However, their activities decrease by 90% after 3 hs of operation at room temperature. $\{Mo(all)\}/Al_2O_3$ catalysts lose their activities in 1 h at 100°C.

$MoO_3/Al_2O_3(ST)$ catalysts. The activity and stability of MoO_3/Al_2O_3 catalysts are much lower than those of catalysts derived from metal complexes that are activated under the same conditions. The activity and stability data for all the catalysts are shown in Table 1.

DISCUSSION

Metathesis of olefins on supported catalysts has been extensively studied from various viewpoints (*2–13*). Much effort has been made to elucidate the role of such parameters as the nature of the support in supported molybdenum complexes, the conditions of activation, and the nature of cocatalysts. However, much less attention has been paid to the dependence of activity upon the number of Mo-atoms in the surface complexes. Two research groups have studied the catalytic system obtained by anchoring to oxide supports of both mononuclear $Mo(C_5H_5)_4$ (*13*) and binuclear $Mo_2(C_3H_5)_4$ allyl molybdenum complexes, (*10*). The reported values of metathesis reaction rate are very close to each other. However, the structure of the surface species of the active catalyst form has not been studied in these works.

The chemistry of organometallic and coordination molybdenum complexes has been well studied (see, for example, Ref. (*22*)). Molybdenum complexes with various Mo oxidation states, natures of ligands, and numbers of metal atoms in the molecule have been synthesized. For preparation of supported catalysts the metal complexes must be, on the one hand, stable in aqueous solutions and not subject to decomposition in air, and, on the other hand, must contain ligands, that do not produce toxic products upon decomposition. These requirements are satisfied, for example, by Mo oxalate complexes.

The oxidation state of molybdenum in complexes of Mo and oxalic acid varies from 6+ to 3+, and the number of Mo atoms, per molecule varies from 1 to 5 (*23*). Most compounds are stable in aqueous solutions, and their synthesis is not complicated. Molybdenum oxalate has been reported as a homogeneous catalyst for olefin epoxidation (*24*).

Acetylacetonate complexes of transition metals are no less interesting from the viewpoint of the synthesis of supported catalysts. The chemistry of β-diketonates of metals has been extensively studied, since they are widely employed in various branches of chemistry and chemical technology. The structure and properties of $MoO_2(acac)_2$, as well as its employment as an Al_2O_3 basic group "titration" reagent (*21*) and as a homogeneous catalyst for various reactions (*26*), have been described (*25*).

The reaction of $MoO_2(acac)_2$ and molybdenum oxalates {$Mo_2(OX)$} and {$Mo_3(OX)$} with the surface of γ-Al_2O_3 proceeds via various mechanisms (*12, 14, 18*). Initial forms of the materials obtained are inactive (in contrast with the {Mo(all)}Al_2O_3 system) in catalysis of olefin metathesis. In order to obtain an active form, all three types of catalyst should be reduced by high-temperature treatment in CO or H_2.

If one proceeds from the oxidation state of Mo^{4+} in an active form of the catalysts (*11*), one may conclude that the thermal pretreatment in CO and H_2 provides for both the reducing of Mo ions in surface species of {Mo(acac)} and {$Mo_2(OX)$} catalysts and the removing of ligands to form vacant sites in a coordination sphere of Mo^{4+} for adsorption of the reacting molecules. Therefore the activation procedure is not adequate for all three types of catalysts. Evidently, after decomposition of the surface oxalate species some fraction of Mo ions is not active in catalysis due to, say, deactivation by carbonaceous deposits. Another possible reason is the formation of nonactive surface species due to noncontrolled processes of penetration of Mo ions into subsurface layers of the support.

A small difference in the activity can be explained through the differences in thermal stability of surface complexes. Thus, the surface oxalate complexes {Mo_2}/Al_2O_3 decompose at higher temperature compared to that of {Mo_3}/Al_2O_3 decomposition. Isolated Mo^{6+} ions that do not have stabilizing chelate ligands are the easiest to be reduced. However, even in this case the temperature that is necessary for formation of the active species (presumably Mo^{4+} ions (*13*)) should not be below 400°C.

Figure 2 illustrates that low-percentage catalysts are not active in olefin metathesis. This result may be explained through the differences in reactivities of γ-Al_2O_3 surface OH-groups for the reaction with the complexes to be supported. It has been reported (*20*) that $MoO_2(acac)_2$ reacts first with the most basic surface OH-groups of γ-Al_2O_3. These surface species seem to be inactive for the catalysis. The reaction of metal complexes with neutral OH-groups leads to the formation of surface species that show a very high catalytic activity for propene metathesis after their reduction with CO or H_2.

On increasing the Mo content in the catalyst, the more acidic OH-groups of alumina interact with Mo complexes. These surface species seem to form poorly active centers (in comparison with neutral OH-groups). In other words, due to the differences in the structure of the surface species formed after reaction of Mo complexes with different types of OH-groups of alumina, the catalytic activity of surface species formed after reduction is different. The detailed structure of these surface species will be discussed in following papers of this series.

Catalysts reduced in CO are more active in comparison with H_2-reduced catalysts (Figs. 1–5). This phenomenon may be explained in the following way. It was found that after injection of propene to the freshly H_2-reduced catalysts, small amounts of alkanes (ethane and propane) were always found in the gas phase. Formation of alkanes seems to result from the interaction of olefines with surface hydride species (*27*), which are nonactive in metathesis. After removal of the gas phase by evacuation and admixture of a new portion of propene, the amount of alkane is sufficiently low and metathesis activity increases. In the case of CO-reduced catalysts the surface Mo carbonyl species seems to be easily transformed into carbenes after contact with propene. Evidently, the different rate of carbene formation for CO- and H_2-reduced catalysts is the main reason for the induction period appearance: maximum activity for the CO-reduced catalysts is achieved in few minutes, but for H_2-reduced catalysts it takes half an hour (Figs. 4 and 5).

The characteristic feature of these catalysts is their relatively long lifetime at low temperatures (Fig. 5). In contrast with the $\{Mo(all)\}/Al_2O_3$ and $MoO_3/Al_2O_3(ST)$ catalysts, the operation period of the catalysts may be as long as 100 h and more at room temperature. However, with the increase of temperature, their lifetime decreases drastically. The temperature coefficient of the catalyst deactivation rate seems to be much greater than that of the propene metathesis reaction. This also seems to be the reason for the maximum in the temperature dependence of the reaction rate (Fig. 3).

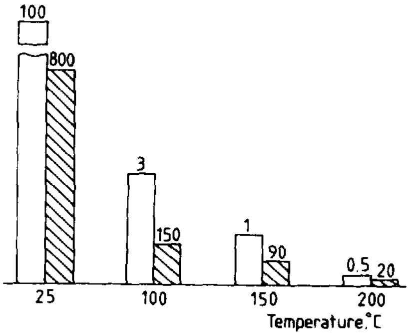

FIG. 6. Temperature dependence of activity and efficiency of $\{Mo_2\}/Al_2O_3$ catalyst, activated with H_2 at 500°C. □, stability (h); □, efficiency (mol C_3H_6/mol Mo).

The above results may be illustrated by referring to catalyst efficiency as a parameter. If the 90% decrease time of the catalyst activity may be taken as a measure of its operation period, the efficiency of the catalyst for 100 h of operation is 800 mol C_3H_6 per mol of Mo (Fig. 6). However, the efficiency of the catalyst at 100°C is as low as 150 mol C_3H_6 per mol of Mo. The increase of reaction temperature up to 150°C leads to an increase of the initial reaction rate (Fig. 3), but the operation period and the efficiency of the catalyst decrease drastically (Fig. 6).

Deactivation of catalysts may be caused by two factors, ethene polymerization and isomerization of olefines followed by growing of the carbon chain due to cometathesis. In fact, in all our experiments an equimolar ratio ethene:butenes was never observed; the amount of ethene was always lower. This is in accordance with the literature (*27*, *28*). Trace amounts of C_{5+} hydrocarbons were also found in the gas phase. Condensation products formed in these reactions may block the active sites. The treatment of deactivated catalysts with H_2 or CO at 500°C regenerates the initial catalytic activity to 80–90%. However, an increase of activity is observed after evacuation of a deactivated catalyst at 500°C (Figs. 4, 5). This result may be interpreted as follows. After the inlet of propene over the reduced samples, active sites in the form of carbene complexes are generated, which gives rise to an initial activity for the catalysts (Fig. 4). The catalysts are deactivated by blocking of active sites with condensation products that do not desorb into the gas phase. Repeated reduction leads to the removal of carbene complexes and practically complete regeneration of the catalysts. Evacuation of deactivated catalysts leads to a thermal decomposition of condensation products. Hydrocarbon radicals seem to be the source of carbene complexes.

CONCLUSIONS

A new method for preparation of Al_2O_3-supported catalysts for olefin metathesis has been developed. The method is based on the anchoring to a support surface of mononuclear $Mo^{VI}O_2(acac)_2$, binuclear $[Mo_2^VO_4(C_2O_4)_2(H_2O)_2]^{2-}$, and trinuclear $[Mo_3^{IV}O_4(C_2O_4)_3(H_2O)_3]^{2-}$ molybdenum complexes. Highly active catalysts for propene metathesis have been prepared by reduction of surface metal complexes with H_2 or CO at elevated temperature. These catalysts have relatively high catalytic stability at low temperatures. The rate of catalyst deactivation increases with increasing temperature faster than that of the catalytic reaction, and this leads to a decrease of the catalyst efficiency at higher reaction temperatures.

Succeeding papers of this series will be devoted to study of the process of catalyst genesis and the nature of the active centers in reduced catalysts.

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