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# Use of Photoreduction for Activation of Silica–Molybdena Catalysts for Propylene Metathesis: Comparison with Thermal Reduction

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Specific activities of silica–molybdena catalysts (1% Mo by weight), prereduced in CO or $H_2$ either photochemically at 300 K or thermally at 773 K, for the propylene metathesis reaction at room temperature are compared. It is found that preliminary photoassisted reduction of $Mo^{6+}/SiO_2$ upon UV irradiation is an effective way to produce active catalysts. Turnover numbers (TON) for photoreduced $Mo/SiO_2$ considerably exceed those for thermally reduced samples (by a factor of 6–10) and are even higher (by a factor of 2–3) than the TON for one of the most active "anchored" organomolybdenum catalysts, $Mo(\eta_3\text{-}C_3H_5)_2/SiO_2$. It is shown that propylene metathesis over photoreduced silica–molybdenum occurs via a Langmuir–Hinshelwood mechanism and catalytically active sites involve $Mo^{4+}$ ions. Poisoning the catalysts by $O_2$, $N_2O$, or NO adsorption is also studied. The possible reasons for higher catalytic activity of photoreduced samples are discussed. A direct comparison is made between the present results and those of M. Anpo, I. Tanahashi, and Y. Kubokawa (*J. Chem. Soc. Faraday Trans. 1* **78**, 2121 (1982)) on the rates of propylene metathesis over $Mo^{6+}$/PVG in $C_3H_6$ atmosphere under UV irradiation.

## INTRODUCTION

The reaction of olefin disproportionation or metathesis ($2R_1CH{=}CHR_2 \rightleftarrows R_1CH{=}CHR_1 + R_2CH{=}CHR_2$), discovered in 1964 by Banks and Bailey (*1*), is still of interest from both the practical and mechanistic viewpoints. The most active solid catalysts for this reaction are those containing surface complexes of Mo, W, or Re, supported on oxides with highly developed surface areas (mainly $Al_2O_3$ and $SiO_2$).

Unreduced silica–molybdena is a poor catalyst for the metathesis reaction: according to Refs. (*2, 3*), impregnated $Mo^{6+}/SiO_2$ catalysts exhibit low activity only at rather high temperatures (673–773 K). However, prereduction of $Mo^{6+}/SiO_2$ in hydrogen, carbon monoxide, or propylene, which is known to produce molybdenum ions in lowered oxidation states, results in an increase in catalytic activity and a decrease in reaction temperature (*4–7*). In this connection a question arises as to what is the oxidation state of molybdenum ions involved in active sites for the metathesis reaction. It seems difficult to answer this question unambiguously in the case of impregnated silica–molybdena catalysts, since thermal reduction at high temperatures occurs nonselectively, leading to the formation of molybdenum ions in various valence and coordination states. For example, Tanaka and co-workers (*7*) believe that coordinatively unsaturated $Mo^{4+}$ ions participate in propylene metathesis. Kadushin *et al.* (*5*) did not rule out this possibility completely, although it was suggested that $Mo^{5+}$ ion pairs unobservable by EPR spectroscopy could be active as well. In Ref. (*5*) an important role of electron transfer from the nearest electron donor to the adsorbed olefin molecule was emphasized.

In our previous works (*8–10*) it has been shown that low temperature (77–300 K) photoreduction of $Mo^{6+}/SiO_2$ is a very effective way to produce reduced molybdenum ions in a particular oxidation state. Coordinatively unsaturated $Mo^{4+}$ ions were created selectively and with high enough

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yields by photoreduction of $Mo^{6+}$ in CO, while UV irradiation in an atmosphere of $H_2$, depending on the wavelength, gave rise to either $Mo^{5+}$ or to $Mo^{4+}$ ions. Taking these data into account the present research was initiated with the objective of comparing properties of the silica–molybdena catalysts activated either by thermal reduction or by photoreduction, as well as to try to find out what valence state of molybdenum ions is responsible for the ability of reduced $Mo/SiO_2$ to catalyze the propylene metathesis reaction. Preliminary results were reported in our earlier paper (*10*).

## EXPERIMENTAL

### *Catalyst Preparation and Pretreatment*

As a supporting material an industrial silica-gel KSK-2-5 with $S = 360$ m$^2$ g$^{-1}$ was used. Major impurities were $Al_2O_3$ (1.02%), $Fe_2O_3$ (0.16%), and CaO (1.45%). $Fe^{3+}$ ions were removed by boiling the silica gel in HCl solution for several hours followed by careful washing of the material with distilled water. The samples of $Mo^{6+}/SiO_2$ (1 wt% Mo) were obtained by impregnation of silica gel with an aqueous solution of ammonium paramolybdate. After it was dried in ambient air at 333–353 K the $Mo^{6+}/SiO_2$ sample was placed in a quartz reactor, which was then sealed to an evacuable gas-circulating system supplied with greaseless metallic valves. The amounts of catalyst in the reactor were 0.18–0.22 g.

The following pretreatment procedure was adopted:

*Step A*. Evacuation to $10^{-4}$ Torr (1 Torr = 133.3 N m$^{-2}$) while continuously raising the temperature (5 K min$^{-1}$) from 300 to 1073 K.

*Step B*. Heating the sample in a circulating flow of dry oxygen ($P_{O_2} = 120$ Torr) at 1073 K for 1–1.5 h, then *in vacuo* at the same temperature for 1.5–2 h. After repeated admission of oxygen ($P_{O_2} = 20$–$50$ Torr) the sample was cooled down to 423 K and evacuated to $10^{-4}$ Torr.

In some cases a modified variant of step B was used: at first the sample was maintained in water vapor at 373–393 K for 2–2.5 h, and then it was treated as in step B, but at 773 K.

The full pretreatment cycle (steps A and B) was done only with the freshly prepared catalyst samples. After the metathesis reaction was carried out the catalysts were regenerated for further experiments by treatment according to step B only.

### *Catalyst Reduction*

Photoreduction of $Mo^{6+}/SiO_2$ in CO or in $H_2$ at pressures of 15–20 Torr was performed at room temperature under UV irradiation with a high-pressure mercury lamp, Model DRSh-1000 (1 kW), equipped with a water filter and a system of quartz lenses to focus the light beam. Irradiation times were varied from 0.5 to 270 min. After completion of the irradiation, the reducing gases were pumped off at room temperature and then the evacuation temperature was raised to 423–473 K. In some experiments a glass filter (BS-10) cutting out wavelengths shorter than 360 nm was used for photoreduction in $H_2$. To provide a more uniform photoreduction the powder catalysts sample was shaken during irradiation using an electromagnetic microvibrator.

Thermal reduction in CO or $H_2$ at pressures of 50–70 Torr was carried out at 773 K for 75–100 min while circulating reducing gas through the catalyst bed. The reduction products ($CO_2$ or $H_2O$) were condensed in a trap cooled with liquid nitrogen. The catalyst was then pumped at 773 K to $10^{-4}$ Torr.

Reduction degrees of molybdenum ions in the catalysts were determined either by measuring the amounts of $CO_2$ formed during photoreduction or thermal reduction in CO or by measuring the amounts of $O_2$ consumed at 773 K during reoxidation of the catalyst prereduced in $H_2$.

### *Catalytic Measurements*

In most experiments catalytic activities of prereduced $Mo/SiO_2$ samples for the propylene metathesis were measured at room temperature with circulation of gaseous mixture through the catalyst. The total reaction volume (the reactor plus the circulation system) was 570 $cm^3$; the initial propylene pressures were in the range of 30–90 Torr. Gaseous mixtures were quantitatively analyzed with a UTI-100 C quadrupole mass spectrometer, which was connected to the circulating system through a leak valve. Mixtures of ethylene, propylene, and *trans*-2-butene of known composition were used for calibration.

### *Gaseous Reactants*

Propylene was purified by a high-pressure distillation process and stored in glass bulbs. Before each run the portion of $C_3H_6$ required to test catalytic activity was further purified by freezing in a cold trap (77 K) with subsequent outgassing at this temperature.

Carbon monoxide was freed from $O_2$ and other contaminants by passage through a column with reduced $Cr^{2+}/SiO_2$ adsorbent and two traps cooled with liquid nitrogen. Hydrogen was purified by diffusion through a red-hot (~1100 K) Pd thimble.

### *Optical Measurements*

UV and visible diffuse reflectance spectra were recorded with a Hitachi Model M-340 spectrophotometer supplied with an integrating sphere attachment. For optical measurements $Mo/SiO_2$ samples were treated in a fused quartz cell as described above.

## RESULTS AND DISCUSSION

### *Kinetics of the Propylene Metathesis Reaction over Reduced $Mo/SiO_2$*

Unreduced $Mo^{6+}/SiO_2$ samples exhibited no appreciable catalytic activity for propylene metathesis at room temperature (Fig. 1a). However, preliminary reduction of these samples in different ways resulted in the appearance of catalytic activity, which could be followed by the time-dependent change in the composition of the circulating gas mixture. Figure 1 shows typical dependences of propylene fractions in reaction mixtures as a function of contact times with the $Mo/SiO_2$ samples preactivated by thermal reduction at 773 K in $H_2$ (curve b), in CO (curves c and d), or by photoreduction at 300 K in CO (curve e). Curves E and B in Fig. 1 correspond to the growth of ethylene and butene concentrations in the course of the propylene metathesis over photoreduced $Mo/SiO_2$ catalyst.

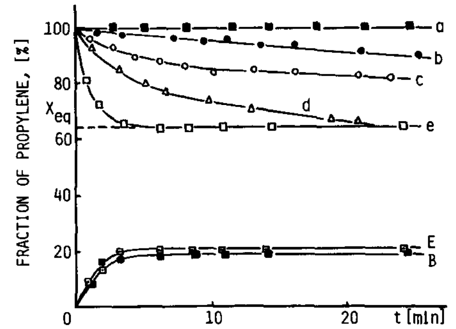


FIG. 1. Time dependences of propylene (a–c), ethylene (E), and butene (B) fractions in gaseous mixtures in the course of the propylene metathesis reaction over $Mo/SiO_2$ catalyst: (a) unreduced; (b) reduced at 773 K in $H_2$ for 90 min; (c) reduced at 773 K in CO for 90 min (pretreatment temperature 773 K); (d) the same as (c) but pretreatment temperature 1073 K; (e) photoreduced at 300 K in CO for 60 min. $X_{eq}$ is the equilibrium propylene fraction.

It is apparent from Fig. 1 that the highest catalytic activity was reached for the photoreduced $Mo/SiO_2$ samples. Thermal reduction in CO made the catalyst more active than reduction in $H_2$. Furthermore, it follows from the data of Fig. 1 that the temperature of thermal reduction in CO had an appreciable influence on the catalytic activities. This effect was studied in more detail (see below).

The lack of distinct initial linear regions on curves c–e of Fig. 1 makes difficult an accurate determination of initial reaction rates and specific activities of the catalyst. Therefore, to obtain more accurate quantitative characteristics of the catalytic activity it is better to use linear transformations of the kinetic curves which can be obtained by applying the Langmuir–Hinshelwood (L-H) model to the kinetic data.

The L-H model for propylene metathesis leads to an expression for the rate of propylene conversion (*11*),

$$-\frac{1}{2}\frac{dC_3}{dt} = k_f\,\theta_3^2 - k_r\theta_2\theta_4,$$

where $C_3$ is the propylene concentration in the gas phase, and $\theta_2$, $\theta_3$, and $\theta_4$ are the fractions of active sites occupied by adsorbed $C_2H_4$, $C_3H_6$, and $C_4H_8$, respectively. $k_f$ and $k_r$ are rate constants of the forward and reverse reactions, respectively.

Taking into account the stoichiometry of the reaction one can express $\theta_2$, $\theta_3$, and $\theta_4$ via concentrations of $C_2H_4$, $C_3H_6$, and $C_4H_8$:

$$\frac{1}{2}(C_3)\frac{dx}{dt} = \frac{k_f K_3^2 (C_3)_0^2[(1-x)^2 - x^2/4K_{eq}]}{[1 + K_3(C_3)_0^2]^2}. \quad (1)$$

Here $K_3$ is the propylene adsorption coefficient, $K_{eq} = k_f/k_r$ is the equilibrium constant, and $x$ is the extent of propylene conversion; i.e., $(1 - x) = (C_3)/(C_3)_0$, where $(C_3)_0$ is the initial propylene concentration in the gas phase.

Let us denote

$$\frac{2k_f K_3^2 (C_3)_0}{[1 + K_3(C_3)_0]^2} = \gamma.$$

Taking into consideration that $x = 0$ at $t = 0$ one can obtain, by integration of Eq. (1),

$$\ln\frac{1 + (1/2\sqrt{K_{eq}} - 1)x}{1 - (1/2\sqrt{K_{eq}} + 1)x} = \frac{\gamma}{K_{eq}}\,t. \quad (2)$$

The linear transformations of kinetic curves b–e of Fig. 1 are presented in Fig. 2, where the values of $\ln[1 + (1/2\sqrt{K_{eq}} - 1)x/1 - (1/2\sqrt{K_{eq}} + 1)x]$ are plotted versus time.

The experimental points fall well enough on straight lines. Taking into account that at $x \to 0$ $(dx/dt)_0 = \gamma$ it is evident that the slopes of these lines characterize the initial rates of the metathesis reaction. Specific activities of the Mo/SiO$_2$ catalysts obtained with different activation modes and reaction conditions are given in the next to last column of Table 1. They are expressed in numbers of $C_3H_6$ molecules converted over one molybdenum ion per one second (turnover numbers, TON ($\Sigma$ Mo)). For the photoreduced catalysts TON referred to one $Mo^{4+}$ ion (TON ($Mo^{4+}$)) are also presented in Table 1 (the last column). The numbers of $Mo^{4+}$ ions in the reduced catalysts were determined by measuring the amounts of $CO_2$ gas evolved during photoreduction of $Mo^{6+}/SiO_2$ in CO, since in our earlier work (*8*, *9*) it has been shown that this process gave rise to predominant formation of $Mo^{4+}$ ions. Naturally, TON ($\Sigma$ Mo) increased with increasing irradiation time in the course of preliminary photoreduction of the catalyst because of the growing concentration of reduced molybdenum ions. At the same time, TON ($Mo^{4+}$) when referred to an identical initial propylene pressure remained practically constant during almost tenfold variation of the $Mo^{4+}$ concentration (Fig. 3).

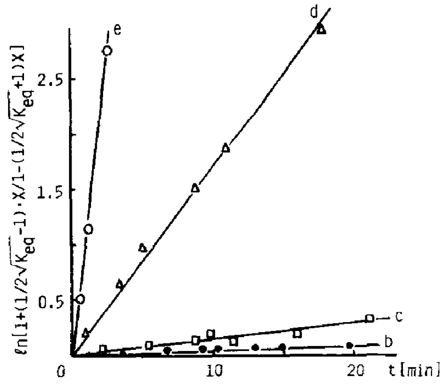


FIG. 2. Linear transformations of curves b–e of Fig. 1.

Determination of TON ($Mo^{4+}$) for the thermally reduced catalyst appears to be a much more difficult problem, since for these samples for some reason (see below) it was not possible to evaluate the number of reduced $Mo^{4+}$ ions.

TABLE 1

Effect of Activation Treatment, Temperature, and Pressure on the Activities of Mo/SiO$_2$ Catalysts in the Propylene Metathesis Reaction

| Temp of Mo$^{6+}$/SiO$_2$ pretreatment (K) | Activation treatment | Reduction time (min) | Reduction degree (%)[a] | Temp of reaction (K) | Initial C$_3$H$_6$ pressure (Torr) | Specific activity (s$^{-1}$) TON ($\Sigma$ Mo) | Specific activity (s$^{-1}$) TON (Mo$^{4+}$) |
|---|---|---|---|---|---|---|---|
| 773 or 1073 | Photoreduction at 300 K in CO | 0.5 | 16 | 300 | 62 | 0.09 | 0.54 |
| | | 58 | 63 | 300 | 85 | 0.42 | 0.67 |
| | | 45 | 65 | 300 | 27 | 0.18 | 0.28 |
| | | 270 | 100 | 263 | 82 | 0.22 | 0.22 |
| 773 | Photoreduction at 300 K in H$_2$ with filtered light ($\lambda \geq 360$ nm) | 70 | — | 300 | 85 | No activity | |
| 1073 | Photoreduction at 300 K in H$_2$ with full light | 60 | 24[b] | 300 | 84 | 0.16 | 0.66 |
| 1073 | Thermal reduction at 300 K in CO | 95 | 64 | 300 | 64 | 0.070 | — |
| | | 90 | 44 | 300 | 70 | 0.048 | — |
| 773 | As above | 75 | 188 | 300 | 80 | 0.024 | — |
| | | 80 | 102 | 300 | 65 | 0.032 | — |
| 773 or 1073 | Thermal reduction at 773 K in H$_2$ | 105 | 20[b] | 300 | 48 | 0.003 | — |

[a] Reduction degree was calculated as the ratio of $N_{CO_2}$ evolved to $N_{Mo^{6+}}$ in the catalyst.

[b] Determined by measuring the amounts of O$_2$ consumed in oxidizing Mo$^{4+}$ ions (see text).

The data of Table 1 (lines 2 and 4) demonstrate that at identical initial propylene pressures the TON (Mo$^{4+}$) for the photoreduced catalysts decreased by a factor of 3 when the temperature was lowered from 300 to 263 K. A rough estimation of activation energy of the metathesis reaction based on these two points gave the value of 19.6 kJ/mol.

TON (Mo$^{4+}$) as a function of initial propylene pressures are depicted in Fig. 4 (curve a). This dependence was used to prove the validity of the above assumption about the metathesis reaction proceeding

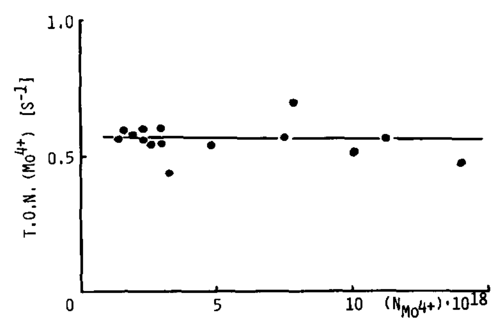


FIG. 3. TON (Mo$^{4+}$) versus numbers of Mo$^{4+}$ ions ($N_{Mo^{4+}}$) for Mo/SiO$_2$ photoreduced in CO.

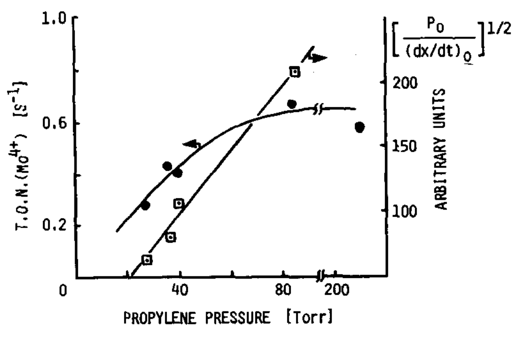


FIG. 4. TON (Mo$^{4+}$) for photoreduced catalyst versus initial propylene pressure.

via a L-H mechanism (*11*). From the equation $(dx/dt)_0 = \gamma$ one obtains

$$\left[\frac{(C_3)_0}{(dx/dt)_0}\right]^{1/2} = \frac{1}{(2K_f)^{1/2}K_3} + \frac{(C_3)_0}{(2K_f)^{1/2}}.$$

Thus, one can expect that $[(C_3)_0/(dx/dt)_0]^{1/2}$ will be a linear function of initial propylene pressures. Figure 4b shows that such a dependence is satisfactorily fulfilled.

The kinetic data shown in Figs. 1–4 were obtained at the first propylene admission onto preliminary reduced Mo/SiO$_2$ samples. After the reaction mixtures were pumped off at room temperture and propylene was repeatedly admitted to the catalyst, conversion of propylene to ethylene and butene again took place. The catalysts kept their activities also on subsequent admissions of new propylene portions without any additional activation. For less active catalysts, for example, those which were activated by thermal reduction in H$_2$ or CO, the initial rates of the metathesis reaction remained practically unchanged after admissions of the second, the third, and the following propylene portions. For the most active photoreduced catalysts a decrease in activity was observed which is probably associated with a partial poisoning of the active sites. As an example, linear transformations of the kinetic curves obtained in the first, the second, and the third propylene admissions onto a Mo/SiO$_2$ sample photoreduced in CO are presented in Fig. 5.

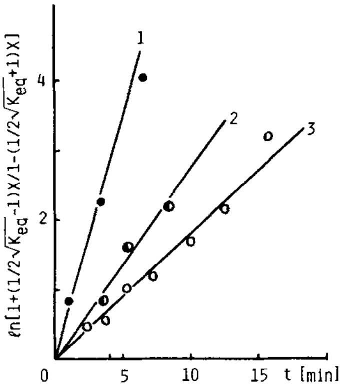
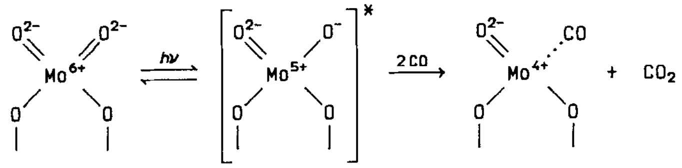


FIG. 5. Linear transformations of the kinetic curves obtained at three successive admissions of $C_3H_6$ onto a Mo/SiO$_2$ sample photoreduced in CO ($P_0$ = 70–72 Torr).

Gradual poisoning of the catalyst which can be deduced from Fig. 5 seems to be quite natural if one takes into account that each active center (Mo$^{4+}$) participates in the reaction a great number of times. For instance, rough estimations show that for the reaction time of ~20 min during three to five successive propylene admissions (2–3) × $10^3$ olefin molecules are converted on each Mo$^{4+}$ ion. It should be stressed that after treatment of Mo/SiO$_2$ samples according to step B (see Experimental) followed by photoreduction or thermal reduction, the activities of the catalysts were fully regenerated.

### *Nature of Active Sites for the Propylene Metathesis Reaction over Photoreduced Catalysts*

In our opinion, the results described above on the activities of the photoreduced catalysts and, in particular, the constancy of TON (Mo$^{4+}$) with variation of Mo$^{4+}$ concentration over a wide range (Fig. 3) can be taken as convincing evidence for the participation of Mo$^{4+}$ ions in the propylene metathesis reaction. These ions are formed under photoreduction of Mo$^{6+}$/SiO$_2$ in CO by a two-electron reduction process according to the scheme proposed in our earlier works (Scheme 1) (*7–9*).



SCHEME 1. The asterisk denotes a short-lived excited state.

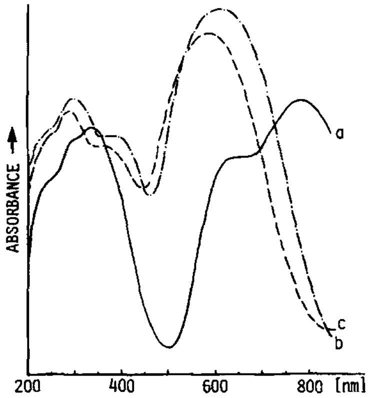


FIG. 6. Diffuse reflectance spectra of Mo/SiO$_2$ sample photoreduced in CO: (a) after outgassing at 423 K; after admission of (b) propylene or (c) ethylene to the sample (a) at room temperature.

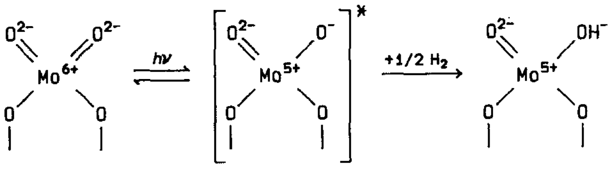
CO molecules which are bound to Mo$^{4+}$ ions could be removed by outgassing the samples at 423 K. Afterward, Mo$^{4+}$ ions either became trigonally coordinated or retained their tetrahedral coordination if a coordination bond with neighboring OH groups or ≡Si—O—Si≡ fragments was formed. This conclusion was drawn in Refs. (*8*, *9*) from an analysis of the diffuse reflectance spectra in the region of the Mo$^{4+}$ *d–d* transition (Fig. 6a).

During photoreduction of Mo$^{6+}$/SiO$_2$ in CO, Mo$^{5+}$ ions are also formed. However, as was shown in Refs. (*8*, *9*), their amounts do not exceed 1–3% of Mo$^{4+}$ concentrations. Considerably higher concentrations of Mo$^{5+}$ ions could be obtained upon exposure of Mo$^{6+}$/SiO$_2$ to radiation of wavelength longer than 360 nm (through a glass filter) in H$_2$ atmosphere at room temperature according to Scheme 2 (*8*, *9*). No appreciable catalytic activity for the propylene metathesis reaction was found for samples reduced in such a way (Table 1). Therefore one may conclude that Mo$^{5+}$ ions do not participate in the propylene metathesis reaction. Upon further irradiation with unfiltered light, in addition to Mo$^{5+}$ ions, Mo$^{4+}$ ions were accumulated in the sample which are formed from Mo$^{5+}$ ions by a consecutive photoreduction process analogous to that described by Scheme 2 (*9*). According to EPR measurements the intensity of the Mo$^{5+}$ signal increased by a factor of 3 as a result of additional irradiation for 1 h. These samples exhibited high catalytic activities, comparable to those of the samples photoreduced in CO (Table 1).

To calculate TON (Mo$^{4+}$) for the catalyst photoreduced in H$_2$ the amount of Mo$^{4+}$ was determined in a parallel experiment in which the number of O$_2$ molecules consumed in reoxidizing the reduced sample at room temperture was measured. It was found that TON (Mo$^{4+}$) for the catalysts photoreduced in H$_2$ or CO were approximately the same under similar experimental conditions.

After adsorption of relatively small amounts of oxidizing gases (O$_2$, N$_2$O, or NO) at room temperature, the catalytic activity of photoreduced samples was irreversibly poisoned. The results of these experiments are summarized in Table 2.

Oxygen is a strong oxidizing agent which is capable of oxidizing both Mo$^{4+}$ and Mo$^{5+}$ ions. At the first stage of oxygen interaction with Mo$^{4+}$, charge transfer complexes (Mo$^{5+}$ . . . O$^{2-}$) were formed which were stable for 2–3 h at 300 K (*9*). They are characterized by an optical absorption band at ~500 nm. The formation of Mo$^{5+}$ . . . O$^{2-}$ complexes is indirectly confirmed by the following experimental findings: (i) $N_{O_2}$ ad-



(A)

SCHEME 2.

sorbed was found to be equal to $N_{Mo^{4+}}$ (Table 2); (ii) oxygen desorption was observed at 423 K, and $N_{O_2(desorbed)} = \frac{1}{2}N_{Mo^{4+}}$. $O_2$ evolution was apparently caused by further oxidation of $Mo^{5+}$ ions:

$$Mo^{5+} \ldots O^{2-} \rightarrow Mo^{6+} + O^{2-} + \tfrac{1}{2}O_2.$$

$N_2O$ is a selective agent for oxidizing $Mo^{4+}$ ions only: it has been shown in Refs. (*8*, *9*) that $N_2O$ adsorption at 300 K was not accompanied by an appreciable change in intensity of the $Mo^{5+}$ EPR signal. At the same time oxidation of $Mo^{4+}$ at temperatures higher than 150 K occurred quantitatively:

$$Mo^{4+} + N_2O \rightarrow Mo^{6+} + O^{2-} + N_2.$$

If the number of $N_2O$ molecules adsorbed by a photoreduced catalyst was approximately equal to $N_{Mo^{4+}}$, it was completely deactivated (Table 2).

An analogous situation was found when a catalyst was poisoned by NO adsorption, if $N_{NO(ads.)} \gg N_{Mo^{4+}}$. In this case as a first step, the reaction proceeded as

$$Mo^{4+} + NO \rightarrow Mo^{6+} \ldots NO^{2-},$$

resulting in the formation of paramagnetic complexes, $Mo^{6+} \ldots NO^{2-}$, which could be detected by EPR (*8*, *12*). Then further transformation occurred according to the scheme

$$Mo^{6+} \ldots NO^{2-} + NO \rightarrow N_2O + Mo^{6+} + O^{2-}.$$

However, if $N_{N_2O} < N_{Mo^{4+}}$ or $N_{NO} < N_{Mo^{4+}}$, the activity of the catalyst partially remained. Moreover, it turned out that TON ($Mo^{4+}$) calculated for the remaining $Mo^{4+}$ ions in the poisoned catalyst were just the same as those for ions in the unpoisoned samples. These results appear to be a good illustration of the high homogeneity of $Mo^{4+}$ ions in photoreduced catalysts. They also clearly support the conclusion made above on the involvement of $Mo^{4+}$ ions in the propylene metathesis reaction.

### *Catalytic Activities of Mo/SiO$_2$ Thermally Reduced in CO or H$_2$*

$Mo^{6+}/SiO_2$ catalysts having low loading of $Mo^{6+}$ ions (up to 1–2%) are hard to reduce by carbon monoxide at 673–773 K. Our preliminary experiments showed that to produce appreciable amounts of reduced molybdenum ions, circulation of the CO gas through the catalyst layer and simultaneous freezing out of $CO_2$ formed in a cold trap (77 K) should be applied.

In Table 1 specific activities (TON ($\Sigma$ Mo)) for catalysts thermally reduced in CO or $H_2$ are given. It follows from these data that: (1) at approximately the same duration of prereduction, activities of the Mo/SiO$_2$ samples reduced in CO were 10–20 times higher than that of the catalyst reduced in $H_2$; (2) raising the temperature of preliminary pretreatment from 773 to 1073 K resulted in an increase in TON ($\Sigma$ Mo) for

TABLE 2

Poisoning of the Catalytic Activity of Photoreduced Mo/SiO$_2$ Samples

| Oxidizing molecule | Initial number of $Mo^{4+}$ ions in catalyst sample | Number of oxidizing molecules adsorbed by catalyst sample | Remaining $Mo^{4+}$ in catalyst sample | Specific activity ($s^{-1}$)[a] | |
|---|---|---|---|---|---|
| | | | | TON ($\Sigma$ Mo) | TON ($Mo^{4+}$) |
| $O_2$ | $1.8 \times 10^{18}$ | $1.8 \times 10^{18}$ | None | No activity | |
| $N_2O$ | $1.1 \times 10^{18}$ | $1.2 \times 10^{19}$ | None | No activity | |
| $N_2O$ | $7.2 \times 10^{18}$ | $2.5 \times 10^{18}$ | $4.7 \times 10^{18}$ | 0.22 | 0.55[b] |
| NO | $1.4 \times 10^{18}$ | $1.7 \times 10^{18}$ | None | No activity | |
| NO | $6.3 \times 10^{18}$ | $5.0 \times 10^{18}$ | $1.3 \times 10^{18}$ | 0.04 | 0.53[b] |

[a] At room temperature.

[b] Initial pressure of $C_3H_6$ was 65 Torr.

samples reduced in CO and had practically no effect on the activity of $Mo/SiO_2$ reduced in $H_2$.

It was impossible for us to calculate TON ($Mo^{4+}$) for thermally reduced catalysts since the number of $Mo^{4+}$ ions ($N_{Mo^{4+}}$) could not be determined in the same simple manner as was done for photoreduced catalysts (by measuring the amounts of $CO_2$ evolved or $O_2$ required for oxidation). This is associated with the following reasons. On one hand, in contrast to photoreduction, the thermal reduction process proceeds nonselectively and leads to the formation of considerable amounts of molybdenum ions having oxidation states different from 4+. Indeed, in a number of papers using EPR (*13–15*), UV–visible optical spectroscopy (*14, 15*), and XPS (*13, 16*), it has been shown that upon heating of $Mo^{6+}/SiO_2$ with molybdena loadings less than 8 wt% in $H_2$ or CO atmosphere at 673–873 K, $Mo^{5+}$ and $Mo^{4+}$ ions in tetrahedral and octahedral coordinations were produced in various proportions. The results of the present study confirmed this conclusion.

On the other hand, in addition to reduction at 773 K in CO, the reaction of CO disproportionation (Boudouard reaction: $2CO \rightleftarrows C + CO_2$) gave a substantial or sometimes even prevailing contribution to the $CO_2$ formation. This may explain why in some cases (see Table 1) the degree of reduction of molybdenum ions, when calculated by the amount of $CO_2$ evolved, considerably exceeded 100%.

It should be noted that the Boudouard reaction occurred more extensively on the samples preheated at 773 K and resulted in the formation of surface carbon species. Therefore it seems reasonable to assume that lower catalytic activities of $Mo/SiO_2$ (773 K), compared to those of $Mo/SiO_2$ (1073 K), might be due to slower diffusion of the olefin molecules to active sites through a thicker carbon film in the case of the former catalyst or to a reduction in the number of sites by the carbon poison.

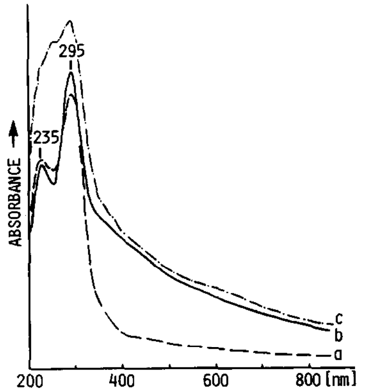


Fig. 7. Diffuse reflectance spectra of $Mo/SiO_2$ sample: (a) unreduced; (b) thermally reduced at 773 K in $H_2$; (c) after $C_3H_6$ admission ($P$ = 35 Torr) to the sample (b) at room temperature.

Optical spectra of the thermally reduced and photoreduced $Mo/SiO_2$ samples differ drastically. As is seen from Fig. 7b, in the spectrum of the sample which was thermally reduced in $H_2$ at 773 K there is no distinct absorption bands associated with reduced molybdenum species. As compared to the spectrum of the unreduced sample (Fig. 7a), which is characterized by two well-developed charge transfer bands $O^{2-} \rightarrow Mo^{6+}$ (at 295 and 235 nm), in the reduced catalyst there is only more or less uniform increase in light absorption in the range 350–850 nm.

In conclusion, it should be briefly pointed out that NO adsorption on $Mo/SiO_2$ (1073 K) thermally reduced in CO also resulted in full deactivation of the samples. Thus, thermally reduced and photoreduced catalysts behave similarly on poisoning by oxidizing gases.

### *Comparison of Activities of Silica–Molybdena Catalysts Activated in Different Ways*

The data on activities of different silica–molybdena catalysts for the propylene metathesis reaction are summarized in Table 3. As a measure of activity TON ($\Sigma$ Mo) were used, since in our opinion this parameter can most objectively characterize the reactivity of the catalysts.

Some comments on Table 3 should be

TABLE 3

Comparison of Activities of Silica–Molybdena Catalysts for the Propylene Metathesis Reaction

| Catalyst | Activation pretreatment | Reaction temp (K) | Initial $C_3H_6$ pressure (Torr) | TON ($\Sigma$ Mo) ($s^{-1}$) | Ref. |
|---|---|---|---|---|---|
| $Mo^{6+}/SiO_2$ | Photoreduction at 300 K in CO | 300 | 85 | 0.42 | This work |
| $Mo^{6+}/SiO_2$ | Thermal reduction at 773 K in CO | 300 | 64 | 0.07 | This work |
| $Mo^{6+}/SiO_2$ | Thermal reduction at 773 K in $H_2$ | 300 | 48 | 0.003 | This work |
| | | 363 | 120 | 0.007 | (*4*) |
| $Mo(\eta_3\text{-}C_3H_5)_2/SiO_2$ | No pretreatment | 363 | 120 | 0.17 | (*4*) |
| $Mo^{4+}/SiO_2$ | Oxidation of $Mo(\eta_3\text{-}C_3H_5)_2/SiO_2$ | | | | |
| | At 673 K in $O_2$, reduction in $H_2$ | 363 | 120 | 0.13 | (*4*) |
| | At 723 K and oxidation at 300 K in $O_2$ | 273 | 21 | 0.075 | (*17*) |

made. It is seen that the activities of photoreduced samples much exceed those of $Mo/SiO_2$ activated by thermal reduction. Note that in this study we did not try to reach the highest possible TON ($\Sigma$ Mo). Evidently, there exist some reserves for this (for instance, an increase in degree of reduction up to ~100% is, in principle, possible).

By photoreduction it became possible to obtain catalysts even more active than those containing "anchored" organomolybdenum complexes. The data in Table 3 demonstrate that even the most active $Mo(\eta_3\text{-}C_3H_5)_2/SiO_2$ is considerably inferior in this respect to photoreduced $Mo/SiO_2$. As was shown in Refs. (*4*, *17*), organic ligands could be removed from $Mo(\eta_3\text{-}C_3H_5)_2/SiO_2$ by an oxidizing–reducing treatment (see Table 3), and thus surface $Mo^{4+}$ ions were produced in a very selective way. However, for these catalysts TON ($\Sigma$ Mo) were also found to be smaller than those for photoreduced silica–molybdena.

It seems that the higher activities of photoreduced catalysts might be connected with the following two reasons. First, due to a higher selectivity of the photoreduction process it is possible to produce much higher concentrations of coordinatively unsaturated $Mo^{4+}$ ions which are active in the metathesis reaction. Second, some specific features of photoreduced $Mo^{4+}$ ions must be taken into account. This may be illustrated by the difference in behavior of photoreduced and thermally reduced $Mo/SiO_2$ samples toward olefin molecules. Propylene adsorption on photoreduced $Mo/SiO_2$ samples at room temperature caused drastic changes in their optical spectra (Fig. 6b). The sample turned to a deep dark-blue color which appears to be evidence for the formation of $C_3H_6$ $\pi$-complexes with $Mo^{4+}$ ions. These complexes are very stable: $C_3H_6$ desorption *in vacuo* was found to occur only at temperatures as high as 573–623 K. After desorption the original optical spectrum of $Mo/SiO_2$ was regenerated.

The products of the propylene metathesis (ethylene and 2-butene) also yielded stable complexes with $Mo^{4+}$ ions, which were destroyed at 573–623 K. Figure 6c shows the spectrum of a $Mo^{4+} \ldots C_2H_4$ complex. It is very similar to that of the $Mo^{4+} \ldots C_3H_6$ complex, although the maxima of the absorption bands in Fig. 6c are slightly shifted toward the blue region. This shift may be interpreted as due to an enhancement of the ligand field caused by ethylene adsorption.

Strong olefin chemisorption in the coordination sphere of $Mo^{4+}$ ions is likely to be accompanied by considerable activation of these molecules. This might be a reason for the increase in their catalytic conversion rates. In contrast to photoreduced samples, after admission of $C_3H_6$, thermally reduced catalysts exhibited only small changes in the UV–visible spectra (Fig. 7). Possibly, this may be associated with lower concentrations of coordinatively unsaturated $Mo^{4+}$ ions in these samples and/or with their coordinative nonuniformity.

The higher TON ($Mo^{4+}$) observed for photoreduced silica–molybdena catalysts, compared to TON ($Mo^{4+}$) of $Mo^{4+}/SiO_2$, prepared by an oxidizing–reducing treatment of $Mo(\eta_3\text{-}C_3H_5)_2/SiO_2$, allow us to assume that there exists a qualitative difference in the properties of molybdenum ions having the same formal oxidation state 4+. Note that in Ref. (*4*) olefin chemisorption on catalysts with anchored molybdenum complexes has not been reported.

Finally, in connection with the high activities of photoreduced $Mo/SiO_2$ catalysts the work of Anpo *et al.* (*18*) should be mentioned, in which upon UV irradiation of $MoO_3$ supported on porous Vycor glass in the presence of propylene the metathesis reaction was found to occur. Unfortunately, TON ($\Sigma$ Mo) were not given in Ref. (*18*). Therefore, to carry out a direct comparison of the catalysts pre-photoreduced in CO and irradiated in $C_3H_6$ atmosphere we reproduced the data of Anpo *et al.* (*18*) for $Mo/SiO_2$ samples used in this study (Fig. 8). It turned out that the rates for the propylene metathesis over prereduced samples were appreciably higher than those for samples under continuous irradiation of $Mo^{6+}/SiO_2$ in $C_3H_6$. In addition, in the latter case the reaction rates were found to decrease drastically when the light was switched off. This fact was explained in Ref. (*18*) by a hypothetical reaction scheme including the interaction of an excited complex $[Mo^{5+} \ldots O^-]^*$ with a $C_3H_6$ molecule to yield an unstable intermediate.

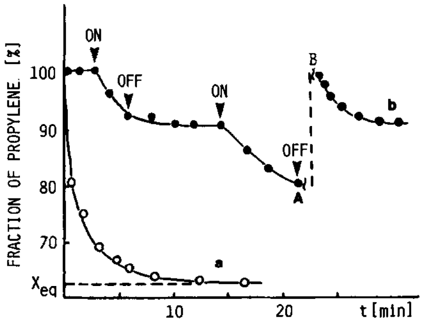


FIG. 8. Kinetics of the propylene metathesis reaction at room temperature: (a) over $Mo/SiO_2$ prephotoreduced in CO; (b) over unreduced $Mo/SiO_2$ upon UV irradiation in the presence of $C_3H_6$. Arrows show the moments when light was switched on or off. Initial propylene pressures were 80–84 Torr. At point A the reaction mixture was evacuated and a new portion of $C_3H_6$ was introduced (point B). $X_{eq}$ is the equilibrium propylene fraction in reaction mixtures.

## CONCLUSIONS

The main conclusion which can be drawn from the results presented in this paper is that preliminary photoassisted reduction is an effective way to activate silica–molybdena catalysts. By means of photoactivation such high activities could be reached as to put this simple and easily available system on a par with the best heterogeneous molybdenum-containing catalysts known so far.

Another important advantage of photoactivated catalysts should also be emphasized: they provide better possibilities for more detailed mechanistic study of the metathesis reaction and for investigation of active sites. Due to the high homogeneity of $Mo^{4+}$ ions in photoreduced catalysts and owing to the possibility of regulating the valence states of reduced molybdenum ions while varying the wavelength of active light, we were able in the present study to develop reliable arguments in favor of the involvement of low-coordinate $Mo^{4+}$ ions in propylene metathesis.

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