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Characterization of Supported Mo(VI)/SiO_2

The Effects of Water Leaching and Support Dehydroxylation

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Two series of Mo(VI)/SiO_2 catalysts were obtained by impregnation with $(NH_4)_6Mo_7O_{24}$ aqueous solutions (impregnated catalysts) and by reaction of $Mo(\eta^3\text{-}C_3H_5)_4$ with OH groups of the SiO_2 surface (fixed catalysts). For each series, the effect of water leaching both on the UV diffuse reflectance spectra and on the photocatalytic properties in the partial oxidation of propane by O_2 were studied. The fractional amount of water-leachable Mo increases with the Mo content for both series of samples but it is significantly higher for the fixed catalysts. An increase in the pretreatment temperature of the SiO_2 support prior to $Mo(\eta^3\text{-}C_3H_5)_4$ fixation increases the percentage of water-removable Mo and indicates that the amount of nonleachable Mo species is associated with the surface OH present on the SiO_2. The nonleachable deposits always contain a large fraction of isolated species with tetrahedral Mo coordination as evidenced by the predominance of the 250-nm band in the UV spectra and in agreement with the photocatalysis results. Conclusions are drawn regarding the structure of the Mo(VI) phase supported on SiO_2.

INTRODUCTION

Transition metal oxides supported on various inorganic oxide supports are widely used as industrial catalysts and have been the object of fundamental research aimed at relating the surface chemistry with their catalytic functions. In this connection several surface models are proposed for supported molybdena catalysts that range from epitaxial surface monolayer to a support surface pimpled with molybdenum polyanion clusters (*1–6*). Because of the acidic character of the aqueous molybdate solutions (pH 5 to 6) used in the catalyst preparation by impregnation methods, the polymeric molybdenum species such as polymolybdate anions present in these solutions are bound to the support surface intact and then polymerize or depolymerize during calcination (*4–8*). In general, it was argued that the heterogeneous and ill-defined nature of the catalysts prepared by impregnation makes them unsuitable for molecular level studies of the relation between their catalytic properties and their surface structure.

A new family of supported transition metal oxide catalysts recently described in the literature is prepared using the facile reaction of superficial OH groups of the support with various organometallic compounds (*9, 10*). It has been claimed that the surface of such catalysts bears a uniform distribution of a single species, the structure of which can be controlled by changing the type of organometallic compound utilized in the synthesis. For example, supported molybdenum catalysts with various structural modifications could be obtained by using $Mo(\eta^3\text{-}C_3H_5)_4$, $Mo_2(\eta^3\text{-}C_3H_5)_4$, $Mo(C_4H_7)_4$, $[Mo(OC_2H_5)_5]_2$, etc. (*8–17*). ESCA studies (*18, 19*) and oxygen chemisorption data (*19, 20*) reveal a greater dispersion of the molybdenum in $Mo(\eta^3\text{-}C_3H_5)_4$-prepared SiO_2 catalysts compared to the impregnated ones. The formation of crystalline MoO_3 was observed in Mo/SiO_2-impregnated catalysts around 2 wt% Mo by Raman spectroscopy and around 5 wt% Mo

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by XRD, whereas the corresponding $Mo(\eta^3\text{-}C_3H_5)_4$-prepared catalysts did not show these spectral features of MoO_3 (*19*). Even at very low loadings (~1 wt% Mo) at least three types of Mo in different environments are observed in Mo/SiO_2-impregnated catalysts compared to the catalysts prepared by $Mo(\eta^3\text{-}C_3H_5)_4$, where only one type of Mo species is suggested (*12–14*). The UV diffuse reflectance spectra of the latter catalysts exhibited only a single band centered at 290 or 303 nm depending on the silica variety used. These bands were assumed to be characteristic of the charge transfer band $Mo^{6+}{=}O^{2-} \rightarrow Mo^{5+}{-}O^{-}$ with Mo in tetrahedral and octahedral symmetry, respectively (*12–14*). On the basis of EXAFS data, however, the 303-nm band was attributed to pentacoordinated or distorted tetrahedrally coordinated Mo (*21*).

Similarly, on the Mo/Al_2O_3 fixed catalysts the single band observed at 281 or 333 nm, depending on the alumina variety, was assigned to tetrahedral and octahedral Mo, respectively (*15–17*).

With respect to photocatalytic properties for the partial oxidation of propane by O_2, Mo/SiO_2 catalysts prepared by impregnation with $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ and by fixation of $Mo(\eta^3\text{-}C_3H_5)_4$ did not exhibit a significant difference below 1 wt%, and it was argued that with both preparative procedures Mo polymerizes on the support. The only difference between the two types of catalysts appears at loadings in excess of 1 wt% and is related to the polymeric phase of Mo with the fixed catalysts having a greater dispersion (*20, 22*) suggesting different structures for the polymeric phase.

Interaction of Mo species with SiO_2 and Al_2O_3 supports is known to be reversible to various degrees depending on loading, preparative procedure, and type of support used. Indeed, even after calcination, sizeable fractions of these supported species can be removed by washing with demineralized water or diluted NH_4OH (*20, 23–27*).

Considerable differences of opinions exist regarding the structure of the molybdenum species present on Mo/SiO_2-fixed catalysts and the interpretation of their UV spectroscopic data. The present communication intends to address these, with a look at the effect of the support dehydration temperature and water leaching on the UV spectra and the photocatalytic activity of these catalysts.

EXPERIMENTAL

Catalyst Preparation

Three series of Mo/SiO_2 catalysts were prepared using commercial grade silica gel (Fisher, S-662) with 99.9% minimum purity. The particle size range of SiO_2 was 60–200 mesh and its surface area was 450 m^2/g.

The first series was prepared by the conventional pore volume impregnation technique (impregnated catalysts) using aqueous solutions (pH around 5 to 6) of high purity $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Anachemia, Ac-630). The main impurities of ammonium paramolybdate were Pb (0.001%) and Mg (0.02%).

The second series of catalysts was made by the reaction between the superficial OH groups of the SiO_2 support and $Mo(\eta^3\text{-}C_3H_5)_4$ complex in *n*-pentane (certified, Fisher, P-393) at ambient temperature (fixed catalysts.) The synthesis of $Mo(\eta^3\text{-}C_3H_5)_4$ as well as the fixation reaction were carried out strictly under oxygen- and humidity-free conditions (*22, 23*). The OH group population of the SiO_2 support was controlled by an *in situ* thermal treatment under a stream of flowing argon (high purity, 99.996%, Linde) at a constant temperature of 200, 300, 400, or 500°C, for 8 h.

The third series was derived from the impregnated and fixed catalysts by leaching them with demineralized water at room temperature.

The leaching procedure was as follows: 1 g of a catalyst sample precalcined in air (500°C, 15 h) was added to 50 ml of demineralized water and the mixture was periodically agitated. After 24 h the water was separated and analyzed for Mo by UV spectroscopy (Hewlett–Packard 8450 UV/VIS spectrophotometer). The detection limit of Mo by this procedure was found to be about 5 ppm. This operation was repeated at least 4 to 6 times until no Mo was detected in the washing solution. It may be estimated that the mass of Mo lost in the last washing was lower than 0.02 wt% of the catalyst sample.

All catalysts were calcined in air at 500°C for 15 h prior to their utilization. The molybdenum contents were determined by X-ray fluorescence (Ortec System) using a ^{241}Am–Ag source and are expressed as weight percents of Mo(wt% Mo).

Reference to the various samples is given by the letter I for impregnated catalysts and F for fixed catalysts followed by the molybdenum loading and, in the case of fixed catalysts, by the support pretreatment temperature. Washed samples are indicated by the symbol W at the end. For example, F-0.35-200W means a washed fixed sample having 0.35 wt% of Mo and prepared from SiO$_2$ preheated at 200°C. Table 1 gives the list of catalysts and percentage of water-removable molybdenum.

Photocatalytic Activity Measurements

The effect of the support dehydration temperature of fixed catalysts and the effect of water leaching of these catalysts on their photocatalytic activity for the partial oxidation of propane (Instrumental grade, 99.5%, Canadian Liquid Air) were studied. The photooxidation reaction was carried out in a differential dynamic reactor under atmospheric pressure in the presence of oxygen

TABLE 1

Mo Contents of Mo(VI)/SiO$_2$ Catalysts before and after Water Leaching

Catalysts before leaching		Catalysts after leaching		Percentage of water-leachable Mo
Sample	Molybdenum loading (wt%)	Sample	Molybdenum loading (wt%)	
I-0.5	0.50	I-0.22W	0.22	56.0
I-0.75	0.75	I-0.29W	0.29	61.3
I-1	1.00	I-0.34W	0.34	66.0
I-2	2.00	I-0.4W	0.40	80.0
I-4	4.00	I-0.63W	0.63	84.3
I-6	6.00	I-0.95W	0.95	84.2
I-10	10.00	I-1.85W	1.85	81.5
F-0.17-200	0.17	F-0.05-200W	0.05	70.6
F-0.38-200	0.38	F-0.1-200W	0.10	73.7
F-0.53-200	0.53	F-0.12-200W	0.12	77.3
F-0.60-200	0.60	F-0.15-200W	0.15	75.0
F-0.63-200	0.63	F-0.14-200W	0.14	77.8
F-1-200	1.00	F-0.21-200W	0.21	79.0
F-1.6-200	1.60	F-0.25-200W	0.25	84.4
F-1.7-200	1.70	F-0.29-200W	0.29	82.9
F-2-200	2.00	F-0.35-200W	0.35	82.5
F-3.35-200	3.35	F-0.49-200W	0.49	85.4
F-4.1-200	4.10	F-0.48-200W	0.48	88.3
F-5.2-200	5.20	F-0.64-200W	0.64	87.7
F-0.44-500	0.44	F-0.06-500W	0.06	86.4
F-2.64-500	2.64	F-0.11-500W	0.11	95.8
F-2.64-400	2.64	F-0.2-400W	0.20	92.4
F-2.85-300	2.85	F-0.34-300W	0.34	88.1

(inert, 99.6%, Linde) and helium (inert, 99.995%, Linde). The total flow rate was 15 cm^3/min and the partial pressures of propane, oxygen, and helium were 305, 200, and 255 Torr (1 Torr = 133.3 N m^{-2}), respectively (*22*). The catalyst (200 mg) was irradiated by a 1000-W xenon lamp (Hanovia, L5179-000) equipped with an ozone-free envelope (emission essentially above 280 nm) and a water filter. The reactants and products were quantitatively analyzed using two gas chromatographs, equipped with a TC and a FI detector, respectively.

Spectroscopy

The catalysts were characterized by UV diffuse reflectance spectroscopy using a Perkin–Elmer Model 559 UV-VIS spectrophotometer equipped with a diffuse reflectance attachment B258. The catalyst samples were prepared in the form of disks by grinding and compressing the catalysts with a force of 10,000 lbs. Spectra were recorded in the range 210–460 nm against a SiO_2 reference.

As shown recently (*8*), the UV diffuse reflectance spectra of SiO_2 supported Mo(VI) are much affected by exposure to water vapor after calcination. In particular with low Mo loadings, the band at 320–330 nm attributed to Mo species in octahedral oxygen coordination appears only after exposure to water vapor. Therefore, the spectra reported in this paper were obtained for samples having been stabilized in air at room temperature for at least 2 weeks after calcination.

All UV diffuse reflectance spectra are reported in terms of the modified Kubelka–Munk function suggested by Kortüm (*28*):

$$F(R'_{\infty,\mathrm{Mo}}) = F(R'_{\infty,\mathrm{sample}}) - F(R'_{\infty,\mathrm{SiO_2}}),$$

with the Kubelka–Munk functions $F(R'_{\infty,\mathrm{sample}})$ and $F(R'_{\infty,\mathrm{SiO_2}})$ given by

$$F(R'_\infty) = \frac{(1 - R'_\infty)^2}{2R'_\infty}.$$

The absolute diffuse reflectance values $R'_{\infty,\mathrm{sample}}$ and $R'_{\infty,\mathrm{SiO_2}}$ were calculated by means of the equations

$$R'_{\infty,\mathrm{sample}} = \left[\frac{R'_{\infty,\mathrm{sample}}}{R'_{\infty,\mathrm{SiO_2}}}\right] \times \left[\frac{R'_{\infty,\mathrm{SiO_2}}}{R'_{\infty,\mathrm{MgO}}}\right] \times R'_{\infty,\mathrm{MgO}},$$

$$R'_{\infty,\mathrm{SiO_2}} = \left[\frac{R'_{\infty,\mathrm{SiO_2}}}{R'_{\infty,\mathrm{MgO}}}\right] \times R'_{\infty,\mathrm{MgO}},$$

where

$\left[\frac{R'_{\infty,\mathrm{sample}}}{R'_{\infty,\mathrm{SiO_2}}}\right]$ = experimentally determined reflectance of the catalyst sample relative to SiO_2

$\left[\frac{R'_{\infty,\mathrm{SiO_2}}}{R'_{\infty,\mathrm{MgO}}}\right]$ = experimentally determined reflectance of the SiO_2 relative to MgO

$R'_{\infty,\mathrm{MgO}}$ = absolute reflectance of MgO (*29*)

RESULTS AND DISCUSSION

Effect of Water Leaching

A major part (50 to 90%) of the supported molybdenum can be removed from the SiO_2 support by water leaching. Figure 1 reports the percentage of water-removable Mo as a function of initial Mo loading, both for impregnated and fixed catalysts. The fractional amount of water-leachable molybdenum increases with the Mo content on most of the range covered for both series of samples and it is significantly higher in the case of the fixed catalysts.

The dehydration temperature of the silica support prior to fixation with Mo(η^3-allyl) complex, affects significantly the percentage of water-removable Mo. This is understood as an indication that nonleachable Mo species are associated with the surface OH present on the support before fixation. Increasing the pretreatment temperature causes a decrease in surface OH concentration and therefore less Mo atoms can be fixed by strong Mo–O–Si bonds. Figure 1A shows the percentage of water-leachable Mo as a function of the support pretreatment temperature. The data at 200°C are interpolated from the corresponding curve on Fig. 1. Extrapolation of the curve on Fig. 1A would indicate a complete dehy-

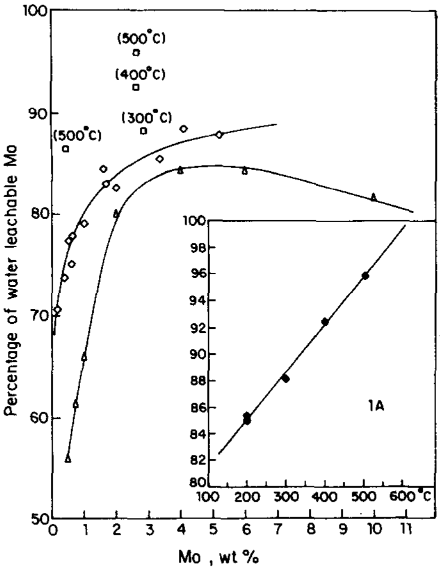

FIG. 1. Percentage of water-leachable Mo as a function of initial Mo loading: (△) impregnated catalysts, (◇) fixed catalysts (T_d = 200°C), (□) fixed catalysts prepared with SiO_2 dehydrated at indicated temperatures. (1A) Percentage of water-leachable Mo as a function of support dehydration temperature (2.7% Mo).

droxylation of SiO_2 only after a pretreatment at a temperature close to 650°C.

The impregnated samples contain more of the nonleachable species in spite of the fact that, at loadings as low as 2%, they contain tiny microcrystals of MoO_3 detected by Lasar Raman spectroscopy. These crystals are segregated at the external surface of the SiO_2 particles, they are not present on fixed catalysts, and they are completely water leachable (*19*).

The UV diffuse reflectance spectra of fixed and impregnated catalysts of various Mo loadings are given in Figs. 2 to 4. In all cases three absorption bands with maxima around 240–245, 290, and 315 nm are observed. The absorption band at 240–245 nm is attributed to Mo^{6+} tetrahedral monomeric species. The band at 290 nm is assigned to the terminal Mo=O groups with low Mo coordination. The band at 315 nm is attributed to the Mo—O—Mo bridging systems of the polymer phase, with Mo in octahedral coordination (*8*, *20*, *22*).

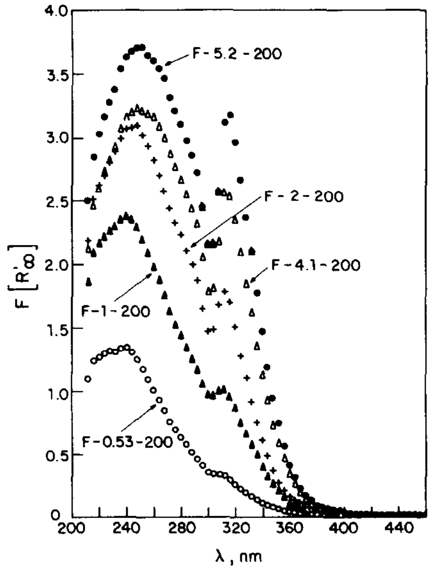

FIG. 2. UV diffuse reflectance spectra of fixed Mo/SiO_2 catalysts of various Mo contents.

Comparing Figs. 2 and 3 shows that at low loadings the bands at 290 and 315 nm are more intense on the impregnated catalysts than on the fixed ones.

Figure 4 illustrates the effect on UV spectra of a change in the support pretreatment temperature. Comparing, for exam-

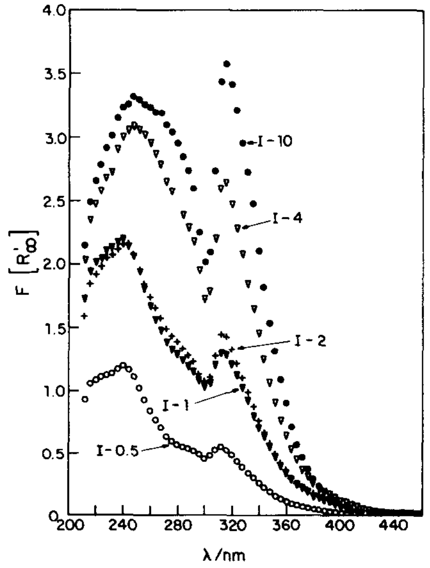

FIG. 3. UV diffuse reflectance spectra of impregnated Mo/SiO_2 catalysts of various Mo contents.

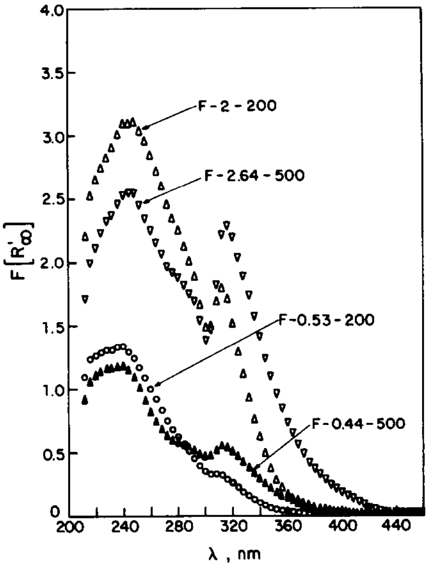

FIG. 4. Effect of support pretreatment temperature on the UV spectra of fixed catalysts of comparable Mo contents.

ple, the spectra of samples F-2-200 and F-2.64-500 shows that the relative intensity of the 240 to 245-nm band decreases whereas the one at 315 nm increases when the pretreatment temperature of the support is raised from 200 to 500°C. The same observation is made at lower loadings when comparing the spectra for samples F-0.53-200 and F-0.44-500. In both cases the band at 290 nm is more pronounced on the F-2.64-500 and the F-0.44-500 spectra, but it is not clear whether this is due to the decrease of the overlapping band at 240–245 nm or to an increase in intensity of the 290-nm band.

It can, however, be concluded from Fig. 4 that as the concentration in surface OH of the support diminishes, so does the proportion of isolated tetrahedral species, more of octahedral polymeric species being formed.

Figures 5 and 6 show the UV spectra of water-leached fixed and impregnated catalysts, respectively. In both cases these spectra show the band at 240 nm as the most pronounced with only a small remainder of the initial 315-nm band (compare with Figs. 2 and 3, respectively). This comparison is illustrated in greater details in Fig. 7, for samples F-0.53-200, I-0.5, and F-0.44-500. The differences between these spectra and those for the corresponding water-leached catalysts (F-0.12-200W, I-0.22 W, and F-0.06-500 W) show that at these low loadings the 290- and 315-nm bands disappear entirely upon leaching. The spectra

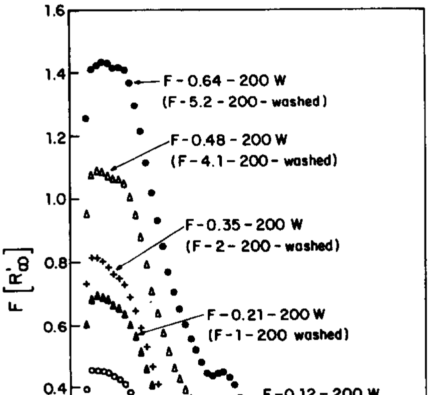

FIG. 5. UV diffuse reflectance spectra of water-leached fixed Mo/SiO₂ catalysts.

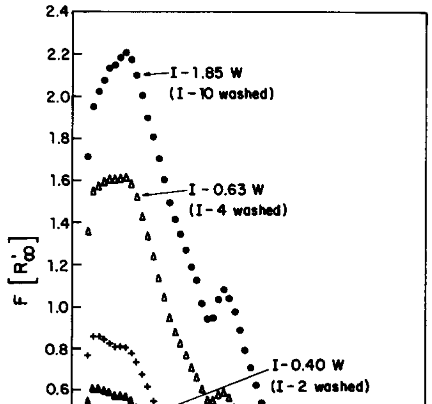

FIG. 6. UV diffuse reflectance spectra of water-leached impregnated Mo/SiO₂ catalysts.

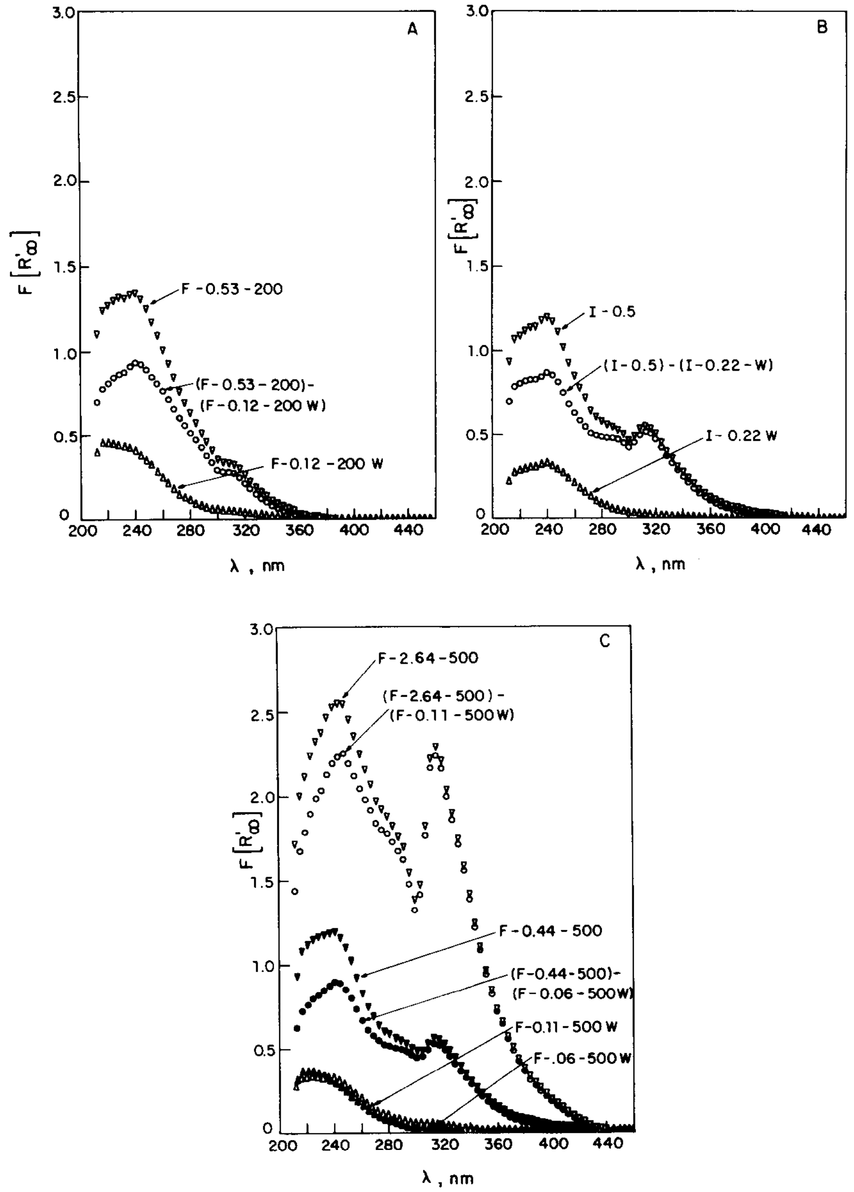

FIG. 7. UV spectra of Mo/SiO_2 catalysts before and after leaching, and their difference spectra: (A) fixed catalysts (T_d = 200°C), (B) impregnated catalysts, (C) fixed catalysts (T_d = 500°C).

for the leached catalysts show that the unleachable Mo species are essentially in tetrahedral coordination. The difference spectra show also that a substantial fraction of the tetrahedral Mo species is water leachable.

Figure 7C gives the spectra for samples F-2.64-500 and its leached daughter F-0.11-500 W. These show that at low OH surface concentration on the support, only a small Mo concentration can be fixed as nonleachable species even though large Mo loadings are realized. In these conditions only isolated tetrahedral species are present in the nonleachable phase. At higher loadings of the leached catalysts prepared by both increasing the initial OH concentration of the support and the Mo initial loading, some octahedral nonleachable species are also observed (see, for example, Fig. 5).

Photocatalytic Oxidation of Propane

(*a*) *Effect of support dehydration temperature.* The steady-state rates of formation of the products of propane photooxidation reaction for Mo/SiO$_2$-fixed catalysts of comparable Mo contents, as a function of support dehydration temperature are given in Figs. 8 to 10. The Mo loading of the catalysts prepared with silica gel pretreated at 500 and 400°C is 2.64 wt% and it is 2.85 wt% for the sample with support pretreated at 300°C. The rates for the 2.64 and 2.85 wt% Mo catalysts made from the 200°C pretreated silica gel were derived from the steady-state rate data given in (*22*), by interpolation.

The oxidation products can be divided into three different groups according to their formation rates as a function of the support dehydration temperature. The rates of formation of CO$_2$, (CH$_3$)$_2$CO, and CH$_3$OH increase up to 400°C and then decrease at 500°C (Figs. 8, 9). They increase continuously for CH$_3$CHO and C$_2$H$_5$CHO (Fig. 10), and in the case of CH$_4$, (CH$_3$)$_2$CHOH, and C$_2$H$_5$OH only minor variations in rate are observed with a possible decrease from 400 to 500°C.

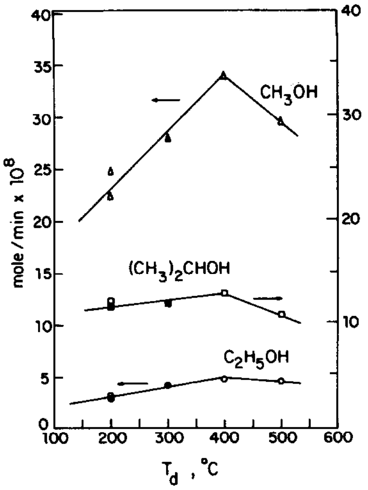

FIG. 9. Steady-state rates of formation of CH$_3$OH, (CH$_3$)$_2$CHOH, and C$_2$H$_5$OH during propane photooxidation on Mo/SiO$_2$-fixed catalysts with comparable Mo contents as a function of support dehydration temperature.

In a recent contribution (*22*), it was proposed that in the photocatalytic oxidation of propane on Mo/SiO$_2$, two mechanisms operate simultaneously. Mechanism No. 1 is responsible for the generation of acetone

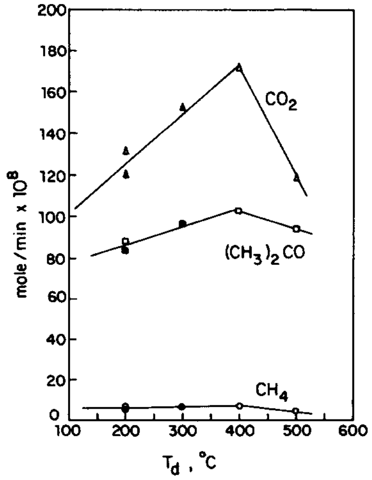

FIG. 8. Steady-state rates of formation of CO$_2$, (CH$_3$)$_2$CO, and CH$_4$ during propane photooxidation on Mo/SiO$_2$-fixed catalysts with comparable Mo contents as a function of support dehydration temperature.

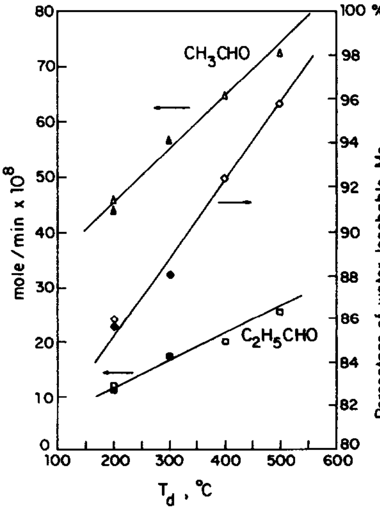

FIG. 10. Steady-state rates of formation of CH$_3$CHO and C$_2$H$_5$CHO during propane photooxidation on Mo/SiO$_2$-fixed catalysts with comparable Mo contents as a function of support dehydration temperature.

TABLE 2

Photocatalytic Oxidation of Propane by O_2 on Mo(VI)/SiO_2: Steady-State Rates of Product Formation

No.	Sample designation	Rate (mol/min × 10^8)							$(CH_3)_2CHOH$ Arbitrary units
		CO_2	CH_3OH	CH_4	CH_3CHO	C_2H_5OH	C_2H_5CHO	$(CH_3)_2CO$	
1	F-2-200	192.0	30.0	12.0	40.2	3.3	10.4	93.5	14.0
2	F-0.35-200W	35.2	3.6	4.9	3.8	N.O.[a]	1.7	14.6	7.0
3	F-0.35-200	88.7	22.0	4.9	11.6	2.5	3.1	50.3	17.3

[a] Not observed.

via the formation of propoxy radicals. When, as in the present study, the light source does not emit at wavelengths below 280 nm, the only site for the formation of propoxy radicals is believed to be the terminal Mo=O group of the polymer phase absorbing at 290 nm. Mechanism No. 2 is responsible for the formation of aldehydes by a route involving propyl and peroxy radicals. The sites for the initiation of mechanism No. 2 are believed to be the Mo—O—Mo bridges with molybdenum in octahedral coordination.

The results presented in Figs. 8–10 are in agreement with these propositions. Figure 10 shows that both rates of propanal and ethanal formation correlate with the amount of water-leachable Mo which is believed to be mostly polymeric molybdate species with Mo in octahedral coordination. As can be easily seen by comparing Figs. 8 and 9 with Fig. 10, the rates of formation of all other products including acetone are not correlated in a simple manner with the content in water-leachable Mo species. In our views this would reflect the complex variation in the concentration of terminal Mo=O species with the changes in dispersion of the Mo polymeric phase as the support pretreatment temperature is varied.

(*b*) *Effect of water leaching.* Table 2 shows typical results for the effect of water leaching of the catalyst on the rates of the photocatalytic partial oxidation of propane under standard conditions. Experiments No. 1 and 2 were conducted in the presence of the photocatalysts F-2-200 and its leached daughter F-0.35-200W. Except for CH_4 and for the minor product isopropanol, the rates of production of other compounds decrease by a factor of 5.5 to 10.7 upon water leaching. This result indicates that most of the Mo species active in photocatalytic oxidation are water leachable.

A further comparison of the results of experiments No. 2 and 3 performed with two fixed catalysts of 0.35 wt% Mo produced by different procedures, is possible from Table 2. Sample F-0.35-200W was produced by water leaching of a 2% Mo sample, whereas F-0.35-200 was obtained by direct fixation of 0.35 wt% Mo. F-0.35-200W is therefore expected to contain mostly monomeric tetrahedral Mo species whereas F-0.35-200 should contain around 70% of water-leachable species, a large fraction of which being polymeric octahedral as well as terminal Mo species.

As with the only exception of CH_4, the rates of generation of the various products of photocatalytic oxidation are much lower (2 to 6 times lower) on F-0.35-200W than on F-0.35-200, it may be safely concluded that the tetrahedral species are not responsible for the observed photocatalytic effect.

This result is in complete agreement with the conclusions of the aforementioned study (*22*).

CONCLUSION

It has been shown that the structure of the Mo(VI) phase supported on SiO_2 can be affected first by the technique of preparation, the fixation technique yielding more leachable species than impregnation. The structure of the fixed catalysts is also dependent on the concentration of surface OH of the support during fixation which can be modified by pretreating the support at various temperatures. Water leaching of both impregnated and fixed catalysts is another means of controlling the surface structure since the polymeric Mo species are almost entirely water leachable. Nonleachable Mo species absorb mostly at 240–250 nm. They are, therefore, considered isolated tetrahedral Mo species, although this assignment is not in full agreement with the literature.

These changes in the structure of the supported molybdic phase are reflected in the photocatalytic properties of the samples in the partial oxidation of propane with oxygen. The photocatalytic results confirm the conclusions of a previous study:

—In the experimental conditions under study, the isolated tetrahedral species do not participate in the photocatalytic process.

—Two different groups in the water-leachable species are, respectively, responsible for the productions of propoxy radicals (terminal Mo═O) and propyl radicals (Mo—O—Mo bridges with Mo in octahedral coordination).

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