JOURNAL OF CATALYSIS **141**, 453–464 (1993)

Characterization and Modeling of the Mo Species in Grafted Mo/SiO_2 Catalysts after Redox Thermal Treatments

CATHERINE LOUIS, MICHEL CHE, AND MASAKAZU ANPO*

*Laboratoire de Réactivité de Surface et Structure, URA 1106 CNRS, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France; and *Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591, Japan*

Received March 25, 1992; revised October 6, 1992

The physicochemical properties of the Mo/SiO_2 catalysts prepared by the grafting method, i.e., by air- and water-free reaction between $MoCl_5$ and hydroxyl groups of silica support followed by a washing step, are compared to those of impregnated Mo/SiO_2 catalysts. Molybdenum solubility and reducibility measurements show that grafted Mo interacts more strongly with silica support than impregnated Mo. Several techniques (Mo^{5+} dispersion measurement by EPR spectroscopy, photoluminescence, methanol oxidation reaction, IR study of CO adsorption) indicate that Mo is better dispersed on the silica surface of grafted samples than of impregnated catalysts. The differences are more important at higher Mo loading (about 1 wt%). On the basis of these results and of those given by the literature, models for the Mo species of the oxidized grafted and impregnated catalysts are proposed. The mechanism of thermal reduction under H_2 is also investigated for grafted Mo/SiO_2 catalysts. An attempt to the rationalization of the changes in the coordination sphere of the Mo^{5+} ions observed by EPR after grafting leads to propose different types of bondings with silica (ionocovalent and coordinative) and to the formation of Mo=O molybdenyl bonds pointing outward.

INTRODUCTION

In earlier works (*1–4*) which were recently reviewed (*5*), the preparation of Mo/SiO_2 catalysts by the grafting method, i.e., by air- and water-free reaction between $MoCl_5$ and hydroxyl groups of silica support followed by a washing step, was described. This reaction was performed in liquid medium (cyclohexane) or in vapor phase. It was shown by EPR and diffuse reflectance spectroscopies that two types of molybdenum are deposited onto silica during the grafting reaction, the first step of the preparation:

(i) Grafted Mo as paramagnetic $\equiv SiOMoCl_4$, where the symbol $\equiv$ designates the three bonds of Si^{IV} with silica.

(ii) Physically adsorbed Mo as a nonparamagnetic Mo_2Cl_{10} dimer; this compound turns blue in air because of its partial oxidation and hydrolysis into molybdenum blues.

In the second preparation step, the sample was washed with water or ammonia solution so as to eliminate the physically adsorbed Mo. The grafted Mo remains bonded to silica but is hydrolyzed and partially oxidized in air, so as to lead to the following species:

$$\equiv SiOMo^{V}(OH)_4 \text{ and } \equiv SiOMo^{VI}(OH)_5.$$

With this preparation method, the bonding between Mo and the support occurs during the grafting reaction at room temperature, whereas with impregnation, the bonding is believed to be formed during calcination at high temperature (*6*), i.e., at a temperature where Mo species can easily migrate onto the support and form aggregates, such as MoO_3. Because of its bonding with the support, molybdenum in grafted catalysts is expected to remain better dispersed than that in impregnated samples even after calcination.

0021-9517/93 $5.00

There is no simple and reliable quantitative method to determine the dispersion of supported oxides. An interesting method has been described by Weller *et al.* for the determination of the dispersion of supported molybdenum on silica (*7–10*). It is based on the determination of the amount of oxygen chemisorbed on reduced catalysts, obtained from the difference between two O_2 adsorption isotherms at 195K, separated by evacuation for 1 hr at 195K. Rodrigo *et al.* (*11*) and Muralidhar *et al.* (*12*) have recently shown that the stoichiometry of the oxygen chemisorption depends on the Mo reducibility, i.e., on the nature of the support and on the preparation method. The results must be therefore interpreted with caution. Another interesting quantitative method was recently proposed by Desikan *et al.* (*13*). It is also based on the oxygen chemisorption, but at a higher temperature, 630K, i.e., at the reduction temperature of the Mo surface species of Mo/SiO_2 catalysts.

A qualitative way for comparing the dispersions of molybdenum is to study the reducibility of the latter and its interaction strength with the support, since these parameters are related to each other. For example, Mo impregnated on alumina is known to be more strongly bonded to the support, better dispersed, and less reducible than Mo impregnated on silica (*11, 12, 14–19*).

In our work, the reducibilities of the grafted and impregnated Mo/SiO_2 catalysts were compared using conventional methods, such as thermogravimetry, hydrogen consumption, and thermoprogrammed reduction. A spectroscopic approach involving different techniques, such as IR, UV–visible diffuse reflectance, EPR, and photoluminescence, was achieved to characterize the interaction between Mo ions in different oxidation states and the silica support and to get another insight into the Mo dispersion. This paper is an attempt to rationalize the results obtained with such different techniques (*1–4, 20–22*). It gives an overview of the characteristics and properties of the grafted Mo/SiO_2 catalysts and compares them to those of impregnated Mo/SiO_2 catalysts.

Models for the Mo species of the oxidized grafted and impregnated catalysts are proposed.

On the basis of the knowledge of the first coordination sphere of the three Mo^{5+} species identified by EPR after thermal reduction of grafted Mo/SiO_2 catalysts (*3, 4, 23, 24*) and of their changes within each other, a model of these species including the second coordination sphere is proposed.

EXPERIMENTAL

Catalyst Preparation

The grafted samples, prepared by a two-step procedure as described in the Introduction and in more detail in (*5*), contain 0.01 to 1.05 Mo wt%. The impregnated samples were prepared from an aqueous solution of ammonium heptamolybdate put in contact with silica. They were dried in air at 80°C with continuous stirring and then calcined in air overnight at 500°C. The Mo loading is between 0.1 to 7 wt%.

The silica Spherosil XOA 400 (400 m^2/g, pore volume = 1.25 cm^3/g, average pore size = 80Å) supplied by Rhône Poulenc (France) was used as support.

Thermal Treatments and Adsorptions

The Mo/SiO_2 catalysts were oxidized under 200 Torr of oxygen at 600°C for 2 hr. The oxygen was evacuated at the same temperature. Then, the samples were reduced under hydrogen at 600°C, either in a closed vessel under 200 Torr of H_2 for 2 hr or under a flow of pure hydrogen. After each treatment, the gas phase was pumped off at 600°C.

Techniques

The description of the techniques which led to results already published can be found in the corresponding papers.

The thermogravimetric experiments were performed with an electrobalance Setaram

Mtb-108 equipped with two quartz vessels containing the pure silica as reference and the sample, respectively. This equipment was connected to a vacuum line. The volumetric experiments were performed using a gauge Texas Instrument-type Bandox which permits the calculation of the hydrogen consumed during the sample reduction in a closed vessel. The water formed during the reduction was trapped by a zeolite. The thermoprogrammed reduction (TPR) experiments were performed with homemade equipment with a heating rate of 7.5°C/min under a mixture of 5% H_2 in argon at a flow rate of 1.6 liters/hr.

In order to conform to the conventions used in solid-state chemistry (*25*), Roman numerals refer to the oxidation states of the ions. However, for reasons of convenience, the formalism of the electric charges is sometime employed, even if the latter do not correspond to the effective charges of the ions.

RESULTS AND DISCUSSION

COMPARED PROPERTIES OF GRAFTED AND IMPREGNATED Mo/SiO$_2$ SAMPLES

Grafted Molybdenum Interacts More Strongly with Silica Than Impregnated Molybdenum

Lower solubility of grafted Mo. Mo grafted onto silica is water resistant (*5*) whereas impregnated Mo is completely solubilized in water and almost completely after calcination (*1–4*), in agreement with the results obtained by Marcinkowska *et al.* (*26*) for impregnated Mo/SiO$_2$. These results indicate that calcination does not lead to the grafting of all the molybdenum impregnated on silica.

Boiling acidic HF-H_2SO_4 mixture completely dissolves silica alone and impregnated Mo/SiO$_2$ samples within a few seconds whereas the grafted Mo/SiO$_2$ is apparently not dissolved after a few minutes (*1–4*). Since the solubility of an oxide gradually increases as one departs from its isoelectric point (*27*), the solubility experiments suggest that the grafted Mo lowers the isoelectric point of the system below that of silica, measured to be around pH 2 (*28*), so as to make the grafted Mo/SiO$_2$ system mostly insoluble in a hot acidic HF-H_2SO_4 mixture. Further experiments are required to probe this hypothesis.

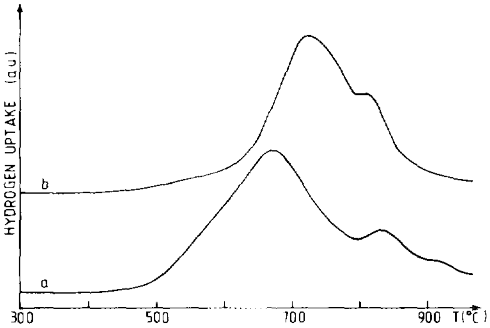


FIG. 1. TPR profiles of Mo/SiO$_2$ catalysts after oxidation under 200 Torr of oxygen at 600°C during 2 hr: (a) impregnated Mo/SiO$_2$ (1.03 wt%), (b) grafted Mo/SiO$_2$ (0.84 wt%).

Lower reducibility of grafted Mo. After reduction at 500°C under hydrogen for 35 hr, the mean oxidation state of Mo measured by volumetry and thermogravimetry is IV for grafted Mo/SiO$_2$ (0.18 wt%) and III to II for impregnated Mo/SiO$_2$ (2 to 7 wt%) (*2–4*). The TPR profiles in Fig. 1 show that the grafted Mo (0.84 wt%) begins to be reduced at a temperature higher than that of the impregnated one (1.03 wt%).

The examination of the carbonyl IR vibration bands arising from CO adsorption on the catalysts reduced at 600°C under hydrogen (*20*) has shown that Mo is present in all the oxidation states from V to 0 for both types of samples (1.06 wt% of grafted Mo, 0.72 wt% of impregnated Mo). A band at 1989 cm^{-1} characteristic of $Mo^0(CO)_6$ results from the gradual segregation of metal clusters by CO. This band is more intense for impregnated Mo/SiO$_2$, indicating a higher reducibility, i.e., there are more numerous and probably larger clusters than in grafted Mo/SiO$_2$.

TABLE 1

Mo^{5+} Dispersion Measurement by EPR Spectroscopy for Grafted and Impregnated Mo/SiO_2 Catalysts

Samples	Mo loading (wt%)	Dispersion (%)
Grafted	0.07	100
	0.18	82
	0.66	95
	1.05	82
Impregnated	0.07	100
	0.17	85
	0.63	78
	1.03	30

Grafted Molybdenum Is More Dispersed Than Impregnated Molybdenum

Higher percentage of Mo^{5+} accessible to oxygen. After thermal reduction of Mo/SiO_2 at 600°C under hydrogen, the oxygen chemisorption at 77K on to Mo^{5+} ions detectable by EPR spectroscopy (paramagnetic $4d^1$ ions) leads to a monoelectronic reduction of oxygen via the following electron transfer reaction:

$$Mo^{5+} + O_2 \rightarrow Mo^{6+}\ O_2^- \quad (1)$$

The decrease in the EPR signal of Mo^{5+} permits the calculation of the percentage of Mo^{5+} ions accessible to oxygen, i.e., the Mo^{5+} dispersion (*1–3*). Table 1 shows that the dispersion of Mo^{5+} ions is higher on the grafted samples than on the impregnated ones. The difference is more drastic for higher Mo loading.

At low Mo loading, all the Mo^{VI} of grafted samples is on the silica surface. A study of the photoluminescence properties of grafted and impregnated Mo/SiO_2 samples has been performed *in situ* on oxidized samples with Mo loading <0.1 wt% (*22*). The analysis of the decay curves of phosphorescence after excitation indicates that the grafted samples possess only one type of Mo-emitting sites, while the impregnated ones contain at least two sites. The emitting site is a tetrahedral dioxomolybdenum species (*29–32*). It may be noted that the octahedral molybdenum species possesses too short a lifetime to be detected (*33–37*). The total quenching of the phosphorescence of grafted samples by CO or O_2 indicates that all the tetrahedral Mo ions are located on the silica surface whereas the incomplete quenching of the phosphorescence of the impregnated samples shows that some tetrahedral Mo ions are not accessible to the gas phase. The likely interpretation (*22*) is that part of the tetrahedral Mo ions of impregnated samples are covered by octahedral Mo species (Table 2).

TABLE 2

Quenching of the Phosphorescence of Grafted and Impregnated Mo/SiO_2 Catalysts by Addition of Oxygen

Mo/SiO_2 catalysts	Oxygen amount (10^{-6} mol/g of catalyst)	Phosphorescence intensity (arbitrary units)
Grafted (0.07 Mo wt%)	Vacuum	63
	4	36
	10	26
	19	19
	29	14
	58	7
	85	0
Impregnated (0.013 Mo wt%)	Vacuum	50
	25	18
	120 or excess	11

TABLE 3

Selectivity of Grafted and Impregnated Mo/SiO_2 Catalysts in the Reaction of Methanol Oxidation Performed at 280°C

Grafted Mo/SiO_2			Impregnated Mo/SiO_2		
Mo loading (wt%)	$S(HCOOCH_3)$ (%)	$S(CH_2O)$ (%)	Mo loading (wt%)	$S(HCOOCH_3)$ (%)	$S(CH_2O)$ (%)
0.07	92	Not detected	0.07	66	24
0.18	94	Not detected	0.17	35	53
0.66	83	10	0.63	73	22
1.05	84	10	0.72	52	43

Methanol oxidation reaction as a test for Mo dispersion. Impregnated and grafted Mo/SiO_2 samples have been tested in methanol oxidation reaction (*21*), which is known to be structure sensitive (*38*, *39*). The higher selectivity in methyl formate for grafted samples compared to impregnated catalysts, whose main product is formaldehyde (Table 3), is explained by their higher Mo dispersion (*21*).

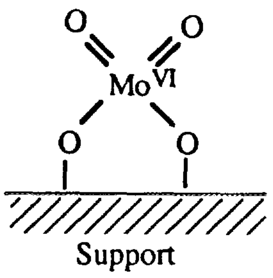
This set of results indicates that grafted molybdenum is less reducible, interacts more strongly with silica, and is more dispersed than impregnated Mo. The differences in Mo dispersion are more important for the highest Mo loadings (about 1 wt%).

Model for the Oxidized Mo/SiO_2 Grafted Samples

The usual model for isolated Mo^{VI} ions in oxidized Mo/Al_2O_3 and Mo/SiO_2 catalysts is a tetrahedral dioxomolybdenum species bonded to the support via two oxygen ligands (e.g., *6*, *13*, *15*, *30*, *40–47*) (Scheme 1).

This model in Mo/SiO_2 catalysts was confirmed by several investigations. On the basis of *in situ* EXAFS and photoluminescence studies, Iwasawa *et al.* (*44*, *45*, *48*) have suggested the presence of MoO_4 dioxo species. The structure was reported to consist of two short Mo=O bonds of distances 0.170 nm and two long Mo-O bonds of distance 0.210 nm. Other photoluminescence studies (*31*, *49*) and theoretical works (*50*) have revealed that the propene metathesis reaction is photoinduced in the presence of Mo/SiO_2 catalysts only if surface tetrahedral dioxo Mo species are present.

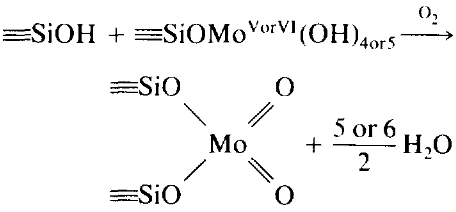
Several authors have recently reconsidered the existence of this species. The analysis of the IR spectra of Mo/SiO_2 samples using isotopic exchange with $H_2{}^{18}O$ led Cornac *et al.* (*51*) to discard the dioxo structure in favor of a mono-oxo structure. The Raman investigations performed by Wachs *et al.* (*52*, *53*) on oxidized Mo/SiO_2 catalysts prepared by different methods (impregnation, grafting with $MoCl_5$ and allylic compounds (*52*), and deposition–precipitation (*53*)) did not show any evidence for the existence of isolated tetrahedral dioxomolybdenum species. Polyoxomolybdates, such as $(Mo_7O_{24})^{6-}$ and $(Mo_8O_{26})^{4-}$, are present in samples hydrated in air, as is MoO_3 for high loadings. Upon dehydration of Mo/SiO_2 catalysts prepared from $Mo_2(\eta_3\text{-}C_3H_5)$ (*52*) or from Mo^{III} deposition–precipitation (*53*),



SCHEME 1

they found that the polyoxomolybdates are transformed into isolated octahedral monooxo Mo^{VI} cations using *in situ* Raman (*52, 53*) and EXAFS data (*53*). It may be noted that Cornac *et al.* (*51*) observed the reverse phenomenon, i.e., the breaking of the Mo-O-X bridge (X = Mo or Si) upon hydration. Desikan *et al.* (*13*) have also characterized oxidized impregnated Mo/SiO_2 samples by *in situ* Raman spectroscopy. They found that the isolated surface Mo species present on their dehydrated catalysts is a distorted tetrahedron in C_{2v} symmetry, with two short Mo=O bonds and two long Mo-O bonds. It may be noted that their *in situ* Raman spectra are different: Wachs *et al.* observed a Raman shift at 994–998 cm^{-1} (*52, 53*) and Desikan *et al.*, one at 955 and 670 cm^{-1} (*13*). The Raman spectra seem to depend on the conditions of sample preparation and of treatment.

The model of tetrahedral dioxo Mo species was found to account for the isolated Mo species of grafted Mo/SiO_2, after oxidizing treatment, on the basis of our photoluminescence results (*22*) described above. However, after the grafting reaction followed by sample washing (*5*), Mo was bound to silica via a single oxygen atom to lead to $\equiv SiOMo^{V}(OH)_4$ and $\equiv SiOMo^{VI}(OH)_5$. These two facts suggest that the second SiO-Mo bond is formed during the oxidizing treatment as a result of the following mechanism:



$$\equiv SiOH + \equiv SiOMo^{V or VI}(OH)_{4 or 5} \xrightarrow{O_2} (\equiv SiO)_2Mo(=O)_2 + \frac{5 \text{ or } 6}{2} H_2O \quad (II)$$

In Fig. 2, a model is proposed for the surface Mo species of oxidized grafted sample containing isolated dioxomolybdenum species and small clusters of octahedral Mo (probably MoO_3, although not detected by DRX). For comparison, a model is also proposed for oxidized impregnated Mo/SiO_2 which gathers the different species identified in the literature (*22, 46, 47, 52, 54, 55*): isolated tetrahedral MoO_4 species in a smaller proportion than those for grafted samples as attested by our results, MoO_3 crystallites, and tetrahedral Mo covered by octahedral Mo. This model concerns dehydrated samples. When the latter is put in air, polymeric Mo species such as silicomolybdic acid (*11, 56*) and/or polyoxomolybdates such as $(Mo_7O_{24})^{6-}$ and $(Mo_8O_{26})^{4-}$ (*51–53*) are formed. The proportion of the different species depends on the Mo loading.

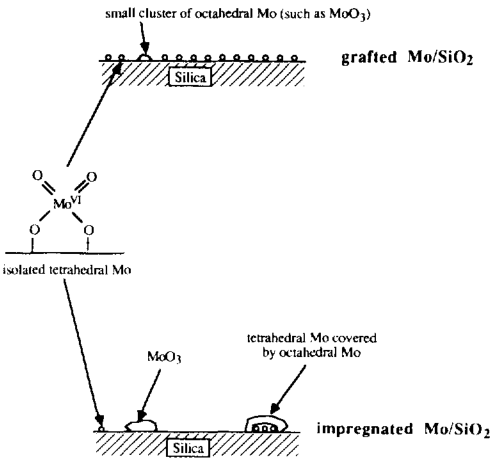


FIG. 2. Models for the Mo species present on oxidized grafted and impregnated Mo/SiO_2 catalysts in dehydrated state.

CHARACTERIZATION OF THE REDUCED Mo/SiO_2 GRAFTED SAMPLES

One of the best techniques to study the coordination sphere of reduced molybdenum is EPR spectroscopy because it deals with the detection of only one Mo oxidation state, the paramagnetic Mo^{5+} ions ($4d^1$) and allows discrimination between different coordinations. EPR spectra of grafted Mo/SiO_2 reduced at 600°C under hydrogen (*3, 4, 23, 24*) have revealed the presence of three types of Mo^{5+} ions (Fig. 3c). The adsorption of probe molecules (H_2O, ^{12}CO, and ^{13}CO) has permitted the characterization of their first

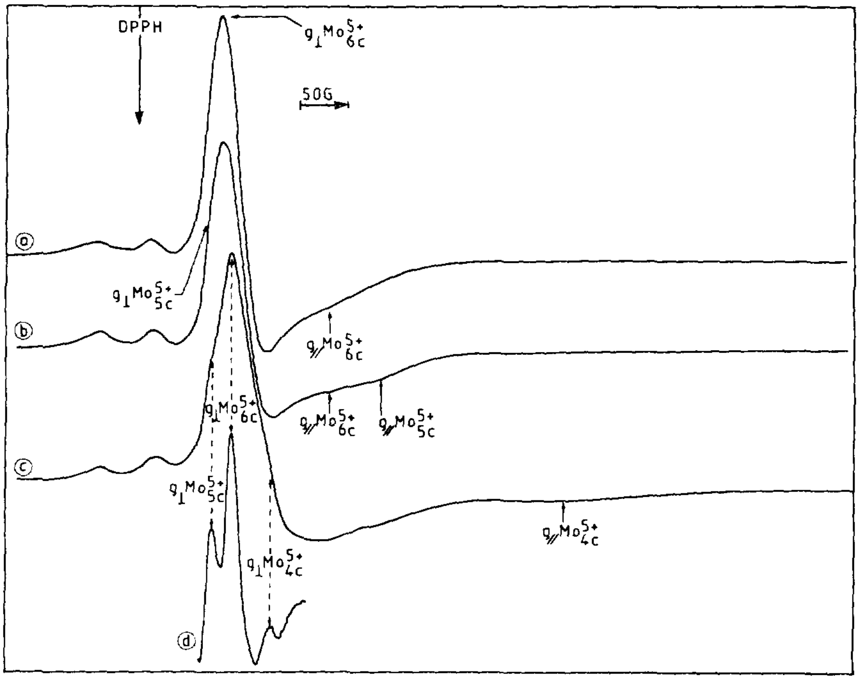
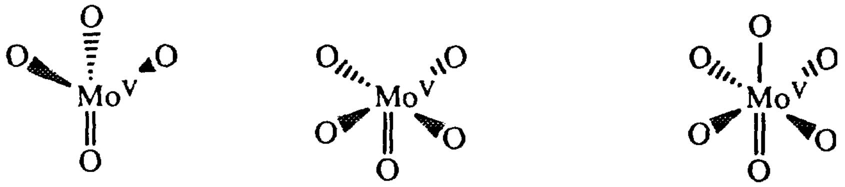


FIG. 3. EPR spectra recorded at 77K of the Mo/SiO$_2$ catalysts prepared by grafting with MoCl$_5$ vapor at 200°C, followed by evacuation: (a) at 200°C for 30 min, (b) at 300°C for 30 min, and (c) at 500°C for 30 min; and (d) third-derivative spectrum of (c). Spectra (c) and (d) may also be obtained after thermal reduction under hydrogen.

coordination sphere (*24*), identified to tetra (Mo^{5+}_{4c})-, penta (Mo^{5+}_{5c})-, and hexacoordinated (Mo^{5+}_{6c}) species, each containing a molybdenyl Mo=O bond (Scheme 2).

The Mo^{5+} spectrum may be observed at the very beginning of the reduction. Upon reduction at 600°C, its intensity passes through a maximum after about 10 hr of reduction and then decreases to reach a plateau after 15 hr while lower oxidation states of Mo are also obtained, as shown above by IR spectroscopy. This result, in agreement with that obtained by Seshadri and Petrakis (*57*) on Mo/γ-Al$_2$O$_3$, suggests that (i) Mo^{5+}

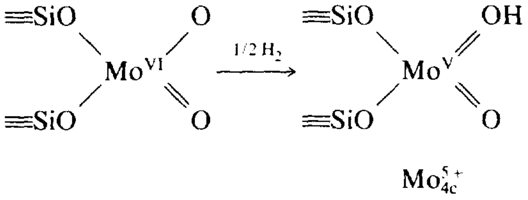


Mo^{5+}_{4c}	Mo^{5+}_{5c}	Mo^{5+}_{6c}
$g_\perp = 1.926$	$g_\perp = 1.957$	$g_\perp = 1.944$
$g_{//} = 1.755$	$g_{//} = 1.866$	$g_{//} = 1.892$

SCHEME 2

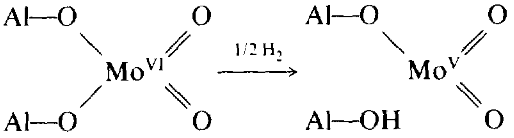
is an intermediate in the reduction path of Mo^{6+} to lower valence states, and (ii) Mo^{5+} is also a residual stable state as indicated by the plateau. It may be noted that the relative abundance of the three Mo^{5+} species is independent on the reduction time (*2*). The Mo^{5+}_{4c} species was detected on grafted $\mathrm{Mo/SiO_2}$ whatever the Mo content (0.18–1.05 wt%) and on impregnated $\mathrm{Mo/SiO_2}$ only when the Mo content was lower than 0.5 wt%.

It is worthwhile to investigate the nature of the ligands beyond the first coordination sphere of Mo^{5+}, i.e., to question how the oxygen ligands bind to silica. The reduction of tetrahedral dioxomolybdenum Mo^{6+} ions may lead to the formation of the tetrahedral Mo^{5+}_{4c} species according to a mechanism analogous to that proposed by Hall and Lo Jacono (*43*) and Giordano *et al.* (*58*) for Mo supported on alumina:



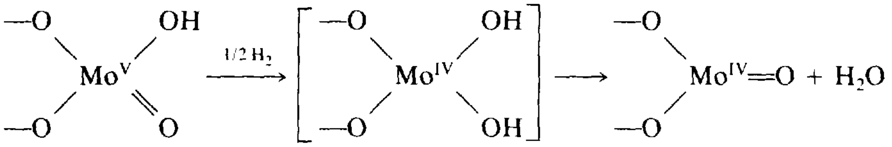
(III)

A recent study by laser Raman spectroscopy on the reduction of $\mathrm{Mo}/\gamma\text{-}\mathrm{Al_2O_3}$ (*59*) has confirmed the existence of the $\mathrm{Mo^V}$-OH species by the presence of the corresponding OH deformation vibration mode. The reduction model in reaction III implies that Mo^{5+}_{4c} is anchored to silica by two bonds and leaves one hydroxyl group and one molybdenyl bond pointing outward from the surface. Seyedmonir and Howe (*46*) have observed by IR a SiO-H vibration band on impregnated $\mathrm{Mo/SiO_2}$ catalysts, whose intensity increases after reduction at 400°C. The increase was attributed to the Si-O-Mo bond cleavage of the polyoxomolybdate phase, producing octahedral Mo^{5+}. They found no evidence for the formation of tetrahedral Mo^{5+} arising from the reduction of isolated tetrahedral Mo^{6+} species. Likewise, Millman *et al.* (*60*) have observed an increase in the Al-OH vibration band during the reduction of $\mathrm{Mo}/\gamma\text{-}\mathrm{Al_2O_3}$ in hydrogen and have suggested that the bond between Mo and the surface oxygen of alumina is broken during reduction:



(IV)

However, the structure of Mo^{5+} in mechanism III is consistent with that of Mo^{5+}_{4c} species which possess an axial symmetry as indicated by its EPR signal. In addition, it may be argued that the increase in the AlO-H (or SiO-H) band intensity may be due to a rehydroxylation of the alumina (or silica) surface owing to the water produced during the reduction. The latter arises from the reduction of Mo^{6+} into Mo^{4+}, according to a reaction also proposed by Hall *et al.* (*43*, *60*) for Mo supported on alumina:

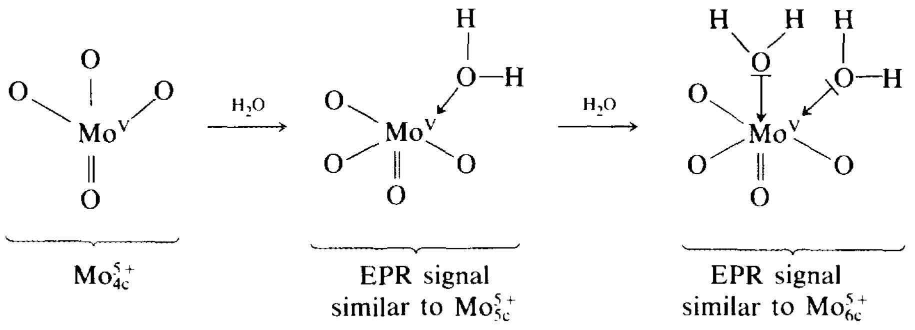


(V)

In consequence, the first step of reduction of grafted $\mathrm{Mo/SiO_2}$, whose main species is an isolated dioxomolybdenum, appears to be the same as that proposed by Hall and Lo Jacono (*43*) (reaction III).

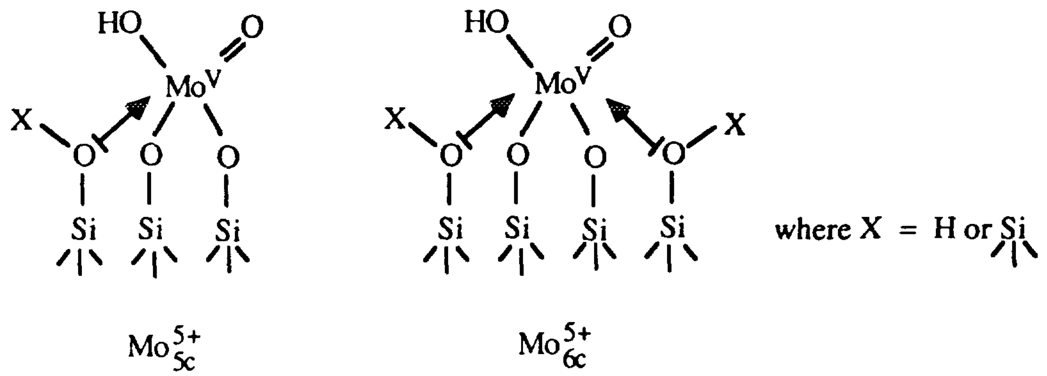
To account for the coexistence of the three Mo^{5+} species after thermal reduction under hydrogen, several remarks need to be made. Their EPR signal has also been observed when a $\mathrm{Mo/SiO_2}$ sample prepared by grafting in vapor phase was submitted to an evacuation at increasing temperatures without any contact with air or water (*4*, *23*). EPR signal, obtained after grafting with $g_\perp$ (1.952) < $g_\parallel$ (1.968) attributed to ≡SiO MoCl$_4$, changes after evacuation at about 200°C (*5*): the $g_\perp$ value becomes larger than $g_\parallel$ due to the replacement of chloride ligands by oxygen ligands (*61*) and the EPR signal shape is similar to that of the Mo_{6c}^{5+} ion. Upon evacuation at 300°C, the signal of Mo_{5c}^{5+} appears and at 500°C, that of Mo_{4c}^{5+} also becomes visible, and the three species coexist (Fig. 3). Another point is that the relative intensity of the Mo_{4c}^{5+} signal increases when the temperatures of reduction and of subsequent evacuation increase (400, 600 and 800°C) (*2*). These experiments show that the formation of vacancies in the Mo^{5+} coordination sphere is favored when the temperature increases.

Conversely, the Mo_{4c}^{5+} signal disappears to the benefit of the increase of the Mo_{5c}^{5+} signal when the sample is left in static vacuum at room temperature for a few hours. In the same way, when water is adsorbed, Mo_{4c}^{5+} is first transformed into a signal similar to that of Mo_{5c}^{5+} which in turn is transformed into one similar to that of Mo_{6c}^{5+} (*23*, *24*). These changes have been interpreted by the admission of a first and then a second water molecule within the Mo_{4c}^{5+} coordination sphere:



(VI)

The binding with H$_2$O molecule is possible via the available doublet of oxygen of the water molecule. The similarity between the signals of hydrated Mo_{4c}^{5+} species and those of Mo_{5c}^{5+} and Mo_{6c}^{5+} means that Mo_{5c}^{5+} and Mo_{6c}^{5+} ions are also bound to one and two oxygen ligands via coordinative bonds, respectively. These oxygen ligands act as H$_2$O



SCHEME 3

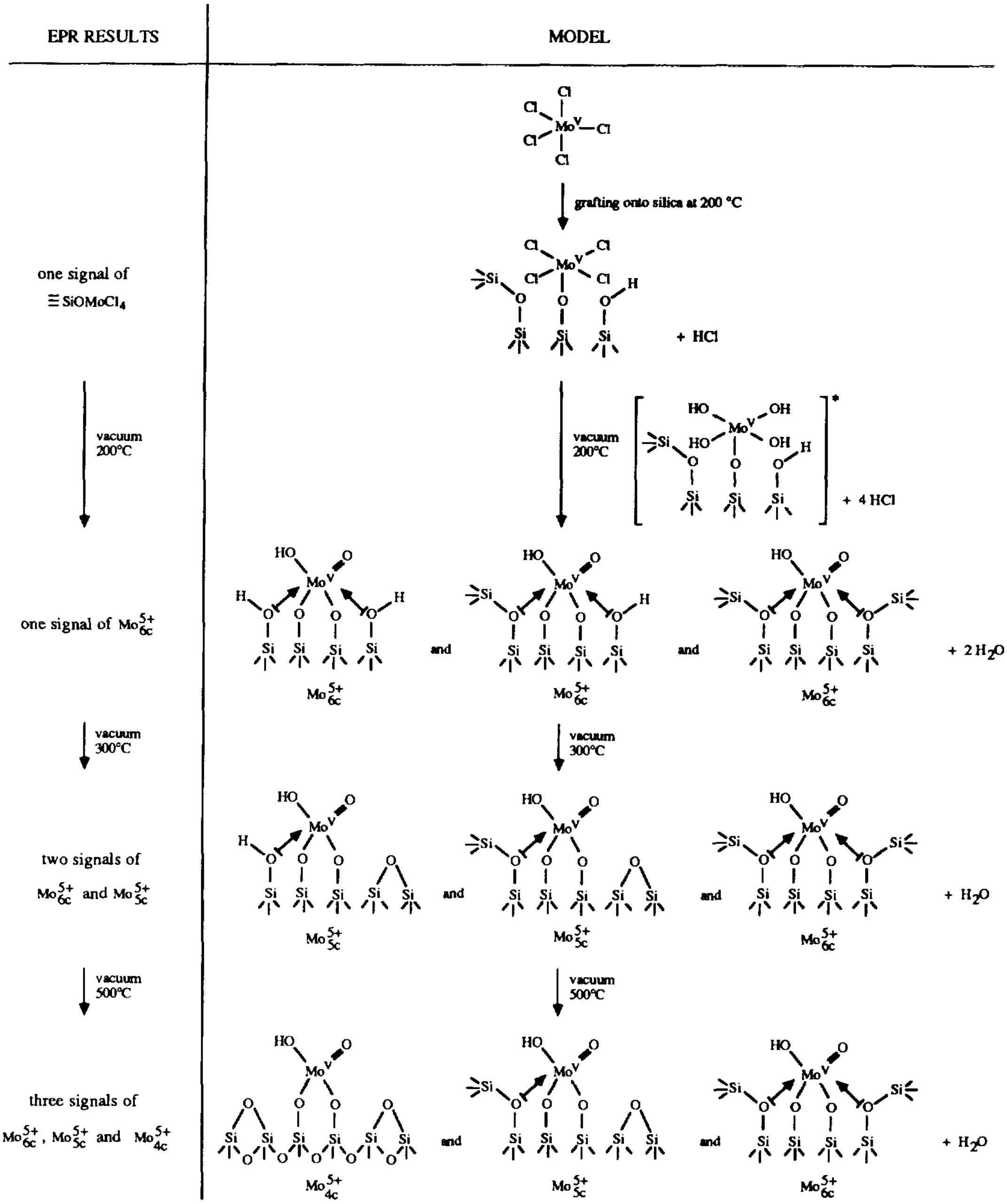


FIG. 4. Model for the changes in the Mo^{5+} coordination sphere observed by EPR (Fig. 3) upon evacuation of the Mo/SiO_2 catalysts prepared by grafting with $MoCl_5$ vapor. *Hypothetical intermediate species not observed by EPR.

from the EPR point of view (*61*). They may belong to neighboring Si-O-H hydroxyl groups or Si-O-Si siloxanes according to Scheme 3.

In consequence, we believe that the ligands Si-OH are responsible for the changes in the Mo^{5+} coordination sphere when the sample is left in static or evacuated at increasing temperatures after grafting: the increase of evacuation temperature induces a stronger dehydroxylation of silica and therefore leads to the formation of Mo^{5+}_{4c} as illustrated by Fig. 4. On the contrary, the disappearance of the Mo^{5+}_{4c} signal when the sample stays at room temperature probably arises from the OH migration on the silica surface (*62*) toward the very reactive Mo^{5+}_{4c} species which transforms successively into Mo^{5+}_{5c} and Mo^{5+}_{6c}.

It may be noted that the representation of silica in Scheme 3 and Fig. 4 is schematic since the atom arrangement in a real silica is not regular and the density of OH groups is lower. A picture of a simulated surface of amorphous silica may be found in Ref. (*63*). On this basis, we have built a model, using molecular systems (Cochranes of Oxford Limited), and found that the Mo^{5+}_{4c} species could be bound to silica via two Si without any steric constraint. These two Si can be adjacent or separated by several -Si-O- sequences. In addition, it is easy to find one or two neighboring Si-O-H or Si-O-Si to coordinate Mo^{5+}_{4c} and transform it into Mo^{5+}_{5c} and Mo^{5+}_{6c}.

The models for Mo^{5+}_{5c} and Mo^{5+}_{6c} (Scheme 3) explain the EPR results recently obtained by Latef *et al.* (*64*): in contrast to ours, they have observed the Mo^{5+}_{4c} signal on impregnated Mo/SiO$_2$ samples with high Mo contents (>1 wt%). However, the sample reduction treatment was slightly different from ours: reduction under a flow of hydrogen at 500°C, then fast quenching to room temperature. It is believed that the hydrogen flow carries away the water produced during reduction and prevents its coordination to Mo^{5+}_{4c}. On the contrary, when their samples were slowly cooled for 3 hr, the Mo^{5+}_{4c} could not be detected because of the migration of OH groups on silica toward Mo^{5+}_{4c} and further transformation of the latter into Mo^{5+}_{5c} and Mo^{5+}_{6c}. It may be noted that Patterson and Taylor (*65*) observed the same EPR spectrum as ours with the three Mo^{5+} species on reduced Mo/SiO$_2$ prepared from steam-deposited MoO$_3$ (5.7 wt%). Unfortunately, the way the sample was evacuated and cooled after the reducing treatment in H$_2$ (60 Torr) at 600°C for 90 min was not described.

CONCLUSION

The properties of grafted Mo/SiO$_2$ catalysts whose preparation has been described earlier (*5*) have been compared to impregnated Mo/SiO$_2$ catalysts: grafted Mo interacts more strongly with the silica support than impregnated Mo and is less reducible. The use of several techniques, such as the Mo^{5+} dispersion measurement by EPR spectroscopy, photoluminescence, methanol oxidation reaction, and IR study of CO adsorption, has shown that grafted Mo is better dispersed onto the silica surface than impregnated Mo, mainly at the highest Mo loadings (about 1 wt%). On the basis of these results, a model for the Mo species of the oxidized grafted catalyst is proposed and compared to the one of impregnated catalyst (Fig. 2). Finally, an EPR study of the Mo^{5+} coordination sphere of the grafted catalysts, performed after thermal reduction under hydrogen, and also during evacuation at increasing temperature, has led to the proposal of a model for these species with different types of bondings with silica (ionocovalent and coordinative) and Mo=O molybdenyl bonds pointing away from the surface (Scheme 3, Fig. 4).

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