

Interaction between molybdena and silica: FT-IR/PA studies of surface hydroxyl groups and pore structure assessment

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Abstract

Silica impregnated in aqueous solutions of ammonium heptamolybdate to achieve different Mo loadings (3–15 wt.%) is studied by the Fourier transform infrared/photoacoustic (FT-IR/PA) technique. Special attention is given to the high frequency region of surface hydroxyl groups. Air calcination at 500°C of the Mo loaded silica caused the evolution of defined features at 3720 and 3550 cm⁻¹ which are attributed to the free and hydrogen-bonded components of a pair of hydrogen-bonded silanol groups. The presence of such silanols on the surface of silica heated at 500°C is attributed to the hydrolysis of open siloxane bridges by the action of constitutional water that is liberated from the bulk interior due to heating at 500°C. The open siloxane represents a site of weakly attached Mo species that escape from the surface upon heating. These detached species are seen as the precursor of MoO₃ detected on the surface (band at 994 cm⁻¹). A surface polymolybdate phase is also detected (band at 970 cm⁻¹) and considered to result from condensation between Mo species adsorbed on the surface.

The effect of fluorination on the interaction between Mo and silica, and the pore structure of the Mo loaded silica are also discussed.

Keywords: FT-IR/PA; Molybdenum-doped silica; Pore structure; Silica; Surface hydroxyls

1. Introduction

The system Mo/SiO₂ finds a wide range of applicability in catalysis, e.g. metathesis of propane [1], propane oxidation [2], methanol oxidation [3], and methane oxidation [4]. Therefore, many physicochemical techniques have been used to investigate the interaction between Mo species and the silica support. Among these techniques IR spectroscopy [1,5–12] which concerned mainly the low frequency region (1100–400 cm⁻¹) is expected to result in bands corresponding to the interacting species. The results of these studies are

thus restricted to recognition of the resulting species, depending on the Mo loadings. Thus, at high Mo loadings (>15% Mo) all the authors agree on the presence of free MoO₃; at intermediate Mo loadings MoO₃ is detected together with other undefined Mo species generally designated as polymolybdates. At low Mo loadings (a few percent) several oxo-Mo species are postulated; pseudo molybdates [7], polymolybdates [7,8], surface polymer molybdate [5] or silicomolybdic acid [6,9].

None of these studies, however, gave due attention to the high frequency region (4000–3500 cm⁻¹) where the surface hydroxyls show their stretching modes of vibration.

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Inspection of this region after Mo loading to different weight percents could help in giving a picture of interaction between Mo and the silica surface.

In the present study, IR spectrometry is used to study the Mo/SiO₂ system at varying Mo loadings, giving attention to the high frequency region together with the previously studied low frequency region. As far as the surface hydroxyls are concerned, it is found interesting to change the extent of surface hydroxylation to throw more light on the role and the nature of surface hydroxyls that interact with Mo species. This is accomplished through subjecting the silica to fluorination before loading with Mo. Low temperature N₂ adsorption data are used to characterize the texture and pore structure of the Mo loaded silica.

2. Experimental

2.1. Materials

A Kieselgel 60 (Merck) silica gel is loaded with different weight percents of Mo by an impregnation technique. Three grams of the gel are stirred in 100 ml of an aqueous solution of ammonium heptamolybdate, (NH₄)₆Mo₇O₂₄·4H₂O, of the appropriate concentration to give samples loaded with 3, 6.6, 9, 12, or 15 wt.% of molybdenum. The Mo loaded solids are dried without washing at 393 K for 12 h, and then calcined at 773 K in air for 16 h. These samples will be designated I, II, III, IV and V, respectively. Fluorination before Mo loading comprised impregnation in 0.2 M NH₄F solution (3 g per 100 ml), washing with distilled water, then drying at 373 K. The prefluorinated samples will be referred to as I-F, II-F, III-F and IV-F.

2.2. Techniques

Infrared spectroscopy

The calcined solid is taken as soon as possible directly from the muffle furnace into a dry nitrogen atmosphered glove box enclosing the photoacoustic cell into which the appropriate sample is placed and then transferred into the IR equipment. The cell is continuously flushed with He gas during the

recording of the spectra. The spectra are obtained on a Nicolet 5-DXB FT-IR spectrometer, equipped with a METC-100 photoacoustic (PA) detector connected to a very sensitive (50 mV Pa⁻¹) Bruel and Kjaer microphone. 300–500 scans were averaged with a scan speed of 0.08 cm s⁻¹ and resolution 4 cm⁻¹.

N₂ adsorption

N₂ adsorption–desorption isotherms are measured on a computer-interfaced Micrometrics Digsorb 2600. The solids are outgassed at 200°C to a residual pressure of 10⁻⁴ Torr, and the weight of the outgassed sample is that used in calculations. A highly pure (99%) N₂ gas is used as adsorbate.

3. Results and discussion

3.1. Infrared spectroscopy

Parent silica

The IR spectrum of the parent silica (silica heated at 500°C) (Fig. 1) displays in the low frequency region bands at 1200–1000 cm⁻¹, 808 cm⁻¹ and 470 cm⁻¹ due to asymmetric stretching, symmetric stretching and bending modes of bulk SiOSi, respectively [13]. The small sharp band at 980 cm⁻¹ is due to Si–OH stretching of surface silanol groups [14,15]. The high frequency region shows a sharp band at 3750 cm⁻¹ due to the stretching vibrations of the isolated (non-interacting) surface silanols [16], preceded by a tail in the range 3700–3500 cm⁻¹ due to hydrogen-bonded silanols. That the hydrogen-bonded groups resulted in no defined maxima has been interpreted in terms of H bonds of different strengths [16].

Mo–silica series

Upon loading with increasing amounts of Mo some new features appear that show dependence on Mo content. Thus, bands at 925, 970 and 994 cm⁻¹ have appeared which increase in intensity with the increase in Mo loading, being barely visible in the case of sample I. These three bands are attributed to Mo–O–Si vibration, terminal Mo=O groups in the surface molybdate phase, and the Mo=O group in the MoO₃ phase, respec-

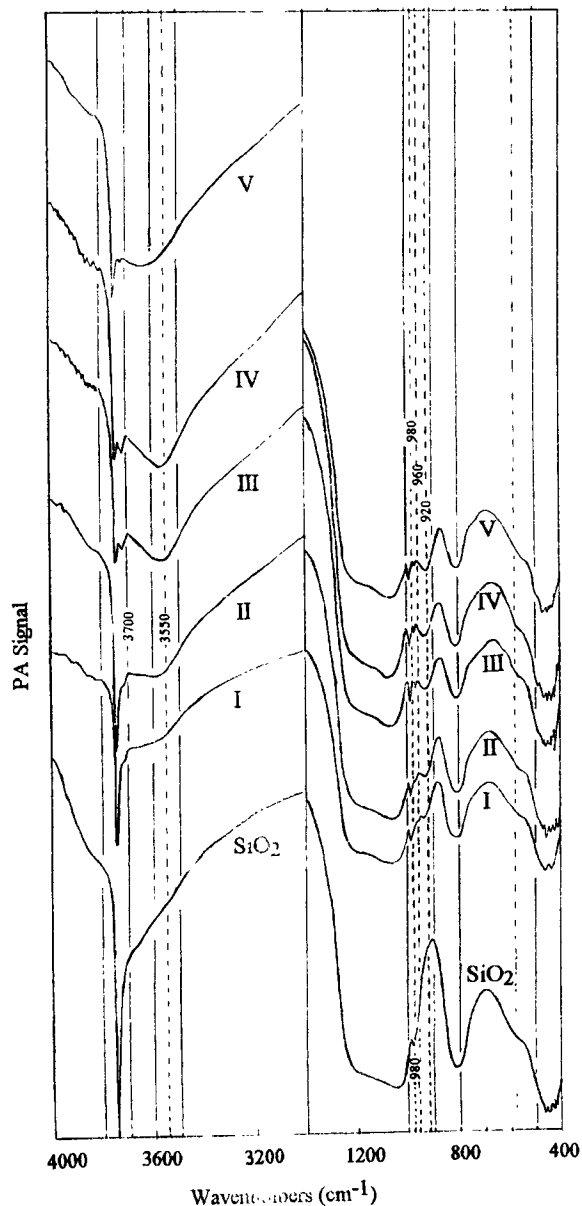


Fig. 1. Infrared spectra of parent silica (500°C) and corresponding samples loaded to different weight percents of Mo.

tively [5]. The band due to MoO_3 (994 cm^{-1}) did not appear exactly at the usual frequency in the case of sample I; probably because of the low content of this species at that low Mo loading, an interference with the band at 980 cm^{-1} (Si–OH) has taken place. This interference vanished with

the increase in Mo loading (Fig. 1). The intense band of SiO_2 around 800 cm^{-1} may mask other bands of MoO_3 expected to appear in the range $800\text{--}900\text{ cm}^{-1}$, also MoO_3 is expected to result in a band in the range $550\text{--}620\text{ cm}^{-1}$ [12], but being broad and adjacent to the intense band of SiO_2 at 470 cm^{-1} its recognition becomes uncertain.

The high frequency region has also been affected by the introduction of Mo to interact with the silica surface. The band at 3750 cm^{-1} underwent a continuous decrease in intensity in parallel with the increase in Mo loading up to 12% (sample IV) after which a relative increase rather than decrease is observed at 15 wt.%. The decrease in this band is accompanied by a change in the character of the tail preceding it. Thus, it is more defined in the case of sample I (relative to parent sample) showing a very broad band in the range $3650\text{--}3500\text{ cm}^{-1}$, and a very small shoulder at 3720 cm^{-1} . These features become more and more evident on increasing the Mo content up to 12% (sample IV). Again the trend ceases at 15% Mo (sample V) where the lower frequency band appeared broader and slightly shifted toward higher frequency, and the band at 3720 cm^{-1} reappeared very small.

The clear increase in intensity of the band at 925 cm^{-1} (Mo–O–Si) with the increase in Mo loading indicates that, in the studied range of Mo loading, as the interacting Mo species increase the interaction with silica surface increases. Moreover, the consecutive appearance of the other two bands (970 and 994 cm^{-1}) with the increase in Mo loading hints that the attributable species depend on the Mo loading and/or the formation of a Mo–O–Si bond. The suggested dependence on the formation of the Mo–O–Si bond conceptually means that the formation of such a bond is a prerequisite for the formation of both surface poly-molybdates and MoO_3 phases.

Groupings of H-bonded silanols should end with free hydroxyls, whose stretching mode is expected to occur at frequencies lower than that of isolated silanols. The occurrence of such terminal hydroxyls is considered negligible only if very large groupings occurred and this becomes likely if OH dimers are considered [17]. Bands at 3720 cm^{-1} and 3530 cm^{-1} are attributed respectively to the free and H-bonded components of such pairs of

H-bonded silanols [15,18]. The continuous evolution of these features on increasing the Mo content from 3 to 12% is a clear manifestation of the increase in formation of such types of H-bonded silanols. It is known that vicinal OH groups that can interact in pairs via H bonding no longer exist on the surface of silica heated to 500°C [19]. Therefore, it is not reasonable to attribute the above mentioned features of H-bonded silanols to groups which have survived the heating to 500°C. Instead, one should consider a situation in which such groups could be generated because of the heat treatment at 500°C.

To account for the decrease in the intensity of the band at 3750 cm⁻¹, due to isolated OH groups, upon interaction with Mo we may assume that the interacting Mo species, MoO₄²⁻, reacts monofunctionally via one oxygen with a single OH. This assumption, however, can not account for the features assigned to hydrogen bonding because of the preparation method used in the present case. The silica is brought to interact with Mo then subjected to heating at 500°C, a temperature that is considered to deplete generally all silanols that are near enough to each other so that they can form strong hydrogen bonds. On the other hand, an isolated OH (3750 cm⁻¹), if it is involved in H bonding with a neighboring OH group (or two such groups), may generate a two-fold effect, namely a decrease in the intensity of the band at 3750 cm⁻¹ and appearance of a band at 3720 cm⁻¹.

An alternative possibility for interaction is a bifunctional condensation with two vicinal OH groups so that the strength of interaction depends on the geometrical distribution of these OH groups. A pair of OH groups which are close together results in strongly held Mo species. A more widely separated pair causes the bonding in Mo–O–Si to be weak so that upon heating to 500°C such bonding is broken and the adsorbed species detach and leave the surface. During the course of heating up to 500°C the other OH groups whose arrangement did not permit them to participate in interaction with Mo species, but still enables them to condense together to evolve water, result in formation of surface siloxane linkages in their positions. The weakly attached species on

leaving the surface create in their positions open siloxane linkages that can be easily hydrolyzed by the action of constitutional water that is liberated from the bulk interior due to heating at 500°C [20]. Each leaving Mo species generates a pair of vicinal OH groups which necessarily contains a terminal hydrogen-bonded OH, because it is formed together with either a siloxane linkage or a still-attached Mo species. This terminal OH group is thus responsible for the band at 3720 cm⁻¹. With the increase in Mo loading the probability of these events increases and so do the features at 3720 and 3550 cm⁻¹. If the position of this newly formed pair is adjacent to an isolated OH, the latter may be perturbed via H bonding which leads to a decrease in the intensity of the band at 3750 cm⁻¹.

The chance that an interacting Mo species will find a pair of adjacent OH groups to form a strongly held species, is higher in narrower pores than in wider ones. Consequently, at low Mo loadings most of the attachment on the surface is expected to be in small pores, and on increasing the Mo loading the groups of lower activity, being widely separated to a greater extent, take part in interaction. Those of the latter type predominate in wide pores, therefore at a high Mo loading, namely 15% (sample V), a great part of the interaction occurs in these wide pores. Being originally weak linkages, they are easily broken which means that most of the OH groups formed in this case are placed in wide pores. As a consequence, a low degree of interruption by the still-attached Mo species decreases the probability of the presence of a terminal H-bonded OH group; in addition a lower probability of being present, beside an isolated OH leads to a lower perturbation of the latter via H bonding. The presence of a very small band at 3720 cm⁻¹ in the case of sample V indicates that very few terminal H-bonded OH groups are present, and the higher intensity of the band at 3750 cm⁻¹ relative to sample IV indicates a lower perturbation via H bonding to the isolated OH groups.

The increase in the features attributed to H-bonded OH groups and the corresponding increase in the band due to MoO₃ (994 cm⁻¹) can be considered as evidence that the weakly attached

Mo species that left the surface are the precursor of the MoO_3 formed.

Fluorinated Mo-silica series

Fluorination caused the absence of the band at 970 cm^{-1} up to 12% Mo loading, and of the band at 994 cm^{-1} up to 6.6%, but the appearance of the band at 925 cm^{-1} , at very reduced intensity, in samples I-F and II-F (Fig. 2). In the high frequency

region, fluorination resulted in the appearance of a band at 3660 cm^{-1} in addition to the bands at 3750 , 3720 and 3550 cm^{-1} which appeared in the case of unfluorinated samples.

Fluorination usually affects the surface through substitution of some surface hydroxyls by fluoride ions. That means a general decrease in the OH density, which decreases the probability of finding vicinal silanols with a geometry that permits easy

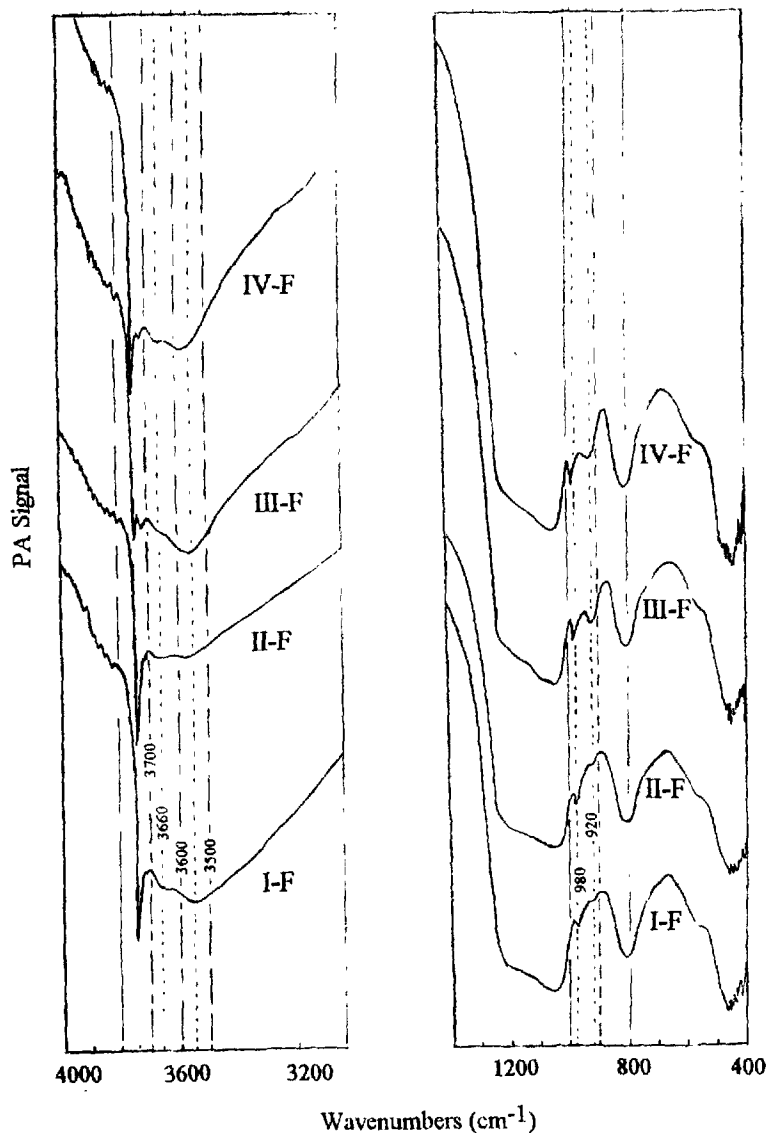


Fig. 2. Infrared spectra of prefluorinated Mo loaded silica series.

interaction with interacting Mo species. Thus, at low Mo loadings a reduced chance for interaction, as proposed, is a consequence of fluorination, as reflected in the reduction of the band at 925 cm^{-1} (Mo–O–Si) in the case of samples I-F and II-F (Fig. 2). On the other hand, the absence of the band at 994 cm^{-1} (MoO_3) in the case of these two samples supports the belief that the formation of MoO_3 depends strongly on the strength of interaction between Mo and the silica surface. In the case of these two samples, the interacting Mo species hardly ever finds a suitable pair of OH groups, which are fewer than in the unfluorinated cases, as reflected in the decreased interaction (Mo–O–Si). The resultant interaction in these cases is therefore the strongest one, and consequently upon heating only a few Mo species detach from the surface and these are not enough to build up appreciable amounts of MoO_3 .

A higher Mo loading, namely 9%, appears enough, in spite of a fluorinated surface, to make the formation of MoO_3 feasible where the interacting Mo species are able to attack the surface and form both strongly held species (925 cm^{-1}), and weakly attached species that are considered as a precursor for MoO_3 formation (992 cm^{-1}). However, careful examination of the band width (925 cm^{-1}) shows that fewer structural variations are present after fluorination (a less broad band) which may be interpreted as restricted distribution of the active OH groups that lead to strong interaction. Presumably, this is also the reason for the absence of the polymolybdate phase (970 cm^{-1}) in all the fluorinated samples. It is thus more probable that polymolybdate formation takes place by condensation between attached species.

Inspecting the high frequency region, we note the features at 3720 and 3550 cm^{-1} are more defined in the case of sample I-F than in sample I, which seems contradictory to the above proposed sequence of events. Nevertheless, it appears that though it is suggested, in the case of sample I-F, that the Mo species responsible for the appearance of these features are few, the interrupting effect of fluoride ions resulted in their enhancement. The fluoride ions caused the newly generated OH groups, though few, to be highly isolated in nature, which is reflected in the more defined appearance

of the features at 3720 and 3550 cm^{-1} . The role of fluoride ions in modifying the surface can be recognized through considering the appearance of the band at 3660 cm^{-1} (Fig. 2) which is attributed to silanols weakly perturbed via H bonding (being not too near to each other) that resist heating up to $\approx 900^\circ\text{C}$ [16]. That can be seen to occur through shifting the electron density because of the higher electronegativity of F atoms and/or through substituting the nearest neighbor OH groups that were able to participate in strong H bonding.

The decrease in intensity of the bands at 3720 and 3550 cm^{-1} in the case of sample II-F relative to sample I-F is accompanied by a relative increase in the intensity of the band at 3750 cm^{-1} . This indicates a lower extent of perturbation to the isolated silanols via H bonding with the newly formed OH groups, which seem to be fewer in number than in the case of sample I-F. This may result if the newly formed OH groups are generated in wider parts of the pores. The crowded situation in narrow pores (due to high density of F ions) means that relative to sample I-F, the excess Mo species are directed to a greater extent to the wider parts in which the regeneration of OH groups causes less perturbation to the isolated OH groups. At a higher Mo loading, such as 9%, the Mo species are enough to attack the surface at many centers of different activities, therefore many species are detached from the surface and are enough to form MoO_3 (992 cm^{-1}). A corresponding situation in this case is that many isolated pairs of OH groups are formed (3720 and 3550 cm^{-1}), and the role of F ions is manifested in the appearance of the band at 3720 cm^{-1} more sharply defined than in the case of sample III (Fig. 2). Fluoride ions seem to enhance the chance of terminal OH group formation in a pair of OH groups.

Again on increasing the Mo loading to 12%, fluorination resulted in a situation similar to that encountered between 3 and 6.6% loadings. We have to emphasize that such a situation is encountered in the case of unfluorinated samples only on increasing the Mo loading from 12% to 15% (Fig. 1). The persistence of the band at 3660 cm^{-1} up to 12% Mo loading (Fig. 2) indicates that the

part of the surface that is affected by fluorination exists at all the levels of loading examined. This part is mainly in narrow pores which agrees with the proposed orientation of Mo species at higher loadings to the wider parts.

3.2. N_2 adsorption

Parent silica

The parent silica shows a type IV isotherm, i.e. a mesoporous solid, with two sloping branches of a type H2 hysteresis loop that closes at $p/p^0=0.52$ (Fig. 3). The mesopores present can be described as tubular pores with openings of some effective and varying radii, r_h , and widened parts with varying radii, r_w , where $r_w > 2r_h$ [21]. Meanwhile, the hysteresis loop illustrates a type H1 character at its higher region where the two branches are parallel to each other, though still sloping. This type of hysteresis loop is generally attributed to a cylindrical pore shape [22].

The specific surface area is derived by applying the BET method in the conventional range of

relative pressures with cross-sectional area of $N_2=16.2 \text{ \AA}^2$. The values of A_{BET} , total pore volume, V_p (calculated as liquid volume at $p/p^0=0.95$), BET C-constant, and the average pore radius, $r_H=V_p/A_{\text{BET}}$ (parallel plate shape) are given in Table 1.

The type of pores present can be identified by using the $V-t$ method [23–25] in which we used the reference t values of Lecloux and Pirard [26] depending on the value of the BET C-constant. The correct choice of the reference data is judged through the agreement between A_{BET} and the area calculated from the $V-t$ plot, A_t (Table 1).

The plot of the parent sample exhibits an upward deviation that starts at $t=5.2 \text{ \AA}$ ($p/p^0=0.38$) and continues with increasing slope up till $t=10.1 \text{ \AA}$ ($p/p^0=0.85$) where it becomes nearly horizontal (Fig. 4). This upward deviation thus represents the capillary condensation in the mesopores present. However, the plot indicates that the isotherm comprises a region of reversible capillary condensation — capillary condensation without hysteresis — between $p/p^0=0.52$ where the hysteresis loop closes and $p/p^0=0.38$ where the upward deviation

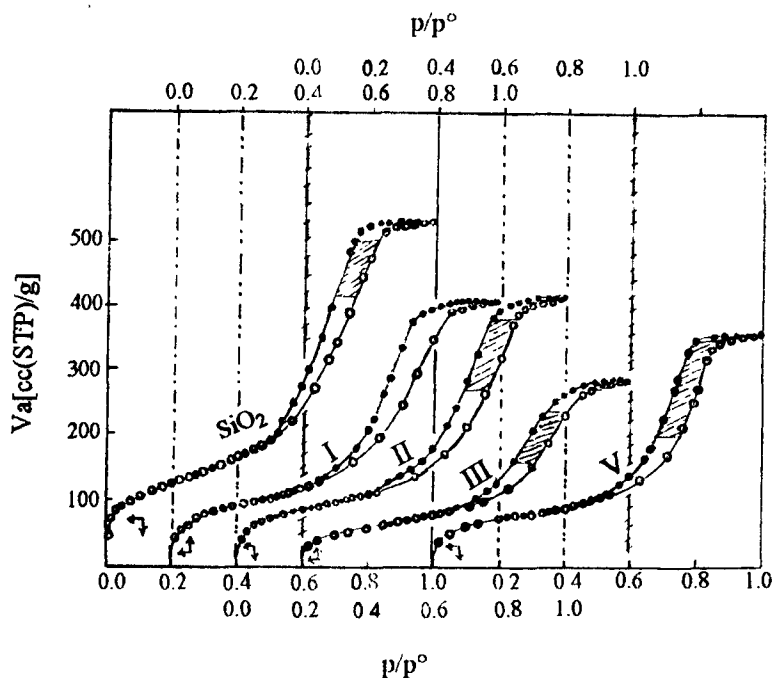


Fig. 3. N_2 adsorption–desorption isotherms (77 K) of parent and Mo loaded silica samples. The shaded region represents type H1 character.

Table 1
Surface characteristics of parent and Mo loaded silicas

Sample	A_{BET} ($\text{m}^2 \text{g}^{-1}$)	A_t ($\text{m}^2 \text{g}^{-1}$)	V_p (ml g^{-1})	BET C-constant	r_H (\AA)	A_{cum} ($\text{m}^2 \text{g}^{-1}$)		V_{cum} (ml g^{-1})		A_{cum} ($\text{m}^2 \text{g}^{-1}$) (Av.)	V_{cum} (ml g^{-1}) (Av.)
						pp	cp	pp	cp		
Silica	457	461	0.8215	77	18.0	435	568	0.8000	0.8397	—	—
3% Mo(I)	329	335	0.6298	82	19.1	314	414	0.6257	0.6597	—	—
6.6% Mo(II)	317	319	0.6355	90	20.0	275	353	0.6209	0.6497	314	0.6357
9% Mo(III)	221	225	0.4355	83	19.8	191	248	0.4205	0.4410	220	0.4307
15% Mo(V)	262	266	0.5549	90	21.7	215	275	0.5079	0.5306	—	—
Silica-F	342	339	0.8292	71	24.2	360	466	0.8209	0.8596	—	—

Subscript cum indicates cumulative; pp and cp indicate parallel plate and cylindrical pore respectively.

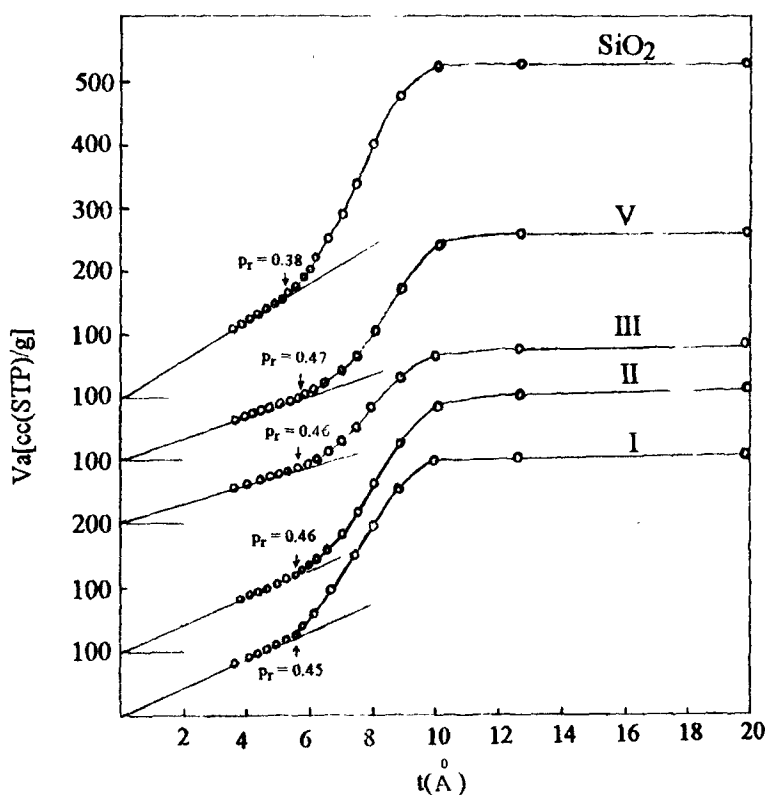


Fig. 4. V - t plots of parent and Mo loaded silica samples.

commences. This reversible capillary condensation can take place in pores of cone and wedge shape [21] having the sizes of wide micropores and/or narrow mesopores [27].

The pore size analysis is achieved using the corrected modelless method developed for meso-

pores [28]. In view of the type H2 character of the hysteresis loop the analysis is conducted using the adsorption branch data [29]. The calculations are continued down to a p/p^0 value at which the correction term proposed by the method was equal to or exceeds the volume desorbed. The parallel

plate model gave much better agreement between experimental and calculated cumulative parameters of volume and area (Table 1).

The pore volume distribution curve, $\Delta V/\Delta r$ vs. r_h (Fig. 5), indicates that the major part of the pore volume is contained in pores of hydraulic radii, r_h , in the range 12.5–32.5 Å, i.e. pore widths in the range 25–65 Å. The most frequent pores are those of $r_h = 17.5$ and 22.5 Å with a maximum at $r_h = 22.5$ Å — the average pore radius, r_H , calculated from A_{BET} and V_p is 18.0 Å (Table 1).

Mo loaded silica

All the Mo loaded samples resulted in type IV isotherms of similar shape (Fig. 3) exhibiting hysteresis loops with nearly parallel and sloping branches, so can be regarded as mixed H1 and H3 types.

A progressive decrease in A_{BET} and V_p accompanied the increase in Mo loading up to 9%; further increase in Mo to 15% resulted in an increase rather than decrease in both parameters. Apparently the decrease in area is more important than that in pore volume where the average pore radius shows an increase upon Mo loading (Table 1). Nevertheless, the similarity displayed in the $V-t$ plots (Fig. 4) indicates that the variable

Mo loading did not affect the pore sizes, but the concordance between the start of the upward deviations in the plots on the one hand, and the closure points of the hysteresis loops ($p/p^0 = 0.45-0.47$) on the other, indicates the blocking of those pores with sizes in the range of narrow mesopores and/or wide micropores. The higher probability of presence of adjacent hydroxyls in narrow pores is thus behind these variations in surface characteristics.

The pore volume distribution curves (Fig. 5) show that at the first level of Mo loading (3%) the pore system has been affected so that pores with $r_h \leq 27.5$ Å are reduced in number. The increase in Mo loading seems to increase the extent of both attachment and escape of Mo species, therefore the pore structure is affected in a complex manner. The pore system in samples II and III, being visualized as an assembly of pores which are composites of cylinders and parallel plates (Table 1), reflects such a complex situation. Meanwhile, the curves imply that the decreases in area and volume in the range 3–9% Mo loading have taken place without change in pore sizes. The maximum in the distribution curve of sample V (15% Mo) is shifted toward a larger size of r_h , and the increase in A_{BET} and V_p recorded in

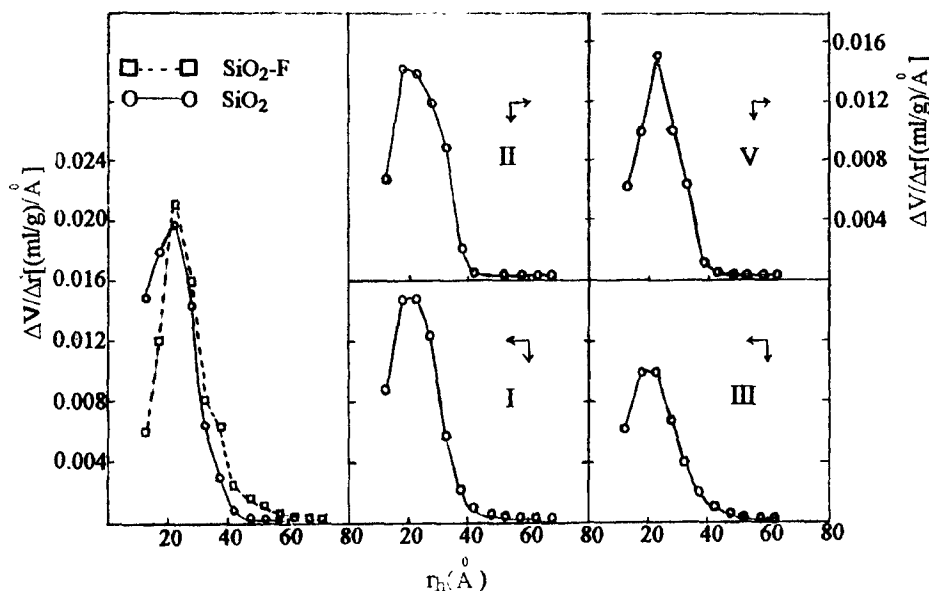


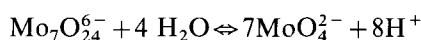
Fig. 5. Pore volume distribution curves ($\Delta V/\Delta r$ vs. r_h) of parent and Mo loaded silica samples.

the case of this sample can be correlated with this shift. At such high loading there is an excess of interacting Mo species which are able to attack the surface hydroxyls residing in wide pores as well, consequently the escaping species leave the surface more freely, resulting in greater area and volume to be measured. Up to 9% Mo the attack takes place mainly in narrow pores which means that the escaping species still prevent a considerable part of the surface from being available to N_2 .

As the population of OH groups is expected to be higher in the narrower pores, therefore upon fluorination the density of F ions will be higher in narrower pores than in the wider ones. The presence of F ions in narrow pores may decrease the number and the size of these pores as a result of increase in bond angles produced by changes in oxygen hybridization [30]. The pore volume distribution (Fig. 5) shows that fluorination caused a decrease in frequency of pores with $r_h \leq 17.5 \text{ \AA}$, and an increase in pores of larger sizes. Moreover, the ratio between the volume adsorbed at $p/p^0 = 0.05$ and the total pore volume was taken [31] as a measure of the fraction of existing fine pores that are full in the very early stages of adsorption. These ratios (as percentage) are 16.9 and 12 for parent and fluorinated silica, respectively. The decrease which occurred, upon fluorination, in A_{BET} but not in V_p (Table 1) is thus because the narrow pores exhibit a high surface to volume ratio. The interaction between the Mo species and silica, as proposed above, requires suitably situated pairs of OH groups whose presence is more probable in narrow pores, consequently the loss which occurred in narrow pores upon fluorination could decrease the probability of this interaction. A comparison of the loss of area caused by Mo loading in the case of samples II and III, with and without fluorination, reflects the lower extent of interaction between the fluorinated silica surface and the interacting Mo species. The A_{BET} values of samples II-F and III-F are $284 \text{ m}^2 \text{ g}^{-1}$ and $215 \text{ m}^2 \text{ g}^{-1}$, respectively which means a decrease in area, upon Mo loading, between 17 and 37%. The decrease in the corresponding cases without fluorination covers a range of 31–52% (Table 1).

4. Conclusions

The interaction between the silica surface and Mo species in an aqueous solution of ammonium heptamolybdate results in the formation of Mo–O–Si bonds of variable strengths. Such a link results from a condensation reaction between a MoO_4^{2-} moiety and a pair of surface silanols which are necessarily vicinal. The aqueous solution furnishes the reacting species through the equilibrium reaction:



The strongest link is that resulting from the involvement of two silanols which are near enough to each other to facilitate the interaction with the Mo species. The strength of the bonding decreases as the separation between the hydroxyls increases. A wider separation between silanols leads to a weakly attached species that detaches from the surface during heating at 500°C , leaving in their place an open siloxane linkage. The constitutional water that is liberated by heating at 500°C hydrolyzes this open siloxane link to produce surface silanols which can form hydrogen bonds with each other. The other silanols that did not participate in bonding with Mo species and are still adjacent to each other are depleted through condensation to evolve water upon heating. The regenerated silanols can be considered as groups that are protected from condensation through their involvement in weak interaction with Mo species. These groups result in features in the high frequency region (3720 and 3550 cm^{-1}) attributed to hydrogen-bonded groups which are believed to be absent from the surface of silica heated at 500°C . The increase in these features with Mo loading and the corresponding increase in MoO_3 formation (band at 994 cm^{-1}) is considered as evidence that the species that left the surface are the precursors of the MoO_3 formed. On the other hand, the formation of a surface polymolybdate phase is seen to result from condensation between Mo species that are still attached to the surface.

The study of surface characteristics revealed that Mo loading results in a greater decrease in surface area than in pore volume. Thus the narrow pores characterized by a high surface to volume ratio

are responsible for these variations. The narrow pores, which accommodate a higher density of suitably situated hydroxyls for interaction with Mo species, represent the most favorable region to be attacked at low levels of Mo loading. The limited space available in these pores in which the interaction with surface hydroxyls and the detachment of weakly bound species took place caused the measured area and volume to decrease progressively with increase in Mo loading. At 15% Mo the content of interacting species seems sufficient to extend the interaction considerably to the wider pores where the escape of the detached species has mostly occurred. This appears as a relative increase in area and volume. Fluorination has thrown more light on the role of adjacent hydroxyls in narrow pores where the extent of interaction with Mo is decreased, resulting in a corresponding loss of area.

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