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Structure and Catalytic Properties of Silica-Supported Polyoxomolybdates

III. 12-Molybdosilicic Acid Catalysts: Vibrational Study of the Dispersion Effect and Nature of the Mo Species in Interaction with the Silica Support

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Silica-supported 12-molybdosilicic acid catalysts prepared by impregnation are studied by IR and Raman spectrometries as a function of the Mo content (Mo wt% varying from 24.6 to 1.2). A dispersion effect is evidenced, especially by Raman spectrometry. The 12-molybdosilicate anion in interaction with the silica support is preserved down to 2% Mo. The results are discussed in relation with ^{29}Si magic-angle-spinning NMR and reactivity studies in the methanol oxidation. © 1992 Academic Press, Inc.

INTRODUCTION

Catalytic oxidation by transition metal oxides has attracted increasing research interest in recent years. Supported metal oxides are usually obtained by impregnation of the support by a precursor solution, followed by calcination at high temperature. In the case of molybdenum compounds, the process generally induces decomposition of the precursor and spillover at the surface, and does not permit control of either the structure, or the dispersion and the nuclearity of the deposit. The sensitivity to molybdenum trioxide structure has been suggested in the mild oxidation of alcohols (*1*). In addition the methanol oxidation is very sensitive to the dispersion of MoO_3 on silica: it was claimed that methylformate is produced by highly dispersed molybdenum ions, whereas aggregates give mainly rise to formaldehyde (*2*). In order to study the relation between the dispersion and the catalytic properties of molybdenum species, it is then suitable to use polyoxomolybdates, which can be considered as simplified oxide models. In many cases, the structure, the nuclearity, and the acido-basic and redox properties of these cluster oxides are well-known (*3*). They are widely used in heterogeneous catalysis (*4*). Moreover, they are soluble in various solvents and can be easily deposited on a support by impregnation, so the structure and the dispersion are expected to be controlled.

Previous works from other teams were already reported concerning the 12-molybdosilicic acid supported on silica (*5–9*), including some physicochemical characterizations and/or catalytic reactivity studies in the partial oxidation of methane. Unfortunately this reaction is performed at a temperature largely higher than the decomposition temperature of the 12-molybdosilicic acid (see Ref. (*10*) on the thermal stability of unsupported and silica-supported 12-molybdosilicic acid), and the physicochem-

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ical characterizations are not fully conclusive. Moreover, with Mo/SiO_2 catalysts obtained by impregnation of silica by heptamolybdate (or eventually hexamolybdate) followed by drying at 120–130°C and calcination in air at 500°C, the presence of 12-molybdosilicic acid was pointed out by several authors, in the case of low Mo contents and in certain conditions (*8, 9, 11–13*). This implies the possibility of building of the 12-molybdosilicic acid from molybdenum oxide and silica, with the assistance of water molecules. From the above studies, it appears that several parameters have an influence on the nature of the Mo-species on the silica surface (treatment temperatures, Mo content, water exposure, etc.). With the aforementioned point of view of using polyoxomolybdates as model compounds (oxide models) for studying the dispersion effect on silica, it is important to perform the study in conditions for which the starting material is stable. In this work a reaction performed at a relatively low temperature, in a range where the 12-molybdosilicic acid is expected to be stable, was therefore chosen: the test reaction of conversion of methanol in presence of oxygen is quite suitable for this purpose, and, in connection with different physicochemical techniques of characterization, can be used as a complementary probe. On this basis, preliminary results on the behavior of samples based on 12-molybdosilicic acid supported on silica have been reported (*10, 13–15*), as well as a recent study by ^{29}Si magic-angle-spinning NMR of these catalysts (*16*). The purpose of this paper is to report a detailed study of the characterization of the silica-supported 12-molybdosilicic acid catalysts by IR and Raman spectrometry and to discuss the results in relation with the information coming from ^{29}Si NMR and catalytic reactivity studies. This reflection is carried out to shed more light on the nature of the Mo species and of their interaction with the silica support as a function of the dispersion.

1. EXPERIMENTAL

1.1. Preparation of Samples

12-molybdosilicic acid $H_4SiMo_{12}O_{40} \cdot 13H_2O$ (noted $SiMo_{12}H$) was prepared and checked using classical methods previously described (*17*).

The silica support (Rhône–Poulenc Spherosil XOA 400, surface area 376 $m^2 g^{-1}$) used for the impregnation was analyzed by thermogravimetry. A first weight loss was observed as soon as the temperature is increased, followed by a plateau between ~150 and ~300°C (water of zeolitic nature, ~4% in weight), and by a second weight loss from ~300 to ~500°C (~1.5% in weight) corresponding to dehydroxylation. This allowed the amount of OH groups to be roughly estimated (about 0.1 mol OH per mol SiO_2). Samples were prepared by stirring SiO_2 and impregnation aqueous solutions of $SiMo_{12}H$ at about 50°C until dryness evaporation. The concentrations of the initial impregnation solutions, in the range 7×10^{-3} mol liter^{-1} to 10^{-1} mol liter^{-1}, were always high enough, even for the lowest Mo content, to avoid degradation of the 12-molybdosilicic acid (checked by UV–visible spectrophotometry at 295 nm); during the impregnation process, the solutions become more and more concentrated: this prevents the degradation of the species, but this can induce a nonuniform deposit on the surface, especially for the high Mo contents. The catalysts were then dried under vacuum at 100°C, and finally kept and handled in air without special precautions against atmospheric moisture. As a consequence, water uptake occurred, to the extent of about 10% in weight as measured by thermogravimetry, whatever the Mo content (water weakly bound, and lost as soon as the temperature is increased). In similar conditions, the silica support reabsorbs the same amount of water. Spectroscopic characterizations were carried out on these samples without any further thermal pretreatment. The final Mo content of the samples referred to as SiMoH-x (x = Mo wt%) was determined by

TABLE 1

Characteristics of Silica-Supported 12-Molybdosilicic Acid Catalysts

Catalyst	wt% Mo	Molar ratio Mo/SiO_2	Molar ratio $SiMo_{12}H/SiO_2$	Molar ratio H^+/SiO_2
SiMoH-25	24.6	0.326	0.027	0.108
SiMoH-17	17.6	0.196	0.016	0.065
SiMoH-9	9.0	0.079	0.0066	0.026
SiMoH-7	7.1	0.072	0.006	0.024
SiMoH-6	6.8	0.055	0.0046	0.018
SiMoH-5	5.0	0.039	0.0032	0.013
SiMoH-2	2.1	0.021	0.00175	0.007
SiMoH-1	1.2	0.009	0.00075	0.003

microanalysis (Service Central de Microanalyse du CNRS, 69390 Vernaison, France). Analytical characteristics of the catalysts of the SiMoH-*x* series are displayed in Table 1.

Mechanical mixtures were also prepared from 12-molybdosilicic acid and silica, with Mo contents similar to those of the impregnated samples, by using a vibrating grinder (agate container, agate balls, 10 min grinding).

1.2. Physicochemical Techniques

1.2.1. Infrared spectrometry (IR). Infrared spectra were recorded on a Perkin–Elmer 283 spectrophotometer (4000–200 cm^{-1}), a Perkin–Elmer 580B spectrophotometer coupled with a data station (4000–200 cm^{-1}), and/or a Perkin–Elmer 1700 interferometer (4000–450 cm^{-1}, scan number 10 to 20), as KBr or RbI pellets.

1.2.2. Raman spectrometry. Raman spectra were run on a Coderg PH0 spectrometer and/or a Jobin-Yvon U1000 spectrometer, equipped with Spectra Physics 164 or Coherent Innova 70 argon lasers (514.5 nm). Classical powder techniques were used, i.e., the capillary tube and the conical sample techniques. Relatively low powers of the laser beam (50 to 100 mW) were used to avoid local reduction and/or destruction of the sample. The reported frequencies, calibrated with respect to plasma lines, are accurate to ± 1 cm^{-1}.

1.2.3. Surface area measurements. Nitrogen/helium (molar ratio 0.3) adsorption–desorption isotherms were measured using a Quantasorb Jr. apparatus. Samples (about 700 mg) were pretreated at different temperatures (from 30 to 400°C) at the atmospheric pressure prior to the measure by the BET method (adsorption at 77 K).

2. RESULTS

2.1. General Considerations

It is well known that the anion $SiMo_{12}O_{40}^{4-}$ (noted $SiMo_{12}$) belongs to the Keggin structure and consists of an SiO_4 tetrahedron surrounded by four Mo_3O_{13} groups formed by three edge-sharing octahedra. These trimolybdic groups are linked together through oxygen atoms. A schematic polyhedral representation of the Keggin unit is presented in Fig. 1, with the four types of oxygen atoms: O_a, oxygen atoms bound to three Mo atoms and to Si; O_b and O_c, bridging oxygen atoms; and O_d, terminal oxygen atoms.

Crystal structure of $SiMo_{12}H$ determined by X-ray diffraction shows that the Keggin units are connected in the crystal through an H-bond network of water molecules and hydrated protons (*18*). Vibrational spectra (IR and Raman) have been already discussed and assigned (*17*): the crystalline framework implies the proximity of the anions, inducing strong anion–anion interactions of electrostatic type, and, as a consequence, an increase of the stretching fre-

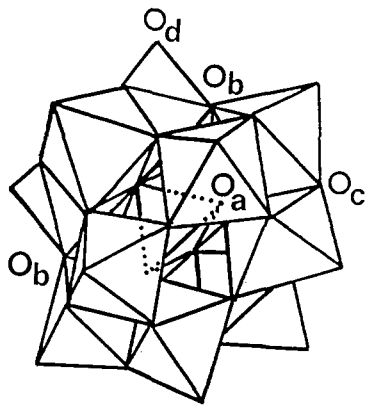

FIG. 1. Schematic polyhedral representation of the Keggin unit: O_a = oxygen atom common to the SiO_4 tetrahedron and to a trimolybdic group, O_b = oxygen atom connecting two trimolybdic groups, O_c = oxygen atom connecting two MoO_6 octahedra inside a trimolybdic group, and O_d = terminal oxygen atom.

quencies νMo–O_d with respect to those of the isolated anions.

2.2. *IR and Raman Characterizations before the Catalytic Reaction*

Initial silica before any treatment exhibits three main IR bands at ~1100 cm^{-1} (broad and very strong), ~800 cm^{-1} (medium), and ~470 cm^{-1} (strong), and a weak band at 976 cm^{-1} [Fig. 2(1)]. A thermal treatment in dry atmosphere at 500°C for several hours induces the disappearance of the weak band at 976 cm^{-1}, the other three ones undergoing only slight shifts. Exposure to air humidity induces again a weak and broad signal at ~960–970 cm^{-1}: such a band can be likely related to surface OH groups, in accordance with previous assignments (*19*). The silica bands partly obscure the typical pattern of $SiMo_{12}H$, leaving, however, some windows to characterize this compound at high Mo contents [Figs. 2(2) and 2(3)]. Subtraction of the absorption of silica is possible for Mo contents ≥9%, showing that the Keggin structure is preserved on the support. This conclusion can be drawn as well from the original spectra, displayed in Figs. 3(1) to 3(3). For the lower Mo contents [Figs. 3(4) to 3(8)], differences are no longer possible, due to the great contrast between the weak signals of the deposited species and the very intense signals of the support: as already explained (*13*), artifact bands can be induced by performing differences in such conditions. As a consequence, for $2 \leq x \leq 9$, the Keggin unit is only characterized by its two highest frequencies (~955 cm^{-1} and ~905–910 cm^{-1}). The ν_{as}Mo–O_c–Mo is obscured by the silica band at ~800 cm^{-1}, and the two low-frequency bands at ~370 and 340 cm^{-1}, characteristic of the α-isomer of the $SiMo_{12}$ anion, are masked on the right side of the strong 470-cm^{-1} band of the silica (they are only visible for Mo contents ≥ 7%). In addition, for the very low contents (<5%), the intensity of the aforementioned OH-band of silica is similar to that of the ν_{as}Mo–O_d, and appears at almost the same frequency: the overlap makes the IR characterization very difficult. For the lowest Mo content ($x = 1$), there is no significant difference between the spectra of the impregnated catalyst and of the support [Fig. 3(8) and Fig. 2(1)].

The IR spectra of the mechanical mix-

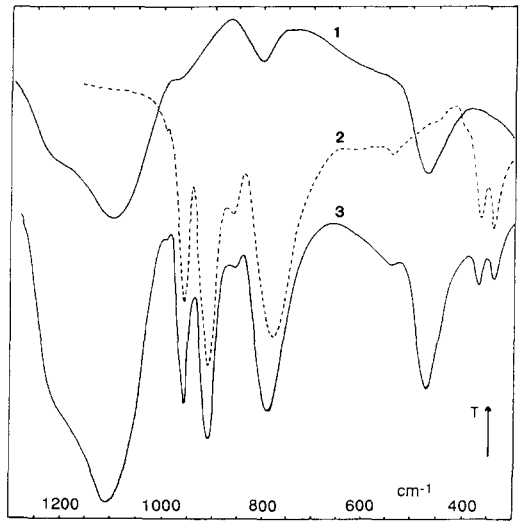

FIG. 2. Infrared spectra (KBr pellets): (1) Silica, (2) unsupported 12-molybdosilicic acid, and (3) SiMoH-25.

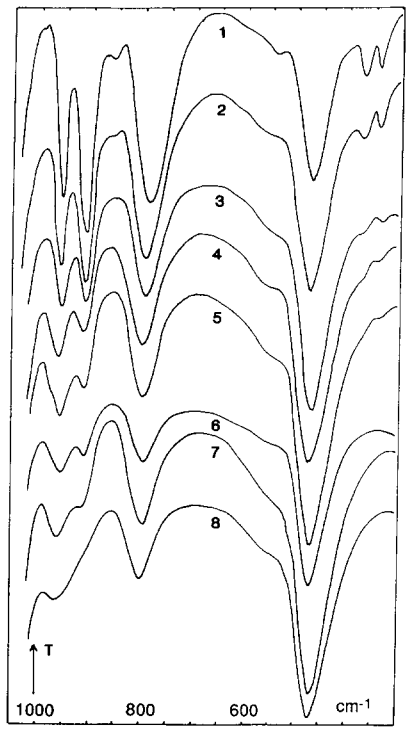

FIG. 3. Infrared spectra of the catalysts of the series SiMoH-x before the catalytic reaction: (1) SiMoH-25, (2) SiMoH-17, (3) SiMoH-9, (4) SiMoH-7, (5) SiMoH-6, (6) SiMoH-5, (7) SiMoH-2, and (8) SiMoH-1.

tures of $SiMo_{12}H$ and SiO_2, with Mo contents similar to those of the SiMoH-x series, give similar results: for the low Mo contents, the Keggin unit on silica can be characterized only by its two highest frequencies (it is impossible to detect $SiMo_{12}H$ unambiguously for contents less than 9% Mo). Some typical spectra are shown in Fig. 4.

With Raman spectrometry, silica does not present bands hindering the characterization of $SiMo_{12}H$: at high Mo content, the Raman spectrum is almost identical to that of $SiMo_{12}H$, as seen in Figs. 5(1) and 5(2). The difficulties remain however important at low Mo contents. It is possible to characterize $SiMo_{12}H$ on the whole spectral range (down to 100 cm^{-1}) for Mo content of 7% [Fig. 5(3)], with however a frequency decrease with respect to unsupported $SiMo_{12}H$ (see Table 2). For lower contents, only the high-frequency part of the spectrum of $SiMo_{12}H$ is evidenced, by using multichannel detection and data accumulations [see, for instance, Fig. 5(4)]. For SiMoH-1, only a weak signal is observed at 975 cm^{-1}. In addition, organized MoO_3, easily characterized by intense Raman bands, was never observed in any of the studied samples.

X-ray diffraction (XRD) data and electron Microscopy (EM) cannot help in the characterization of the samples, since impregnation yields amorphous deposits on the support: the XRD diagrams do not present any lines of crystalline phase, whatever the Mo content, and crystalline forms are also never observed by EM measurements (*15*).

2.3. IR and Raman Characterizations after the Catalytic Reaction

The catalysts of the SiMoH-x series were tested in the conversion of methanol in presence of oxygen: the results were already published in previous works (*10, 13–15*).

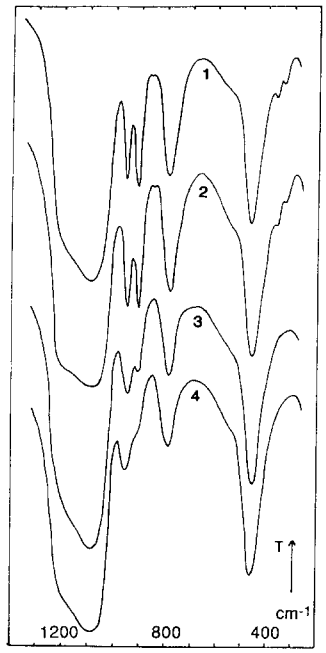

FIG. 4. Infrared spectra (KBr pellets) of some mechanical mixtures of $SiMo_{12}H$ and SiO_2: (1) 30% Mo, (2) 12% Mo, (3) 5% Mo, and (4) 2% Mo.

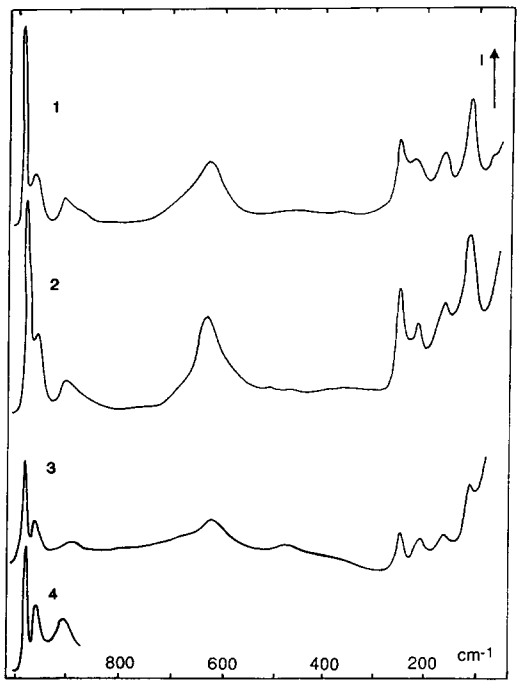

FIG. 5. Raman spectra of unsupported $SiMo_{12}H$ and some catalysts of the series SiMoH-x (1) unsupported $SiMo_{12}H$ (from Ref. (*14*)), (2) SiMoH-25, (3) SiMoH-7, and (4) SiMoH-2.

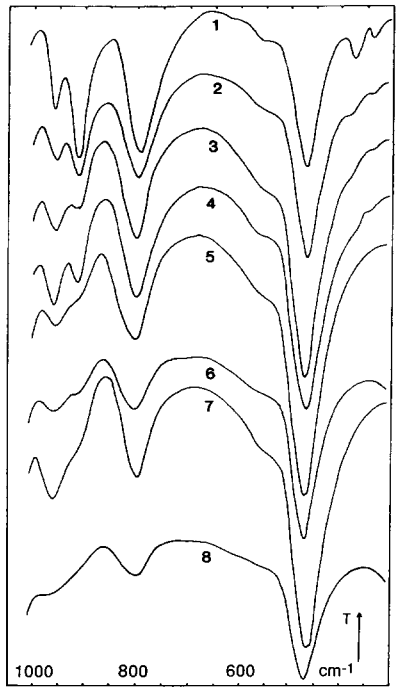

FIG. 6. Infrared spectra (KBr pellets) of the catalysts of the series SiMoH-x after the catalytic reaction: (1) SiMoH-25, (2) SiMoH-17, (3) SiMoH-9, (4) SiMoH-7, (5) SiMoH-6, (6) SiMoH-5, (7) SiMoH-2, and (8) SiMoH-1.

The samples were pretreated under O_2 at 140°C, and the test reaction was conducted at 250°C. All the samples undergo a reduction (color turns from yellow-greenish to light blue), which does not permit measurement of Raman spectra, since the incident beam is absorbed by the reduced sample. The catalytic reaction does not induce significant changes in the infrared spectra of the samples: typical spectra displayed in Fig. 6 essentially differ from those shown in Fig. 3 by the broadening of the bands. A possible reoxidation can occur at the end of the reaction (methanol flow is stopped before oxygen) and/or during the IR sampling. In any case, the relative invariance of the IR spectra after the catalytic test is rather consistent with the fact that the reaction is a surface process and implies that the bulk starting catalyst is preserved. Given this assumption, the blue color could be due to a molybdenum blue.

3. DISCUSSION

All the results presented above can be discussed in relation with those obtained by

TABLE 2

Highest Raman Frequency (cm^{-1}) in Unsupported and Silica-Supported $SiMo_{12}H$

$SiMo_{12}H$	SiMoH-25	SiMoH-17	SiMoH-9	SiMoH-7	SiMoH-6	SiMoH-5	SiMoH-2	SiMoH-1
988	986	983	982	982	982	982	981	975

the reactivity studies in the methanol oxidation and by ^{29}Si NMR. The unsupported acid gives essentially dimethyl ether (*10*). It is catalytically active from 160°C and presents no deactivation and no significant changes of the selectivities for the products of transformation of methanol under different pretreatments up to 280°C. At high coverages, the silica-supported samples behave as unsupported $SiMo_{12}H$: easy access to the acidic protons favors the dehydration of methanol with formation of dimethyl ether (acidic catalysis). On the contrary, for the low Mo contents, the catalytic character is essentially redox, with increased selectivity for formaldehyde, at least down to 2% Mo.

From the results of the Raman spectrometry technique, the Keggin unit is unambiguously preserved at high and medium coverages ($x \geq 7$), with, however, a frequency decrease of ν_sMo–O_d when decreasing the Mo content (see Table 2, showing also that the frequency remains constant from $x = 9$ to $x = 2$). Only the high-frequency region of the spectra is observed for the low Mo contents [three bands for SiMoH-2, Fig. 5(4); one band for SiMoH-1]. The band at the highest frequency could be interpreted as ν_sMo–O_d: as the water content is the same for all samples, and as this water is only weakly bound, it is likely that the frequency decrease with respect to unsupported $SiMo_{12}H$ is essentially due to a weakening of the anion–anion interactions by the formation of isolated $SiMo_{12}$ units. According to the shape of the pattern for SiMoH-2, this assumption seems reasonable; however, for SiMoH-1, taking into account the sudden decrease of the frequency, the assignment of the unique band observed to ν_sMo–O_d of isolated $SiMo_{12}$ anions remains questionable.

It is now helpful to consider the results of the recent study by ^{29}Si magic-angle-spinning NMR of $SiMo_{12}H$ and of the catalysts of the SiMoH-x series (*16*). Unsupported $SiMo_{12}H$ is characterized by a unique isotropic line at -74.5 ± 0.1 ppm, and a spin-lattice relaxation time T_1 of about 16 s. For the supported samples of the series SiMoH-x, T_1 decreases dramatically (down to 0.3 s for $x \leq 17$). Correlatively a slight high-frequency shift with respect to unsupported $SiMo_{12}H$ is observed. For high Mo contents, for instance SiMoH-25, two ^{29}Si NMR signals are evidenced [two sites corresponding to unperturbed $SiMo_{12}H$ (site 1, $\delta \approx -74.5$ ppm, long T_1), and to another species (site 2, $\delta \approx -74.3$ ppm, short T_1)]. Taking into account the value of δ for the species in site 2, and the very weak frequency shift with respect to the unsupported $SiMo_{12}H$, the species in site 2 is likely assumed to be closely related to a Keggin unit. As it was demonstrated that for high Mo contents ($x \geq 7$) the IR and Raman spectra are consistent with the presence of $SiMo_{12}H$, with only slight frequency shifts which accompany the impregnation process, the second NMR signal (Si in site 2) can be assigned to a Keggin anion slightly perturbed by the support (weak electrostatic interaction with the OH_2^+ groups of the silica). Since this signal assigned to a perturbed 12-molybdosilicate anion is detected down to 2% Mo (SiMoH-2), it is now possible to consider that the aforementioned interpretation of the partial Raman pattern for $2 \leq x < 7$ (only the high-frequency region is observed) as characteristic of isolated $SiMo_{12}$ anions is therefore quite likely. This is also confirmed by the constant value of ν_sMo–O_d (within the experimental error) in the range $2 \leq x \leq 9$.

This interpretation is also consistent with the catalytic behavior: in the samples with low Mo content, hydrated protons from the 12-molybdosilicic acid may be more and more trapped through an electrostatic interaction between the surface and the polyanion via the formation of Si-OH_2^+ groups when increasing dilution. As a consequence, the number of Brønsted-acid sites may decrease, inducing the decreasing of the acidic character.

Our model of $SiMo_{12}$ anions electrostatically attracted by the Si–OH_2^+ groups has now to be examined with a topological point

of view by considering the OH groups of the silica. With the rough assumption that the Si centers of the silica are arranged in triangles sharing their sides (Si–Si = ~3.06 Å), a surface area of ~800 $m^2 g^{-1}$ can be calculated, a result only about two-fold higher than the experimental one (376 $m^2 g^{-1}$). This means that this silica could be essentially considered as a surface support (two layers), without any inaccessible core. This type of fractal model is consistent with those described by Legrand *et al.* (*19*). On this fractal support, the OH groups can be randomly distributed, and eventually packed in clusters, as already pointed out (*20*). These clusters could be formed of triangles or squares (distances close to 3–4 Å). The Keggin anions can be considered as balls with a "radius" of about 5.2 Å (*17*). The negative charges of the quasi-spherical Keggin anions are located on the external oxygen atoms. From geometrical considerations taking into account the distances between these oxygen atoms, the attraction of the Keggin ball to clusters of protonated OH groups is possible and can be easily realized. (The distances between the nearest external oxygen atoms are in the range between 2.56 and 2.80 Å. Whatever the position of the ball, there are always triangles of oxygens with side lengths in this range). Assuming that the monolayer coverage is obtained by a close packing of the anions on the silica surface (*10, 13*), one ball is associated with about 20 accessible surface Si centers (i.e., 40 Si centers, taking into account the two layers), as seen in Fig. 7(1). For each 12-molybdosilicate anion $SiMo_{12}$, there are four H^+ eventually capable of acting on the surface OH groups. As mentioned above, there are about 0.1 mol OH per mol SiO_2, i.e., one OH per 10 Si centers. If an interaction occurs between these OH groups and the protons, giving rise to OH_2^+ groups, there are therefore not enough OH groups to complete the interaction, even with a less-charged polyanion such as $PMo_{12}O_{40}^{3-}$ noted PMo_{12} (1 OH/10 Si corresponds to 2 OH_2^+/polyanion: $SiMo_{12}$ needs four OH_2^+, and PMo_{12} only three OH_2^+). A monolayer approximation is therefore not a suitable model. In a recent study by ^{31}P NMR of silica-supported 12-molybdophosphoric acid catalyst (*21*), the correlation between the T_1 relaxation times and the Mo content indicates that the saturation of the interaction sites occurs for 10% in weight Mo, corresponding to ~0.025 mol H^+ per mol Si, i.e., three H^+ per 120 Si, or one polyanion PMo_{12} per 120 Si, and one polyanion per 60 surface Si centers (only one-half of the Si centers is available). As a consequence, there are enough OH groups which are randomly distributed, but only a part of them (those which are sterically favorable) can be available for the interaction with both the Keggin anions and the protons: such a situation is schematically drawn in Fig. 7(2). Because of the difficulty in measuring the T_1 relaxation times of ^{29}Si nuclei at low contents for silica-supported 12-molybdosilicic acid catalysts (see below), such an estimation of the Mo content corresponding to the saturation of the interaction sites for this kind of catalysts can be only very roughly obtained. This saturation likely also occurs for about 10% Mo, i.e., for about 0.03 to 0.04 mol H^+ per mol Si (see Table 1), i.e., one polyanion $SiMo_{12}$ per 60 surface Si centers. As for the silica-supported 12-molybdophosphoric acid catalysts, only a part of the OH surface groups is engaged in the protonation process, and the surface repartition of $SiMo_{12}$ anions seems to be similar to that of PMo_{12} anions (three protons trapped). As a consequence, for the SiMoH-*x* series, all the protons are not trapped in the interaction $SiMo_{12}/Si–OH_2^+$. Those which remain accessible for the dehydration of methanol (about one proton per polyanion) induce a persistence of acidic catalysis, even at low Mo contents. There is a repartition of the protons between the silica support and the polyanion: those favorably located on the OH groups can interact with $SiMo_{12}$ (three protons per polyanion) and are not accessible for acidic catalysis, the

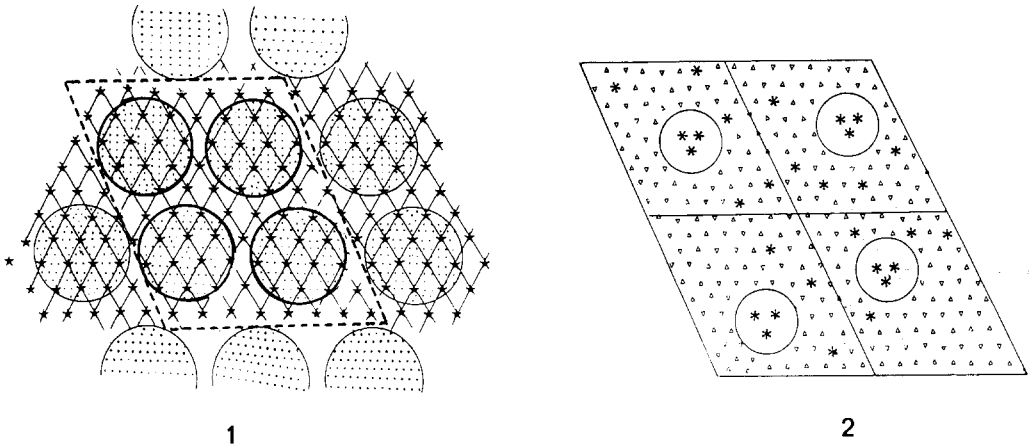

FIG. 7. Schematic representation of the packing of $SiMo_{12}$ anions on the silica surface (1) "monolayer" coverage (close packing approximation): ★ = Si centers and ○ = $SiMo_{12}$ anions; (2) possible configuration of the interaction between $Si-OH_2^+$ and $SiMo_{12}$: △ = Si centers, * = OH groups randomly distributed on the surface, and ○ = $SiMo_{12}$ anions.

other ones can favor the dehydration of methanol.

The above model explaining the interaction between polyanions and silica is further supported by the catalytic behavior of the samples. Let us recall some reactivity results from the 12-molybdosilicic acid catalysts in the test reaction of conversion of methanol in presence of oxygen (*10, 13–15*). Some of these results are displayed in Table 3. For the unsupported acid, the redox activity estimated from formaldehyde formation is about 10^{-2} mol/h/gMo, and the acidic activity estimated from dimethyl ether formation is about $3.5\ 10^{-2}$ mol/h/gMo (*10, 13, 15*). When this bulk material is submitted to thermal treatments up to 400°C, MoO_3 is formed and the corresponding redox and acidic activities become 1.5×10^{-2} mol/h/gMo and 4×10^{-3} mol/h/gMo, respectively (*10*). Redox activities are similar for both $SiMo_{12}H$ and MoO_3, and the more acidic

TABLE 3

Activities in the Methanol Conversion and Surface Areas of Some Catalysts

Sample	Surface area (m^2/g Mo)[a]	Activity (mol/h/g Mo)		Normalized activity (mol/h/m^2 Mo)		Normalized activity (mol/h/mol Mo)	
		Oxidation	Acidic	Oxidation	Acidic	Oxidation	Acidic
$SiMo_{12}H$ treated at 144°C	5.5	10^{-2}	3.5×10^{-2}	1.8×10^{-3}	6.3×10^{-3}	90	310
MoO_3 from $SiMo_{12}H$ treated at 400°C	5.1	1.5×10^{-2}	4×10^{-3}	2.9×10^{-3}	7.8×10^{-4}	150	39
SiMoH-5	500[b]	5×10^{-2}	6×10^{-2}	10^{-4}	1.2×10^{-4}	5	6

[a] In the text, surface area is expressed in m^2/g of compound.
[b] Calculated from the surface of the Keggin balls.

activity for $SiMo_{12}H$ seems essentially due to the protons. With this assumption, as there is one proton per three Mo, the activity associated with each proton is comparable to the redox activity (about 10^{-2} mol/h/gMo). These activities seem weaker than those of the supported catalysts of the series SiMoH-x. However, by considering that the methanol conversion is a surface reaction, a normalization taking into account the surface area is required since all the Mo centers are not available in the unsupported compounds. With well-crystallized hydrated $SiMo_{12}H$, the surface area is very low, and increases with increasing the temperatures of the pretreatments (see Table 4 and Experimental part). The surface areas are 3.5 m^2 g^{-1} for $SiMo_{12}H$ treated at 144°C, 0.2–0.3 m^2 g^{-1} for MoO_3 (commercial grade), and 3.4 m^2 g^{-1} for MoO_3 obtained from thermal decomposition of $SiMo_{12}H$ (*22*). Consequently, after normalization [activities are now expressed in mol/h/m^2 (of active site), and/or mol/h/mol (of active site)], the redox and acidic activities become respectively 1.8×10^{-3} and 6.3×10^{-3} mol/h/m^2 Mo (or 90 and 310 mol/h/mol Mo) for unsupported $SiMo_{12}H$, and 2.9×10^{-3} and 7.8×10^{-4} mol/h/m^2 Mo (or 150 and 39 mol/h/mol Mo) for MoO_3. Considering now a well-dispersed catalyst, such as SiMoH-5, the normalization has been carried out by considering the surface of the Keggin balls: the corresponding normalized activities are respectively 10^{-4} mol/h/m^2 Mo (or 5 mol/h/mol Mo) (redox) and 1.2×10^{-4} mol/h/m^2 Mo (or 6 mol/h/mol Mo) (acidic). The comparison with unsupported $SiMo_{12}H$ and MoO_3 leads to assume that the activity strongly depends on the number of interacting centers: the more dispersed the Mo centers, the weaker the activity. Moreover because of the equivalence of redox and acidic activities, it seems that there is always one untrapped proton per one $SiMo_{12}$ that induces acidic character, even for well-dispersed catalysts (see Table 3). Our model of surface OH groups interacting with polyanions seems useful at least down to 2% Mo.

TABLE 4

Evolution of the Surface Area of $SiMo_{12}H$ with Respect to the Temperature of the Pretreatments Performed Prior to the BET Measurement (See Experimental Part)

Temperature (°C)	Duration (h)	Surface area (m^2/g of compound)
30	2	0.2
60	1	0.5
110	0.5	1.9
150	0.5	3.5
250	0.5	3.7
280	0.5	3.5

We have now to consider the very low Mo contents ($x < 2$). Owing to the low natural abundance (4.7 atom %) of ^{29}Si, to its chemical dilution in the polyoxoanion (1.5 wt%), and to its dilution in the supported samples, very long spectrometer time is required for low coverages: e.g., 19 h to get a weak signal characteristic of $SiMo_{12}$ for SiMoH-2. As said above, it can be considered with confidence that the Keggin unit is present on the silica surface at least down to 2% Mo. However, without quantitative determination (extremely time-consuming, as explained in Ref. (*16*), this does not exclude the simultaneous presence of another polyoxomolybdate phase. At lower loading, the highly selective ^{29}Si NMR fails to give information on the nature of the species on the surface. Only Raman spectrometry gives information in the form of a unique signal at 975 cm^{-1}. It is however very difficult to conclude unambiguously on the true nature of the molybdenum species with such a weak proof. When considering the sudden decrease of the $\nu_s Mo{-}O_d$ frequency for SiMoH-1 with respect to the constant value observed for the Mo contents in the range $x = 9$ to $x = 2$ (see Table 2), we are tempted to consider that the Keggin units no longer exist on the silica support for $x = 1$, and that a new species is formed on the surface. Among the known polyoxomolybdic species, only those containing the trimolybdic

group, fragment of the Keggin unit (see Fig. 1), present an Mo-terminal O band in this frequency range (*23*). We could suggest that the eventual polyoxomolybdate phase induced by the degradation of the Keggin unit at low loading could be constituted at least of trimolybdic groups connected together.

For SiMoH-1, methyl formate is the main product formed in the reaction of methanol oxidation (*13–15*). The results obtained on silica-grafted molybdenum catalysts (*2*) suggest that the selectivity for methyl formate could be used as a dispersion-sensitive probe. In this assumption, we could consider that the dispersion is better for SiMoH-1 than for SiMoH-2, with, in both cases, $SiMo_{12}$ anions on the surface. However, as there is only little change in the formation of methyl formate down to 2% Mo, followed by a sudden increase for SiMoH-1, this assumption seems questionable. Moreover, in samples obtained by calcination at 500°C of silica-supported hexamolybdate catalysts (*13*), lowering the Mo content induces as well the increase of selectivity for methyl formate: in this case a polyoxomolybdate phase different from the Keggin unit is formed. The formation of methyl formate could be favored by well dispersed surface Mo centres, not aggregated in compact structures such as the Keggin structure, but arranged in trimolybdic groups well dispersed on the silica surface. The high selectivity for methyl formate could be the sign of the partial degradation of the Keggin unit. A dispersion probe for the Keggin unit could be rather the spin–lattice relaxation time T_1, as suggested by Thouvenot *et al.* (*16*), or the formation of formaldehyde in the test reaction of oxidation of methanol (*10, 13–15*).

CONCLUSION

This study evidences the effect of dispersion on the surface state of 12-molybdosilicic acid catalysts supported on silica, and shows the importance of using several complementary techniques, in order to make the identifications more valuable.

Because of the strong absorptions of silica, IR spectrometry is only efficient at high coverages. Raman spectrometry is a more powerful technique, but needs help from ^{29}Si NMR to be more convincing at coverages $2 \leq x < 7$. Indeed both Raman and NMR techniques bring complementary information which, in connection with the reactivity studies, afford a better knowledge of the surface of the impregnated samples. At high loadings, there is no ambiguity with the Raman data: the spectrum is similar to that of unsupported $SiMo_{12}H$. At this level, NMR distinguishes two kinds of $SiMo_{12}H$: one similar to unsupported $SiMo_{12}H$, the other interpreted as $SiMo_{12}H$ in interaction with silica. For SiMoH-7, both techniques are consistent with isolated $SiMo_{12}$ anions in interaction with silica. At lower loadings (down to 2%), the NMR signal is quite consistent with the presence of the Keggin unit, implying that the partial Raman pattern is due to $SiMo_{12}H$.

Interaction of $SiMo_{12}$ anions with silica through $Si–OH_2^+$ groups decreases the number of accessible Brønsted-acid sites, and favors the progressive change of catalytic character (predominant redox catalysis at low Mo contents). All the results (Raman, NMR, and catalytic reactivity) suggest SiMoH-2 as a model of isolated Keggin anions in interaction with the silica surface.

The most important conclusion is the preservation of the Keggin unit when deposited by impregnation on the silica for Mo contents down to 2% in weight (at lower contents partial degradation is likely), and its interaction with the support evidenced by decreases in the Raman frequencies and in the T_1 relaxation times, and by a change in the catalytic character in the methanol oxidation.

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