

Structure and Catalytic Properties of Silica-Supported Polyoxomolybdates

II. Thermal Behavior of Unsupported and Silica-Supported 12-Molybdosilicic Acid Catalysts from IR and Catalytic Reactivity Studies

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Thermal behavior of unsupported and silica-supported 12-molybdosilicic acid (with Mo loadings of 17.6 and 9 wt%) are studied by IR spectrometry and catalytic reactivity in the methanol oxidation reaction. In the case of the unsupported acid (SiMo_{12}H), IR and catalytic reactivity measurements show that the destruction of the Keggin unit is rather abrupt in the temperature range 300–320°C (collapse of the acidic character in catalysis, formation of MoO_3 evidenced by IR). The thermal stability of SiMo_{12}H is reduced by ~20–30°C when supported on silica, and the destruction of the Keggin unit extends over a larger temperature range. The nature of the Mo oxo species responsible for the redox activity after thermal treatments at temperatures higher than 330°C is discussed. © 1990 Academic Press, Inc.

INTRODUCTION

Catalytic applications of heteropolyanions have attracted increasing interest in the last decade (1). Catalysts based on polyoxometalates related to the Keggin structure have been particularly studied: these compounds with both acidobasic and redox properties have been shown to be efficient in a wide variety of chemical processes.

In a previous paper (2), we used 12-molybdosilicic acid (SiMo_{12}H) supported on silica for studying the effect of dispersion on the catalytic properties through the test reaction of methanol oxidation. At high Mo loadings, the acidic catalytic character related to the formation of dimethylether is predominant. It dramatically decreases at loadings less than 10 wt% Mo. At low loadings, the catalytic reaction is mainly of the redox type, as inferred from the formation of oxidized products, formaldehyde in particular.

A correlation between the catalytic data and the dispersion of SiMo_{12}H was proposed (2): the low acidity at low loadings could arise from an interaction of silica and molybdosilicic acid through the OH surface groups and the acidic protons.

The test reaction was conducted at 230 and 250°C, and the samples were characterized before and after the reaction by vibrational spectrometry. At high and medium loadings (down to 7 wt% Mo), the Keggin unit is preserved. At lower loadings, only the high-frequency bands are observed, and are consistent either with isolated $\text{SiMo}_{12}\text{O}_{40}^{4-}$ anions (SiMo_{12}), or with constitutive fragments of the Keggin unit (trimolybdic groups) in interaction with silica. It appears that the stability of the Keggin unit on the silica support is questionable at low loadings.

The problem of the thermal stability of the heteropolyanions has been studied for a long time by numerous teams. We have

already pointed out (3) that, under dynamic heating, the temperatures at the beginning of decomposition of the Keggin structure compounds depend on the heteroatom (Si, P, Ge, etc.), on the metal atom (W or Mo), and on the cation: in the case of the acids and of the tetraalkylammonium salts, these temperatures lie in the range 200–350°C. Under static heating for several hours, the decomposition occurs, of course, at lower temperatures, depending on the level and the duration of the thermal treatment.

What happens now when these compounds are deposited on a support such as silica? According to Öhlman *et al.* (4, 5), the thermal stability of the heteropolyanions decreases when supported on silica; moreover, the lower the concentration on the support, the lower the stability. In contrast, Moffat *et al.* (6, 7) conclude a stabilization of the heteropolyanions by the support: 12-molybdophosphoric acid and 12-molybdosilicic acid are found to be stable up to 570°C when supported on silica. Similar conclusions are proposed by Chumachenko *et al.* (8, 9) and Goncharova *et al.* (10): silica stabilizes SiMo_{12}H up to 600°C. In view of the contradictory results, it appeared timely to reinvestigate the question.

Consequently this paper deals with the thermal behavior of unsupported and silica-supported SiMo_{12}H , by means of infrared spectrometry and catalytic reactivity in the test reaction of methanol oxidation. Both approaches, simple but efficient, can be used as sensitive means of probing surface changes. Two supported samples already studied in our previous work (2) were chosen because their Mo content allows unambiguous Keggin unit characterization (17.6 and 9 wt% Mo). So both support and concentration effects on the thermal stability are expected to be probed.

1. EXPERIMENTAL PART

1.1. Preparation of Samples

12-molybdosilicic acid $\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ (abbreviated SiMo_{12}H) was prepared

according to a method previously described (3). The silica support (Rhône-Poulenc XOA 400, surface area $376 \text{ m}^2 \cdot \text{g}^{-1}$) was impregnated with aqueous solutions of SiMo_{12}H . Two supported samples were prepared by stirring SiO_2 and impregnation solutions at $\sim 50^\circ\text{C}$ until dryness evaporation. The catalysts were then dried under vacuum at 100°C . The final Mo contents of the samples referred to as SiMoH-17.6 and SiMoH-9 were 17.6 and 9% in weight, respectively, as determined by microanalysis techniques (Service Central de Micro-analyse du CNRS, 69390 Vernaison, France). In the approximation of close packing of anions on the silica surface, the Mo contents of the two studied samples correspond to 0.5 and 0.25 monolayer, respectively.

1.2. Thermal Treatments

For infrared studies, each catalyst (either unsupported SiMo_{12}H or supported catalysts) was heated in air, in platinum crucible, at different temperatures from 250 to 500°C (temperatures controlled by a thermocouple located near the crucible in the furnace). At first, the samples were heated at 250°C and maintained at this temperature for 2 h. After having cooled the sample in a desiccator, the IR spectrum was recorded. Then the samples were submitted to a similar procedure at a higher temperature (heating at this temperature for 2 h, cooling, recording of the IR spectrum). The same operation was repeated until the final temperature (500°C) was reached.

For catalytic measurements, each catalyst packed in the reactor was heated at different temperatures of treatment from 250 to 500°C for 2 h under O_2 without admission of the reagent mixture ($\text{He}/\text{O}_2/\text{CH}_3\text{OH}$). Then, it was cooled to 250°C , the temperature at which the reagent mixture was admitted and the catalytic test conducted. As for the infrared studies, the operation was repeated until the final treatment temperature was reached. The temperatures of the different thermal treatments were

controlled by a thermocouple located near the glass reactor.

1.3. Infrared Spectrophotometry (IR)

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer (4000–200 cm^{-1}) as KBr pellets.

1.4. Catalytic Measurements

Oxidation of methanol was used as test reaction. The experimental conditions were previously described (11). All the test reactions were conducted at 250°C. The stabilization of the activity of the catalysts was reached after about one half hour.

1.5. Thermogravimetry (TG)

Thermogravimetry was carried out in air on a Cahn RG electrobalance equipped with a Kipp & Zonen Micrograph BD5 recorder coupled with a BA5 channel selector (sample weight 1–10 mg; heating rate 5°C/min; sensitivity and reproducibility better than 5 μg).

2. RESULTS

2.1. Unsupported SiMo_{12}H Behavior

2.1.1. Infrared studies. IR spectra are shown in Fig. 1. The spectrum of the untreated SiMo_{12}H (Fig. 1a) is consistent with the previously published results (3). All the characteristic features of the Keggin structure are observed (957, 904, 855, 770, ~535, 370, 340 cm^{-1} ; see Ref. (3) for assignments). This structure is preserved after thermal treatments up to ~300°C (Fig. 1b,c,d). From 310°C upward, some bands of molybdenum trioxide MoO_3 begin to appear (996, 860, 600, 366 cm^{-1}), showing the beginning of the destruction of the Keggin unit (Fig. 1e). After a thermal treatment at 320°C (Fig. 1f), a mixture of MoO_3 and SiMo_{12}H is clearly evident. Above 340°C, only the bands of MoO_3 are observed in the IR spectra (Fig. 1g,h,i,j) (SiO_2 , as a decomposition product, is formed in such small amounts that it is not evidenced by IR). Increasing the treatment temperature leads to a better crystallinity of

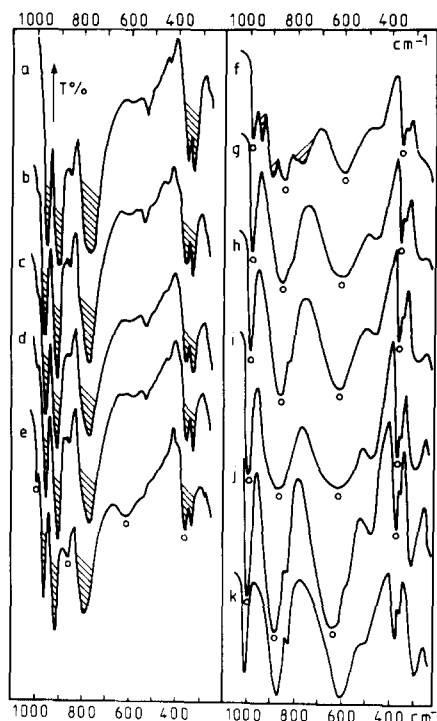


FIG. 1. IR spectra of SiMo_{12}H after different thermal treatments (for 2 h) (hatching: SiMo_{12}H ; (O) MoO_3): (a) Untreated SiMo_{12}H ; (b) 250°C; (c) 280°C; (d) 300°C; (e) 310°C; (f) 320°C; (g) 340°C; (h) 370°C; (i) 400°C; (j) 500°C; (k) MoO_3 (commercial grade Prolabo).

the oxide formed, and, thus, to better defined spectra. Some shifts of the band frequencies with respect to those of the commercial orthorhombic trioxide MoO_3 (Fig. 1k) are observed: we have already pointed out (11) that these shifts are probably related to water and crystallization effects.

2.1.2. Reactivity. The results of the catalytic behavior of SiMo_{12}H after successive thermal treatments at different temperatures from 250 to 400°C are reported in Table 1. Analysis of the curves of selectivities (Fig. 2) and activities (Fig. 3a) as a function of the treatment temperature allows definition of two regions of different catalytic behaviors, the first from 250 to 310°C and the second from 310 to 400°C. In the first region, acidic catalysis is predominant: dimethyl ether is the main product formed (selectivity

TABLE 1

Selectivities and Activities of SiMo_{12}H after Thermal Treatments at Different Temperatures (Test Conducted at 250°C)

SiMo_{12}H T ($^\circ\text{C}$)	Selectivities (%)					Total activities (mmol/h/g Mo)	Conversion (%)
	1	2	3	4	5		
230	11	2	9	74	4	37	7
250	12	3	6	72	7	49	8
280	22	4	8	64	2	49	8
300	24	6	5	64	1	87	13
310	24	5	5	64	2	126	13
320	60	8	17	14	1	28	8
330	59	7	19	14	1	25	8
350	59	8	18	14	1	26	8
400	59	8	18	14	1	24	7

Note. 1, CH_2O ; 2, HCOOCH_3 ; 3, $(\text{CH}_3\text{O})_2\text{CH}_2$; 4, $(\text{CH}_3)_2\text{O}$; 5, $\text{CO}_2 + \text{CO}$.

$\geq 64\%$). Between 250 and 310°C , the activity increases and reaches a maximum at 310°C . The second region is characterized by a sudden collapse of the activity, and a change of the catalytic properties. Redox catalysis becomes predominant: the selectivity for mild oxidation products is greater than 85%, while that for dimethyl ether decreases down to 14%. The increase of the selectivity for methylal is consistent with the formation of MoO_3 , according to the mechanism proposed by Chung *et al.* (12). The catalytic behavior can be correlated to the TG curve

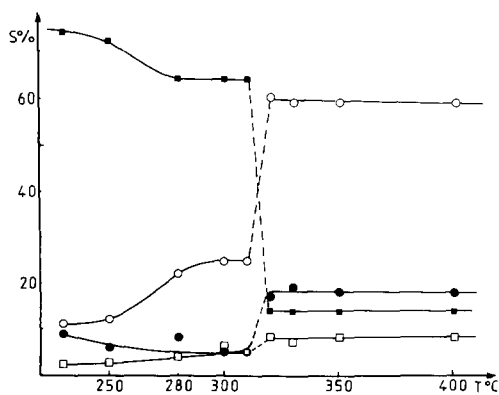


FIG. 2. Selectivities of SiMo_{12}H versus thermal pre-treatment temperature (test conducted at 250°C): (○) CH_2O ; (□) HCOOCH_3 ; (●) $(\text{CH}_3\text{O})_2\text{CH}_2$; (■) $(\text{CH}_3)_2\text{O}$.

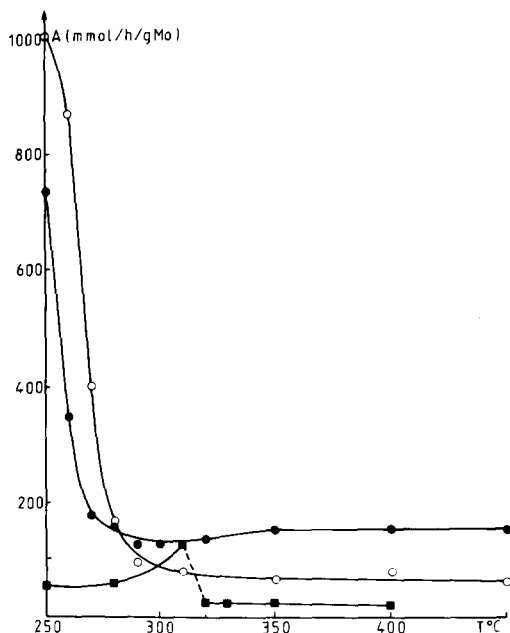


FIG. 3. Total activities (mmol/h/gMo) of unsupported and silica-supported SiMo_{12}H catalysts versus thermal pretreatment temperature (test conducted at 250°C): (■) unsupported SiMo_{12}H ; (○) SiMoH-17.6 ; (●) SiMoH-9 .

of SiMo_{12}H (Fig. 4): the loss of acidic protons under the form of "constitution water" occurs in the same temperature range, in which a mixture of SiMo_{12}H and MoO_3 is expected.

2.2. Silica-Supported SiMo_{12}H Behavior

2.2.1. Infrared studies. Infrared spectra of the two SiMoH-17.6 and SiMoH-9 samples before and after several thermal treatments are shown in Fig. 5 and 6. Silica exhibits three main bands at $\sim 1100\text{ cm}^{-1}$ (broad and very strong), $\sim 800\text{ cm}^{-1}$ (medium), and

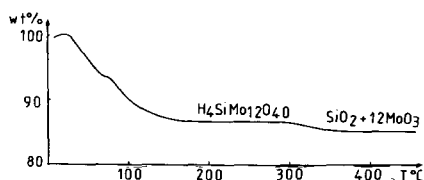


FIG. 4. TG curve of $\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ (heating rate: $5^\circ\text{C}/\text{min}$; sample weight: 8.356 mg).

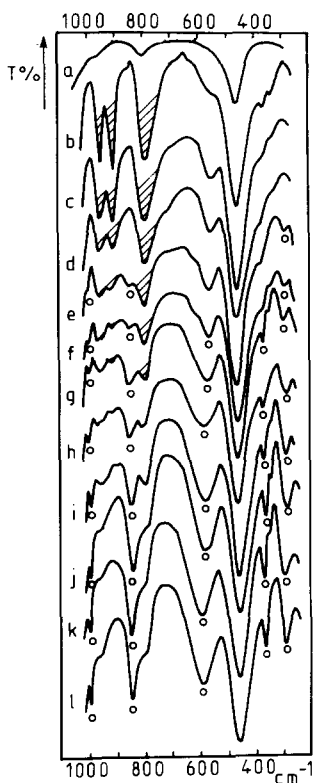


FIG. 5. IR spectra of SiMoH-17.6 after different thermal treatments (for 2 h) (hatching: SiMo₁₂H; (○) MoO₃): (a) silica; (b) untreated SiMoH-17.6; (c) 250°C; (d) 270°C; (e) 290°C; (f) 300°C; (g) 315°C; (h) 320°C; (i) 345°C; (j) 355°C; (k) 430°C; (l) 500°C.

~470 cm⁻¹ (strong) (Fig. 5a). From the reasons developed in a previous paper (11), the results have been discussed from the original spectra, without subtracting the silica background.

The IR spectrum of SiMoH-17.6 before any treatment exhibits the bands of unsupported SiMo₁₂H, with insignificant frequency shifts (Fig. 5b). Both SiMo₁₂H and silica contribute to the band at ~800 cm⁻¹. The contribution of SiMo₁₂H in the 650–400 cm⁻¹ region (Fig. 1b) is partly obscured by the strong silica band at 470 cm⁻¹, and appears as a broad shoulder on this band. After thermal treatments at 250 and 270°C (Fig. 5c,d), the Keggin unit is preserved, with however a significant broadening of the

characteristic bands (Mo-terminal O stretch at ~960 cm⁻¹, and Si–O stretch at ~910 cm⁻¹ (3)). This broadening may be correlated to the increase of the dispersion of the species. An evolution of the shoulder pointed out above toward a band at ~560 cm⁻¹ is also observed. From 290°C upward, the bands characteristic of MoO₃ begin to appear (Fig. 5e and following), and become more and more predominant. The bands due to SiMo₁₂H progressively disappear; a change in the relative intensities of the two bands at 960 and 910 cm⁻¹ is also observed. Above 355°C (Fig. 5j,k,l), only bands of MoO₃ are visible, with a shoulder at ~960 cm⁻¹ which could be assigned to silica OH groups and/or a surface polyoxomolybdate (11, 13–18).

Exactly like that of SiMoH-17.6, the IR spectrum of SiMoH-9 (Fig. 6a) before any treatment shows the preservation of the Keggin unit. Thermal treatments rapidly induce important modifications in the spectra. After treatments at 250 and 270°C (Fig. 6b and c), the relative intensities of the two bands at 960 and 910 cm⁻¹, characteristic of the Keggin structure, are changed with respect to those of the untreated sample. When the temperature is increased, the band at 910 cm⁻¹ tends to progressively disappear (Fig. 6d and following). After treatments at 400 and 500°C, it remains only a band at 960 cm⁻¹, which, as for SiMoH-17.6, could be associated with silica OH groups (at least up to 300°C) and/or surface polyoxomolybdate, and a band at ~560–570 cm⁻¹, which could also be related to such a surface species. Whatever the temperature of the thermal treatment, bands characteristics of MoO₃ are never observed.

2.2.2. *Catalytic reactivity.* The results of the catalytic behavior of SiMoH-17.6 and SiMoH-9 after successive thermal treatments at different temperatures from 250 to 450°C are reported in Tables 2 and 3. Selectivities as a function of the treatment temperature are displayed in Fig. 7 and 8. Activities (Fig. 3b,c) are expressed with respect to the molybdenum weight, in order

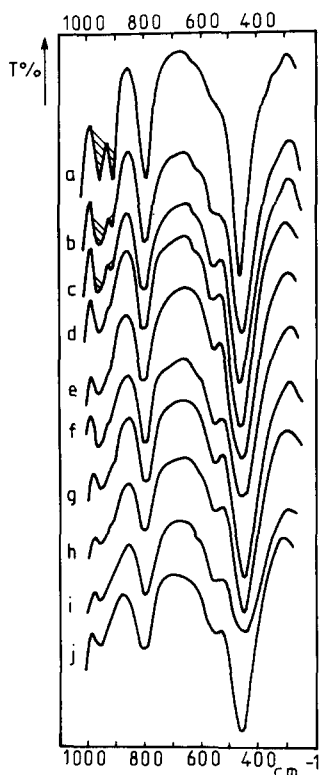


FIG. 6. IR spectra of SiMoH-9 after different thermal treatments (for 2 h) (hatching: SiMo_{12}H): (a) untreated SiMoH-9; (b) 250°C; (c) 270°C; (d) 285°C; (e) 300°C; (f) 320°C; (g) 345°C; (h) 360°C; (i) 400°C; (j) 500°C.

TABLE 2

Selectivities and Activities of SiMoH-17.6 after Thermal Treatments at Different Temperatures (Test Conducted at 250°C)

SiMoH-17.6 <i>t</i> (°C)	Selectivities (%)					Total activities (mmol/h/g Mo)	Conversion (%)
	1	2	3	4	5		
250	18	4	12	66	0	1004	9
260	28	5	13	53	1	869	8
270	32	8	21	38	1	400	7
280	36	11	30	22	1	183	5
290	39	25	26	9	1	96	5
310	43	35	16	4	2	80	6
350	41	42	12	3	2	64	5
400	35	49	12	2	2	80	6
450	37	47	11	2	3	60	6

Note. 1, CH_2O ; 2, HCOOCH_3 ; 3, $(\text{CH}_3\text{O})_2\text{CH}_2$; 4, $(\text{CH}_3)_2\text{O}$; 5, $\text{CO}_2 + \text{CO}$.

TABLE 3

Selectivities and Activities of SiMoH-9 after Thermal Treatments at Different Temperatures (Test Conducted at 250°C)

SiMoH-9 <i>t</i> (°C)	Selectivities (%)					Total activities (mmol/h/g Mo)	Conversion (%)
	1	2	3	4	5		
250	20	6	10	63	1	736	7
260	31	10	17	41	1	344	5
270	32	15	20	32	1	174	5
280	38	27	14	19	2	153	7
290	45	25	18	10	2	125	6
300	49	27	13	8	3	127	7
320	46	32	12	7	3	135	8
350	44	36	12	5	3	150	8
400	49	32	12	5	2	151	9
450	44	35	12	6	3	151	9

Note. 1, CH_2O ; 2, HCOOCH_3 ; 3, $(\text{CH}_3\text{O})_2\text{CH}_2$; 4, $(\text{CH}_3)_2\text{O}$; 5, $\text{CO}_2 + \text{CO}$.

to get a direct relation between the methanol transformation and the amount of Mo deposited on the support.

The catalytic behavior of SiMoH-17.6 and SiMoH-9 is characterized by an activity higher than that in the case of unsupported SiMo_{12}H , probably by favoring the accessibility of Keggin units through a dispersion effect, and, consequently, by increasing the number of active sites. In both cases, the selectivity for dimethyl ether strongly decreases as soon as the temperature of the

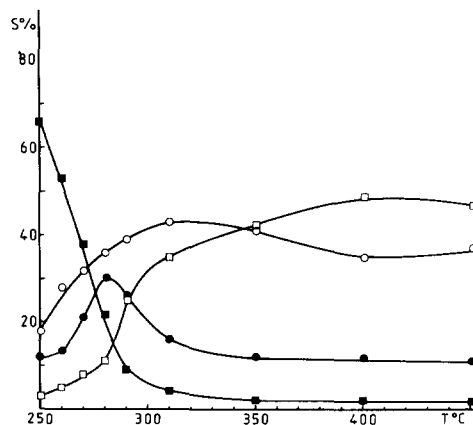


FIG. 7. Selectivities of SiMoH-17.6 versus thermal pretreatment temperature (test conducted at 250°C): (○) CH_2O ; (□) HCOOCH_3 ; (●) $(\text{CH}_3\text{O})_2\text{CH}_2$; (■) $(\text{CH}_3)_2\text{O}$.

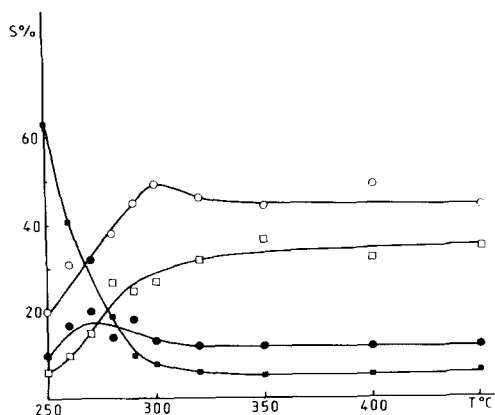


FIG. 8. Selectivities of SiMoH-9 versus thermal pre-treatment temperature (test conducted at 250°C): (○) CH₂O; (□) HCOOCH₃; (●) (CH₃O)₂CH₂; (■) (CH₃)₂O.

thermal treatment is increased. It stabilizes at a low level (less than 5%) after treatments at temperatures higher than 310°C. Simultaneously the selectivities for oxidation products (formaldehyde, methyl formate) increase for treatments between 260 and 310°C, and stabilize for treatments at higher temperatures. The activities of the two samples exhibit the same shape as a function of the treatment temperature. For SiMoH-17.6 and SiMoH-9, the treatment temperatures at which the redox activity become higher than the acidic activity ("turning points") are respectively ~280 and 270°C. Activities (expressed with respect to Mo weight) of SiMoH-9 over 290°C are higher than those of SiMoH-17.6 under the same conditions. This is perhaps due to a better dispersion of the active sites in the case of SiMoH-9, and to the fact that MoO₃, which is known to have little activity, is formed in the case of SiMoH-17.6.

3. DISCUSSION

3.1. Unsupported SiMo₁₂H Behavior

Both IR and catalytic reactivity studies give information about the thermal stability of unsupported SiMo₁₂H. In both cases, two regions are defined. The first one, up to ~300–310°C, corresponds to the stability domain of SiMo₁₂H (preserved IR spectrum,

predominant acidic catalysis). The second one (above 320°C) is characterized by a predominant redox activity due to the formation of MoO₃. The increase of activity when increasing the temperature of the thermal treatments (up to 310°C) is paralleled with the fact that the selectivities do not vary significantly in the same temperature range. From these results, it is likely that the same species, namely SiMo₁₂H, is responsible for the activity, enhanced through an increase of the number of the active sites. This increase of activity is now being investigated. In a narrow temperature range (300–320°C), the IR spectra are consistent with a mixture of MoO₃ and SiMo₁₂H, which agrees with the above statement considering that SiMo₁₂H remains the active species. As pointed out above, this behavior could be correlated to the TG curve of SiMo₁₂H (Fig. 4).

3.2. SiO₂-Support Effect

In the case of unsupported SiMo₁₂H, the abrupt collapse of the acidic character has been related to the destruction of the Keggin unit. In the case of the supported catalysts SiMoH-17.6 and SiMoH-9, the dramatic decrease of the selectivity for dimethyl ether, showing the fall of acidic character of the catalysts, can also be interpreted by the destruction of the Keggin unit on the support. The infrared data are also consistent with this conclusion. The Keggin unit destruction arises at lower temperatures for the supported catalysts than for the unsupported one. *From these results, we can suggest that the thermal stability of SiMo₁₂H is reduced when supported on the silica used in this work.* There is no marked effect of concentration on the thermal stability. Both supported catalysts exhibit similar behaviors: the decomposition occurs in a temperature range wider than that of the unsupported catalyst. The support induces higher activity, but reduced thermal stability.

Let us now point out the differences in the behavior of unsupported and supported catalysts. In the case of the unsupported acid, thermal decomposition leads to a mix-

ture of silica and MoO_3 , the latter being the only species responsible for the catalytic activity. The change of the catalytic character from acidic to redox after thermal treatments arises in the narrow range 300–320°C, with a turning point at $\sim 310^\circ\text{C}$. For supported catalysts, MoO_3 is characterized only for SiMoH-17.6. For SiMoH-9, there are probably not enough Mo centers to constitute repetitive units on a long range to characterize organized tridimensional orthorhombic MoO_3 . The catalytic behaviors of both catalysts are, however, rather similar, with turning points at ~ 270 – 280°C . This similarity probably results from the fact that they contain the same active species. As pointed out above, IR spectra of both series of thermally treated supported catalysts exhibit some features (960 – 970 cm^{-1} and $\sim 560\text{ cm}^{-1}$) which could be assigned to surface OH group vibrations and/or polyoxomolybdate ones. The existence of a surface polyoxomolybdate has already been postulated by several teams (11, 13–18). The true nature of this species is not yet completely elucidated because of the few elements of characterization and because of the difficulty in obtaining quantitative repartition of molybdenum between the different species possibly present on the surface, especially at low contents. Anyway, this species is likely similar to that formed by calcination at 500°C of silica-supported hexamolybdate catalysts (11): the same IR band characteristic of $\text{Mo}-\text{O}_{\text{terminal}}$ stretch appears at $\sim 960\text{ cm}^{-1}$ and redox catalysis is evident in the methanol oxidation test, leading to formol and methyl formate formation. The distribution of the mild oxidation products has been previously related to the dispersion of the active Mo centers on the silica surface (19). Different pathways were evidenced: for catalysts with Mo centers in close interaction (poorly dispersed catalysts, MoO_3), formaldehyde easily desorbs, and is the main oxidation product; on the contrary, highly dispersed Mo centers favor the spillover to silica of formaldehyde, which can react with methoxy groups,

leading to methyl formate via a hemiacetal intermediate. For the two supported catalysts SiMoH-17.6 and SiMoH-9, the differences between the distribution of mild oxidation products can also be related to the capability of spillover. For SiMoH-17.6, the amount of Mo deposited on the support allows us to obtain heaps of tridimensional MoO_3 , separated by silica surfaces which are only partially covered by Mo oxo species, as bidimensional polymer polyoxomolybdate. For SiMoH-9, the Mo centers are likely only engaged in the same kind of species; indeed, as MoO_3 is not present, the repartition of Mo centers is more uniform, with higher coverage silica surface than in the case of thermally treated SiMoH-17.6 samples. This situation, unexpected since the Mo content is lower, favors the formation of formaldehyde (close interactions between the Mo centers). Further investigations are in progress to obtain a better picture of the distribution of molybdenum between the different surface species.

CONCLUSION

This study allows us to draw the following conclusions.

First, the silica support used in this work does not stabilize the 12-molybdosilicic acid. The decomposition of the Keggin unit occurs at a lower temperature (under our working conditions, decrease of ~ 20 – 30°C , slightly depending on the concentration on the support) than that of the unsupported acid.

Second, the decomposition suddenly occurs in the case of the unsupported acid; crystals crumble more and more in a narrow range of temperature, with simultaneous formation of MoO_3 . At the temperature of decomposition, the process is very rapid, and all the polyanion mass is destroyed. On the contrary, in the case of silica-supported catalysts, the aggregates of Keggin units deposited on the surface do not decompose simultaneously; a damping effect occurs over the support. The decomposition not

only happens at a lower temperature, but also more slowly.

Third, the thermal treatments induce the formation of MoO_3 only in the case of unsupported SiMo_{12}H and high-loaded catalyst (17.6 wt% Mo). In the case of the supported catalyst with 9 wt% Mo, MoO_3 is never observed, whatever the temperature and the duration of the thermal treatment. The redox activity of thermally treated silica-supported catalysts is probably due to the presence of a polymer surface polyoxomolybdate, similar to that obtained by calcination at 500°C of silica-supported hexamolybdate catalysts (11).

Finally, the approach we have taken leads to the conclusion that SiMo_{12}H is the active species, responsible for the formation of dimethyl ether. This is strong evidence that a heteropolymolybdate in the solid state is catalytically active *in its full integrity* in the temperature range used. In addition, we can design acidic or redox catalysts, the switch from acidic to redox being controlled either by the Mo content (2), or by the treatment temperature.

Catalytic reactivity studies, coupled with IR spectroscopy, appear to be very sensitive means of probing surface changes.

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