# Properties of Molybdate Species Supported on Silica

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Molybdenum species have been deposited on a high surface area silica by the impregnation method and further calcination at 500 °C in air. Mo loading was varied from 0-10 wt % Mo. I.r., u.v.-visible, XPS and EDX-STEM techniques have been used to characterize the nature of the molybdenum species as a function of Mo loading. At low Mo content (< 3 wt % Mo) interaction between silanol groups and molybdate ions occurred resulting in the formation of monomeric tetrahedral  $MoO_4^{2-}$ species with a u.v. band near 245 nm. For intermediate loadings (3-8 wt %) polymeric octahedral molybdate species were identified with a u.v. band near 340 nm. At high Mo content crystallites of MoO<sub>3</sub> were also observed. Catalytic properties for both isopropyl alcohol conversion in air at 100 °C and propene oxidation at 400 °C were studied as a function of Mo loading. It was observed that the catalysts are acidic as evidenced by isopropyl alcohol dehydration into propene at low Mo content and their activity increased with Mo content following the amount of MoO<sub>4</sub><sup>2-</sup> species. Polymeric molybdate species were observed to exhibit mainly redox-type properties as evidenced by isopropyl alcohol oxidative dehydrogenation into acetone and by propene oxidation into propanal (electrophilic attack) and into acrolein (allylic-type reaction). MoO<sub>3</sub> crystallites were observed to exhibit usual properties of unsupported MoO<sub>3</sub> catalysts.

The even spreading of an oxide over another oxide acting as a support is an interesting phenomenon for comparison with lumps of the oxide on the support. The state of the art has already been largely studied,<sup>1,2</sup> in particular for  $MoO_3$ ,  $WO_3$  or  $V_2O_5$  deposited on various supports, such as  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $SnO_2$ , MgO etc. A question arises whether there exists an interaction or even a chemical bonding between the metallic ion or oxide and its support. One may reasonably expect different catalytic properties depending on the dispersion state of the oxide on the support and/or on the interaction between the molybdenum species and its support.

Many researchers were interested in using preparation methods able to ensure good dispersion of molybdenum on the catalyst. When Mo loading was increased, first the formation of isolated monomeric  $MoO_4^{2-}$  (tetrahedral environment), then polymeric isopolymolybdate species (octahedral environment) and finally of  $MoO_3$  crystallites deposited on the surface were postulated.<sup>1.3,4</sup> One may then reasonably expect different catalytic properties.<sup>5</sup> This holds true for many reactions as a function of Mo content, as for instance for metathesis of propene,<sup>6</sup> for propene oxidation,<sup>7</sup> methanol oxidation<sup>8</sup> or methane oxidation.<sup>9</sup> The nature of the molybdenum species remains not clearly established and depends on the preparation and calcination conditions. Some of the prominent studies involve data from electronic spectra and titration,<sup>9b, 10-12</sup> from Raman spectra<sup>3, 13</sup> and e.s.r. spectroscopy data.<sup>11, 14</sup>

Different procedures may be used for depositing active compounds on a support. The

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more classical way consists of impregnating the support with an aqueous solution of ammonium heptamolybdate at a given pH (kept constant or not during the preparation) and then in calcining the solid in air to get rid of ammonia. Particular attention has to be paid to the isoelectric point of the support (IEPS) which influences the primary interaction of the support surface with the ionic precursor of the deposited compound as emphasized by Brunelle.<sup>15</sup> The surface charge of the support suspended in an aqueous medium is controlled by the equilibrium

### $Me - OH_2^+ \rightleftharpoons MeOH \rightleftharpoons Me - O^-$

shifted to the left or the right when decreasing or increasing the pH of the solution, respectively. Anion adsorption (as required for molybdate adsorption) should thus occur if the pH of the solution is adjusted at a value below the IEPS of the support equal to 2 for silica.<sup>16,17</sup>

Other preparation procedures consisted of having organometallic complexes of Mo such as  $Mo(\pi-C_3H_5)_4$  reacting with a support<sup>18,19</sup> or in grafting a Mo compound by chemical reaction with surface active groups of the support.<sup>20,21</sup> For instance,  $MoCl_5$  in the gaseous phase or dissolved in cyclohexane was contacted with hydrated silica resulting in a chemical reaction with silanol groups and well dispersed Mo ions on the support.

Another technique consisted of calcining at relatively high temperature (e.g. 500 °C) a mechanical mixture of  $MoO_3$  and a support such as  $SiO_2$ ,  $TiO_2$ ,  $SnO_2$  etc.<sup>22,23</sup> The low melting temperature of  $MoO_3$  allowed it to spread regularly as a thin layer or tiny particles on the support as evidenced by the disappearance of the X-ray diffraction pattern due to  $MoO_3$  crystallites.

In the present work our interest has been focussed on the effect of Mo loading on spectroscopic features and catalytic properties of Mo ions deposited on silica. A wide variety of physical techniques have been used, namely X.r.d., XPS, i.r., u.v.-visible and EDX-STEM. Catalytic properties for isopropyl alcohol transformation in air and for propene oxidation have been studied in order to try to determine which catalytic features correspond to a given Mo ion environment. The impregnation method has been chosen as a preparation procedure. However, for comparison some samples have also been prepared either by calcining a mechanical mixture or by ionic exchange.

### Experimental

#### Preparation of Samples

Aerosil Degussa silica ( $S = 380 \text{ m}^2 \text{ g}^{-1}$ ) impregnated with an aqueous solution of ammonium heptamolybdate (AHM) to get a wet slurry, was stirred in order to homogenize the slurry and then dried at 110 °C without washing. The samples were finally calcined in flowing air at 500 °C for 15 h. The chemical composition of the samples is given in table 1.

#### **Physical Techniques**

U.v.-visible spectra were recorded at room temperature using a Lambda 9 Perkin-Elmer spectrometer working in diffusion reflectance mode with  $BaSO_4$  as a reference. I.r. spectra were recorded with a 580 A Perkin-Elmer spectrometer using a self-supported wafer technique to characterize the vibrational modes of the different compounds in activation and reaction conditions.

XPS data were obtained with a Hewlett-Packard HP 5950 A spectrometer, with the sample powder pressed on a soft indium sample holder. Flood gun accessory was used when necessary to try to eliminate the charging effect due to the electron ejection under

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samples	Mo content (wt%)	Mo/Si atom %
Il	0.6	0.38
I2	1.2	0.76
13	2.3	1.51
I4	3.45	2.27
15	5.0	3.41
I6	6.55	4.54
I7	8.5	6.06
18	10.3	7.57

Table 1. Chemical composition of impregnated						
and 500 °C calcined samples as determined by						
atomic absorption						

the X-ray beam over an insulator. The samples were outgassed in the spectrometer  $(10^{-8} \text{ Torr}^{\dagger})$  without any other treatment.

EDX-STEM analyses were performed using a Vacuum Generators HB O 5B emissiongun high-resolution electron microscope. The solid samples were embedded in an epoxy resin and cut into very thin sections (thickness < 100 nm) with a microtome. The electron beam may be focussed in very small parts of the sample ( $30 \times 40$  nm) or in large domains (*e.g.*  $0.1 \times 0.2 \mu$ m).

## **Catalytic Properties**

They were studied for three reactions, namely: (a) isopropyl alcohol dehydration to propene; (b) isopropyl alcohol oxidative dehydrogenation to acetone and (c) propene oxidation into acrolein, propanal, ethanal and  $CO_2$ . All reactions were conducted under atmospheric pressure in a differential flow microreactor made of a Pyrex U tube (8 mm i.d.) with 100 mg catalyst. Reactions (a) and (b) were carried out simultaneously with isopropyl alcohol vapour (2.24%) in air. The gas flow was  $0.3 \text{ cm}^3 \text{ s}^{-1}$  and the temperature was varied between 100 and 120 °C to keep a low conversion level (< 1%). Reaction (c) was conducted with a total gas flow equal to 1 cm<sup>3</sup> s<sup>-1</sup> and the following pressure ratio  $O_2$ : propene: N<sub>2</sub> equal to 100:100:560. Temperature was varied between 360 and 400 °C. Analysis was performed by gas chromatography FID for hydrocarbons and oxygenates, catharometer for carbon oxides.

# **Experimental Results**

### U.V.-Visible Spectroscopy Data

Diffuse reflectance spectra for samples I1 to I8 are shown in fig. 1. The absorption near 245 nm may be assigned to tetrahedral monomeric  $MOO_4^{2-}$  species and the one at 340 nm to octahedral polymeric molybdate species.<sup>10,12</sup> The changes in the intensity at 245 and 340 nm vs. Mo content are represented in fig. 2. It appears, as expected, that monomeric molybdate species are formed first with a plateau reached for sample I4 *i.e. ca.* 3.4 wt% Mo. Polymeric molybdate species are present mainly for sample I5 and further with a maximum intensity near I6, *i.e.* 6.5 wt% Mo. MoO<sub>3</sub> crystallites exhibit broad absorption spectra between 200 and 400 nm whose intensity depends on the crystallite size.

Hydroxyl groups of silica may also be detected by u.v.-visible spectroscopy without

† 1 Torr = 133.322 Pa.



Fig. 1. Diffuse reflectance u.v.-visible spectra of MoO<sub>3</sub>-SiO<sub>2</sub> impregnated samples as a function of Mo loading. Intensities expressed in Kubelka-Munk units.



Fig. 2. Variation of u.v.-visible band intensities vs. Mo loading: (a) at 245 nm (Td), (b) at 340 nm (Oh).

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Fig. 3. Diffuse reflectance n.i.r. spectra in the hydroxyl group region for sample I2 evacuated at 200 °C.



Fig. 4. Variations of u.v.-visible band intensity at 1380 nm vs. Mo loading.

or with outgassing the samples as one usually does in i.r. spectroscopy. Typical spectra are shown in fig. 3 with a band at 1380 nm  $\equiv$  7245 cm<sup>-1</sup> corresponding to the mode  $2v_{OH}$  with  $v_{OH} = 3740$  cm<sup>-1</sup> as evidenced by i.r. spectroscopy, the difference being due to the anharmonicity factor and a band at 2208 nm  $\equiv$  4530 cm<sup>-1</sup> corresponding to  $v_{OH} + \delta_{Si-OH} = 3740 + 790$  cm<sup>-1</sup>.

The variations of the intensity of the 1380 nm band vs. Mo loading are given in fig. 4. It clearly appears that a Mo compound reacted with OH groups of silica particularly at low Mo content. Extrapolating the first four points to 0 one gets ca. 3 wt % Mo, *i.e.* a value close to that of the plateau obtained for monomeric  $MOO_4^{2-}$  species intensity in fig. 2. One may then suggest the following reaction

$$2H^{+} + MoO_{4}^{2-} + 2 \equiv Si - OH \xrightarrow{\Xi Si} Mo \xrightarrow{FO} H_{2}O.$$
(1)  
$$\equiv Si^{-O} Mo \xrightarrow{FO} H_{2}O.$$
(1)

In such a model one  $MoO_4^{2-}$  species neutralises two silanol groups. The protons arose from the equilibrium reaction

$$Mo_{2}O_{24}^{6-} + 4H_{2}O \rightleftharpoons 7MoO_{4}^{2-} + 8H^{+}$$

$$\tag{2}$$

which is shifted towards the right-hand side when the dilution or pH value increases. One usually admits that a silica surface contains ca. 2.2 silanol groups  $nm^{-2}$ .<sup>24</sup> On a 380 m<sup>2</sup> g<sup>-1</sup> silica used as a support 3 wt % Mo corresponds roughly to 0.5 Mo atom  $nm^{-2}$ . If relation (1) applies one should then neutralise one silanol group  $nm^{-2}$  against 2.2 usually present on a silica support.<sup>25</sup> This point will be discussed later.

### I.R. Spectroscopic Data

I.r. was used complementarily to the u.v.-visible spectroscopy to characterize molybdenum species.<sup>6,25</sup> Two frequency ranges were analysed: (i) the OH frequency  $(3500-3800 \text{ cm}^{-1})$  range with an absorption band near 3740 cm<sup>-1</sup> due to silanol groups. This band was observed to decrease with Mo concentration disappearing for the 3.45 wt% Mo sample (I4). (ii) The low-frequency range 600–1100 cm<sup>-1</sup> corresponding to absorptions due to molybdate species and silica bands (1100 and 800 cm<sup>-1</sup> for SiO<sub>2</sub>). Polymolybdate species are known to exhibit absorption bands at 975 and 885 cm<sup>-1</sup>, MoO<sub>3</sub> at 998 cm<sup>-1</sup> and 870 cm<sup>-1</sup>.

For low Mo content (e.g. sample I4) the band at  $975 \text{ cm}^{-1}$  was observed alone indicating that molybdate species are present while  $MoO_3$  is not. For high Mo content (e.g. sample I8) the bands at 975 and  $885 \text{ cm}^{-1}$  due to polymolybdate species and at  $998 \text{ cm}^{-1}$  due to  $MoO_3$  were observed all together. If reduction by hydrogen or methanol was performed at 200 °C the 998 cm<sup>-1</sup> band disappeared while the other two remained. This indicates that the covalency of the Mo=O bands decreased due to the reduction of  $MoO_3$  particles.<sup>26</sup>

### **XPS** Data

This technique was used in order to gain some information about Mo species at the surface of a silica support, since it is sensitive to the top layers of the material (up to 2 nm in depth). However aerosil silica support of high surface area  $(380 \text{ m}^2 \text{ g}^{-1})$  corresponds to small silica balls *ca*. 4 nm in diameter, *i.e.* the technique cannot be considered as truly a surface technique for such small particles.

The Mo 3d doublet was observed to be unresolved particularly for low Mo loading

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Fig. 5. XPS Mo 3d doublet for sample  $I_2$  and  $I_7$ .

and to be resolved only for relatively high loading (> 6 wt %) (fig. 5). The lack of resolution has already been observed and largely discussed.<sup>27-33</sup> Several explanations have been proposed: (i) the presence of more than one Mo(vI) species with different chemical characteristics, (ii) electron transfer between Mo ions and the support due to strong bonding<sup>34</sup> and (iii) differential charging effect between the support and the supported species due to different and poor electrical conductivities.

The first explanation seems reasonable since other techniques have shown the existence of several Mo ion environments. The second explanation should eventually lead to a chemical shift and not to a line broadening and can be ruled out. The third explanation may hold true for well dispersed Mo species since relaxation of electrons within very dispersed and isolated species is strongly hindered.

Another explanation could be that the broadening of the peaks is due to strong coulombic and exchange interaction between 3d electrons and electrons from the ligands or 4s or 4p Mo levels. Nefedov<sup>35</sup> has shown that high exchange interaction results in a broadening of each line of multiplets (*e.g.*  $3d_{3/2}$  and  $3d_{5/2}$ ) and to displacement of the weighted centre of the multiplets (*i.e.* to a change in multiplet line splitting).

Several authors have suggested that silicomolybdic acid (SMA:SiH<sub>4</sub>Mo<sub>12</sub>O<sub>40</sub>) compound is formed at the surface of the support at low Mo coverage as identified by Raman spectroscopy (bands at 980 and 650 cm<sup>-1</sup>) and by its yellow colour.<sup>9b.10</sup> The formation of such a well defined species cannot explain the lack of Mo 3d doublet resolution. We are therefore of the opinion that differential charging effects of well dispersed and isolated molybdenum species and the presence of tetrahedral MoO<sub>4</sub><sup>2-</sup> species bonded to silica and of octahedral polymolybdate species may explain these broad spectra. Note that quantitative XPS data are not relevant because of the too small silica particle size (4 nm in diameter) with respect to the mean free path of the electrons (*ca.* 2 nm).

### **EDX-STEM Study**

Several samples have been studied by microanalysis in order to determine the changes in chemical composition along the same particle or between different species. Rather heterogeneous Mo ion spreading was observed for all samples even at low Mo contents.

This shows that Mo ions are not deposited regularly on the surface. For instance for sample I6 (6.55 wt % Mo or 4.5 atom %) one gets Mo atom % in the range 4–9 and domains much richer in Mo (30–55 Mo atom %) presumably due to the presence of polymolybdate on the surface at some peculiar location.

Several samples prepared by other means were also studied. If one mixes  $4\% \text{ MoO}_3$  per weight with SiO<sub>2</sub> and analyses the sample after catalytic reaction no mixing between MoO<sub>3</sub> and SiO<sub>2</sub> was detected by EDX-STEM. In contrast if the same mechanical mixture was calcined under air flow at 400 °C for 15 h mixing between MoO<sub>3</sub> and SiO<sub>2</sub> was observed with particles exhibiting various Mo % contents from 1 to 15. If ionic exchange was performed by contacting ammonium heptamolybdate aqueous solution with SiO<sub>2</sub> at a pH maintained to 1 or 9 (in regards to the IEPS of silica) and eliminating the excess solution before calcination at 500 °C one gets a rather homogeneous Mo distribution on silica from 0.5 to 1.2 Mo atom % with a few Mo rich crystallites (against 2 Mo atom % from chemical analysis).

It may then be concluded that calcination in air of intimate mixtures of  $MoO_3$  and  $SiO_2$  results in a more homogeneous spreading of Mo species over the  $SiO_2$  support than the impregnation techniques. This holds true also for grafted samples.<sup>8</sup>

### **Catalytic Results**

Isopropyl alcohol conversion in the presence of air has been studied in the temperature range 80–120 °C. The main products<sup>36,37</sup> are propene formed by dehydration reaction (acid-type reaction), acetone formed by oxidehydrogenation (redox-type reaction) and  $CO_2$  (total oxidation). The amount of isopropyl alcohol transformed into propene and acetone at 100 °C at stationary state is plotted *vs*. Mo content in fig. 6. It is important to note that propene was formed first and increasingly with Mo content at variance with acetone which started to be formed for higher Mo content (> 4 wt %). These results clearly indicate that active sites are different for the two reactions and that the acid-type reaction is favoured at low Mo content.

Another striking feature is seen in fig. 7 where the variations of apparent activation energy values for both products, propene and acetone, are plotted vs. Mo loading. Both activation energies increase with Mo content, reach a maximum and then a plateau. From the reaction rate and the activation energy values, it is possible to have an estimate of active site density D on the catalyst surface.<sup>38</sup> If it is assumed that the transition state between a reactant and a product for a reaction is the same for all catalysts, one may write:

$$D = (k Tr/h) \exp(E_a/RT)$$

k, h and R being the universal constants, r the rate of reaction measured under zeroorder conditions and  $E_a$  the activation energy, the activation entropy being taken equal to zero. The site density was then observed to increase sharply with Mo content for propene after 1 wt% Mo and for acetone after 3 wt% Mo with a maximum near 5 wt% for both products, followed by a sharp decrease and a plateau for loading larger than 6.5 and 8.5 wt%, respectively.

These results indicate that isopropyl alcohol dehydration occurred when monomeric  $MoO_4^{2-}$  species were present while oxide hydrogenation was observed only in the presence of polymeric molybdate species. Both types of species appeared to exhibit high active site density by comparison with  $MoO_3$  particles. This suggests that the surface is covered with an homogeneous active site population.  $MoO_3$  particles exhibit both dehydration and oxidative dehydrogenation properties with low active site density.

For the propene oxidation reaction experimental results are summarized in table 2 and in fig. 8. Several points have to be noted. First, selectivity in acrolein first decreases with Mo loading and reaches a plateau for loading higher than 5 wt %. Another striking



Fig. 6. Propene (+) and acetone (×) formation in isopropyl alcohol+air reaction at 100 °C vs. Mo loading expressed in mol% isopropyl alcohol converted.



**Fig. 7.** Variations of the activation energy values for propene (dashed curve), acetone (point curve) formation in isopropyl alcohol + air reaction at 100 °C vs. Mo loading.

feature is the selectivity in propanal which is very low for pure  $SiO_2$  or  $MOO_3$  and thus mechanical mixtures and important (30–50%) for impregnated, grafted and calcined mechanical mixture samples. This clearly shows that the reaction mechanism differs depending on the surface Mo species. If one determines the active site density, as

	Mo (wt %)	conversion (%)	selectivity (%)				
samples <sup>a</sup>			propanal	acrolein	ethanal	CO2	
I1	0.55	0.063	40	31	19	10	
12	1.03	0.18	42	29	16	13	
13	2.05	0.13	53	21	16	10	
15	4.72	0.57	52	18	15	15	
I6	6.65	2.9	53	18	21	8	
17	7.9	2.6	46	18	23	13	
18	10.2	1.45	32	20	26	22	
MI	2.53	0.064	19	39	11	31	
M2	2.50	0.11	31	25	13	31	
IA	3.06	0.25	38	30	13	26	
IB	3.59	0.37	26	23	18	12	
MoO <sub>2</sub>	100.00	0.03	2	35		63	
SiO,	0.0	0.003	14	40	20	27	

Table 2.	Propene oxidation at ca.	400 °C (100 mg cataly	$st, C_{3}H_{6}:O_{2}:N_{2} =$	100:100:560,	flow rate
		$1 \text{ cm}^3 \text{ s}^{-1}$			

<sup>a</sup> M1: mechanical mixture, M2 = M1 calcined at 400 °C in air flow, IA: impregnated at pH 1 and further calcined at 500 °C, IB: impregnated at pH 9 and further calcined at 500 °C.



Fig. 8. Formation of propanal (+) and acrolein (×) in propene oxidation at 400 °C expressed in propene conversion mol%.

discussed above, one observes a sharp increase above 5 wt % Mo with a maximum near 7.5 and a steady state above 9 wt % Mo for propanal formation and the same evolution above 7 wt %, maximum near 9 wt % and steady state above 10 wt % Mo for acrolein formation. These results indicate that surface Mo species influence selectivity and active site density due to both their nature (monomeric, polymeric) and their concentration.

These features have to be compared with structure sensitivity of oxides for partial oxidation reactions.<sup>39</sup> Note also (fig. 8) that the activity for both propanal and acrolein increased sharply above 5 wt% and reached a maximum near 7.5 wt%.

### Conclusion

Catalytic properties for propene oxidation and isopropyl alcohol conversion clearly depend on the reaction itself and the local (short-range) and long-range Mo ion environments.

At low Mo loading ( < 3 wt % Mo) tetrahedral monomeric  $MoO_4^{2-}$  species are formed first by interaction of heptamolybdate ions with silanol groups as schematized below and can be seen in reactions (1) and (2).

Silicomolybdate acid  $(SiH_4Mo_{12}O_{40})$  observed by other authors<sup>9b.10</sup> was not detected in our case. However isopropyl alcohol dehydration, which is an acid-type reaction, was observed to depend strongly on the presence of tetrahedral monomeric Mo species, indicating that these species have an acidic character.

For intermediate Mo loadings (3-8 wt % Mo) polymeric molybdate species are present either on top of the monomeric ones or more probably by their condensation. These species exhibit both dehydration and oxidative dehydrogenation features for isopropyl alcohol and both allylic and electrophilic attack properties for propene oxidation giving relatively high yield in propanal in the latter case.<sup>40</sup>

At high Mo loading (> 8 wt % Mo) MoO<sub>3</sub> particles are formed on SiO<sub>2</sub> support. These particles exhibit usual catalytic properties of unsupported MoO<sub>3</sub>.

The main conclusions which we may draw from our results are summarized below. (i) The short-range environment of  $Mo^{6+}$  cations greatly influences catalytic properties. On silica support at low Mo loading monomeric  $MoO_4^{2-}$  tetrahedral species exhibit acid-type properties. At intermediate Mo loading, polymeric octahedral molybdate species exhibit enhanced oxide-hydrogenative and electrophilic attack properties. At high Mo loading,  $MoO_3$  crystallites supported on SiO<sub>2</sub> are formed and exhibit usual and well known catalytic properties of unsupported  $MoO_3$  for partial oxidation of propene and isopropyl alcohol conversion reactions. (ii) It is not possible to extrapolate long-range order properties of oxides to short-range order properties as one would like for modelling by very small clusters. This is due both to the difficulty of preparing very dispersed active species which are not modified by the interaction with the support, even as inert as silica and to the fact that the catalytic properties of active sites greatly depend on their short- or long-range order.<sup>39</sup>

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