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EPR and Diffuse Reflectance Studies of the Physico-chemical Phenomena Occurring during the Preparation of Mo/SiO$_2$ Catalysts by the Grafting Method

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Mo/SiO$_2$ catalysts were prepared by the grafting method, i.e., by air- and water-free reaction between MoCl$_5$ and hydroxyl groups of silica support. This reaction may be performed either in a liquid medium (cyclohexane) or in the vapor phase. It is shown by EPR and diffuse reflectance spectroscopies that two types of molybdenum were deposited onto silica during the grafting reaction: (i) grafted Mo as $\equiv$SiOMoCl$_4$ ($g_\perp = 1.952$ and $g_\parallel = 1.968$), and (ii) physically adsorbed Mo as the diamagnetic Mo$_2$Cl$_{10}$ dimer; this compound turns blue in air because of both its partial oxidation and hydrolysis to form the so-called molybdenum blues. After the grafting reaction itself, the second step involves washing by water or ammonia solution. The physically adsorbed Mo is eliminated and the grafted Mo remaining on the silica is hydrolyzed and partially oxidized in air, so as to lead to the following species: $\equiv$SiOMo^{V}(OH)$_4$ or $\equiv$SiOMo^{VI}(OH)$_5$. In consequence, at the very end of the preparation, only the grafted Mo species remains on the silica and the sample color is brown. The catalytic behavior of the unwashed and washed catalysts in the reaction of methanol oxidation emphasizes the differences in the Mo species. The unwashed sample containing molybdenum blues behaves like a polycrystalline MoO$_3$ catalyst, producing mainly methylal at low reaction temperature (230°C) and formaldehyde at higher temperature (280°C), whereas the washed one, containing only grafted Mo, produces mainly methylformate and, to a lower extent, formaldehyde.

INTRODUCTION

Although the characterization and reactivity studies of supported molybdenum catalysts have been the topic of numerous investigations for a number of years (*1–5*), detailed studies on the coordination sphere of molybdenum species have been scarce (*6–12*). The reason is that the samples are usually prepared by conventional impregnation and that the different phenomena occurring during the preparation are very difficult to control, leading to an ill-defined supported phase (*1, 13–17*). The grafting method, which consists of the air- and water-free reaction between MoCl$_5$ and hydroxyl groups of silica support (*9, 10, 18–20*), leads to a better control of the preparation and to better-defined catalysts than impregnated ones.

The present paper is an attempt to give a comprehensive *qualitative* description of the mechanism of grafting in the context of recently published results (*9, 10, 18–20*) and of additional experiments. After each step of the preparation, the catalysts were tested in the reaction of methanol oxidation. The other paper of this series (*21*) will deal with the study of the physico-chemical properties of the grafted catalysts after calcination and after reduction, and the comparison with catalysts prepared by impregnation. In particular, it will be shown that grafted Mo is much better dispersed and in stronger interaction with silica than impregnated Mo and behaves differently in the reaction of methanol oxidation (*22*).

In order to follow the conventions used in solid chemistry (*23*), roman numbers are used to designate the oxidation states of the

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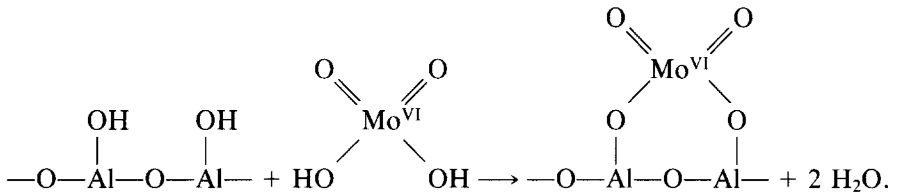
ions. However, for the sake of convenience, the formalism of electric charges is sometimes employed, even if the latter are not the effective charges of the ions.

GENERAL BACKGROUND ON PREPARATION TECHNIQUES

The supported molybdenum catalysts are usually prepared using one of the three main methods: impregnation, ion exchange, and grafting. Their principle and respective advantages and disadvantages are briefly described.

Impregnation Method

In the impregnation method, the support is put into contact with an aqueous solution of molybdenum salt, usually ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$), then dried and calcined. The contact time of the solution with the support and the drying and calcination conditions strongly influence the Mo distribution (*1, 13, 15, 24*). A few investigators have focused their efforts on the study of the first step of preparation and have successively proposed the incipient wetness technique (*25*) and the impregnation via displacement of an immiscible liquid (*26*). During the drying step, usually performed at about 100°C, the metal salt is reformed from the individual solvated cations and anions and redistributed on the support in a way which depends both on the drying rate and the support porosity (*27, 28*). During the calcination step performed in air or oxygen at about 500°C, three phenomena may occur on supported Mo catalysts: (i) the migration of the impregnated salt onto the support surface (*29–32*, and Refs. therein), (ii) its decomposition into oxide, and (iii) the formation of ionocovalent bonding between the Mo species and the support, leading to their grafting. The support through its hydroxyl groups acts as a reactant (*33*). A typical example for the Mo/γ-Al_2O_3 system can be written as follows (*34*):



(1)

In addition, Mo can migrate into the bulk of supports such as TiO_2 (*35, 36*) and SnO_2 (*37, 38*). In consequence, several molybdenum species whose nature depends on the Mo content, the type of support, and the thermal treatment may be formed: isolated tetrahedral $(MoO_4)^{2-}$, MoO_3 crystallites, and surface polymeric species such as polyoxomolybdates (*3, 39–41*). In addition, silicomolybdic acid ($H_4SiMo_{12}O_{40}$) may be formed on a silica support (*3, 39, 42–44*) and $Al_2(MoO_4)_3$ on an alumina support (*45, 46*).

For studying the coordination sphere of supported molybdenum, it is necessary to restrict as much as possible the number of Mo species and prepare catalysts with a high dispersion of isolated Mo ions. This involves the choice of suitable preparation methods, which have been the subject of recent attempts of rationalization (*9, 33, 47, 48*). The ion exchange or impregnation with equilibrium adsorption is one of these methods.

Ion Exchange

When solid oxides are in aqueous solution, an amphoteric dissociation of the surface hydroxyl groups can occur as follows:

$$\begin{aligned} SOH_2^+ &\rightleftharpoons SOH + H^+, \quad K_1 \\ SOH &\rightleftharpoons SO^- + H^+, \quad K_2, \end{aligned} \tag{2}$$

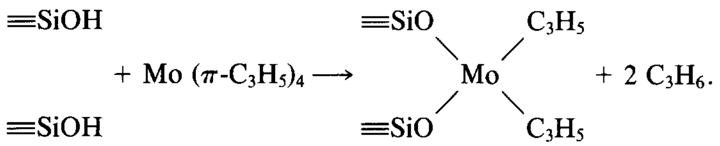
where K_1 and K_2 are the acidity constants. At a pH = $(pK_1 + pK_2)/2$, called the isoelectric point of the solid surface (IEPS) (*49*), positive charges balance negative charges at the oxide surface ($[SOH_2^+] = [SO^-]$). The IEPS of γ-Al_2O_3 is found to be at pH 6–8 and that of SiO_2 at pH 1–2 (*49*). At pH below the IEPS, the surface is positively charged and anion adsorption can occur. Conversely, at pH above the IEPS, the negatively charged surface adsorbs cations only. Those ion adsorption properties can be used to prepare catalysts from solutions of metal salts (*33, 47, 50*), the pH acting as a surface charge selection switch (*48*). It may be noted that in contrast to impregnation, ion exchange leads to the electrostatic adsorption of one type of ions, at the exclusion of the corresponding counterions.

To exchange reasonable amounts of the anionic precursors of molybdenum, the solution pH must be smaller by several pH units from the IEPS of the support, otherwise the support exchange capacity is too low (*33*). Anionic exchange has been largely performed on alumina (*51–56*) and on titania (*57, 58*), but to the best of our knowledge not on silica, because of its too-low IEPS (pH 1-2).

Grafting

A more effective route to prepare highly dispersed Mo onto silica support is the grafting method. It consists of the formation of an iono-covalent bonding between Mo and the support during the first step of preparation, in contrast to impregnation and ion exchange, for which this type of bonding may appear in subsequent steps. This Mo–support interaction is expected to inhibit the Mo migration and aggregation during calcination and other thermal treatments, and to lead to a highly dispersed molybdenum. This approach involves neutral molecular species as precursors.

Yermakov and co-workers (*59, 60*) and Iwasawa *et al.* (*61–66*) and more recently others authors (*42, 67–69*), have used organometallic precursors such as Mo(π-$C_3H_5)_4$ or $Mo_2(\eta^3$-$C_3H_5)_4$ to prepare supported Mo catalysts. The reaction occurs at room temperature according to the following mechanism:



(3)

Roberge and co-workers (*67*) have found that in fact most of the Mo were not really anchored onto the support surface since 70 to 90% of the Mo could be eliminated by washing the calcined sample with water.

The method described in the present work involves a chemical reaction between molybdenum pentachloride and surface silanol groups of silica. Si–O–Mo bonds are created and HCl is evolved. The reaction must be performed under air- and water-free conditions, because $MoCl_5$ is easily oxidized and hydrolyzed into the following compounds:

$$MoCl_5 + \tfrac{1}{2}O_2 \longrightarrow MoOCl_4 + \tfrac{1}{2}Cl_2 \quad (\textit{70})$$

$$MoCl_5 + H_2O \longrightarrow MoOCl_3 + 2\ HCl \quad (\textit{70, 71})$$

$$MoOCl_3 + H_2O \longrightarrow \text{hydrolyzed compounds} \quad (\textit{72})$$

$$MoOCl_4 + H_2O \longrightarrow \text{molybdenum blues} \quad (\textit{73, 74}). \tag{4}$$

In a very first study (*75*), $MoCl_5$ was treated with a suspension of silica in chloroform. The catalyst was then washed with chloroform, further hydrolyzed with water vapor, and finally dried at 120°C. The samples obtained were blue. Later, we found (*18*) that this color was due to the formation of molybdenum blues (mixed valence oxide-hydroxides containing Mo^{V} and Mo^{VI} ions (*76–78*)) which were not grafted (*18, 19*) but could be eliminated by washing with water.

Then, the grafting method was improved, using MoCl$_5$ as vapor (*19, 20*) or dissolved in cyclohexane (*18, 20*). Both methods led to catalysts with the same characteristics. Cyclohexane was chosen as a solvent because (i) it is almost the only one in addition to chloroform able to dissolve MoCl$_5$ without any reaction of solvolysis or dissociation (for example, CCl$_4$ is supposed to decompose MoCl$_5$ to lower chlorides and Cl$_2$ (*79*)), (ii) it leads to the grafting of larger amounts of Mo than chloroform (*18, 19*).

The choice of MoCl$_5$ is particularly attractive since it is a monomeric and paramagnetic species (Mo^{5+}, $4d^1$) both in vapor phase and in solution (*80*), i.e., detectable by EPR spectroscopy. Molybdenum chloride forms a diamagnetic dimer Mo$_2$Cl$_{10}$ in the solid state (*81*). Mo^{5+} can be used as an effective probe to monitor via EPR spectroscopy the changes in its coordinating sphere during the grafting process.

The second important step of the catalyst preparation is the washing by water or ammonia solution. Its goal is twofold, i.e., to hydrolyze the Mo–Cl bonds of the grafted molybdenum and to eliminate weakly bonded molybdenum.

EXPERIMENTAL

Catalyst Preparation

The following procedure was adopted for the preparation of grafted Mo/SiO$_2$ catalysts:

Grafting. In an inflatable glove box purged with dry nitrogen, dehydrated cyclohexane (200 cm^3), MoCl$_5$ (1 g), and silica previously dehydroxylated at 400°C (5 g) are introduced in an erlenmeyer. It is closed with a cork connected to a rubber balloon with an overpressure of dry nitrogen. The apparatus is removed from the glove box and the mixture stirred at room temperature: in contact with MoCl$_5$, cyclohexane becomes reddish and the silica gradually turns orange-red. The experiment is complete when the solution is colorless after about six hours. Two remarks can be made: (i) 1 g of MoCl$_5$ for 5 g of silica corresponds to a theoretical loading of 6 wt% Mo on silica. This loading is smaller than the maximum of 45 wt% Mo calculated from the number of hydroxyl groups of silica and assuming a 1 : 1 stoichiometry (about 7 OH/100 Å^2) for a silica prepared by precipitation such as ours (Spherosil XOA 400) and dehydroxylated at 400°C (*82*)). As is shown in the Results section, the amount of grafted Mo is much lower than expected. (ii) 1 g of MoCl$_5$ is not fully soluble in 200 cm^3 of cyclohexane in absence of silica. The solution of cyclohexane is however colorless at the end of the preparation and this is explained as follows. The Mo deposition onto silica lowers the molybdenum concentration in the solution and shifts the dissolution equilibrium to the right so that all the MoCl$_5$ is finally dissolved.

Washing. The sample is then opened to air, filtered, and dried at room temperature. It turns blue. Then, the solid is washed by soaking in water (several days) or in ammonia solution (100 cm^3 of a 1 *M* solution for 5 g of sample, contact time usually 5 min), followed by filtration. Relevant details will be given in the Results section. Finally, the sample is dried at room temperature. Its color is pale brown to brown.

In the second method with MoCl$_5$ vapor, the reactor consists of two glass ampules kept *in vacuo* and separated by a breakable seal; they contain silica previously dehydroxylated at 400°C (1 to 2 g) and MoCl$_5$ (about 1 g), respectively. After breakage of the seal, the reactor is introduced in a furnace at 200°C. MoCl$_5$ vapor reacts with silica, which becomes red-orange. After grafting, the sample is washed in the same way as described above. The reactor may be equipped with both an EPR tube and a UV cell in order to monitor the grafting process by EPR and diffuse reflectance spectroscopies (*19, 20*). This preparation method was therefore performed to investigate *in situ* the grafting reaction.

The Spherosil XOA 400 silica supplied by Rhône Poulenc (France) was used as support. This is a precipitated silica with a surface area of 400 m^2/g, a porous volume of 0.9 cm^3/g, and a mean pore diameter of 80 Å (*83*). Chemical analysis reveals 400 ppm of Ca and 900 ppm of Na. Cyclohexane labelled "Normapur" from Prolabo (France) has a purity higher than 99.8%. It is dehydrated by stirring in the presence of zeolite 4A, previously dehydrated overnight at 350°C. $MoCl_5$ (99% purity) was purchased from Merck (Germany). Water soluble molybdenum blues used as reference compounds in this study were prepared by Dr. Michel Fournier (*84*).

Techniques

The EPR spectra were recorded either at room temperature or at 77 K on a Varian spectrometer model E-3 operating at 9.3 GHz (*X* band). It was equipped with a subharmonic generator (Telmore instrument) using multiple field modulations for recording third derivative spectra (*85*). The g values were measured relative to a DPPH reference ($g = 2.0036$).

The diffuse reflectance spectra were recorded in the range 220–2500 nm with a 5270 Beckman spectrometer equipped with an integration sphere and a double monochromator. $BaSO_4$ was used as reference.

The chemical analysis of the samples were performed at the Centre de Microanalyse du CNRS, Vernaison (France).

The catalytic reaction of methanol oxidation was carried out in an isothermal fixed-bed microreactor under atmospheric pressure and at temperature between 230 and 280°C, with a mixture of methanol, oxygen, and helium in the molar ratio (7/19/74%). The reaction is performed in differential conditions, i.e., with a conversion lower than 10%. More details may be found in (*22*). Before reaction, the samples were pretreated in a flow of oxygen at 420°C for 6 hr. Selectivity to a product i (S_i in %) is defined as the ratio between the number of methanol moles transformed into i and the overall number of moles of methanol transformed during the same time. The total activity A_T is the overall number of moles of methanol transformed per hour and gram of catalyst. The activity A_i for the formation of a product i is calculated as follows: $A_i = A_T \times S_i/100$.

RESULTS

Precursors before Grafting

$MoCl_5$ dissolved in dehydrated cyclohexane exhibits an isotropic signal of Mo^{5+} ($g = 1.952$) with 6 hyperfine lines separated by a coupling constant of 51.5 Gauss at room temperature (Fig. 1a). The hyperfine structure arises from the interaction of the unpaired electron spin with the nuclear spins ($I = 5/2$) of the ^{95}Mo and ^{97}Mo isotopes, which have about the same magnetic moment (natural abundance 15.8 and 9.6%, respectively) (*86*). Recorded at 77 K, the isotropic signal broadens and the hyperfine structure is no longer observed. This isotropy at 77 K indicates that the Mo^{5+} ligand field induced by the 5 Cl groups is highly symmetric.

The silica dehydroxylated at 400°C exhibits a charge transfer band at 260 nm in the UV region and two vibration bands at 1365 and 2190 nm in the near infrared (7300 and 4560 cm^{-1}, respectively) (Fig. 2a). The first vibration band corresponds to the first overtone of the O–H stretching mode of silanol groups. The fondamental vibration ν_{OH} is near 3600–3750 cm^{-1}, depending on the location and the type of silanol sites, single or geminal, free or hydrogen bound, external or internal. The second vibration band is the combination mode ($\nu_{OH} + \delta_{OH}$)

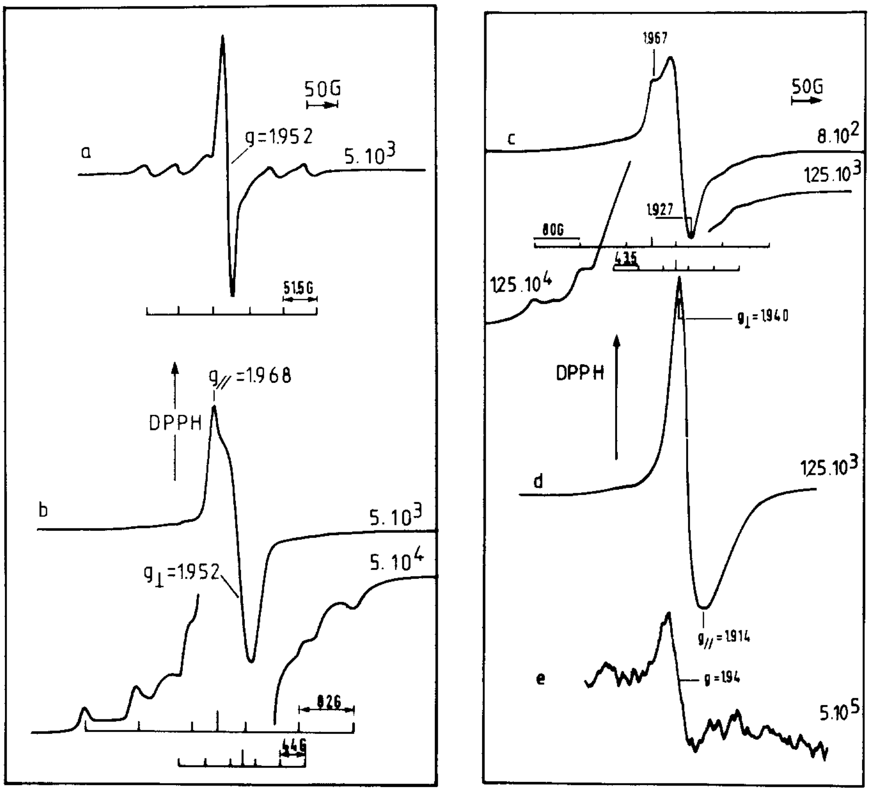


FIG. 1. EPR spectra recorded at 300 or 77 K of (a) MoCl$_5$ diluted in dehydrated cyclohexane (300 K); (b) Mo/SiO$_2$ catalyst during grafting with MoCl$_5$ vapor (EPR-G) (77 K); (c) Mo/SiO$_2$ catalyst after exposure to ambient air (EPR-A) (77 K); (d) molybdenum blues (77 K); (e) Mo/SiO$_2$ catalyst after washing (EPR-W) (77 K).

whose bending mode frequency is at about 800 cm^{-1} (*82, 87–89*).

Grafting Reaction

The grafting reaction was investigated using the vapor phase preparation. When silica is heated at 200°C in the presence of MoCl$_5$, an EPR signal (EPR-G) appears on the silica. Its intensity increases to become constant after about 20 hr of heating, although MoCl$_5$ is far to be totally consumed (Fig. 1b). The signal is anisotropic ($g_\perp$ = 1.952 and $g_\parallel$ = 1.968) surrounded by hyperfine structure composed of 6 lines due to the odd ^{95}Mo and ^{97}Mo isotopes. The coupling constants are $A_\perp$ = 44 and $A_\parallel$ = 82 Gauss. The spectrum shape does not depend on the recording temperature (77 or 300 K).

The diffuse reflectance spectrum of the system also changes during grafting (DRS-G) (Fig. 2b). In the near infrared, both bands at 1356 and 2190 nm decrease while others appear in the UV–visible range at 255, 280, 365, 460, and 625 nm. Their intensities reach a maximum after about 20 hr of grafting, as for the EPR spectrum. The ≡SiO–H vibration bands, however, do not disappear completely.

During the grafting step, in vapor phase or cyclohexane, the samples turn orange-red and HCl is evolved. HCl was detected by its characteristic smell and by the color change of a pH indicator paper located at the outlet of the rubber bag after grafting. In the following, the results deal with samples prepared by either method, i.e., in vapor phase or cyclohexane.

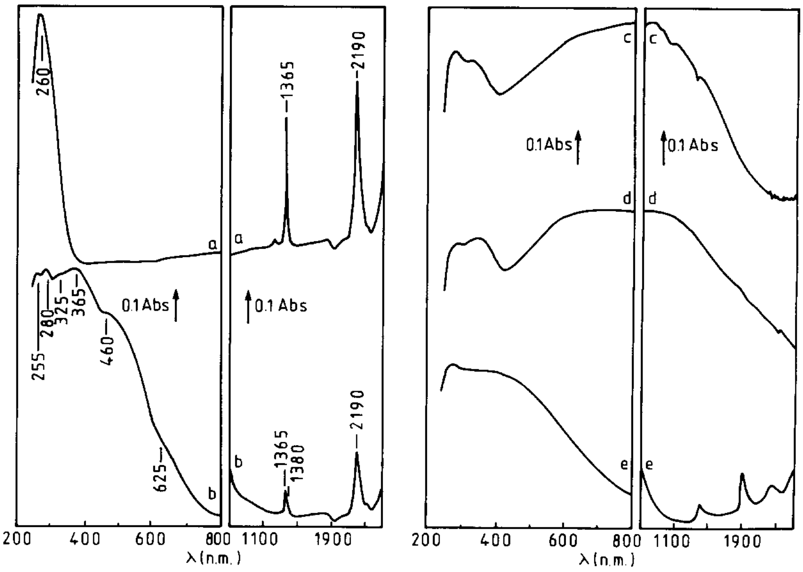


FIG. 2. Diffuse reflectance spectra recorded at room temperature of (a) silica dehydrated at 400°C; (b) Mo/SiO_2 catalyst after grafting at 200°C with $MoCl_5$ vapor during 20 h (DRS-G); (c) Mo/SiO_2 catalyst after exposure to ambient air at 25°C (DRS-A); (d) molybdenum blues; (e) Mo/SiO_2 catalyst after washing with water (DRS-W).

Exposure to Ambient Air

The samples gradually turn blue upon exposure to air. The EPR spectrum of the blue samples (EPR-A) (Fig. 1c) is different from the one obtained during the grafting reaction (EPR-G) (Fig. 1b). Its intensity is stronger and its shape more anisotropic with the apparent g values $g_\perp = 1.927$ and $g_\parallel = 1.967$. A broad and intense band centered at 600–1000 nm appears in the absorption spectrum (DRS-A) (Fig. 2c). This band is similar to that of the molybdenum blues (Fig. 2d). It may be noted that the molybdenum blues exhibit an anisotropic EPR signal ($g_\perp = 1.940$, $g_\parallel = 1.914$) (Fig. 1d). Chemical analysis reveals the presence of chlorides in the samples (Table 1).

Washing Step

After exposure to air, the samples are soaked in water. Gradually, the solution turns blue and the solid brown or pale brown. This step may last several days for the blue color to disappear, and it is necessary to renew the water several times. Afterwards, the samples are dried at room temperature. Their diffuse reflectance (DRS-W) and EPR (EPR-W) spectra have changed again: the broad band at 600–1000 nm is no longer visible while another one at 400–500 nm is observed (Fig. 2e). The EPR spectrum has strongly decreased in intensity and because of the low signal/noise ratio, it was not possible to determine the g values with accuracy (Fig. 1e).

During the washing step, the molybdenum content of the samples decreases, e.g., from 4.7 wt% before washing, to less than 1 wt% after washing. The change in sample color and the decrease in the Mo content indicate that the blue Mo species, weakly bonded to silica, can be eliminated by washing so as to only leave the grafted molybdenum on the surface which is brown.

Chemical analysis reveals that all the chlorides were not eliminated upon washing; their content can exceed the molybdenum one (Table 1). In consequence, washing by water did not succeed in hydrolyzing

TABLE 1

Mo and Cl Content of Grafted Catalysts before and after Washing

Sample	Color	Mo		Cl		Molar Cl/Mo
		(wt%)	(10^{-3} mol./g)	(wt%)	(10^{-3} mol./g)	
Before washing[a]	Blue	2.21	23	0.82	23	1
After washing by ammonia sol. (a few min.)	Brown	0.66	6.9	<0.1[b]	—	—
After washing by water (few hours)	Pale brown	0.07	0.73	0.34	9.59	13

[a] After drying in air at room temperature.

[b] Cl detection limit = 0.1 wt%.

all the Mo–Cl bonds of the grafted Mo, but only permitted the elimination of the weakly bonded molybdenum characterized by its blue color.

The washing with ammonia solution was found to be more effective than that with water since: (i) the blue color instantaneously disappears to leave brown samples. The washing solution remains colorless, (ii) the chlorides are no longer detected on the samples by chemical analysis (Table 1), and (iii) it is possible to prepare samples with larger Mo contents (1–2 wt%) than with washing by water (≤1 wt%). However, the Mo content is dependent on the washing time (Table 2).

Methanol Oxidation Reaction

After calcination at 420°C, one unwashed (7.42 wt% Mo) and one washed (0.66 wt% Mo) catalyst were tested in the reaction of methanol oxidation, in the conditions described in experimental part. The analysis of the calcined samples by electron microscopy (TEM) and XRD reveals the presence of crystalline MoO_3 on the unwashed sample which is not detected on the washed one (*21*).

TABLE 2

Mo Content of Grafted Catalysts versus the Washing Time with 1 *M* Ammonia Solution

Time	Sample color	Mo content (wt%)
0	Blue	6.17
A few seconds	Brown	—
6 min	Brown	1.18
30 min	Brown	0.44
2 hours	Brown	0.32
5 hours	Sandy brown	0.19

The catalytic results are summarized in Table 3. The total activity is of the same order of magnitude for the two catalysts. The main difference in behavior is their selectivity. The main product is methylal (54%) at 230°C and formaldehyde at 280°C (37%) for the unwashed catalyst, and methylformate (98 to 83%) for the washed sample.

DISCUSSION

Grafting Reaction

The role of the silica OH groups in the grafting reaction is attested by the decrease in intensity of the vibration bands at 1365 and 2190 nm of the $\equiv$SiO–H groups (Figs. 2a,b). The intensity does not decrease in parallel, likely because their extinction molecular coefficient ε are different (Table 4). In addition, these bands do not completely disappear but broaden during the reaction: the band at 1365 nm exhibits a shoulder at 1380 nm. This fact reveals the presence of unreactive OH groups. They may be either internal OH present in precipitated silica or

TABLE 3

Catalytic Properties of Unwashed and Washed Grafted Mo/SiO_2 in the Reaction of Methanol Oxidation

Samples:	Unwashed Mo/SiO_2 (7.42 wt% Mo)			Unwashed Mo/SiO_2 (0.66 wt% Mo)			Silica	
T(°C):	230	260	280	230	260	280	230	260
$A(CH_2O)$	1.63	4.50	6.87	—	0.96	2.3	0.07	0.11
$A(HCOOCH_3)$	1.59	2.77	5.55	6.05	12.98	18.59	0.09	0.36
$A(CH_3O)_2CH_2$	4.60	4.91	2.98	—	—	—	—	—
$A(CH_3OCH_3)$	0.75	1.78	2.88	0.07	0.22	0.38	0.03	0.07
$A(CO_2)$	—	0.01	0.04	0.05	0.41	1.08	0.07	0.11
$A(CO)$	—	—	0.14	—	—	—	—	—
A_T	8.57	13.97	18.46	6.17	14.56	22.37	0.19	0.54
$S(CH_2O)$	19.3	32.2	37.2	—	6.6	10.4	—	—
$S(HCOOCH_3)$	17.8	19.9	30.1	98	89.1	83.1	46.1	58.3
$S(CH_3O)_2CH_2$	53.9	35.1	16.1	—	—	—	—	—
$S(CH_3OCH_3)$	8.9	12.7	15.6	1.1	1.5	1.7	15.1	16.1
$S(CO_2)$	—	0.1	0.2	0.9	2.8	4.8	38.8	25.6
$S(CO)$	—	—	0.8	—	—	—	—	—
Conversion (%)	1.8	3.4	4.9	3.0	7.1	10.8	0.3	0.6

Note. The activities A_i and A_T are expressed in mol h^{-1} (g of catalyst)$^{-1}$ × 10^3; the selectivities S_i are expressed in percent.

the companion OH of geminal silanol which cannot react because of steric hindrances (*82*, *88*). They also may be some so called "OH of internal surface," i.e., surface OH exchangeable by D_2O but not accessible for bigger molecules (*82*).

The similarities between the *g* values and the hyperfine structure of the EPR signal obtained after grafting (EPR-G) and those of $MoCl_5$ and various Mo^{5+} species found in the literature (Table 5) indicate that the EPR-G signal also arises from Mo^{5+} ions. In addition, this result shows that during grafting, $MoCl_5$ transforms into a species with the same oxidation state and that the grafting reaction is not of a redox type.

The EPR-G signal (Fig. 1b) exhibits an axial symmetry, i.e., a lower symmetry than that of $MoCl_5$ (Fig. 1a). This decrease in symmetry shows that the grafting process modifies the first coordination sphere of $MoCl_5$. The EPR *g* values are close to those of the molybdenyl species $(MoOCl_4)^-$ (Table 5). The fact that $g_\parallel > g_\perp$ indicates that chloride ligands are still present in the Mo^{5+} coordination sphere. For Mo^{5+} sur-

TABLE 4

$\equiv$SiO-H Vibration Bands Characteristics of Silica, before and after Grafting (without Air Exposure)

	Band width (nm)		Relative intensity $I_{(\nu+\delta)}/I_\nu$
	ν (1365 nm)	$(\nu + \delta)$ (2190 nm)	
Before grafting	40	80	1.21
After grafting	80	210	2.5

TABLE 5

EPR Parameters of Various Mo^{5+} Ions

Sample	$g_\perp$	$g_\parallel$	$g_\parallel - g_\perp$	$A_\perp$	$A_\parallel$	Ref.
Mo/SiO_2 (EPR-G)	1.952	1.968	0.014	44	82	This work
$MoCl_5$	1.952			51.5		This work
$(MoOCl_4)^-$	1.950	1.967	0.017	35.45	72.8	(*90*)
$(MoOCl_5)^{2-}$	1.940	1.963	0.023	32.6	74.7	(*91*)
$MoOCl_4 \cdot (H_2O)$	1.935	1.970	0.035	—	—	(*92*)

TABLE 6

UV-visible Electronic Transitions of Mo/SiO$_2$ Catalyst During Grafting and of Reference Compounds

Samples	Mo/SiO$_2$	MoCl$_5$	(MoOCl$_4$)$^-$	(MoOCl$_5$)$^{2-}$
State	solid	gas	in solid AsPh$_4$MoOCl$_4^*$	in solid (NH$_4$)$_2$(MoOCl$_5$)
Ref.	this work	*(94)*	*(90)*	*(95)*
Electronic Transitions λ (nm) and Assignment	≅625 (shoulder)	658 $E'' \to E'$	650 $B_2 \to A_1$	725 $^2B_2 \to {}^2E(I)$
	≅460	470	444 $B_2 \to B_1$	425 $^2B_2 \to {}^2B_1$
	365	360 $E'' \to A_1'$	377 $B_2 \to E$	375 $^2B_2 \to {}^2E(II)$
	325 (shoulder)			312
	280	280 charge transfer		280 charge transfer
	255	235		240 (shoulder)

* AsPh$_4$: tetraphenylarsonium

rounded by oxygen ligands, $g_\parallel$ is always smaller than $g_\perp$ *(93)*. It must be added that the hyperfine coupling constants given here are now correct and differ slightly from those published earlier *(10, 11, 20)*.

The absorption bands of molybdenum after grafting (DRS-G) are also compared to those of MoCl$_5$ in gaseous phase, and (MoOCl$_5$)$^{2-}$ and (MoOCl$_4$)$^-$ in solid state (Table 6). Transitions in spectrum DRS-G are common to both MoCl$_5$ and (MoOCl$_4$)$^-$.

All these observations: (i) the decrease in the ≡SiO–H band intensity, (ii) the similarities between both the EPR and the diffuse reflectance spectra of Mo (EPR-G, DRS-G) and those of the model compound (MoOCl$_4$)$^-$, (iii) the conservation of the oxidation state V for molybdenum, and (iv) the HCl evolvement during grafting, lead us to suggest the grafting reaction

$$\mathrm{Mo^VCl_5} + {\equiv}\mathrm{SiOH} \rightarrow {\equiv}\mathrm{SiOMo^VCl_4} + \mathrm{HCl}, \quad (5)$$

during which molybdenum is bonded to the support via a single oxygen. It was mentioned above that the UV–visible spectrum (DRS-G) also exhibits bands corresponding to that of MoCl$_5$. The fact that MoCl$_5$ is not observed in the EPR-G spectrum (Fig. 1b) suggests that it is deposited as a diamagnetic solid state dimer Mo$_2$Cl$_{10}$.

In consequence, there are two kinds of Mo on the silica surface after grafting:

—chemically grafted Mo as ≡SiOMoCl$_4$.

—physically adsorbed Mo as Mo$_2$Cl$_{10}$.

Exposure to Ambient Air

When exposed to ambient air after grafting, the samples turn blue. This change is accompanied by the appearance of a band at 600–1000 nm (Fig. 2c) in the diffuse reflectance spectrum (DRS-A). It is analogous to the one observed with molybdenum blues (Fig. 2d), which was attributed to an intervalence charge transfer band arising from electron hopping between Mo^{V} and Mo^{VI} *(96)*. The similarity between these spectra suggests that the physically adsorbed Mo$_2$Cl$_{10}$ is partially hydrolyzed and oxidized in ambient air so as to lead to the formation of Mo species analogous to molybdenum blues, according to reactions (4). The transformation of nonparamagnetic Mo$_2$Cl$_{10}$ into paramagnetic molybdenum blues is consistent with the increase in intensity of the EPR spectrum when the sample is exposed to air (Fig. 1c). However, its g component values, $g_\perp = 1.927$ and $g_\parallel = 1.967$, with $g_\parallel > g_\perp$, and its shape are different from those of the molybdenum blues used as reference for diffuse reflectance spectroscopy, with $g_\perp = 1.940$ and $g_\parallel =$

1.914, and $g_\perp > g_\parallel$ (Fig. 1d). These differences in g values probably result from the fact that these molybdenum blues arising from Mo_2Cl_{10} in contact with air, still contain some chlorides, as attested by the chemical analysis (Table 1).

It may be noted also that molybdenum blues is a generic term which describes several compounds with the same basic structure but whose mean Mo oxidation state varies between V and VI, e.g., $MoO_{2.0}(OH)$ and $MoO_{2.5}(OH)_{0.5}$ *(97)*. Some of them are water soluble, others are not *(76–78)*. Since the many attempts to characterize solid molybdenum blues compounds have been frustrated by the difficulty of separating them *(78)*, it is expected that their EPR parameters will also depend on the type of molybdenum blues.

The EPR spectrum (EPR-A) (Fig. 1c) is therefore interpreted as the superposition of:

—a main EPR signal due to a compound analogous to molybdenum blues, i.e., with mixed valence (Mo^V–Mo^{VI}), arising from partial oxidation in air of physically adsorbed Mo_2Cl_{10},

—and probably, the signal (EPR-G) of grafted molybdenum (Fig. 1b). It probably remains unchanged in exposure to ambient air, because protected by a layer of molybdenum blues and/or stabilized by the support.

The analysis of the hyperfine structure of spectrum EPR-A does not furnish any other information. Its coupling constants are similar to those of the grafted Mo (EPR-G). However, it is not possible to exclude that they could not also correspond to those of molybdenum blues, because the latter could not be determined with accuracy in Fig. 1d. The constants could in any case be different from those of our molybdenum blues containing chlorides.

Washing Step

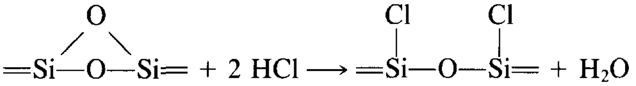
The change in the sample color, the lower Mo content (Table 1), and the disappearance of the intervalence band at 600–1000 nm (Fig. 2e) after washing indicate that the molybdenum blues are eliminated by washing, so as to only leave the grafted molybdenum, which gives a brown color to the sample. This result confirms that the molybdenum blues are weakly bonded to silica.

The time of washing is much shorter with washing by water than by ammonia, probably because two different phenomena are involved: water dissolves molybdenum blues, as attested by the blue color of the solution, while a basic solution such as ammonia, potassium, or sodium hydroxide transforms molybdenum blues in solution or in suspension into red-brown molybdenum hydroxide, $MoO(OH)_3$, which precipitates *(76, 98, 99)*. In our experiments, the precipitate was not observed and the ammonia solution remained colorless. The precipitation of $MoO(OH)_3$ onto silica can be excluded, otherwise the Mo content on silica would not have decreased (Table 2). The saturation concentration of $MoO(OH)_3$ was probably not reached; unfortunately, no relevant data could be found in the literature. In consequence, the higher efficiency of washing with ammonia solution is related to the faster transformation of molybdenum blues into $MoO(OH)_3$ than their solubilization in water. Another explanation would be that both silica and molybdenum blues are more negatively charged in the 1 *M* ammonia solution than in pure water. Therefore, stronger repulsive forces between silica and molybdenum blues develop at increasing pH, explaining why ammonia-washing is more efficient than water-washing.

The Mo content after ammonia washing (a few minutes) may exceed the one obtained after water washing (several days) (Table 1). That suggests that a slow solubilization of the brown grafted molybdenum occurs in water. Table 2 suggests that it is also the case for ammonia-washed samples if washing is extended. Therefore, the criterion of washing, leading to grafted Mo only, is the color change of the samples. In consequence, a washing time selected so as to permit the color change will limit the extent of grafted Mo solubilization.

The Mo content of the samples (<2 wt% for ammonia-washed samples) is much lower than the maximum loading of 6 wt% expected (see Experimental). It may be due to the fact that all the OH groups do not react with MoCl$_5$, as proved by the remaining unreacted OH bands in the near IR range (Fig. 2b). In addition, silanols or siloxane bridges can react with HCl (*100*) formed during grafting,

$$\equiv\mathrm{SiOH} + \mathrm{HCl} \longrightarrow \equiv\mathrm{SiCl} + \mathrm{H_2O}$$



$$=\mathrm{Si}\overset{\mathrm{O}}{\overbrace{-\mathrm{O}-}}\mathrm{Si}= + 2\,\mathrm{HCl} \longrightarrow =\overset{\mathrm{Cl}}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{Si}}}= + \mathrm{H_2O} \qquad (6)$$

and thus decrease the number of sites available for grafting. This last point also explains the trapping of chlorides by the support even after washing with water. Indeed, chemical analysis reveals that all the chlorides were not eliminated during washing by water and that the molar ratio Cl/Mo increases up to more than 10 after washing (Table 1). These results indicate that the chlorides located on silica are not drastically affected by the elimination of physically adsorbed Mo during washing.

The water-washed sample exhibits an absorption band at 400–500 nm characteristic of the *d–d* transition of Mo^{5+} ions (*75, 101, 102*) and a band at 280–300 nm due to the ligand to metal charge transfer transitions $O^{2-} \rightarrow Si^{4+}$ and $O^{2-} \rightarrow Mo^{6+}$ (*101, 103, 104*) (Fig. 2e). The latter band results from the oxidation of grafted molybdenum during washing. This oxidation is confirmed by the decrease in intensity of the EPR Mo^{5+} signal (EPR-W) (Fig. 1d). The intervalence band at 1100 nm, observed for the brown Lindqvist isopolyanion $(Mo_6O_{19})^{3-}$ containing 1 Mo^{5+} and 5 Mo^{6+} in interaction (*93*), is not detected in our samples, suggesting that Mo^{5+} ions are isolated from Mo^{6+} ions.

The brown color of the samples after washing is probably due to the presence of Mo^{5+} species because oxidized Mo/SiO$_2$ samples containing only Mo^{6+} ions are white (*21*). These grafted Mo^{5+} species probably possess a structure close to those of Mo(OH)$_5$ or MoO(OH)$_3$ which both are brown (*98*).

The following structure is proposed for brown grafted Mo^{5+} and Mo^{6+} ions:

$$\equiv\mathrm{SiOMo^{V}Cl_4} \xrightarrow{\text{hydrolysis}} \equiv\mathrm{SiOMo^{V}Cl_{4-x}(OH)_x} \qquad (7)$$

$$\equiv\mathrm{SiOMo^{V}Cl_4} \xrightarrow[\text{+ oxidation in air}]{\text{hydrolysis}} \equiv\mathrm{SiOMo^{VI}Cl_{4-x}(OH)_{x+1}}. \qquad (8)$$

For ammonia-washed samples, the Mo–Cl and the Si–Cl bonds are totally hydrolyzed as proved by chemical analysis (Table 1), suggesting a value of 4 for x.

Another group, Fricke *et al.* (*6*), have also studied the grafting reaction of MoCl$_5$ with silica under different experimental conditions (Aerosil Degussa silica 200 m^2/g dehydroxylated at 600°C, CCl$_4$ as solvant). By titration of HCl evolved during hydrolysis with water vapor in the absence of air, they also found that molybdenum is grafted via one bond to the support. However, the authors did not take into account in their calculation the presence of weakly bonded molybdenum species which are also hydrolyzable and therefore able to produce HCl. They did not consider the chlorides adsorbed on the silica surface. In consequence, it seems that their HCl titration value results from a compensating effect.

These authors have obtained samples containing 4.3 wt% after grafting. After grafting, their EPR signal analogous to ours (Fig. 1b) was also attributed to $\equiv SiOMoCl_4$. According to the authors, the signal intensity corresponds to 10% of the total Mo and the other 90% Mo correspond to grafted diamagnetic dimers,

$$2\equiv SiOH + 2\ MoCl_5 \longrightarrow (\equiv SiO)_2\ Mo_2Cl_8 + 2\ HCl, \quad (9)$$

which, in contact with water vapor, are hydrolyzed as follows:

$$(\equiv SiO)_2\ Mo_2Cl_8 \xrightarrow{2\ H_2O} 2\equiv SiOH + 2\ (MoOCl_4)^- + 2\ H^+. \quad (10)$$

The rupture of the $\equiv$Si–OMo bonds leads to the formation of the paramagnetic $(MoOCl_4)^-$, responsible for the increase in the EPR signal intensity. Their interpretation does not explain why the $\equiv$Si–OMo bonds of the dimer species are broken while those of the $\equiv SiOMoCl_4$ monomers are not. We rather suggest that their dimer species were not really grafted but physically adsorbed as Mo_2Cl_{10}. In the presence of water vapor admitted without oxygen, Mo_2Cl_{10} was transformed into the paramagnetic $Mo(OH)Cl_4$ monomer, responsible for the increase in the EPR signal intensity. Only the $\equiv SiOMoCl_4$ monomer was really grafted, i.e., 10% of the 4.3 wt% Mo content. This content is in the same range as our sample loading.

Methanol Oxidation Reaction

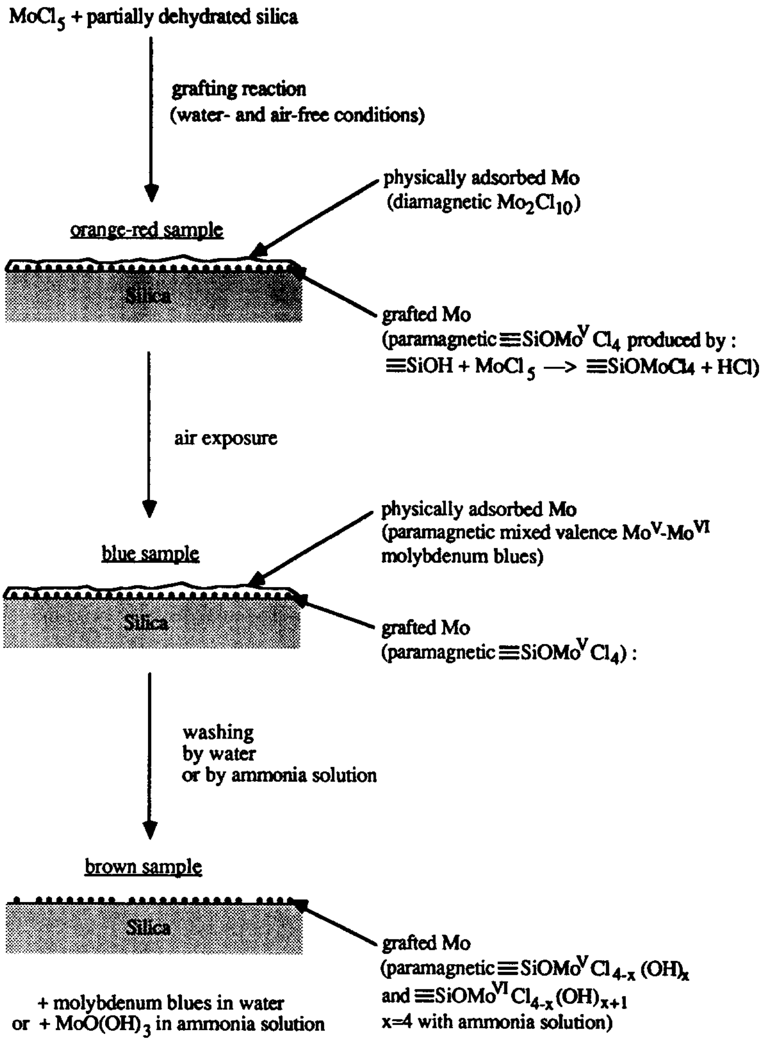
In order to emphasize the differences between washed (brown samples containing grafted Mo) and unwashed Mo/SiO_2 catalysts (samples containing molybdenum blues), they were tested after calcination in the reaction of methanol oxidation. This reaction was found by Tatibouët *et al.* (105, 106) to be sensitive to the structure of MoO_3, which means that the selectivity depends on the exposed faces. They have found that the basal (010) face of MoO_3 is highly selective for the formation of formaldehyde whereas the side (100) face leads to methylal, and the apical (001) and (101) faces are selective in dimethyl ether. As shown in other papers (*21, 22*), this reaction also provides information concerning the Mo dispersion.

The unwashed and washed catalysts are found to behave totally differently (Table 3). According to the results of Tatibouët and Germain (*107, 108*) and Bennett and coworkers (*109*) the unwashed catalyst behaves as massive MoO_3. The presence of MoO_3 on the unwashed calcined sample was in fact detected. It results from the oxidation of molybdenum blues. The formation of methylal and dimethylether on the unwashed catalyst is related to the acidic character of MoO_3. It decreases when the reaction temperature increases and the redox character becomes stronger, as attested by the increasing selectivity to methylformate and formaldehyde (*105, 106*). Tatibouët *et al.* have not observed the formation of methylformate on MoO_3. According to a previous work (*22*), the methylformate formation is due to the presence of the silica support. However, the formation of methylformate and formaldehyde on washed catalysts suggests a redox catalytic behavior only. In addition to that, the high selectivity to methylformate compared to that to formaldehyde indicates a state of high Mo dispersion (*21, 22*). The presence of grafted Mo as main species on washed samples prevents the formation of MoO_3 and leads to a totally different catalytic behavior from that on unwashed catalysts.

CONCLUSIONS

The preparation by grafting occurs in two steps, summarized as follows and also in Scheme 1:

—the *grafting* namely, a reaction between $MoCl_5$ and the OH groups of silica performed in the absence of air: brown grafted Mo as $\equiv SiOMo^VCl_4$ is formed according to reaction 5. In the same time, diamagnetic Mo_2Cl_{10} is physically adsorbed. The sample is orange-red. After



SCHEME 1

grafting, the sample put in air, turns blue, due to the transformation of Mo_2Cl_{10} into molybdenum blues (reaction (4)). The grafted Mo probably remains unchanged.

—the *washing* in ammonia solution: the molybdenum blues are completely eliminated and the grafted Mo is completely hydrolyzed into $\equiv SiOMo^{V}(OH)_4$; part of these species are also oxidized into $\equiv SiOMo^{VI}(OH)_5$. The sample color is brown. In water, the washing procedure requires much longer times, and the chlorides are not totally hydrolyzed. Extended washing time in both water and ammonia leads to the solubilization of grafted Mo, therefore it is necessary to adjust the washing time according to the color change.

The catalytic behavior of the catalysts before and after washing, in the reaction of methanol oxidation, is different and confirms the presence of different molybdenum species. Unwashed catalysts containing mainly molybdenum blues, transformed into MoO_3 after calcination prior to the reaction, behaves as massive MoO_3, i.e., possesses an acidic character, as revealed by the presence of methylal and dimethylether in the reaction products. Washed catalyst containing grafted Mo species which are not transformed into MoO_3 by calcination behaves as a redox catalyst, forming mainly methylformate, and formaldehyde to a lower extent.

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