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Studies on Catalytically Active Surface Compounds

IV. Preparation of Mo/SiO$_2$ Catalysts from MoCl$_5$ Studied by ESR and UV-vis Spectroscopy[1]

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The preparation steps of silica-supported molybdenum catalysts have been followed by ESR and uv-vis spectroscopy. It is shown that the reaction of MoCl$_5$ with silanol groups of the support leads to dimeric (the main part) and monomeric surface Mo species. On adsorbing H$_2$O a surface "solution layer" is formed allowing a fast tumbling of Mo^{5+} ions. Simultaneously, the concentration of isolated Mo^{5+} ions is increased; however, it does not exceed about 10% of the total Mo concentration. The final hydrolyzing process which includes drying at 378 K in air produces partly oxidized catalysts containing polymolybdate complexes. Although the interaction between the molybdenum species and the silica surface has been described as being relatively weak, no indication has been found that adsorption of water vapor causes any structural changes within the polymeric Mo complexes or its bonding to the surface. Adsorption of wet HCl causes ligand exchange which is accompanied by destruction of the polymeric molybdenum complexes.

INTRODUCTION

Catalytic systems containing molybdenum as the active element receive continuous attention and have been the subject of numerous investigations. With supported catalysts, special attention has been focussed upon their surface structure and the changes under various conditions. In addition, the interaction between molybdenum ions and the support (mainly Al$_2$O$_3$ or SiO$_2$) has been considered. Though a great number of methods have been used the detailed structure of these catalysts is still not settled. The preparation of the catalysts is often performed by impregnation of the support with aqueous solutions of molybdenum compounds and it is uncertain whether or not there is a specific interaction between the active component and the support (resulting in a high molybdenum surface dispersion). It is often concluded that molybdenum is aggregated on the surface of the support (*2–4*). Other authors have concluded that when using organometallic compounds (such as Mo(π-C$_3$H$_5$)$_4$) the formation of oxide clusters on the support surface is less probable (*5, 6*).

The use of MoCl$_5$ in nonaqueous solutions for the preparation of the catalyst seems to be of some advantage compared with the impregnation method. Due to the specific reaction of MoCl$_5$ with SiOH groups a high dispersion of Mo ions on the surface should be expected and, in addition, the initial state of the catalyst and the changes caused by the preparation procedure (in particular by the adsorption of water vapor) can be studied. Various authors who used MoCl$_5$ paid only little attention to these questions (*7–9*). The aim of the present work is first to contribute some detailed information on problems connected with the preparation procedure using MoCl$_5$ and second to characterize the state of molybdenum on the support surface in

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[1] For Part III, see Ref. (*1*).

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the final catalyst using ESR and uv-vis spectroscopy.

EXPERIMENTAL

Mo/SiO_2 catalysts have been prepared under protection of argon by reaction of granulated SiO_2 (Degussa Aerosil-200, S = 200 m^2/g) with $MoCl_5$ dissolved in CCl_4. Steps and conditions as well as some characteristics of the sample are shown in Table 1.

The detailed procedure was as follows. SiO_2 was calcined in air at 873 K for 10 h. In order to exclude the influence of air the sample was repeatedly evacuated and argon treated. The resulting SiO_2 has a SiOH concentration of about 0.42–0.48 mmole OH/g (*10*). The reaction of $MoCl_5$ (in slight excess compared to the SiOH concentration) with SiO_2 was carried out in boiling CCl_4 under argon atmosphere for 2–4 h (depending on the desired Mo concentration). The remaining solution was removed over a frit and the brown reaction product was twice washed with CCl_4 and dried in a stream of dry argon. In order to obtain an air stable catalyst hydrolysis was carried out by means of a stream of wet argon. During this treatment layers of different color move through the catalyst in the following sequence: brown → white-grey → olive-brown → blue, while HCl was produced and conveyed with the argon stream. After 8 h argon was substituted by air and HCl was desorbed at 295 K during 24 h treatment. The final drying process was carried out at 378 K for 12 h. The total Mo concentration of the sample was 4.3 wt%. Though the influence of the Mo concentration has not been studied in detail samples prepared without excess of $MoCl_5$ and with lower Mo concentrations (down to 1.0%) show similar results and are therefore not regarded separately in this paper. The final catalyst is blue and is designated the hydrolyzed sample.

$MoCl_5$ is easily hydrolyzed in moist atmosphere to form MoO^{3+} species. This reaction includes the formation of 2 mole HCl (or a Cl : Mo ratio of 3 for the catalyst). As a medium value of about 4 is found for the Cl : Mo ratio the following reaction may be assumed as the first preparation step:

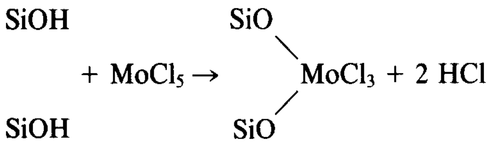
$$SiOH + MoCl_5 \rightarrow SiOMoCl_4 + HCl \qquad (Cl:Mo{=}4) \quad (1a)$$

In addition, the reaction of $MoCl_5$ with geminal ($Si(OH)_2$) or vicinal $(SiOH)_2$ groups according to (1b) cannot be rules out

TABLE 1

Preparation Data for Mo/SiO_2 Catalysts

Reaction step	Conditions	Color	Cl : Mo ratio (catalyst)
1. Reaction	SiO_2 + $MoCl_5$ in boiling CCl_4 under argon (HCl-evolution)	Brown	3.7–4.2
2. Hydrolysis	(a) + H_2O (HCl formation in wet argon stream 8 h, 295 K)	White-grey Olive-brown	
	(b) − HCl (in wet air stream 24 h, 295 K)	Blue ↓	2
3. Drying	Dry air stream (12 h, 378 K)	Blue	0



$$\begin{matrix} SiOH \\ \\ SiOH \end{matrix} + MoCl_5 \rightarrow \begin{matrix} SiO \diagdown \\ MoCl_3 \\ SiO \diagup \end{matrix} + 2\,HCl$$

$(Cl:Mo{=}3)$ (1b)

but should be of minor importance. Due to the limited number of SiOH groups the maximum concentration of Mo obtained for catalysts prepared by this method is about 4.6 wt%.

In order to avoid any influence of oxygen or moisture the catalyst was stored in argon atmosphere (after the first reaction step). The ESR sample tube and uv-vis cuvette were filled via a side arm or by means of a glove box, respectively. ESR measurements were carried out with a ZWG ERS-220 spectrometer at 77 K and 293 K. DPPH and NMR markers were used for the calibration of the magnetic field and for the calculation of g and A values. A $CuSO_4 \cdot 5H_2O$ crystal served as spin standard, the spin concentration being determined by double integration. Ultraviolet-vis spectra were taken with a Beckman DK 2A spectrometer.

RESULTS

ESR Spectroscopy

The X-band spectrum of the unhydro-

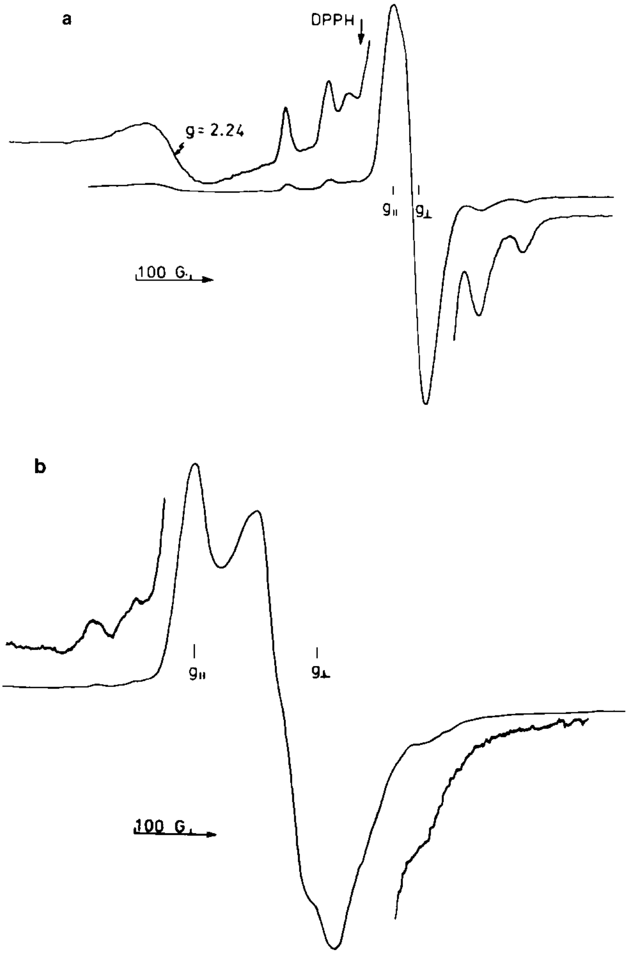


FIG. 1. $MoCl_5/SiO_2$ catalyst (brown) in argon atmosphere. (a) ESR spectrum at 77 K (X-band); (b) ESR spectrum at 293 K (Q-band).

lyzed brown sample is shown in Fig. 1a. It differs strongly from the spectra of Mo^{5+} of partially reduced Mo catalysts known from the literature (*11–14*) (see also Fig. 6). The asymmetric central line ($g_\perp$ = 1.948, $g_\parallel$ = 1.967) is surrounded by several hyperfine structure (hfs) lines which result from the two molybdenum isotopes ^{95}Mo and ^{97}Mo of natural abundances of 15.78 and 9.60%, respectively, both with the nuclear spin I = 5/2. An additional single line at g = 2.24 is also observed but is not identified. Though the hfs lines are slightly better resolved at 77 K the whole spectrum is nearly temperature independent. The main characteristic of the signal is the relative magnitude of the components of the g tensor which shows $g_\parallel > g_\perp$. This is confirmed by the Q-band spectrum which improves the assignment of the central axial line (Fig. 1b). Hfs lines are again resolved in the Q-band spectrum but less clearly. The adsorption of water vapor on the sample without evacuation results in a slow change of its color from brown to white-grey. Simultaneously, the room temperature spectrum changes its line shape (Fig. 2a). An isotropic spectrum is observed now, consisting of a single symmetric line and 6 hfs lines with the following parameters: g_{iso} = 1.952, A_{iso} = 53.8 G. The spectrum at 77 K is axial with $g_\perp$ = 1.947, $g_\parallel$ = 1.972, $A_\perp$ = 43.6 G, and $A_\parallel$ = 81.3 G (Fig. 2b). This "solution-like" behavior is accompanied by an increase in intensity of

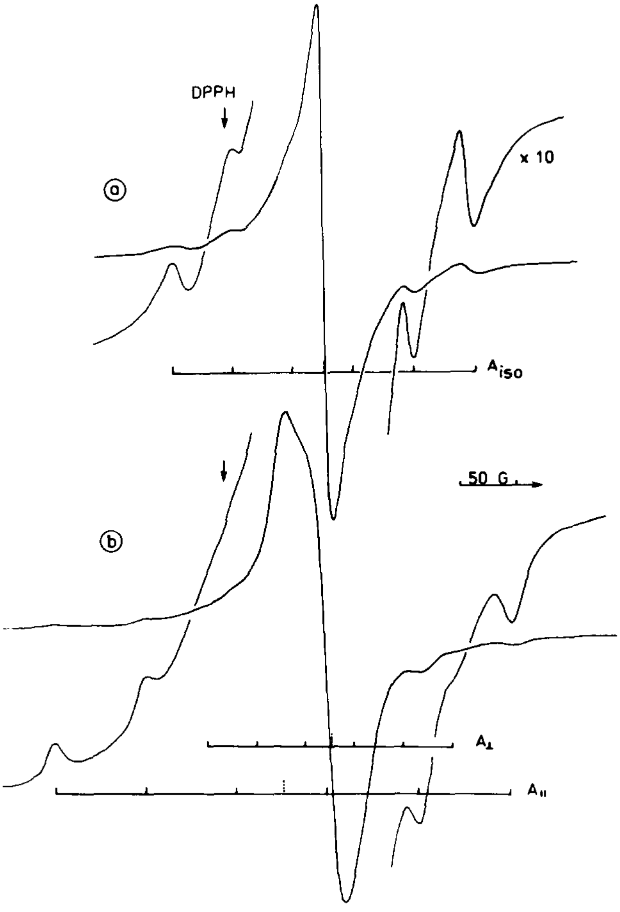


FIG. 2. Mo/SiO₂ sample after adsorption of water vapor (white). ESR spectra at (a) 293 K and (b) 77 K.

nearly one order of magnitude.

Evacuation after adsorption of water vapor caused a blue color of the sample and the resolution of the whole Mo^{5+} spectrum decreased (see Fig. 8). The ESR parameters of this spectrum have not been estimated because of too great uncertainty of the resonance positions. Chemical analysis has shown that the sample is still not fully hydrolyzed ($Cl : Mo \approx 2$). Therefore, an additional treatment in wet oxygen at 378 K was carried out in the sample tube which simulates the "usual" hydrolyzing treatment in a stream of wet argon and air. This sample does not contain any chlorine; the blue color still remains. The axial spectrum, however, now shows $g_{\parallel} < g_{\perp}$ ($g_{\perp} = 1.939$, $g_{\parallel} = 1.910$) which is the normal case for partially reduced samples (Fig. 3).

Ultraviolet-vis Spectroscopy

Ultraviolet-vis spectra after various steps of preparation are shown in Fig. 4. Spectrum 4a (brown sample) shows absorption in the 18,000–28,000 cm^{-1} region with a distinct maximum at 25,500 cm^{-1}. Shoulders at 21,000 cm^{-1} (intense), 13,000 cm^{-1} (weak), and 14,700 cm^{-1} (weak) were resolved. At shorter wavelengths a broad charge transfer band with a maximum at 35,000–36,000 cm^{-1} was observed. The characteristics of the spectrum suggest the existence of more than one Mo^{5+} species. Similarities in the 24,000–25,000 cm^{-1} region characteristic for dimeric Mo complexes in solution (*15*) are obvious (Fig. 5). Already at the beginning of hydrolysis (white-grey sample) the spectrum changes markedly; in particular the absorption in the dimeric region (20,000–26,000 cm^{-1}) is diminished (Fig. 4b). The positions of the other bands are summarized in Table 2. After proceeding with hydrolysis the sample became blue (the olive-brown intermediate product has not been studied). A strong absorption band at 12,000 cm^{-1} (intervalence charge transfer absorption) and a shoulder at 16,000 cm^{-1} are characteristic. Further hydrolysis and drying in air did not change the spectrum remarkably even when the sample was calcined at 623 K in air (Fig. 4d).

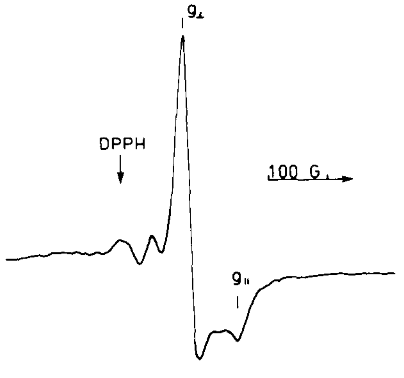


FIG. 3. Mo/SiO_2 sample after treatment in O_2/H_2O at 378 K (blue), ESR spectrum at 77 K.

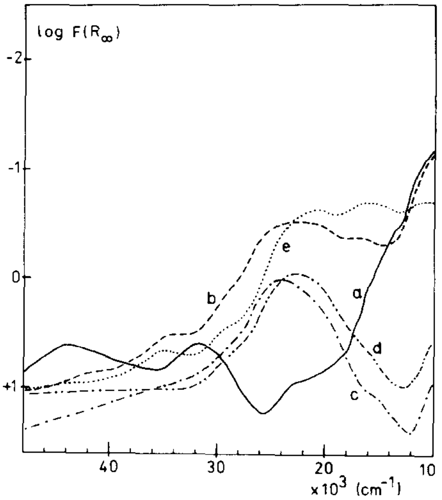


FIG. 4. Ultraviolet-vis spectra of Mo/SiO_2 catalysts. Changes of the spectrum under various conditions: (a) $MoCl_5/SiO_2$ (unhydrated); (b) H_2O adsorption on (a); (c) evacuated after (b); (d) Mo/SiO_2 (hydrated); (e) after adsorption of wet HCl on (d).

DISCUSSION

The Reaction of $MoCl_5$ with SiO_2

$MoCl_5$ exists in the dimeric Mo_2Cl_{10} form as a solid substance but becomes a monomer when dissolved in CCl_4 (*16*). Therefore, under the chosen conditions, one may simply expect the reaction of monomeric $MoCl_5$ with SiOH groups as stated in Eq. (1) producing a high dispersion of Mo^{5+} ions

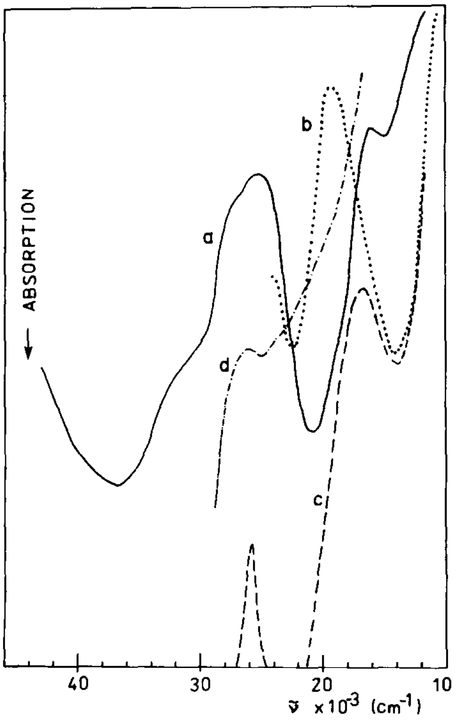


FIG. 5. Ultraviolet-vis spectra of Mo complexes in solutions: (a) $MoCl_5$ in CCl_4; (b) $[MoOCl_5]^{2-}$; (c) $\{[MoOCl_4]_2O\}^{4-}$; (d) solution (c) further diluted by addition of H_2O.

on the SiO_2 surface. ESR spectra of this catalyst show the signal of uncoupled, i.e., isolated, Mo^{5+} ions (Fig. 1) with the parameters $g_\parallel = 1.967$ and $g_\perp = 1.948$. Following De Armond *et al.* (*17*) and Che *et al.* (*18*) $g_\parallel$ strongly reflects the nature of the ligands, showing $g_\parallel > g_\perp$ for chlorine and $g_\parallel < g_\perp$ for oxygen ligands. Because the spacing (about 270 G) between high and low field hfs lines (m_I = 3/2 and −3/2) is clearly not a multiple of the hfs constant A the hfs could not be designated. Q-band measurements (Fig. 1b) or lowering of the Mo content to 1% do not increase the resolution in any way. Therefore, as a reasonable speculation, the overlap of two different Mo^{5+} signals with slightly different ESR parameters is assumed. An estimation of the Mo^{5+} signal intensity shows that only about 1% of the total Mo concentration is detected by ESR spectroscopy both at 300 and 77 K. This

TABLE 2

Ultraviolet-vis Spectra[a]

Sample	Color	Band positions (cm^{-1})						
(a) $MoCl_5/SiO_2$	Brown	13,000(sh)			21,000(sh)	25,500	35,500	
$MoCl_5/SiO_2(+H_2O)$	White-grey	14.500		18,200		28,000(sh)	32,700	
$MoCl_5/SiO_2(-HCl)$	Blue	12,000	16,000(sh)			28,000(sh)	33,000	
Mo/SiO_2 (hydrolyzed)	Blue	12,000–14,000				28,000	(Broad)	
Mo/SiO_2 (HCl ads.)	White-grey	12,800		18,900		28,600(sh)	32,300	
(b) $MoCl_5/CCl_4$	Red		15,200		21,200	27,000(sh)	31,000(sh)	37,000
$[MoOCl_5]^{2-}$	Green		14,500		22,700	{Not measured}		
$\{[MoOCl_4]_2O\}^{4-}$	Dark brown		14,200		23,000 (broad)			
$\{[MoOCl_4]_2O\}^{4-}$ (H_2O diluted)	Light-brown					25,000		

[a] (a) Mo/SiO_2 catalyst (4.3 wt% Mo); (b) Mo compounds in solutions.

agrees with the findings of other authors on supported molybdenum catalysts (*2, 19, 20*). Abdo *et al.* (*2*) explained this by strongly interacting Mo^{5+} ions not detectable in the temperature range between 4.2 and 560 K. Due to the proposed reaction mechanism (1) this result is unexpected for catalysts prepared from $MoCl_5$.

According to Bader and Westland (*16*) uv-vis spectra of $MoCl_5$ vapor and a $MoCl_5/CCl_4$ solution are nearly identical, indicating that $MoCl_5$ is monomeric in a solution of CCl_4. Figure 5a corresponds to their spectra allowing the same conclusion. This is also confirmed by the spectrum of $[MoOCl_5]^{2-}$ dissolved in concentrated HCl which also represents monomeric Mo^{5+} ions (*15*). It does not exactly agree with the $MoCl_5/CCl_4$ spectrum but slight band shifts may originate from incorporated oxygen in the $[MoOCl_5]^{2-}$ complex. If water is added, dimerization to $\{[MoOCl_4]_2O\}^{4-}$ occurred (brown solution) causing no band shift but a strong increase of the 22,700 cm^{-1} band whereas the 14,500 cm^{-1} band is not affected (Fig. 5c). If this solution is further diluted with H_2O the strong absorption between 21,500 and 25,000 cm^{-1} decreased and is replaced by a band at 25,500 cm^{-1} (Fig. 5d). Haight (*15*) has excluded further aggregation of Mo under these conditions.

Returning now to the brown sample of the Mo^{5+}/SiO_2 catalyst (Fig. 4a) the uv-vis spectrum shows distinct differences compared to any solution spectrum. The most remarkable observation is a strong absorption in the 18,000 to 28,000 cm^{-1} region with a shoulder at about 21,000 cm^{-1} and a maximum at 25,500 cm^{-1}. The position of the shoulder agrees with the maximum of the $MoCl_5/CCl_4$ solution spectrum and is therefore ascribed to the presence of monomeric, i.e., isolated, Mo^{5+} ions as already shown in the ESR spectra. The appearance of the strong 25,500 cm^{-1} absorption band not visible in the $MoCl_5/CCl_4$ spectrum is obviously the product of the surface reaction of $MoCl_5$ with SiOH groups. Surprisingly the maximum at 25,500 cm^{-1} coincides with that in highly diluted $\{[MoOCl_4]_2O\}^{4-}$ (Fig. 5d). The nature of this effect which might result from the high dilution in both substances, is not fully clear. It allows us, however, to conclude that in both cases the Mo complexes are dimers. This agrees also with the observation that more than 90% of Mo^{5+} ions were not detected by ESR. As a consequence Eq. (1) has to be completed:

$$\begin{matrix} \mathrm{SiOH} \\ \\ \mathrm{SiOH} \end{matrix} + 2\,MoCl_5 \rightarrow (SiO)_2Mo_2Cl_8 + 2\,HCl \qquad (Cl:Mo=4) \quad (2)$$

It should be pointed out, however, that the detailed reaction mechanism is still unknown, although, the reaction of monomeric $MoCl_5$ with SiOH followed by dimerization on the SiO_2 surface is suggested (*21*). Strong coupling of two Mo^{5+} ions may provide either a diamagnetic Mo_2 complex as proposed for $Mo(CO)/\gamma\text{-}Al_2O_3$ catalysts (*22*) or a paramagnetic dimer complex (*23*) with undetectable broad ESR lines. However, because no further investigations have been undertaken with regard to this problem the model character of the proposed reaction should be emphasized.

It should be mentioned that the catalyst in the unhydrolyzed state (brown sample) is extremely sensitive toward oxygen or moisture. Despite storage in argon atmosphere oxidation could not be completely ruled out: this, however, had no influence on the Mo^{5+} ESR signal.

Hydrolysis

Adsorption of water vapor on the brown sample within the ESR sample tube or the uv-vis cuvette changed the color from brown to white-grey and caused strong changes of ESR and uv-vis spectra (Figs. 2 and 4b). The temperature-dependent Mo^{5+} signal consisting of 6 hfs lines and a central intense narrow line at room temperature shows the Mo^{5+} species undergoing fast tumbling in a solution-like surface layer at this temperature (Fig. 2a). At 77 K this motion is frozen, resulting in an axial solid state spectrum (Fig. 2b). This effect showing that the Si–OMo^{5+} bond is destroyed is known for silica-supported vanadium catalysts (*24*) but has not been observed for molybdenum catalysts. The parameters of both spectra agree with those of Mo^{5+} complexes in liquid and frozen solution (Table 3), namely $[MoOCl_4]^-$ or $[MoOCl_5]^{2-}$ (*25, 26*).

During the adsorption of water vapor a significant increase of the Mo^{5+} spin concentration by about one order of magnitude is observed, showing that the concentration of Mo^{5+} monomers has increased and is greater in the "solution layer" than on the dry surface. This agrees with the uv-vis spectrum which shows a strong decrease of the dimer band at 25,500 cm^{-1} (Fig. 4b).

Hare *et al.* (*23*) by means of susceptibility and ESR measurements have shown that formation of MoO^{3+} monomers is promoted in strong acidic solutions (6–12 *M* HCl). Suggesting that the detected solution layer is also strongly acidic caused by H$^+$ formation during hydrolysis,

$$(SiO)_2Mo_2Cl_8 \xrightarrow{2\,H_2O} 2\,SiOH + 2\,[MoOCl_4]^- + 2\,H^+ \quad (3)$$

the equilibrium of the reaction will be shifted to the right side. The result is an increased concentration of monomeric $[MoOCl_4]^-$ anions. Evacuation caused the reverse process but left the blue color. This irreversibility of the color change which is additionally documented both in the ESR and uv-vis spectra is obviously connected with the formation of stable $(Mo{=}O)^{3+}$ bonds.

An additional treatment in wet oxygen at 378 K produced a chlorine-free sample. The Mo^{5+} signal ($g_\perp = 1.939$, $g_\parallel = 1.910$) (Fig. 3) and uv-vis spectrum are similar to that of partially reduced (*11*) and hydrolyzed samples (Figs. 4 and 6).

Hydrolyzed Samples and Influence of Cl$^-$ Ligands

Due to the uncontrolled oxidation during

TABLE 3

ESR Data of Mo Catalysts after Various Treatments

Sample treatment	Color	$g_\perp$	$g_\parallel$	g_{iso}[a]	HFS-Splitting (G)			Reference
					$A_\perp$	$A_\parallel$	A_{iso}[a]	
1. $MoCl_5/SiO_2$								
Unhydrolyzed	Brown	1.948[b]	1.967[b]	—			—	This work
H_2O adsorbed	White-grey	1.947	1.972	1.952	43.6	81.3	53.8	This work
Vac. 1 h, 773 K	Grey-blue	1.941	1.883	—	—	—	—	This work
$+H_2O$ ads.	Grey-blue	1.939	1.968	1.949	39.6	81.2	52.8	This work
H_2O/O_2 1 h, 378 K	Blue	1.939	1.910	—	—	—	—	This work
$[MoOCl_4]^-$		1.95	1.967	—	37.9	77.9	51.3	(*25*)
$[MoOCl_5]^{2-}$		1.938	1.970	1.946	36.4	79.7	49.9	(*26*)
2. Mo/SiO_2								
Hydrolyzed	Blue	1.936	1.894	—	36.0	80.0	—	This work
Vac. 1 h, 773 K	Blue	1.941	1.865	—	—	—	—	This work
HCl adsorbed	White-grey	1.944	1.968	1.948	42.8	82.0	52.2	This work
$^{95}Mo/SiO_2$								
Reduced		1.940	1.882	—	44	98	—	(*12*)
$Mo_6O_{19}^{2-}$	Brown	1.930	1.919	—	34.5	80.5	—	(*18*)

[a] Room temperature spectrum.

[b] Estimated from the Q-band spectrum (Fig. 1b): $g_\perp = 1.938$, $g_\parallel = 1.972$.

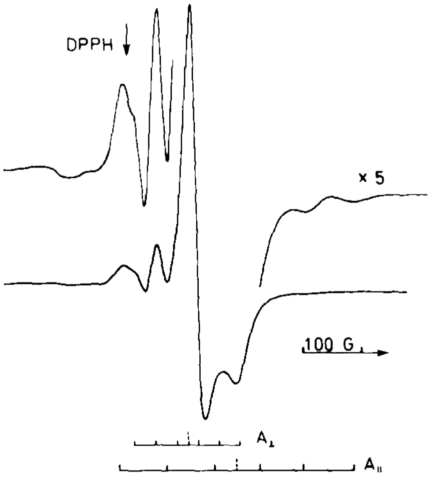


FIG. 6. Mo/SiO_2 catalyst, hydrolyzed and dried at 378 K (blue). ESR spectrum at 77 K.

hydrolysis and drying the Mo^{5+} concentration does not amount to more than about 10% of the total Mo concentration. ESR (Fig. 6) and uv-vis spectra (Fig. 4d) agree with those reported earlier for similar partially reduced Mo catalysts (*9, 11, 27*). The uv-vis spectrum shows absorption in the visible region with a maximum at about 12,000–13,000 cm^{-1} which is attributed to an intervalence charge transfer band. The broad absorption at shorter wavelengths with a shoulder at 30,000–33,000 cm^{-1} has also been found for MoO_3 and points to distorted octahedral coordination. Further considerations on the coordination in supported Mo catalysts and mechanical mixtures of structurally known Mo compounds will be presented in a forthcoming paper (*28*).

As to the Mo^{5+} ESR signal the following parameters were estimated from the spectrum: $g_\perp = 1.936$, $g_\parallel = 1.894$, $A_\perp = 36.0$ G, and $A_\parallel = 80.0$ G which, however, differ from those calculated by Che *et al.* (*12*) from the reduced ^{95}Mo-enriched Mo/SiO_2 sample. A square pyramidal coordination of C_{4v} symmetry is often supposed for the local symmetry of Mo^{5+} ions (*29, 30*); however, Abdo *et al.* (*31*) have concluded from crystal field considerations that also a local field of tetrahedral symmetry with tetragonal distortion would accord with the experimental findings.

Regardless of the amount of adsorbed water, Mo^{5+} ions of hydrated, but chlorine-free samples do not move within the surface solution layer (fast tumbling) as could be shown for VO^{2+} ions in V/SiO_2 (*24*) and V–P/SiO_2 (*32*) catalysts. In order to check the HCl influence a hydrolyzed blue sample was evacuated and a small amount of wet HCl was adsorbed. This treatment changed the sample color from blue to white-grey and increased the signal intensity and the line-shape of Mo^{5+} ions indicating a solution spectrum (Fig. 7) also shown after H_2O adsorption on the original brown sample (Fig. 2). One may therefore conclude that the state of Mo^{5+} ions in both white-grey

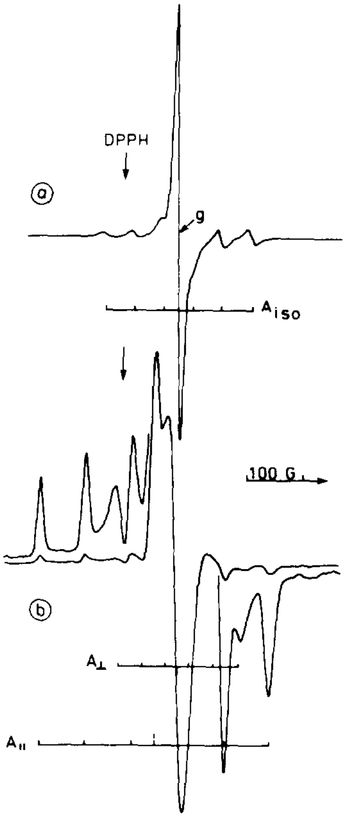


FIG. 7. Mo/SiO_2 sample hydrolyzed as in Fig. 6 but after room temperature adsorption of wet HCl. ESR spectra at (a) 293 K and (b) 77 K.

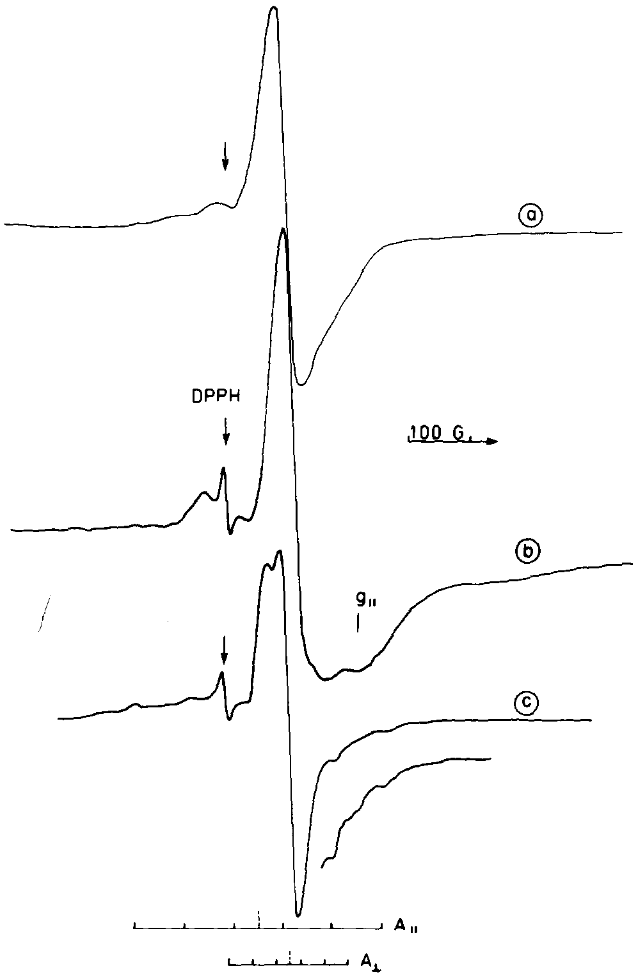


FIG. 8. $MoCl_5/SiO_2$ catalyst, unhydrolized, after vacuum treatment at (a) room temperature; (b) 773 K; (c) 773 K and adsorption of water vapor.

samples is the same. HCl desorption at room temperature restores the original blue color and spectral parameters. van Reijen and Cossee (*33*) have shown by means of ESR measurements that if HCl is adsorbed on Cr/SiO_2 catalysts, chlorine substitutes for oxygen as a ligand showing $g_{\|} > g_{\perp}$ for the Cr^{5+} signal. The same effect is shown here for Mo/SiO_2 catalysts. In agreement with recent Raman and uv-vis studies (*3, 34, 35*) it is therefore concluded that Mo species are aggregated on the SiO_2 surface in the form of polymolybdates. This structure cannot be destroyed by water adsorption whereas wet HCl causes ligand exchange destroying Mo–O–Mo as well as Si–O–Mo bridges, at least partially. As one consequence the concentration of Mo^{5+} monomers able to rotate within the surface solution layer is increased.

An additional remark should be made on the relative magnitudes of the *g*-tensor components of the Mo^{5+} spectra. As shown for chlorine-containing Mo complexes in various solutions, a predominant influence of the spin-orbit coupling constant λ_L of the ligands is observed (*13, 18, 21, 22*), causing $g_{\|} > g_{\perp}$. However, when studying vacuum-treated $MoCl_5/SiO_2$ catalysts a divergence is observed. Figure 8 shows spectra of the unhydrolyzed sample after evacuation at 293 K (a) and 773 K (b) followed by water adsorption (c). The result is contradictory because $g_{\parallel} < g_{\perp}$ is evident for the evacuated sample (b) and $g_{\parallel} > g_{\perp}$ after water adsorption. If evacuation removed the Cl$^-$ ligands then the spectrum after water adsorption should also show $g_{\parallel} < g_{\perp}$; if not then the former spectrum is possibly not in agreement with the model. High temperature vacuum treatment strongly changes the coordination of Mo^{5+} species. This is indicated by a shift of $g_{\parallel}$ from 1.894 to 1.865 for the hydrolyzed sample and from 1.967 to 1.883 for the unhydrolyzed sample (Table 3). Since the relation

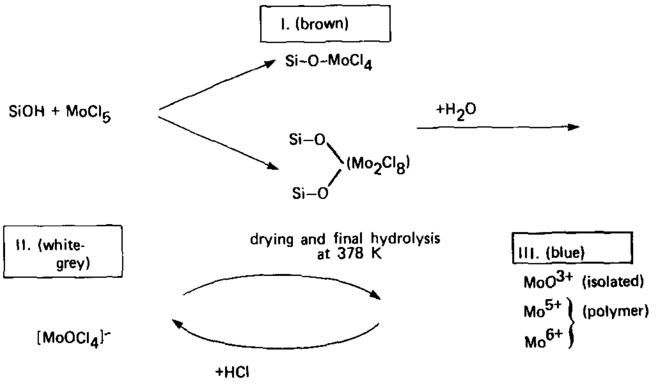
$$g_{\parallel} \sim \frac{\lambda_L}{\Delta E(b_2 \rightarrow b_1)}$$

has been derived for Mo^{5+} complexes (*17*) one may suppose that a change of the energy splitting ΔE caused by coordinative distortions might overcompensate the influence of λ_L. In any event, the experimental result shows that the interpretation of the relative g-values of chlorine-containing solid Mo^{5+} complexes should be regarded with care.

CONCLUSIONS

It is shown that in contrast to the expected high dispersion of isolated Mo ions on the surface of SiO$_2$, Mo ions are mainly present in the dimeric form already after the reaction of MoCl$_5$ with SiOH groups. The amount of isolated Mo^{5+} ions detected by ESR is rather low and in no case exceeds 10% of the total Mo concentration. During hydrolysis a rearrangement of Mo ions within a surface solution layer is observed, resulting in an increasing concentration of monomer Mo^{5+} ions. Drying of the catalysts produces mainly polymeric Mo complexes which are not influenced by water adsorption.

If, however, wet HCl is adsorbed the polymeric complexes are partly destroyed as well as their bonding to the surface, again forming a surface solution layer with an increasing concentration of isolated Mo^{5+} ions and fast tumbling of these ions. After evacuation the original spectrum is restored showing that the reaction is reversible. Therefore, the preparation process may be described schematically as follows:



It is supposed that the step I → II is irreversible because of incorporation of oxygen. Further species not detected by ESR or identified in the uv-vis spectra are probably present.

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