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ESR Evidence of Tetracoordinated Mo_{4c}^{5+} Species Formed on Reduced Mo/SiO_2 Catalysts Prepared by Impregnation

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Tetracoordinated Mo_{4c}^{5+} species have been detected by ESR on reduced Mo/SiO_2 catalyst prepared by a conventional ammonium heptamolybdate impregnation. Their detection was possible only after reduction in pure hydrogen flow at high temperature (773 K), followed by quenching. These species are very reactive, as water or oxygen impurities cause the Mo_{4c}^{5+} signal to disappear very rapidly. The ESR lineshape of the Mo_{4c}^{5+} species is reversibly modified when hydrogen is switched to helium at 643 K ($g_{\parallel}$ changes from 1.822 to 1.769) without any change in the signal intensity. Quantitative estimation of the Mo_{4c}^{5+} species, based on the Curie law, has been made. The effect of sample calcination has also been investigated. © 1989 Academic Press, Inc.

INTRODUCTION

Interest in Mo/SiO_2 catalysts has been restimulated by the discovery that they are active and selective catalysts for methane oxidation into methanol (*1*). In recent years, supported Mo/SiO_2 catalysts have been extensively studied by various characterization techniques (*2*). In particular, ESR is a powerful technique for studying Mo^{5+} ions in this system, having often been used to study the development of Mo^{5+} species during the different steps of treatments or to compare different preparative procedures of these catalysts (*3–8*). With silica as a support for the Mo species, it is possible to discriminate among the different ESR lines of the Mo^{5+} species, since they are relatively narrow, whereas with alumina as support (*9–11*), broader lines have been observed. This can be explained by magnetic interaction and/or a shorter relaxation time related to the structural properties of the adsorbed species (*9–12*). Nevertheless, in many cases, the ESR signals and spectral features observed with Mo/SiO_2 are often left unassigned due to a lack of adequate information, and definitive determination of the symmetries of Mo^{5+} ions responsible for the signals is difficult. However, on grafted Mo/SiO_2 catalysts, three different Mo^{5+} species have recently been detected by ESR and discussed in terms of hexa-, penta-, or tetracoordinated ions (Mo_{6c}^{5+}, Mo_{5c}^{5+}, and Mo_{4c}^{5+}) (*13*). The Mo_{6c}^{5+} and Mo_{5c}^{5+} species are respectively in octahedral and square pyramidal environments. Interestingly, the new Mo_{4c}^{5+} species have been proposed to generate O^- reactive oxygen species from N_2O decomposition (*14, 15*).

The present work will show that all these species exist on impregnated catalysts after thermal reduction, but that they are extremely dependent on the observation conditions due to their extreme reactivity. In addition the effects of various calcination and reduction treatments will be described. Finally, attempts to obtain quantitative information about the relative proportion of the new Mo_{4c}^{5+} species will be discussed.

EXPERIMENTAL

Catalyst Preparation and Pretreatment

The silica support (Aerosil 200 Degussa) was mixed with pure water at 298 K, dried

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at 383 K in air, and stirred to obtain an agglomerated support suitable for impregnation. This support was then impregnated with a $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution; the excess solution was evaporated and the solid was dried at 383 K in air for 16 h. Afterwards, the sample was calcined at 773 K for 16 h under air flow (C designates a calcined sample). The analysis gave 1.5% Mo by weight (which corresponds to 9.4×10^{19} atoms g^{-1}).

In order to evaluate the effect of the calcination on the ESR signals, a part of the impregnated sample was directly reduced under H_2 flow, without any previous calcination (NC designates a noncalcined sample).

For this catalyst, the molybdenum surface coverage on silica is undoubtedly below the "monolayer limit." This point has been confirmed by XPS measurements on a similar series of samples with various Mo loadings (*16*); furthermore, this series of samples has recently been characterized by several other techniques and by acidimetric titration, in correlation with methane oxidation (*17*). In the present paper, we report in more detail the influence of sample treatments on the ESR signals (lineshape and intensities), without any variation of molybdenum coverage.

Both samples (C and NC) were reduced in a flow of pure hydrogen (5 liters/h) at 773 K. Hydrogen was purified by trapping water at 195 K (solid CO_2) and passing the gas through a Pt/zeolite column to eliminate oxygen impurities.

Reductions were performed in a 20-mm-o.d. quartz fixed-bed reactor usually containing 0.1 g of catalyst. A 4-mm-o.d. quartz tube was joined to the reactor for the sample to be transferred into the ESR cavity. The system allows the reactor isolation under controlled atmosphere during an ESR experiment and the restoration of the pretreatment gas flow using a by-pass to purge the reactor inlet. Hydrogen, helium, and oxygen gases were supplied by l'Air Liquide, France.

ESR Measurements

The ESR spectra were recorded on a Varian E109 spectrometer at 9.36 GHz (X band) with a rectangular dual cavity (TE_{104}). Modulations at 100 and 10 kHz were used respectively in both channels with modulation amplitudes of 16 G for the Mo sample and 1 G for the standard sample. The hf power was chosen in order to prevent any signal saturation.

The spectra were systematically recorded at room temperature and 77 K in all cases. The spin concentrations and g factors were calculated by comparison with Varian "strong pitch" (3×10^{15} spins cm^{-1}; $g = 2.0028$). To calculate the spin concentrations, the intensities have been corrected by the Curie law (intensities proportional to $1/T$) and calibrated with the strong pitch at 298 K. The spectra have been digitized and integrated twice by using a microcomputer SORD 100 in order to calculate the spin concentrations (the error margin on the relative spin concentration can be estimated to less than 10%). Additional details about these estimations have been published previously (*16*).

RESULTS AND DISCUSSION

ESR Mo^{5+} Species

Both the NC and the C samples were reduced at 773 K under H_2 flow from 15 min to 7 h, and then cooled to 298 K and isolated under H_2 before ESR measurements. This treatment will be referred to as STS, signifying "stable state." For the NC sample, the corresponding ESR spectrum recorded at 298 K is reported in Fig. 1a. We observe characteristic ESR Mo^{5+} signals whose lineshapes are identical to those of C samples. (The effect of calcination is characterized only by an important drop in the signal intensities: see Table 3 later in the text and the ensuing discussion.) No major modification of the spectra occurs at 77 K (Fig. 1b), and between 298 and 77 K the total ESR intensities have been found to be proportional to $1/T$. These signals (see Ta-

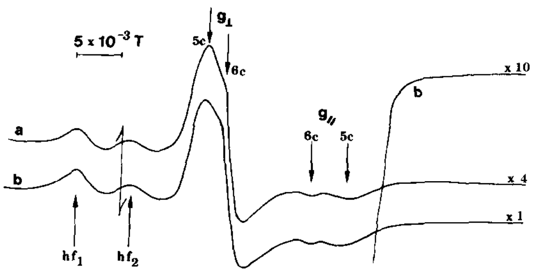

FIG. 1. Mo^{5+} ESR signals (NC sample) after 773 K/H_2 flow reduction (7 h), and slow cooling to 298 K (3 h): stable state STS. (a) 298 K ESR spectrum. (b) 77 K ESR spectrum.

ble 1 for $g_\perp$ and $g_\parallel$ factors) are similar to ESR Mo^{5+} signals described elsewhere on impregnated (*3–8, 20, 21*) or on grafted (*13–15*) samples (the Mo^{5+}_{5c} signal is the dominant one in our case). Moreover, as observed, the spectra exhibit a hyperfine structure (hfs) which results from the two molybdenum isotopes ^{95}Mo and ^{97}Mo (spin $\frac{5}{2}$; natural abundance 15.78 and 9.60%, respectively) with about the same magnetic moment (*4–6, 13, 20*). In particular, a previous study with ^{95}Mo-enriched Mo/SiO_2 samples (*4*) showed unambiguously that the low-field peaks belong to hfs (hf_1 and hf_2 in Fig. 1). The hfs high-field peaks observed in Ref. (*4*) are much less intense than the low-field peaks, so with natural isotopic molybdenum ratio samples, these high-field weak peaks disappear, and only $g_\parallel$ components of the zero nuclear spin molybdenum are detected in the high-field region, as has already been proposed in numerous works (*3–8, 13, 14, 20, 21*). Furthermore, in Fig. 1 the left-hand side of the spectra can be discussed in the same terms as in Ref. (*13*); i.e., hf_1 and hf_2 belong to Mo^{5+}_{5c} and Mo^{5+}_{6c} signals, respectively, the Mo^{5+}_{5c} signal being more intense than the Mo^{5+}_{6c} signal and hf_1 more intense than hf_2.

After reduction at 773 K and immediate quenching to 298 K in H_2, different ESR spectra have been recorded and are shown for the NC sample in Fig. 2. These spectra exhibit four important features different from the STS spectra:

(i) the total intensities for Mo^{5+}_{6c} and Mo^{5+}_{5c} signals, measured at 298 K (Fig. 2a), are much lower than in the corresponding STS;

(ii) the Mo^{5+}_{6c} population is now higher than that of the Mo^{5+}_{5c} (Fig. 2a);

(iii) at 77 K other Mo^{5+} species appear, characterized by a new $g_\parallel$ factor at about

TABLE 1

The g Factors of the ESR Signals of Mo^{5+} Obtained after H_2 Reduction at 773 K[a]

Catalyst state		STS[b]	UNS (H_2)[c]	UNS (He)[d]
Mo^{5+}_{6c}	$g_\perp$	1.945	$\underline{1.945}$	$\underline{1.945}$
	$g_\parallel$	1.891	$\underline{1.891}$	1.891
Mo^{5+}_{5c}	$g_\perp$	$\underline{1.959}$	1.959	1.959
	$g_\parallel$	$\underline{1.863}$	1.863	1.863
Mo^{5+}_{4c}	$g_\perp$		1.927	1.927
	$g_\parallel$		1.822 (4c′)	1.769 (4c)

[a] Underlined values correspond to the dominant species.

[b] STS indicates stable state obtained after reduction.

[c] UNS (H_2) indicates state obtained after quenching of the reduced samples to 298 K in H_2.

[d] UNS (He) indicates state obtained after quenching in helium.

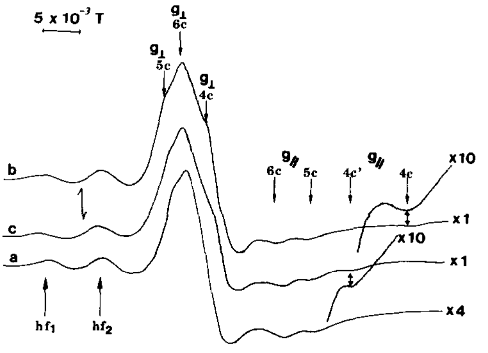

FIG. 2. Mo^{5+} ESR signals (NC sample) after 773 K/H_2 flow reduction (7 h) and quenching to 298 K: unstable state UNS. (a) 298 K ESR spectrum (H_2 or He). (b) 77 K ESR spectrum (H_2); $g_\parallel$ 4c′ component is observed (1.822). (c) 77 K ESR spectrum (15-min He flow at 643 K just after reduction and quenching to 298 K in He); $g_\parallel$ 4c component is observed (1.769).

1.82 and a visible modification of the $g_\perp$ zone (Fig. 2b, Table 1).

(iv) the Curie law is not obeyed between 77 and 298 K.

These features are still similar for C and NC samples, with just a drop in intensities for the C sample (Table 3). Such states will be symbolized as UNS (unstable states).

The new Mo^{5+} species observed at 77 K are easily identified as Mo^{5+}_{4c} species previously observed only at low temperature (77 and 4.2 K) on grafted samples (*13, 14*) (Table 2) (similar general shape and temperature dependence are observed in both cases). The $g_\perp$ values are identical, but $g_\parallel$ is higher in our case; this point is correlated with the presence of H_2 atmosphere and will be discussed below. Analogies with ESR signals of tetrahedral Mo^{5+} species detected after UV photoreduction of impregnated Mo/SiO$_2$ samples, reported by Pershin *et al.* (*7*) can also be found (Table 2), but some important differences from our UNS appear, i.e., narrower linewidths in their case (which allowed observation of isotropic coupling with a proton, a point to be discussed below, and an important distortion of the species that could be distinguished on this ESR signal. Thus, the best agreement with our observations can be found with the ESR signal of tetracoordinated Mo^{5+}_{4c} ions produced by thermal treatment of grafted samples, reported by Louis *et al.* (*13*). In that work, the Mo^{5+}_{4c} coordination sphere had been further elucidated by ESR, using adsorbed ^{13}CO as a probe molecule. This experiment allowed identification of two vacancies within the coordination sphere of the Mo^{5+}_{4c} species.

In the UNS, the fact that the Curie law is not obeyed between 77 and 298 K is due to the presence of these Mo^{5+}_{4c} species (which cannot be detected at 298 K). Thus the differences between 77 and 298 K Mo^{5+} spin concentrations correspond to the Mo^{5+}_{4c} content (such an estimate is more accurate than the deconvolution of the different lines). For both NC and C samples in the UNS, the absolute numbers of spins (stationary after 7 h reduction at 773 K) have been reported in Table 3^a for the 298 K signals (Mo^{5+}_{6c} + Mo^{5+}_{5c}) and in Table 3^b for the 77 K signals (Mo^{5+}_{4c} + Mo^{5+}_{5c} + Mo^{5+}_{6c}). The absolute numbers of Mo^{5+}_{4c} species are deduced from the differences ((*b*) − (*a*)). The absolute numbers of spins for STS are also indicated in Table 3.

TABLE 2

Comparison of g Factors Observed for Tetracoordinated Mo^{5+} Species on Mo/SiO$_2$ Catalysts, According to the Experimental Conditions

Mo/SiO$_2$ preparation	Treatment	ESR sample atmosphere	$g_\perp$	$g_\parallel$	$\Delta H_{1/2}$ G for $g_\parallel$ component	Ref.
Impregnated (ammonium paramolybdate)	Thermal reduction in H_2 flow at 773 K	Quenching in H_2	1.927	1.822 (4*c*′)	>100	This work
Impregnated (ammonium paramolybdate)	Heating for 15 min in He flow at 643 K after thermal reduction	Quenching in He	1.927	1.769 (4*c*)	>100	This work
Grafted	Thermal reduction	Vacuum	1.926	1.755	>100	(*13*)
Impregnated (ammonium paramolybdate)	Photoreduction	H_2	$g_1^T = 1.811$ $g_2^T = 1.929$ $g_3^T = 1.952$ With a hyperfine splitting ~15 G (proton coupling)		~25	(*7*)

TABLE 3

Mo^{5+} Spin Concentrations ($\times 10^{-17}$ spins/g) after 7-h H_2 Reduction at 773 K (STS and UNS)

State	ESR measurement	298 K[a]	77 K[b]	Mo^{5+}_{4c}[c]
NC	STS	34	34	0
	UNS (H_2 or H_e)	6	18	12
C	STS	12	12	0
	UNS (H_2 or H_e)	3.75	7.5	3.75

[a] Total number of spins at 298 K.

[b] Total number of spins at 77 K.

[c] Number of spins for Mo^{5+}_{4c} species ((*b*) − (*a*)).

For both samples (C and NC) the observation of the UNS depends in a similar way on the reduction temperature. A lower reduction temperature (573 K) produces only Mo^{5+}_{6c} and Mo^{5+}_{5c} species, even after a 7-h reduction treatment. After such a mild reduction and quenching to room temperature, intensities always follow the Curie law. Thus, the UNS observation is not only correlated with the quenching procedure, but also with a further evolutionary step of the catalyst, i.e., a reduction at a temperature higher than 573 K.

Thus, the existence of Mo^{5+}_{4c}, which is evidenced on impregnated Mo/SiO_2 catalysts, is strongly dependent on the treatment of the solids. However, observation of similar Mo^{5+}_{4c} species with grafted (*13*) or impregnated samples suggests that Mo^{5+}_{4c} ESR signal existence is practically independent of the nature of the deposited Mo species, as already observed for Mo^{5+}_{6c} species (*4*). Generally, ESR characterization mainly concerns the first coordination sphere of Mo^{5+} ions, which is in direct interaction with Si atoms in the grafted samples. Under our preparation conditions, silicomolybdic acid (SMA) formation mainly occurs (*17*), as also evidenced by others (*18*), and the analogy between both ESR results is not surprising. Nevertheless, molybdenum in the grafted samples is well dispersed and the relative proportion of Mo^{5+} species observed by ESR is in fact much higher in grafted samples than in our impregnated samples for similar thermal reduction treatments and molybdenum contents (*19*).

Effect of Atmosphere

The effect of an inert gas (He) or reactive oxygen and water were studied next to further investigate the properties of the Mo^{5+}_{4c} species on both the NC and the C samples. First, the effect of He was studied. Starting with an STS pretreatment, the samples were heated for 15 min in a helium flow at 643 K. We observed an important drop in Mo^{5+} signal intensities and we obtained a new state which is about the same as the UNS (see Fig. 2 and Table 3): the formation of Mo^{5+}_{4c} is still obvious and the signal intensities are identical in the UNS and in this new state. Just a small variation in g values can be observed (particularly for $g_{\parallel}$). A reverse shift in $g_{\parallel}$ values is then observed when hydrogen is let in at 643 K just after a helium treatment ($g_{\parallel}$ values for Mo^{5+}_{4c} are respectively 1.769 (4c) in He and 1.822 (4c′) in H_2 (Fig. 2, Table 1). This change in the $g_{\parallel}$ value can still be reversed by readmission of He at 643 K, making the 1.822 component disappear quickly while the 1.769 component is restored.

Although the 1.769 component is in the range of the previously observed Mo^{5+}_{4c} on grafted samples (*13, 14*), to our knowledge the 1.822 component had never been reported after thermal reduction. This effect of hydrogen does not affect the Mo^{5+}_{4c} ESR signal intensity; thus, it is possible that molecular H_2 interacts weakly and reversibly with Mo^{5+}_{4c} species without drastic modification of their relaxation time. Such weak complexes have been proposed with nickel complexes (*22*) and recently with iridium complexes (*23*). The $g_{\parallel}$ value we observed in H_2 is curiously similar to the $g^{T}_{\parallel}$ value obtained by Pershin *et al.* after photoreduction (Table 2, (*7*)). Furthermore, an interaction with protons was also indicated by these authors under these conditions, but the protons belong to OH groups and this effect cannot be compared with the present results. It is probable that photoreduction in H_2 causes the breaking of Si–O–Mo bonding, giving tetrahedral $\gtrdot Mo^{5+}$–OH species which cannot be obtained by thermal reduction, and a further comparison with our results of Ref. (*13*) is not possible.

A rapid disappearance of Mo^{5+}_{4c} occurs when exposed to small quantities of oxygen in helium at 298 K. In that case the O_2^- ESR spectra are also detected at 77 K (g_1 = 2.0176; g_2 = 2.0096; g_3 = 2.0043) (Fig. 3). Persistence of the Mo^{5+}_{5c} ESR signals is in good agreement with the work of Zhan *et al.* (*20*), who established that oxygen preferentially attacks sites other than five-coordinated species.

Let us now discuss the significant loss of the Mo^{5+} signal intensities after heating STS at 643 K under He flow. The disappearance of Mo^{5+} is correlated with the elimination of water. This can be demonstrated by the quick inverse evolution observed with wet H_2 or He at 298 K. In so doing the STS is restored and we essentially observe Mo^{5+}_{6c} species. Thus, the loss of intensity which occurs when STS is heated can be correlated with a dehydroxylation process. The variation in the ESR response factor for Mo^{5+} can be explained by the disappearance of some Mo^{5+} species produced by OH elimination, as previously reported for Mo catalysts supported on γ-Al_2O_3 (*24*). The effect of water on Mo^{5+}_{4c} and Mo^{5+}_{5c} signals is well described in the literature (*13, 14*) and water interaction explains the differences reported above between the STS and the UNS observation conditions. For example, with the NC samples, the STS is obtained after 3 h in "pure" H_2 flow (5 liters/h) containing a residual relative water pressure of 2.3×10^{-6} (195 K equilibrium vapor pressure is assumed) which corresponds to 3×10^{17} H_2O molecules. This value is just slightly higher than the Mo^{5+}_{4c} content in our sample (10^{17} spins for a 0.1-g sample).

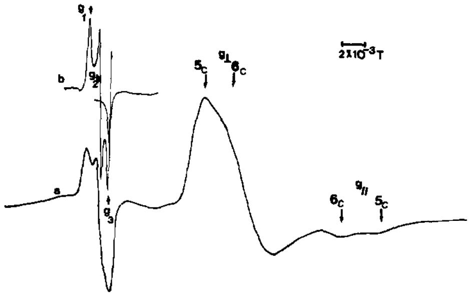

FIG. 3. ESR spectra (77 K) of Mo^{5+} and O_2^- species after oxygen adsorption at 298 K in the UNS. (a) With 16-G modulation amplitude. (b) with 4-G modulation amplitude.

Thus, the UNS is very sensitive to the nature and purity of the gas in contact with the catalysts, mainly because of the important reactivity of the Mo^{5+}_{4c} species.

Effect of Calcination

No differences in the g factors have been observed in any state (STS or UNS) between the C and NC samples. However, the calcination decreases the intensities of all signals. In particular, in the STS, the total amount of Mo^{5+} species detected by ESR is divided by 3 for the calcined sample (Table 3). Generally, the Mo^{5+} species observed by ESR are often considered a small part of the total Mo^{5+} ions when compared with those observed by other characterization techniques (*5, 25*). The existence of strongly coupled Mo^{5+}, which cannot be detected by ESR, is currently invoked to explain the discrepancy.

In the present case, XPS measurements on the NC sample, reduced under the same conditions (*26*), have shown that a major part (45%) of the Mo remained as Mo^{6+}, whereas an important proportion of Mo^0 (30%) was detected. Thus, it can be deduced that the other intermediary oxidation states, and in particular Mo^{5+} ions, are effectively in low content in our NC sample. Furthermore, a similar result was obtained with the C sample by XPS (*19*), giving a distribution of 40% Mo^{6+} and 50% Mo^0. In that sample, the amount of intermediary oxidation states is lower than that in the NC sample, in accordance with our ESR observations.

These results suggest that the calcination partly destroys the SMA-supported entities, leading to molybdenum oxide whose reduction is more facile, rapidly giving Mo^0.

Thus, the support does not stabilize these destroyed Mo anions, as might be supposed for low surface coverages (*27*); however, the anionic entities which have not been destroyed are stabilized and lead to the Mo^{5+} ESR signals. As the existence of these species is likely to be dependent on preparation conditions, such different procedures may account for some of the discrepancies with the literature results.

CONCLUSION

This work gives ESR evidence of the existence of tetracoordinated Mo_{4c}^{5+} on impregnated Mo/SiO_2 catalysts. These species have been observed on samples treated under a dry hydrogen flow, at temperatures commonly used in catalyst reduction (above 573 K, the dehydration process is responsible for Mo_{4c}^{5+} formation). These species are very reactive (with water and O_2 traces) and are in reversible interaction with H_2; as a consequence they might be reactive catalytic sites. The absolute concentrations for Mo^{5+} species have been calculated. All the observable Mo^{5+} species are magnetically isolated (according to the Curie law) and they belong to silicomolybdic entities which are present in higher contents when the catalyst is not calcined before the reduction.

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REFERENCES

1. Liu, H. F., Liu, R. S., Liew, K. U., Johnson, R. E., and Lunsford, J. H., *J. Amer. Chem. Soc.* **106,** 4117 (1984).

2. For example, see (a) Marcinkowska, K., Rodrigo, L., Kaliaguine, S., and Roberge, P. C., *J. Catal.* **97,** 75 (1986); (b) Alsdorf, E., Hanke, W., Schnabel, K. H., and Schreier, E., *J. Catal.* **98,** 82 (1986).

3. Gonzalez-Elipe, A. R., Louis, C., and Che, M., *J. Chem. Soc. Faraday Trans. 1* **78,** 1297 (1982).

4. Che, M., McAteer, J., and Tench, A. J., *J. Chem. Soc. Faraday Trans. 1* **74,** 2378 (1978).

5. Fricke, R., Hanke, W., and Ohlmann, G., *J. Catal.* **79,** 1 (1983).

6. Howe, R. F., and Leith, I. R., *J. Chem. Soc. Faraday Trans 1* **69,** 1967 (1973).

7. Pershin, A. N., Shelimov, B. N., and Kazanskii, V. B., *Kinet. Katal.* **20,** 1298 (1979).

8. Narayana, M., Zhan, R. Y., and Kevan, L., *J. Phys. Chem.* **89,** 636 (1985).

9. Hall, W. K., *in* "Proceedings, 4th Climax Molybdenum Co. Conference, 1982" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 224.

10. Abdo, S., Lo Jacono, M., Clarkson, R. B., and Hall, W. K., *J. Catal.* **36,** 330 (1975).

11. Hall, W. K., and Lo Jacono, M., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 246. The Chemical Society, London, 1977.

12. Martini, G., *J. Magn. Reson.* **15,** 262 (1974).

13. (a) Louis, C., and Che, M., *J. Phys. Chem.* **91,** 2875 (1987); (b) Che, M., Louis, C., and Tatibouet, J. M., *Polyhedron* **5,** 123 (1986).

14. Che, M., Dyrek, K., and Louis, C., *J. Phys. Chem.* **89,** 4526 (1985).

15. Che, M., Dyrek, K., and Louis, C., *J. Phys. Chem.* **89,** 4531 (1985).

16. Latef, A., Elamrani, R., Gengembre, L., Aissi, C. F., Kasztelan, S., Barbaux, Y., and Guelton, M. *Z. Phys. Chem. NF,* **152,** 93 (1987).

17. Barbaux, Y., Elamrani, R., Payen, E., Gengembre, L., Bonnelle, J. P., and Grzybowska, B., *Appl. Catal.* **44,** 117 (1988).

18. For example, (a) Klimchuk, E. G., Shelimov, B. N., and Kazanskii, V. B., *Izv. Akad. Nauk. Kaz. SSSR Ser. Khim.* **7,** 1488 (1983); (b) Castellan, A., Bart, J. C. J., Vaghi, A., and Giordano, N., *J. Catal.* **42,** 162 (1976); (c) Stencel, J. M., Diehl, J. R., D'Este, J. R., Makovsky, L. E., Rodrigo, L., Marcinkowska, K., Adnot, A., Roberge, P. C., and Kaliaguine, S., *J. Phys. Chem.* **90,** 4739 (1986).

19. Latef, A., Thesis, Lille (1987).

20. Zhan, R. Y., Narayana, M., and Kevan, L., *J. Chem. Soc. Faraday Trans. 1* **81,** 2083 (1985).

21. Giamello, E., Theobald, F., Naccache, C., and Védrine, J., *J. Chim. Phys.* **75,** 305 (1978).

22. Olivier, D., Richard, M., Che, M., Bozon-Verduraz, F., and Clarkson, R. B., *J. Phys. Chem.* **84**, 420 (1980).

23. Crabree, H., Lavin, M., and Bonneviot, L., *J. Amer. Chem. Soc.* **108**, 4032 (1986).
24. Payen, E., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Mol. Struct.* **143**, 259 (1986).
25. Mendelovici, L., and Lunsford, J. H., *J. Catal.* **94**, 37 (1985).
26. Leclercq, G., Romero, T., Pietrzyk, S., Grimblot, J., and Leclercq, L., *J. Mol. Catal.* **25**, 67 (1984).
27. Masson, J., and Nechtschein, J., *Bull. Soc. Chim. Fr.*, **10**, 3933 (1968).