JOURNAL OF CATALYSIS **139**, 142–152 (1993)

# Mo/$Al_2O_3$ Catalysts Prepared via Metal Complex Precursors

## 2. Sorption of Metal Complexes by the Support Surface

O. V. KLIMOV, M. A. FEDOTOV, AND A. N. STARTSEV

*G. K. Boreskov Institute of Catalysis, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russian Federation*

Received October 14, 1991; revised May 11, 1992

The interaction of metal complexes $MoO_2(C_5H_7O_2)_2$, $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$, and $(NH_4)_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$ with the surface of γ-$Al_2O_3$ was studied by NMR spectroscopy on the nuclei $^{95}Mo$, $^{27}Al$, $^{17}O$, $^{14}N$, and $^{13}C$, while the composition of surface species formed was studied by IR spectroscopy. The interaction between molybdenum acetylacetonate and the support surface occurs according to the mechanism of ligand substitution, whereas the sorption of oxalate complexes of Mo is shown to occur according to both the mechanism of ligand substitution and the mechanism of ion exchange. In all cases aluminum complexes having the respective chelate ligands have been found in the mother solution. © 1993 Academic Press, Inc.

## INTRODUCTION

In Part 1 (*1*) the catalytic properties of catalysts prepared by the anchoring to a γ-$Al_2O_3$ surface of the complexes $MoO_2(C_5H_7O_2)_2$, $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$, and $(NH_4)_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$ (denoted correspondingly as {Mo(acac)}, {$Mo_2$(OX)}, {$Mo_3$(OX)}) with different nuclearity and oxidation state of Mo atoms have been studied. The supported catalysts after reduction in CO or $H_2$ are characterized by a high activity and stability in the reaction of propylene metathesis at low temperatures.

Supported Mo catalysts are widely used in oil refining and other chemical processes. The most popular method for preparing these catalysts is impregnation of the support with an aqueous solution of ammonium paramolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (APM) (*2*). However, when dissolving APM in water, an intricate equilibrium sensitive to pH, concentration, and temperature occurs (*3*). Moreover, after contact of the solution with $Al_2O_3$, APM dissociates into monomers (*4*) and Al ions of the support go into solution (*5*). For this reason, during sorption a whole set of surface species with different structure and composition is formed on the support surface. With this connection it is interesting to use for the catalyst preparation Mo compounds that are as stable as possible in the solution and could keep the structure of the initial complexes on the support surface. The choice of {Mo(acac)}, {$Mo_2$(OX)}, and {$Mo_3$(OX)} as the objects of investigation is specified by this fact.

A large number of Mo complexes with different ligands, oxidation state of Mo, and a different number of Mo atoms in the molecule have been studied by NMR spectroscopy (see, for example, Ref. (*6*)). At the same time other techniques allow us to study the different molybdate anions which are present inside and outside the support pores (*7*). Thus one may observe the formation of surface species of heterogeneous catalysts even at the stage of impregnation. The use of the NMR method makes it possible to identify the compounds in the solution during the anchoring of Mo complexes to the surface of $Al_2O_3$ and to describe the chemical reactions proceeding between the support and the complexes. IR spectroscopy gives us additional information on the structure of the active species of the hetero-

0021-9517/93 $5.00

geneous catalysts, although its application is somewhat restricted by $Al_2O_3$ absorption at frequencies less than 1000 $cm^{-1}$. In the present work the interaction of {Mo(acac)}, {$Mo_2$(OX)}, and {$Mo_3$(OX)} with the surface of γ-$Al_2O_3$ has been studied by NMR and IR spectroscopies.

## EXPERIMENTAL

NMR spectra were recorded on a CXP-300 Bruker spectrometer at 40.7 ($^{17}$O), 21.68 ($^{14}$N), 75.47 ($^{13}$C), 19.56 ($^{95}$Mo), and 78.2 ($^{27}$Al) MHz with the accumulation rate being 50, 20, 0.08, 20, and 10 Hz, respectively.

IR spectra were recorded on a Specord 75IR spectrometer (pellet with KBr).

γ-$Al_2O_3$ with $S_{BET}$ = 220 $m^2/g$ has been used; its pore volume is 0.7 $cm^3/g$, and its size fraction is 0.5–0.25 mm. The support has been preliminarily calcined in air at $T$ = 550°C for 8 h.

The details of the preparation of the molybdenum complexes are described in Part I (*1*). The Mo concentrations in the solutions before and after sorption are given in Table 1. In all cases, 80 ml of the solution was added to 22 g of γ-$Al_2O_3$. Adsorption was conducted for 24 h at room temperature. After sorption the solid phase was separated on a filter. $Mo/Al_2O_3$ catalysts (designated as {Mo(acac)}/$Al_2O_3$, {$Mo_2$(OX)}/$Al_2O_3$, {$Mo_3$(OX)}/$Al_2O_3$) were washed with pure solvent many times and dried in vacuum at 80°C; the Mo content on the support surface was then determined. After sorption the Mo content in the solution was also determined. Finally the solution was evaporated in vacuum to the initial concentration and NMR spectra were recorded.

To identify the products of interaction between the complexes and γ-$Al_2O_3$, samples without Mo were prepared for comparison:

(a) Oxalic acid (1 g) was dissolved in 80 ml of water, then 22 g of γ-$Al_2O_3$ was introduced into the solution and kept for 24 h at room temperature; after this the support was separated on a filter, washed many times, and dried in vacuum at 80°C. The sample is designated as {OX}/$Al_2O_3$. The solution containing the products of interaction of oxalic acid with γ-$Al_2O_3$ was evaporated in vacuum to 0.1 of the initial volume (designated subsequently as {OX}).

(b) γ-$Al_2O_3$ (22 g) was treated with 80 ml of benzene containing 2.0 g of acetylacetone (designated below as Hacac) for 24 h at room temperature. Then it was separated on a filter, washed with pure benzene many times, and dried in vacuum (sample {Hacac}/$Al_2O_3$).

## RESULTS

Following sorption of the Mo complexes on γ-$Al_2O_3$ the solution becomes decolorized and the support is colored yellow ({Mo(acac)}), brown ({$Mo_2$(OX)}), or black-brown ({$Mo_3$(OX)}). Note that the color of the catalyst in a dry state differs greatly from that of the initial complexes. In all three cases of impregnation no precipitation has been visually observed. The time for the contact of solutions with the support (24 h) was long enough to achieve equilibrium. The material balance of the sorption process is given in Table 1.

### {*Mo(acac)*} + $Al_2O_3$ *System*

The assignment of peaks in the NMR spectra of the {Mo(acac)} solution is given in Table 2 (solution A). The $^{95}$Mo NMR signal is represented by a narrow and symmetrical peak with a chemical shift (CS) of 4 ppm relative to $MoO_4^{2-}$. This is typical for Mo complexes of general composition $MoO_2L_2$, where $L$ is a chelate oxygen-containing ligand and corresponds to the oxidation state of Mo(VI) (*8*).

In {Mo(acac)} Mo is in a distorted octahedral environment. On the basis of structural data (*9*) one may single out three pairs of atoms having close distances of Mo–O—1.68 ± 0.02, 1.98 ± 0.02, and 2.20 ± 0.02 Å. In this respect in the $^{17}$O NMR spectrum of solution A, three peaks of equal intensity were found, wherein the greatest CS corresponds to the shortest Mo–O distance (*10*).

For asymmetrical disposition of the ligand

TABLE 1

Material Balance of the Sorption Process of Mo Complexes by the Support Surface

| | {Mo(acac)} | {$Mo_2$(OX)} | {$Mo_3$(OX)} |
|---|---|---|---|
| Mo concentration in the initial solution (mg/ml) | 6.6 | 17.7 | 16.6 |
| Mo concentration in the solution after sorption (mg/ml) | 1.0 | 3.4 | 2.0 |
| Mo content in the catalyst (mass %) | 2.0 | 5.2 | 4.9 |
| Extraction degree of Mo from the solution (%) | 85 | 81 | 88 |
| Amount of Mo in the initial solution (mg) | 528 | 1416 | 1328 |
| Summary amount of Mo after sorption (mg) | 530 | 1420 | 1324 |

around the central atom the $^{13}$C NMR spectrum is represented by five peaks, with two methyls $-CH_3$ (27 and 25 ppm), two $\rangle$C–O groups (197 and 185 ppm), and one vinyl fragment –CH= (105 ppm).

The location and intensity of the above peaks did not change even after sorption (Table 2, solution B). Differences in chemical shifts do not exceed the experimental error. Lack of change in the $^{95}$Mo NMR spectrum of the solutions before and after sorption in the presence of equilibrium between Mo compounds in the solutions and on the support surface are evidence for the conservation of the Mo (VI) oxidation state.

In addition to the initial complex NMR spectra of solution B, there are a number of peaks whose appearance is due to the liberation into the solution of the reaction products between {Mo(acac)} and γ-$Al_2O_3$.

TABLE 2

$^{95}$Mo, $^{27}$Al, $^{17}$O, $^{13}$C NMR Data of Benzene Solution of {Mo(acac)}.

| | δ (ppm) | | | |
|---|---|---|---|---|
| | $^{95}$Mo | $^{27}$Al | $^{17}$O | $^{13}$C |
| | | (A) Initial solution | | |
| {Mo(acac)} | 4.1 | — | 1025;337;243<br>(1) (1) (1) | 197;185;105; 27; 25<br>(1) (1) (1) (1) (1) |
| Benzene | — | — | — | 128 |
| | | (B) Solution after sorption | | |
| {Mo(acac)} | 5.0 | — | 1025;337;243<br>(1) (1) (1) | 195;185;104; 27; 24<br>(1) (1) (1) (1) (1) |
| {Al(acac)$_3$} | — | 0.2 | 267 | 190; 101; 26<br>(2) (1) (2) |
| Hacac | — | — | 269 | — |
| $H_2O$ | — | — | 12 | — |
| Benzene | — | — | — | 128 |
| Standard | $MoO_4^{2-}$ | $Al(H_2O)_6^{3+}$ | $H_2O$ | $Si(CH_3)_4$ |

*Note*. The conventional intensity of the respective peaks is given in brackets.

Van Veen *et al.* (*11, 12*) have shown that this interaction proceeds with the splitting off of the acetylacetonate ligands. Acetylacetone liberated into the solution reacts with the support and probably forms aluminum tris-acetylacetonate $Al(C_5H_7O_2)_3$ (designated as $Al(acac)_3$) and water. All these products were found in solution B (Table 2).

In the $^{17}O$ NMR spectrum the peak at 12 ppm was assigned to the oxygen atom of water. The signal at 247 ppm corresponds to the enol form of acetylacetone (*13*).

In the $^{13}C$ NMR spectrum the signals of free Hacac are masked by more intense signals from acac ligands coordinated to Mo and Al. In solution B there is no keto form of Hacac because it has negligible concentration under the experimental conditions (*14*).

The $^{27}Al$ NMR signal with CS = 0 ppm resembles aluminum tris-acetylacetonate (*15*). For high symmetry of ligands surrounding Al in $Al(acac)_3$ (*16*) one expects only one peak in the $^{17}O$ NMR spectrum (CS = 267 ppm) and three peaks in the $^{13}C$ NMR spectrum with intensity ratio 2 : 1 : 2 (CS = 190, 101, 26 ppm corresponding to $>$C–O, –CH=, $-CH_3$ groups).

The splitting off of a ligand from the initial complex under support on the $\gamma$-$Al_2O_3$ surface is confirmed by IR-spectroscopy data (Fig. 1). The absorption bands of the catalyst {Mo(acac)}/$Al_2O_3$ coincide completely with the spectrum of {Hacac}/$Al_2O_3$. This apparently accounts for the presence of acac ligands in both samples that are coordinated only to Al atoms of the support. Note that this spectrum differs greatly from that of the initial {Mo(acac)}.

*{$Mo_2(OX)$} + $Al_2O_3$*

When an aqueous solution of {$Mo_2(OX)$} is contacted with $Al_2O_3$ a fast extraction of Mo from the solution is observed and simultaneously the pH of the solution increases (Fig. 2). The sorption rate depends on the Mo concentration in the solution and the impregnation temperature. The main part of the Mo is sorbed during the first 1–2 h. More continuous exposure of the support in the solution does not result in any noticeable changes of the Mo concentration in the solution or on the support. The degree of Mo extraction from the impregnating solution decreases from 90 to 50% under equilibrium

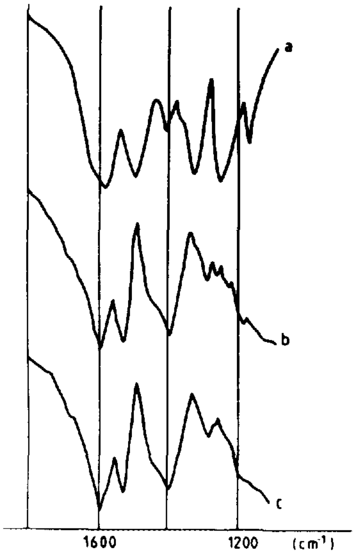


FIG. 1. IR spectra of (a) {Mo(acac)}, (b) {Mo(acac)}/$Al_2O_3$, (c) {Hacac}/$Al_2O_3$.

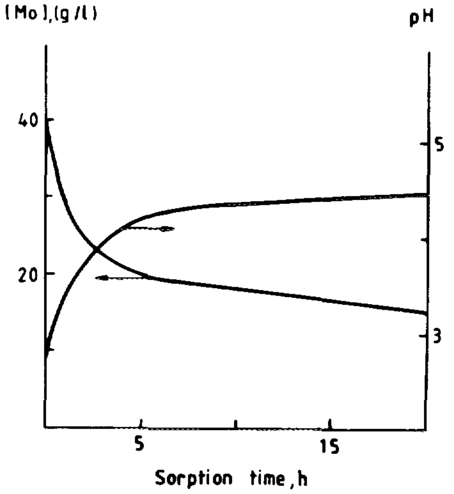


FIG. 2. Variations of pH and Mo concentration in the impregnating solution during {$Mo_2(OX)$} sorption by $\gamma$-$Al_2O_3$.

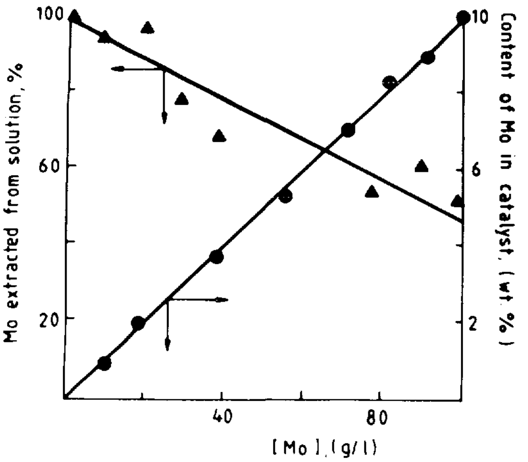


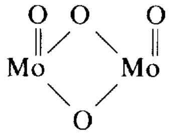
FIG. 3. Equilibrium sorption of $\{Mo_2(OX)\}$ by $\gamma$-$Al_2O_3$.

conditions when increasing the concentration of the initial solution from 10 to 90 g of Mo/liter (Fig. 3). In this case the Mo content over the support approaches 10%, which is close to the monolayer filling of the surface.

The NMR data of the aqueous solution $\{Mo_2(OX)\}$ (Table 3, solution C) are the same as those published earlier for $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ (*17*). In the $^{95}$Mo NMR spectrum the narrow signal with CS = 525 ppm is typical for aqueous solutions of binuclear complexes of Mo(V) having a $Mo_2O_4$ framework whose CS is situated in the range 400–600 ppm (*6*).

For the peaks in the $^{17}$O NMR spectrum the following assignments are made according to Ref. (*16*): CS = 925 ppm, Mo = O; 556 ppm, $\mathrm{Mo}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Mo}$, 292 and 224 ppm; O atoms of the oxalate ligand coordinated to Mo with the peak of CS = 224 ppm corresponding to the Mo–O bond. In the $^{14}$N NMR spectrum the signal at 325 ppm is related to the hydrazonium cation $(N_2H_5)^+$.

These are no new signals in the $^{95}$Mo NMR spectrum of the solution after sorption (Table 3, solution D). The equilibrium between molybdenum compounds in the solution and on the surface is evidence for the fact that $\{Mo_2(OX)\}$ interacts with $\gamma$-$Al_2O_3$ without changing the oxidation state of Mo(V) and decomposing



framework. This was confirmed by EXAFS-spectroscopy data which showed that the distance Mo–Mo = 2.55 Å typical for the initial complex is kept in the surface species (*18*).

The interaction of $\{Mo_2(OX)\}$ with the support is accompanied by large changes in the $^{17}$O NMR spectra (Table 3, Fig. 4). Alongside peaks of the initial complex a number of new signals appeared and the position of lines on the CS scale changed also. The relative intensity of resonances from oxygen atoms of oxalate ligands grew noticeably (Fig. 4). As potential products of the reaction between $\{Mo_2(OX)\}$ and $Al_2O_3$ one may expect oxalate complexes of aluminum. It is impossible to obtain Al oxalate in a pure form (*19*). For this reason the solution $\{OX\}$ was used as a sample for comparison. For the NMR spectra of $\{OX\}$ the following assignments have been made:

$^{27}$Al: CS = 16, 12, 6, 0 ppm; Al complexes of general formula $[Al(OH)_{2y}(C_2O_4)_{3-y}]^{3-}$, ($y$ = 0–3), where the smallest CS agrees with the largest value of $y$ (*20*).

$^{17}$O: CS = 290 and 213 ppm; oxalate ligand; 30 and 16 ppm; OH-groups, bonded to Al.

New resonances that appeared in the spectra of solution D are identical with signals of oxalate complexes of Al (Fig. 4). Some differences in the intensity of the $^{27}$Al spectra are accounted for by a higher concentration of oxalate ion in solution D as compared with $\{OX\}$. In the NMR spectra of the initial solution (C) there are no signals of free oxalic acid. Hence, the occurrence of aluminum oxalate in the solution after sorption may be caused only by the splitting of oxalate ligands from $\{Mo_2(OX)\}$. However, in the IR spectra of the catalyst $\{Mo_2(OX)\}/Al_2O_3$ the absorption bands are

TABLE 3

$^{95}$Mo, $^{27}$Al, $^{17}$O, $^{14}$N NMR Data of Aqueous Solutions of {$Mo_2$(OX)}, {$Mo_3$(OX)}, and {OX} (OX)—solution for comparison with {OX}. Below cs the chemical shift value in brackets the conventional intensity, is given.

| | δ (ppm) | | | |
|---|---|---|---|---|
| | $^{95}$Mo | $^{27}$Al | $^{17}$O | $^{14}$N |
| (C) Initial solution of {$Mo_2$(OX)} | | | | |
| {$Mo_2$(OX)} | 525 | — | 925;556;292;224<br>(1) (1) (2) (2) | 325 |
| (D) Solution C after sorption | | | | |
| {$Mo_2$(OX)} | 525 | — | 925;556 ······<br>(1) (1) | 325 |
| {Al(OX)}$^a$ | — | 16;12;6;0 | 286;213; 30; 16<br>(10)(10) (1) (2) | — |
| (E) Initial solution of {$Mo_3$(OX)} | | | | |
| {$Mo_3$(OX)} | 1038 | — | 740;498;300;241<br>(3) (1) (6) (6) | 353 |
| (F) Solution E after sorption | | | | |
| {$Mo_3$(OX)} | 1040 | — | 740;490; ······ | 353 |
| {Al(OX)}$^a$ | — | 16;12;6;0 | 292;213; 30; 16<br>(10)(10) (1) (2) | — |
| (OX) Solution for comparison with {OX} | | | | |
| (OX) {Al(OX)}$^a$ | — | 16;12;6;0 | 292;213; 30; 16<br>(10)(10) (1) (2) | — |

[a] By {Al(OX)} designated aluminum oxalate with common formula $[Al(OH)_{2y}(C_2O_4)_{3-y}]^{3-}$, where $y$ = 0, 1, 2, 3.

assigned to the vibrations of carboxyl groups (Fig. 5). The presence of a band at 1400 $cm^{-1}$ (stretching of the $COO^-$ group) in the spectra of the catalyst and the initial complex testify to the conservation of ligand coordinated to Mo, because in free oxalic acid and the sample {OX}/$Al_2O_3$ these vibrations are characterized by bands at 1440 and 1425 $cm^{-1}$, respectively (*21*).

### *{$Mo_3$(OX)} + $Al_2O_3$*

Sorption of {$Mo_3$(OX)} by the $Al_2O_3$ surface is characterized by the same regularities as {$Mo_2$(OX)}. Namely, at the initial moment a fast extraction of Mo from the solution is observed (Fig. 6) and in 1–2 h the sorption rate slows down and equilibrium is attained. When increasing the concentration of the impregnation solution the degree of Mo extraction from the solution decreases (Fig. 7), and at Mo concentration 100 g/liter monolayer filling of the support surface is achieved.

NMR data of {$Mo_3$(OX)} are presented in Table 3 (solution E). The position of the $^{95}$Mo NMR signal (CS = 1038 ppm) is typical for complexes of Mo(IV) with a $Mo_3O_4$ framework, whose CS lies in the range 1000–1200 ppm (*6*).

The following assignments for the peaks in the $^{17}$O NMR spectrum may be made according to the structure of $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O_4)_3] \cdot 4H_2O \cdot 0.5H_2C_2O_4$ (*22*): 740 ppm, $\mu_2$ – O; 489 ppm, $\mu_3$ – O; 300 and 241 ppm, oxygen atoms of oxalate ligand coordinated to Mo. The signal in the $^{14}$N NMR spectrum with CS = 353 ppm corresponds to the ammonium cation.

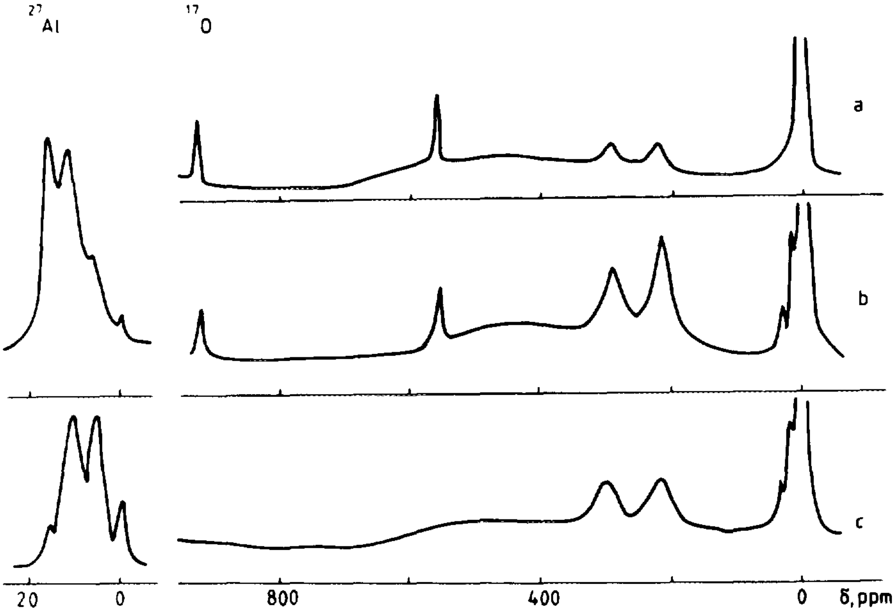


FIG. 4. $^{27}$Al and $^{17}$O NMR spectra of solutions (a) {Mo$_2$(OX)}, (b) the same after sorption, (c) {OX}.

All the changes in the NMR spectra of {Mo$_3$(OX)} solutions before and after sorption (Table 3, solutions E and F, respectively) are similar to those mentioned above for {Mo$_2$(OX)}. When there is no free oxalic acid in the initial solution (E), after sorption solution F contains a great amount of aluminum oxalates; i.e., the anchoring of {Mo$_3$(OX)} to the support is accompanied by ligands splitting off. At the same time coincidence of absorption bands in the IR spectra of catalyst {Mo$_3$(OX)}/Al$_2$O$_3$ and the initial {Mo$_3$(OX)} with a large difference from the spectra of the sample {OX}/Al$_2$O$_3$ (Figs. 5c, 5d, and 5e) points to the fact that oxalate ligands coordinated to molybdenum are present in the surface species.

## DISCUSSION

Sorption of metal compounds by the surface of oxide supports is a complicated physicochemical process. On one hand, it may be an electrostatic interaction between ions from electrolyte solutions and the charged surface of the oxides (*3*). On the other hand, the sorption of metal complexes may proceed according to various chemical mechanisms (*23*, *24*). Ligand substitution and ion exchange seem to be basic mechanisms for sorption of Mo compounds by an Al$_2$O$_3$ surface. Ligand substitution means the exchange of ligands of the metal complexes for functional groups of the support. The mechanism of ion exchange that is the most widespread in the literature is that of exchange of ions of the dissociated compound for the ions of the support surface. Evidently this classification is conventional enough, because both mechanisms have much in common and in some cases they supplement each other.

The interaction of the neutral complex {Mo(acac)} from a nonpolar solvent with the Al$_2$O$_3$ surface appears to be a typical example of metal complex sorption according to the mechanism of ligand substitution. In fact, this interaction is accomplished with the participation of OH-groups of the support (*11*, *12*), and as a result acetylacetone is liberated into the solution. Hence, the

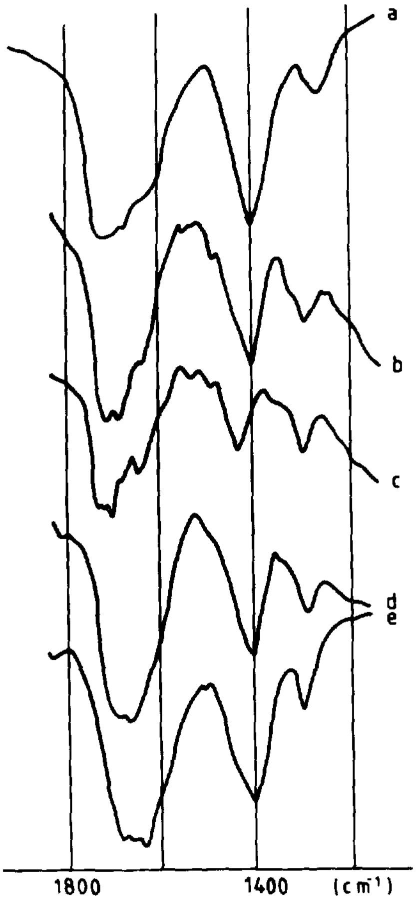
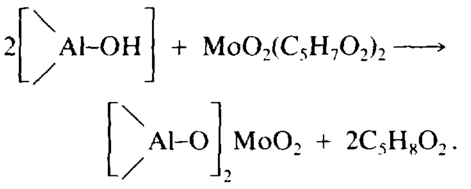


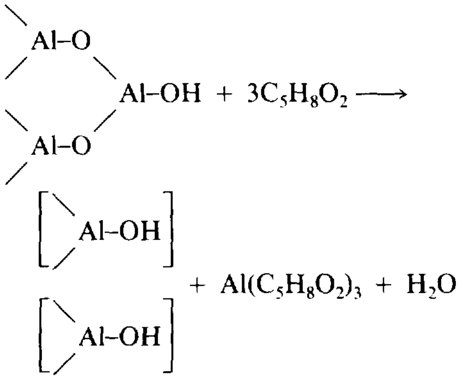
FIG. 5. IR spectra of (a) {$Mo_2(OX)$}, (b) {$Mo_2(OX)$}/$Al_2O_3$, (c) {OX}/$Al_2O_3$, (d) {$Mo_3(OX)$}/$Al_2O_3$, (e) {$Mo_3(OX)$}.

chemical reaction may be considered as a substitution of acetylacetonate ligands in the coordination sphere of Mo for the support macroligand:



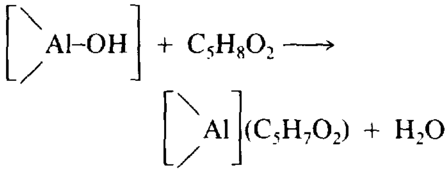
(1)

The acetylacetone formed then interacts with surface OH-groups of the support, for instance according to the scheme



(2)

or according to the scheme



(3)

The sorption of ionic oxalate complexes of Mo(V) and Mo(IV) proceeds in a very different way. As a result of ion exchange a hydrazonium or ammonium cation is substituted by a macrocation of the support, for example, according to the following schemes:

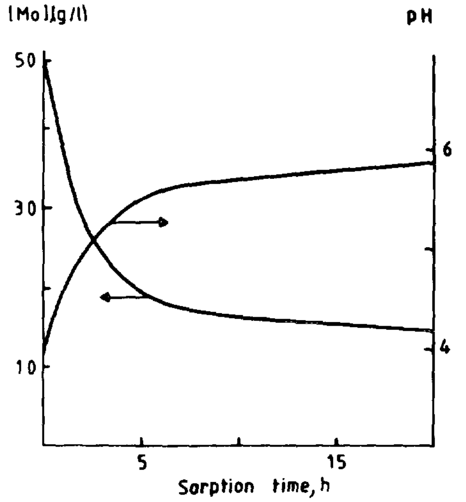


FIG. 6. Variations of pH and Mo concentration in the impregnating solution during {$Mo_3(OX)$} sorption by γ-$Al_2O_3$.

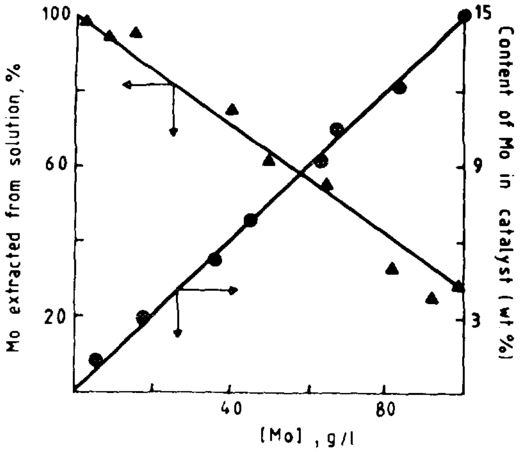


FIG. 7. Equilibrium sorption of {Mo$_3$(OX)} by γ-Al$_2$O$_3$.

$$2\left[{>}\text{Al-OH}\right] + [N_2H_5]_2^+[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-} \longrightarrow \left[{>}\text{Al}\right]_2^+[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-} + 2N_2H_5OH \quad (4)$$

$$2\left[{>}\text{Al-OH}\right] + [NH_4]_2^+[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-} \longrightarrow \left[{>}\text{Al}\right]_2^+[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-} + 2NH_4OH. \quad (5)$$

Both the pH of the solution increasing during sorption and the IR data (Fig. 5) speak in favor of these schemes of interaction. However, aluminum oxalates found in the solution testify to a more complicated character of the interaction between Mo oxalates and the Al$_2$O$_3$ surface. As the sorption of these complexes is carried out from acid solutions, then in consequence of protonation of surface OH-groups, according to the scheme (*6*)

$$\left[{>}\text{Al-OH}\right] + H^+ \longrightarrow \left[{>}\text{Al-OH}_2\right]^+, \quad (6)$$

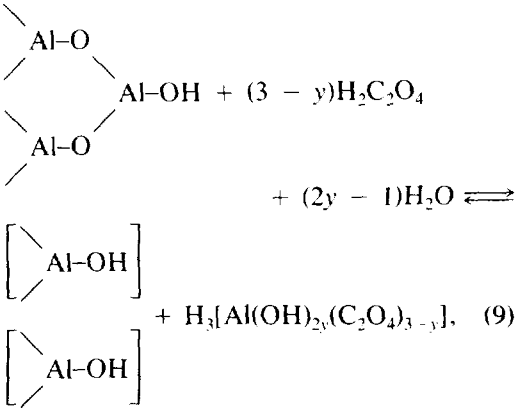
the support surface receives (+) charge. Ligand substitution seems to take place alongside the mechanism of ion exchange. This substitution may be realized according to the schemes

$$2x\left[{>}\text{Al-OH}_2\right]^+ + [Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-} \rightleftharpoons \left[{>}\text{Al-O}\right]_{2x}[Mo_2O_4(C_2O_4)_{2-x}(H_2O)_2] + xH_2C_2O_4, \quad (7)$$

where $x$ = 1, 2, and

$$2x\left[{>}\text{Al-OH}_2\right]^+ + [Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-} \rightleftharpoons [\text{Al-O}]_{2x}[Mo_3O_4(C_2O_4)_{2-x}(H_2O)_2] + xH_2C_2O_4, \quad (8)$$

where $x$ = 1, 2, 3. Oxalic acid formed can interact with the support surface according to the scheme



$$\begin{array}{l}{>}\text{Al-O}\\ \qquad\quad {>}\text{Al-OH}\\ {>}\text{Al-O}\end{array} + (3-y)H_2C_2O_4 + (2y-1)H_2O \rightleftharpoons \begin{array}{l}\left[{>}\text{Al-OH}\right]\\ \left[{>}\text{Al-OH}\right]\end{array} + H_3[\text{Al}(OH)_{2y}(C_2O_4)_{3-y}], \quad (9)$$

where $y$ = 0, 1, 2, 3.

In addition, a fraction of the oxalic acid seems to remain coordinated to the Al of the support:

$$2\left[{>}\text{Al–OH}\right] + H_2C_2O_4 \longrightarrow \left[{>}\text{Al–}\right]_2[C_2O_4] + 2H_2O. \quad (10)$$

All the above reactions (1)–(10) are at equilibrium. To shift the equilibrium to the side of the formation of surface species it is necessary to wash the catalyst carefully with a pure solvent.

## CONCLUSIONS

The interaction between the neutral complex of Mo(VI), $MoO_2(C_5H_7O_2)_2$, and $\gamma$-$Al_2O_3$ surface is realized via substitution of acetylacetonate ligands by the support macroligand. The anchoring of anion oxalate complexes of Mo(V) and Mo(IV) is carried out not only by their exchange with OH-groups of the support, but also via partial substitution of the oxalate ligand by the support macroligand.

The interaction of Mo complexes of various metal nuclearity and metal oxidation state with the alumina surface followed by reduction of the surface species formed in CO or $H_2$ resulted in approximately equal activity of catalysts in the olefin metathesis reaction (*1*). This could mean that:—the surface reaction is accomplished with the destruction of a basic framework of the supporting complexes resulting in the formation of similar (in the structure and nearest environment of a central atom) surface species;

—the surface reaction occurs via a redox mechanism resulting in the formation of surface species containing Mo in the same oxidation state;

—high-temperature pretreatment leads to the formation of a similar active center independently of the structure of the direct precursor of the active component; or

—the reaction of olefin metathesis is a structurally nonsensitive one and can occur on the active centers of any nuclearity.

The data demonstrate that the first suggestion is hardly probable. In the following papers of this series, other possible explanations of the phenomenon mentioned will be analyzed.

## REFERENCES

*1.* Startsev, A. N., Klimov, O. V., and Khomyakova, E. A., *J. Catal.* **139,** 134 (1993).

*2.* Hall, W. K., *in* "Proceedings, 4th International Conference on the Chemistry and Uses of Molybdenum," p. 224. Climax Molybdenum Co., Ann Arbor, MI, 1982.

*3.* Kasztelan, S., Payen, E., Toulhoat, H., Grimblot, J., and Bonnelle, J. P., *Polyhedron* **5,** 157 (1986).

*4.* Luthra, N. P., and Cheng, W-C., *J. Catal.* **107,** 154 (1987).

*5.* Brunelle, J. P., *Pure Appl. Chem.* **50,** 1211 (1978).

*6.* Gheller, S. F., Hambley, T. W., Brownlee, R. T. S., O'Connor, M. J., Snow, M. R., and Wedd, A. G., *J. Am. Chem. Soc.* **105,** 1527 (1983).

*7.* Sarrazin, P., Mouchel, B., and Kasztelan, S., *J. Phys. Chem.* **93,** 904 (1989).

*8.* Capparelli, M. V., Piggott, B., Thorpe, S. D., Wong Swee, F., and Sheppard, R. N., *Inorg. Chim. Acta* **106,** 19 (1985).

*9.* Krasochka, O. N., Sokolov, J. A., and Atovmyan, L. O., *J. Strukt. Khim.* **16,** 696 (1975). [In Russian]

*10.* Miller, K. F., and Wentworth, R. A. D., *Inorg. Chem.* **18,** 984 (1979).

*11.* Van Veen, J. A. R., *J. Colloid Interface Sci.* **121,** 214 (1988).

*12.* Van Veen, J. A. R., Jonkers, G., and Hesselink, W. H., *J. Chem. Soc. Faraday Trans. I* **85,** 389 (1989).

*13.* Belyaev, A. V., Venediktov, A. B., Fedotov, M. A., and Khranenko, S. P., *Koord. Chim.* **11,** 794 (1985). [In Russian]

*14.* Folkendt, M. M., Weis-Lopez, B. E., Chauvel, J. P., and True, N. S., *J. Phys. Chem.* **89,** 3347 (1985).

*15.* Lewinski, J., and Pasynkiewicz, S., *Inorg. Chim. Acta* **130,** 23 (1987).

*16.* Hon, P. K., and Pfluger, C. E., *J. Coord. Chem.* **3,** 67 (1973).

*17.* Startsev, A. N., Shkuropat, S. A., Klimov, O. V., Fedotov, M. A., Kolosov, P. E., Fedorov, V. K., Degtyarev, S. P., and Kochubey, D. I., *Koord. Khim.* **17,** 229 (1991). [In Russian]

*18.* Startsev, A. N., Klimov, O. V., Shkuropat, S. A., Kolosov, P. E., Fedorov, V. K., Degtyarev, S. P., and Kochubey, D. I., *React. Kinet. Catal. Lett.* **41,** 339 (1990).

*19.* Tikhonov, V. N., "Analititcheskaya chimiya aluminiya," p. 18. Nauka, Moscow, 1971.

*20.* Tchernyshov, B. N., and Konshin, V. V., *Koord. Khim.* **13,** 1066 (1988). [In Russian]

*21.* Klimov, O. V., Krivoshchekova, E. A., and Startsev, A. N., *React. Kinet. Catal. Lett.* **42,** 95 (1990).

22. Bino, A., Cotton, F. A., and Dori, Z., *J. Am. Chem. Soc.* **100,** 5352 (1978).
23. Summers, J. C., and Ausen, S. A., *J. Catal.* **52,** 445 (1978).
24. Zymbal, T. V., Alt, L. Ya., Doronin, V. P., and Duplyakin, V. K., *in* "Proceedings, 5th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, Novosibirsk, 1986," p. 687. VNU Science Press, Utrecht, The Netherlands, 1986.