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Catalytic Activity of Reduced MoO_3/α-Al_2O_3 for Hexanes Reforming

II. Catalytic Activity and Mechanistic Approach Using ^{13}C Tracer Studies and Probe Molecules

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The catalytic activities of 4-methyl-1-pentene and of the corresponding alkane, 2-methylpentane, are compared on two series of reduced MoO_3 catalysts supported on α-type-Al_2O_3, prepared either by impregnation with Na_2MoO_4 or by the slurry impregnation method starting from MoO_3. The reduction of these samples depends on the molybdenum oxide content and therefore on the interaction with the alumina surface. The use of probe molecules, such as 3,3-dimethylbut-1-ene (dibranched containing a quaternary carbon atom), 2,3-dimethylbut-2-ene (dibranched with two tertiary carbon atoms), 4-methyl-1-pentene (monobranched with a tertiary carbon atom), 1-hexene (linear), and cyclohexene (cyclic), combined with ^{13}C tracer studies leads to the conclusion that isomerization mainly occurs on acidic sites via surface alkoxy intermediates, resulting in protonated cyclopropane species. From the correlation with XPS measurements, it can be concluded that Mo(V) species are responsible for acidic isomerization and that Mo(IV) and Mo(II) species exhibit metallic dehydrogenation properties. Nevertheless, metallic isomerization via metallocyclobutane intermediates should be considered when reduction at high temperature occurs.

Key Words: **MoO_3/α-type-Al_2O_3; comparison of hexenes and 2-methylpentane reactivity; ^{13}C studies; isomerization mechanism; alkoxy intermediates; protonated cyclopropane species.**

I. INTRODUCTION

It is well known that supported molybdenum oxides are active for many reactions, such as methane (1) and methanol (2) oxidation, hydrotreatment (hydrodesulfurization (3, 4) and hydrodenitrogenation (5)), metathesis (6), or hydrocarbon hydrogenation (7) and hydrogenolysis (8). Molybdenum oxide catalysts were used extensively many years ago for hexene reforming and the mechanisms were discussed in detail (9, 10). Molybdenum-based catalysts also show some activity in hydrocarbon skeletal isomerization (11), depending on the reductant activation treatment. The activities and isomerization selectivities for hexanes and hexenes can be associated with specific Mo oxidation states. In previous works, the mechanism of hydrocarbon isomerization on molybdenum powder has been explained by a metallic mechanism proceeding by the bond shift through a metallacyclobutane-type intermediate. But another mechanism can be considered, such as a bifunctional mechanism, in which dehydrogenation–hydrogenation occurs on metallic sites and skeletal isomerization takes place on acidic sites.

The previous part of this paper (Part I) (12) mainly dealt with preparation and characterization methods, especially XPS measurements, of two series of MoO_3/α-Al_2O_3 catalyst samples after activation (reduction) treatments at 350, 450, and 700°C. In this work, hexane and hexene skeletal rearrangement mechanisms are studied using probe molecules and ^{13}C labeling techniques and are correlated with specific Mo oxidation states, depending on the molybdenum concentration and reduction conditions.

II. EXPERIMENTAL

II.1. Catalyst Samples

Four catalyst samples varying by preparation method and by MoO_3 loading were tested. The first series, Cat1 was prepared by impregnation with Na_2MoO_4 and the second series, Cat2, by the slurry impregnation method (SIM). The preparation methods have been described in more detail in the first part of this paper (12). For each preparation method, different MoO_3 loadings were achieved:

—0.08% MoO_3/α-Al_2O_3, denoted Cat1a (corresponding to 0.04 eq of monolayer or 1.7×10^{13} Mo atom/cm^2)
—5.4% MoO_3/α-Al_2O_3, denoted Cat1b (2.50 eq monolayer or 1.3×10^{15} Mo/cm^2)
—1.2% MoO_3/α-Al_2O_3, denoted Cat2a (0.60 eq monolayer or 2.8×10^{14} Mo/cm^2)
—5.2% MoO_3/α-Al_2O_3, denoted Cat2b (2.40 eq monolayer or 1.2×10^{15} Mo/cm^2)

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II.2. Apparatus and Procedures

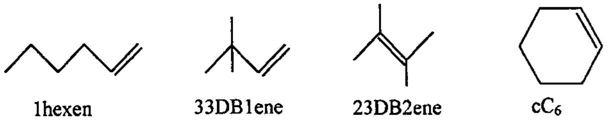
The experiments were carried out with 300 mg of catalyst powder in a glass system, as described before (13). Reactions were performed at 350°C under 760 Torr (1 Torr = 133.3 N mm^{-2}) of hydrogen at a flow rate around 50 cc/min. Tests were performed at three activation temperatures: 350, 450, and 700°C. After catalytic activation by hydrogen, the temperature was brought to 350°C (reaction temperature) and 5 μl of reactant was injected into the quartz reactor at constant pressure (around 6.5 Torr) in flowing H_2 (or He in some cases). Two catharometers were inserted upstream and downstream of the reactor, their signals representing the hydrocarbon pressure as a function of time. When the pulse of hydrocarbon had passed the reactor, a sample was taken off "online" and the product distribution was recorded by GC analysis (Varian 3300) over a dimethylsulfoxane column (50 cm long and 0.53-mm internal diameter) (Chrompack CP-SIL-5CB) with a flame ionization detector and a flux of helium as the gas carrier. It must be mentioned that all the products were hydrogenated before they were analyzed by GC.

Before the catalytic tests were performed, the samples were treated under hydrogen at 350, 450, and 700°C and the evolution of catalytic properties versus temperature and time of reduction was observed.

II.3. Probe Molecules

The main hydrocarbons used for catalytic tests on stream were 4-methyl-1-pentene (4M1Pen) and 2-methylpentane (2MP). The different reaction products obtained from 4M1Pen and 2MP are summarized in Scheme 1, as all the products were hydrogenated before being analyzed by GC.

The comparison of these two reactants allows us to obtain information about acidic and metallic properties of bifunctional catalysts, because in the first step 2-methylpentane needs metallic sites to dehydrogenate and react, unlike olefin, for which only acidic sites are necessary. So, on acidic catalysts, the olefin reacts faster than the corresponding saturated hydrocarbon (14).



SCHEME 2

To study the influence of the structure of the reactant (Scheme 2), the reactivities of 1-hexene (1hexen) (linear), 4-methyl-1-pentene (4M1Pen) (monobranched with a tertiary carbon atom), 3,3-dimethylbut-1-ene (33DB1ene) (dibranched with a quaternary carbon atom), 2,3-dimethylbut-2-ene (23DB2ene) (dibranched with two tertiary carbon atoms), and cyclohexene (cC_6) (cyclic) were compared.

II.4. Labeled Hexanes

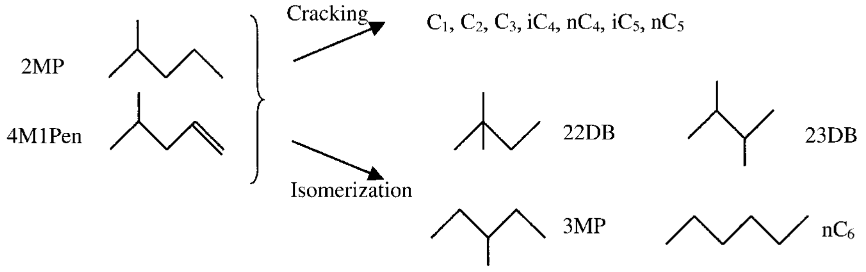
The experiments were performed by replacing commercial hexanes by labeled ones with ^{13}C in the classical flow system already described in (13). Labeled hexanes were synthesized by catalytic dehydration of the corresponding labeled alcohols, obtained by the Grignard reaction. The resulting olefins were then hydrogenated to yield the labeled hexanes (15). The procedure used, the calculation of the isomer isotopic species distributions, and the location of the ^{13}C atom in the molecules have already described elsewhere (16). The different isotopic species were characterized by GS-MS.

II.5. Calculations

The total conversion, α_t (%), is defined as the percentage of reactant transformed. The selectivity, S (%), of a product is given as the percentage of this product among all the products formed. The total reaction rate, r (mol/s · g), is defined as the number of moles of reactant transformed per second per gram of catalyst (13). Starting from 2MP or from 4M1Pen, the $3MP/nC_6$ ratio can be representative of the acidity of the catalyst, because under these conditions the reaction leads to the most stable carbocation yielding 3MP (17).

III. CATALYTIC RESULTS

The catalytic experiments with 4M1Pen and 2MP were carried out on the four catalyst samples, Cat1a, Cat1b,



SCHEME 1

Cat2a, and Cat2b, at a given reaction temperature of 350°C, for reduction temperatures of 350, 450, and 700°C and for different reduction times. Each sample was tested under helium prior to any reduction treatment. Detailed studies of the results focused on Cat1b and Cat2a. Catalytic results concerning Cat1a and Cat2b will be mentioned only briefly without any corresponding figures being given.

The reactivity and comparison of all the probe molecules were tested only on Cat2a (1.2%$MoO_3/\alpha\text{-}Al_2O_3$), which was the most reactive and the most stable for 4M1Pen and 2MP reactions.

Catalytic behaviors during activation treatments were correlated to surface species distributions, determined by XPS, only for Cat1b and Cat2a.

III.1. Activity of Cat1a (0.08% $MoO_3/\alpha\text{-}Al_2O_3$)

Reduction at 350°C was not enough to adequately activate the catalyst, because even after 23 h the total conversion for 4M1Pen reaction reached only 4%. Nevertheless, the isomerization selectivity was high (around 90%) and the $3MP/nC_6$ ratio greater than 20. Under these activation conditions, 2MP was not transformed.

Reduction at 450°C was much more efficient because after 2 h the catalyst sample exhibited a total activity of 10% and a very high selectivity (around 98–99%). After 20 h of reduction the catalyst seemed to become stable with a total conversion of 20%, an isomerization selectivity around 99%, and a $3MP/nC_6$ ratio around 10. After an activation of 5 h, 2MP began to be converted; the conversion reached 6% after 20 h of reduction.

Activation at 700°C for 2 h led to an increase of the total conversion, which reached 40 and 10% respectively for 4M1Pen and 2MP, the isomerization selectivities being unchanged. At both activation temperatures, 450 and 700°C, 4M1Pen reacted faster than 2MP, while the $3MP/nC_6$ ratio remains high in both cases.

XPS measurements were unsuccessful because the MoO_3 content was too low to be detected.

The activity of Cat1a was tested under helium flux for 4M1Pen and 2MP without any previous reduction. No activity was detected in either case.

III.2. Activity of Cat1b (5.4% $MoO_3/\alpha\text{-}Al_2O_3$)

III.2.1. Reactivity of 4M1Pen. The catalytic properties starting from 4M1Pen, associated with the surface species distributions, determined by XPS measurements during reduction at 350 and 450°C, are represented in Figs. 1a and 1b and Figs. 2a and 2b, respectively. Compared to Cat1a, the total conversion at the beginning of activation is much more important, whatever the reduction temperature (350 or 450°C), but the sample deactivated after a few hours of reduction. This deactivation was much more rapid when the activation temperature was increased. The same tendency was observed for the isomerization selectivity, which was very high at the beginning of activation (>95%) and decreased to 55% after 25 h/H_2 at 350°C and to 40% after 23 h/H_2 at 450°C.

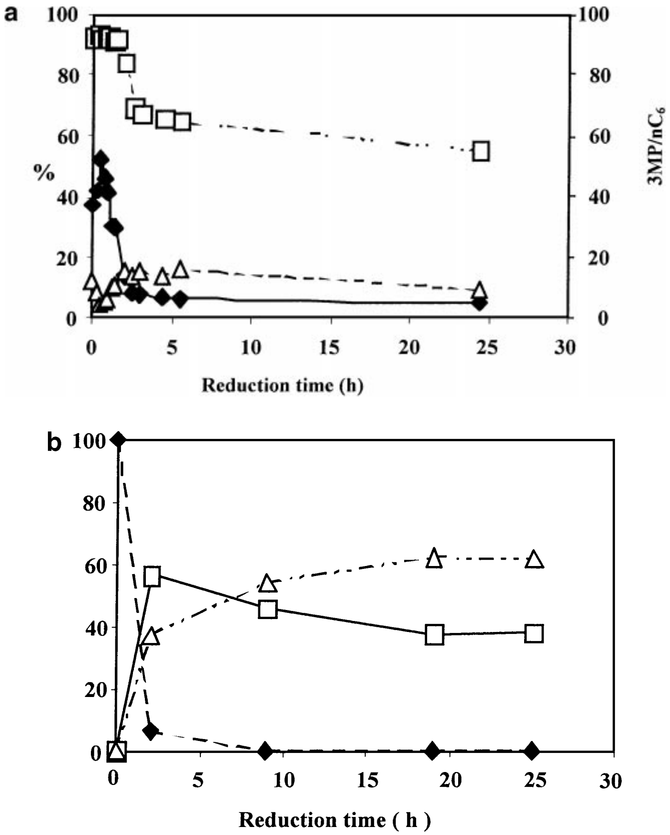


FIG. 1. (a) Conversion (◆), isomerization selectivity (□), and $3MP/nC_6$ ratio (△) at $T = 350$°C versus reduction time (h) at 350°C on Cat1b (5.4% $MoO_3/\alpha\text{-}Al_2O_3$). (b) Distribution of Mo surface species on Cat1b (5.4% $MoO_3/\alpha\text{-}Al_2O_3$): Mo(VI) (◆), Mo(V) (□), and Mo(IV) (△) versus reduction time (h) at 350°C.

The XPS measurements show (Fig. 1b) that Mo(VI) is the only surface species present on the initial catalyst before activation. This species decreased rapidly in the course of reduction and was not detectable after 9 h/H_2 at 350°C. The disappearance of Mo(VI) was accompanied by the appearance and increase of Mo(V) and Mo(IV). In the beginning, after 3 h/H_2 at 350°C, the amount of Mo(V) was higher than the amount of Mo(IV). After 25 h/H_2 at 350°C the concentration of Mo(IV) was the greatest and the ratio between Mo(V) (38%) and Mo(IV) (62%) was stable.

It must be noted that XPS spectra concerning activation at 450°C (Fig. 2b) were performed on the sample after 23 h/H_2 at 350°C (presented in Fig. 2a). Reduction at 450°C resulted in a decrease of Mo(V) surface species and in the appearance of metallic Mo (25% after 5 h/H_2 at 450°C), whereas the proportion of Mo(IV) did not change.

An activation of 2 h/H_2 at 700°C (results not shown in this paper) totally suppressed the activity for 4M1Pen.

XPS measurements show mainly Mo(IV) (60%), Mo(0) (34%), and Mo(V) (6%).

XPS spectra after calcination, after 9 h/H_2 at 350°C, after 25 h/H_2 at 350°C + 5 h/H_2 at 450°C, and after the previous treatments + 1 h/H_2 at 700°C are given in Figs. 3a, 3b, 3c, and 3d, respectively (the detailed spectra have already been shown in the previous paper (12)).

III.2.2. Comparison of the reactivity of 4M1Pen and 2MP. Comparisons of total conversions and product distributions of 2MP and 4M1Pen after 1.5 h of activation at 350°C and 4 h/H_2 at 450°C are presented respectively in Tables 1a and 1b.

Reduction at 350°C for 1.5 h/H_2 showed high isomerization selectivities, when starting both from 4M1Pen and from 2MP with 3MP/nC_6 ratios around 9, confirming the acidic character of this sample at the beginning of reduction. In addition to 3MP, which is the most important isomer, there was a large proportion of 2,3-dimethylbutane (23DB). Nevertheless, the olefin reacted around 10 times faster than the saturated hydrocarbon, meaning that after 1.5 h of reduction only a few metallic sites leading to alkane dehydrogenation were present. Among the cracking products, propane seemed predominant.

For reduction at 450°C, in both cases, total conversions were low, around 4%, and the reaction rates were very close. Compared with activation at 350°C, the isomerization selectivity decreased greatly (33–40%), although the 3MP/nC_6 ratio was only slightly lower. Among the cracked products, methane was present in a large majority and originated

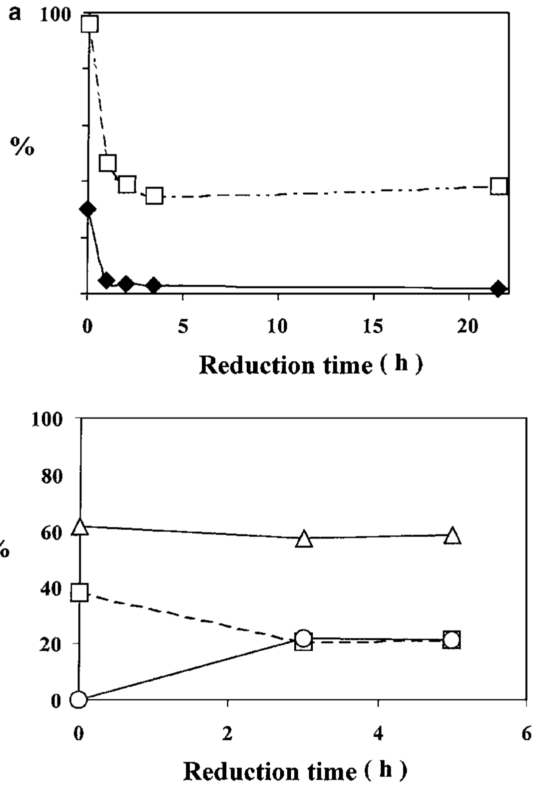


FIG. 2. (a) Conversion (◆) and isomerization selectivity (□) at $T =$ 350°C versus reduction time (h) on Cat1b (5.4%$MoO_3/\alpha\text{-}Al_2O_3$) at 450°C. (b) Distribution of Mo surface species on Cat1b (5.4%$MoO_3/\alpha\text{-}Al_2O_3$): Mo(V) (□), Mo(IV) (△), and Mo(0) (○) versus reduction time (h) at 450°C.

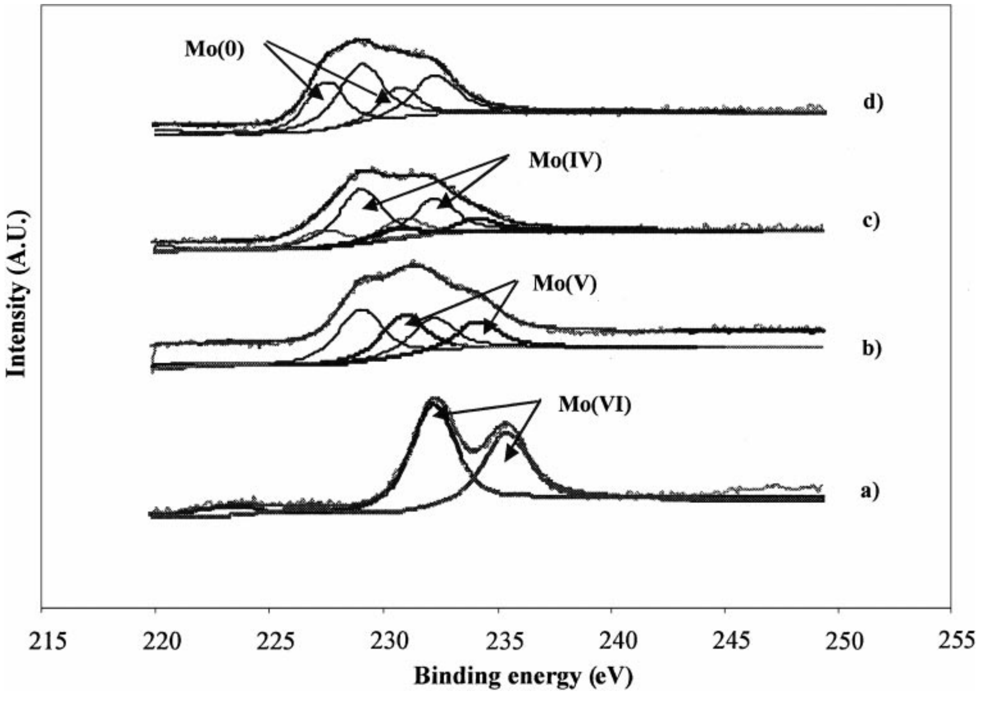


FIG. 3. XPS spectra of the Mo(3*d*) region of Cat1b: (a) calcined sample; (b) after 9 h/H_2 at 350°C; (c) after (b) + 16 h/H_2 at 350°C + 5 h/H_2 at 450°C; (d) after (c) + 1 h/H_2 at 700°C.

TABLE 1

Comparison of Total Conversion (%), Total Reaction Rate (*r*), and Product Distribution (%) of 2MP and 4M1Pen at 350°C on Cat1b (5.4%MoO_3/α-Al_2O_3)

Reactant	α_t (%)	Si (%)	r (μmol/(s g^{-1}))	3MP/nC_6	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	22DB	23DB	3MP	nC_6
(a) After 1.5 h/H_2 at 350°C															
2MP	5.2	96.8	0.03	8.8	0.7	0.2	1.0	0.6	0.0	0.5	0.2	0.0	35.1	55.3	6.2
4M1Pen	41.8	97.6	0.32	9.1	0.4	0.3	1.7	0.5	0.0	0.3	0.2	0.5	32.5	58.6	6.5
(b) After 4 h/H_2 at 450°C															
2MP	3.5	33.0	10^{-2}	4.6	22.7	3.0	16.0	4.1	1.3	10.0	9.9	0.0	5.5	22.8	5.0
4M1Pen	3.8	39.2	2×10^{-2}	4.7	26.5	1.8	15.0	5.1	0.5	2.1	10.7	0.0	4.8	28.4	6.0

from terminal carbon–carbon bond breaking, characteristic of metallic hydrogenolysis properties, in contrast to internal carbon–carbon rupture, more characteristic of acidic cracking. Nevertheless, it must be noted that the amount of propane remains significant.

As for 4M1Pen, reduction at 700°C resulted in no activity.

III.2.3. Reaction under helium. Before reduction treatment, Cat1b was tested by replacing the hydrogen flux with helium and keeping the other experimental conditions constant. The results are shown in Table 2.

Only isomers are formed starting from 4M1Pen, with a high 3MP/nC_6 ratio, showing that the catalyst exhibited very strong acidic properties before reduction, although the total conversion was lower than that after 1.5 h/H_2 at 350°C (41.8%). Otherwise, as has been shown in Part I, heating this sample under helium at 350°C leads to the appearance of 30% Mo(V) species.

III.3. Activity of Cat2a (1.2% MoO_3/α-Al_2O_3)

III.3.1. Reactivity of 4M1Pen. As shown in Fig. 4a for activation at 350°C, the Cat2a catalyst sample exhibited activity around 15% immediately after the first few minutes of reduction, this total conversion being constant after 48 h/H_2 at 350°C. In the same manner, the isomerization selectivity of 98%, as well as the 3MP/nC_6 ratio of about 12, was constant after 2 days of activation. So isomerization seems to take place on acidic sites. In the initial oxidic form of the catalyst, only Mo(VI) species were detected (Fig. 4b). But contrary to Cat1b, these species were not completely reduced, even after 20 h/H_2 at 350°C. After 3 h of activation at 350°C, the surface consisted of 33% Mo(VI), 37% Mo(V), and 30% Mo(IV). These proportions were quite constant in the course of reduction, except for a slight increase of Mo(IV), which becomes predominant after 20 h.

Activation at 450°C (Fig. 5a) led to the same behavior as activation at 350°C, with high isomerization selectivity (98%), but with a better conversion than reduction at 350°C (40% vs 15%). The catalyst was very stable, even after more than 100 h under hydrogen. The 3MP/nC_6 was slightly lower than that for activation at 350°C.

TABLE 2

Total Conversion (%) and Product Distribution (%) of 4M1Pen at 350°C on Cat1b (5.4%MoO_3/α-Al_2O_3) under Helium Flux before Reduction

Reactant	α_t (%)	Si (%)	3MP	nC_6	3MP/nC_6
4M1Pen	10.0	100.0	98.0	2.0	49.0

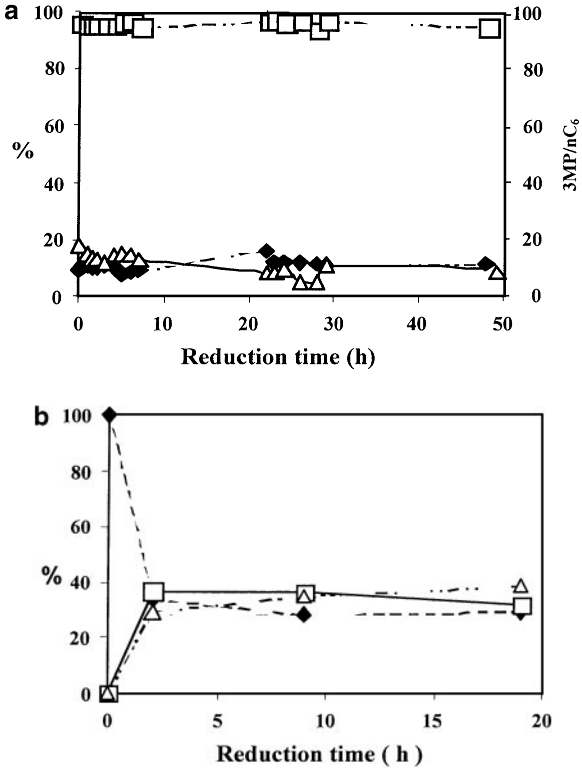


FIG. 4. (a) Conversion (◆), isomerization selectivity (□), and 3MP/nC_6 ratio (△) at $T = 350$°C versus reduction time (h) at 350°C on Cat2a (1.2%MoO_3/α-Al_2O_3). (b) Distribution of Mo surface species on Cat2a (1.2%MoO_3/α-Al_2O_3): Mo(VI) (◆), Mo(V) (□), and Mo(IV) (△) versus reduction time (h) at 350°C.

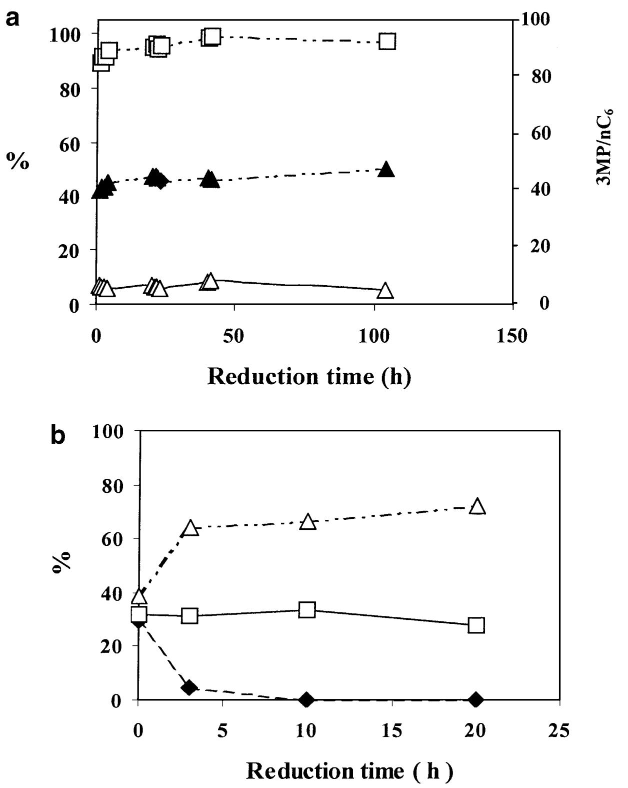


FIG. 5. (a) Conversion (▲), isomerization selectivity (☐), and 3MP/nC_6 ratio (△) at $T = 350°C$ versus reduction time (h) at 450°C on Cat2a (1.2%MoO_3/α-Al_2O_3). (b) Distribution of Mo surface species on Cat2a (1.2%MoO_3/α-Al_2O_3): Mo(VI) (◆), Mo(V) (☐), and Mo(IV) (△) versus reduction time (h) at 450°C.

Figure 5b, presenting the distribution and evolution of Mo states at 450°C, shows that the Mo(VI) surface species were completely reduced after 10 h/H_2 at 450°C. It seems that Mo(VI) species disappear in favor of Mo(IV), whereas the Mo(V) concentration remains the same after 20 h.

Reduction for 2 h/H_2 at 700°C (Table 3c) led to an increase of the total conversion starting from 4M1Pen (55%), whereas the isomerization selectivities, the 3MP/nC_6 ratios, and the product distribution remained constant. XPS measurements indicated the presence of Mo(IV) (34%), Mo(V) (6%), and Mo(II) (60%). These results have already been presented in Part I (12).

III.3.2. Comparison of the reactivity of 4M1Pen and 2MP. 2MP was not converted when the catalyst sample was activated by hydrogen at 350°C. Comparisons of total conversions and product distributions of 2MP and 4M1Pen after 1 h of activation at 450°C and 100 h/H_2 at 450°C are represented respectively in Tables 3a and 3b.

As for 4M1Pen, the total conversion, the isomerization selectivity, and the 3MP/nC_6 ratio are very stable starting from 2MP in the course of reduction. A comparison of the specific transformation rate, *r*, shows that 4M1Pen reacted between six and seven times faster than the saturated hydrocarbon at the beginning of reduction at 450°C, confirming the acidic properties of this catalyst. On the other hand, after 100 h/H_2 at 450°C this ratio was lower (between 2 and 3). The detailed product distribution was the same starting from 2MP or from the corresponding olefin, whatever the time under hydrogen. The 3MP/nC_6 ratio was the same for 2MP and 4M1Pen, the value being slightly lower after 100 h of reduction. Among the isomers, 3MP is the most important, with relatively high values for 23DB. Furthermore, about 1.5–2.5% 22DB with a quaternary carbon was detected.

Reduction (2 h/H_2) at 700°C (Table 3c) led to an increase of the total conversion, which reached 25% (when starting from 2MP), while isomerization selectivity and the 3MP/nC_6 ratio remained the same. For this high reduction temperature, the saturated hydrocarbon reacted about as rapidly as its corresponding olefin.

III.3.3. Reaction under helium. The product distribution corresponding to replacing hydrogen by helium for Cat2a is very similar to the one obtained on Cat1b (III.2.3, Table 2); this means 100% isomerization selectivity into

TABLE 3

Comparison of Total Conversion (%), Total Reaction Rate (*r*), and Product Distribution (%) of 2MP and 4M1Pen on Cat2a (1.2% MoO_3/α-Al_2O_3)

Reactant	α_t (%)	Si (%)	r (μmol/(s g^{-1}))	3MP/nC_6	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	22DB	23DB	3MP	nC_6
(a) After 1 h/H_2 at 450°C															
2MP	10.4	95.6	0.03	6.8	0.9	1.0	1.5	1.0	0.6	1.9	2.3	2.5	17.2	62.0	9.1
4M1Pen	44.7	98.0	0.20	6.7	1.0	1.0	2.0	1.1	0.7	2.6	2.5	2.4	14.2	62.8	9.4
(b) After 100 h/H_2 at 450°C															
2MP	12.8	98.6	0.08	5.3	0.3	0.2	0.6	0.4	0.3	0.7	0.5	1.3	14.2	67.8	12.8
4M1Pen	48.3	96.8	0.22	6.1	0.2	0.5	0.9	0.8	0.3	0.6	0.6	1.8	15.0	68.0	11.2
(c) After 2 h/H_2 at 700°C															
2MP	25.0	98.6	0.14	5.3	0.1	0.1	0.6	0.4	0.1	0.5	0.5	0.8	14.2	69.5	13.3
4M1Pen	55.0	96.8	0.22	6.07	0.1	0.1	0.6	0.4	0.1	0.3	0.1	0.5	15.5	70.50	11.8

3MP and nC_6. However, the conversion was a little lower (8%) and the $3MP/nC_6$ ratio much higher (around 100). The addition of water (not represented here) led to a considerable decrease of the $3MP/nC_6$ ratio, to values around 10.

The activation energies for isomerization of 4M1Pen were determined on both Cat1b (5.4% MoO_3/α-Al_2O_3) and Cat2a (1.2% MoO_3/α-Al_2O_3), after respectively 2 and 50 h of reduction at 350°C. In both cases, they were about 15–20 kcal/mol.

In the same manner, studies of deactivation as a function of the reaction time were performed at 350°C, although the corresponding curves have not been given in this paper. Cat2a deactivated rapidly (after a few hours at 350°C), as is generally the case for acidic catalysts without any metallic function. On the other hand, on Cat1b, the deactivation was less rapid, as long as there was no Mo(0) present.

III.3.4. Reactivity of probe molecules. To obtain more information about the reaction mechanisms occurring on Cat2a, a comparison between some probe molecules was performed after more than 100 h of reduction at 450°C, which corresponded to a relatively stable catalyst sample. As under such conditions 4M1Pen was more reactive than the saturated hydrocarbon, several hexenes have been compared. The experimental conditions (catalyst weight and reaction temperature) were chosen so that the conversion, about 10%, could be considered very close to the initial distribution. The product distributions starting from 3,3-dimethylbut-1-ene (33DB1ene) (dibranched with a quaternary carbon), 2,3-dimethylbut-2-ene (23DB2ene) (dibranched with two tertiary carbon atoms), 4-methyl-1-pentene (4M1Pen) (monobranched with a tertiary carbon atom), 1-hexene (linear), and cyclohexene (cyclic) are shown in Table 4 in the order of decreasing conversion.

Dibranched hexenes reacted better than monobranched hexenes, which reacted more easily than linear and cyclic ones. Between 23DB2ene and 33DB1ene, the reactant with a quaternary carbon obtained better conversion. It is shown in Table 4 that starting from 33DB1ene, 23DB was the most abundant isomer formed (94%), followed by 2MP (6%). No other isomers were detected at initial conversion. On the other hand, 23DB2ene yielded mainly 2MP (97.3%) with a low proportion of 22DB (2.7%). It was already noted previously that 3MP was the main product observed from 4M1Pen, much more important than the other isomer formed, the nC_6. Concerning 1-hexene, the two isomers were 2MP (85.6%) and 3MP (14.4%).

TABLE 4

Comparison of Product Distribution (%) of Probe Molecules at 200°C on Cat2a (1.2% MoO_3/α-Al_2O_3) after 100 h/H_2 at 450°C

	Product					
	22DB	23DB	2MP	3MP	nC_6	MCP
33DB1ene	—	94.0	6.0	—	—	—
23DB2ene	2.7	—	97.3	—	—	—
4M1Pen	—	—	—	92.1	7.9	—
1hexen	—	—	85.6	14.4	—	—
cC_6	—	—	—	—	18.0	82.0

Cyclohexene mainly gave another cyclic product, MCP (82%), and a linear one, nC_6; in this case no branched products were detected. Whatever the starting noncyclic reactant, no MCP was detected, meaning that isomerization did not occur via a methylcyclopentane intermediate mechanism.

III.4. Activity of Cat2b (5.2% MoO_3/α-Al_2O_3)

The detailed catalytic activities of Cat2b for 4M1Pen and 2MP conversion are not given here, because their behavior was the same as that for Cat2a (5.4% MoO_3/α-Al_2O_3) prepared by wet impregnation with Na_2MoO_4, i.e.,

—a total conversion after a few minutes of activation between 30 and 40%, depending on the activation temperature;

—a very high isomerization selectivity at the beginning of reduction;

—4M1Pen reacting around 10 times faster than 2MP at the beginning of reduction at 350°C, this difference decreasing with extended reduction;

—a rapid deactivation appearing after 3 h when activation was performed at 350°C and after 30 min when activation was at 450°C;

—comparable reaction rates starting from 4M1Pen and 2MP when activation was at 450°C;

—a non-negligible decrease of the isomerization selectivity in favor of cracking in methane;

—XPS studies showing that Mo(VI) was rapidly reduced, already at 350°C, first to Mo(V) and mainly Mo(IV), and then further to Mo(0).

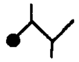
IV. ^{13}C TRACER STUDIES

Isomerization of 2-methylpentane (2-^{13}C) was studied on Cat1b (5.4% MoO_3/α-Al_2O_3) after 2.5 h of activation at 450°C and Cat2a (1.2% MoO_3/α-Al_2O_3) after 20 h/H_2 at 450°C. The amount of catalyst was chosen so that the conversion, about 10%, could be considered very close to the initial distribution. The selectivity of each isotopic isomer produced and the total isotopic distributions are summarized in Tables 5 and 6, respectively.

The tracer experiments performed on Cat2a showed that the main isotopic species produced (Table 5) were 23DB(2-^{13}C) (34.0%) and 3MP(2-^{13}C) (30.6%), followed by 3MP(3-^{13}C) (14.4%). Among nC_6 isotopic species, the distributions obtained (Table 6) corresponded to a quasi-statistical distribution of the ^{13}C atom. Unusual products such as nC_6(1-^{13}C) (35.7%), 3-methyl(^{13}C)pentane (7.4%), and 2-methyl(^{13}C)pentane (5.0%) were detected.

TABLE 5

Selectivity of Each Isotopic Isomer Produced from Labeled 2-Methylpentane () at $T = 350°C$ on Cat1b (after 2.5 h/H_2 at 450°C) and Cat2a (after 20 h/H_2 at 450°C) Samples: Cat1b (5.4% MoO_3/α-Al_2O_3); Cat2a (1.2% MoO_3/α-Al_2O_3)

											
Cat2a	7.6	34.0	—	—	—	3.6	14.4	30.6	3.5	3.5	2.8
Cat1b	2.1	19.4	—	—	—	0.0	8.9	29.9	1.0	28.8	9.9

Note. Reactions were performed at 350°C under 1 atm (1 atm = 1.013 × 10^5 Pa) of hydrogen at a flow rate around 50 cm^3/min.

In the case of Cat1b, the main isotopic species were 3MP(2-^{13}C) (29.9%), then nC_6(2-^{13}C) (28.8%), 23DB(2-^{13}C) (19.4%), and 3MP(3-^{13}C) (8.9%). The nC_6 isotopic species revealed that the statistical distribution disappeared. Almost no unusual isotopic species were observed.

It has already been shown that on acidic catalysts a statistical distribution of the ^{13}C atom occurs, meaning that the molecules undergo many rearrangement reactions before desorption, which was, in this case, the rate-determining step. Indeed, on acidic systems, the reactions through the carbenium ion were fast and the desorption of the reaction products was much more difficult. So an increase in the metallic character led to a higher desorption rate and to an isotopic distribution further away from the statistical distribution.

As was already noted when the activities of 4M1Pen and 2MP on samples Cat2a and Cat1b were compared, the two catalysts exhibited acidic properties, although the acidity became minor for the second in the course of reduction in favor of an increase in metallic properties.

On the other hand, it is well known that the self-isomerization on acidic systems of 3-methylpentane (3-^{13}C) into 3-methylpentane (2-^{13}C) by a 1,2-ethyl shift is very fast and proceeds through a carbenium ion mechanism (Scheme 3a). So one can suppose that if the carbenium ion rearrangement is very fast and if the desorption rate is low, the ethyl shift described in Scheme 3a will be equilibrated. So if this assumption is right, the 3MP(2-^{13}C)/3MP(3-^{13}C) ratio should be close to 2, which corresponds to the equilibrium value (Scheme 3b).

IV.1. On Cat1b (5.4% MoO_3/α-Al_2O_3)

The 3MP(2-^{13}C)/3MP(3-^{13}C) value of 3.3 was very close to the nC_6(2-^{13}C)/nC_6(3-^{13}C) value of 2.9. Moreover, as the isomerization of 3MP into nC_6 was slow and the self-isomerization of 3MP very fast (not shown in this paper), one can suppose that nC_6(2-^{13}C) and nC_6(3-^{13}C) were issued in successive steps via the adsorbed 3MP(2-^{13}C) intermediate. Nevertheless, no further consecutive steps are implied because almost no unusual isotopic species such as 3-methyl(-^{13}C)pentane, 2-methyl(-^{13}C)pentane, or 2MP(4-^{13}C) were observed.

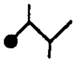
IV.2. On Cat2a (1.2% MoO_3/α-Al_2O_3)

In this case, the distribution obtained corresponds to a quasi-statistical distribution of the ^{13}C atom. Furthermore, on this catalyst, which is known to exhibit a stronger acidic character than Cat1b, unusual isotopic species like 3-methyl(-^{13}C)pentane and 2-methyl(-^{13}C)pentane have been produced, the presence of this exo labeling (mainly in the case of 2-methyl(-^{13}C)pentane) can very well be explained via an acidic isomerization mechanism implying cyclopropane-like intermediates (18) as well as successive steps in the isomerization pathway. Moreover, the 3MP(2-^{13}C)/3MP(3-^{13}C) ratio is 2, showing that the self-isomerization by an ethyl shift is equilibrated; this is a result of the low desorption rates.

The isotopic isomer distributions show that the metallic cyclic isomerization is not predominant; indeed, in this case the main isotopic species, when starting from 2MP

TABLE 6

Isotopic Species Distributions from Labeled 2-Methylpentane () at $T = 350°C$ on Cat1b (after 2.5 h/H_2 at 450°C) and Cat2a (after 20 h/H_2 at 450°C) Samples: Cat1b (5.4% MoO_3/α-Al_2O_3); Cat2a (1.2% MoO_3/α-Al_2O_3)

											
Cat2a	18.3	81.7	5.0	89.0	6.0	7.4	29.6	62.9	35.7	35.7	28.6
Cat1b	9.8	90.2	2.0	97.0	1.0	0.0	22.9	77.1	2.5	72.5	24.9

Note. Reactions were performed at 350°C under 1 atm (1 atm = 1.013 × 10^5 Pa) of hydrogen at a flow rate around 50 cm^3/min.

SCHEME 3

(2-^{13}C), would have been 3MP(3-^{13}C), as already observed on Pt/Al_2O_3 catalysts (19).

V. DISCUSSION

The discussion will focus on three main points:

1. The surface reducibility;
2. the nature of the active sites and their role in hexane (or hexene) rearrangements;
3. the isomerization mechanism.

V.1. *The Surface Reducibility*

According to previous discussions detailed in Part I of this paper, Cat1a (0.08% MoO_3/α-Al_2O_3) contains a large majority of monomeric molybdates species in tetrahedral coordination, in very strong interaction with the surface. Thus, Mo(VI) species are difficult to reduce. Furthermore, the low molybdenum content, yielding to a low concentration of active species, explains why this sample exhibited poor activities for 4M1Pen and 2MP conversion.

On the other hand, the surface molybdenum species present on Cat1b (5.4% MoO_3/α-Al_2O_3) and Cat2b (5.2% MoO_3/α-Al_2O_3)) were mainly bulklike MoO_3. That is why, according to the XPS spectra (III. 2.1), Mo(VI) species were easily reduced at 350°C to Mo(V) and Mo(IV), which became predominant and to Mo(0) after 3 h at 450°C. So metallic molybdenum is correlated with deactivation of the catalyst.

The surface of Cat2a (1.2% MoO_3/α-Al_2O_3) contains isolated monomeric molybdate species in tetrahedral coordination and well-dispersed polymolybdates in octahedral coordination, in interaction with the surface. That is why this catalyst is more difficult to reduce and why it needed to be treated at 450°C for several hours to observe the complete disappearance of Mo(VI) (III.3.1). On the other hand, it has been demonstrated on MoO_3/Al_2O_3 catalysts (20) using ISS, XPS, and Raman spectroscopy that, for low reduction temperatures, the following reduction scheme is obtained:

$$\text{Isolated tetrahedral molybdate Mo(VI)} \rightarrow \text{Mo(IV)},$$
$$\text{Polymolybdate octahedral Mo(VI)} \rightarrow \text{Mo(V)} \rightarrow \text{Mo(IV)}.$$

This explains the higher proportion of Mo(V) at the beginning of reduction at 350°C. On these catalyst samples, even after a reduction for 2 h at 700°C, no Mo(0) was detected.

It must be noted that from Part I it can be deduced that there is no formation of a determined $Al_2(MoO_4)_3$ compound before and after reduction treatments.

V.2. *The Nature of Active Sites in Alkanes Reforming*

It has been shown in this paper by XPS measurements that only Mo(VI) species were present on the initial catalyst before any reduction treatment. Catalytic tests under helium performed on the initial oxidic form on Cat1b and Cat2a showed very strong acidic character (3MP/nC_6 between 50 and 100) and only isomer products. Compared to the same samples at the beginning of reduction at 350°C, the acidic properties were much more pronounced, but the total conversion was lower. XPS studies, after a thermal heating under helium at 350°C, revealed the appearance of non-negligible amounts of Mo(V) species (30%) (Part I). At this stage it can be postulated that thermal heating under an inert gas leads to the formation of unsaturated Mo(V) species which act as Lewis acid sites. Otherwise, the addition of water leads to a decrease of the 3MP/nC_6 ratio to values around 10.

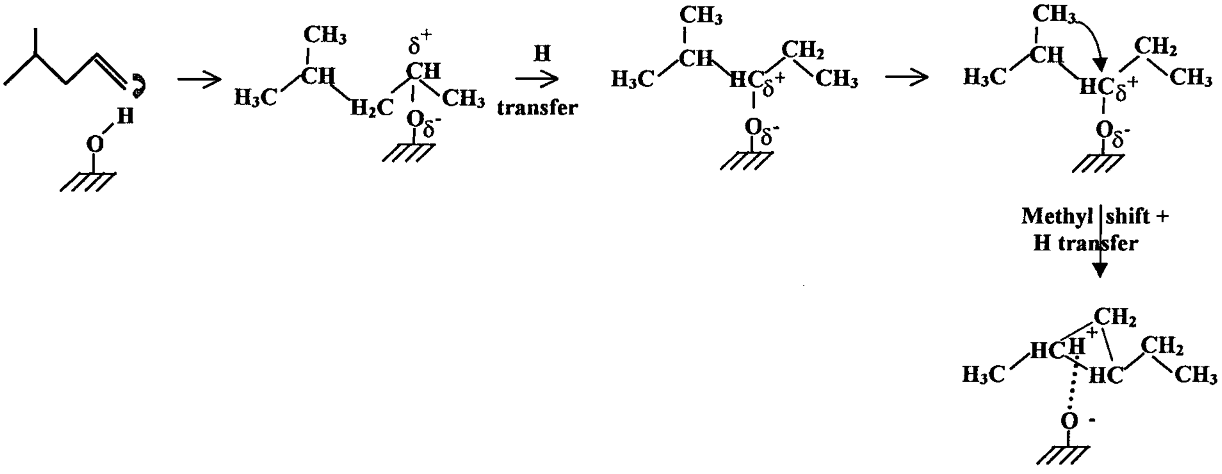
Whatever the catalyst sample, at the beginning of reduction 4M1Pen reacted faster than 2MP, but in both cases the isomerization selectivity and the 3MP/nC_6 ratio were very close and relatively high. This means, first, that the catalysts exhibited acidic properties and that the differences in reaction rates only came from the low number of metallic sites necessary to dehydrogenate the alkane (2MP) to isomerize. Correlation with XPS studies show that in the first moment of reduction there is a majority of Mo(V) at the surface. On the other hand, the proportional increase of Mo(IV) species is associated with the detection and the increase of metallic dehydrogenation properties, which appear as similar reaction rates for 4M1Pen and 2MP reactions.

In the same manner deactivation of the sample with a high molybdenum content can be correlated with the appearance of metallic molybdenum accompanied only by cracking into C_1 (resulting in a decrease of the isomerization selectivity), the 3MP/nC_6 ratio remaining about the same.

The presence of Mo(II) on Cat2a after 2 h/H_2 at 700°C, which species has already been detected on reduced MoO_3/Al_2O_3 catalysts (8) for propane hydrogenolysis, seems to exhibit metallic dehydrogenation properties.

V.3. *The Isomerization Mechanism*

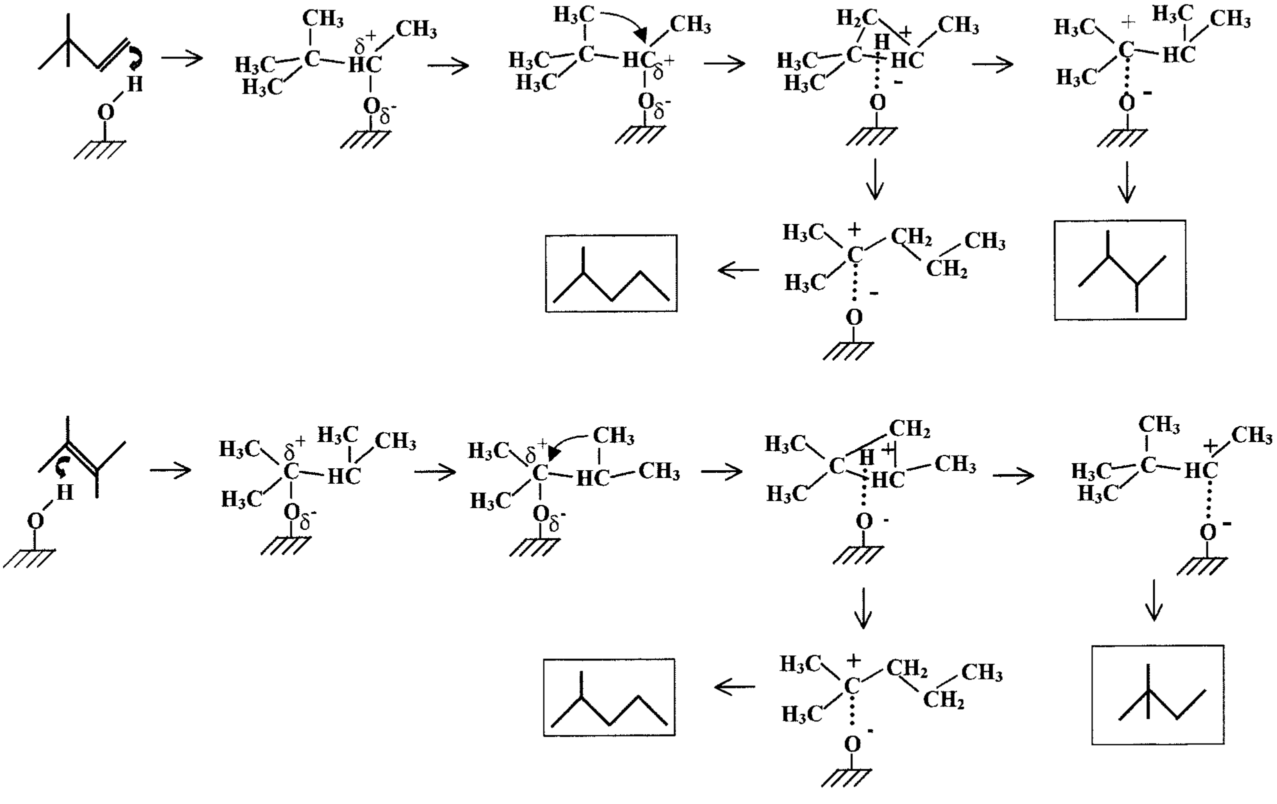
It has been shown in this paper, looking at the product distributions, that the isomerization mechanism implies



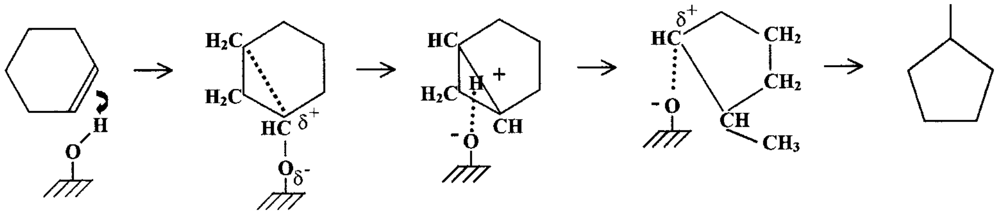
SCHEME 4. Formation of a protonated cyclopropane-like ring from alkoxy species, starting from 4M1Pen.

acidic sites, whatever the catalyst sample and the reduction treatment. However, it is necessary to take into account the interaction with the surface, which is not necessarily the case with a classical mechanism implying carbenium ions. That is why the isomerization mechanisms were interpreted using the presence of O–H surface groups leading to alkoxy species as intermediates (21, 22) (Scheme 4) when an olefin approaches the surface. This alkoxy species, when strongly polarized up to its ionic form (21, 23, 24), can behave as a protonated cyclopropane intermediate. This cyclopropane-like intermediate can explain the formation of some isomers without a primary carbenium ion formation.

If we consider the product distributions, starting from the probe molecules (III.3.4, Table 4), it is shown that 33DB1ene only gives 23DB (94%) and 2MP (6%). These observations are well explained via the initial formation of a polarized alkoxy intermediate, as represented in Scheme 5. Indeed, as the C–O bond is polarized, the starting alkoxy intermediate is constituted by a secondary-like carbenium and the two resulting products imply tertiary carbenium



SCHEME 5



SCHEME 6

ions. Nevertheless, the formation of 23DB is favored because of the stability induced by the inductive effect (25) of the isopropyl group in comparison with the inductive effect of the propyl group, yielding to 2MP. It must be noted that via a classical acidic mechanism the presence of 2MP cannot be explained because it would need the intervention of a starting primary carbocation.

In the same manner, starting from 23DB2ene, the alkoxy mechanism allows the exclusive formation of 22DB and 2MP, this last being produced in a greater proportion because it is the result of the transformation of a tertiary carbenium into a tertiary one, whereas the formation of 33DB would imply the presence of a resulting secondary carbenium ion.

The alkoxy mechanism can also explain the formation of MCP (Scheme 6).

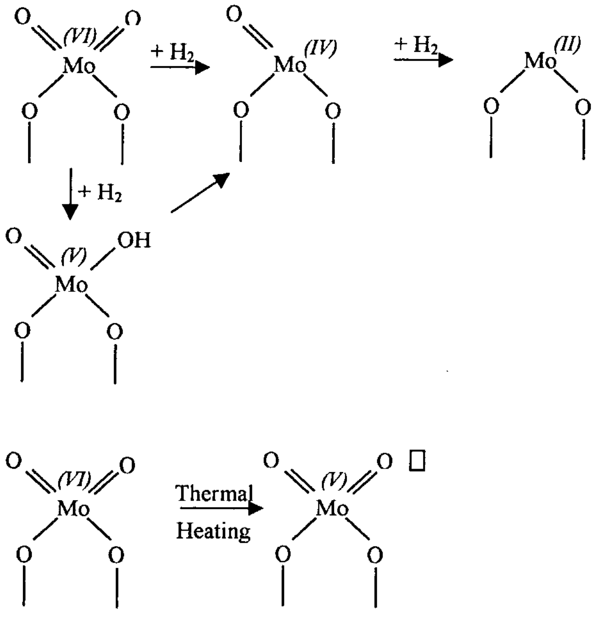
However, a metallic path of isomerization implying metallocycles, especially metallocyclobutanes, cannot be totally excluded, as these intermediates have already been proposed on bulk tungsten (26, 27) or molybdenum oxides (28). But if such a metallic isomerization pathway is probable, it may be limited on supported molybdenum oxides, under mild reduction conditions, as is shown by the low conversion of the 2MP saturated hydrocarbon. Somehow, this reaction scheme may become more significant for reduction under more severe conditions, i.e., at 700°C or for long reduction times at 450°C. Anyway, the acidic isomerization pathway is predominant on supported systems, as has been confirmed by the ^{13}C labeling experiments and by the low values of isomerization activation energies (about 15–20 kcal/mol); indeed, it has already been shown in other systems (29) that the isomerization activation energies are higher when metallocyclobutane intermediates are involved (about 40 kcal/mol). Lower values of 15–20 kcal/mol are more typical of acidic isomerization.

The MCP-like intermediate can be excluded, because MCP was never detected in the reaction products when starting from noncyclic hydrocarbons.

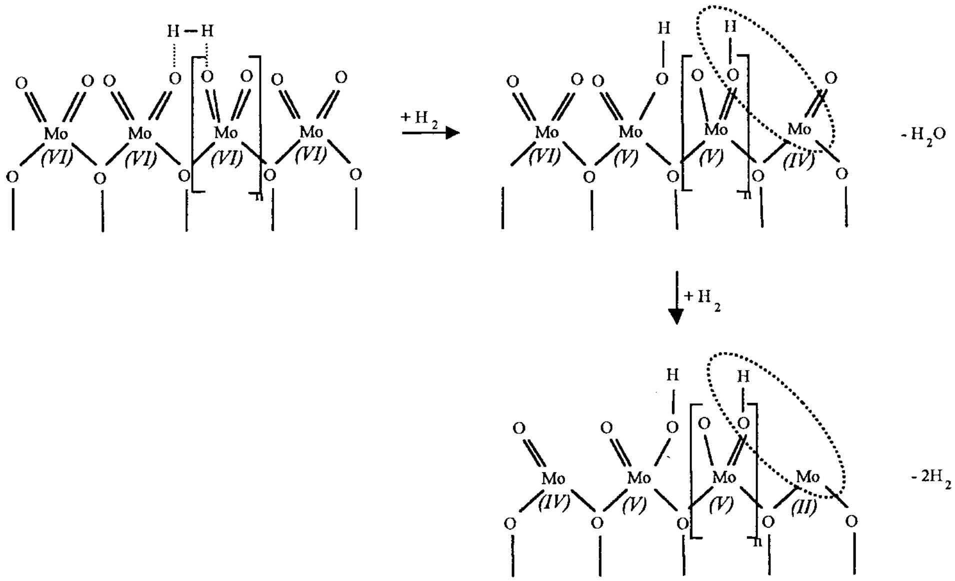
VI. CONCLUSIONS

The different results issued from various characterizations (XRD, TPR, BET, and XPS) performed in Part I, correlated with the study of hexane and hexene reforming and with the ^{13}C tracer experiments, led to the following conclusions:

- At the beginning of reduction, the catalysts exhibit very few metallic properties, but almost only acidic ones. The extent of reduction of the catalyst sample is a function of the molybdenum content, that is, of the nature of the interactions of molybdena with the support. So in the course of reduction, metallic properties appear more rapidly when the Mo concentration is increased, because in this case the catalyst behaves as bulk MoO_3, which is easier to reduce than a surface layer of molybdena.
- The isomerization takes place mainly on acidic sites and implies alkoxy species as intermediates, although the presence of metallic isomerization via metallocyclic intermediates cannot be excluded when reduction occurs at high temperature. These alkoxy species can be strongly polarized, depending on the acidity strength of the catalyst, and yield to protonated cyclopropane-like species, explaining the product distributions obtained from different probe molecules.
- Correlation with XPS measurements allows us to postulate that the Mo(V) surface species are responsible for



SCHEME 7



SCHEME 8. Reduction of polymolybdates surface species leading to dual sites.

acidic isomerization. These species can be of the Lewis type (coordinative unsaturated sites) when heated under helium gas or/and of the Brønsted type (O–H surface groups) after reduction. At this stage no suppositions can be made on the role of Mo(VI) surface species. Mo(IV) and Mo(II) species (although this species is only observed at 700°C for a surface layer reduction) obtained on further reduction exhibit metallic dehydrogenation properties. These different molybdenum species are represented in Scheme 7. So from these observations it can be deduced that reduction of a bulklike structure rapidly gives Mo(IV) species, responsible for the appearance of bifunctional properties. Unfortunately, these catalyst samples deactivate rapidly because of further reduction into Mo(0). In the case of the reduction of a surface layer, this bifunctional behavior only appears for more severe reduction conditions; these catalyst samples are very stable, because there is no formation of Mo(0).

- The notion of dual sites in the case of bifunctional mechanism can be proposed. Scheme 7 only represents the reduction steps considering isolated monomolybdates species. However, under our conditions the presence of polymolybdates must be considered and thus the association and proximity of different Mo species in the course of reduction, as represented in Scheme 8. So the proximity of Mo(V)–Mo(IV) and/or Mo(V)–Mo(II) can act as dual sites; that is, adsorption of the reactant may occur on both acidic and metallic sites.

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