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Selective isomerization of 2-methylpentane and 4-methyl-1-pentene over the molybdenum oxide supported on aluminum orthophosphate

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ABSTRACT
In this work, we have focused our attention on catalytic activity and selectivity of Molybdenum oxide supported $AlPO_4$ (MoAlP) since studies on this kind of catalysts are much fewer and its composition seems to lead to better acid characteristics. The $AlPO_4$ (AlP) used as a support was synthetized by coprecipitation and the catalysts MoAlP (4 wt %) was prepared by impregnation of AlP with the ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. This system was characterized in detail using BET surface area measurement, porosimetry, X-ray diffraction (XRD), FTIR spectroscopy, Temperature Programmed Reduction (TPR) and X-ray Photoelectron Spectroscopy (XPS). BET and porosimetry analysis showed that this solid is mesoporous. TPR and XPS indicated an in situ reduction of this catalyst by hydrogen at 450°C which enabled to reduce Mo(VI) to lower oxidation states. The catalytic activities and isomerization selectivity's of 2-methylpentane (2MP) and 4-mthyl-1-pentene (4M1Pene) using MoAlP system, at atmospheric pressure yield a mixture of cracked and isomerized compounds were interpreted in terms of dual sites on the catalyst surface. The mechanism of hydrocarbon isomerization on MoAlP has been explained by a bifunctional mechanism, in which dehydrogenation - hydrogenation occurs on metallic sites and skeletal isomerization takes place on acidic sites. From correlation with XPS measurements, it can be concluded that Mo(V) species are responsible for acidic isomerization and that Mo(IV) species exhibit metallic dehydrogenation properties.

1. Introduction

The increasing interest in improving environmental protection and promoting efficiency of automotive motors encourages the formulation of new catalysts and development of new processes for gasoline production. Considering that branchedchain alkanes have higher octane numbers than linear alkanes, the use of gasoline that contains higher proportions of these compounds is an alternative in obtaining fuel with the required characteristics [1,2]. These compounds are an alternative to replace some additives normally used in gasoline to increase the octane number. Usually, they are obtained by isomerization reactions, which employ bifunctional catalysts formed by platinum supported over acid catalysts, usually platinum over chloride alumina [3–5].
The mixed aluminum orthophosphates are important materials that have application in several fields; they have been reported as catalysts for a wide range of reactions [6-20]. The catalytic behavior of these solids is due to their aspect acid-basic. Those properties play an important role in its catalytic aspect; some reactions require acid sites while others occur on basic sites. Moffat and coll. [21] showed that the phosphor atom functions as Lewis acid in $AlPO_4$ and that the acidity of Brönsted is due to the protons attached to the oxygen atoms on its

surface. Modification of aluminum starting salt [7] calcination at high temperatures [6-9], addition fluoride or sulfate ions [8] and the incorporation of other metals [18-22]improve the physico-chemical properties and catalytic activities of $AlPO_4$. In many cases, the catalytic performance is greatly dependent on the nature of the metal oxides, the metal oxide/$AlPO_4$ ratio, the method of preparation and operating conditions [6-22].

The majority of supported Mo catalysts are prepared by deposition of ammonium heptamolybdate on alumina. This salt is transformed partially into molybdate ions by interaction with basic OH groups of the alumina during impregnation. During calcination of the catalyst, molybdate ions react with OH groups under formation of stable Al-O-Mo bonds and release of water. Interaction between ammonium heptamolybdate or molybdate ions with OH groups of the support was the subject of numerous, spectroscopic studies confirming that the formation of an MoO_3 over layer is accompanied by gradual consumption of free OH groups [23-27]. It is believed that density and availability of OH groups and the MoO_3 loading are important factors controlling the formation of the resulting surface structures.

In this work, we have focused our attention on catalytic activity and selectivity of molybdenum oxide supported on aluminum orthophosphate, since studies on this kind of catalysts are much fewer and its composition seems to lead to better acid characters. This system was prepared and characterized in detail using BET surface area measurement, X-ray diffraction, IR, TPR and XPS. In situ XPS measurements as a function of reduction time VS temperature have been performed, allowing a detailed study of the reducibility of MoAlP.

The catalytic activities and isomerization selectivities of 2MP and 4M1Pene can be related to the specific Mo oxidation. The mechanism of hydrocarbon isomerization on MoAlP has been explained by a bifunctional mechanism, in which dehydrogenation - hydrogenation occurs on metallic sites and skeletal isomerization takes place on acidic sites, through a dimethylcyclo-propane intermediates.

2. Materials and methods

2.1. *Chemical Preparation*

All chemical products were of highest commercially available purity. Aluminum nitrate, orthophosphoric acid and ammonia were obtained from Merck.

$AlPO_4$ support (AlP) with a ratio of Al/P of 1 was obtained from aluminum nitrate and orthophosphoric acid by precipitation with aqueous ammonia until pH = 5 was reached.

$$\mathrm{Al(NO_3)_3, 9H_2O} \; + \; \mathrm{H_3PO_4} \xrightarrow{NH_3} \mathrm{AlPO_4, nH_2O} \; + \; \mathrm{NH_4NO_3}$$

The precipitate was allowed to stand at room temperature for 10h. After filtration, it was washed several times with distilled water. Then, the precipitate was dried at 100°C for 24hours and calcined at 400°C for 24hours.The MoAlP system was prepared by wet impregnation using an aqueous ammonium heptamolybdate solution (Merck, min 99%). After soaking the system in this solution for 2hours and evaporating the water the impregnated support was dried at 100°C for 24hours and then calcined in dry air at 400°C for 24hours.

2.2.*Physico-chemical characterisation*

2.2.1. Textural properties

The porous texture of AlP and MoAlP was characterized by analysis of nitrogen adsorption-desorption isotherms, determined at the boiling temperature of liquid nitrogen. The instrument used was a Sorptomatic Carlo Erba controlled by computer. The analysis of the isotherms was performed in accordance with the methodology proposed by Lecloux [28-29].

2.2.2. XRD analysis

X-Ray diffraction patterns were obtained with a Philips PW 1050 diffractometer using Ni-filtre radiation (λ_{Cu} = 1,5406 Å).

2.2.3. FTIR analysis

IR spectra were run in a Fourrier Nicolet 205 spectrometer on 1% samples in KBr pressed disks. The window of absorption is included between 4000 and 400 cm^{-1}.

2.2.4. TPR analysis

Temperature Programmed Reduction (TPR) measurements were carried out an automatic XSORB (Gira) apparatus. The catalyst (500mg) of catalyst was placed in a quartz reactor and it was reduced in stream of 5% H_2/Ar at a constant flow rate. The reduction temperature was increased from room temperature up to 900°C with a uniform heating of 5°C/min. The H_2 consumption was measured with a thermal conductivity detector.

2.2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoemission spectra (XPS) were obtained using an ESCA III VG instrument with Al Kα radiation. The binding energies of different Mo oxides were in agreement with those reported in the literature [30-35].

2.3. *Catalytic properties*

The catalytic study was carried out in a microcatalytic pulse reactor which was packed with catalyst held by small plugs of pyrex glass wool.The catalyst in the reactor was first reduced under H_2 flow of at a flow of 40ml/min at 450°C and standardized at 380°C for 2hours. 5µl of reagents was injected periodically into the reactor at a flow rate of 40ml/min.The reaction product were analyzed with Hewlett-Packard gas chromatograph equipped with a flame ionization detector using a capillary column (dimethyl siloxane, diameter 0,25mm and 60m in length). The total conversion, α (%) 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 product formed. In the reaction with 2MP or 4M1Pene, the 3MP/n-Hex ratio can be representative of the acidic aspect of the catalyst, because under these conditions the reaction leads to the most stable carbocation yielding 3MP [36].

3. Results and discussion

3.1. Physico-chemical characterisation

3.1.1. Textural properties

A porous texture study of AlP and MoAlP shows that these those systems are essentially mesoporous. The adsorption isotherms were classified as a type IV according to the BDDT classification [37] and the t-plot (which compares the nitrogen adsorption isotherm obtained on the studied porous solid and the standard isotherm determined on non-porous solids) presents a positive deviation from straight line, which is characteristic of mesoporous. This observation is confirmed by the type A hysteresis characteristic of cylindrical pores, according to Lippens and Boer's classification [38].The surface areas calculated by the generalized t-method (S_t) was found to tally with those obtained by the BET method (S_{BET}) (table I). The two samples have the same paces for the isotherms and the t diagrams. This means that the molybdenum does not assign the texture or the morphology of the support and consequently the geometry of the pores.

Table 1: Surface areas S_{BET} and S_t, pore volume (V_p) and pore volume distribution of AlP and MoAlP calcined at 400°C

Catal.	**SBET (m^2/g)**	**S_t (m^2/g)**	**V_p (cm^3/g)**	**Pore volume distribution (vol. %)**						
				>20 nm	***16-20***	***12-16***	***10-12***	***8-10***	***6-8***	***<6 nm***
AlP	129.5	129.2	0.55	18.79	20.69	26.04	19.50	11.10	3.87	0.01
MoAlP	129.6	122	0.65	53.03	20.98	12.75	7.24	3.51	2.35	0.13

The nitrogen adsorption as a function of the relative pressure was important for MoAlP comparatively to AlP. This must be due to the increase in of mesoporous concentration as confirmed by the results of table I. The examination of those results shows that the two samples are constituted principally of mesoporous.

3.1.2. X-ray diffraction (XRD)

This technique was adopted to ascertain cristallinity of the sample $AlPO_4$ and also to observe any possible changes in its structure that can occur during temperature treatment or impregnation. The characteristic diffractogram patterns for this solid calcined at temperatures lower than 850°C did not exhibit any peaks. Moreover, $AlPO_4$ or Mo/$AlPO_4$ (4Mo wt%) samples calcined at temperatures higher than 850°C showed several peaks indicating the crystalline structure of the sample. The later corresponds to the pseudo hexagonal one of tridymite, identified by its characteristic reflection at d = 4.4Å (2θ = 20.2°), d = 4.15Å (2θ = 21.4°) and d = 3.88Å (2θ = 22.9°).

Besides this, the bands became sharper as the treatment temperature increased up to 1050°C. In this sense, it has been reported that $AlPO_4$ tridymite usually exhibits abnormal XRD patterns, characterized by the presence or absence of some diffraction and by variations in intensity [39].

3.1.3. Infrared spectroscopy (IR)

Allspectra of AlP (treated at different temperatures) and MoAlP exhibited bands at 1200 - 650 cm^{-1} and all of these modes are relevant for PO_4^{3-} groups. In addition, the spectrum presents bands at 3430 and 1650 cm^{-1} (wide and intense) and was ascribed to O-H in -plane-bending vibration and O-H stretching vibrations respectively. These bands are departed with increasing temperature of calcination. An additional band was present at 700 cm^{-1} and can be attributed to Al-O bonds in combination with P-O bond groups. Examination of the spectrum of MoAlP and AlP treated at 400°C shows no important differences between the two samples.

3.1.4. Temperature Programmed Reduction (TPR)

The Temperature Programmed Reduction (TPR) of AlP calcined at 400°C does not present any hydrogen consumption indicating that AlP is irreducible in the range of temperature studied. On the other hand, the TPR spectra of MoAlP shown in figure 1, revealed that, at temperatures higher to 500°C, three reduction peaks. The first at 520°C is assigned to the reduction of Mo(VI) into Mo(V), the second at 700°C is due to the transformation of Mo(V) to Mo(IV) and the third one at 898°C is related to the transformation of Mo(IV) to Mo(0). The total consumption of hydrogen for these three steps is about 1,47.10^{-3}mol/g.

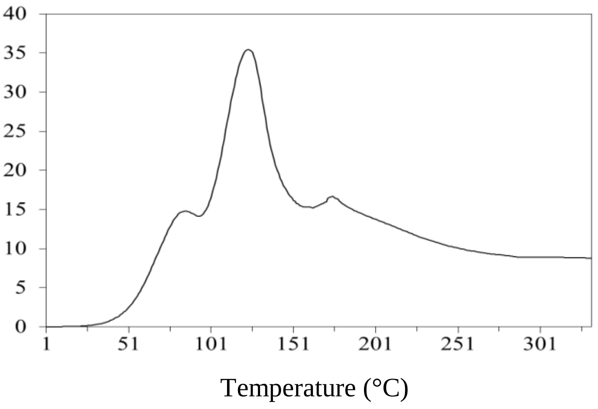


Figure 1: TPR pattern MoAlP

3.1.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to provide information on the oxidation state of Mo based AlP catalyst as a function of time and temperature reduction treatments. The Mo3d orbital band developed for MoAlP before any treatment with H_2 (Figure 2a) consists of a single doublet ($3d_{5/2}$ - $3d_{3/2}$) having binding energies values characterizing Mo in the state Mo(VI) observed at 231.9 and 235.2eV. The doublet $3d_{5/2}$ - $3d_{3/2}$ binding energies of reduced MoAlP catalyst shifts to lower values when the temperature and time of its reduction were increased.

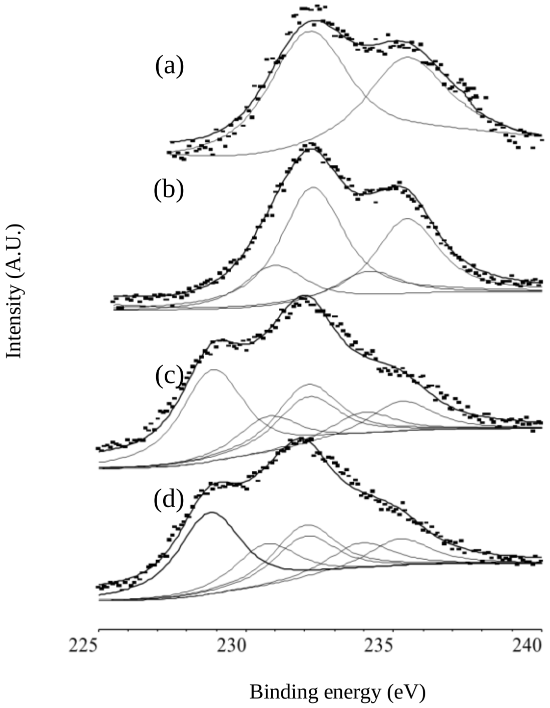


Figure 2 : The XPS of MoAlP 3d following different temperatures of in-situ treatments with H_2 for 2hour: (a) before any treatment, (b) 350°C, (c) 450°C, (d)

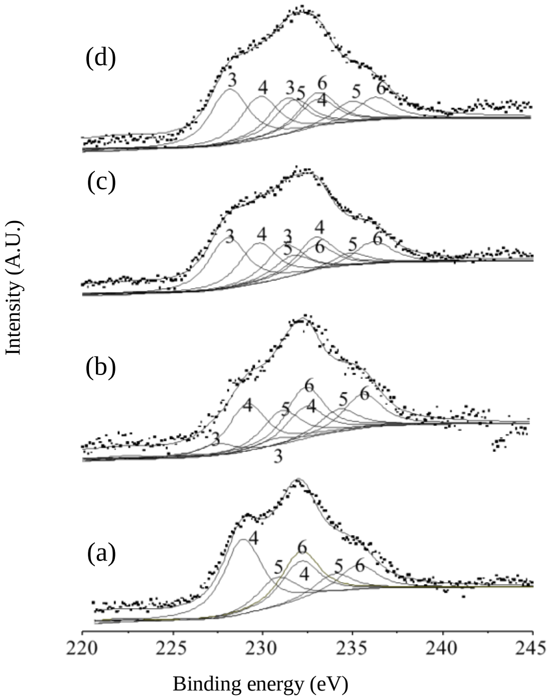


Figure 3 : The XPS of MoAlP 3d following different times of in-situ treatments with H_2 at 450°C: (a) 2h, (b) 4h, (c) 12h, (d) 17h.

An in-situ treatment of MoAlP by H_2 at 350°C for 2hours results in a partial reduction of Mo(VI) to two lower valence states with the $3d_{5/2}$ and $3d_{3/2}$ measured at 233.9 and 230.7 eV. Under these conditions the Mo(VI) is still more abundant than Mo(V) (Figure 2b). Further reduction by H_2 for 2hours of the same sample at increased temperature (450°C, 550°C) results in an increase in Mo(IV) (doublet 4) and Mo(V) (doublet 5) (51.8% Mo(IV), 20.8% Mo(V) and 27.4% Mo(VI)) as compared to Mo(VI) (doublet 6) (Figures 2c and 2d).

In situ reduction by hydrogen at 450°C for 4hours results in apparition of other peaks at 227,2 and 230,4 eV (Figure 3b) characteristic of Mo(III) (doublet 3). However, the reduction by hydrogen at 450°C for 12 and 17hours results in considerable decrease in the Mo(VI) relative concentration, as compared to Mo(V), Mo(IV) and Mo(III) (Figures 3c and d).The evolution of surface Mo species as a function of reduction time at 450°C is shown in figure 3. It is clear that the Mo(VI) surface concentration decreases rapidly during the first 2hours of reduction, accompanied at the same time with an increase of Mo(V) and Mo(IV). Then Mo(VI) contribution continuous to decrease slightly with reduction time at 450°C. After 4h/H_2 at 450°C the decay of Mo(V) is accompanied by an inverse of Mo(III). At higher time of reduction at 450°C no metallic molybdenum has been detected.

3.2. Catalytic properties

3.2.1. Optimization of the reaction conditions

The extreme sensitivity of the surfaces of catalysts to treatment, the nature of the active sites and mechanisms of reaction leads us to study the following objectives :

- The preparation of a surface conditioned by an appropriate reduction, which requires optimization of experimental conditions to check for side effects (diffusion phenomena, heterogeneity of the catalytic bed etc.).
- The determination of intrinsic catalytic properties of the catalysts with respect to various hydrocarbons contact reactions (alkanes, alkenes and cyclane).

The catalytic experiments were carried out on the MoAlP catalyst at a given reaction temperature of 380°C. Each catalytic reaction has been repeated several times in order to ensure reproducibility of results using a pulse catalytic reactor mode.

3.2.1.1. Effect of the amount of the catalyst

We studied the catalytic properties of four amount of the catalyst (100, 150, 200 and 250mg) in transforming the 2MP on MoAlP previously treated in situ under hydrogen (40cm^3/ min) at 450°C for 17 hours. For each of these amounts we conducted a series of catalytic tests at 380°C by injection of 5µl of 2MP. Between two catalytic tests the catalyst is purged with a hydrogen flow for 30min at 380°C.

Whatever the catalyst mass, we noticed that the selectivity isomer products has decreased from 73 to 62% (Figure 4a) and remains almost constant during the first six experiments (equivalent to 3 hours under hydrogen). The ratio 3MP / n-Hex is also independent of the mass of the catalyst and is stable in the first six tests (Figure 4b). In Figure 4c, it appears that, contrary to what was expected, the rate is lower as the mass of catalyst is important. So it seems that the number of active sites for the reaction of 2MP is different for each of the four masses, although they have been treated in the same conditions.

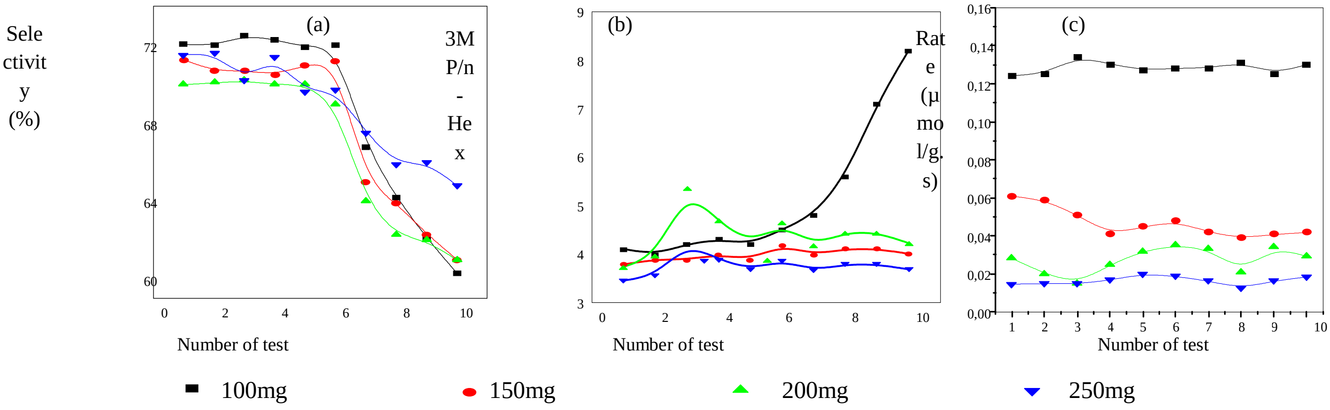


Figure 4 : Evolution of the selectivity, the ratio of the 3MP/n-Hex and rate of reaction with the number of catalytic testing at 380°C on different masses of catalyst in the isomerization of 2MP

Tableau 2 : Effect of the amount of the catalyst in the isomerization of 2MP

Amount (mg)	**α(%)**	**r (µmol/g.s)**	**C_1**	**C_2**	**C_3**	**iC_4+nC_4**	**iC_5+nC_5**	**22DMB**	**23DMB**	**3MP**	**n-Hex**	**MCP**	**CH**	**Siso(%)**	**3MP/n-Hex**
100	9.27	0.12	7.5	2.2	13.4	1.6	3.2	0	9.9	48.9	11.6	1.1	0.6	72.1	4.2
150	6.79	0.07	7.7	2.4	13.4	1.9	3.5	0	10	48.4	10.8	1.2	0.7	71.1	4.48
200	4.24	0.03	7.3	2.6	13	1.9	3.5	0	11.1	47.2	11.5	1.2	0.7	71.7	4.1
250	2.7	0.02	7.7	2.2	13.3	1.8	4.1	0	10	48	11.1	1.1	0.7	70.9	4.32

3.2.1.2. Effect of reduction time

Having in mind the XPS results concerning the reduction of MoAlP by H_2 as a function of temperature and reduction time, we reported the catalytic results obtained using MoAlP before and after reduction at different times.

Before reduction

The first catalytic test (before reduction), carried out on MoAl after calcination at 400°C during 24 hours and keeping the temperature at 380°C (temperature of the reaction) under hydrogen, does not reveal any activity.

After reduction

A reduction of catalyst at 450°C during 2 hours induces a weak activity and various evolutions of the catalytic behavior can be distinguished according to the duration of the treatment under hydrogen and as an example, we notice that under the experimental conditions chosen, the selectivity in isomer products increases until reaching a maximum of 72% at the end of 17 hours of reduction.

- The treatment of 100mg of catalyst under hydrogen at various periods ($0 < T < 17h$) led to an increase of activity (Table 3). In this time interval of reduction, the isomer product mainly formed is the 3MP.
- For the formed products of cracking, we notice a certain stability of the propane selectivity during the 17 hours of reduction. The ethane and butanes (iC4 + nC4) are formed in equivalent proportions ($\approx$ 2.5%). The iC4/nC4 ratio is worth approximately 3, this ratio gives an account of the probability of successive reactions which occur on the surface of the catalyst, i.e. the nC_4 does not seem to be formed directly from the 2MP, its formation would require at least two C-C breakings of the reagent.

When we extend the time of reduction beyond 17 hours, a fall of the selectivity in isomer products and an increase of the activity (Table 3) are observed. The decrease of the selectivity in isomer products is accompanied, consequently, with an increase in the quantity of the products of cracking. The methane selectivity reaches more than 35% which seems to indicate that the intermediate species of reaction are strongly bound to the surface and undergo a multiple cracking before desorption.

Table 3: The influence of reduction time under hydrogen at 450°C on the reactivity and the product distribution of the reaction with 2MP at 380°C.

reduction time (h)	α(%)	**r (µmol/g.s)**	**C_1**	**C_2**	**C_3**	**iC_4+nC_4**	**iC_5+nC_5**	**22DMB**	**23DMB**	**3MP**	**n-Hex**	**MCP**	**CH**	**Siso (%)**	**3MP / n-Hex**
2	2.91	0.039	6.9	3.4	0	1.1	2.4	0	11.7	52.6	12.1	0	0	76.4	4.38
4	3.62	0.049	7.7	2.2	14.1	4.7	2.5	0	13.8	44.2	10.8	0	0	68.8	4.1
8	7.19	0.097	6.5	3.2	12.8	4	2.5	0	11.1	47.2	11	1.1	0.6	71	4.3
12	9.89	0.131	8.8	3.3	11.8	4	2.6	0	9.7	42	13.8	2.4	1.6	69.5	3.04
17	9.27	0.12	7.5	2.2	13.4	1.6	3.2	0	9.9	48.9	11.6	1.1	0.6	72.1	4.2
23	11.43	0.154	10	5.6	16.1	4.5	3.7	0	8.6	34.5	7.9	4.9	4.4	60.3	4.37
36	28.72	0.386	22	10.2	8.8	9.2	10	0	5.5	22.4	7.8	2.2	1.8	39.7	2.87
40	38.01	0.511	25.3	15	9.5	13.1	13.7	0	3.4	13.1	4.6	1.2	1.1	23.4	2.85
44	43.09	0.579	29	19.3	11.1	13.6	12.3	0	1.2	8.4	3.7	0.8	0.6	14.7	2.27
48	51.02	0.986	35.4	19.5	12.9	15	12.4	0	0.1	2.9	1.4	0.2	0.2	4.8	2.07

C1: methane; C2: ethane; C3: propane; iC4: iso-butane; nC4: n-butane; iC5: iso-pentane; nC5: n-pentane; 22MB: 2,2-dimethylbutane, 23MB: 2,3-dimethylbutane 2MP: 2-methylpentane; 3MP: 3-methylpentane; n-Hex: n-hexane; MCP: methycyclopentane, CH: Cyclohexane, α : total conversion and S_{iso}: selectivity in isomerized products.

3.2.1.3. Apparent activation energy

In order to ensure that we work under reaction conditions where the reaction rate is governed by chemical kinetics and not by diffusion phenomena due to transport of the material, we calculated the apparent activation energy in studying the evolution of MoAP 100mg of activity treated in hydrogen at 450°C for 17 hours depending on the reaction temperature. These conditions were chosen because they allow the production of stable surfaces for several hours under hydrogen (3 hours).

Tests according to the temperature (between 350 and 450°C) were carried out on a catalyst 100mg sample and confirm the stability of the surface. The apparent activation energy is obtained by plotting the curve Ln r = f (1 / T) according to the law Arrhenius:

$$r = A\exp\frac{-E_a}{RT}$$

Ea : the apparent activation energy,
r : the reaction rate (μmol/g.s),
A : the pre-exponential factor,
R :*the ideal gas constant*
T : the reaction temperature (°C).

The overall activation energy calculated in this study is 20.16kcal/mol. This value is characteristic of a bifunctional acid catalysis which allows us to show that the reaction rate is not governed by a diffusion regime in the reaction temperature range chosen ($350°C<T_{reaction}<450°C$) [2].
From these results of the optimization of the experimental conditions for studying the catalytic properties of MoAlP in isomerization of the 2MP, we have:

- shown that the activity of the catalyst depends on its mass. Better conversion is achieved with a 100mg mass.
- highlighted the existence of a heterogeneity in the catalytic bed during the treatment of the catalysts under hydrogen. This heterogeneity is a function of the mass of catalyst introduced into the reactor.
- highlighted the evolution of the catalytic properties of the catalysts during their reduction in hydrogen. Good selectivity is obtained after reduction for 17 hours at 450°C.
- prepared a stable surface for several hours under a hydrogen stream by 100mg of catalyst reduction during 17 hours at 450°C and checked that under these experimental conditions ($350°C<T_{reaction}<450°C$) the rate of reaction is not governed by diffusion phenomena.

All these findings led us to use a catalyst 100mg mass treated in hydrogen at 450°C for 17 hours for our study of intrinsic MoAlP developed in following the article.

3.2.2. Reactivity of 2MP on MoAlP reduced for different periods at 450°C

In order to know if, during the experiment with successive pulses, the regular injections of the 2MP contribute, by deposit of hydrocarbon residues on the surface of the catalyst or by the formation of a phase of the carbide type (MoC_x) or the oxycarbide (MoO_xC_y), to a modification of the catalytic behavior of MoAlP observed according to the time of reduction or if, only the reduction of the surface of MoAlP is at the root of this behavior. We placed various solid samples under hydrogen flow at 450°C during 2, 8, 12, 17 and 23 hours then we carried out a catalytic test on each one of them.
The comparison of the results shown in table 4 with those obtained during the successive pulses experiments (Table 3) allows us to notice that the evolution of the catalytic behavior of MoAlP with regard to the reaction of the 2MP in terms of the duration of reduction under hydrogen, during the reduction of catalyst, is the same whether we carry out regular or irregular injections of the 2MP.
The modifications of the catalytic behavior are, therefore, induced by the reduction under hydrogen of the surface of the catalyst, which probably leads to the development of molybdenum oxides. This is also proved by the analysis of the catalyst before and after the catalytic test. Indeed, the analysis by means of infra-red spectroscopy and X-rays diffraction of MoAlP before and after the catalytic test, did not reveal any modification thereof. The experiments concerning the reactivity of the 2MP on MoAlP showed that:

- The catalytic properties of MoAlP vary during their reduction under hydrogen.
- The unreduced surface of MoAlP is inactive in the reaction of transformation of the 2MP but becomes active after reduction.

The catalytic behavior of this catalyst evolves in terms of the oxidation degree of molybdenum at the surface. We then move from a surface possessing isomeric properties primarily leading to the formation of the 3MP, to a surface of metallic nature fostering cracking:

- The reduction of initial surfaces by hydrogen leads at first to the formation of hydro-dehydrogenation sites, which we allocate to Mo^{4+} species, allowing the reactivity of the 2MP according to a bifunctional mechanism.
- The reduction of Mo^{4+} to Mo^{3+} results in an important diminution of the selectivity in isomer products and the preferential methane formation resulting from an extensive successive cracking of the 2MP.

Table 4: The effect of time reduction under hydrogen on product distribution in the conversion of 2MP at 380°C.

reduction time (h)	α(%)	r (µmol/g.s)	C_1	C_2	C_3	iC_4+nC_4	iC_5+nC_5	22DMB	23DMB	3MP	n-Hex	MCP	CH	Siso (%)	3MP / n-Hex
2	2.21	0.03	7	3.6	11.7	1.3	2.6	0	12.1	50.3	11.4	0	0	73.8	4.41
8	8.01	0.11	7.3	3.8	13.1	3.6	2.7	0	12.3	45.2	12	0	0	69.5	3.76
12	10.15	0.14	8.8	3.5	11.4	3.5	2.5	0	10.5	45.1	10.9	2.7	1.1	70.3	4.14
17	11.12	0.15	7.5	3.3	14.3	2.3	1.5	0	10.3	48	11.6	1	0.4	71.3	4.14
23	12.53	0.17	11.1	6.1	17	5.4	4.3	0	7.5	32.5	8.3	5.3	2.5	56.1	3.91

3.2.3. Reactivity of the 4M1Pene on MoAlP

We have presented in this paragraph the reactivity of the 4M1Pene on MoAlP in order to have additional information to understand the reaction mechanisms.

We have studied, according to the same experimental procedure as for the 2MP ($m_{catalyst}$ = 100mg, $T_{reaction}$ = 380°C, hydrogen flow = 40cm^3), the catalytic properties of MoAlP by experiments with successive pulses. In the case of the 4M1Pene and of the MCP, we have placed a hydrogenator on the outlet side of the reactor in order to hydrogenate the olefinic products before the analysis by CPG.

The unreduced MoAlP catalyst has not led to any transformation of the saturated molecules (2MP, 3MP and n-Hex). However, it presents a certain activity under the reaction mixture (H_2 + 4M1Pene) and an important selectivity in 3MP (87.7%).

In table 5, we illustrated the results of the tests carried out on the unreduced surfaces within the 4M1Pene as reagents.

Table 5 : Reactivity and products distribution in the conversion of 4M1Pene at 380°C on MoAlP

Catal.	α(%)	r (µmol/g.s)	C_1+C_5	C_2+C_4	C_3	22DMB	23DMB	2MP	3MP	n-Hex	MCP	CHA	Siso(%)	3MP / n-Hex
MoAlP unreduced	4.8	0.068	1.2	0.9	0.3	0	5.8	0	87.7	4.1	0	0	97.6	21.4
MoAlP reduced at 450°C/17H	0.16	12.2	12.5	4.8	13.0	0	13.4	0	42.5	10.6	1.8	1.4	69.7	4.01

The distribution in products of reaction is completely a feature of an acid isomerization mechanism by the formation of the carbonium ion according to the following scheme:

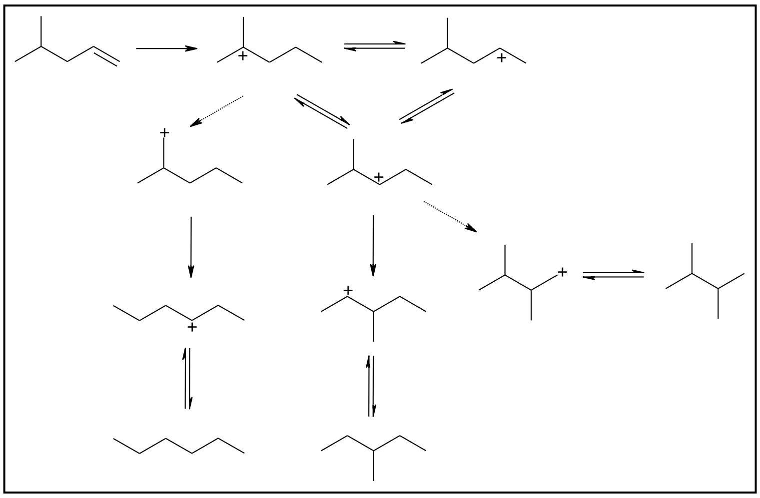


Figure 5: Isomerization of the 4M1Pene in 23DMB, 3MP and n-Hex by an acid mechanism by formation of carbonium ions according to Garin and Coll, [40]

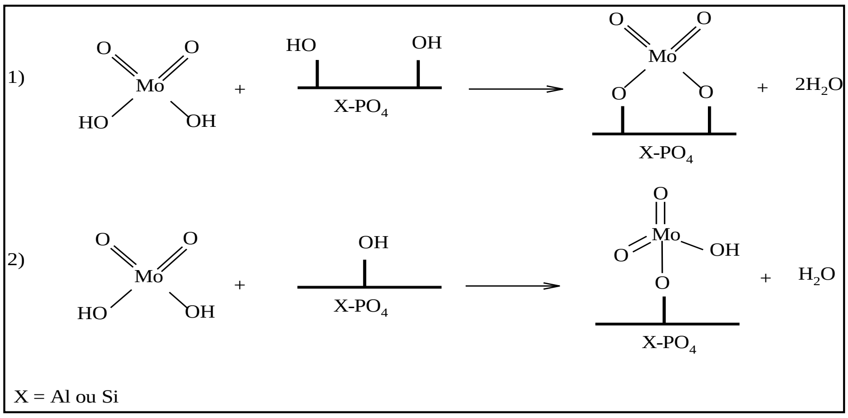
The preferential formation of the 3MP is explained by the great stability of the secondary carbocation compared to the primary carbocation necessarily induced to form the n-Hex or the 23DMB.

The results resulting from the characterization by XPS of unreduced surfaces, enable us to suggest that the active sites in the isomerization of the 4M1Pene within 380°C are sites of Brönsted (OH groups) created during the adsorption of hydrogen on the surface, The inactivity of this solid in the reaction of the 2MP can be explained by the absence of sites of hydro-dehydrogenation able to dissociate the C-H bonds of the alkane to form an olefin according to a bifunctional mechanism.

4. Discussions and mechanisms

Throughout this study we have noticed that:

- The calcined surface of MoAlP is active under the reaction mixture (H_2 + 4M1Pene) contrary to the mixtures of the 2MP with H_2 for which a modification by hydrogen is necessary to the development of the active sites. The important selectivity in isomer products (97,6%), the high 3MP/n-Hex ratio isomers (≈22) is typically a feature of an acid monofunctional catalysis with formation of carbonium ions as an intermediate of reaction.
- The fact that no treatment of activation of surfaces under hydrogen is necessary to the development of their activities indicates that the acid sites responsible for the isomerization of the 4M1Pene are formed at the moment of the calcination of catalyst. According to Vit [26-27] two types of sites can be created at the time of the calcination of catalysts based on molybdenum oxide: acid sites of Lewis or of Brönsted according to the scheme of figure 6. We then propose the formation, at the level of surface, at the time of the calcination under air at 400°C, primarily of acid sites of Lewis Mo^{6+}. The passage of a hydrogen flow would lead to the formation of acid sites of Brönsted (OH) by adsorption of hydrogen on the surface, the thing which would explain the gain of activity in this case. A transformation of acid sites of Lewis into acid sites of Brönsted is also conceivable,
    - The results obtained by XPS of the MoAlP system suggested the presence on the surface of polymeric molybdate species where molybdenum is in a tetrahedral environment.



1- Reaction of a molybdenum atom with two OH groups to form an acid site of Lewis,
2- Reaction of a molybdenum atom with an OH groups to form an acid site of Brönsted.

Figure 6 : molybdate Species where molybdenum is in a tetrahedral environment [26-27]

When the catalytic tests are carried out on reduced surfaces at 450°C during 17hours, the conversion is more important than that obtained on calcined surfaces in the case of the 4M1Pene. The proportion of the 3MP is weaker, which results in a decrease of the 3MP/n-Hex (≈4) ratio, we can suppose that these differences in activity and distributions in isomer products following the under hydrogen treatment are bound to a modification of nature and number of acid sites initially present on the surface of calcined catalyst. This evolution of the catalytic properties can be allotted to the formation of Mo^{4+} cations, as observed in XPS. The surfaces are characterized, whether the reagent is the 2MP or the 4M1Pene, by some selectivity in high isomer products (>70%), a 3MP/n-Hex≈ 4 ratio and a better activity in the case of olefin. These distributions in reaction products and the difference of the transformations speeds of both the 2MP and the 4M1Pene are features of a bifunctional acid catalysis. We allot the hydro-dehydrogenating nature to the Mo^{4+} cations and the isomeric function of olefins to the OH groups which are present at the level of surface.

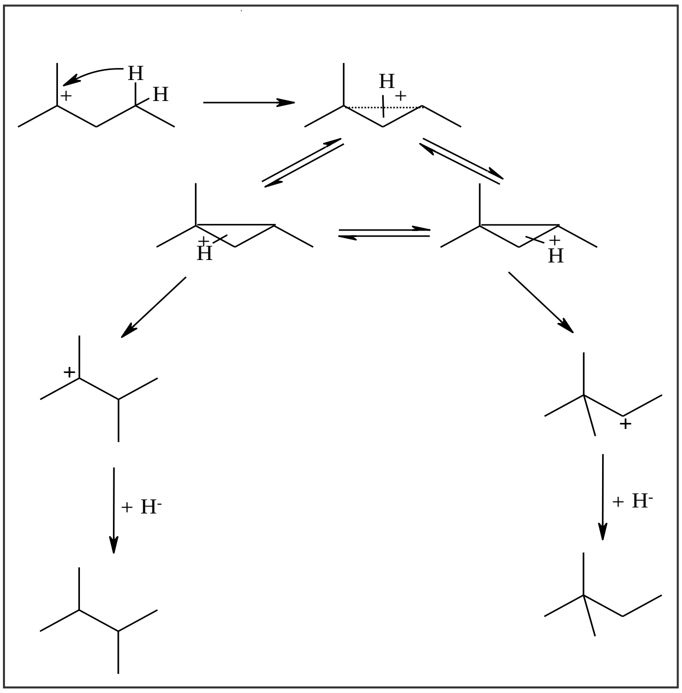


Figure 7: Mechanism with cyclopropanic complexes

The isomerization of the 2MP or the 4M1Pene is carried out by a succession of reactions which can be gathered in two stages. A first stage corresponds to the formation of the tertiary carbocation. In a second stage, the load of the carbocation interacts with the "carbon-hydrogen" bond σ located in position γ in order to give cyclopropanic complexes (Figure 7) which can be in resonance between 3 mesomeric forms which do not have the same stability because of the number of methyl groupings in α of the positively-charged center. Consequently, the formed carbonium ions do not have same stability since they are tertiary or secondary. Hence the difficulty in obtaining the 22DMB arises.

Conclusion

From the foregoing results obtained in the conversion of 2MP and 4M1Pene at 380°C, with hydrogen at atmospheric pressure, it was clear that the MoO_3 supported $AlPO_4$ catalyst the content of which in molybdenum oxide is close to a monolayer (4% w) had interesting properties of isomerization as well alkanes as alkenes.

The Characterization of MoAlP system by XPS led us to suggest the presence on the surface of polymeric molybdate species where molybdenum is in a tetrahedral environment, we also noticed a diffusion of molybdenum in the carrier during the treatment in hydrogen at 450°C.

A correlation between the results of physicochemical characterizations of MoAlP and distributions of the reaction products allowed us to assign some of the active sites in oxide phases. Thus the mechanistic approach of our study led us to postulate:

- The coexistence of Lewis's acid sites (Mo^{5+} stemming from the reduction of the cations Mo^{6+}) and of acid sites of Brönsted (group OH) on the surfaces of phosphates. These sites would be responsible for the isomerization of skeleton olefins according to an acid nonfunctional mechanism bringing in intermediate species.
- The appearance of a metallic function with the reduction of Mo^{5+} in Mo^{4+} and an evolution of the strength of the acid sites. In this case the system becomes active in the isomerization of alkanes as well as alkenes and presents important catalytic properties. To explain the distributions of products of reaction, we proposed the coexistence of a mechanism bifunctional with the participation of the molybdenum cations (metallic function responsible for the hydro-dehydrogenation) and groups OH (acid function responsible for isomerization).

References

1. P.J. Kuchar. J.C. Bricker. M.E. Rhine. R.S. Haizmann. *Fuel Process. Technol*. 35 (1993) 183.
2. M. Belloum. Ch. Travers. J.P. Bournonville. *Rev. de L'Institut Français du Pétrole* 46 (1991) 89.

3. J.K. Lee. H.K. Rhee. Catal. Today 38 (1997) 235.
4. A. Van of Runstraat. J.A. Kamp. P.J. Stobbelaar. J.V. Grondelle. S. Krijnen. R.A.V. Santen. *J. Catal*. 171 (1997) 77.
5. A.K. Aboul-Gheit. S.A. Ghoneim. A.A. Al-Owais. *Appl. Catal. A: Gen*. 170 (1998) 277.
6. F. M. Bautista, J. M. Campelo, D. Luna, J. M. Marinas and A. A. Romero, *Appl. Catal*. A96 (1993) 175-199.
7. J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, *J. Catal*. 111 (1988) 106-119.
8. F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas, A. A. Romero, J. A. Navio and M. Macias, *J. Catal*. 145 (1994) 107-125.
9. F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas and A. A. Romero, *Appl. Catal*. A 104 (1993) 109-135.
10. J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, *J. Catal*. 102 (1986) 447-451.
11. J. M. Campelo, A. Garcia, J. F. Herencia, D. Luna, J. M. Marinas and A. A. Romero, *J. Catal*. 151 (1995) 307-314.
12. J. M. Campelo, R. Chakraborty and J. M. Marinas, *Catal. Lett*. 54 (1998) 91-93.
13. F. M. Bautista and B. Delmon, *Appl. Catal*. A 130 (1995) 47-65.
14. A. Blanco, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas and A. A. Romero, *J. Catal*. 137 (1992) 51-68.
15. F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas and A. A. Romero, React. *Kinet. Catal*. Lett. 57 (1996) 61-70.
16. J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, *Appl. Catal*. 10 (1984) 1-17.
17. F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas, M. C. Moreno and A. A. Romero, *Appl. Catal*. 170 (1998) 159-168.
18. J. W. Bae, S. M. Kim, S. H. Kang, K. V. R. Chary, Y. J. Lee, H. J. Kim, K. W. Jun. *J. Mol.Catal. A: Chemical* 311 (2009) 7–16.
19. M. Kacimi, M. Ziyad, L. F. Liotta, *Catalysis Today* 241 (2015) 151-158.
20. O. Ouariach, M. Kacimi and M. Ziyad, *Appl. Catal*. A General, Volume 503 (2015) 84-93.
21. J. B. Moffat, R. Vetriel and B. Viswamathan, *J Mol Catal* 30 (1985) 171-180.
22. K. Mtalsi, T. Jei, M. Montes and S. Tayane, *J. Chem. Technol. Biotechnol*. 76 (2001) 128-138.
23. V. Keller, F. Barath and G. Maire, *J. Catal*. 189 (2000) 269-280.
24. M. E. Harlin, L. B. Backman, A. O. I. Krause and O. J. T. Jylhä, *J. Catal*. 183 (1999) 300-313.
25. N. Giordano, A. Vaghi, J. C. J. Bart and A. Castellan, *Symposium on the Mechanisms of Hydrocarbon Reactions, Siofok, Hungary, June* (1973) 245-263.
26. Z. Vit and M. Zdrazil, *J. Catal*. 171 (1997) 305-312.
27. Z. Vit, *Surf. Interface Anal*. 27 (1999) 861-864.
28. A. J. Lecloux, in *Catalysis Science and Technology*, Ed by J. R. Anderson and M. Boudart, Springer-Verlag, Berlin Vol 2 (1981) 171-227.
29. A. Lecloux, and J. P. Pirard, *J. Colloid. Interface Sci*. 70 (1979) 265-281.
30. D. S. Zingg, L. E. Markovsky, R. E. Tischer, F. R. Brow and D. M. Hercules, *J. Phys. Chem*. 84 (1980) 2898-2906.
31. R. B. Quincy, M. Houalla, A. Proctor and D. M. Hercules, *J. Phys. Chem*. 94:1 (1990) 520-1526.
32. M. Yamada, J. Yasumaru, M. Houalla and D. M. Hercules, *J. Phys. Chem*. 95 (1991) 7037-7042.
33. A. Katrib, V. Logie, M. Peter, P. Wehrer, L. Hilaire and G. Maire, *J Chim Phys* 94 (1997) 1923-1937.
34. A. Katrib, P. Leflaive, L. Hilaire and G. Maire, *Catal. Lett.* 38 (1996) 95-99.
35. Y. Holl, R. Touroude, G. Maire, A. Muller, P. A. Engelhard and J. Grosmangin, *J. Catal*. 104 (1987) 202-210.
36. F. Garin, V. Keller, R. Ducros, A. Muller and G. Maire, *J. Catal*. 166 (1997) 136-147.
37. S. Brunauer, L. S. Deming, W. S. Deming and E. Teller, *J. Am. Chem. Soc*. 62 (1940) 1723.
38. B. C. Lippens and J. H. de Boer, *J. Catal.* 4 (1965) 319.
39. F. d'Yvoire, C. R. *Acad. Sci. Paris. Ser*. C 247 (1958) 297.
40. F. Garin, V. Keller, R. Ducros, A. Muller et G. Maire, *J. Catal.*166 (1997) 136.

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