



Catalytic activity-surface structure correlation of molybdenum-based catalysts

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ABSTRACT

Controlled reduction temperature of equivalent 5 monolayer of molybdenum trioxide deposited on TiO₂ enabled us to obtain two distinct, well-defined states of molybdenum surfaces. The reduction was performed using hydrogen. A stable bifunctional (metal–acid) MoO₂(H_x)_{ac} phase is obtained at reduction temperature of 673 K. In this phase, the metallic function consists of delocalized π electrons over Mo atoms placed along the C-axis of the deformed rutile structure of MoO₂. The acidic function consists of Brønsted Mo–OH group(s). At reduction temperature of 873 K, a metallic Mo(0) state is obtained. The metallic function consists of large particle sizes (clusters) of Mo atoms. Hydroisomerization of *n*-hexane and 1-hexene to methyl pentanes and dimethyl butanes are obtained on the bifunctional phase. On the other hand, hydrogenation, hydrocracking and formation of benzene occur on the metallic Mo(0) state. Aromatization of cyclohexene and cyclohexane is performed by the bifunctional MoO₂(H_x)_{ac} surface at 623–673 K reaction temperatures. The absence of such aromatization catalytic processes in the case of *n*-hexane and 1-hexene on MoO₂(H_x)_{ac} is attributed to the fact that cyclization of 1-hexene to cyclohexene, the pathway for benzene formation, is structure-sensitive catalytic process. It occurs on the Mo(0) large particle size(s). Apparently, molybdenum Mo–Mo atoms placed along the C-axis (atomic wire) in MoO₂(H_x)_{ac} phase do not favor this cyclization process. On the contrary, aromatization of cyclohexene and cyclohexane are structure-insensitive catalytic processes.

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1. Introduction

Hydroisomerization of C₅–C₆ light alkanes is an important catalytic process that increases the octane number of the gasoline pool and eliminates undesired aromatic compounds. In general, platinum-based catalysts deposited on chlorinated alumina or zeolite(s) are the most commonly used in the industry and in fundamental research [1–3]. In these catalysts, platinum is present in the form of finely dispersed particles deposited on the surface of alumina or zeolite(s) substrates. In the case of *n*-hexane reactant, the catalytic isomerization process has been rationalized in terms of the bifunctional mechanism [4]. Dehydrogenation of *n*-hexane and hydrogenation of the isomerized olefin are performed by the metallic function of the Pt particles. On the other hand, acidic function is responsible for the isomerization of the produced olefin via carbenium ion mechanism. Aromatization of *n*-hexane to benzene, occurs on Pt-based catalysts as a by-product [5]. The formation of benzene is temperature dependent. The maximum selectivity of *n*-hexane aromatization is obtained at 723 K [6]. Increasing concern and strict environmental regulations, world-

wide imply the elimination of toxic benzene from gasoline. In previous works, we have presented new types of catalytic systems as possible replacement of Pt-based catalysts for the isomerization of light alkanes [7–10]. The catalytic active phase is designated as MoO₂(H_x)_{ac} (M = Mo, W) bifunctional phase. In this system, the metallic function is rationalized in terms of delocalized π electrons above the M–M atoms placed along the C-axis of the deformed rutile structure of MO₂. Since hydrogen is present in the reaction mixture, Brønsted acidic function(s) M–OH are formed on the surface following the dissociation of hydrogen molecules by the MO₂ metallic function. Catalytic performances of the MoO₂(H_x)_{ac} system in terms of hydroisomerization of alkanes are equal or better than those obtained by the Pt-based catalysts. Interestingly, benzene was not formed as a by-product of *n*-hexane reactions on this bifunctional system at reaction temperatures up to 673 K. Moreover, it was possible to produce metallic Mo(0) surface following reduction temperature increase beyond 673 K. In this work, we present two well-defined MoO₂(H_x)_{ac} and Mo(0) catalytic systems obtained at different reduction temperatures. Benzene was formed as a by-product of *n*-hexane reaction on the metallic Mo(0) phase at reaction temperatures above 653 K. This is not the case in the bifunctional MoO₂(H_x)_{ac} phase. Apparently, *n*-hexane transformation to benzene is surface structure-sensitive catalytic reaction. To elucidate these catalytic processes, we have conducted a systematic study involving the reaction of 1-hexene,

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cyclohexene and cyclohexane, considered as possible reaction intermediates for *n*-hexane aromatization, using both $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ and $\text{Mo}(0)$ systems.

In situ characterization by XPS-UPS techniques were employed to identify the chemical composition of the upper surface layers responsible for the catalytic activity of the systems under investigation. Surface morphology is obtained using high resolution transmission electron microscopy (HRTEM).

2. Experimental

2.1. Catalyst preparation

The equivalent 5 monolayers of molybdenum trioxide were deposited on TiO_2 using ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (99.9%) supplied by STREM Chemicals. Titanium dioxide TiO_2 is Degussa P-25 (25% rutile) with pore volume of $0.5\text{ cm}^3/\text{g}$ and BET surface area of $50 \pm 5\text{ m}^2/\text{g}$. Supported catalyst is prepared by impregnating the appropriate amount of molybdenum in ammonium heptamolybdate salt, following the method described by Pines et al. [11].

2.2. Catalytic tests

The catalytic experiments were performed using 100 mg of the catalyst in a fixed bed quartz reactor. These processes were conducted in pulse mode under continuous hydrogen flow rate of $40\text{ cm}^3/\text{min}$. The catalytic products were analyzed by gas chromatography using 100 m (Petrocol-DH) column and a flame ionization detector. Catalytic experiments were repeated several times in order to ensure the reproducibility of the results

2.3. Catalysts characterization

Characterization of the samples by XPS was conducted using VG Scientific ESCALAB-200 spectrometer. The radiation source was an Mg K α operating at a power of 300 W (15 kV, 20 mA). UPS He(I) resonance 584 Å radiation of 21.217 eV was employed for the VB energy region measurements. Vacuum in the analysis chamber was below 7×10^{-9} mbar during all measurements. In situ reduction was conducted in a high-pressure gas cell housed in the preparation chamber, with hydrogen flow rate at 200 mL/min. Binding energies were based on the carbon contamination C 1s at 284.8 eV within an experimental error of ± 0.1 eV. High resolution transmission electron microscopy measurements were conducted using 3010 JEOL instrument.

3. Results and discussion

3.1. Characterization of the catalysts by surface techniques

The XPS-UPS experiments of the $\text{MoO}_3/\text{TiO}_2$ before and after hydrogen reduction at different temperatures were carried out in situ to avoid any re-oxidation of the sample following its exposure to air. Assignment of the different molybdenum oxidation states is done based on the XPS of the Mo ($3d_{3/2,5/2}$) spin-orbit components binding energies. These BEs are at 235.85 and 232.65 eV for MoO_3 , 234.9 and 231.7 eV for Mo_2O_5 , 232.3 and 229.1 eV for MoO_2 , 230.85 and 227.7 eV for $\text{Mo}(0)$ [12]. Moreover, molybdenum dioxide is characterized by additional structure in terms of the presence of two π (0.4 eV) and σ (1.4 eV) bands in the VB energy region [13]. Therefore, additional information concerning the presence of MoO_2 phase in the upper 4–5 monolayers of the sample surface could be obtained from the UPS spectrum.

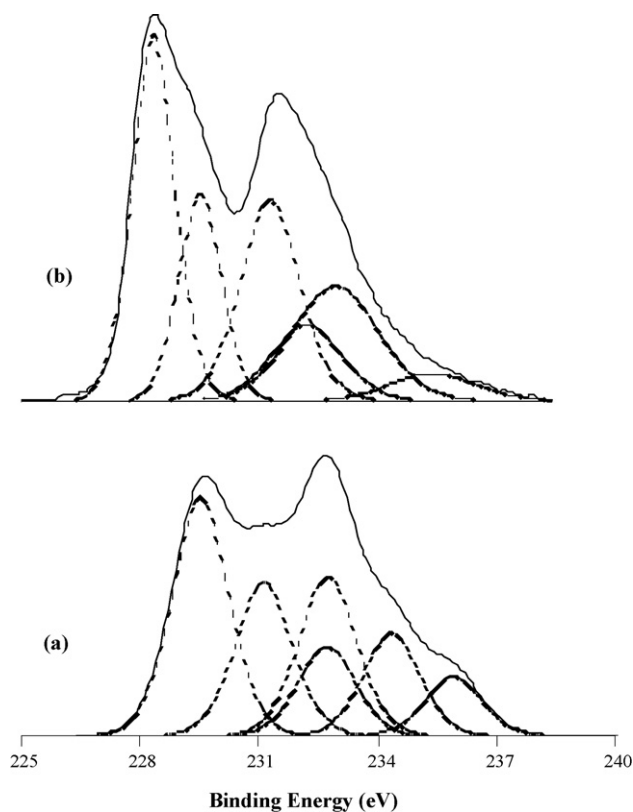


Fig. 1. The XPS of Mo (3d) in $\text{MoO}_3/\text{TiO}_2$, (a) after reduction at 673 K for 2 h and (b) after reduction at 873 K for more than 24 h.

The XPS of the $\text{MoO}_3/\text{TiO}_2$ sample prior to any reduction treatments shows the presence of two distinct spectral lines at 235.85 and 232.65 eV, characteristics of the MoO_3 phase. In situ sample exposure to hydrogen at 673 K for 12 h results in the formation of MoO_2 . The presence of this phase is characterized by the Mo ($3d_{3/2,5/2}$) at 232.3 and 229.1 eV (Fig. 1a) as well as the π and σ bands, measured at 0.4 and 1.4 eV (Fig. 2a). Moreover, aside from the main oxide oxygen spectral line at 530.6 eV, a shoulder at 531.6 eV was observed (Fig. 3a). The presence of this low intensity spectral line is attributed to the presence of Brønsted Mo-OH acidic group(s) on the sample surface. The formation of the Brønsted acidic group(s) is rationalized as follows: dissociation of hydrogen by MoO_2 metallic function produces active H atoms which are bonded to surface oxygen. Therefore, the presence of both metallic and acidic functions on the Mo-Mo atoms placed along the C-axis of the deformed rutile structure of MoO_2 produces a bifunctional (metal-acid) structure represented by $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ phase. The arrays of these Mo atoms in this new structure could be observed in Fig. 4. It is important to note that this bifunctional structure once it is prepared, is very stable at different reaction temperatures up to 673 K. Continuous reduction of the sample up to 873 K for 24 h results in the formation of metallic $\text{Mo}(0)$ state. This state is characterized by the Mo spin-orbit components at 230.85 and 227.7 eV (Fig. 1b). It was observed that the pure $\text{Mo}(0)$ metallic state could not be obtained upon extended reduction of the sample at 876 K. Some dioxide and trioxide species remain unreduced. Also, the morphology of the surface has drastically changed as could be observed from the HRTEM micrograph (Fig. 5). Large clusters are present on the sample surface as compared to atomic wires in the case of $\text{MoO}_2(\text{H}_x)_{\text{ac}}$.

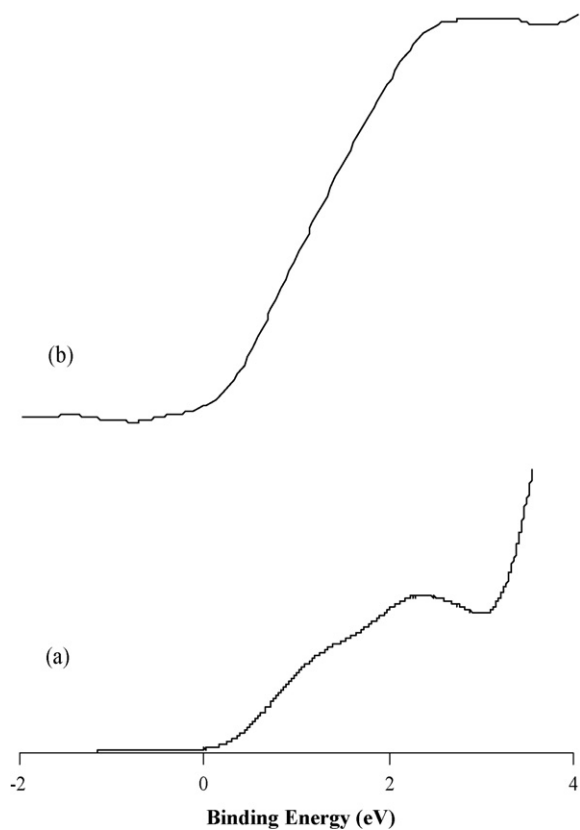


Fig. 2. The UPS of the VB in $\text{MoO}_3/\text{TiO}_2$, (a) after reduction at 673 K for 2 h and (b) after reduction at 873 K for more than 24 h.

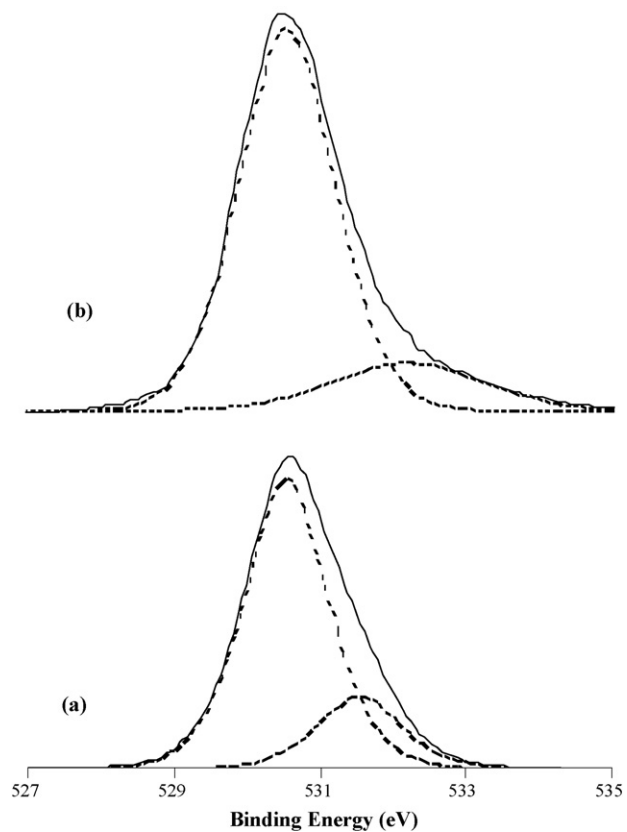


Fig. 3. The XPS of the O 1s in $\text{MoO}_3/\text{TiO}_2$, (a) after reduction at 673 K for 2 h and (b) after reduction at 873 K for more than 24 h.

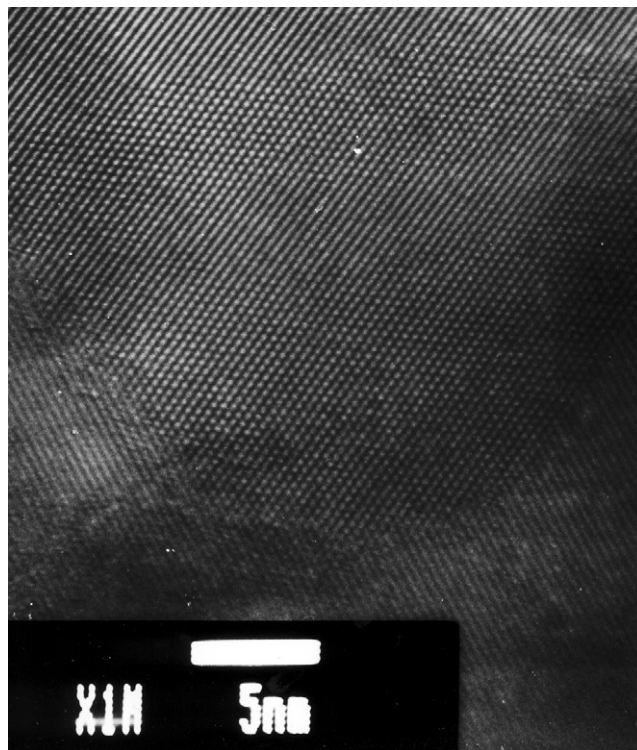


Fig. 4. HRTE micrograph for $\text{MoO}_3/\text{TiO}_2$ after reduction at 673 K.

3.2. Catalytic results

The catalytic reactions of *n*-hexane, 1-hexene, cyclohexene (CHE) and cyclohexane (CH) as a function of reaction temperature on the bifunctional and the metallic Mo(0) surfaces will be presented.

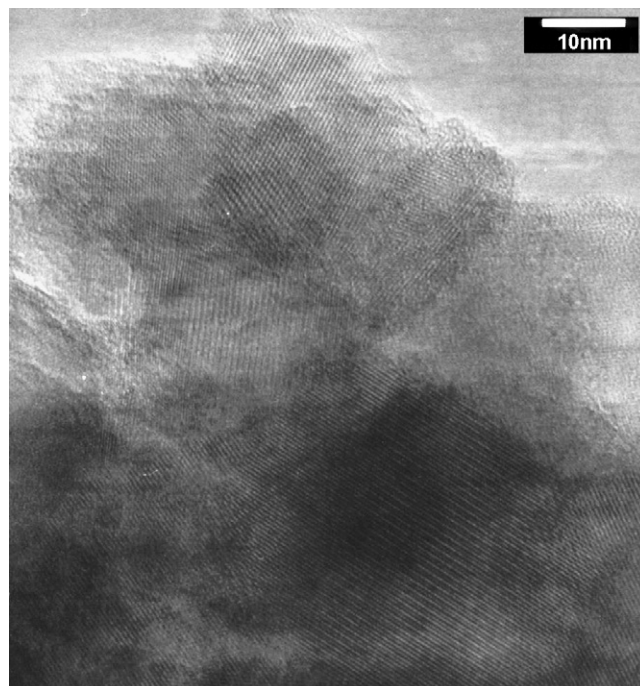
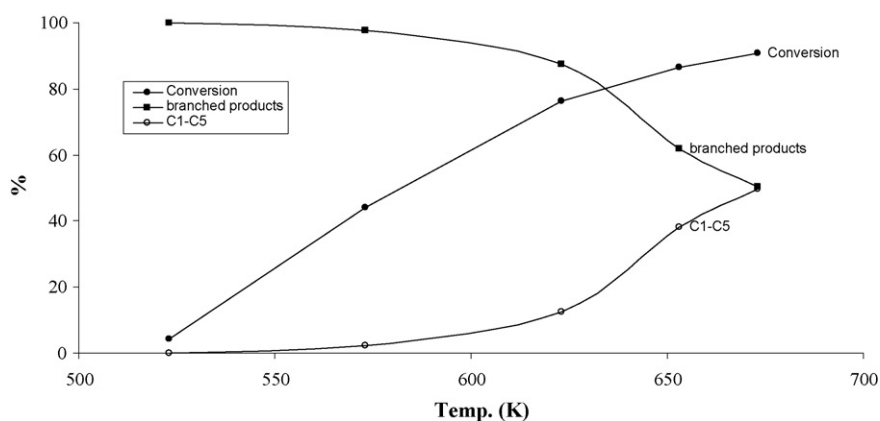


Fig. 5. HRTE micrograph for $\text{MoO}_3/\text{TiO}_2$ after reduction at 873 K.

Table 1Products distribution of *n*-hexane as a function of reaction temperature on MoO₃/TiO₂ after reduction at 873 K for more than 24 h

	Reaction temperature (K)												
	523	573	623	653	673	693	713	723	733	753	773	823	873
Conversion	0.6	0.6	2.4	7.1	14.2	24.1	32.2	39.7	49.4	61.2	73.4	92.3	100
Distribution of branched products (%)													
iC4+iC5	0	0	0	2.6	3.5	5.1	5.4	4.9	4.2	2.5	0.6	0	0
2,2 DMB+2,3 DMB	0	0	0	0	0	0	0	0	0	0	0	0	0
2MP	0	18.6	28.8	23.3	16.0	9.8	5.5	3.1	1.5	0.4	0	0	0
3MP	37.2	37.0	24.3	16.6	11.0	7.0	4.1	2.5	1.3	0.4	0	0	0
Distribution of cracked isomers (%)													
C1–C5 += Cps	0	0	38.6	53.8	66.0	73.3	78.0	78.1	78.6	74.7	86.3	98.4	100
MycycloC5	62.8	44.5	8.6	2.3	1.0	0	0	0	0	0	0	0	0
C6H6	0	0	0	1.4	2.3	4.8	6.9	8.9	11.5	17.8	14.0	1.6	0
Toluene	0	0	0	0	0	0	0	2.5	2.9	4.2	1.4	0	0

**Fig. 6.** Products distribution of *n*-hexane as a function of reaction temperature on MoO₃/TiO₂ after reduction at 673 K for 12 h.

3.2.1. The *n*-hexane reactant

The catalytic activity of *n*-hexane on previously reduced MoO₃/TiO₂ by hydrogen at 673 K for more than 12 h has been studied as a function of reaction temperature. As could be observed from Fig. 6, a conversion of 42.2% to mono- and di-branched isomers has been observed at 673 K. The conversion increases as the reaction temperature increases to reach 97.6% at 673 K (Fig. 6). However, the selectivity in isomerization decreases from 96% at 573 K to 25.7% at 673 K in favor of cracking products. Central C3–C3 bond dissociation seems to be the dominant catalytic process at higher reaction temperatures. Regardless of the reaction temperature, the ratio of 2MP to 3MP isomers remains almost constant at the thermodynamic equilibrium value of 1.4.

In the case of metallic Mo(0) surface obtained at 873 K reduction temperature, *n*-hexane molecules undergo different catalytic

processes at different reaction temperatures up to 873 K (Table 1). Traces of mono-branched 2MP and 3MP were obtained at temperatures between 573 and 713 K. The major products are C1–C5 cracking products. The drastic decrease in mono-branched and total absence of di-branched isomers at reaction temperatures between 573 and 673 K, as compared to the bifunctional phase, is attributed to the absence of the acidic function in this dominant metallic Mo(0) state. Dehydrogenation of *n*-hexane will take place at these reaction temperatures. Apparently, isomerization of the produced olefin does not occur due to the absence of the acidic function as rationalized in term of the bifunctional mechanism. Aromatization of *n*-hexane, yielding benzene, is obtained at reaction temperatures between 653 and 823 K. Such catalytic process was not observed in the case of MoO₂(H_x)_{ac} phase. The absence of benzene formation on the

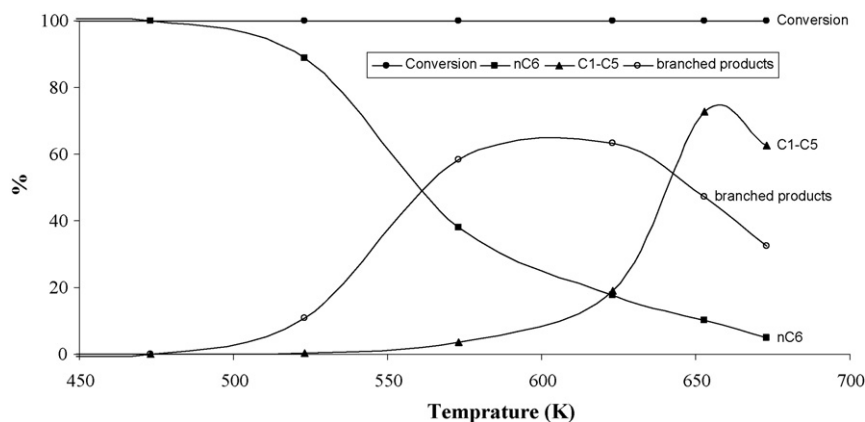
**Fig. 7.** Products distribution of 1-hexene as a function of reaction temperature on MoO₃/TiO₂ after reduction at 673 K for 12 h.

Table 2
Products distribution of 1-hexene as a function of reaction temperature on MoO₃/TiO₂ after reduction at 873 K for more than 24 h

	Reaction temperature (K)												
	523	573	623	653	673	693	713	723	733	753	773	823	873
Conversion	100	100	100	100	100	100	100	100	100	100	100	100	100
C1–C3	0	0.1	1.1	3.4	7.5	15.7	26.5	32.8	42.1	56.6	73.5	100	100
iC4+iC4+=+C4	0	0.1	0.9	2.8	5.8	11.0	15.5	15.9	15.1	9.1	4.5	0	0
iC5+iC5+=+C5	0	0.2	0.8	2.1	3.7	5.9	6.4	5.4	3.8	1.4	0.6	0	0
iC6+iC6=	0	0.3	2.5	5.5	7.9	8.7	7.7	5.6	3.2	0	0	0	0
C6	100	99.2	94.6	85.9	74.5	56.6	37.3	28.9	19.2	7.0	3.0	0	0
C6H6	0	0	0	0.2	0.7	2.1	5.2	8.4	12.2	20.4	15.3	0	0
Me C ₆ H ₅	0	0	0	0	0	0	1.5	3.0	4.2	5.4	3.2	0	0

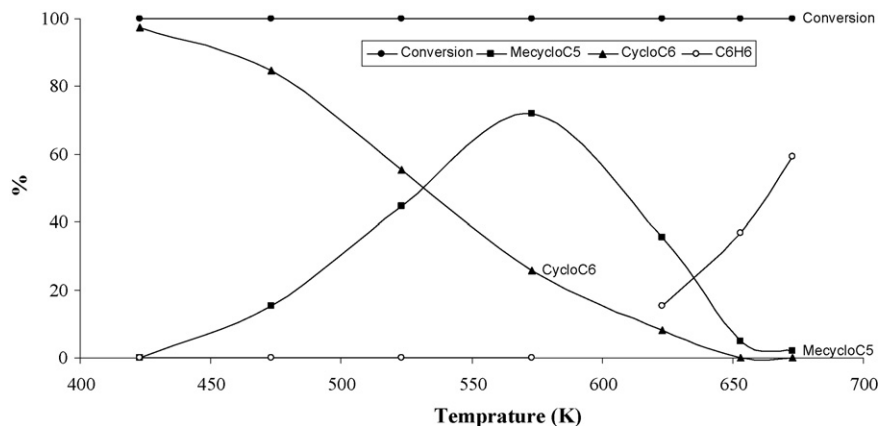


Fig. 8. Products distribution of cyclohexene as a function of reaction temperature on MoO₃/TiO₂ after reduction at 673 K for 12 h.

bifunctional phase could be attributed to either the limited strength of the metallic function or the morphology of the surface structure or both. In order to define the factor(s) which affect the aromatization of *n*-hexane, the catalytic studies of 1-hexene, cyclohexene and cyclohexane were performed on both catalytic systems.

3.2.2. The 1-hexene reactant

Complete conversion of 1-hexene molecules on MoO₂(H_x)_{ac} phase, regardless of the reaction temperature, has been observed (Fig. 7). Up to 523 K, the dominant catalytic process is the hydrogenation of 1-hexene to *n*-hexane. However, at 523 K, mono- and di-branched isomers were formed. This corresponds to thermodynamic requirements for the isomerization of the hexane olefin as observed in the case of the isomerization of *n*-hexane to these branched isomers. The maximum selectivity in isomerization products occurs at 623 K. It is interesting to note that regardless of the reaction temperature, or the isomerization selectivity, the 2MP to 3MP products ratio corresponds to the thermodynamic equilibrium value. At higher reaction temperatures up to 673 K, the isomerization selectivity decreases in favor of cracking products.

In the case of the metallic Mo(0) state, obtained following the reduction of MoO₃/TiO₂ at 873 K for more than 24 h, complete

hydrogenation of 1-hexene molecules is obtained at reaction temperatures up to 623 K (Table 2). At higher reaction temperatures, hydrogenation of 1-hexene decreases in favor of cracking products. In addition, benzene and toluene are formed in similar manner to what is observed in the case of *n*-hexane reactant on the same catalyst surface. In this case, a slight increase in the relative concentration of benzene is observed. This is due, in part, to the fact that the dehydrogenation process of *n*-hexane to hexene is not required in this case. Most probably, this dehydrogenation process corresponds to the first step in the mechanism of *n*-hexane transformation to benzene. Toluene is formed in a very low concentration at reaction temperatures between 713 and 773 K. The absence of acidic function(s) in this dominant Mo(0) state accounts for the negligible formation of mono- and di-branched C6 isomers.

3.2.3. Cyclohexene (CHE) reactant

At reaction temperature of 473 K, cyclohexene molecules are completely converted to cyclohexane on MoO₂(H_x)_{ac} phase (Fig. 8). The metallic function of the catalyst is responsible for this hydrogenation process. Isomerization to methyl cyclopentane (MCP) is performed at higher reaction temperatures to reach a selectivity of 72.1% at 573 K. This catalytic process is the result of ring shortening to methyl cyclopentane by the acidic function followed by hydro-

Table 3
Products distribution of cyclohexene as a function of reaction temperature on MoO₃/TiO₂ after reduction at 873 K for more than 24 h

	Reaction temperature (K)															
	423	473	523	553	573	623	653	673	693	713	723	733	753	773	823	873
Conversion	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
C1–C3	0	0	0	0	0	0	0.2	0.5	0.5	0.9	1.6	2.6	5.7	15.4	82.7	100
MecycloC5	0	0	0.4	1.0	1.3	1.6	0.5	0.2	0	0	0	0	0	0	0	0
C ₆ H ₆	0	0	0	0.9	1.9	41.4	73.3	86.8	93.8	96.2	96.3	95.6	92.3	82.8	17.3	0
CycloC6	100	100	99.6	98.1	96.8	57.0	25.6	12.5	5.4	2.6	1.4	0.9	0.4	0	0	0
MeC ₆ H ₅	0	0	0	0	0	0	0	0	0	0.3	0.6	0.9	1.6	1.8	0	0

Table 4Products distribution of cyclohexane as a function of reaction temperature on MoO₃/TiO₂ after reduction at 873 K for more than 24 h

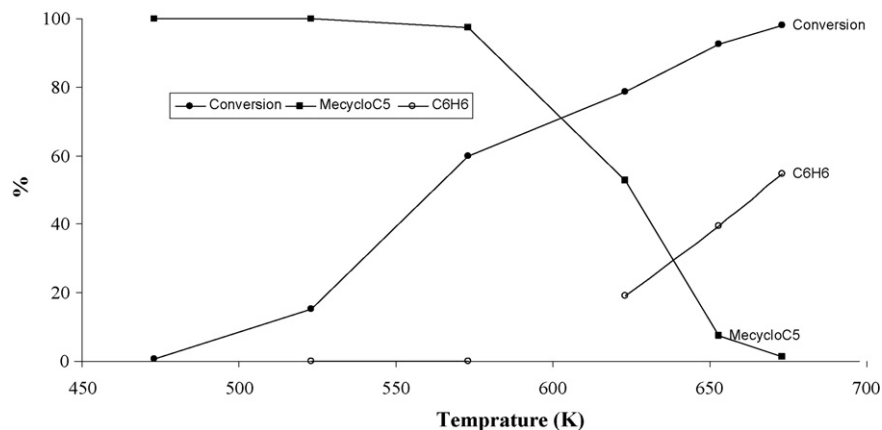
	Reaction temperature (K)												
	523	573	623	653	673	693	713	723	733	753	773	823	873
Conversion	0	0.3	7.4	26.1	43.8	59.6	76.6	76.1	81.4	88.4	92.6	96.5	100
C1–C3	0	0	0	0.5	0.6	0.8	2.0	1.9	2.3	4.2	9.6	62.9	98.4
MecycloC5	0	0	2.9	0.7	0	0	0	0	0	0	0	0	0
C ₆ H ₆	0	100	97.1	98.9	99.3	99.1	97.8	98.0	96.8	94.3	88.7	37.0	1.5
CycloC6=	0	0	0	0	0	0	0	0	0	0	0	0	0
MeC ₆ H ₅	0	0	0	0	0	0	0	0	0.8	1.3	1.7	0	0

genation to MCP performed by the metallic function. Interestingly, a 15.4% in selectivity of benzene is observed at 623 K. The selectivity in the formation of benzene increases as a function of reaction temperature to reach 59.2% at 673 K. These results clearly indicate that the metallic function in MoO₂(H_x)_{ac} is sufficient for the aromatization of cyclohexene to benzene. As a result, it could be stated that the absence of such catalytic process in the case of 1-hexene on the same catalytic phase is simply due to the difficulty in the cyclization of 1-hexene to cyclohexene. Apparently, the cyclization of 1-hexene occurs on the metallic Mo(0) surface at reaction temperatures above 653 K as discussed earlier. Therefore, it is suggested that cyclization of 1-hexene is structure-sensitive catalytic process. In the case of the Mo(0) state, the molybdenum atoms are present in clusters in which 1-hexene molecules undergo cyclization followed by aromatization to benzene. Meanwhile, in MoO₂(H_x)_{ac} phase, molybdenum atoms are present in form of arrays of single atoms (atomic wire), on which cyclization process is not possible. Structure-sensitive effect on the different catalytic processes involving cyclohexene hydrogenation and dehydrogenation as well as skeletal rearrangement reactions, involving dehydrogenation, isomerization, cyclization and aromatization of paraffinic hydrocarbons over platinum (111) and platinum (100) were clearly demonstrated by using sum frequency generation (SFG) [14].

Aromatization of cyclohexene yielding benzene over metallic Mo(0) surface starts at 553 K and reaches a maximum of 96.2% in selectivity at 713 K reaction temperature (Table 3). High selectivity in benzene formation from the reaction of cyclohexene as compared to 1-hexene on Mo metallic surface is a clear indication that cyclization process of 1-hexene is structure-sensitive process. Hydrogenation to cyclohexane is achieved at low temperatures as compared to the dehydrogenation processes.

3.2.4. Cyclohexane (CH) reactant

The first catalytic activity of cyclohexane on MoO₂(H_x)_{ac} phase with a 0.8% in conversion to MCP is observed at 473 K (Fig. 9).

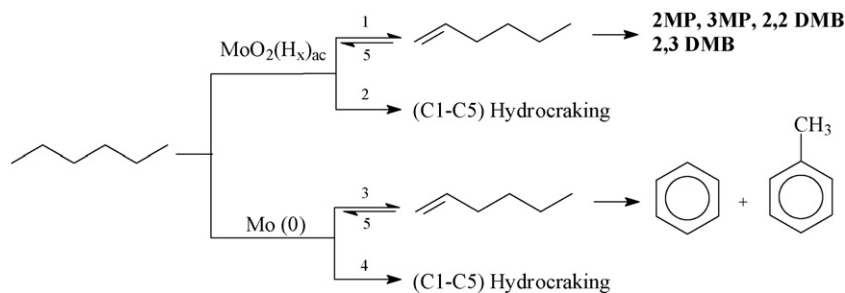
**Fig. 9.** Products distribution of cyclohexane as a function of reaction temperature on MoO₃/TiO₂ after reduction at 673 K for 12 h.

The conversion increases as a function of reaction temperature to reach 59.9% at 573 K, while the selectivity to MCP remains very high at 97.5%. At 623 K reaction temperature, a selectivity of 19% in benzene is similar to what observed in the case of cyclohexene. A maximum of 98% in conversion with 54.7% selectivity to benzene were obtained at 673 K. At high reaction temperatures, the dehydrogenation on the metallic function seems to be more favored than the isomerization to MCP on the Brønsted acidic function(s) of MoO₂(H_x)_{ac}. The catalytic performances of this Mo bifunctional phase in terms of conversion, selectivity and stability are better than what is obtained in the case of Pt deposited on tungsten or zirconium oxides [15].

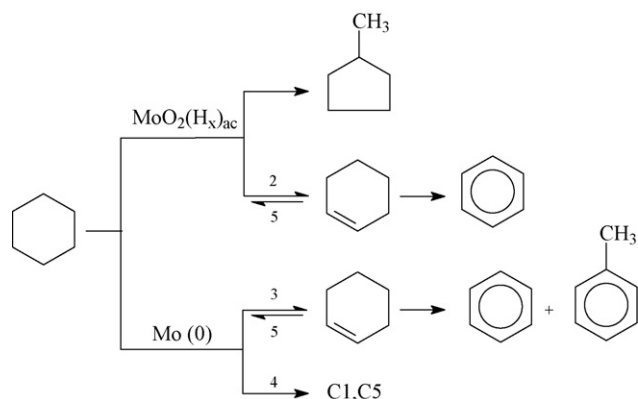
The absence of MCP formation from the reaction of cyclohexane over Mo(0) surface is expected. Aromatization to benzene seems to be the dominant catalytic process regardless of the reaction temperature (Table 4). A conversion of 81.4% and 96.8% selectivity to benzene is obtained at 733 K. This metallic Mo(0) surface seems to be an efficient catalyst for hydrogen production from cyclohexane.

3.3. General discussion

From the above catalytic results of *n*-hexane, 1-hexene, cyclohexene and cyclohexane over the bifunctional MoO₂(H_x)_{ac} and Mo(0) states, it was revealed that catalytic reactions are dependent on the catalyst surface structure and reaction temperature. Hydroisomerization catalytic reactions of *n*-hexane to mono- and di-branched molecules of relatively high octane numbers occur over MoO₂(H_x)_{ac} as represented in Scheme 1, pathway (1). High values of conversion and selectivity in isomerization products were obtained. Hydrocracking (2) occurs at high reaction temperatures. On the metallic Mo(0) state, different catalytic reactions are performed. At low reaction temperatures between 523 and 573 K, a very low conversion of *n*-hexane to MCP is obtained. However, at reaction temperatures above 573 K, aromatization to benzene and to lesser extent to toluene is performed (3). The absence of *n*-hexane



Scheme 1. Different catalytic reactions pathways of *n*-hexane on $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ and $\text{Mo}(0)$ surfaces.



Scheme 2. Different catalytic reactions pathways of cyclohexane on $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ and $\text{Mo}(0)$ surfaces.

aromatization catalytic reactions over $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ is attributed to the fact that cyclization of hexene molecule(s), produced by the dehydrogenation of *n*-hexane, to cyclohexene is not performed by the Mo atoms placed along the C-axis. This cyclization catalytic process is structure-sensitive which is performed over cluster structure of Mo atoms present in $\text{Mo}(0)$. Catalytic reactions of 1-hexene over $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ and $\text{Mo}(0)$ are similar to those of *n*-hexane except that hydrogenation process to *n*-hexane (5), is performed on both Mo catalytic systems at relatively low reaction temperatures.

In the case of cyclohexane (Scheme 2), isomerization to MCP (1) occurs on the bifunctional $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ phase at reaction temperatures between 473 and 673 K. Aromatization of cyclohexane to benzene (2) is performed by the metallic function of $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ at 623–673 K. This was not the case in the reaction of *n*-hexane and 1-hexene on the same catalyst. This is due to the inhibition of hexene cyclization to cyclohexene on this well-defined surface of Mo arrays of atoms in $\text{MoO}_2(\text{H}_x)_{\text{ac}}$. Very high conversion of cyclohexane to benzene occurs on the metallic $\text{Mo}(0)$ state. This could be considered as a good catalyst for cyclohexane aromatization and for the production of hydrogen. Catalytic reactions of cyclohexene and cyclohexane over $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ and $\text{Mo}(0)$ are comparable except at low reaction temperatures, at which hydrogenation of cyclohexene is observed. Conversions of cyclohexene at different temperatures are higher by comparison to cyclohexane as expected on the basis that the first dehydrogenation catalytic process to cyclohexene, required for aromatization, is already performed.

4. Conclusions

Two well-defined molybdenum surface states were obtained following controlled reduction of $\text{MoO}_3/\text{TiO}_2$ by hydrogen at different temperatures. A bifunctional $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ phase is obtained at

reduction temperatures between 653 and 673 K. On the other hand, a metallic $\text{Mo}(0)$ state is obtained at 873 K. The surface morphology of the two Mo states differs considerably. In the $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ phase, the Mo atoms are placed along the C-axis (atomic wire) of the deformed rutile structure of MoO_2 , while in the case of $\text{Mo}(0)$ state the Mo atoms are present in the form of large particles (clusters). Hydroisomerization of *n*-hexane occurs on the bifunctional phase, while *n*-hexane aromatization to benzene and hydrocracking are dominant catalytic reactions in the case of $\text{Mo}(0)$ state. Similar reactions were observed in the case of 1-hexene. In the case of cyclohexene and cyclohexane, isomerization reactions to MCP occur at reaction temperatures between 473 and 573 K, while dehydrogenation reactions to benzene occur on the $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ phase at reaction temperatures between 573 and 673 K. Very high conversions and high selectivity to benzene were observed for the reactions of these molecules over the metallic $\text{Mo}(0)$ state. The absence of *n*-hexane and 1-hexene aromatization on $\text{MoO}_2(\text{H}_x)_{\text{ac}}$ phase is attributed to the fact that cyclization of 1-hexene to cyclohexene is structure-sensitive catalytic process. It does not take place on the molybdenum atoms placed along the C-axis (atomic wire) in $\text{MoO}_2(\text{H}_x)_{\text{ac}}$. This is an important advantage of the Mo bifunctional phase as compared to Pt-based catalysts, in which benzene is formed due to the sintering problem. However, large particle size(s), present in $\text{Mo}(0)$ state seem to favor this cyclization process. Therefore, the cyclization catalytic process is considered as a rate determining step in aromatization of 1-hexene and *n*-hexane to benzene.

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