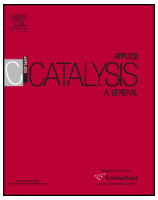
Applied Catalysis A: General 475 (2014) 497–502

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Tailoring acid–metal functions in molybdenum oxides: Catalytic and XPS-UPS, ISS characterization study

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ARTICLE INFO

Article history:
Received 3 October 2013
Received in revised form 5 February 2014
Accepted 5 February 2014
Available online 14 February 2014

Keywords:
$MoO_{2-x}(OH)_y$ catalyst
XPS-UPS, ISS
Acid, metal functions
2-Propanol
Cyclohexane

ABSTRACT

Formation of acid, metal and metal–acid (bifunctional) functions in titania-supported molybdena following controlled partial reduction of MoO_3 using hydrogen at different temperatures are monitored by a combination of surface XPS-UPS, ISS techniques. Addition of controlled amount of sodium or potassium alkali metals to the bifunctional $MoO_{2-x}(OH)_y/TiO_2$ (MoTi) enabled to neutralize the Brønsted acid Mo-OH functions. Sodium or potassium molybdenum bronze metallic function is formed following the addition of the alkali metal to the Mo salt following its calcination at 773 K. The catalytic functions of these MoTi and Na, KMoTi systems were evaluated for the dehydration/hydrogenation, oxidation reactions of isopropanol to acetone as well as the ring shortening of cyclohexane to methylcyclopentane MCP and its oxidative dehydrogenation to benzene.

1. Introduction

Certain catalytic reactions such as dehydration of alcohols, hydrogenation of olefins and isomerization of alkanes are performed by specific acid, metal or both, metal–acid (bifunctional) catalytic functions. Identification of the chemical structure(s) having these functions present on the outermost surface layer in heterogeneous catalysts constitutes a major challenge. Several spectroscopic and physical techniques as well as catalytic reactions are employed for such objective. The major difficulty relies on the fact that catalytic active site(s) are formed in situ following specific catalyst activation procedure(s) of the initial compounds. In other words, exposure of the catalyst to air will cancel its effect due to modification of its chemical structure. Consequently, characterization results in this case will be misleading. In previous works [1–3], we have reported the formation of a metal–acid (bifunctional) system following controlled partial reduction by hydrogen of bulk or supported MoO_3 on TiO_2 (MoTi). Identification of these catalytic function(s) to specific molybdenum chemical species is based on, in situ, characterization using XPS-UPS, ISS and FT-IR techniques in parallel to its catalytic activity of well-defined catalytic reactions. In this catalytic MoTi system, titania is employed as a support in order to increase the surface area and add mechanical strength to Mo oxide catalyst.

Optimization of the MoTi catalytic performances in terms of acid, metal or both metal–acid functions toward specific catalytic reactions is achieved by defining the exact experimental conditions of preparation and activation of the catalyst. Moreover, addition of controlled amount of alkali metals such as sodium, potassium and cesium in view of enhancing the metallic properties of MoTi is evaluated for well-known catalytic reactions. This methodology consists of in situ characterization-catalytic activity measurements conducted in the same experimental conditions. In this work, we have added small amounts of sodium or potassium to the impregnated molybdenum salt on titania. Catalyst activation and performances were studied for the different catalytic reactions of 2-propanol and cyclohexane. Several types of catalytic reactions take place in these systems. Each of them is performed by specific catalytic function(s) at certain experimental conditions. Association of each catalytic reaction in the above systems with the active catalytic function(s) in MoTi and modified MoTi by Na or K alkali metals constitutes the primary objective of this work.

Dehydration of propanol and isomerization of cyclohexane are typical catalytic reactions performed by Brønsted acid function(s) [4–6]. On the other hand, dehydrogenation of 2-propanol to acetone, hydrogenation of an olefin to saturated hydrocarbon and dehydrogenation of cyclohexane to benzene are performed by metallic function(s).

In order to get more insight about the formation and suppression of Brønsted acid function, addition of small amount of alkali metals such as sodium or potassium to the molybdenum oxide is used. It is expected in this case that Na or K atoms will replace the hydrogen

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http://dx.doi.org/10.1016/j.apcata.2014.02.006
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in MoOH, if any, and lead to the suppression of the acid function(s) in the catalytic system. Moreover, calcination of the modified systems is expected to produce sodium and potassium molybdenum bronzes of certain metallic property [7,8]. The proposed, in situ, surface chemical structure-catalytic activity methodology will enable to identify the chemical process(es), responsible for the formation of specific catalytic active site(s). Moreover, very weak electronic interaction, if any, takes place between the partially reduced MoOx ($x < 3$) and the titania surface as evaluated by the XPS of Ti(2p) after each treatment. This is compared to strong electronic interaction (SMSI) which takes place with the alumina support and results in the formation of aluminum molybdate complex [9,10].

2. Experimental

2.1. Catalyst preparation

The equivalent of 5 monolayers of molybdenum trioxide were deposited on TiO_2 using ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (99.9%) supplied by STREM Chemicals. Titanium dioxide, TiO_2, is Degussa P-25 (25% rutile) with a pore volume of 0.5 cm^3/g and a BET surface area of 50 ± 5 m^2/g. The reported error margin of 10% by the supplier covers widely the experimental value of 52 m^2/g performed in the laboratory. Supported catalysts are prepared by impregnating the appropriate amount of molybdenum in ammonium heptamolybdate salt following the method described by Pines et al. [11]. The exact amount of the molybdenum (0.3 g of salt per gram of the support) is dissolved in distilled water followed by the impregnation procedure. The excess water has been eliminated by evaporation then the catalyst is dried at 383 K for 8 h and eventually calcined at 773 K for 12 h. It is worth mentioning that the loaded ammonium heptamolybdate was quantitatively decomposed into MoO_3 species during the calcination process as characterized by XPS. 2.5% concentration by mass of sodium or potassium, in form of $NaNO_3$ and KNO_3 with respect to Mo were added following post-impregnation of the dried heptamolybdate-impregnated TiO_2 pellets prior to the calcination process at 773 K. In situ reduction of the MoO_3/TiO_2 system before and after Na and K additions in a flow of 40 cm^3 H_2/min as a function of temperature was carried out in different ways in order to elucidate the surface structure and its stability in relation to catalytic activity. The hydrogen gas was a 99.9% pure product of KOAC (Kuwait).

2.2. Catalyst characterization

X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific ESCALAB-250Xi spectrometer. The radiation source was monochromatic of AlKα operating at the power of 300 W (15 kV, 20 mA). Ultraviolet Photoelectron Spectroscopy (UPS) He(I) resonance 584 Å radiation of 21.217 eV was employed for the Valence Band (VB) energy region measurements. Vacuum in the analysis chamber was better than 7×10^{-9} bar during all measurements. In situ reduction was carried out in a high-pressure gas cell housed in the preparation chamber. Binding energies were based on the carbon contamination C 1s at 284.8 eV within an experimental error of ±0.2 eV. Ion scattering spectroscopy (ISS) measurements were performed on the same test sample using He^+ with a kinetic energy of 1 keV.

2.3. Catalyst tests

Time on stream catalytic reactions under atmospheric hydrogen pressure was studied. The reactant (2-propanol or cyclohexane) was drawn from the reservoir throw HPLC pump of flow rate of 0.1 ml/min then it passed through vaporizer and eventually it passed over a fixed bed quartz reactor containing either MoTi or Na, K modified MoTi catalytic systems. A continuous H_2 flow of 40 cm^3/min was allowed through 500 mg of the catalyst which contains 65 mg of Mo. The reaction mixture was separated and analyzed with an on-line gas chromatograph Chemito, India 1000 equipped with a Petrocol-DH column and a flame ionization detector.

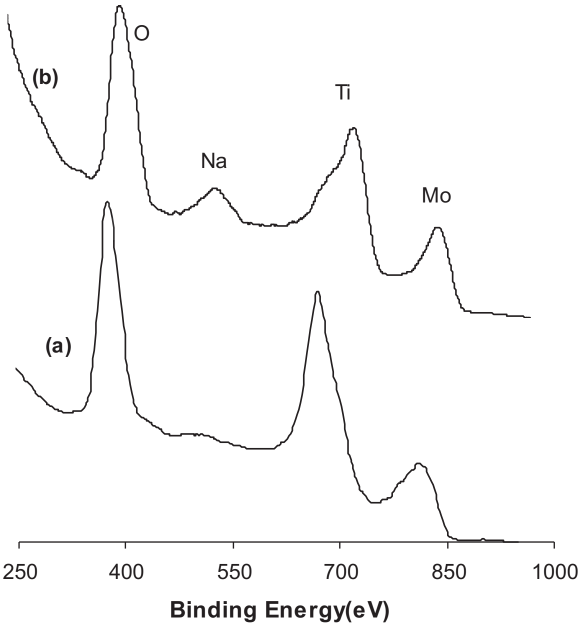


Fig. 1. ISS spectrum after hydrogen reduction at 673 K for MoTi (a), NaMoTi (b).

3. Results and discussion

3.1. Catalyst characterization

Characterization of the active metal–acid functions in partially reduced MoO_3 deposited on TiO_2 using XPS-UPS and ISS techniques was reported in previous works [3]. Addition of controlled amounts of Na or K to the MoTi structure and its effect on these functions will be reported. Moreover, extended reduction of MoO_3 to the metallic Mo(0) and its effect on the dehydrogenation of cyclohexane to benzene will be studied.

3.1.1. ISS spectra

Elemental composition of the outermost surface structure of MoTi, NaMoTi and KMoTi systems determined by ISS technique, following in situ exposure of each sample to hydrogen at 673 K for 12 h reveals the presence of the alkali metal, Mo, Ti and oxygen (Fig. 1 and Table 1). The presence of titanium as part of the surface can be attributed to the inhomogeneous deposition of Mo on TiO_2 substrate. Most probably, the Mo oxide is present in form of aggregate needle like crystallites structure as postulated by Bond et al. [12].

Table 1
ISS relative intensities of catalysts elements composition following its exposure to hydrogen at 673 K for 12 h.

Catalyst	% O	% Ti	% Mo	% Na	% K
MoTi	49	38	13	–	–
NaMoTi	45	31	16	8	–
KMoTi	47	23	22	–	8

Table 2
Characteristic BE, relative intensities, surface areas and alkali Na and K metals atomic ratio in different catalysts employed in this research work.

Catalyst	MoO_3		Mo_2O_5		MoO_2		Mo(IV)/Mo(VI)/Mo(VI) relative intensities	Surface area (m^2/g)	Atomic ratio	
	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$			Na/Mo	K/Mo
MoTi after calcinations	236.28	233.08					0/0/1	33.9		
MoTi after hydrogen reduction at 573 K	236.38	233.18	234.68	231.58	232.78	229.59	0.57/0.32/0.11	–		
MoTi after hydrogen reduction at 673 K	236.08	232.88	234.68	231.48	232.88	229.68	0.56/0.31/0.13	47.8		
NaMoTi after hydrogen at 673 K	235.88	232.68	234.98	231.78	232.18	229.08	0.80/0.14/0.06	45.5	0.13	
KMoTi after hydrogen at 673 K	–	–	–	–	232.6	229.42	1/0/0	49.0		0.09

3.1.2. XPS-UPS spectra

Calcination of equivalent 5 monolayers of ammonium heptamolybdate deposited on TiO_2 (MoTi) surface at 773 K enabled to convert all Mo to MoO_3 structure (Fig. 2a). In situ exposure of the sample to hydrogen at different temperatures up to 673 K results in gradual reduction of MoO_3 as follows: $MoO_3 \rightarrow Mo_2O_5 \rightarrow MoO_2$ characterized by Mo $3d_{5/2,3/2}$ spin–orbit coupling at 233.1, 236.3 eV (MoO_3), 231.7, 234.9 eV (Mo_2O_5) and 229.1, 232.3 eV for MoO_2 (Fig. 2b). A stable structure takes place at 673 K, at which the three Mo(VI), Mo(V) and Mo(IV) states co-exist at a certain stoichiometric ratio regardless of exposure time of the sample to hydrogen (Table 2). The MoO_2 with its metallic properties constitutes the outermost surface layer (Fig. 1c). Further increase in the reduction temperature to 873 K results in the reduction of molybdenum to the metallic Mo(0) state characterized at 227.7 and 230.9 eV of Mo $3d_{5/2,3/2}$ spin–orbit components. Moreover, the surface area increased from 47.8 m^2/g at 673 K to 60.0 m^2/g at 773 K (Table 2). It is interesting to note that addition of alkali metal improves the reduction process of MoO_3 to the MoO_2 structure at 673 K (Fig. 2d) as compared to pure MoO_3/TiO_2 system (Fig. 2c). The exact reason(s) for such difference in the reduction process can be attributed to the formation of discrete entities of the modified system such as Na_2MoO_4 in the process of calcination of the system at 773 K. Consequently, partial depolymerization of the polymolybdate, present on the sample surface, will take place in the reduction process by hydrogen [3].

The UPS of the calcined MoTi sample does not show any density of state at the Fermi level (Fig. 3a). This is in agreement with the insulating properties of MoO_3. Sample exposure to hydrogen at 673 K for 12 h results in the presence of two structures at 0.4 and 1.4 eV (Fig. 3b), assigned to the π and σ spectral lines in MoO_2 structure [13,14]. The specific metallic properties of MoO_2 deformed rutile structure is the result of the delocalized π electrons above the Mo atoms. Taking into consideration the limited UPS depth analysis of few angstroms (Å) as compared to XPS, it is concluded that MoO_2, having metallic properties, is constituent of the outermost surface layer of the partially reduced MoTi sample. On the other hand, the Brønsted Mo-OH acid function is observed in form of O 1s shoulder at 531 eV as well as FT-IR measurements [3,15].

The two π and σ spectral lines are also observed in the case of modified MoTi by alkali metals (Fig. 3c and d). In this case, the metallic function of MoO_2 remains unaffected. However, Brønsted Mo-OH is suppressed due to the replacement of the acidic Mo-OH hydrogen by the metal Na or K atoms [3].

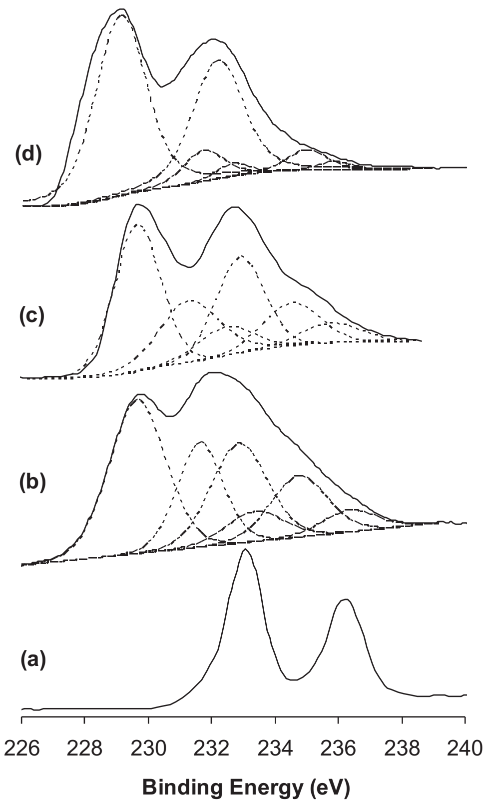


Fig. 2. XPS of Mo(3d) energy region of calcined MoTi at 773 K (a), after reduction by hydrogen of MoTi at 573 K for 2 h (b), after reduction by hydrogen MoTi at 673 K for 2 h (b), after reduction of NaMoTi by hydrogen at 673 K for 2 h (d).

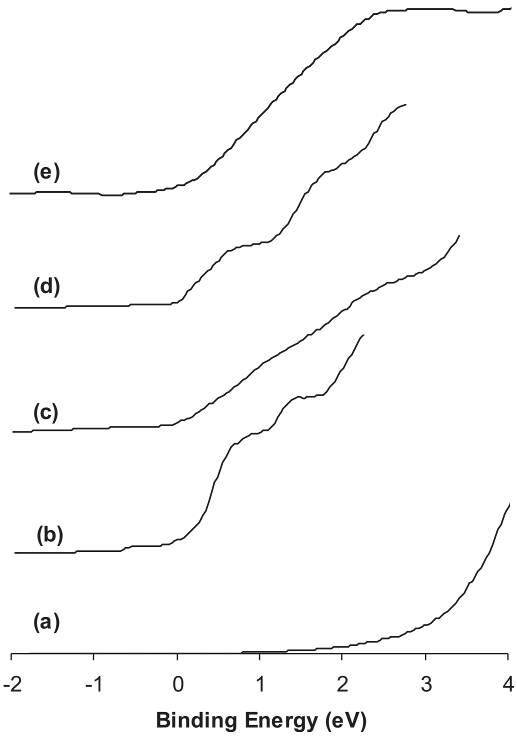


Fig. 3. UPS of calcined MoTi at 773 K (a); after reduction by hydrogen for 12 h at 673 K: MoTi (b), NaMoTi (c), KMoTi (d); after reduction by hydrogen for 12 h at 873 MoTi (e).

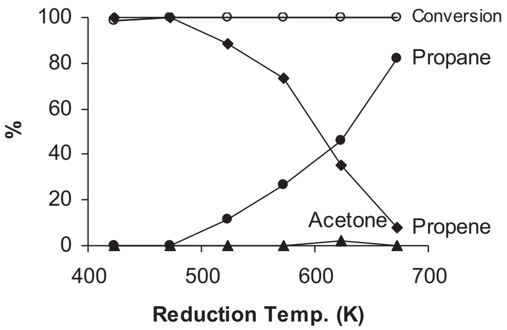


Fig. 4. Variation of the 2-propanol conversion and selectivity to main reaction products during the 2-propanol catalytic reaction as a function of calcined MoTi reduction temperature for 1 h each. The reaction temperature is the same as the reduction temperature.

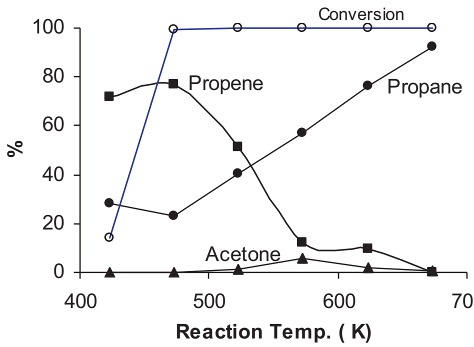


Fig. 5. Variation of the 2-propanol conversion and selectivity as a function of reaction temperature to main reaction products during the 2-propanol catalytic reaction on reduced MoTi by hydrogen at 673 K for 12 h.

3.2. *Catalytic measurements*

The formation of metal and acid functions following the exposure of MoO_3/TiO_2 to hydrogen at 673 K for 12 h is represented in a new $MoO_{2-x}(OH)_y/TiO_2$ bifunctional structure. The modification of this system by the addition of 2.5% by mass of alkali Na or K metals will be evaluated using well-known catalytic reactions of 2-propanol, cyclohexene and cyclohexane.

3.2.1. *2-Propanol*

The main catalytic reactions of 2-propanol performed by either acidic, metallic or both functions are dehydration to propene (acidic), followed by its hydrogenation to propane (metallic). A more difficult reaction is the dehydrogenation to acetone performed by a metal function. In the case of calcined MoTi system at 773 K and prior to the reduction treatment by hydrogen, complete conversion of 2-propanol to propene takes place at 423 K (Fig. 4). This is in agreement with FT-IR measurements related to the presence of Brønsted type acid functions in MoTi prior to hydrogen reduction [3]. Gradual increase in the reduction temperature up to 673 K for 1 h each under hydrogen is carried out. It is worth to mention that the reaction temperature, in this case, is the same as the reduction temperature. A conversion of 100% of 2-propaol is obtained regardless of the reduction (reaction) temperature up to 673 K. However, the selectivity to propene and propane varies as a function of reaction temperature. Although all the reacted 2-propanol molecules were dehydrated to propene at 423 K, part of the produced propene (11.6%) were hydrogenated to propane at 523 K. A maximum of 81.7% in propane selectivity at 100% conversion were obtained at 673 K (Fig. 4) These results are consistent with the relative increase of metal function concentration on the surface of the sample expressed in terms of the reduction of MoO_3 to MoO_2 as observed by XPS (Fig. 2) [15]. Furthermore, the conversion and selectivity remain unchanged at 673 K as a function of reaction time. In other words, hydrogenation of propene to propane is related to the reduction process of MoO_3 to MoO_2 which reaches a stable state at 673 K as demonstrated by XPS-UPS and catalytic results [2]. In this context, it is of interest to compare the catalytic performances of the MoTi system upon its gradual reduction as discussed above and its direct reduction at 673 K for 12 h. Indeed, in the direct reduction process at 673 K, interpreted as the formation of the bifunctional $MoO_{2-x}(OH)_y/TiO_2$, the conversion of 2-propanol is 13.8% at 423 K reaction temperature (Fig. 5) as compared to 100%, obtained in the gradual process (Fig. 4). Moreover, the nature of products in both reduction processes is different. Only propene product is obtained in the gradual reduction protocol, as compared to 72% propene and 28% propane in the direct one (Fig. 5). These results are interpreted as follows: In the direct reduction process at 673 K, a stable bifunctional (metal–acid) structure in form of $MoO_{2-x}(OH)_y/TiO_2$ is formed. Thus, catalytic activity of this system is controlled by kinetic and thermodynamic effects. Apparently, the relative concentration of the Brønsted acid sites on the surface of this bifunctional system is less than in the calcined MoTi prior to the reduction process. Catalytic performances of the bifunctional system toward 2-propanol is studied as a function of reaction temperature. Complete conversion of 2-propanol takes place beyond 450 K reaction temperatures with continuous increase in propane concentration to reach 92.5% at 673 K (Fig. 5). It is worth mentioning that no acetone is produced on MoTi before and after hydrogen treatments regardless of the reaction temperature. Apparently, dehydrogenation of 2-propanol to acetone requires stronger metallic function, high DOS structure, than what is present in form of π delocalized electrons in $MoO_{2-x}(OH)_y/TiO_2$.

The catalytic behavior of MoTi following the addition of 2.5% of Na or K alkali metal is completely different than the unmodified MoTi system. Different types of metallic characters seem to be formed on the NaMoTi or KMoTi surfaces depending on the reduction temperature (Figs. 6 and 7). Acetone formation takes place at reduction-reaction temperatures between 423 and 523 K with a maximum of 54.2% in selectivity and 10.7% conversion at 423 K in NaMoTi. Higher conversion of 38.1% and 50.9% selectivity to acetone was obtained at 473 K in the case of KMoTi (Fig. 7). The acetone selectivity decreases to 1.0% while the conversion increases to 100% at 573 K (Figs. 6 and 7). In parallel, a propene selectivity of 38.3% is observed at 423 K and increases to 99.0% at 573 K. Partial hydrogenation of the formed propene takes place at higher temperatures than 573 K with a maximum of 55% at 673 K (Figs. 6 and 7). The above mentioned catalytic results of Na, KMoTi as a function of

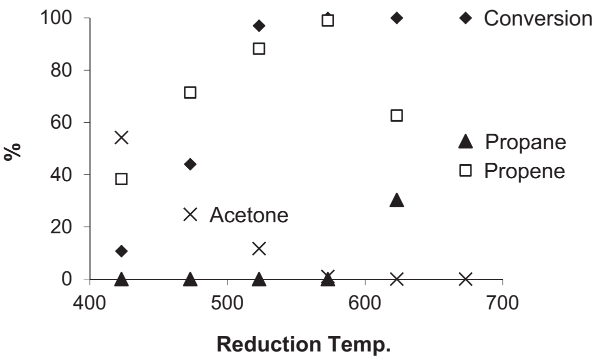


Fig. 6. Variation of the 2-propanol conversion and selectivity to main reaction products during the 2-propanol catalytic reaction as a function of calcined NaMoTi reduction temperature. The reduction process is 1 h for each temperature. The reaction temperature is the same as the reduction temperature.

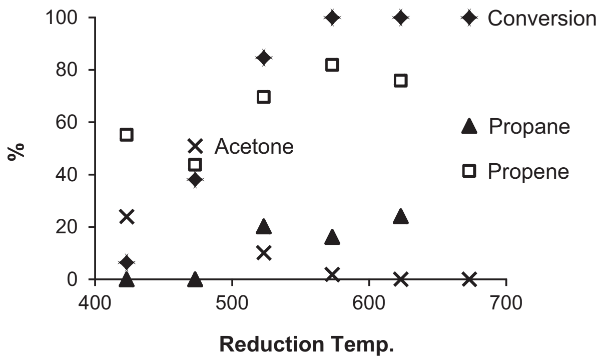


Fig. 7. Variation of the 2-propanol conversion and selectivity to main reaction products during the 2-propanol catalytic reaction as a function of calcined KMoTi reduction temperature. The reduction process is 1 h for each temperature. The reaction temperature is the same as the reduction temperature.

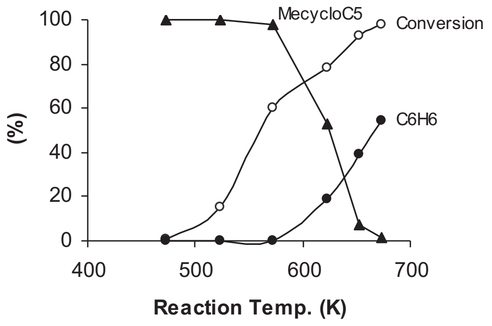


Fig. 8. Variation of cyclohexane conversion and selectivity as a function of reaction temperature to main methylcyclopentane and benzene reaction products during cyclohexane catalytic reaction on reduced MoTi by hydrogen at 673 K for 12 h.

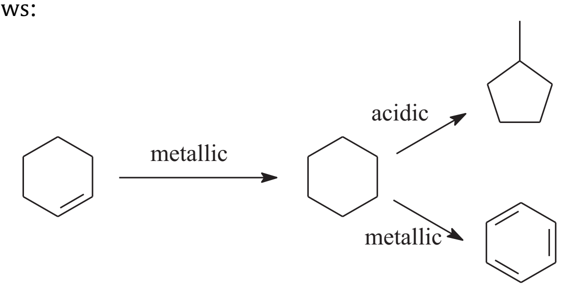
reduction temperature could be interpreted as follows: addition of the alkali Na or K alkali metal to the MoO_3/TiO_2 system and its calcination at 773 K seem to result in bronze formation with specific metallic character [7,8]. Moreover, Brønsted acid function(s) are present on the sample surface as revealed by FT-IR measurements [3]. These bronze metallic and Brønsted acid function(s) are respectively responsible for the 2-propanol dehydrogenation to acetone as well as its dehydration to propene.

3.2.2. *Cyclohexene and cyclohexane*

The different catalytic functions formed on the surface of MoTi and modified by the addition of alkali metals such as NaMoTi will be evaluated for the possible catalytic reactions of cyclohexene and cyclohexane. Hydrogenation of cyclohexene, ring opening and dehydrogenation of cyclohexane are performed by metallic function(s). On the other hand, isomerization of cyclohexane is catalyzed by acid function. Dehydrogenation of cyclohexane to benzene represents a safe and practical way of hydrogen storage and transportation.

Platinum based catalysts are the most common and widely used systems for dehydrogenation/hydrogenation of hydrocarbon compounds. The active site, responsible for the dehydrogenation of cyclohexane to benzene is attributed to finely dispersed particles deposited on the surface of nanomaterials supports [16] or carbon black supports covered with microporous silica layers [17]. The objective of microporous silica layers support is to avoid the catalyst deactivation due to Pt particles sintering. Also, gold, palladium and gold–palladium catalysts were employed for such objective [18]. Molybdenum deposited on various oxide supports were also employed for the dehydrogenation of cyclohexane to benzene [19]. Mo/Cr–Al–O catalyst was found to be effective in cyclohexane dehydrogenation. The active phase is attributed to Mo^{6+} and Cr^{3+} species present on the catalyst surface. On the other hand, Platinum deposited on MoO_2 is found to have relatively high selectivity toward methylcyclopentane ring opening [20].

In the case of stable bifunctional $MoO_{2-x}(OH)_y/TiO_2$ structure, obtained following exposure of MoO_3/TiO_2 to hydrogen at 673 K for 12 h, a conversion of 100% of cyclohexene and a selectivity of 97.5% to cyclohexane were obtained at 423 K reaction temperature. Produced cyclohexane undergo two possible catalytic reactions, these are isomerization to methylcyclopentane MCP and dehydrogenation to benzene. Catalytic results show that isomerization activity to methylcyclopentane is catalyzed first with a selectivity of 15.4% at 473 K. It increases to 72.1% at 573 K, while the conversion remains constant at 100%. To note at this point that ring opening of produced MCP did not take place in this case. Dehydrogenation to benzene seems to be more difficult. A selectivity of 15.4% is obtained at 623 K and reaches a maximum of 59.2% at 673 K. The sequence of cyclohexene reactions performed by specific catalytic functions of the bifunctional $MoO_{2-x}(OH)_y/TiO_2$ system could be summarized as follows:



It is worth mentioning that ring opening catalytic process activity is very low to negligible in this case.

The catalytic activity of the $MoO_{2-x}(OH)_y/TiO_2$ bifunctional system toward cyclohexane has been studied as a function of reaction temperature. Initial activity of 0.8% of the system in form of cyclohexane isomerization to methylcyclopentane MCP has been observed at 473 K. The conversion increases to 59.9% with 97.5% of MCP at 573 K (Fig. 8). Dehydrogenation of cyclohexane to benzene starts at 623 K reaction temperature. Benzene product selectivity of 54.7% and 98% conversion were obtained at 673 K. These results clearly demonstrate that isomerization of cyclohexane to MCP, catalyzed by the Brønsted acid function of $MoO_{2-x}(OH)_y/TiO_2$ is easier than the dehydrogenation process to benzene performed by the metallic function of this catalytic system. The effect of metal function particle size such as the delocalized π electrons along the Mo–Mo atoms in deformed rutile structure of MoO_2 in $MoO_{2-x}(OH)_y/TiO_2$ in comparison with the relatively large aggregates of Mo atoms in the Mo(0) metallic state is investigated. Further increase in the reduction temperature of MoTi carried out under hydrogen up to 873 K for more than 12 h enabled to convert all the Mo atoms to the elemental Mo(0) state as revealed by the XPS of the Mo(3d) energy region as well as the UP spectrum. In other words, the relative density of states at the Fermi level is substantially increased (Fig. 3d). The dehydrogenation activity of cyclohexane on this Mo(0) system starts also at 623 K with a conversion of 7.4% and 97.1% selectivity to benzene formation (Fig. 9). At 733 K reaction temperature, the conversion increases to 81.4%, while the benzene selectivity remains constant at 97%. Apparently, 623 K reaction temperature is the energy barrier for the dehydrogenation of cyclohexane on this Mo based catalysts. Isomerization of cyclohexane to MCP did not take place on the Mo(0) due the absence of Brønsted acid function(s) formation on the surface of this system.

Addition of alkali Na or K alkali metals to MoTi system results in the suppression of the Brønsted acid function(s) formation, as discussed above, is confirmed in the case of cyclohexane reactant.

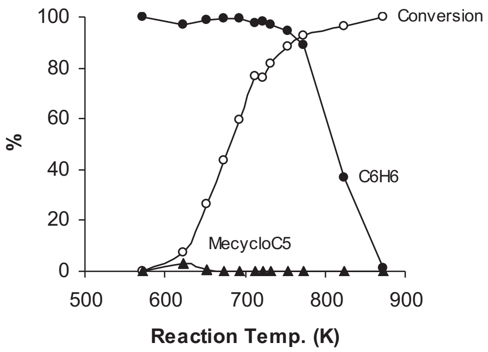


Fig. 9. Variation of cyclohexane conversion and selectivity as a function of reaction temperature to main methylcyclopentane and benzene reaction products during cyclohexane catalytic reaction on reduced MoTi by hydrogen at 873 K for 12 h.

No isomerization to MCP is observed. In fact, catalytic activity of the order of 13% cyclohexane conversion to benzene starts at 673 K on Na or K modified system. At higher reaction temperatures than 750 K, the alkali metal modified MoTi system behaves in similar way to the unmodified system in terms of dehydrogenation of cyclohexane to benzene. This is attributed to the reduction of MoO_3 to Mo(0) state.

4. Conclusions

Combination of adequate surface XPS-UPS, ISS techniques and well characterized catalytic reactions in terms of acid and metal functions requirements enabled to define the catalytic activity–chemical structure relationship in heterogeneous Mo oxides based catalysts. Formation of metal, acid and bifunctional metal–acid functions in partially reduced by hydrogen of MoO_3 deposited on TiO_2 at different temperatures were characterized, in situ, by XPS-UPS, ISS surface techniques as well as specific catalytic reactions carried out at the same experimental conditions.

Identification of the presence of acid, metal or both metal–acid functions in MoO_3/TiO_2 (MoTi) structure following its exposure to hydrogen at 673 K for 12 h clearly demonstrates the presence of stable $MoO_{2-x}(OH)_y/TiO_2$ bifunctional catalytic system. Addition of small amount of Na or K alkali metal results in the suppression of Brønsted acid function(s) as demonstrated by catalytic and spectroscopic characterization measurements.

Complete conversion of 2-propanol on the bifunctional $MoO_{2-x}(OH)_y/TiO_2$ catalyst takes place at reaction temperatures between 473 and 673 K. Two consecutive catalytic processes in terms of dehydration to propene, performed by the Brønsted acid function, followed by its hydrogenation to propane, were performed by the metallic function. The relative concentration of propane increases from 23.3% at 473 K to 92.5% at 673 K reaction temperature. In the case of cyclohexene, a conversion of 100% and 97.5% selectivity to cyclohexane were obtained at 423 K reaction temperature on $MoO_{2-x}(OH)_y/TiO_2$ catalyst. Moreover, 15.4% of the produced cyclohexane at 473 K is isomerized to methylcyclopentane and increases to 72.1% at 573 K. On the other hand, dehydrogenation of the produced cyclohexane to benzene takes place at higher reaction temperature with a maximum of 59.2% at 673 K. Further reduction of the bifunctional $MoO_{2-x}(OH)_y/TiO_2$ under hydrogen at 873 K enabled to produce the elemental Mo(0) structure. A conversion of 81.4% of cyclohexane to mainly benzene with a selectivity of 97% was obtained at 733 K reaction temperature.

Acknowledgements

The support by Kuwait University through research grant # SC03/09 and *GFS project # GS02/08* is gratefully acknowledged.

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