

Catalytic Hydrogenation Reactions on Molybdenum Oxide

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Abstract

Partially reduced molybdenum trioxide deposited on titania under hydrogen at 673 K for 12 h enabled to convert several surface atomic layers to the catalytically active bifunctional (metal-acid) $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ (MoTi) structure. The formed metallic function is the result of π bonding between adjacent Mo-Mo atoms placed along the C-axis of the rutile structure of MoO_2 . Delocalization of these π electrons produces a wire like atomic metal. This resembles in a way, the small Pt particles deposited on a support. Moreover, dissociated hydrogen atoms are bonded to sample surface oxygen to produce Brønsted acid Mo-OH function(s). These metal-acidic properties have been tested for several catalytic reactions requiring one or both catalytic functions. In this order, 2-propanol species could be considered as a model test of the acidic function via dehydration of the molecule to propene, while hydrogenation of the produced propene to propane is performed by the metallic function. Moreover, hydrogenation of 2-propanol to acetone, requires relatively strong metallic function. In this order, addition of small amount of alkali metal like rubidium will suppress the acidic function in $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ and enhance the metallic function strength. The performance of the metallic function alone in this case will be evaluated. Titanium dioxide is employed in this catalytic system as a support. It does not have any catalytic effect. Association of XPS-UPS, ISS surface techniques with catalytic performances of this catalytic MoTi system will be presented.

Keywords

$\text{MoO}_{2-x}(\text{OH})_y$ Catalyst, XPS, Acid-Metal Functions, Hydrogenation, 2-Propanol

1. Introduction

Hydroisomerization and hydrogenation reactions of light naphtha compounds are of special interest in terms of improving the octane number of these compounds [1]. In general, these catalytic reactions are carried out using

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finely dispersed noble metals such as Pd, Pt, Rh [2]-[5]. Hydroisomerization process of these compounds requires both the metallic and acidic functions. Several problems are encountered using these noble metals based systems such as highly dispersed fine particles preparation, sintering and poisoning by sulfur and other trace metals. A molybdenum oxide based catalyst of bifunctional (metal-acid) $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ (MoTi) properties has been prepared [6]-[8]. Controlled reduction by hydrogen of MoO_3 deposited on TiO_2 at 673 K results in the partial reduction of MoO_3 to MoO_2 , characterized by *in-situ* XPS-UPS techniques. The metallic properties of this system are attributed to the delocalized π bonding between adjacent Mo atoms placed along the C-axis of the deformed rutile structure of MoO_2 [Jones]. The specific morphology of these metallic-like π electrons is comparable to the metallic properties of finely dispersed Pt or Pd-nanoparticles. Furthermore, hydrogen molecules are dissociated by this metallic function. Consequently, bonding of the hydrogen atoms to surface oxygens results in the formation of Brønsted acid Mo-OH function(s). Both metallic and acidic sites are present on the catalyst surface. This is to be compared of commonly prepared bifunctional catalysts using the metallic properties of noble metals deposited on acidic supports such as zeolites or Al_2O_3 . In this catalytic $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ system, TiO_2 support provides larger surface area to the Mo phase and mechanical strength to the catalyst.

In this research work, we provide some catalytic hydrogenation reactions of C5-C7 alkenes. The catalytic performances of both acidic and metallic functions in terms of dehydration/hydrogenation of 2-propanol will be presented. Suppression of the Brønsted acid Mo-OH function(s) is achieved by the addition of controlled amount of alkali metal such as K or Rb.

2. Experimental

2.1. Catalyst Preparation

The equivalent of 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 a pore volume of $0.5 \text{ cm}^3/\text{g}$ and a BET surface area of $50 \pm 5 \text{ m}^2/\text{g}$. Supported catalysts are prepared by impregnating the appropriate amount of molybdenum in ammonium heptamolybdate salt following the method described by Pines *et al.* [9]. After impregnation, the catalyst is calcined at 773 K which enabled to convert the molybdenum compound to MoO_3 as characterized by XPS. Small amount of 2.5% by mass of rubidium with respect to Mo were added to the impregnated catalyst. Catalyst activation is achieved following *in-situ* reduction of the $\text{MoO}_3/\text{TiO}_2$ system in a flow of $40 \text{ cm}^3 \text{ H}_2/\text{min}$. was carried out at 673 K. The hydrogen gas was a 99.9% pure product of KOAC (Kuwait).

2.2. Catalyst Characterization

Characterization of the samples by XPS was conducted using VG Scientific ESCALAB-250Xi spectrometer. The radiation source was monochromatic of Al $K\alpha$ operating at a power of 300 W (15 kV, 20 mA). UPS He(I) resonance 584 \AA 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 carried out in a high-pressure gas cell housed in the preparation chamber, with hydrogen flow at 120 mL/min. Binding energies were based on the carbon contamination C1s at 284.8 eV within an experimental error of ± 0.2 eV.

Ion scattering measurements were performed on the same 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 was drawn from the reservoir through 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 the catalyst. A continuous H_2 flow of $40 \text{ cm}^3/\text{min}$ 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.

3. Results and Discussion

3.1. XPS-UPS, ISS Catalyst Characterization

X-ray photoelectron spectroscopy XPS, UPS and Ion Scattering ISS techniques are the most appropriate surface

techniques which enable to define the nature and composition of the outermost surface layers, responsible for the catalytic activity of a system. Characterization experiments were carried out *in-situ* at the same conditions of catalytic measurements. The assignment of the different oxidation states of Mo oxides is based on the Mo ($3d_{3/2}$, $5/2$) spin-orbit components. These energies are at 235.85, 232.65 eV for MoO_3 , 234.9, 231.7 eV for Mo_2O_5 and 232.3, 229.1 eV for MoO_2 . Continuous sample exposure to hydrogen as a function of reduction temperature results in the formation of large Mo (0) crystallites at 873 K. This metallic state of Mo is characterized by Mo(3d) spin-orbit components at 230.85 and 227.7 eV.

Two well-defined spectral lines at 235.9 and 232.7 eV were observed (**Figure 1(a)**) in the case of calcined Mo salt deposited on TiO_2 . These lines are assigned to the Mo (3d) spin-orbit components of MoO_3 . *In situ* exposure of the sample to hydrogen at 673 K for 12 h shows the presence of more complex structure of the Mo (3d) energy region (**Figure 1(b)**). Deconvolution of this band reveals the presence of three Mo oxides states. The most intense Mo ($3d_{3/2,5/2}$) at 232.3 and 229.1 eV is assigned to MoO_2 . Lower concentration states of Mo_2O_5 and MoO_3 are also present. Most probably, the MoO_2 structure constitutes the outermost surface structure of the sample. This statement is based on the fact that the XPS of the valence band following sample reduction at 673 K (**Figure 2(b)**) reveals the presence of DOS structure at the Fermi level, characteristic of the conductive π electrons of MoO_2 . This DOS structure (0.4 eV) at the surface of the sample is well defined in the UP spectrum (**Figure 3(b)**). Consequently, it is concluded that Mo_2O_5 is present in the interphase between surface MoO_2 and unreduced MoO_3 in the bulk.

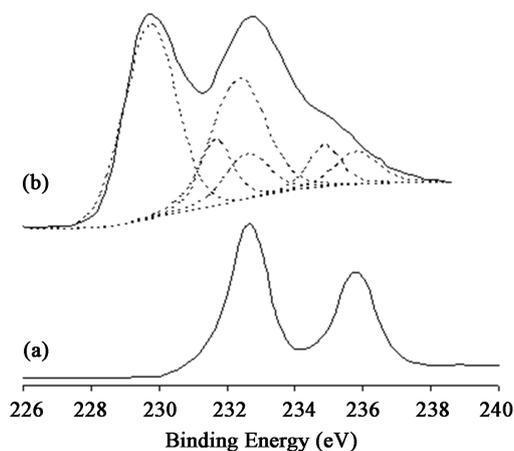


Figure 1. Mo(3d) region of $\text{MoO}_3/\text{TiO}_2$ 5 layers (a) before treatment (b) after reduction at 673 K for 12 h.

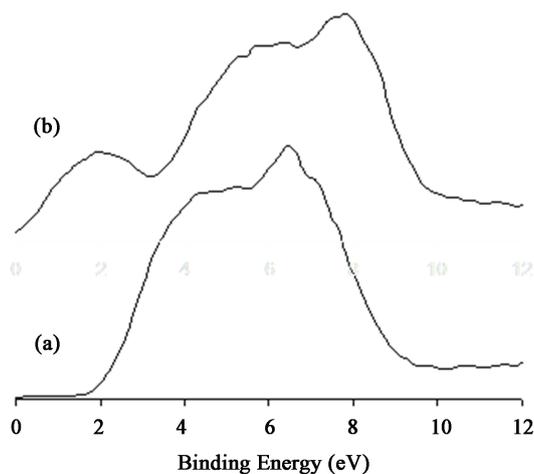


Figure 2. XPS of the valence band of 5 layers $\text{MoO}_3/\text{TiO}_2$ (a) before treatment (b) after reduction at 673 K for 12 h.

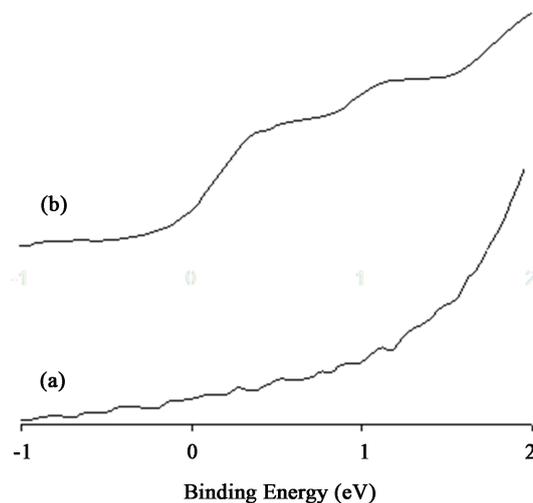


Figure 3. UPS of 5 layers MoO₃/TiO₂ (a) before treatment (b) after reduction at 673 K for 12 h.

In the case of the reduced sample by hydrogen at 673 K (**Figure 4(b)**), the oxygen 1 s energy region shows the presence of a shoulder at 531.4 eV beside the main oxide oxygen. This is attributed to the formation of Brønsted acid Mo-OH function(s) on the sample surface. The Mo-OH formation takes place in a sequence of processes in which hydrogen molecules were dissociated by the delocalized π electrons to hydrogen atoms. Bonding of the produced active hydrogen atoms to surface oxygen results in the formation of Brønsted acid Mo-OH groups. As a result, a bifunctional MoO_{2-x}(OH)_y/TiO₂ structure is obtained. The XPS of the Ti 2p energy region before and after hydrogen reduction does not show any changes in neither the binding energy nor the spectral lines shape (**Figure 5(a)** and **Figure 5(b)**). In fact, TiO₂ is employed in this case as a support in order to increase the surface area and provide mechanical strength to the Mo catalyst. ISS spectra of the Mo sample shows the presence of Mo, Ti and oxygen on the sample surface before and after reduction (**Figure 6(a)** and **Figure 6(b)**). This indicates that Mo does not completely cover the TiO₂ surface, This is due, most probably to the formation of needle like crystallite structure of Mo on TiO₂ as observed by Bond *et al.* [10].

3.2. Catalytic Measurements

Hydrogenation catalytic reactions of C5 - C7 alkenes and dehydration/ hydrogenation of 2-propanol will be presented.

3.2.1. 1-Pentene

Complete conversion of 1-pentene to n-pentane takes place on the bifunctional MoO_{2-x}(OH)_y/TiO₂ at 423 K (**Figure 7**). Although the conversion remains unchanged at higher reaction temperatures, isomerization of the produced pentane to isopentane takes place. At 623 K, 54.9% of the hydrogenated n-pentane molecules undergo isomerization to iso-pentane via carbenium ion mechanism requiring both metal-acid functions [11]. At higher reaction temperature, hydrocracking reactions producing C1-C3 hydrocarbon species are favored. It is interesting to note that different catalytic behavior takes place using large Mo (0) crystallites. Hydrocracking C1-C3 products are dominant. Also, no isomerization process to i-C5 is observed. This is attributed, in part, to the relatively strong metallic function in Mo (0). Isomerization to iso-pentane cannot be performed due to the absence of the acidic function. Similar catalytic behavior to Mo (0) has been observed in the case of the addition of trace alkali metals such as K, Rb, Cs to the molybdenum oxide and reduced at 673 K. The promoter alkali metal in this case suppress the Brønsted acid Mo-OH in favor of Mo-OA (A = Rb).

3.2.2. 1-Hexene

In similar way to what is observed in the case of 1-pentene, complete hydrogenation of 1-hexene molecules to n-hexane over MoO_{2-x}(OH)_y/TiO₂ takes place at 423 K. However, at higher reaction temperature, part of the produced n-hexane molecules are isomerized to mainly 2 and 3-methylhexane with a ratio 2 MP/3 MP = 1.5 in

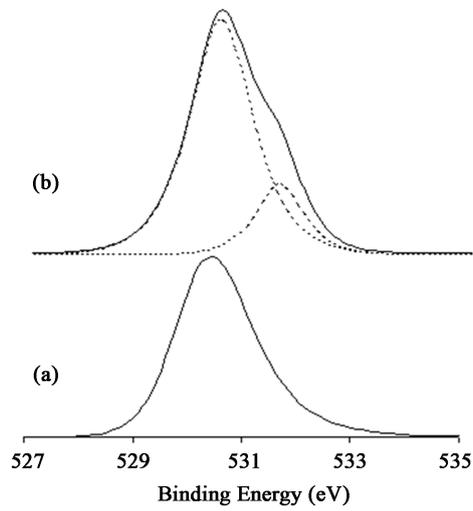


Figure 4. O1s region of 5 layers MoO₃/TiO₂ (a) before treatment (b) after reduction at 673 K for 12 h.

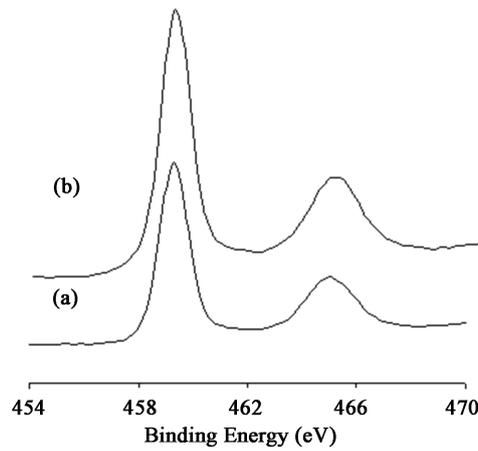


Figure 5. Ti 2P region of 5 layers MoO₃/TiO₂ (a) before treatment (b) after reduction at 673 K for 12 h.

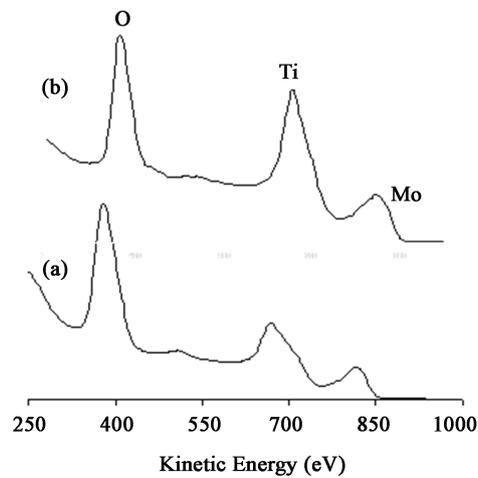


Figure 6. ISS of 5 layer MoO₃/TiO₂ (a) before treatment (b) after reduction at 673 K for 12 h.

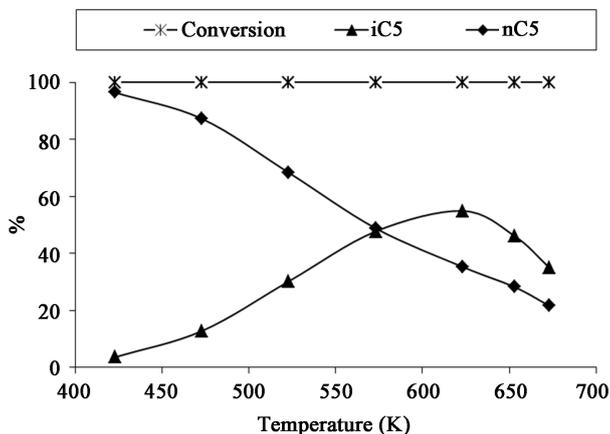


Figure 7. Hydrogenation and isomerization of 1-pentene on $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ as a function of reaction temperature.

agreement with the thermodynamic ratio. Also and to lesser extent, 2,2 and 2,3 dimethylbutane isomerizations products were obtained. Beyond 623 K reaction temperature, hydrocracking products are favored.

3.2.3. 1-Heptene

Although complete hydrogenation of 1-heptene to heptane takes place at 423 K, in similar way to 1-pentene and 1-hexene catalytic reactions, considerable decrease in the hydrogenation process in favor of hydrocracking products at higher reaction temperature of 523 K is observed. This is due, most probably, to the size of the heptene molecule. Hydroisomerization of 1-heptene to mainly 2 and 3-methylhexanes with ratio 2 MH/3 MH is close to unity is observed. The selectivity of these isomers reach a maximum of 45% at 573 K reaction temperature. These catalytic results clearly demonstrate that concerted sequences of catalytic process in terms of hydrogenation followed by isomerization reactions (dehydrogenation/isomerization of the olefin/hydrogenation) take place on this bifunctional Mo oxide catalyst.

3.2.4. 2-Propanol

The catalytic behavior of 2-propanol is generally used to determine the redox properties of oxide catalysts [12]. In this respect, three reactions could take place depending on the nature and strengths of the catalyst active sites. Dehydration of 2-propanol to propene is performed by the acidic site [13] [14]. On the other hand, hydrogenation of the produced propene to propane is performed by metallic function. More difficult dehydrogenation of 2-propanol to acetone is performed by a metallic function of certain strength. Complete conversion of 2-propanol to propene takes place at 423 K using the bifunctional $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ system. This conversion remains total at higher temperatures up to 673 K. However, at 523 K, 11.6% of the formed propene molecules are hydrogenated to propane. This hydrogenation process increases as a function of the reaction temperature to reach 81.7% at 673 K. The concerted dehydration/hydrogenation process is clearly demonstrated in this case. This is in agreement with the surface characterization of the $\text{MoO}_{2-x}(\text{OH})_y/\text{TiO}_2$ system as a bifunctional (metal-acid) system. Dehydrogenation of 2-propanol to acetone was not observed in this Mo system. However, addition of small amount (2.5%) of Rb to the $\text{MoO}_3/\text{TiO}_2$ after calcination enabled to obtain 47% of acetone at 473 K reaction temperature. In this Rb modified system, a drastic decrease in the dehydration/hydrogenation processes takes place. This is due to the suppression of the acidic function by the alkali metal addition. The catalytic activity and stability of this system has been tested for several days, time on stream experiments without any observed changes in its performances. Extended research for other catalytic reactions is underway.

The above data clearly demonstrate the excellent concordance of catalytic activity-surface XPS-UPS, ISS characterization techniques in identifying the type and, to some extent, the relative strength of the catalytic active sites in a given system.

4. Conclusions

In situ XPS-UPS, ISS surface characterization enabled to define the chemical state of Mo following the calcina-

tion at 773 K of ammonium heptamolybdate deposited on TiO₂. It was found that the calcination process at 773 K of both systems enabled to convert all Mo salt to MoO₃ state. However, *in-situ* hydrogen reduction results in partial conversion of MoO₃ to MoO₂ in the case of MoO₃/TiO₂. The molybdenum dioxide is present in form of bifunctional (metal/acid) MoO_{2-x}(OH)_y/TiO₂(MoTi) structure. The acidic function could be suppressed by the addition of small amount of an alkali metal such as rubidium.

The bifunctional catalytic properties of MoTi and the only metallic properties of the modified system were evaluated for the hydrogenation catalytic reactions of C5 - C7 linear alkenes and 2-propanol. Complete hydrogenation takes place at 423 K, followed by hydroisomerization processes performed by the metal-acid functions of the catalyst. Dehydration of 2-propanol to propene is the easiest catalytic process performed by the Mo-OH acidic function, followed by the hydrogenation of the produced olefin to alkane, is performed by the metallic function of the system. Dehydrogenation of 2-propanol to acetone was not observed using Mo oxide catalyst alone. It required the addition of small concentration of Rb to initiate this reaction at 423 K.

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