Surface electronic structure-catalytic activity correlation of partially reduced molybdenum oxide(s) for the isomerization of light alkenes and alkanes

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Abstract. Catalytic activity-surface electronic structure correlation was carried out using surface XPS-UPS techniques. In situ reduction by hydrogen, were carried out at similar experimental conditions to those employed for the catalytic reactions. In the case of MoO$_3$ deposited on TiO$_2$, the reduction to MoO$_2$ state with the bifunctional MoO$_2$(H$_x$)ac phase on its surface starts at 573 K and reaches a stable state at temperatures between 653-673 K. In the case of alumina support, a strong metal-support interaction takes place during the catalyst preparation, leading to Al$_2$(MoO$_4$)$_3$ complex formation as characterized by XRD. The reduction process(s) of this complex by hydrogen as a function of temperature is different from what is observed in the case of titania support. The changes in the chemical structure of the sample surface in both systems were tested for the catalytic reactions of 1-pentene and n-pentane.

1. Introduction

Hydroisomerization of C5-C6 light alkanes is an important catalytic process in order to increase the octane number and improve the motor engine working conditions [1]. The transformation of n-pentane to isopentane takes place in several consecutive catalytic steps, summarized in terms of bifunctional (metal-acid) mechanism [2]. The most commonly employed catalyst in industry for such objective consists of finely dispersed platinum particles deposited on acidic support such as chlorinated alumina or zeolite. Dehydrogenation of pentane and hydrogenation of the isomerized olefin are performed by the metallic function, while isomerization of the olefin takes place on the acidic function. We have introduced a new type of bifunctional catalysts based on molybdenum and tungsten dioxides [3-5]. The catalytic performances of these systems are comparable and have several advantages as compared to the Pt catalysts. The dioxide species such as MoO$_2$ has deformed rutile crystal structure. It is obtained, in general, as a result of controlled reduction of MoO$_3$ by hydrogen as a function of temperature. The metallic property of this MoO$_2$ phase is attributed to the delocalization of the $\pi$ electrons above the Mo atoms placed along the C-axis. This metal function is observed as density of states DOS at the Fermi level in the UPS spectrum. Dissociation of hydrogen by this metallic function produces active H atoms which are bonded to surface oxygen to form Brönsted Mo-OH acid group(s). As a result, a bifunctional MoO$_2$(H$_x$)ac phase is produced on the sample surface. Different catalytic reactions could take place in the case of 1-pentene and n-pentane depending on the nature of the catalyst active site(s) present on the sample surface [6].

XPS-UPS are the most appropriate surface techniques which enable to identify the presence of different chemical species on the outermost surface layer. In the case of MoO$_2$, this structure is identified in terms of the Mo (3d$_{5/2}$, s$_{5/2}$) spin-orbit components, measured at 232.3 and 229.1 eV, while the metallic character is observed as a DOS structure at the Fermi level in the UPS spectrum. Moreover, the formation of the Brönsted Mo-OH acidic site(s) is observed in the O1s XP spectrum at 531.6 eV.
2. Experimental
Molybdenum trioxide of high purity (99.5%) was supplied by STREM Chemicals. The equivalent of 5 monolayer of molybdenum trioxide, determined by lattice surface area of 20 Å², was deposited on TiO₂. Characterizations of the samples by XPS-UPS were conducted using VG Scientific ESCALAB-200 spectrometer. XPS data and curve fitting were analyzed using ECLIPS VG V 2.1 supplied with the instrument. Peaks are fitted in the symmetric mode. Gauss/Lorentz ratio is used taking into consideration the full width at half maximum FWHM, height ratio and peak center with the largest peak as a reference. Experimental details are given elsewhere [5].

3. Spectroscopic characterization of the catalysts
XPS-UPS surface techniques are employed in order to define the surface structures of partially reduced molybdenum oxide deposited on titania and alumina surfaces.

3.1. MoO₃/TiO₂
In order to define the nature of the Mo chemical species produced following MoO₃/TiO₂ exposure to hydrogen at different temperatures, we present the UPS-XPS spectra of bulk MoO₂ (Figure 1) and MoO₃ (Figure 2). It is important to note that commercial MoO₂ as received is covered by few layer(s) of MoO₃ on its surface. It requires reduction by hydrogen at 653 K for several hours in order to reduce some of surface MoO₃ to MoO₂.

The XPS-UPS spectra of the Mo 3d, O1s and the valence band of the prepared catalyst prior to its reduction is typical of the MoO₃ state. This state is defined by the Mo (3d₁/₂,5/₂) spin-orbit components at 235.85 and 232.65 eV (Figure 3a)[7]. Exposure of the sample, in situ, to hydrogen at 573 K for 2 h results in partial reduction of few upper surface MoO₃ layer to Mo₂O₅, measured at 234.9 and 231.7 eV (Figure. 3b). More sensitive UPS, shows the presence of DOS structure at the Fermi level. The absence of the MoO₂ structure in the XPS (3d) energy region is attributed to a relatively low concentration of this state at this reduction temperature. However, the presence of MoO₂ could be clearly observed in the Mo(3d) XP spectrum and UPS, following sample reduction at 673 K for 2 h, (Figure 3c). An additional spectral line at 531.6 eV, beside the main oxide oxygen at 530.5 eV, is also observed. This is assigned to the Brønsted Mo-OH acidic group(s) formed on the sample surface [8]. The presence of both the metallic and acidic functions
in the same chemical species is characterized by the bifunctional MoO$_2$(H$_x$)$_{ac}$ phase as the outermost surface layer.

![Figure 3. The XPS-UPS of MoO$_3$/TiO$_2$ (a) after calcination (b) after reduction at 573 K (c) after reduction at 653 K](image)

### 3.1.2. MoO$_3$/Al$_2$O$_3$

The XPS-UPS spectra of the equivalent of 5 monolayer of MoO$_3$ deposited on Al$_2$O$_3$ shows that Mo is present in the valence state Mo(VI) such as MoO$_3$. However, XRD of this system shows that all the Mo is present as aluminum molybdate Al$_2$(MoO$_4$)$_3$ complex. In such complex structure, the Mo(3d) BE is similar to bulk MoO$_3$. Apparently, strong metal-support interaction occurs between Mo and the alumina surface during the process of catalyst preparation. This might explain the difficulty of reducing Mo(VI) to lower valence state(s) following sample exposure to hydrogen at different temperatures. The extent of the reduction of Mo(VI) to Mo(IV) in MoO$_3$/Al$_2$O$_3$ is much less than what is observed in the case of MoO$_3$/TiO$_2$. In the case of the alumina support, some localized Mo(VI) is reduced to Mo(IV) state.

### 4. Catalytic results and discussion

In the following, we present a comparative study of the catalytic activities of partially reduced, at

| Reaction temperature (K) | 373 | 423 | 473 | 523 | 573 | 623 | 653 | 673 |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Conversion              |     |     |     |     |     |     |     |     |
| (94.7)                  | 93.8| 93.6| 93.6| 98.7| 100 | 100 | 100 | 100 |
| Selectivity % (branched products) |     |     |     |     |     |     |     |     |
| (100)                   | 96.9| 91.9| 90.6| 56.7| 56.8| 56.8| 56.8| 56.8 |
| Distribution (branched products, %) |     |     |     |     |     |     |     |     |
| iC4                     |     |     |     |     |     |     |     |     |
| (0)                     | 0   | 0.8 | 1.5 | 2.2 | 2.2 | 4.3 |     |     |
| iC5                     |     |     |     |     |     |     |     |     |
| (0)                     | 0.8 | (0) | (0) | (0) | (0) | (0.5)| (0.5)| (0.4)|
| ΣiC5                    |     |     |     |     |     |     |     |     |
| (100)                   | 94.0| 84.6| 80.5| 23.5| 0   | 0   |     |     |
| Others                  |     |     |     |     |     |     |     |     |
| (0)                     | 0   | 1.5 | 2.5 | 1.2 | 0   | 0   |     |     |
| Distribution (hydrogenation and cracking products, %) |     |     |     |     |     |     |     |     |
| C1-C4                   |     |     |     |     |     |     |     |     |
| (0)                     | 0   | 1.8 | 3.6 | 2.1 | 4.2 | 4.2 |     |     |
| C5                      |     |     |     |     |     |     |     |     |
| (0)                     | 3.1 | 6.3 | 5.8 | 47.2| 39.0| 39.0|     |     |

Table 1. Product distribution of 1-pentene on 0.5 g partially reduced Mo/TiO$_2$ and (MoO$_3$/Al$_2$O$_3$)
different temperatures, of MoO$_3$ deposited on either titanium or aluminum oxides towards 1-pentene and n-pentane reactants. Depending on the reduction (reaction) temperatures, two types of catalytic reactions of 1-pentene take place on MoO$_3$ deposited on either TiO$_2$ or Al$_2$O$_3$.

At reduction (reaction) temperatures between 423-523 K, a conversion of more than 90 % to olefin isomerization products is observed (Table 1) similar catalytic behavior of MoOx is observed using both supports. This catalytic behavior is attributed to different Lewis, and probably Brønsted acid site(s) associated with Mo$_2$O$_5$ oxide. However, at higher reduction temperatures between 573 to 653 K, hydrogenation of 1-pentene to n-pentane, as well as its isomerization to iso-pentane take place. In this case, the two supports systems differ. A selectivity of 23.9 % in iso-pentane is observed at 573 K in the case of MoO$_3$/TiO$_2$ as compared to only 4.1 % for MoO$_3$/Al$_2$O$_3$. The same trend is observed at higher reduction and reaction temperatures. This major difference between the two catalytic systems is attributed to the ease of reduction of the catalytically inactive MoO$_3$ to MoO$_2$ with the bifunctional MoO$_2$(H$_x$)$_{ac}$ phase as the outermost surface layer at temperatures between 573-653 K of using TiO$_2$ support. Meanwhile, in the case of MoO$_3$/Al$_2$O$_3$, a fraction of Mo(VI) is reduced to MoO$_2$, due to strong metal-support interaction.

The difference in the reduction process of MoO$_3$ to MoO$_2$ between the two supports could be clearly observed in the case of the transformation of n-pentane to iso-pentane. Such catalytic reaction requires the presence of a bifunctional (metal-acid) phase. A continuous increase in conversion of n-pentane to iso-pentane takes place as a function of reduction (reaction) temperature on MoO$_3$/TiO$_2$. A conversion of 60.1 % and 90.9 % selectivity to iso-pentane is obtained following catalyst reduction by hydrogen at 653 K for 12 h. On the contrary, the conversion of n-pentane to iso-pentane on MoO$_3$/Al$_2$O$_3$ remains very low regardless of the reduction and reaction temperature.

5. Conclusions
Characterization by XPS-UPS and XRD of the equivalent 5 atomic layers of MoO$_3$ deposited on TiO$_2$ and Al$_2$O$_3$ enabled us to identify the reduction process of MoO$_3$ by hydrogen as a function of temperature. On titania support, molybdenum trioxide is partially reduced to MoO$_2$ at temperatures up to 573 K. At higher temperatures, molybdenum dioxide is formed, with the bifunctional MoO$_2$(H$_x$)$_{ac}$ phase as the outermost surface layer. This bifunctional phase catalyze the transformation of n-pentane to iso-pentane.

In the case of alumina support, a strong metal-support interaction between Mo and the alumina surface results in the formation of aluminum molybdate Al$_2$(MoO$_4$)$_3$ complex. Only part of the surface is reduced to MoO$_2$ at high temperature. As a result, the catalytic performance of this system is much weaker than what is observed in the case of titania support.

6. References
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