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Isomerization reactions of *n*-hexane on partially reduced MoO_3/TiO_2

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Abstract

Isomerization of *n*-hexane on partially reduced MoO_3 deposited on TiO_2 was carried out using different masses of the catalyst. Consistent catalytic behaviour in terms of conversion and isomerization selectivity was observed regardless of the mass of the catalyst. A typical conversion of 80% and 90% of selectivity in isomerization products was obtained at 623 K, 0.7 h^{-1} LHSV and 15 bar hydrogen pressure. The major isomerization products are 2MP and 3MP present at the thermodynamic equilibrium ratio. Di-branched 2,2-DMB and 2,3-DMB were also obtained in the range of 18% of the isomerization products. The products distribution is comparable to that reported for Pt based catalysts. No changes were observed in the catalyst activity following its exposure to the hydrocarbon reactant for 60 days.

Keywords: MoO_3; TiO_2; Bifunctional catalysis; Isomerization of *n*-hexane; LHSV

1. Introduction

Catalyzed hydroisomerization reactions of light fractions from normal paraffin such as *n*-hexane have been rationalized in terms of a bifunctional mechanism [1]. The dehydrogenation of the saturated hydrocarbon bond and the hydrogenation of the isomerized olefin are performed by a metallic function of certain strength. On the other hand, isomerization of the olefin takes place on an acidic function. Platinum deposited on a support associated with an acidic function catalysts are the most commonly used systems in the industry as well as in the fundamental research [2–6]. Highly dispersed Pt on chlorinated alumina or zeolites are the main catalysts used in the industry for the isomerization of C5–C6 light alkanes. On the other hand, platinum associated with sulfated zerconia Pt (PtSZ) is also under consideration for such objective [4,6]. Several problems are associated with the Pt based catalysts. Beside its relatively high costs, toxic benzene is formed as a by-product. Moreover, the introduction of chlorine causes severe corrosion problems. Also, platinum is sensitive to sulfur poisoning.

In previous works, [7–12], we have introduced new catalytic systems based on partially reduced molybdenum or tungsten trioxides as a bulk or deposited on TiO_2. The catalytic active species has been identified as the MO_2 (M=Mo, W) phase. The delocalized π electrons over the M–M atoms placed along the *C*-axis of the deformed rutile structure of the MO_2 phase produce a metallic function of equivalent strength to the highly dispersed Pt particles. Dissociation of hydrogen by this metallic function to H atoms results in the formation of Brönsted M–OH on the sample surface. As a result, a bifunctional $MO_2(H_x)_{ac}$ outermost surface layer is produced. In a separate work, Rodrigues-Gattorno et al. [13] using different characterization techniques, X-ray diffraction, Raman spectroscopy, thermal analysis and HRTEM, have confirmed the bifunctional catalytic behaviour of the active molybdenum oxide species. Hydroisomerization of C5–C7 alkanes and olefins, dehydration of isopropanol and isomerzation/dehydrogenation of methylcyclohexane, at the microreactor level, were carried out on these systems [7–12]. XPS–UPS are the most appropriate surface techniques in order to define

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the presence of the metallic character of a given chemical species. It is observed as a density of states (DOS) at the Fermi-level with a maximum at 0.4 eV for MoO_2 . High resolution UPS spectrum clearly shows the presence of the metallic π and σ bands between adjacent M–M atoms in the deformed rutile structure of MoO_2. Moreover, the presence of Brönsted acidic (–OH) groups on the surface is observed in the form of O1 s at 531.6 eV as compared to the oxide O1 s at ~530.5 eV [8]. In this work, we present the XPS–UPS as well as HRTEM characterizations of the catalytic active phase in the case of partially reduced MoO_3 deposited on TiO_2. In order to envisage the use of this catalytic system at the industrial level, larger amounts of the catalyst than the laboratory microreactor scale should be employed. Moreover, the catalytic experiments will be carried out at different range of parameters such as pressure, reaction temperatures and contact time (LHSV). The use of TiO_2 extrudate as a support is important in order to increase the surface area of the active phase and avoids pressure drop which results from the use of bulk MoO_3 powder. It is important to note that titanium dioxide alone has no catalytic activity towards *n*-hexane reactant regardless of the experimental conditions.

2. Experimental

The equivalent of five monolayers of molybdenum trioxide (19.65% by mass) were deposited on TiO_2 using ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (99.9%) supplied by STREM Chemicals. Titanium dioxide TiO_2 is Degussa P-25 (25% rutile) with pore volume of 0.5 cm^3/g and BET surface area of $50 \pm 5\ m^2/g$. Supported catalyst is prepared by impregnating the appropriate amount of molybdenum in ammonium heptamolybdate salt, following the method described by Pines et al. [14]. Different concentrations of MoO_3, which correspond to the equivalent 1–3 monolayers did not yield consistent catalytic results. Further research work, using different characterization techniques, is underway in order to elucidate the relation between the Mo relative concentration in MoO_3/TiO_2 versus the conversion and selectivity in isomerization products. The catalytic experiments were performed using different amounts ranging from 100 mg to 15 g of the catalyst in fixed bed reactors. A commercial bench scale Xytel of India catalytic unit equipped with a Stainless steel reactor of 235 cc is employed for the catalytic experiments. Alumina balls and or silicon carbide were employed to dilute the large amounts of the catalysts, the catalyst was loaded into the reactor and gradually the pressure was raised to 15 bar. After that the catalyst was reduced at 653 K for 12 h in hydrogen flow of 45 SLPH (stand. liter per hour).

Time on stream experiments were carried out for several days in order to study the stability of the active surface under continuous flux of hydrogen and hydrocarbon reactant. Different experimental parameters such as hydrogen flow rate, pressure, reaction temperature as well as LHSV were also studied . Catalytic products were analyzed by gas chromatography using 100 m (Petrocol-DH) column and a flame ionization detector. 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 carried out in a high-pressure gas cell housed in the preparation chamber, with hydrogen flow at 200 mL/min. Binding energies were based on the carbon contamination C1s at 284.8 eV within an experimental error of ± 0.2 eV.

High resolution transmission electron microscopy HRTEM measurements were carried out using a JEM3010 JEOL instrument.

3. Results and discussion

3.1. Characterization by XPS–UPS and HRTEM

In the following, we present the XPS–UPS spectra of the catalytic active phase following controlled reduction of MoO_3/TiO_2 by hydrogen at 653 K for more than 6 h. This corresponds to the experimental procedure carried out in order to activate the catalyst system. The assignment of the oxidation states of different Mo oxides is based on the Mo ($3d_{3/2,5/2}$) spin-orbit components. These energies are at 235.85 and 232.65 eV for MoO_3, 234.9 and 231.7 eV for Mo_2O_5, 232.3, 229.1 eV for MoO_2, and 230.85 and 227.7 eV for Mo(0) [15]. As observed from Fig. 1, the exposure of the MoO_3/TiO_2 sample to hydrogen

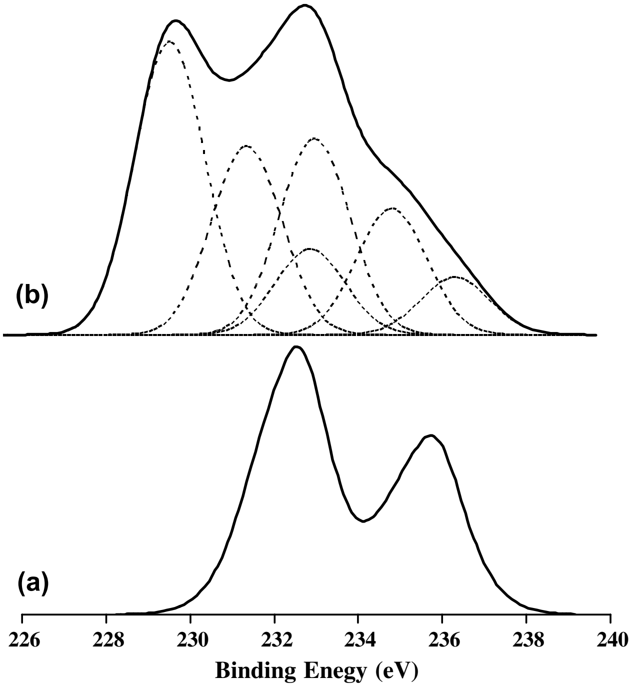

Fig. 1. The XPS of the Mo(3d) energy region of MoO_3/TiO_2 before (a) and following its reduction by hydrogen at 653 K for 2 h.