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Catalytic activity of Mo oxide before and after alkali metal addition for methylcyclohexane and methylcyclopentane compounds

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ABSTRACT

Different catalytic reactions of methylcyclohexane MCH are performed depending on the nature of the catalytic active site (s) and experimental conditions. Ring contraction RC catalytic processes, producing dimethylcyclopenanes DMCP's of high octane numbers as compared to MCH are catalysed by acidic function of zeolites systems such as HY. Better activity, selectivity and stability concerning these RC reactions were obtained using Pt/HY catalyst. At higher reaction temperature, dehydrogenation of MCH to toluene and hydrocracking reactions are catalyzed by Pt. Comparable catalytic behavior is obtained using a bifunctional (metal–acid) $MoO_{2-x}(OH)_y/TiO_2$ (MoTi) system. Different metallic character strength is observed following the suppression of the Brønsted acid Mo—OH function(s) to $MoO_{2-x}(OA)_y/TiO_2$ (*A* = Na, K, Rb) by the addition of small amount of alkali metal A. Rubidium addition seems to be the most performant in the dehydrogenation of MCH to toluene. The metallic functions in MoTi and modified AMoTi are not efficient for RO in MCP. In-situ characterization of the different oxidation states of Mo at different experimental conditions were conducted using in-situ XPS–UPS techniques.

1. Introduction

In general, Catalytic reactions are rationalized in terms of acidic, metallic or bifunctional catalysts. Methylcyclohexane MCH, undergo several types of catalytic processes requiring the presence of either acidic, metallic or both metal–acid (Bifunctional) functions. The most commonly used catalysts for such objectives are acid catalysts such as zeolites and platinum based systems at specific experimental conditions. In this respect, the principal catalytic reactions of MCH are: ring contraction (RC)-isomerization producing different non aromatic dimethylcyclopentanes (DMCP) of higher octane number as compared to MCH [1]. The isomerization reactions are catalyzed by Brønsted acid function(s) such as the zeolite HY catalyst. However, beside the instability of the zeolite catalysts, considerable increase in the relative concentration of the highest octane number 1,1-DMCP is achieved using the bifunctional Pt/HY as compared to HY zeolite alone. It is supposed that platinum, in this case, activates the hydride transfer step [1–3]. Less desired ring opening (RO) processes leading to heptane and 2, 3- methylhexanes, of much lower octane number, seem to require stronger metallic function(s) catalytic systems. Bimetallic catalysts such as Pt–Rh supported on chlorinated alumina acidic support for example, appear to be the most active for RO reactions. This catalytic process is rationalized in terms of bifunctional mechanism in which MCH is isomerized to diverse dimethylcyclopentanes DMCP, catalyzed by the acidic function as first step, followed by RO performed by relatively strong metal function [4–5]. Dehydrogenation of MCH to toluene as well as cracking reactions are performed by metallic function of highly dispersed platinum particles [6]. In the case of methylcyclopentane MCP, catalyst particle size in terms of relative high density of active site(s) as well as the nature of the catalytic active species are important in defining the order and magnitude of activity and selectivity [7–10].

Platinum is widely used in catalysis due, in part, to its specific metallic properties. However, platinum is rare and expensive. It is also difficult to prepare it in finely dispersed particles deposited on an acidic or carbon supports [11]. Moreover, Pt undergoes sintering at certain experimental conditions which results in drastic changes in its catalytic properties. It is also sensitive to poisoning by sulfur and other heavy trace metals present in crude oil cuts reactant(s). Possible replacement of Pt becomes a subject of importance from scientific and economical points of views. In this respect, in-situ partial reduction by hydrogen at 673 K of molybdenum trioxide deposited on titanium dioxide enabled to produce a bifunctional (metal–acid) $MoO_{2-x}(OH)_y/TiO_2$ (MoTi) catalyst [12–14]. In this system, the metallic function consists of delocalized π electrons

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above the Mo–Mo atoms placed along the C-axis of the deformed rutile structure of MoO_2. It is important to note that metallic electrons are delocalized on arrays of atoms, an atomic like wire. This is in comparison to highly dispersed Pt particles deposited on a support. On the other hand, Brønsted acid Mo—OH function(s) are formed on the sample surface following hydrogen dissociation by the π metallic function to active hydrogen atoms which are bonded to surface oxygen Mo—OH. The Brønsted acid groups were characterized by in-situ IR spectra of adsorbed pyridine molecules [13,14]. Hydrogen reduction of the sample at 873 K for 12 h results in the formation of relatively large Mo(0) metallic aggregates. Suppression of the Brønsted acid function(s) in $MoO_{2\text{-}x}(OH)_y/TiO_2$ could be achieved by controlled addition of relatively small amount (2.5%) of alkali metals such as Na, K [13,14] Rb. In-situ XPS–UPS characterization of the different states of molybdenum trioxide deposited on TiO_2 pellets, were performed following in-situ hydrogen reduction at different temperatures. The catalytic properties of the Mo based catalysts before and after modifications by alkali metals, $MoO_{2\text{-}x}(OA)_y/TiO_2$ (A = Na, K, Rb) for the well-defined catalytic reactions of MCH and MCP will be presented in comparison with the reported data using HY zeolite and Pt/HY based catalytic systems.

2. Experimental

2.1. Catalyst preparation

A wet impregnation method using ammonium heptamolybdate salt has been used in the preparation of five monolayers MoO_3 supported TiO_2 salt following the method described by Pines et al. [15]. An appropriate amount of this salt was completely dissolved in excess distilled water. This salt solution was then poured into the corresponding amount of TiO_2 in a rotary evaporating flask with continuous mixing for 30 min, and then the solution was completely dried under vacuum at 343 K. After that an appropriate amount of each sodium, potassium and rubidium nitrate salt was separately dissolved in excess distilled water. The solution was added with continuous mixing to the dry mixture for 30 min. The resultant solution was completely dried under vacuum at 343 K. The prepared catalyst was then placed in electric oven at 383 K overnight. Finally, the calcination step was carried out using a tube furnace (F21100/ USA) through the passing air at 773 K for 12 h. The sample was cooled in argon atmosphere and then was kept dry over silica gel.

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). 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 C1s at 284.8 eV within an experimental error of 0.2 eV.

2.3. Catalyst tests

Time on stream catalytic reactions under atmospheric hydrogen pressure was studied. The reactant was drawn from the reservoir throw HPLC pump of flow rate of 0.1 mL/min then it passed though vaporizer and eventually it passed over a fixed bed quartz reactor containing either MoTi or Na, K, Rb modified MoTi (AMoTi) 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.

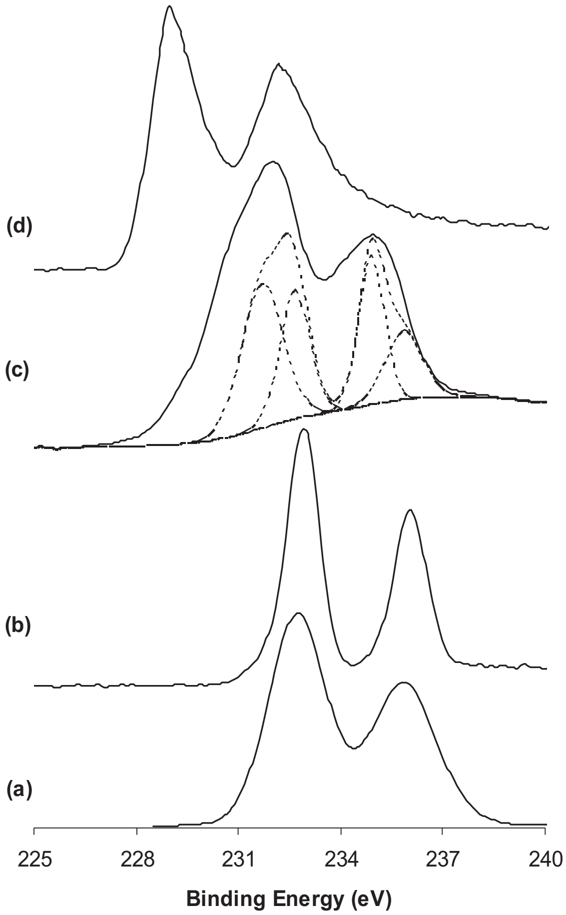

Fig. 1. XPS of Mo(3d) energy region after calcination at 773 K of MoTi (a), RbMoTi (b), after hydrogen reduction of RbMoTi at 473 K (c), after hydrogen reduction of RbMoTi at 673 K (d).

3. Results and discussion

3.1. Catalyst characterization

Characterization of the active metal-acid functions in partially reduced MoO_3 deposited on TiO_2 as well as the modified system by the addition of small amounts of alkali metals, using XPS--UPS, ISS, FT-IR techniques was reported in previous works [13–14]. To elucidate the effect of changes in the relative density of the metallic active site(s) in relation with the catalytic activity of the system, the changes in the XPS of the VB of the uppermost surface layer in parallel with the Mo (3d) spin-orbit components before and after in-situ hydrogen reduction at different temperatures will be reported. In this study, we report data related to the addition of rubidium Rb to the Mo catalyst (RbMoTi).

3.2. XPS spectra

Calcination of equivalent 5 monolayers of ammonium heptamolybdate deposited on TiO_2 (MoTi) surface at 773 K enabled to convert all Mo atoms to MoO_3 with Mo ($3d_{3/2,5/2}$) spin-orbit components at 235.8 and 233.6 eV (Fig. 1a). The VB energy region does not show any density of states at the Fermi level (Fig. 2a). This is in agreement with the insulating properties of MoO_3 structure. Similar results were obtained in the case of the Rb modified MoTi