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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.

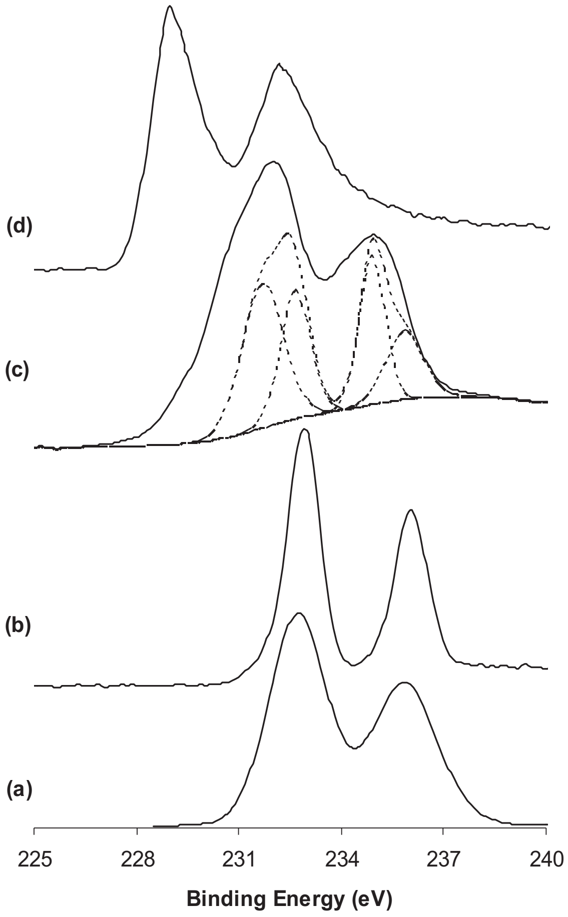

Fig. 1. XPS of Mo(3d) energy region after calcination at 773 K of MoTi (a), RbMoTi (b), after hydrogen reduction of RbMoTi at 473 K (c), after hydrogen reduction of RbMoTi at 673 K (d).

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

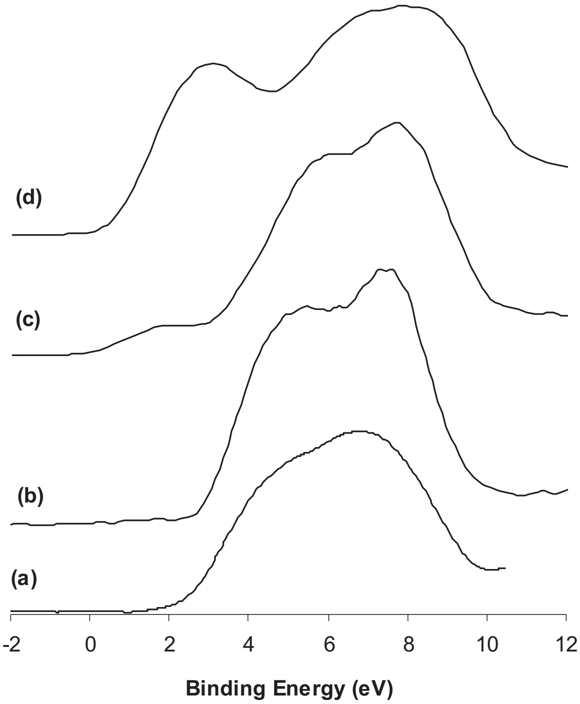

Fig. 2. XPS of the VB energy region after calcination at 773 K of MoTi (a), RbMoTi (b), after hydrogen reduction of RbMoTi at 473 K (c), after hydrogen reduction of RbMoTi at 673 K (d).

(Fig. 1b). In-situ exposure of the sample to hydrogen at 473 K for 2 h enabled to partially reduce MoO_3 to Mo_2O_5 state (Fig. 1c). Low concentration of MoO_2 could be observed in form of DOS at the Fermi level in the VB energy region (Fig. 2c). Extended exposure of the sample to hydrogen at 673 K for 12 h results in the conversion of MoO_3 to MoO_2 state, characterized at 232.3 and 229.1 eV (Fig. 1d). The presence of MoO_2 could also be identified as DOS structure in the valence band (Fig. 2d). The presence of the π and σ energy levels, characteristics of the MoO_2 state, could also be observed in the UPS of RbMoTi after hydrogen reduction at 673 K (Fig. 3b). To note at this point that the reduction process by hydrogen of MoTi and RbMoTi seems to be different. In the case of the unmodified MoTi system, only part of MoO_3 is converted to MoO_2 at 673 K for 12 h, whereas most if not all of MoO_3 in RbMoTi are converted to MoO_2. Apparently, molybdenum deposition on titania surface in MoTi takes place in form of aggregate needle like crystallites structure as postulated by Bond et al. [16]. So, only the upper MoO_3 surface layers are converted to MoO_2. In the case of alkali metal addition to MoTi, discrete entities of the modified system such as Rb_2MoO_4 could be formed in the calcination process 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. Titanium dioxide is employed as a support in order to increase the surface area of the Mo active phase and inherit mechanical strength to the catalyst without any involvement in the catalytic activity of the system. The Ti($2p_{3/2,1/2}$) binding energies at 458.5 and 464.2 eV did not change after the calcination of the Mo salt or the modified one by the addition of Rb as could be observed in Fig. 4.

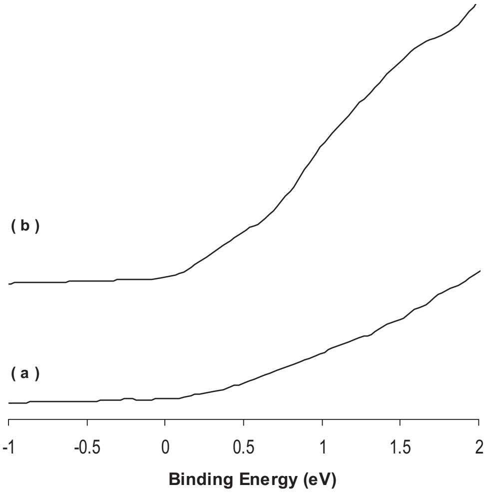

Fig. 3. UPS of Rb modified Mo catalyst RbMoTi after calcination at 773 K (a), after in-situ hydrogen reduction at 673 K for 12 h (b).

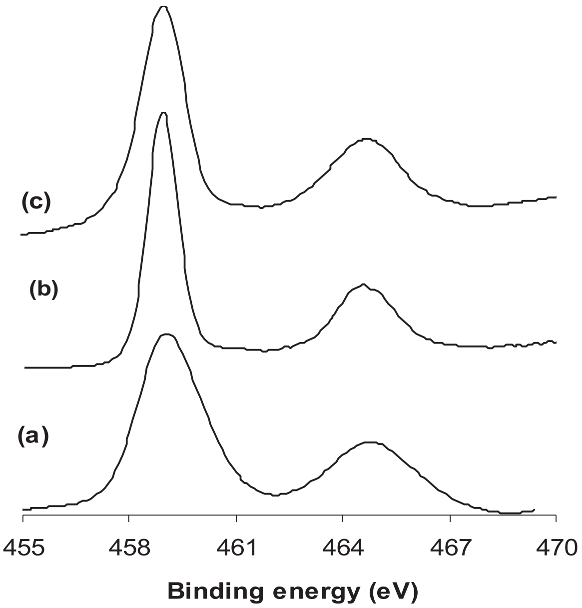

Fig. 4. XPS of Ti(2p) energy region after calcination at 773 K of MoTi (a), RbMoTi (b), after hydrogen reduction of RbMoTi at 673 K (c).

Table 1
Isomerization reactions of MCH and products distribution on 0.5 g MoTi reduced at 673 K for 12 h, hydrogen flow 40 mL/min.

Products/Selectivity	Reaction temperature (K)			
	573	623	653	673
Conversion%	27.4	46.3	74.7	88.8
1,1DMCP	9.5	5.7	1.4	0.4
Trans 1,3DMCP	23.1	12.9	3.0	0.9
Cis 1,3DMCP	19.8	11.6	2.8	0.8
Trans 1,2DMCP	23.9	13.7	3.3	1.1
Et CP	21.5	10.0	2.5	0.8
Toluene	2.2	46.2	77.8	81.7
Others	0	0	9.1	14.1

Table 2
Comparative RC isomerization products distribution of MCH performed by Pt/HY at 533 K (ref.1) and MoTi at 573 K.

Products/Selectivity	MoTi	Pt/HY
Conversion%	27.4	29.2
1,1 DMCP	9.5	13.3
Trans 1,3 DMCP	23.1	15.6
Cis 1,3 DMCP	19.8	16.0
Trans 1,2 DMCP	23.9	26.0
Et CP	21.5	27.0

Table 3
Isomerization reactions of MCH and products distribution on 0.5 g A MoTi (*A* = Na, K, Rb) reduced at 673 K for 12 h, hydrogen flow 40 mL/min.

Reaction Temp. (K)	573				623				653				673			
2.5AMoO$_3$/TiO$_2$	Mo	Na	K	Rb	Mo	Na	K	Rb	Mo	Na	K	Rb	Mo	Na	K	Rb
Conversion,%	27.4	0.8	0.7	0.9	46.3	5.8	12.9	21.0	74.7	13.2	30.3	57.3	88.8	20.3	42.5	76.2
DMCP	76.3	0.0	0.0	0.0	43.8	0.0	0.0	0.0	10.5	0.0	0.0	0.0	3.2	0.0	0.0	0.0
Toluene,%	2.2	100	100	100	46.2	100	100	100	77.8	100	100	98.6	81.7	100	97.5	96.3
Et CP,%	21.5	0.0	0.0	0.0	10.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	0.8	0.0	0.0	0.0
Cracking, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.2	0.0	0.0	1.4	14.3	0.0	2.5	3.7

3.3. *Catalytic measurements*

The catalytic properties of the bifunctional (MoTi) and MoO$_{2\text{-}x}$(OA)$_y$/TiO$_2$ (*A* = Na, K, Rb) AMoTi will be evaluated for the catalytic reactions of MCH and MCP.

3.3.1. *Methylcyclohexane MCH*

The main catalytic reactions of MCH could be summarized as follows: Ring contraction RC leading to different dimethylcyclopentanes DMCP isomerization products of relatively high octane numbers as compared to MCH. These isomerization reactions are performed by acidic function such as HY or bifunctional, mainly Pt deposited on zeolite Pt/HY catalysts [1]. Dehydrogenation to toluene is performed by a metallic function. On the other hand, ring opening RO, producing 2, 3- methylhexanes and heptane, of lower octane number than MCH, are performed by metallic function. Furthermore, RO catalytic reactions seem to be more difficult and require a catalyst of high hydrogenolysis activity such as Ir/SiO$_2$ or a bimetallic Pt–Rh deposited on acidic support. It is of interest to compare the bifunctional MoTi and the metallic AMoTi catalytic properties of the Mo systems concerning RC isomerization, dehydrogenation and RO catalytic reactions of MCH, to the commonly used zeolites and supported noble metals catalysts.

The catalytic reactions of MCH performed by MoTi as a function of reaction temperature up to 673 K are presented in Table 1. The conversion increases from 27.4% at 573 K to 88.8% at 673 K. However, two major types of catalytic reactions take place in this reaction temperature region. At low temperature of 573 K, isomerization ring contraction RC reactions are dominant, while MCH dehydrogenation to toluene relative concentration increases as a function of reaction temperature. Ring contraction dimethyl and ethylcyclopentanes constitute 97.8% of reaction products, and 2.2% of toluene at 573 K (Table 1). This to be compared with less than 10% of isomerization products and 81.7% toluene obtained at 673 K. The RC isomerization selectivity at low reaction temperature is attributed to the Brønsted acidic groups in agreement to what is obtained using zeolite HY and Pt/HY catalysts [1]. However, dehydrogenation of MCH to toluene seems to be more difficult to dissociate C—H chemical bond, performed by the metallic function of MoTi at relatively high reaction temperature. The addition of a metallic function such as Pt to the unstable zeolite HY catalyst enhances the stability of the catalyst performances. This is attributed to a higher rate of hydrogen transfer accelerated by the Pt metal [1]. This is what expected to take place concerning the metallic function in MoTi. It is worth mentioning that catalyst activity and selectivity are completely reproducible at any reaction temperature following ascending or decreasing in reaction temperature up to 673 K. Most probably, this is due to the atomic wire like metallic π electrons above the Mo–Mo atoms placed along the C-axis of the deformed rutile structure of MoO$_2$ based system, on which hydrocarbon poisoning species are not permanently adsorbed. This is not the case using the zeolite HY catalyst in which the activity drastically decreases after 6 h time on stream experiment [1].

It is of interest to notice the comparable RC isomerization products distribution trend, obtained by MoTi at 573 K with those using Pt/HY at 533 K (Table 2). The contribution of the metallic function of MoTi at this 573 K reaction is obvious from the presence of low concentration of toluene.

Different catalytic behavior of MCH takes place on the modified MoTi by alkali metals AMoTi (Table 3). There is almost no catalytic activity at 573 K reaction temperature as compared to the unmodified MoTi system. Furthermore, the catalytic activity remains relatively low at reaction temperatures up to 673 K. The main reaction product is the dehydrogenation process to toluene.

A conversion of 76.2% and selectivity of 96.3% to toluene were obtained at 673 K using the RbMoTi catalyst. The complete absence of dimetylcyclopentanes isomerization products in this case (Table 3), is due to the absence of the Brønsted acid function(s). Addition of Rb seems to enhance the metallic function strength of MoTi.

3.3.2. *Methylcyclopentane MCP*

Ring opening inactivity of the bifunctional MoTi and metallic AMoTi, Mo(0)Ti catalysts towards MCH reactant seems to prevail in the case of MCP. Apparently, strong metallic function(s) in form of large particle size of noble metals such as Pt and Ir or bi-metallic systems is required for such catalytic processes. The most selective products in this case are 2 and 3-methylpentanes and hexane [7–9,17–19]. Moderate catalytic activity in form of ring opening/ enlargement followed by dehydrogenation to benzene takes place in the case of the metallic Mo(0)Ti at 873 K. A conversion of 7.8% and 29.6% selectivity to benzene were obtained at 673 K reaction temperature. Although the conversion increases as a function of reaction temperature, benzene selectivity does not exceed 35%. Low concentration of the order of 10% of MCH is obtained at 773 K. Much lower activity is observed in the case of the modified AMoTi system. This could be considered as a demonstration that ring opening-ring enlargement require the presence of an acid function as well as relatively strong metallic function such as bimetallic noble metals deposited on acidic support.

4. Conclusions

In situ XPS–UPS characterization enabled to define the chemical state of Mo following the calcination at 773 K of ammonium heptamolybdate deposited on TiO$_2$, modification of this system by the addition of small amount of rubidium and in-situ hydrogen reduction at different temperatures. It was found that the calcination process at 773 K of both systems enabled to convert all Mo salt to MoO$_3$ state. However, in-situ hydrogen reduction results in partial conversion of MoO$_3$ to MoO$_2$ in the case of MoO$_3$/TiO$_2$. This is attributed to presence of MoO$_3$ in a needle like crystal structure. The molybdenum dioxide is present in form of bifunctional (metal/acid) MoO$_{2\text{-}x}$(OH)$_y$/TiO$_2$ (MoTi) structure. On the contrary, the majority of MoO$_3$ in the Rb modified system is converted to MoO$_2$. This is due to formation of isolated RbMoO$_4$ structure. In the case of Rb modified system, the Brønsted Mo—OH acid function is suppressed due to hydrogen replacement by the Rb atom (MoO$_{2\text{-}x}$(ORb)$_y$/TiO$_2$.

The bifunctional catalytic properties of MoTi and the only metallic properties were evaluated for the catalytic reactions of methylcyclohexane and methylcyclopentane. It was found that in the case of MCH reactant at relatively low temperatures, the bifunctional MoTi catalytic behaviour and performances are similar to Pt/HY. The main catalytic reactions in this case are RC isomerization of MCH to different dimethylcyclopentanes DMCP of relatively high octane number. However, at higher reaction temperatures, dehydrogenation of MCH to toluene is obtained. High conversion of 88.8 % and 81.7 selectivity to toluene is obtained at 673 K using the bifunctional MoTi system. In the case of the Rb modified system, RC reaction leading to the formation of DMCP isomers was not observed regardless of the reaction temperature. This is a clear demonstration of the suppression of the Brønsted acidic function in RbMoTi. Titanium dioxide is employed as a support in order to increase the surface area and add mechanical strength to the catalyst. In general, it could be concluded that the bifunctional $MoO_{2-x}(OH)_y/TiO_2$ system could be considered as possible replacement of the Pt/HY catalyst for ring contraction and isomerization of MCH and other naphtenic molecules.

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