

Reforming of hydrocarbons on partially reduced MoO₃/TiO₂

S. Al-Kandari¹, H. Al-Kandari², A. M. Mohamed¹, F. Al-Kharafi¹, A. Katrib^{1*}

¹Chemistry Department, Kuwait University, Safat, Kuwait

²College of Health Sciences, Public Authority for Applied Education and Training (PAAET),
Faiha, Kuwait

*corresponding author: ali.katrib@ku.edu.kw

Introduction

Hydroisomerization of C5–C6 light alkanes is an important catalytic process that increases the octane number of the gasoline pool and eliminates undesired aromatic compounds. We introduce a new catalytic systems based on partially reduced molybdenum or tungsten trioxides as a bulk or deposited on TiO₂. The delocalized p electrons over the M–M atoms placed along the C-axis of the deformed rutile structure of the MO₂ 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 Brønsted M–OH on the sample surface. As a result, a bifunctional MO₂(H_x)_{ac} outermost surface layer is produced.

Materials and Methods

The equivalent of 5 monolayers of MoO₃ deposited on TiO₂ has been prepared by impregnating the right amount of molybdenum in ammonium heptamolybdate salt (Strem Chemicals). TiO₂ is Degussa P-25 (25% rutile) with pore volume of 0.5 cm³ g⁻¹ and BET surface area of 50 ± 5 m²g⁻¹. Catalytic reactions were studied by introducing the reactant as pulses of 5 mL at constant pressure, over a fixed-bed quartz reactor under atmospheric hydrogen pressure.

Results and Discussion

The exposure of the MoO₃/TiO₂ sample to hydrogen at 653 K reduces some of MoO₃ to Mo₂O₅ and MoO₂ (Figure 1). Most probably, the surface upper layer(s) consist of MoO₂, while Mo₂O₅ is present in the inter-phase. The UPS spectrum clearly shows the presence of a DOS structure (0.4 eV) at the Fermi-level characteristic of the metallic π electrons of the MoO₂.

A typical conversion of 80% and 90% of selectivity in isomerization products was obtained at 623 K. 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.

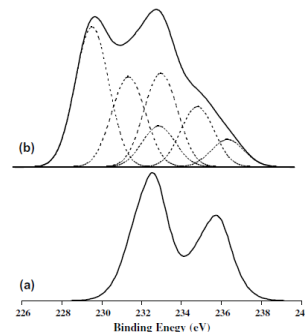


Figure 1 The XPS of the Mo(3d) energy region of MoO₃/TiO₂ before (a) and following its reduction by hydrogen at 653 K for 2 h.

Table 1 isomerization reaction of products distribution of n-hexane (0.1 mL/min) as a function of reaction temperature on MoO₃/TiO₂ partially reduced at 673 K for 12 h; hydrogen flow 45 SLPH at 15 bar.

	Reaction temperature (K)		
	573	623	653
Conversion	34.5	80.1	82.2
Selectivity, %	92.9	88.2	80.3
Hydrogenolysis (C1–C4) %	7.1	11.8	19.7
2MP/3MP	1.4	1.5	1.4
2,2-DMB/2,3-DMB	0.6	1.3	1.6
Distribution (branched isomers, %)			
iC4	0.3	0.7	1.6
iC5	0.7	3.8	8.0
2,2-DMB	3.8	10.6	11.6
2,3-DMB	6.2	8.4	7.3
2MP	48.1	38.8	30.4
3MP	33.7	25.9	21.4

Significance

Catalytic performances of the MO₂(H_x)_{ac} system in terms of Hydroisomerization of alkanes are comparable to those obtained by the Pt-based catalysts. Interestingly, benzene was not formed as a by-product of n hexane reactions. Moreover, the bifunctional state shows considerable resistance to corrosion by sulphur and water.

References

1. F. Gault, Adv. Catal. 30 (1980) 1.
2. A. Woortsch, Z. Paal, J. Catal. 185 (1999) 192.
3. U.B. Dimirci, F. Garin, Catal. Lett. 76 (2001) 45.
4. A. Katrib, P. Leflaive, L. Hilaire, G. Maire, Catal. Lett. 38 (1996) 95.