

Epoxidation of cyclohexene catalyzed by mixed oxides V₂O₅-TiO₂ as catalyst and TBHP as an oxidant

D. Lahcene^{1,2,3}, A. Choukchou-Braham², C. Kappenstein³ et L. Pirault-Roy³

¹Département de technologies, Faculté des Sciences et technologies, université de Bechar, BP 417 Route Kenadsa Béchar 08000 Algérie.

²Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculté des Sciences, Université A. Belakaid, B.P. 119 Tlemcen 13000, Algérie

³LACCO UMR 6503, Laboratoire de Catalyse, Faculté des Sciences Fondamentales et Appliquées, 86022 Poitiers Cedex, France
E-mail address: drissino@yahoo.fr

Introduction

Catalytic liquid-phase epoxidation of cyclohexene is a commercially important reaction used to produce cyclohexene oxide, which is an essential organic intermediate in the production of fine chemicals. Moreover, the production of epoxides paves the way to the development of mild and green chemical processes for the synthesis of adipic acid, the raw materials used in the production of nylon 6,6 [1]. The use of heterogeneous catalysts for cyclohexene oxidation and TBHP (tert-butyl hydroperoxide) as an oxidant has been demonstrated, with formation of 2-cyclohexene-1-one, 2-cyclohexene-1-ol, and trans-cyclohexane-1,2-diol beside cyclohexene oxide [2-5].

Experimental

Starting materials

Titanium butoxide (Ti(OC₄H₉)₄; Aldrich, 97 %), vanadyl acetylacetonate (VO(C₅H₇O₂)₂; Merck), propanol-2 (99,5 %, Merck), and acetic acid (Prolabo, 100 %). cyclohexene (Aldrich, 98 %), heptane (Fluka), tert-butyl hydroperoxide solution (Aldrich; 5.5 mol L⁻¹ in decane)

Synthesis of V₂O₅-TiO₂

Typical procedure for 10 wt.-% V₂O₅-TiO₂ sample: the mixed oxide was prepared by an acid-catalyzed sol-gel process [6] using 0.8750 g (0.00330 mol) of vanadyl acetylacetonate VO(acac)₂ dissolved in water under stirring for 15 min. Then a mixture containing titanium butoxide (23.0056 g, 0.0676 mol), acetic acid (0.5 ml) and propanol-2 (50 ml) were added into the solution while stirring. The obtained green gel was dried at 60 °C and then calcined at 500 °C for 4 h (5 °C.min⁻¹) under air in a muffle furnace.

The prepared catalysts are analyzed by ICP-OES and characterized by different physico-chemical techniques: infrared spectroscopy (IR), X-ray diffraction (XRD), thermal analysis (ATG-ATD) and specific surface area determination (BET). They are evaluated for epoxidation of cyclohexene using tert-butyl hydroperoxyde (TBHP) as the oxidizer.

The reaction mixture was analyzed by gas chromatography (GC), taking aliquots at different reaction times. A Varian GC-450 gas chromatograph equipped with a CP-wax-52 B (25 m x

0.32 x 1.2 μm) column and a flame ionization detector (FID) was used. Consumption of TBHP was determined by iodometric titration.

Results/Discussion

The mixed oxide series presents the crystalline structure of TiO₂ anatase phase. BET analysis shows a medium surface area decreasing from 73 to 19 m² g⁻¹ when V₂O₅ content rises from 5 to 20 wt.-%. The results of pyridine adsorption followed by FT-IR indicate that the catalysts display identical surface acid densities, independently of the V₂O₅ content, and both Brønsted and Lewis acid sites are present on their surfaces.

Table 1 presents a summary of catalytic activity and selectivity for cyclohexene oxidation. The presence of V₂O₅ increases the catalyst efficiency and leads to a selectivity change from cyclohexenol (blank test) to epoxide with a maximum for 15 wt.-% V₂O₅. The influence of other active phases supported on titanium oxide and solvents are currently under progress.

Table 1: Effect of catalyst composition on cyclohexene oxidation with TBHP

	Conversion (%)	Selectivity (%)				
		epoxide	C ₆ enol	C ₆ enone	C ₆ one	trans-C ₆ diol
blank test	10	0	100	0	0	0
TiO ₂	13	6	88	4	2	0
5 % V ₂ O ₅	33	50	40	5	4	1
10 % V ₂ O ₅	35	68	6	12	10	4
15 % V ₂ O ₅	46	75	6	10	6	3
20 % V ₂ O ₅	38	74	6	11	7	2

* epoxide: cyclohexene oxide; C₆enol: 2-cyclohexenol ; C₆enone: 2-cyclohexenone ;

C₆one: cyclohexanone; trans-C₆diol: trans-1,2-cyclohexanediol

* Reaction conditions: 3 mL of cyclohexene, 25 mL of heptane (solvent), 5 mL of TBHP in decane, 100 mg catalyst; 70 °C, 6 h and 460 rpm.

References.

- [1] J. M. Thomas, R. Raja, *Aust. J. Chem.*, **2001**, 54, 551-560.
- [2] L. M. González, A. L. Villa de P., C. Montes de C., A. Sorokin, *Tetrahedron Lett.*, **2006**, 47 (36), 6465-6468.
- [3] S. Wang, Q. Yang, Z. Wu, M. Li, J. Lu, Z. Tan, C. Li, *J. Mol. Catal. A: Chemical*, **2001**, 172 (1-2), 219-225.
- [4] D. D. Agarwal, R. Rastogi, L. Sharma, *J. Indian Che. Soc.*, **1991**, 68 (10), 566-8.
- [5] M. Reichinger, W. Schmidt, M. W. E. v. d. Berg, A. Aerts, J. A. Martens, C. E. A. Kirschhock, H. Gies, W. Grünert, *J. Catal.*, **2010**, 269 (2), 367-375.
- [6] S. Klein, S. Thorimbert, W. F. Maier, *J. Catal.*, **1996**, 163 (2), 476-488.