Catalytic oxidation of cyclohexane to cyclohexanone and cyclohexanol by tert-butyl hydroperoxide over Pt/oxide catalysts

I. REKKAB-HAMMOUMRAOUI, A. CHOUKCHOU-BRAHIM, L. PIRAULT-ROY, and C. KAPPENSTEIN
Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculté des Sciences, Université A. Belkaid, B.P. 119 Tlemcen 13000, Algeria
3LACCO UMR CNRS 6505, Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculté des Sciences, 80022 Poitiers Cedex, France

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Abstract. Heterogeneous oxidation of cyclohexane with tert-butyl hydroperoxide was carried out on Pt/oxide (Al2O3, TiO2, and ZrO2) catalysts in the presence of different solvents (acetic acid and acetonitrile). The catalysts were prepared using Pt(NH3)2(NO2)2 as a precursor and characterized by chemical analysis using the ICP-AES method. XRD, TEM, FTIR and BET surface area determination. The oxidation reaction was carried out at 70°C under atmospheric pressure. The results showed the catalytic performance of Pt/Al2O3 being very high in terms of turnover frequency.

Keywords. Oxidation; cyclohexane; platinum; TBHP; cyclohexanol; cyclohexanone.

1. Introduction

A mixture of cyclohexanone and cyclohexanol known as K/A oil is obtained by cyclohexane oxidation. These two compounds are important intermediates in the manufacture of nylon 6 and nylon 6-6 which have become important reference materials in the industrial production of polymers, and the demand has expanded over the last few years. The industrial scale preparation of cyclohexanone and cyclohexanol is carried out by oxidation of cyclohexane or by hydrogenation of phenol (Schuchardi et al., 1993, 2001; Lu et al., 2005). The earlier process is carried out at around 150°C and 1–2 MPa pressure, employing metal cobalt salt or metal-boric acid as homogeneous catalyst worldwide. The drawback of this process is that the oxidation must be operated in 3–6% conversion of cyclohexane to maintain a high selectivity (75–80%) for the K/A oil (Ingold 1989; Sawatari et al., 2001). Many attempts have been made to synthesize more efficient catalysts for the oxidation of cyclohexane. Bellifa et al. (2006) used a V2O5–TiO2 catalyst which resulted in an 8% conversion and a 76% selectivity to cyclohexanone using acetic acid as solvent and acetone as initiator. Copper (II) complexes were used with H2O2 to give a total yield of 69.9% of cyclohexanone, cyclohexanol and other products in 24 h (Silva et al., 2007). The use of Co3O4 nanocrystals gave a 7.6% conversion yielding cyclohexanol and cyclohexanone at 120°C in 6 h with molecular oxygen (Zhou et al., 2005). A chromium-containing complex, CrCoAPO–2(C6H5COOH) (Masters et al., 2001) gave a 50% conversion, yielding 55%, 8%, 15% and 22% selectivities towards cyclohexanol, cyclohexanone, adipic acid and others, respectively at 115°C and 1 MPa of oxygen. The Co/ZSM-5 catalyst (Yuan et al., 2006) was reported to give about 10% mol conversion and 97% selectivity to cyclohexanone and cyclohexanol at 120°C and 1 MPa pressure of O2. A zirconium complex bonded to modify carboate silica gel gave a product distribution ratio of 6:1 of cyclohexanol/cyclohexanone mixture with 21% conversion at 200°C (Anisita and Kamat, 2004). Titanium silicate (Reddy and Sivasankar, 1991) gave 27.8 mol% conversion with selectivities of 44 mol% %, 45 mol% and 11 mol% towards cyclohexanol, cyclohexanone and other products, respectively in 5 h reaction at 100°C with hydrogen peroxide as oxidant. The Au/Al2O3 system using molecular oxygen in a solvent free system resulted in 12.6% conversion with a selectivity of 52.6% for cyclohexanone and 32.1% for cyclohexanol (Xu et al., 2007). A similar use of Au/MCM-41 with oxygen resulted in 19% conversion with 21.3% and 6% selectivity towards cyclohexanol, cyclohexanone and other products, respectively (La et al., 2004). Ebadi et al. (2007) reported Fe, Mn and Co/Fe supported on gamma-alumina as catalysts for aerobic oxidation of cyclohexane in the gas phase under atmospheric pressure. They obtained 38% of selectivity for cyclohexanone and cyclohexanol with 29% conversion of cyclohexane. Recently, Yao et al. (2006) reported a conversion of 95% over Ce–MCM-41 at 100°C over 12 h; this gave 82% selectivity to cyclohexanol. Sathivel and Selvan (2002) reported

Author for correspondence (chbm@univ-tlemcen.dz)