

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

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**Abstract.** Heterogeneous oxidation of cyclohexane with *tert*-butyl hydroperoxide was carried out on Pt/oxide (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>) catalysts in the presence of different solvents (acetic acid and acetonitrile). The catalysts were prepared using Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> as 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 cyclohexanol and cyclohexanone is carried out by oxidation of cyclohexane or by hydrogenation of phenol (Schuchardt *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 V<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub> catalyst which resulted in an 8% conversion and a 76% selectivity to cyclohexanol using acetic acid as solvent and acetone as initiator. Copper (II) complexes were used with H<sub>2</sub>O<sub>2</sub> to give a total yield of 68.9% of cyclohexanol, cyclohexanone and other products in 24 h (Silva *et al* 2007). The use of Co<sub>3</sub>O<sub>4</sub> 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-5(CH<sub>3</sub>COOH) (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 1.0 MPa pressure of O<sub>2</sub>. A zirconium complex bonded to modify carbamate silica gel gave a product distribution ratio of 6.6:1 of cyclohexanol/cyclohexene mixture with 21% conversion at 200°C (Anisia and Kumar 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 a 5 h reaction at 100°C with hydrogen peroxide as oxidant. The Au/Al<sub>2</sub>O<sub>3</sub> system using molecular oxygen in a solvent free system resulted in 12.6% conversion with a selectivity of 52.6% for cyclohexanol and 32.1% for cyclohexanone (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 (Lu *et al* 2004). Ebadi *et al* (2007) reported Fe, Mn and CoPc supported on gamma-alumina as catalysts for aerobic oxidation of cyclohexane in the gas phase under atmospheric pressure. They obtained 38% of selectivity for cyclohexanol and cyclohexanone 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. Sakthivel and Selvam (2002) reported

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