Preparation of heterogeneous vanadium (VO\(^{2+}\)) catalyst for selective hydroxylation of cyclohexane by molecular oxygen

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A vanadium(II) Schiff base ligand, [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex bonded on carbamate-modified silica gel, has been synthesized. The liquid-phase oxidation reaction of cyclohexane with this catalyst was found to give cyclohexanol at moderate condition (reaction temperature 200 °C, pressure 23.8 atm, catalyst concentration 1.0% and 16 h of reaction time) with considerably higher specificity (18:1 ratio with cyclohexanone and negligible acid formation). The catalyst has been tested for 200 h of reaction and the leaching of the metal occurs negligibly.

KEY WORDS: vanadium (VO\(^{2+}\)) catalyst; selective hydroxylation; cyclohexane hydroxylation.

1. Introduction

Hydrocarbons are cheaply available from the chemical and petrochemical industry and their functionalization through oxidation [1,2] using molecular oxygen poses a present-day challenge in modern catalysis. In earlier works of catalysis, metals and their salts were dissolved in nonvolatile liquids, dispersed on solid phase, and were called supported liquid-phase catalysts (SLPCS) [3]. When employed in liquid-phase oxidation, there is excessive metal leaching and, as a result of this, there has been an effort to anchor transition metals and their complexes on suitable supports [4]. Transition metal carboxyls have been directly connected with organic polymers like polyvinyl pyridine or a suitably modified support with donor groups [5]. There are examples of covalent anchoring, ionic bonding, physical adsorption and chemisorption, and covalent anchoring has been reported to be the most efficient. However, even from these, under the reaction condition of liquid-phase oxidation, metals do get leached [6].

Air oxidation of cyclohexane is industrially carried out using unsupported cobalt catalyst and, in its presence, at least five products (adipic acid, succinic acid, gallic acids, cyclohexyl acetate and cyclohexyl mono-adipate) are formed in addition to cyclohexanol and cyclohexanone [7]. In addition to this, there is an induction time, which is reduced in the presence of promoters like acetaldehyde, cyclohexanone, cyclohexanol and azobisisobutyronitrile. Reactions have also been carried out in the presence of cobalt zeolite, CoA-PO-Catalyst [8], which gives acids (like valeric acid and butyric acid) in sufficient quantities [9]. As a variation of this, nano-structured iron and cobalt oxides have been used as catalysts and recently, on using those supported on titania, the products were formed in extremely mild reaction conditions [10] (1 atm, 70 °C) and consisted of a mixture of cyclohexanol and cyclohexanone in the ratio of 1.5 to 1.0. Unsupported vanadium complexes have also been studied as a catalyst for oxidation of cyclohexane. Several complexing agents have been reported and all have been shown to give a mixture of cyclohexanol and cyclohexanone in comparable amount at mild reaction conditions [11].

In this paper, we report a heterogeneous vanadium complex catalyst supported on carbamate-modified silica gel. This hydroxylates cyclohexane using molecular oxygen in moderate reaction conditions giving cyclohexanol in preponderance. After 16 h of the reaction in batch reactors, the catalyst was removed before distillation at 110 °C. This gave 13 ml of the product with distillate having only cyclohexane, as confirmed by GC analysis. The product was subjected to GC-MS analysis and it showed cyclohexanol (78.95%), cyclohexanone (4.53%), succinic acid (6.74%) and unidentified esters (9.78%) and the observed product distribution is entirely different from the literature. The analysis showed the formation of cyclohexanol and cyclohexanone in the ratio of 18:1 and with no induction period. There is negligible acid (1.2% succinic acid) formed and the metal leaching in 200 h of reaction time is negligible.

2. Experimental

The catalyst reported in this work has been synthesized by the following four-step procedure. In the

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first step, benzoyl isocyanate was synthesized by the reaction of sodium azide NaN₃ (16.8 g, 0.26 g·mole) with the same number of moles of benzoyl chloride C₈H₇COCl (35 ml, 0.30 g·mole) at 0 °C and its FTIR spectrum matched with the literature. The filtrate was reacted with 5.0 g of silica gel [12], its FTIR spectrum given in figure 1(a) at 40 °C for 6 h. The carbamate group bound on the silica gel was confirmed by FTIR, given in figure 1(b) (aromatic –CH at 3030 cm⁻¹, –NH group at 1599 cm⁻¹, C=O at 1693 cm⁻¹), and the extent of reaction estimated by the butyl amine method [13]. In the second step, the complexing agent was