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Solvent-free oxidation of benzyl alcohol over chromium orthoborate

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Abstract

The use of $CrBO_3$ in the catalytic liquid phase oxidation of benzyl alcohol (BzOH) has been investigated for the first time. The reaction was performed under solvent-free conditions without employing any oxidant. Benzaldehyde (BzH), dibenzyl ether (DBzE) and benzyl benzoate (BzB) were obtained as the major reaction products. Influence of the reaction parameters (reaction time, temperature and the amount of catalyst) on the catalytic performance has been studied. A mechanism operating over acidic boron sites has been suggested.

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Keywords: $CrBO_3$; Benzyl alcohol oxidation; Heterogeneous catalysis; Solvent-free catalysis; Benzaldehyde

1. Introduction

Catalytic oxidation of BzOH to BzH is a fundamental process since BzH is an important raw material in perfumery and pharmaceutical industries. Traditionally, manganese and chromium salts have been used as stoichiometric oxidants in this process. These catalysts are not only expensive but have serious toxicities. The general production process involves either the hydrolysis of benzyl chloride or oxidation of toluene in chlorinated hydrocarbons [1]. Formation of BzH is the first step in this oxidation process and further oxidation leads to the production of benzoic acid (Scheme 1) with side reactions leading to other products like toluene, DBzE, dibenzyl acetal and BzB [2]. Solvent-free and selective oxidation of BzOH to BzH is therefore attractive in both economical and environmental aspects.

Gas phase oxidation of BzOH by gold catalysts [3] and by copper chromium aluminum borate catalysts [4] have been reported however the control of selectivity for a particular oxidation product is difficult in the vapor phase. Many heterogeneous catalysts have been developed recently for the liquid phase solvent-free oxidation of BzOH; such as hydrotalcite-like solids (HT)/layered double hydroxides [5,6] Ru–Mn–Fe–Cu–O [7], supported metal nanoparticles [8–11], zeolite-supported Au and Au–Pd catalysts [2], W and Mo compounds [12–14] and transition metal oxides [15]. Most of these catalytic systems use molecular oxygen or hydrogen peroxide as oxidant. A comparison of their performances and catalytic reaction conditions is summarized in Table 1.

The catalytic activity of transition metal borates are mostly given in patent formulations. Zirconyl-cobalt borate, zirconyl-nickel borate and vanadyl-cobalt borate systems were found useful for the esterification of olefins [16]. A process for the production of alkylene oxides from olefins in the presence of transition metal borate catalysts, oxygen and a non-polar, aromatic organic solvent via one-step, direct oxidation has been described [17]. The catalytic behavior of two mixed-valence borates, ferroferriborate (Fe_3BO_5) and magnesium ferroferriborate (Fe_2MgBO_5), was studied in ethyl acetate oxidation [18]. To the authors′ knowledge, no information is available in the literature about the catalytic activity of chromium orthoborate. In this work, the use of $CrBO_3$ as a heterogeneous catalyst has been tested for the first time and benzyl alcohol oxidation reaction, which is a well-known acid catalyzed reaction [1], has been chosen as the test reaction. The

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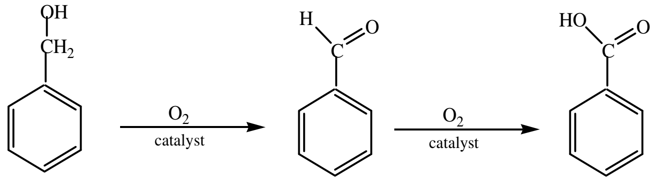

Scheme 1. Oxidation of BzOH.

experiments have been performed in solvent-free conditions without employing any oxidizing agent other than the air present in the reflux atmosphere. The influence of the reaction parameters (reaction time, temperature and the amount of catalyst) on the catalytic performance of chromium orthoborate are reported.

2. Experimental

Chromium orthoborate was prepared by heating $Cr_2(SO_4)_3 \cdot 15H_2O$ and H_3BO_3 (Cr:B = 1:3 mole ratio) in an ash oven at 1000 °C for 12 h. The obtained calcite-type $CrBO_3$ [19] displayed all the characteristic XRD reflections indexed in ICDD-15-0663. Commercial BzOH (Riedel) was used after distillation. The oxidation reaction was performed in a magnetically stirred three-neck flask equipped with a thermometer and reflux condenser. In a typical reaction, the flask was charged with BzOH (10 mL) and $CrBO_3$ was added in a prescribed amount (0.2–1.0 g). The system was heated at a prescribed temperature (25–165 °C) for a period of 7 h. The solid catalyst was then separated and the reaction products were analyzed by GC–MS. The analysis was performed with a Shimadzu GCMS-QP5050A instrument (Optima column, 5–1.0 μm, 50 m × 0.32 mm), temperature range: 80–250 °C (20 °C/min), carrier gas: helium (1 mL/min). Peak areas were correlated with a calibrant mixture containing benzyl alcohol and benzaldehyde and quantification of the products was achieved by assuming equal response factors for the components of the reaction mixture. FT-IR spectra were measured in KBr matrix with a Perkin Elmer spectrum one instrument.

3. Results and discussion

The solvent-free liquid phase catalytic performance of $CrBO_3$ in BzOH conversion was found to be comparable with some of the heterogeneous catalysts reported for the same oxidation reaction (Table 1). No additional oxidant such as oxygen flow or H_2O_2 was used in the experiments. The green $CrBO_3$ was easily recovered and no coloration in the reaction mixture was observed throughout the catalytic reaction to indicate the leaching of chromium species into the liquid phase. Thus the system is truly heterogeneous in nature.

Chromium orthoborate crystallizes in a distorted face centered structure with discrete BO_3^{3-} ions occupying the octahedral positions [19,20]. The reaction is most probably catalyzed by the Lewis acid sites associated with the coordinatively unsaturated surface boron atoms. The very robust nature of $CrBO_3$ against strong oxidants [20] has prompted us to assume that the low oxidation state Cr(III) centres are probably not involved in the catalytic reaction. The role of boron was confirmed by comparing the FTIR spectrum of the recovered catalyst with that of the fresh catalyst (Fig. 1). The broad and strong bands observed in the 1100–1600 cm^{-1} region in the spectrum of the fresh catalyst

Table 1
Solvent-free oxidation of BzOH to BzH over some heterogeneous catalysts

Catalyst	BzOH/catalyst	Reaction conditions	Conversion[a]	Selectivity[b]	Reference
HT-like solids	10.0 mL/0.5 g	210 °C, 5 h, $O_2 = 6\ cm^3/min$	16.8–50.9	70.1–99.7	[5]
$Mg–Al–HT/MnO_4^-$	52 mmol/0.5 g	197 °C, 5 h, $surfactant_{(aq)}$	~50	~100	
Mg–Al–HT			4.7	100	[6]
$KMnO_4$			28.5	84.4	
Ru–Mn–Fe–Cu–O	5 mmol/0.1 g	60 °C, 48 h	–	Yield:85%	[7]
Al Mo 20	5 mL/0.5 g	Reflux, 6 h	96.9	52	[12]
$Au–Pd/TiO_2$	Liter/10^{-5} mol	100 °C, 8 h, $O_2 = 0.2$ MPa	74.5	91.6	[10]
Au/ZSM 5	40 mL/0.2 g	100 °C, 7 h, $O_2 = 6\ cm^3/min$	13.5	65	[2]
Au/U_3O_8	29 mmol/0.1 g	130 °C, 5 h, $O_2 = 0.1$ MPa	53	95	[11]
TAPO-Mo	10.8 g/0.5 g	Reflux, 1.7 h, 15% H_2O_2	93.6	90.5	[13]
MnO_2	20 mL/0.5 g	80 °C, 3 h, $O_2 = 0.1$ MPa	37.7	98.6	
Co_2O_3			11.7	87.2	[15]
Fe_2O_3		Microwave assisted	6.7	80.8	
$CrBO_3$	10 mL/0.5 g	100 °C, 4 h	41	51	This work

[a] (Moles of BzOH converted)/(moles of BzOH loaded) × 100%.
[b] (Moles of BzH formed)/(moles of BzOH converted) × 100%.

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