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Liquid Phase Oxidation of Benzhydrol by Using Nano Crystalline Iron Supported on Ceria Mixed Oxide Catalysts.

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ABSTRACT

Simple oxidation of benzhydrol was carried out by using TBHP over nanocrystalline iron supported on ceria prepared by hydrothermal method showed high yield of desired product, selectivity and improvement in reaction time.

Keywords: Nanocrystalline, hydrothermal, oxidation, benzhydrol

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INTRODUCTION

Now days nanocatalysis has huge importance and many organic transformations have been carried out more efficiently by using nanocrystalline metal oxides as catalysts. High catalytic uses of these oxides are due to high surface area, recyclability, and easy work up procedure with nonhazardous nature of these catalysts. Many catalytic methods have been developed for oxidation of alcohols based on different transition metals such as Pd [1-3], Cu [4], Ru [5], Co [6] and Au [7,8].

A number of CeO_2-based systems such as CeO_2-ZrO_2, CeO_2-Al_2O_3, CuO-CeO_2-Al_2O_3, CeO_2-SiO_2, CeO_2-La_2O_3, CeO_2-HfO_2, Pd-CeO_2 and Au-CeO_2 have been examined for their catalytic properties [9-10]. Recently efforts have also been made to synthesize nanoparticles of ceria having better physicochemical properties for diverse applications [11,12].

Given the effects of trivalent ions and those of smaller size on the structure and properties of catalysts, there is considerable scientific interest in the introduction of M^{3+} (e.g., Fe^{3+}) ions into the ceria lattice [13]. This addition of trivalent transition metals (Fe, Mn, Ni, Cu, etc.) has been reported to enhance the interaction of CO_2 in O_2-releasing reactions at lower temperatures. CeO_2–MO_x (Fe, Mn, Ni and Cu) solid solutions with high melting points and high conductivities of O^{2-} are some of the most reactive ceramics known and are used as resistive-type O_2 sensors for exhaust gas from automobiles [14]. The catalytic activity of CeO_2–Fe_2O_3 in the synthesis of 3-pentanone from 1-propanol has been investigated [15]. Recently, iron-based catalytic systems have been designed for use in the gas phase epoxidation of propylene, utilizing nitrous oxide as a selective oxidant [16].

A 'green' process of oxidation, using hydrogen peroxide as the oxidant, is the most attractive oxidation technology for selective organic syntheses [17-18]. Hydrogen peroxide is a favorable and clean oxidant for various oxidation reactions [19]. It overcomes the disadvantage of the traditional toxic inorganic oxidants [20], like MnO4.

In order to prevent the formation of unwanted waste and toxic reagents, the use of inexpensive and less toxic iron complexes together with hydrogen peroxide represents an ideal combination for such oxidations.
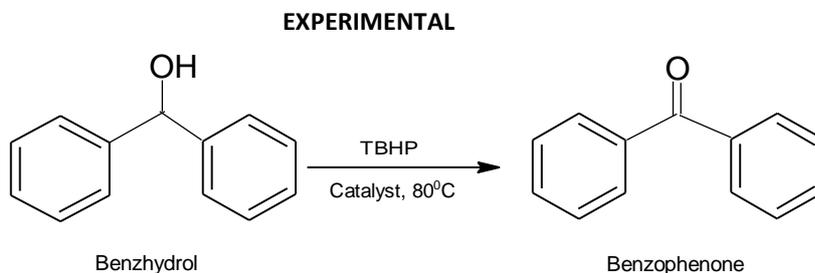
Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of benzhydrol and p-substituted benzhydrols by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied [21]. In the recent years, studies of oxidation of various organic compounds using heteropoly acids and polyoxometalates especially those with Keggin-type structure under homogeneous and heterogeneous reaction conditions have attracted considerable attention of the researchers [22].

In the present study liquid phase oxidation of benzhydrol has been carried out under a variety of reaction conditions over Fe/CeO_2 mixed oxide catalysts. Already studied and characterized iron–ceria catalysts were used for oxidation of benzhydrol using H_2O_2 as the oxidant was carried out, and the effects of reaction temperature, amount of catalysts and solvent were also investigated. Herein, we report the nano Fe/CeO_2 as an efficient and environmentally benign catalyst for oxidation reaction.

MATERIALS AND METHODS

1 M Cerium nitrate solution was mixed with 100 ml of 30 % H_2O_2 under vigorous stirring in an ice bath. After 10 min ammonia solution was added to this mixture and the color changes to dark brown. The solution was stirred at 3000 rpm for 4h. The precipitates formed from the solution were aged for a day and turned yellow after aging. Then this solution was decanted and the wet precipitates were washed using ethanol several times until the pH was near neutral region. The wet precipitates were filled to 80 vol. % in a Teflon vessel held in an outer pressure vessel made of stainless steel. After the vessel was sealed, it was placed in a thermostatic oven and heated at 200^0C for 6 h. The final products were re-washed several times with ethanol and dried at 80^0C for 12 h. Finally, sample was calcined at 650^0C for 5 h to get the nanocrystalline CeO_2 and characterized by various techniques such as XRD, TEM, FT-IR [23]. The X-ray diffraction pattern was acquired for different angle (2θ) range between 10 to 80° with speed 2° per min, using (Bruker D8-Advance X-

ray diffractometer) with CuKα radiation (1.5418 A^0). The measured diffraction angles were consistent with the standard XRD patterns of CeO_2, with extra peak of Fe_2O_3 indicating the incorporation of Fe on CeO_2. The size of nanocrystalline CeO_2 powder was around 10-12 nm obtained from X-ray line broadening using the Scherrer equation (D = 0.9¢ cos ᵃ). The TEM was observed on a Philips CM 200, operating at 20-200 kV accelerating voltage and having resolution up to 2.4. The size of nano CeO_2 obtained from TEM is 8-10 nm having spherical shape.

EXPERIMENTAL

Benzhydrol   Benzophenone

The reaction of oxidation of benzhydrol to benzophenone was carried out at various temperatures using TBHP as oxidant and benzene as solvent. The effect of the reaction temperature was studied by adding the Fe/CeO$_2$ nanocatalyst added to the reaction mixture involving benzhydrol (2mmol), aqueous TBHP (2mmol) and 10 ml benzene as solvent. The mixture was then heated to 60^{0}C, 80^{0}C, 100^{0}C respectively and then progress of reaction was monitored by TLC and GC.

Effect of Temperature

At 60^{0}C the catalytic reaction was quite low with benzhydrol conversion 48.42% at the end of 6h. The conversion increases upto 63% with 100% selectivity when the reaction was carried out at 80^{0}C. At 100^{0}C the conversion was again considerably decreases as compared to 80^{0}C. The effect of oxidant and amount of catalyst was studied on the oxidation of benzhydrol. Benzophenone was found to be main product with trace of byproducts. With H_2O_2 as the oxidant there was no conversion of benzhydrol was observed in the reaction. The reaction conditions including conversion of benzhydrol and product selectivity is given below in table 1.

Effect of Amount of Catalyst

The reaction of oxidation of benzhydrol to benzophenone was carried out at various amounts of catalysts using TBHP as oxidant and benzene as solvent in Fig.1

The reaction has been carried out at three different catalyst amount using benzene as the solvent. As amount increases the conversion as well as selectivity also increases. This may be due to the increase in amount of iron in the reaction. The maximum product selectivity (100%) was achieved with 0.2 gm of Fe/CeO$_2$ catalyst. As the amount of catalyst was increased the conversion of benzhydrol increases but selectivity decreases. The results were shown in the form of bar diagram. By comparing the results, it concluded that the best results of oxidation of benzhydrol were obtained with 0.2g of the catalyst.

Effect of Solvents

The reaction of oxidation of benzhydrol to benzophenone was carried out at various solvent by using, TBHP as oxidant given in table 2.

The reaction was carried out using different solvents to improve conversion of benzhydrol and selectivity of benzophenone. The effect of the various solvents acetonitrile, dichloroethane, Toluene, Benzene and DMSO respectively was studied by using Fe/CeO$_2$ catalyst and the reaction mixture was heated at 80^{0}C. The maximum benzophenone Selectivity was achieved with benzene. By changing the solvent resulted in the lowering of benzophenone selectivity. The DMSO showed higher selectivity but the conversion was less. There was no any typical trend found in the reaction as might be the effect of catalyst was more on the reaction.

Table 1: Effect of temperature on oxidation of Benzhydrol using Fe/CeO$_2$ catalyst

Sr. No.	Temperature (^{0}C)	% Conversion	% Selectivity of Product
1	60^0	48	89
2	80^0	63	100
3	100^0	47	95

Reaction conditions: Benzhydrol: TBHP- 1:1, Solvent: Benzene, time- 6h, Catalyst- 0.2g

Table 2: Effect of solvents on conversion of Benzhydrol using Fe/CeO$_2$ as catalyst

Sr.No.	Solvents	% Conversion	% Selectivity Benzophenone
1	Acetonitrile	63.64	89.36
2	Dichloroethane	60.00	92.38
3	Toluene	53.47	69.81
4	Benzene	63.15	99.98
5	DMSO	16.70	99.94

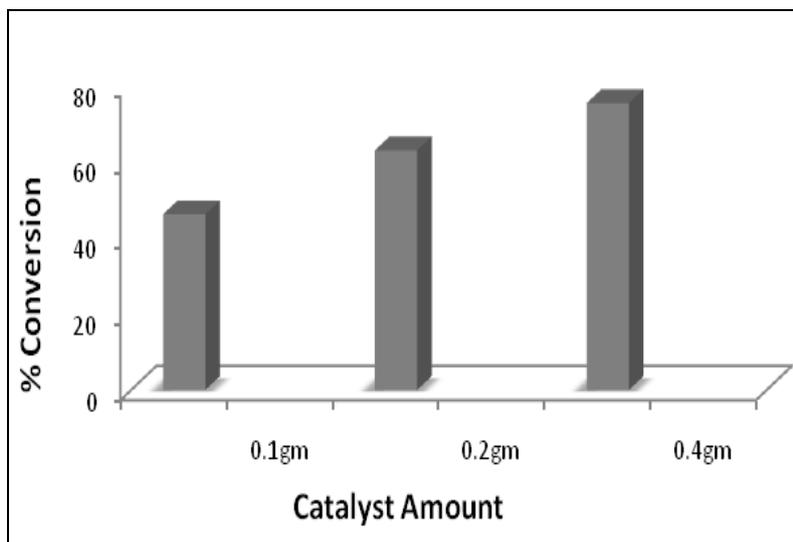Reaction conditions: Benzhydrol : TBHP- 1:1, time- 6h , catalyst- 0.2g , Temp.-80^{0}C

Figure 1: Effect of amount of catalyst on conversion of benzhydrol.

CONCLUSIONS

The oxidation of benzhydrol using TBHP as oxidant over Fe/CeO$_2$ nanocrystalline mixed oxide catalyst gives a product benzophenone with minor byproducts.

Optimized temperature for oxidation of benzhydrol was 80^{0}C gave higher conversion as well as selectivity for benzophenone. The imperative role played by various reaction parameters in deciding the catalytic efficiency is well established and each parameter has optimum value in order to acquire maximum activity. At lower amount of catalyst the conversion was higher with higher selectivity. In addition, the commercial availability and low cost of the reagent, high yields of the products, mild reaction conditions, easy

workup and short reaction times are noteworthy advantages of this method and make this reagent practical bench-top oxidant.

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