

## Research Article

# Zeolite Encapsulated Nanocrystalline CuO: A Redox Catalyst for the Oxidation of Secondary Alcohols

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Zeolite encapsulated nanocrystalline CuO is synthesized and characterized by powder XRD and HRTEM analyses which clearly show that the particles are less than 15 nm and the nanoparticles are highly dispersed. This nano CuO encapsulated CuY zeolite is used as catalyst in the oxidation of aromatic secondary alcohols. CuY zeolite acts as an efficient support for nano CuO, by stabilizing it and preventing its aggregation. Plausible mechanisms for the formation of the various products are also given.

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## 1. INTRODUCTION

Nanostructured materials present great promise and opportunities for a new generation of materials with improved and tailorable properties for applications in sensors, optoelectronics, separation, and catalysis. Catalysts in many cases are nanoscale particles, and thus catalysis is a nanoscale phenomenon [1, 2]. Significant progress has been made in recent years in controlling the size of nanoscale materials and in understanding their unique size-dependent catalytic properties [3]. In this context, controlling the shape of nanoparticles is also an equally important aspect of desired catalyst synthesis [4]. Nanostructured materials, especially nanometal oxides such as MgO, CuO, Al<sub>2</sub>O<sub>3</sub>, CaO, BaO, SrO, ZnO, and TiO<sub>2</sub>, exhibit great promise and opportunities for a new generation of materials with improved and tailorable properties for applications in sensor development, optoelectronics, separation, and catalysis studies [5]. Among these nanometal oxides, CuO has gained advantages because of its higher catalytic activity in many oxidation processes [6].

Various preparation methods to ultrafine CuO have been reported [7–10]. Bandara et al. [11] have reported the synthesis of highly stable CuO incorporated TiO<sub>2</sub> and these catalysts have higher catalytic activity in the photocatalytic reduction of H<sub>2</sub>O under sacrificial conditions. Liquid-phase oxidation of benzene to phenol catalyzed by CuO supported Al<sub>2</sub>O<sub>3</sub> has been reported by Miyahara et al. [12]. They

have also reported that CuO supported Al<sub>2</sub>O<sub>3</sub> prepared by coprecipitation of Cu(NO<sub>3</sub>)<sub>2</sub> · H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O inhibits the leaching of Cu species in comparison with the Cu catalysts supported by the impregnation method on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MCM-41, and so forth. Mixed oxides of Cu-Mn derived from calcination of Cu-Mn-hydrotalcite precursors are reported to be promising catalysts for the total combustion of toluene [13].

Oxidative decomposition of benzene and its methyl derivatives catalyzed by copper and palladium ion-exchanged Y-type zeolite is reported by Becker et al. [14]. They have observed the presence of microcrystalline CuO phases in the catalyst by EXAFS experiments and the equilibrium between Cu(I) and CuO is probably the rate determining step for the oxidation reaction.

Velu et al. [15] have utilized MCM-41 mesoporous molecular sieves containing copper and zinc for the selective oxidation of alcohols to aldehydes. They have also observed the presence of finely dispersed CuO inside the channels of MCM-41 which produce overoxidation products, namely, CO<sub>2</sub> and H<sub>2</sub>O. Lin and Wang [16] have reported the oxidation of 2-chlorophenol catalyzed by CuO/ZSM-48 derived from the calcination of Cu<sup>2+</sup>-exchanged in zeolite at 500°C. For the cation exchange, they have used Cu(OCOCH<sub>3</sub>)<sub>2</sub> in aqueous solution. They have also reported that the oxidation efficiency of 2-chlorophenol in the supercritical water is efficiently enhanced by the presence of CuO in the zeolite.

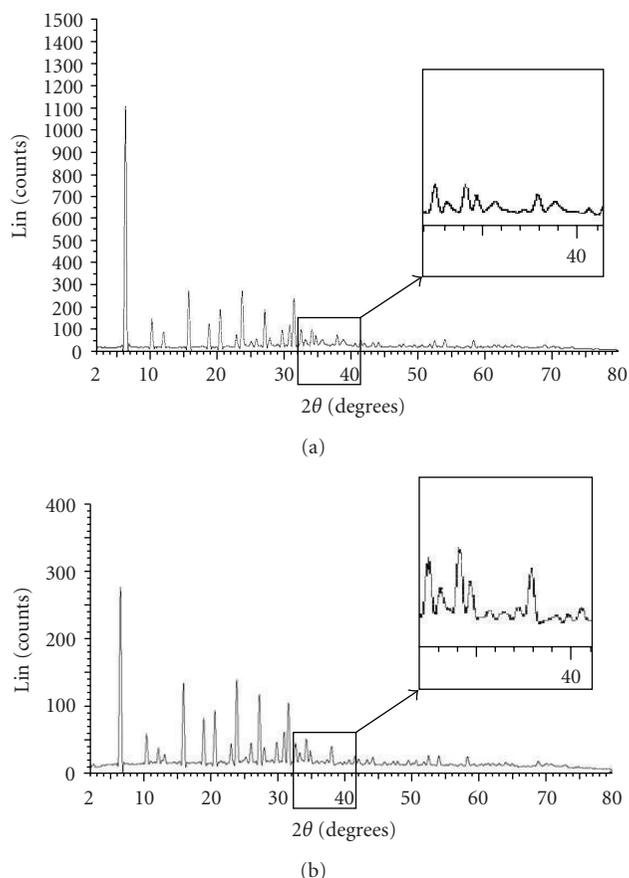


FIGURE 1: Powder XRD patterns of (a)  $\text{Cu}^{2+}$  exchange Y-zeolite, and (b) zeolite encapsulated nanocrystalline CuO.

In earlier reports for preparation of CuO containing zeolites, calcination procedure is utilized (calcination of  $\text{Cu}^{2+}$ -exchanged zeolite at  $500^\circ\text{C}$ ) and only microcrystalline CuO phases are observed. However, there are no reports for the syntheses of nanocrystalline CuO in the supercage of Y-zeolite. The shape and size of the zeolite cavities, particularly the cages and polar active sites are expected to stabilize the CuO nanoparticles and thus prevent their aggregation. Hence, in the present study, it is proposed to synthesize nanocrystalline CuO encapsulated inside the supercages of Y-zeolite and to study its catalytic activity in the oxidation of alcohols.

## 2. EXPERIMENTAL METHODS

### 2.1. Preparation of zeolite encapsulated nanocrystalline CuO

Zeolite encapsulated nanocrystalline CuO was synthesized from  $\text{Cu}^{2+}$ -exchanged Y-zeolite. About 2 g of  $\text{Cu}^{2+}$ -exchanged Y-zeolite were taken in a round-bottomed flask containing 10 mL of deionized water and they were heated to  $80^\circ\text{C}$  in a water bath. To the hot mixture, 2 mL of 10% sodium hydroxide solution was added with constant stirring. First, the bluish green  $\text{Cu}^{2+}$ -Y-zeolite becomes dark blue by

the formation of  $\text{Cu}(\text{OH})_2$ , then it changed in situ into black colour by the formation of CuO. The mixture was stirred at room temperature for 6 hours and then it was separated by centrifuging. It was washed thrice with water, centrifuged, and the precipitate was dried in an air oven at  $100^\circ\text{C}$ .

### 2.2. Oxidation of secondary alcohols

Zeolite encapsulated nanocrystalline CuO 300 mg was activated in a muffle furnace at  $450^\circ\text{C}$  for 6 hours. The hot zeolite was immediately transferred into 5 mL of n-hexane to avoid absorption of water. Then, 100 mg of benzhydrol were loaded into the zeolite by stirring it in a magnetic stirrer. After loading, n-hexane was evaporated with rotovapor and then it was dried. Alcohol-loaded zeolite was uniformly packed in a sample loading unit and it was fitted into the reactor. Oxygen was allowed to flow into the reactor with a rate of 1 mL/min. The temperature of the reactor was maintained at  $200^\circ\text{C}$ . After 1 hour, the products condensed on the receiver and also on zeolite were extracted with dichloromethane and the mass balance was noted. Then, the reaction mixture was analyzed in GC, and the products were characterized in GC-MS.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of zeolite encapsulated nanocrystalline CuO

In this paper, zeolite encapsulated nanocrystalline CuO is synthesized by the addition of NaOH solution to a suspension of  $\text{Cu}^{2+}$ -exchanged zeolites. Here, the procedure similar to that reported by Cao et al. [10] is adopted. They have used CTAB as capping agent which prevents the aggregation of nanoparticle. But in our study, the shape of the supercage and its polar active sites are likely to prevent the aggregation of nanocrystalline CuO and consequently no capping agent is used. Formation of CuO from  $\text{Cu}^{2+}$  is characterized by its powder XRD and its nano form is confirmed by HRTEM analysis. The prepared nanocrystalline CuO encapsulated CuY zeolite is characterized by AAS, powder XRD, SEM, and HRTEM analyses, and the observed results are given below.

AAS analysis of CuO encapsulated CuY zeolite shows 8.4 wt% of copper present in the zeolite. However, with this result alone, it is difficult to come to a conclusion about the percentage of CuO and  $\text{Cu}^{2+}$  (as a cation) presents inside the zeolite. Powder XRD pattern of  $\text{Cu}^{2+}$ -exchanged and zeolite encapsulated nanocrystalline CuO is given in Figure 1. The presence of peaks corresponding to CuO (at  $2\theta = 34$  and  $2\theta = 38$ )<sup>16</sup> confirms the presence CuO in the zeolite. Pure  $\text{Cu}^{2+}$ -Y zeolite also has small peaks that corresponding to CuO and this may be due to the formation of trace amount of CuO by partial oxidation of  $\text{Cu}^{2+}$  to CuO during cation exchange and drying the cation-exchanged sample in an air oven. There have been no other changes in the other diffraction peaks of the zeolite and the crystallinity of the zeolite is maintained even after the base treatment of the zeolites.

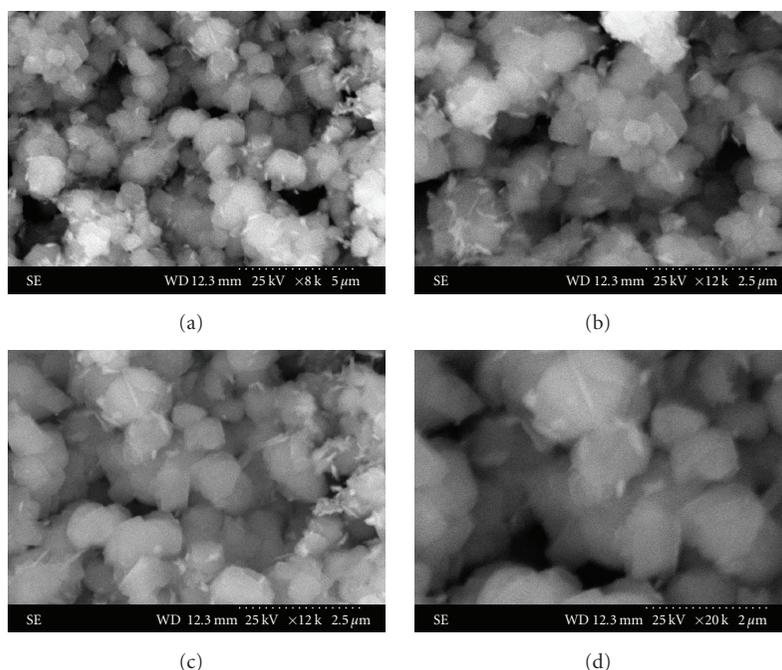


FIGURE 2: SEM images of zeolite encapsulated nanocrystalline CuO at different magnifications.

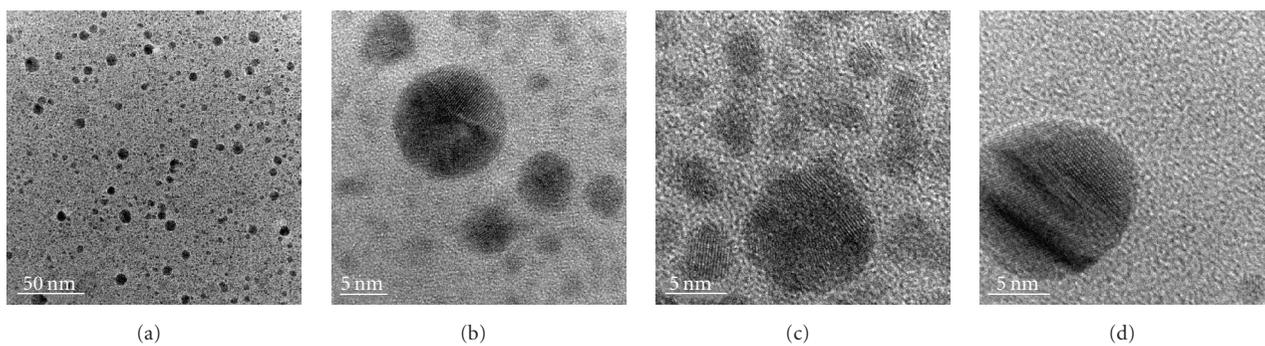


FIGURE 3: HRTEM images of zeolite encapsulated nanocrystalline CuO at different magnifications.

SEM analysis of zeolite encapsulated nanocrystalline CuO shows the surface morphology of the zeolite (Figure 2). Zeolite particles are found to be present as granules of particle size  $\sim 500$  nm. HRTEM images of zeolite encapsulated nanocrystalline CuO at different magnifications are given in Figure 3. These figures clearly show that the CuO particles are in nanometer range ( $<15$  nm) and most of the particles (which are less than 2 nm) are embedded inside the zeolite materials (Figures 3(b) and 3(c)). These CuO nanoparticles are also spherical in shape. Few other particles in the range of 15 nm are also found and this is attributed to the passage of high energy beam during the HRTEM analysis and consequent cage-escape and aggregation of CuO nanoparticles.

HRTEM images reveal that nanocrystalline CuO particles are highly dispersed and no aggregation or cluster formation occurs. This may be due to the interaction between the

zeolites active sites and the CuO surface, which have high surface energy due to its smaller size [17]. Further, the formation of the nanocrystalline CuO inside the supercages of Y-zeolite was confirmed by the BET pore-size and pore volume of the CuY-zeolite. The pore size and pore volume of CuY-zeolite before and after nano CuO formation are 16.11 Å, 0.3179 cc/g and 15.19 Å, 0.2608 cc/g, respectively. The decrease in the average pore diameter and the pore volume clearly indicates the formation of nanocrystalline CuO within the supercages of zeolite without damaging the zeolite crystal structure.

CuO has been widely used as a catalyst for the oxidation of alcohols and aromatic hydrocarbons [12–15]. Here, zeolite encapsulated nanocrystalline CuO is used for the oxidation of aromatic alcohols. Since CuO is mildly basic and zeolites are mildly acidic, this combination will provide an acid-base bifunctional catalyst. In addition, zeolite supercages will also

TABLE 1: Zeolite encapsulated nanocrystalline CuO catalyzed oxidation of alcohols<sup>(a)</sup>.

S. No	Substrate	Catalyst	% Conversion <sup>(b)</sup>	% of products				X <sup>(c)</sup>
				2	3	4	5	
(1)	Benzoin	CuOY	100	92.2	—	—	—	7.8
(2)	Benzhydrol	CuOY	100	29.1	70.9	—	—	—
(3)		CuOY <sup>(d)</sup>	nil	—	—	—	—	—
(4)		Cu <sup>2+</sup> Y	21.0	28.7	71.3	—	—	—
(5)		NaY	11.2	—	100	—	—	—
(6)		CuO	100	100	—	—	—	—
(7)		Y-zeolite-CuO <sup>(e)</sup>	100	90.0	8.4	—	—	1.6
(8)	1-Phenylethanol	CuOY	100	—	—	84.9	—	15.1
(9)		CuO	78.0	100	—	—	—	—
(10)	Hydrobenzoin	CuOY	100	—	—	—	100	—
(11)	Benzyl alcohol	CuOY	13.7	100	—	—	—	—

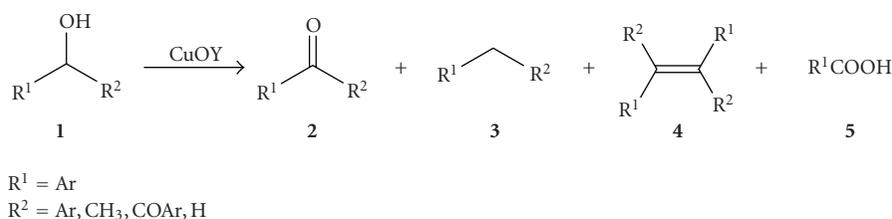
<sup>(a)</sup> Substrate loaded zeolite heated in solid phase reactor at 200°C for 1 hour under oxygen atmosphere.

<sup>(b)</sup> Analyzed in GC, error limit  $\pm 3\%$ .

<sup>(c)</sup> Unidentified products.

<sup>(d)</sup> Reaction carried out at 100°C.

<sup>(e)</sup> Physical mixture of Y-zeolite and CuO.



SCHEME 1

provide closer proximity between substrates, adjacent acidic, and basic sites which is expected to increase the rate of the reaction. In general, catalytic activity of CuO is maximum at higher temperature and hence, we have developed a solid-phase reactor provided with constant flow of oxygen. The results obtained for the oxidation of various aromatic alcohols using zeolite encapsulated nanocrystalline CuO are given in Table 1 and Scheme 1.

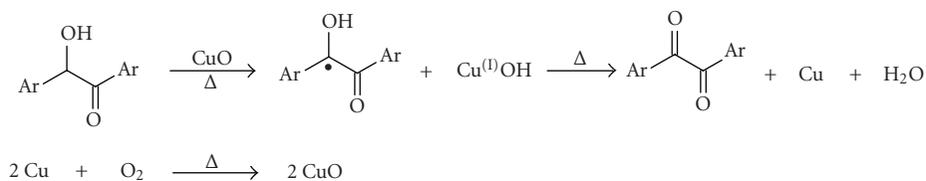
In the oxidation of benzoin with zeolite encapsulated nanocrystalline CuO in the solid phase reactor, the oxidation product, namely, benzil is formed in good yield. But with benzhydrol, benzophenone, and diphenylmethane, the oxidized as well as reduced products, respectively, are formed. However, at a lower temperature (100°C), there is no reaction (Table 1, entry 3). With only Cu<sup>2+</sup>-exchanged zeolite, the conversion is lower and a similar product ratio is observed. Hence, it is likely that at an elevated temperature, Cu<sup>2+</sup> in oxygen atmosphere may have been oxidized to CuO. Similarly, when studied in NaY zeolite also, the conversion is very low and only the reduced product is observed. In the presence of pure CuO, only the oxidized product is formed exclusively.

When 1-phenylethanol is subjected to oxidation under the same conditions, the oxidative-coupled product an alkene (1,2-dimethylstilbene) is formed. Hydrobenzoin, an

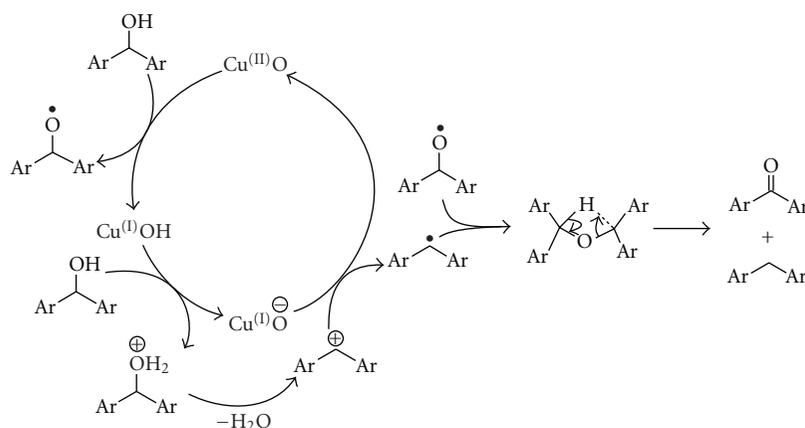
aromatic diol, undergoes overoxidation to produce benzoic acid. With an aromatic primary alcohol, namely benzyl alcohol, the conversion is very low (Table 1, entry 10). It is likely that because of its lower boiling point, it may be vaporized before it reacts with the catalyst as it is found to be condensed on the receiver. Thus, this method is found to be efficient only for alcohols having higher boiling points.

### 3.2. Mechanism for the oxidation of alcohols

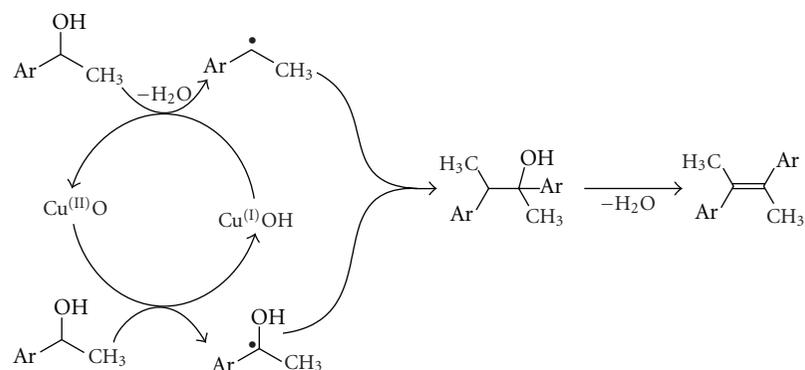
Nagase et al. [18] have studied the dynamic oxidation states of copper in the course of carbon monoxide oxidation over powdered CuO and Cu<sub>2</sub>O in a gas mixture of 5% CO/He and air (O<sub>2</sub>) by means of an appropriate combination of evolved gas analysis, thermogravimetry, XRD, and FT-IR in the temperature range of room temperature to 350°C. They have observed the reduction of CuO to Cu and the stepwise oxidation of Cu→Cu<sub>2</sub>O→CuO from the XRD spectra of the products after each process. Hence, the oxidation state of copper changes thermodynamically between CuO, Cu<sub>2</sub>O, and Cu as a function of temperature and oxygen atmosphere. This redox behavior and the difference in oxygen defects, oxygen holes, and oxygen adsorption species in these oxidation states are thought to be the reason for the high activity or selectivity of the copper catalyst.



SCHEME 2: Proposed mechanism for the oxidation of benzoin catalyzed by zeolite encapsulated nanocrystalline CuO.



SCHEME 3: Proposed mechanism for the oxidation/reduction of benzhydrol catalyzed by zeolite encapsulated nanocrystalline CuO.



SCHEME 4: Proposed mechanism for the coupling of 1-phenylethanol catalyzed by zeolite encapsulated nanocrystalline CuO.

Earlier Sheikh and Eadon [19] have reported the vapor-phase oxidation of alcohols to aldehydes and ketones by cupric oxide as a catalyst. They have proposed a homolytic cleavage of C–H and O–H bonds for the oxidation of alcohols catalyzed by CuO. A similar mechanism may also be proposed in our case too, when benzoin is oxidized to benzil (Scheme 2). In this process, CuO is proposed to be reduced to Cu, and this Cu may undergo aerial oxidation to regenerate CuO.

Benzhydrol behaves differently with CuO encapsulated CuY zeolite. With pure CuO, benzhydrol gives benzophenone as the sole product. However, with CuO encapsulated CuY zeolite, the oxidized product benzophenone as well as the reduced product, diphenylmethane, is obtained. It is rel-

evant to note that under supercritical water, diarylmethanols and its derivatives are transformed into diarylmethanes and diarylketones [20]. This disproportionation is considered to proceed via a hydrogen transfer from bis(diarylmethyl)ether intermediate. The same group has also reported the formation of diarylalkanes from diarylketones under supercritical 2-propanol [21]. Earlier, Gribble et al. [22] have reported the reduction of diarylketone with  $\text{NaBH}_4$  in  $\text{CF}_3\text{CO}_2\text{H}$  to yield diarylmethane.

Zeolite plays a vital role in the oxidation/reduction of benzhydrol. In the oxidation of benzhydrol with pure CuO, benzophenone is formed as the sole product. However, in presence of CuY zeolite, diphenylmethane, the reduced product is also formed. To account for this, it is proposed

that zeolite supercage provides closer proximity between the reactants resulting in the formation of the intermediate bis(diarylmethyl) ether. This ether undergoes disproportionation to form alcohol and ketone (see Supplementary Figure available online at doi:10.1155/2008/257691). A plausible mechanism is proposed for the oxidation/reduction of benzhydrol catalyzed by CuO encapsulated CuY zeolite (Scheme 3). To confirm this, a control experiment was also performed with a physical mixture of Y-zeolite and CuO. Here, a vastly different products distribution was obtained with only 8.4% of reduced product and the remaining being the oxidized product. This clearly indicates that the acid-base bifunctionality is due to encapsulation of CuO inside the zeolite framework.

In the oxidation of benzhydrol, hydrogen transfer to CuO takes place involving homolytic cleavage of hydroxyl group. This reduces Cu(II) to Cu(I) which can readily eliminate H<sup>+</sup>. This H<sup>+</sup> will protonate benzhydrol which followed by dehydration forms the corresponding cation. This cation may be reduced by the Cu(I) to diphenylmethyl radical. Combination of this with the initially formed diarylmethyleneoxy radical leads to the formation of bis(diarylmethyl) ether intermediate. Disproportionation of this intermediate proceeds, through intramolecular hydrogen transfer to give diarylmethane and diarylketone. The redox behavior of Cu provides a useful regeneration of the catalyst.

In the case of 1-phenylethanol, 1,2-dimethylstilbene is formed as the major product. To account for this, the following mechanism is proposed (Scheme 4). Here, 2,3-diphenyl-2-butanol intermediate is proposed which may undergo dehydration to form the alkene.

#### 4. CONCLUSIONS

Zeolite encapsulated nanocrystalline CuO (particle size less than 15 nm) is synthesized successfully and is characterized by powder XRD, SEM, and HRTEM analyses. The nanoparticles are highly dispersed. This CuOY is used as catalysts in the oxidation of aromatic alcohols. Secondary alcohols undergo oxidation to a greater extent and primary alcohols react very slowly. With benzhydrol, disproportionation takes place leading to both oxidation as well as reduction products (benzophenone and diphenylmethane, resp.). CuY zeolite acts as an efficient support for nano CuO, by stabilizing it and preventing its aggregation. The process is also significant in that it is a new method for the synthesis of diphenylmethane, a useful material in spice production and also an important intermediate in drug and organic synthesis [23]. Plausible mechanisms for the formation of the various products are also given.

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