



Selective Catalytic Oxidation of Benzyl Alcohol by Sol-Gel Synthesized Nano Copper Aluminate

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Nano copper aluminate spinel catalyst prepared by sol-gel technique using citric acid as gelling agent and sintered at 900 °C was characterized by XRD, FT-IR, SEM to identify the structural phases, stretching frequencies, surface morphology and particle size, respectively. The prepared catalyst was used for the selective oxidation of benzyl alcohol to benzaldehyde in presence of hydrogen peroxide as the oxidant. The effect of solvent, reaction time and amount of catalyst on the catalytic oxidation of benzyl alcohol was studied. Formation, percentage yield and turnover number of benzaldehyde were confirmed by gas chromatography and ammonia chemisorption data. Without using the catalyst or the solvent, very low yield of benzaldehyde was observed. Highest conversion and turnover number of benzaldehyde was observed using acetonitrile as the solvent.

Key Words: Copper aluminate, Spinel, Sol-gel process, X-Ray diffraction, Catalytic oxidation, Benzyl alcohol.

INTRODUCTION

Aluminum-based spinels constitute an interesting class of oxide ceramics with important technological applications and are prepared by various methods like solid state reaction, co-precipitation, sol-gel and hydrothermal method¹⁻⁴. Among them, the sol-gel method is an attractive technique, because it produces pure and ultra-fine powders at low temperatures⁵. Among all kinds of spinels, aluminate spinels have high thermal stability, high mechanical resistance, hydrophobicity and low surface acidity⁶. These properties make them promising catalytic or carrier materials for active metals in substitution for more traditional systems. Among the spinels, copper aluminate (CuAl₂O₄) is found to be an efficient catalyst in a number of catalytic oxidation reactions⁷⁻¹⁰. In CuAl₂O₄, Cu²⁺ ions are highly dispersed in the Al₂O₃ matrix. Generally, it is accepted that the Cu²⁺ ion present in CuAl₂O₄ acts as an active site in the catalytic reactions¹¹. However, the literature on the usage of copper aluminate for the catalytic oxidation of alcohols is silent.

Recently nanomaterials are more active in catalytic reactions because of the high number of surface atoms and they frequently carry surface atoms with special local environment and enhanced chemical activity¹². Hence nanometal aluminate spinels can be developed for its application related to catalytic activities. Oxidation of benzyl alcohol to benzaldehyde is a practically important reaction for the production of chlorine-

free benzaldehyde that is required in the perfumery and pharmaceutical industries. Studies on the catalytic vapour-phase oxidation of benzyl alcohol to benzaldehyde¹³ have been reported and in this process significant carbon loss in the form of carbon oxides is a major environmental problem¹⁴.

Traditionally, the oxidation of alcohols is performed using stoichiometric amounts of oxidants, such as permanganate, chromate or bromate¹⁵. These methods produce a large amount of waste and are unacceptable in view of green chemical practices. To solve this problem, various catalytic systems using environmentally benign oxidants like hydrogen peroxides, organic peroxides and molecular oxygen under homogeneous as well as heterogeneous conditions have been developed in the last two decades.

Recently, transition metal nanoparticle-catalyzed aerobic alcohol oxidations have been investigated and many have shown high catalytic activities and good selectivities^{16,17}. Though the utilization of molecular oxygen as an oxidant is highly effective, there are certain limitations like requirement of sophisticated instrumentation and the use of precious elements as catalysts.

Hydrogen peroxide has also emerged as a popular oxidant in the past few decades. The liquid phase catalytic oxidation of alcohols using hydrogen peroxide as an oxidant using various catalysts like tungstate complex, titanium silicalite-I, FeBr₃ and cobalt(II) complexes has been reported in literature¹⁸⁻²¹. Dijkstra *et al.*²², have reported the polymer immobilized

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as an efficient catalyst for the oxidation of alcohols using hydrogen peroxide as an oxidant. Although the use of TEMPO in homogeneous phase is well established, but its reusability is questionable.

All the above methods have advantages like higher yields and selectivity. But some of the major problems encountered in these methods include the difficulty associated with the method of preparation and high cost of the catalysts especially in case of catalysts using precious metals. Hence there is still significant demand for the green and effective catalysts, which can activate a wide range of substrates and can be used under mild conditions and exploration of new oxidizing agents remains a challenging area of research in organic synthesis.

Therefore liquid-phase oxidation of benzyl alcohol to benzaldehyde is preferable than the vapor phase oxidation. In this paper, we report the synthesis, characterization and selective catalytic oxidation of benzyl alcohol to benzaldehyde using nano copper aluminate spinel as the catalyst.

So far from literature^{18,23} it is found that very low yield of benzaldehyde is formed by using hydrogen peroxide (H_2O_2) as the oxidant for the oxidation of benzyl alcohol and TBHP (*tert*-butyl hydroperoxide) was reported as the best oxidant. But in the present study, H_2O_2 is proved to be a better oxidant for benzyl alcohol and 100 % selective oxidation of benzyl alcohol to benzaldehyde is reported. Also the influence of reaction time, solvent and amount of catalyst has been investigated.

EXPERIMENTAL

Catalyst preparation and characterization: Calculated amounts of copper nitrate and aluminum nitrate of analytical grade were dissolved in distilled water and citric acid was added as the gelling agent. The resulting solution was stirred at room temperature for 2 h to get clear and transparent solution. This clear solution was kept for gelation at 100 °C for 12 h followed by calcinations at 600 °C for 5 h. The powders were then sintered at 900 °C for 5 h.

The structural studies of the catalysts prepared were carried out using a Philips X'pert diffractometer for 2θ values ranging from 0-80° using $CuK\alpha$ radiation at $L = 0.154$ nm. A Perkin Elmer infrared spectrophotometer was used for the determination of the surface functional groups. The surface morphology of the nano copper aluminate was observed on a Leo-Jeol scanning electron microscope at the desired magnification. The nitrogen adsorption-desorption isotherms of the catalyst were measured using an automatic adsorption instrument (Quantochrome Corp. Nova-1000 gas sorption analyzer). The specific surface area (m^2/g) of the catalyst was calculated using BET equation^{24,25}. The pore size distribution was determined using the BJH (Barrett, Joyner and Halenda) method. In addition the *t*-plot method^{26,27} was applied to calculate the micropore volume and surface area. The total pore volume was estimated as liquid volume of adsorbate adsorbed at a relative pressure (P/P_0) of 0.09. All surface area measurements were calculated from the nitrogen adsorption isotherms by assuming the area of the nitrogen molecule to be 0.162 nm².

Catalytic test: The liquid phase reaction was carried out in a three necked round bottom flask equipped with a reflux

condenser and thermometer preheated at 70 °C in presence of copper aluminate catalyst. In a typical catalytic oxidation, 10 mmol of hydrogen peroxide as the oxidant was added along with the copper aluminate catalyst of different weights and the contents were heated at 80 °C using different solvents like *n*-hexane, chlorobenzene and acetonitrile for 6-10 h. The course of the reaction was monitored by TLC using petroleum ether-ethyl acetate (9:1 v/v) as the solvent system and the percentage yield along with turnover number of the product was confirmed by gas chromatography.

The oxidized product after the catalytic reaction is collected and studied using Agilent GC spectrometer. The column used for the study was DB wax column (capillary column) of length 30 mm and helium was used as the carrier gas.

To calculate the number of active sites TPD measurements were carried out using Chemisorb 2750 TPD from which the turnover number was calculated. Turnover number is the number of moles of benzyl alcohol converted per mole of the catalyst.

RESULTS AND DISCUSSION

Catalyst characterization: The XRD pattern of nano copper aluminate catalyst (Fig. 1) showed the spinel phase with cubic structure (JCPDS:33-0448). There are no additional reflections due to the related phases of CuO or Al_2O_3 were present and there by confirming the formation of pure spinel phase. The average crystallite size was calculated using Scherrer formula²⁸ and is found to be 15.56 nm.

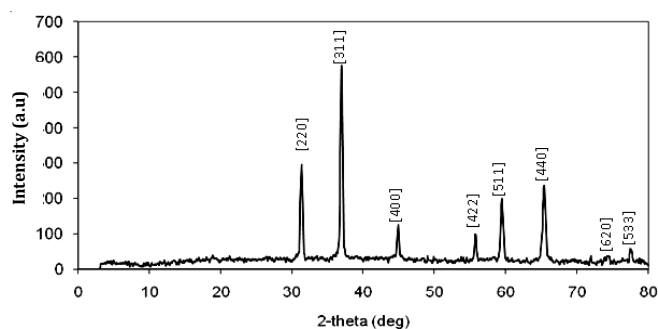


Fig. 1. XRD pattern of the nano copper aluminate spinel catalyst

The FT-IR spectrum exhibited a broad band near 3400 cm^{-1} due to -OH stretching vibration of a free hydrogen bonded hydroxyl groups and a second typical absorption region at 1630 cm^{-1} is assigned to the deformative vibration of water molecules, which is most probably due to water absorption during the compaction of the powder specimen with KBr ²⁹. The metal oxygen stretching frequencies in the range of 1000-400 cm^{-1} are associated with the vibrations of Al-O, Cu-O-Al bonds. Two bands at 560 and 678 cm^{-1} observed are due to the copper aluminate spinels. These bands correspond to the AlO_6 unit, which build up the $CuAl_2O_4$ spinel and indicate the formation of $CuAl_2O_4$ spinels³⁰.

The visual observation of spatial relationships between the component phases in the nano copper aluminate is of particular importance in attempts to study their catalytic activity. The surface morphology of nano copper aluminate catalyst as shown in Fig. 2 which depicts the intergranular porous structure of the catalyst qualitatively. The SEM-

micrographs reveal the porous nature of the catalyst where the pores are in the range of 0.5-3.0 μm . The highly porous nature of the catalyst is a necessary criterion for a good catalyst. It is also observed from the image that the smaller grains are connected with each other and/or aggregate to some extent with well developed porosity.

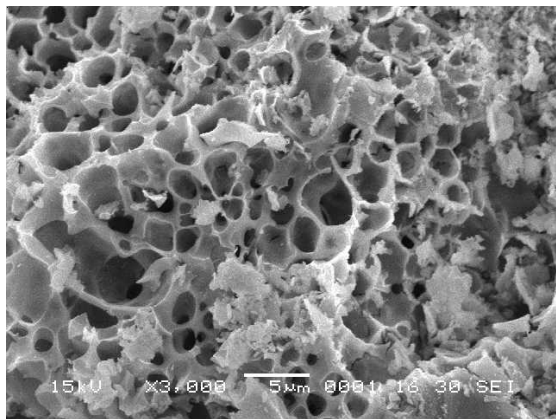


Fig. 2. SEM image of nano copper aluminate

Fig. 3 represents the typical nitrogen adsorption/desorption isotherm of nano copper aluminate at 77 K. It shows the presence of a hysteresis loop at high relative pressures and shape of the isotherm corresponding to type IV according to IUPAC classification^{26,27}. Fig. 4 shows the pore size distribution of the nano copper aluminate catalyst from which, it is found that the catalyst has only a mesoporous character with pore size in the mesopore range of $2 < d < 50$ nm. The amount of nitrogen adsorbed was found to be $50.65 \text{ cm}^3/\text{g}$. The specific surface area, pore volume and pore size distribution of the copper aluminate catalyst are listed in Table-1. From the values, it is observed that the copper aluminate catalyst prepared in the present study has only mesopores, which facilitated the catalytic oxidation of benzyl alcohol.

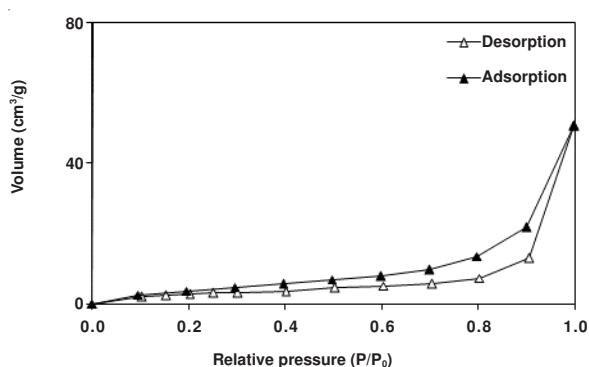


Fig. 3. Nitrogen adsorption/desorption isotherm of nano copper aluminate

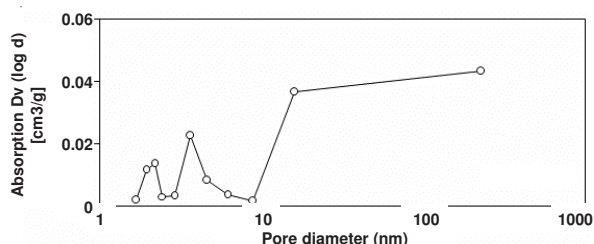


Fig. 4. Pore size distribution of nano copper aluminate spinel catalyst

TABLE-1
SURFACE AREA PARAMETERS OF NANO
COPPER ALUMINATE CATALYST

Surface area parameters	
S_{BET} (m^2/g)	10.46
S_{mic} (m^2/g)	0.000
S_{meso} (m^2/g)	10.46
Total pore volume (cm^3/g)	0.078
Micropore volume (cm^3/g)	0.000
Mesopore volume (cm^3/g)	0.078
Average pore diameter (nm)	29.97

Catalytic oxidation of benzyl alcohol using copper aluminate catalyst

Effect of reaction time: The liquid phase oxidation of benzyl alcohol was carried out using hydrogen peroxide as the oxidant along with 0.5 g copper aluminate catalyst using different solvents like *n*-hexane, chlorobenzene and acetonitrile at different time intervals of 6, 8, 10 and 14 h. The only product obtained was benzaldehyde which confirms the 100 % selectivity of the catalyst. Fig. 5 depicts the influence of reaction time on the conversion of benzyl alcohol by copper aluminate catalyst. At the initial stage of the reaction a rapid increase in the conversion of benzyl alcohol is observed and at longer reaction run time, the catalyst gets slowly deactivated. The oxidation of benzyl alcohol to benzaldehyde was carried out using hydrogen peroxide as the oxidant along with nano copper aluminate catalyst of different weights (0.50, 0.75 and 1.00 g) using different solvents like *n*-hexane, chlorobenzene and acetonitrile at different time intervals and the percentage yield of the products is shown in Table-2.

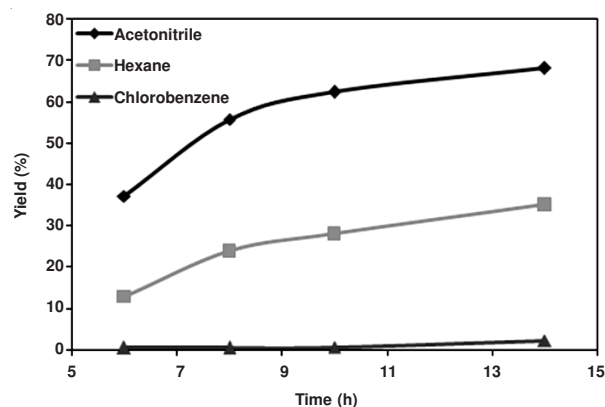


Fig. 5. Effect of reaction time on the yield % of benzaldehyde for different solvents

Effect of solvent: When the reaction was carried out in the absence of any solvent, very less amount of formation of benzaldehyde was observed (1 %). Subsequently, the reaction was carried out using different solvents like *n*-hexane, chlorobenzene and acetonitrile. The percentage yield of the product at different time intervals in the presence of different solvents using different amounts of nano copper aluminate catalyst (0.50, 0.75 and 1.00 g) is given in Table-2 and the effect of solvent on the turnover number is given in Table-3. From the results, it is found that as the polarity of the solvent increases the conversion percentage of benzaldehyde decreases. It would have been caused by the competitive adsorption of the solvent

TABLE-2
AMOUNT OF CATALYST, REACTION TIME AND PERCENTAGE YIELD OF BENZALDEHYDE IN *n*-HEXANE, ACETONITRILE AND CHLOROBENZENE

Amount of catalyst (g)	Reaction time (h)	Yield of benzaldehyde in solvents (%)		
		<i>n</i> -Hexane	Acetonitrile	Chlorobenzene
0.50	6	12.8	37.2	0.4
	8	23.8	55.6	0.4
	10	27.9	62.3	0.5
0.75	6	35.2	41.3	0.4
	8	42.4	62.0	0.6
	10	59.2	75.0	1.1
1.00	6	51.5	65.1	0.8
	8	77.8	97.3	0.9
	10	87.8	100	2.1

All the reactions were done with 10 mmol benzyl alcohol, 10 mmol H₂O₂, at 80 °C for various reaction times.

TABLE-3
EFFECT OF SOLVENT ON THE PERCENTAGE YIELD AND TON OF NANO COPPER ALUMINATE CATALYST

Solvent	Temp. (°C)	Conversion (%)	TON
Acetonitrile	80	100	3500
Hexane	80	87.8	2436
Chlorobenzene	80	2.1	1190
No catalyst/Solvent	80	1	28

All the reactions were done with 10 mmol benzyl alcohol, 10 mmol H₂O₂, 1 g catalyst, at 80 °C, for 10 h.

and hydrogen peroxide on the surface of the catalyst. By the increase in solvent polarity, solvent will be more easily adsorbed in the active site of the catalyst than the hydrogen peroxide³¹.

Although acetonitrile has the highest polarity it gave a maximum conversion of benzyl alcohol to benzaldehyde in present study, as it activates H₂O₂ by forming a perhydroxyl anion (OOH⁻) that nucleophilically attacks the nitrile to generate a peroxy-carboximidic acid intermediate. This intermediate is a good oxygen transfer agent. In addition, acetonitrile has a comparatively good solubility power for both the organic substrate as well as the aqueous H₂O₂³².

Effect of the amount of catalyst: The percentage yield of benzaldehyde obtained using 0.50, 0.75 and 1.00 g of CuAl₂O₄ catalyst in presence of different solvents is shown in Table-2. No formation of benzaldehyde was observed in the absence of the catalyst.

From Table-2, it is inferred that when the amount of the catalyst is increased from 0.5-1.0 g, the percentage of formation of benzaldehyde was also increased and a complete oxidation (100 %) of benzyl alcohol to benzaldehyde is possible using acetonitrile as the solvent and 1 g of the nano copper aluminate catalyst when the reaction time is kept as 10 h.

Catalyst reusability: In order to study the possibility of reusability, the catalyst was filtered off from each run and washed several times with *n*-hexane and dried at 120 °C in an air oven for 3 h. The reusability of the catalyst was checked for five consecutive runs of the oxidation of benzyl alcohols under the identical conditions. The percentage yield *versus* number of cycles checked for the reusability of the catalyst is shown in Fig. 6.

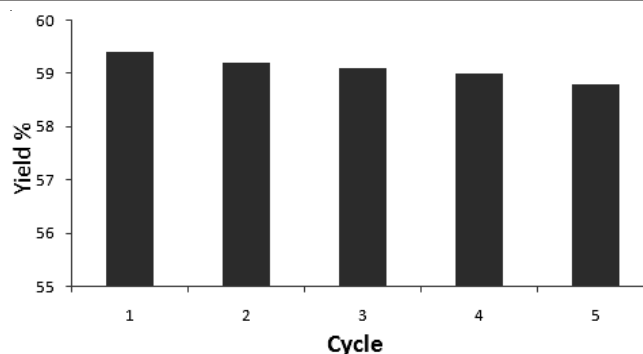


Fig. 6. Reusability studies of the catalyst

Conclusion

Nano copper aluminate spinel catalyst was synthesized by sol-gel method. The sintered precursors yielded pure nano copper aluminate spinel catalyst, which is found to be highly porous. The particle size of the catalyst was found to be 15 nm. The formation of spinel phase was confirmed by XRD and FT-IR. The catalytic oxidation of benzyl alcohol to benzaldehyde is carried out in presence of H₂O₂ using 0.5, 0.75 and 1 g of the catalyst and varying the solvents as *n*-hexane, acetonitrile and chlorobenzene. Without using the catalyst or the solvent very low yield of benzaldehyde was observed. When the amount of the catalyst is increased to 1 g, the percentage of formation of benzaldehyde was also increased. The highest yield of benzaldehyde was obtained using 1 g of the catalyst in acetonitrile medium at 80 °C for 10 h. The ready availability of the reagents and ease of preparation, together with high yields are the salutary features of this approach and hence the procedure is versatile particularly in cases where rapid and mild oxidation of alcohols is required.

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