Synthesis, characterization, scale-up and catalytic behaviour of Co_3O_4 nanoparticles

MANPREET SINGH*, N K RALHAN and SUKHDEEP SINGH

Department of Chemistry, Eternal University, Baru Sahib (H.P.) 173 101, India

MS received 28 February 2014; revised 4 July 2014

Abstract. Highly uniform cobalt oxide (Co_3O_4) nanoparticles were synthesized via thermal decomposition of cobalt hydroxy carbonates with particle size around 16 ± 1 nm. The process gives reproducible results in batches of 1–5 kg. The particles show good catalytic activity for the oxidation of oxalic acid and benzaldehyde under mild temperature conditions. The characterization was performed by X-ray diffractometry (XRD), Transmission electron microscopy (TEM), Fourier-transform infrared (FT-IR) spectrum and Nuclear magnetic resonance (NMR). The XRD measurements show cubic spinel phase and Debye–Scherrer relation was used to measure average particle size. The convenience of the production of catalyst can be exploited for its large-scale production and use in laboratories, R&Ds and industries.

Keywords. Cobalt oxide; nanoparticles; calcination; oxidation.

1. Introduction

There is being increasing interest in the field of catalytic selective oxidation in liquid phase owing to its industrial interests.¹ For oxidation reactions, transition metal oxides are known to be having promising catalytic activity.² Our interest is being in the search of an efficient catalyst for redox reactions. In the group of transition metal oxides, the nanostructured cobalt oxide (Co_3O_4) spinels are of special interest due to their relatively low cost, high thermal stability, ease of preparation of high surface area^{3–13} and many applications in different areas such as catalysts,^{14–16} sensors^{17–19} and batteries.^{20–22} A range of different morphologies had been used to synthesize Co_3O_4 including nanospheres, nanocubes, nanofibres and mesoporous structures.^{23–27} The properties of thus prepared oxides are strongly morphology dependent which determines the structural parameters such as quality of crystal, particle size and surface area.²⁸

Co_3O_4 is a p-type semiconductor and its spinel structure is based on cubic close packing array of oxide ions in which Co(II) ions occupy the tetrahedral 8a sites and Co(III) ions occupy the octahedral 16d sites.²⁹ Out of different crystal faces of Co_3O_4 , the naturally exposed surface of Co_3O_4 is the (110) crystal face and it plays an important role in the catalytic oxidation of CO, ethylene and methane combustion.³⁰ It has also been observed that Co_3O_4 readily oxidizes carbon monoxide to CO_2 by a dynamic oxygen transfer from the air.³¹ At the same time the Co_3O_4 as such or supported over alumina, silica or titania^{32,33} are the catalyst of choice for Fischer–Tropsch synthesis of hydrocarbons from a mixture of carbon monoxide and hydrogen.

Co_3O_4 nanoparticles synthesized via thermal decomposition of cobalt hydroxyl carbonate has been observed as a versatile oxidizing agent as such and as well as assisted by oxygen (air, O_2) or oxygen donors (H_2O_2) for a variety of organic compounds, e.g., aldehydes (formaldehyde, acetaldehyde, benzaldehyde, glucose, etc.), acids (formic acid, oxalic acid) and others like carbon monoxide, methanol and azodyes (methyl orange). Many of these compounds are volatile organic compounds (VOCs) whose presence is considered harmful.

Little information is available for the synthesis of Co_3O_4 in bulk/large scale and that too in grams. The few references of Co_3O_4 on large-scale production includes Co_3O_4 supported on substrates such as ceramics, silicon^{34,35} and pure Co_3O_4 without any substrate support synthesized through solvothermal process.³⁶ In literature, Co_3O_4 have been reported for both selective oxidation^{37,38} and reduction^{39,40} purpose. The catalyst reported in this paper is found to be having promising oxidative nature which is confirmed from the oxidation of oxalic acid and benzaldehyde under mild conditions. The Co_3O_4 nanoparticles produced were further scaled-up to pilot plant level (1–5 kg batches). The so produced batches show similar properties and uniform distribution of nanoparticles.

2. Experimental

2.1 Materials and methods

Cobalt sulphate heptahydrate (28.1 g; 0.1 M) of analytical grade was dissolved in demineralized water (100 ml) followed by slowly addition, with stirring, an aqueous solution

*Author for correspondence (manpreetrisam19@gmail.com)

of sodium hydroxide:sodium carbonate (1:1 w/w) in demineralized water. The pH was adjusted to 8.0 ± 0.2 . The precipitated hydroxy carbonate of cobalt was repeatedly washed with demineralized water to free from sulphate ions and then dried at $80\text{--}85^\circ\text{C}$. The dried cobalt hydroxy carbonate was calcined at $300\text{--}350^\circ\text{C}$ in a ceramic crucible for 2 h.

2.2 Scale-up

The scale-up of the material was achieved by the reaction of cobalt sulphate solution (2.3 kg, 10.0 M) in 50 L demineralized water that was precipitated by adding an aqueous solution of sodium hydroxide:sodium carbonate (1:1 w/w) and adjusted to $\text{pH } 8.0 \pm 0.2$, filtered, washed with demineralized water to free from sulphate ions, air dried and then calcined in specially designed ceramic boats having capacity to hold 1 kg of cobalt hydroxy carbonates.

2.3 Characterization

The spectrum of Co_3O_4 nanoparticles were studied in the infrared region by Fourier-transform infrared (FT-IR) spectroscopy using a Nicolet Avatar 5700 system. The structure of the catalyst was studied by X-ray diffraction (XRD) using X-Pert PROsystem. The morphology of the catalyst was studied by transmission electron microscopy (TEM) using Hitachi H-7500.

2.4 Catalytic activity

2.4a Oxidation of oxalic acid: Seven-hundred and eighty milligrams of oxalic acid and 1 g of Co_3O_4 nanoparticles were taken in a 100 ml closed lid measuring flask and was filled up to the mark using double distilled water. Series of five different sets were prepared and ultrasonicated with a gap of 15 min each at 25, 35, 45, 55 and 65°C . Ultrasonication of each set was followed by stay time of 2 h. After 2 h, 5 ml of the aliquot from each sample is taken and titrated against $\text{M}/100 \text{ KMnO}_4$ using 25 ml distilled water and 20% H_2SO_4 . The readings observed for the titration were recorded and are shown in table 1 and figure 4.

2.4b Oxidation of benzaldehyde: Co_3O_4 nanoparticles were used for the selective oxidation of benzaldehyde to benzoic acid. One pot liquid phase oxidation of benzaldehyde to benzoic acid was performed in a 250 ml flask. In each test 0.2 g of the nanocatalyst was added to 2 ml benzaldehyde and 40 ml double distilled water. Reactions were carried out under refluxing using small condenser and digitally controlled stirrers at (mild temperature conditions) 60°C for 3, 4 and 6 h. The crystals of benzoic acid prepared were separated, washed with double distilled water and air dried. The identity of the products was confirmed by comparing their melting points and NMR data with those reported in literature. The so obtained yields are shown in table 2.

Table 1. Titration results at different temperatures and time periods for the oxidation of oxalic acid.

Catalyst	Reaction time (min)	Result (ml)
<i>At 25°C</i>		
Co_3O_4	0	10.0
Co_3O_4	15	8.3
Co_3O_4	30	8.3
Co_3O_4	45	8.3
Co_3O_4	60	8.3
<i>At 35°C</i>		
Co_3O_4	0	10.0
Co_3O_4	15	8.3
Co_3O_4	30	8.3
Co_3O_4	45	7.8
Co_3O_4	60	7.7
<i>At 45°C</i>		
Co_3O_4	0	10.0
Co_3O_4	15	7.9
Co_3O_4	30	6.0
Co_3O_4	45	5.8
Co_3O_4	60	4.1
<i>At 55°C</i>		
Co_3O_4	0	10.0
Co_3O_4	15	5.0
Co_3O_4	30	4.8
Co_3O_4	45	3.7
Co_3O_4	60	2.6
<i>At 65°C</i>		
Co_3O_4	0	10
Co_3O_4	15	2.1
Co_3O_4	30	1.8
Co_3O_4	45	1
Co_3O_4	60	0.4

Table 2. Yield obtained at different time periods for the oxidation of benzaldehyde.

Benzaldehyde (ml)	Co_3O_4 nanoparticles (mg)	Time (h)	Benzoic acid (yield) (%)
2	200	3	35
2	200	4	50
2	200	6	70

2.5 NMR analysis

An NMR spectrum of benzoic acid was recorded on Bruker Avance II 400 NMR spectrometer. The confirmation of the peaks of benzoic acid was made by comparing with standard NMR spectra.

3. Results and discussion

Figure 1 shows the FT-IR spectra of Co_3O_4 nanoparticles. Peaks at 574.32 and 669.33 cm^{-1} correspond to the vibration

of metal–oxygen (Co–O) bond due to Co_3O_4 spinel oxide.⁴¹ The peak at 1634.46 cm^{-1} and a broad band at 3433.09 cm^{-1} are assigned to O–H stretching and bending modes of water.⁴²

Figure 2 shows the XRD spectra of Co_3O_4 nanoparticles. The spectrum reveals reflections of the cubic structure of the spinel with Fd3m space group. The lattice parameter is calculated from the most intense peak (311) and the values of lattice constant a (Å) is found to be 8.066. The values of lattice parameter are found to be close to JCPDCS reference card no. 42-1467 (8.083 Å). The average crystallite sizes for the most intense peak [(311) plane] were calculated from the XRD data using Scherrer formula and are found to be $16 \pm 1\text{ nm}$. The X-ray density of prepared specimen was calculated and is 6.10 g cm^{-3} which are very close to the value reported in JCPDCS reference card no. 42-1467. The

Figure 1. FT-IR spectra of Co_3O_4 nanoparticles.

Figure 2. XRD pattern of Co_3O_4 nanoparticles.

X-ray density of prepared specimens was calculated using the relation

$$\left[d_x = \frac{ZM}{Na^3} \right],$$

where Z is the number of molecules per unit cell, M the molecular weight, a the lattice parameter and N the Avogadro's number.

The surface morphology of the Co_3O_4 nanoparticles was studied using transmission electron microscopy (TEM). The high-resolution TEM images in figure 3 shows that the observed particle size is uniform, homogeneous and in good agreement with XRD results having average particle size of $16 \pm 1\text{ nm}$. Similar morphology was achieved even up to pilot plant level, i.e., 1–5 kg batches. This indicates that the method employed is easy and convenient for pilot plant level and can be possible for the synthesis of Co_3O_4 nanoparticles on a large scale.

The cobalt and oxygen percentage in Co_3O_4 spinel is 73.4 and 26.5, respectively, whereas the observed cobalt percentage in the cobalt oxide nanoparticles synthesized via thermal decomposition was found to be 64.18 using complexometric titrations. The percentage of cobalt along with its FT-IR, XRD and TEM support it as Co_3O_4 spinel nanoparticles with particle size of $16 \pm 1\text{ nm}$. The lower percentage of Co in the Co_3O_4 spinels but well-defined nanoparticles in TEM and supported by XRD is indicative of highly adsorbed oxygen on its surface and hence are capable of dynamic oxygen transfer for oxidative and allied reactions.

Co_3O_4 spinels exhibited higher oxidation activity so a series of experiment with the material was designed to determine its effect on oxalic acid. Figure 4 shows five different sets for the oxidation of oxalic acid at five different temperatures (25, 35, 45, 55 and 65°C) on $\text{M}/100\text{ KMnO}_4$ (ml) concentration vs. time (minutes) graph. The pattern of the lines indicated that Co_3O_4 nanoparticles oxidized oxalic acid with ease even at mild temperature conditions. However under the similar conditions of concentration and temperature, the extent of oxidation increases in the order $25^\circ\text{C} < 35^\circ\text{C} < 45^\circ\text{C} < 55^\circ\text{C} < 65^\circ\text{C}$. On moving from 25°C to 65°C , the amount of titrant consumption decreases indicating that

Figure 3. TEM images of Co_3O_4 nanoparticles.

Figure 4. Graphical representation for the oxidation of oxalic acid.

the oxidation of the oxalic acid increases in the order $25^{\circ}\text{C} < 35^{\circ}\text{C} < 45^{\circ}\text{C} < 55^{\circ}\text{C} < 65^{\circ}\text{C}$ for the respective sets. The reactivity of the material is strictly dependent on the structural properties as determined by the morphological structure. Wang *et al*⁴³ reported that the strength of the Co–O bond weakens with the increase in specific surface area on Co_3O_4 which in turn makes reduction easy by promoting more lattice oxygen desorption from Co_3O_4 . The effect of time and temperature is also shown in table 1 and figure 4.

A series of experiment with Co_3O_4 nanoparticles was also designed to study the oxidation effect of Co_3O_4 spinels on benzaldehyde. It was found that even at mild temperature conditions Co_3O_4 spinels had oxidized benzaldehyde to benzoic acid in good yield. The observed m.p. of benzoic acid crystals was in match with the standard m.p. (122.41°C). The time-dependent oxidation effect and yield is shown in table 2. It was found that the reaction was time dependent. As the time increases, the yield of benzoic acid increases. The NMR spectrum reveals the formation of pure product with high selectivity. The dynamic oxygen transfer properties of Co_3O_4 had been attributed to the weak Co–O bond and a fast exchange between molecular oxygen and lattice oxygen.⁴⁴ The yield of benzoic acid was found to be 70%. The results obtained under mild conditions had proved that the synthesized Co_3O_4 nanoparticles have good oxidation properties which can be further improved to achieve the products in high yield at mild temperature and pressure conditions. And work is going on in this direction.

The comparison of the available oxygen and oxygen required for the reactions was calculated from the stoichiometric calculations and it was found that for complete oxidation of benzaldehyde (2.12 g; 0.02 m), the required oxygen (320 mg; 0.02 m) has been provided by Co_3O_4 nanoparticles and in a concerted manner by absorbing oxygen from the atmosphere and transferring to benzaldehyde whereas the oxidation of oxalic acid with Co_3O_4 nanoparticles has been

followed at four different temperatures to optimize the best condition for the oxidation and it has been observed that the oxidation proceeds best at 65°C .

4. Conclusion

Co_3O_4 nanoparticles formed are equally uniform and non-contaminated. Further the simplicity and ease of the reaction condition developed in the above method is very useful for scale-up and production of material in larger batches (1–5 kg) and make material available for study of applications of Co_3O_4 nanoparticles. The convenience of the production of catalyst can be exploited for its large-scale production and use in laboratories, R&Ds and industries. The Co_3O_4 nanoparticles have been found to be useful catalysts for dynamic oxygen transfer reactions. The capacity of Co_3O_4 nanoparticles to oxidize oxalic acid and benzaldehyde indicates that they can be used as catalyst. However, there is also the possibility of further improving the catalytic behaviour of Co_3O_4 nanoparticles for using it as catalyst and work is going on in this direction.

Acknowledgements

We thank Eternal University, Himachal Pradesh, SAIF-Panjab University, Chandigarh, USIC-Himachal Pradesh University, Shimla and Tinchem Enterprises (www.tinchementerprises.in), for their liberal support.

References

1. Bavykin D V, Lapkin A A, Kolaczowski S T and Plucinski P K 2005 *Appl. Catal. A: Gen.* **288** 175
2. Taghavimoghaddam J, Knowles G P and Chaffee A L 2012 *J. Mol. Catal. A: Chem.* **358** 79
3. Hall A K, Harrowfield J M, Hart R J and McCormick P G 1996 *Environ. Sci. Technol.* **30** 3401
4. Jia M, Su G, Zheng M, Zhang B and Lin S 2010 *Sci. China Chem.* **53** 1266
5. Jia M, Su G, Zheng M, Zhang B and Lin S 2011 *J. Nanosci. Nanotechnol.* **11** 2100
6. Lichtenberger J and Amiridis M D 2004 *J. Catal.* **223** 296
7. Öberg T, Bergbäck B and Filipsson M 2008 *Chemosphere* **71** 1135
8. Ollis D F, Pelizzetti E and Serpone N 1991 *Environ. Sci. Technol.* **25** 1522
9. Schetter G, Horch K, Stuetzle R, Brunner H and Hagenmaier H 1990 *Organohalogen Compd.* **3** 165
10. Zacheis G A, Gray K A and Kamat P V 2001 *J. Phys. Chem. B* **105** 4715
11. Zhang L, Zheng M, Liu W, Zhang B and Su G 2008 *J. Hazard. Mater.* **150** 831
12. Zhang L, Zheng M, Zhang B, Liu W, Gao L, Ba T, Ren Z and Su G 2008 *J. Environ. Sci.* **20** 1523
13. Zhang X and Savage P E 1998 *Catal. Today* **40** 333

14. El-Shobaky G, Doheim M, Ghosza A and El-Boohy H 2002 *Mater. Lett.* **57** 525
15. Liu Q, Liu C-X, Nie X-L, Bai L and Wen S-H 2012 *Mater. Lett.* **72** 101
16. Zhu J, Kailasam K, Fischer A and Thomas A 2011 *ACS Catal.* **1** 342
17. Cao A-M, Hu J-S, Liang H-P, Song W-G, Wan L-J, He X-L, Gao X-G and Xia S-H 2006 *J. Phys. Chem. B* **110** 15858
18. Dai C-L, Chen Y-C, Wu C-C and Kuo C-F 2010 *Sensors* **10** 1753
19. Wöllenstein J, Burgmair M, Plescher G, Sulima T, Hildenbrand J, Böttner H and Eisele I 2003 *Sens. Actuators B: Chem.* **93** 442
20. Kim H, Seo D-H, Kim S-W, Kim J and Kang K 2011 *Carbon* **49** 326
21. Hu C, Guo J, Wen J and Yangxi P 2013 *J. Mater. Sci. Technol.* **29** 215
22. Wu Z-S, Ren W, Wen L, Gao L, Zhao J, Chen Z, Zhou G, Li F and Cheng H-M 2010 *ACS Nano* **4** 3187
23. Feng J and Zeng H C 2003 *Chem. Mater.* **15** 2829
24. He T, Chen D, Jiao X, Xu Y and Gu Y 2004 *Langmuir* **20** 8404
25. Jiang Y, Wu Y, Xie B, Xie Y and Qian Y 2002 *Mater. Chem. Phys.* **74** 234
26. King S, Hyunh K and Tannenbaum R 2003 *J. Phys. Chem. B* **107** 12097
27. Lakshmi B B, Patrissi C J and Martin C R 1997 *Chem. Mater.* **9** 2544
28. Lin S, Su G, Zheng M, Jia M, Qi C and Li W 2011 *J. Hazard. Mater.* **192** 1697
29. Jing X, Song S, Wang J, Ge L, Jamil S, Liu Q, Mann T, He Y, Zhang M and Wei H 2012 *Powder Technol.* **217** 624
30. Xu X L and Li J Q 2011 *Surf. Sci.* **605** 1962
31. Lin H-K, Chiu H-C, Tsai H-C, Chien S-H and Wang C-B 2003 *Catal. Lett.* **88** 169
32. Elbashir N, Dutta P, Manivannan A, Seehra M and Roberts C 2005 *Appl. Catal. A: Gen.* **285** 169
33. Viswanathan B and Gopalakrishnan R 1986 *J. Catal.* **99** 342
34. Jiang J, Liu J P, Huang X T, Li Y Y, Ding R M, Ji X X, Hu Y Y, Chi Q B and Zhu Z H 2009 *Cryst. Growth Des.* **10** 70
35. He L, Li Z and Zhang Z 2008 *Nanotechnology* **19** 155606
36. Xiao Y, Liu S, Li F, Zhang A, Zhao J, Fang S and Jia D 2012 *Adv. Funct. Mater.* **22** 4052
37. Jagadeesh R V, Junge H, Pohl M-M, Radnik Jr, Brückner A and Beller M 2013 *J. Am. Chem. Soc.* **135** 10776
38. Chun S W, Jang J Y, Park D W, Woo H C and Chung J S 1997 *Korean J. Chem. Eng.* **14** 216
39. Novochinsky II, Chernavsky P, Ryabchenko P and Lunin V 1998 *Catal. Lett.* **51** 191
40. Meng B, Zhao Z, Wang X, Liang J and Qiu J 2013 *Appl. Catal. B: Environ.* **129** 491
41. Li Y, Zhao J, Dan Y, Ma D, Zhao Y, Hou S, Lin H and Wang Z 2011 *Chem. Eng. J.* **166** 428
42. Zhou L, Xu J, Miao H, Wang F and Li X 2005 *Appl. Catal. A: Gen.* **292** 223
43. Wang C-B, Tang C-W, Gau S-J and Chien S-H 2005 *Catal. Lett.* **101** 59
44. Montoya A and Haynes B S 2011 *Chem. Phys. Lett.* **502** 63