



Investigating Oxidation of Formaldehyde Over Co_3O_4 Nanocatalysts at Moderate Temperature

MANPREET SINGH^{1*} and KAMAL KISHORE¹

¹Department of Chemistry, Akal College of Basic Sciences, Eternal University,
Baru Sahib, Sirmour-173101, H.P., India.

*Corresponding author E-mail: manpreetrisam19@gmail.com

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ABSTRACT

Formaldehyde is considered as one of the major contributor to global air pollution having extreme toxicity even at very low concentrations in air. Evidently, efficient processes and effective materials for the abatement of formaldehyde at low temperature are of great significance. In this paper, we report the comparative study for the catalytic oxidation of formaldehyde in aqueous medium at moderate temperature conditions (20-40 °C). The catalysts used are nanoparticles of Co_3O_4 synthesized via chemical combustion, sol-gel autocombustion, thermal decomposition and hydrothermal route with particle size 21 ± 1 nm, 39 ± 1 nm, 16 ± 1 nm and 25 ± 1 nm respectively. The characterization of the synthesized nanocatalysts was performed by X-ray diffractometry (XRD), Transmission electron microscopy (TEM), Fourier-transform infrared (FT-IR) spectrum. The XRD measurements confirm the cubic spinel phase of Co_3O_4 nanoparticles. Mechanism for the oxidation of formaldehyde has also been proposed.

Keywords: Nanoparticles, Cobalt oxide, Catalytic oxidation, Formaldehyde.

INTRODUCTION

Volatile organic compounds (VOCs) with boiling points ranging between room temperature and 260 °C are considered as major contributors to global air pollution¹. They are the main contributors to photochemical smog, secondary aerosol and many VOCs (such as benzene and toluene) are found to be harmful to living beings due to their toxic, malodorous, mutagenic and carcinogenic nature^{2,3}. Formaldehyde emitted widely from building

and decorative materials is becoming a major pollutant and it also has photochemical activity in atmosphere⁴. Formaldehyde is considered harmful to human health if it exceeds safe limitations. Serious health problems such as burning sensation in the eyes, irritation in throat, difficulty in breathing and even pernicious diseases such as nasopharyngeal or nasal cancer can be caused because of excessive exposure to a formaldehyde polluted environment⁵. Due to its effects on human health and environment, its emission reduction is of significant interest particularly at room temperature.



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Several methods have been used to control formaldehyde oxidation^{6,7} but catalytic oxidation is considered as one of the best alternative as it converts formaldehyde into non harmful carbon dioxide and water. Therefore, it is desirable to synthesize catalysts that can oxidize formaldehyde. It has been found that transition metal oxides (Fe_2O_3 , MnO_2 , NiO and Co_3O_4) and rare earth metals or composite oxides (CeO_2 , LaMnO_3 and LaFeO_3) have been used to catalytically oxidize formaldehyde. However, these catalysts operate at high temperatures i.e. 200-300 °C and their catalytic efficiency is inadequate for technological adaptation⁸⁻¹⁰. Au based catalysts have shown high activity towards catalytic oxidation of formaldehyde at moderate temperatures¹¹⁻¹⁴ but their high cost limit their use. Thus, the catalytic oxidation of formaldehyde using low cost catalysts at low/moderate temperatures is still a desirable goal. Nano-structures of inorganic materials can lead to novel magnetic, optical, electronic and catalytic properties as compared to their bulk counterparts^{15,17}. It has been assumed that these materials may possess numerous edges and corners for adsorption and activation of reaction or possess several kinds of active sites, which may exhibit different reactivities and typically higher activity.

Nano Co_3O_4 with morphologies such as tube, sheet, belt, rod, sphere and pore has shown excellent catalytic performance and is used in various fields¹⁸⁻²². Morphology and structure of Co_3O_4 has an important role in the catalytic performance of the catalyst²³⁻²⁵. Co_3O_4 is a p-type semiconductor and its spinel structure is based upon 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 sites²⁶. 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 oxidation²⁷. It has also been observed that cobalt oxide readily oxidizes carbon monoxide to CO_2 by a dynamic oxygen transfer from the air²⁸. In this paper, nano cobalt oxides synthesized via, chemical combustion, sol-gel autocombustion, thermal decomposition and hydrothermal method are comparatively studied for the catalytic oxidation of formaldehyde under mild/moderate temperature conditions (20-40 °C) in aqueous medium. A general mechanism for the oxidation of formaldehyde on the surface of nanocatalyst has also been proposed.

EXPERIMENTAL

Chemicals were purchased from Merck & Co, India. All the chemicals were of analytical grade and used without further purification. Double distilled water was used in all the experiments.

Chemical Combustion

Cobalt nitrate (0.1 mol; 29.103 g) and ethylene glycol/polyethylene glycol (EG/PEG) in stoichiometric proportions were dissolved and stirred followed by the addition of urea (0.1 mol, 6.0g). The temperature was raised up to 70 °C and stirring was continued until combustion occurred. The powder was crushed, grounded and then washed with water and methanol to remove any unwanted impurities. The product obtained was then dried and further annealed at 600 °C in ceramic crucible in a programmed furnace so as to obtain a pure crystalline phase. The crystalline powder obtained is designated as Co_3O_4 -CC.

Sol-gel Autocombustion

Stoichiometric amount of cobalt chloride (0.1 mol) and citric acid were dissolved in ethanol:water (1:5) solution and was continuously stirred. The pH of the solution was adjusted to 7 using ammonia. The solution was then heated and stirred continuously to transform it into xerogel. At a proper temperature, ignition started and the dried gel burnt it in a self-propagating combustion manner until whole the gel was burnt out completely to form a loose powder. The desired powder was calcined at 450 °C for three hours. The crystalline powder obtained is designated as Co_3O_4 -SG.

Thermal Decomposition Method

The material and method used to prepare nano cobalt oxide via thermal decomposition method has already been published²⁹. The crystalline powder obtained is designated as Co_3O_4 -TD.

Hydrothermal Method

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05 mol) was dissolved in 40 ml distilled water followed by stirring for about one hour. KOH was added as precipitating agent to increase the pH up to 13 followed by stirring for half an hour to prepare a homogenous sol. Whole material was then transferred to a teflon vessel of capacity 100 ml and was kept in a stainless steel

autoclave which in turn was put in a programmed furnace at 180 °C for 48 hours. The precipitates so obtained were washed with water and ethanol to remove the suspended impurities and were subjected to heating for 8 regular hours at 80 °C in a programmed oven. The crystalline powder obtained is designated as Co₃O₄-HT.

Characterization

The spectrum of Co₃O₄ nanoparticles were studied in the infrared region by Fourier transform infrared spectroscopy (FTIR) using a Nicolet Avtar 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.

Catalytic Activity

Oxidation of Formaldehyde: 10 ml HCHO (1%), 20 ml K₂Cr₂O₇ (0.1 M) solution and 100 ml dil. H₂SO₄ were taken in a closed lid 250 ml conical flask. To this flask, 100 mg of the synthesized metal oxide nano catalysts were added. The solutions were ultrasonicated for 5 minutes at three different temperatures i.e. 20, 30 and 40°C followed by filtration using sintered glass crucibles and the filtrate was titrated against 0.1 M mohr salt solution using diphenyl amine as an indicator. Appearance of green color gave the end point. The comparison was done with the blank observation i.e. without the catalyst.

The readings obtained for the titration were recorded and are shown in Table 1 and Fig. 4 respectively.

RESULTS AND DISCUSSION

The FTIR spectrum of the Co₃O₄ nanostructures synthesized via chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal method (Co₃O₄-HT) are shown in Figure 1.

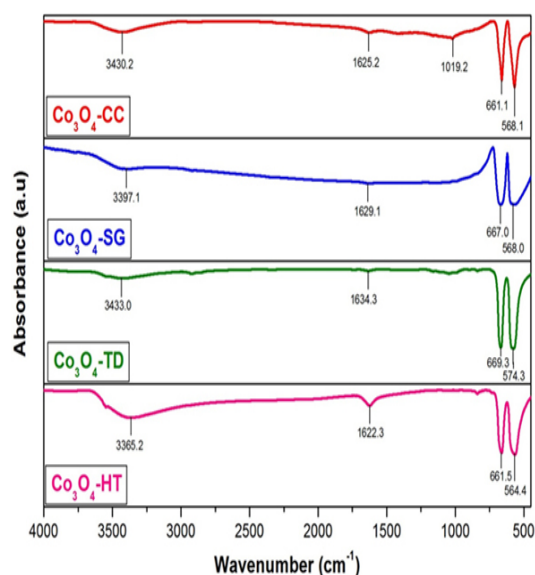


Fig. 1. FTIR spectra of Co₃O₄ nanostructures synthesized by chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal (Co₃O₄-HT) method

Table 1: Titration results for the oxidation of formaldehyde by Co₃O₄ nanocatalysts synthesized via chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal (Co₃O₄-HT) method

S. No.	Catalyst	20 °C (in ml)	30 °C (in ml)	40 °C (in ml)
1	Without Catalyst	15.0	13	9.8
2	Co ₃ O ₄ -CC	10.4	8.8	7.1
3	Co ₃ O ₄ -SG	7.3	6.6	5.4
4	Co ₃ O ₄ -TD	6.7	5.8	4.2
5	Co ₃ O ₄ -HT	7.7	6.1	4.0

The Figure clearly represents the metal-oxygen absorption bands, characteristic of cubic spinel structure of Co₃O₄. The absorption peaks at

568.1 cm⁻¹ and 661.1 cm⁻¹ (Co₃O₄-CC), 568.0 cm⁻¹ and 667.0 cm⁻¹ (Co₃O₄-SG), 574.3 cm⁻¹ and 669.3 cm⁻¹ (Co₃O₄-TD) and 564.4 cm⁻¹, 661.5 cm⁻¹

(Co₃O₄-HT) represents stretching vibrations of metal–oxygen (Co–O) bonds and confirm the formation of the Co₃O₄ spinel oxide. The minor peak at 1019.27 cm⁻¹ observed in Co₃O₄-CC sample may be attributed to C-H stretching vibrations from EG/PEG30. The broad bands near 3430.2 cm⁻¹ (Co₃O₄-CC), 3397.1 cm⁻¹ (Co₃O₄-SG), 3433.0 cm⁻¹ (Co₃O₄-TD) and 3365.2 cm⁻¹ (Co₃O₄-HT) correspond to stretching vibrations of hydrated water. The less intensive bands at 1625.2 cm⁻¹ (Co₃O₄-CC), 1629.1 cm⁻¹ (Co₃O₄-SG), 1634.3 cm⁻¹ (Co₃O₄-TD) and 1622.3 cm⁻¹ (Co₃O₄-HT) are attributed to bending vibration of water molecules³¹.

The XRD pattern of Co₃O₄ nanostructures synthesized via chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal method (Co₃O₄-HT) are shown in Fig. 2. XRD graphs indicate the formation of polycrystalline spinel phase. All diffraction peaks in this pattern could be indexed to a cubic spinel Co₃O₄ with lattice parameter $a = 8.083 \text{ \AA}$ (JCPDS No. 42-1467) and correspond to (111), (220), (311), (222), (400), (422), (511), and (440) reflections of cubic spinel Co₃O₄ with Fd3m [227] space group.

The average crystallite sizes for the most intense peak [(311) plane] were calculated from the XRD data using Scherrer formula and were found to be 21 nm, 39 nm, 16 ± 1 nm and 24 nm for Co₃O₄-CC, Co₃O₄-SG, Co₃O₄-TD and Co₃O₄-HT respectively. The X-ray density of prepared specimens was calculated using equation 1:

$$\left[d_x = \frac{ZM}{N a^3} \right] \quad (1)$$

Where Z is the number of molecules per unit cell, M the molecular weight, a the lattice parameter and N the Avogadro's number. Sharp peaks in the pattern suggest that the sample has good crystallinity indicating the formation of pure Co₃O₄ spinel phase.

The TEM images of Co₃O₄ nanostructures synthesized via chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal method (Co₃O₄-HT) are shown in Figure 3.

The observed micrograph shows homogeneity and uniformity. The high-resolution TEM images shows that the Co₃O₄ nanoparticles are having almost cubical shape with mean crystallite size 21 nm, 38 ± 1 nm, 16 ± 1 nm and 25 ± 1 nm for Co₃O₄-CC, Co₃O₄-SG, Co₃O₄-TD and Co₃O₄-HT respectively. There is consistency between the values observed by TEM and XRD.

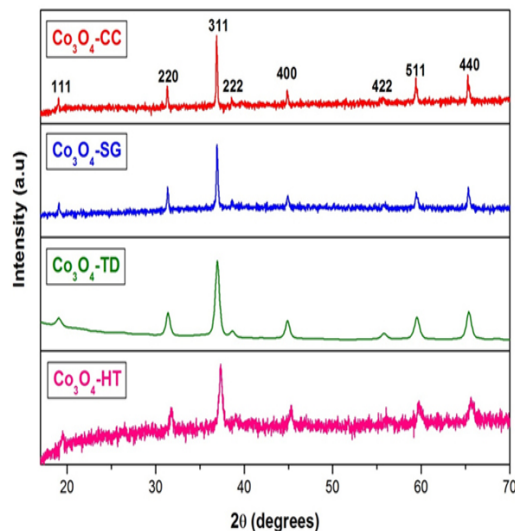


Fig. 2. XRD pattern of Co₃O₄ nanostructures synthesized by chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal (Co₃O₄-HT) method

A series of experiment were designed in order to study the comparative catalytic oxidation of formaldehyde by Co₃O₄ synthesized via chemical combustion (Co₃O₄-CC), sol-gel autocombustion (Co₃O₄-SG), thermal decomposition (Co₃O₄-TD) and hydrothermal method (Co₃O₄-HT). To study the reaction in aqueous medium and at moderate temperature conditions (20-40 °C) was the area of interest. The results of the experiment are shown in Table 1 and Figure 4.

Figure 4 represents the oxidation of 1% HCHO using all synthesized nanocatalysts at 20, 30 and 40 °C where Co₃O₄-CC, Co₃O₄-SG, Co₃O₄-TD and Co₃O₄-HT represents Co₃O₄ synthesized by chemical combustion, sol-gel autocombustion, thermal decomposition and hydrothermal method respectively. The graph represents that all the

synthesized catalysts have the capacity to oxidize formaldehyde. This may be attributed to the fact that nanomaterials increase the exposed surface area of the active component of the catalyst thereby enhancing the contact between reactants and catalyst. The oxidation by each catalyst is compared with the blank reading of 0.1 M $K_2Cr_2O_7$.

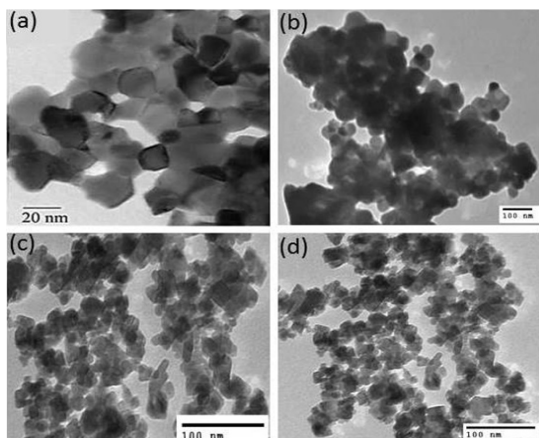


Fig. 3. TEM images of Co_3O_4 nanocatalysts synthesized via (a) chemical combustion (Co_3O_4 -CC), (b) sol-gel autocombustion (Co_3O_4 -SG), (c) thermal decomposition (Co_3O_4 -TD) and (d) hydrothermal (Co_3O_4 -HT) method

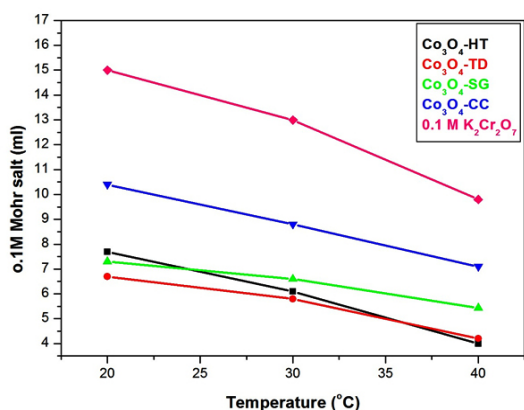


Fig. 4. Oxidation of formaldehyde by Co_3O_4 nanocatalysts synthesized via chemical combustion (Co_3O_4 -CC), sol-gel autocombustion (Co_3O_4 -SG), thermal decomposition (Co_3O_4 -TD) and hydrothermal (Co_3O_4 -HT) method

It is found that with the increase in temperature, rate of reaction increases i.e as the temperature increases, the catalytic activity of the catalyst increases. Thus, under similar conditions of concentration and temperature, the extent of oxidation increases in the order $20^\circ C < 30^\circ C < 40^\circ C$. However,

the catalytic performance is markedly influenced by the methods employed for the synthesis of nanocatalysts. It is observed that catalyst annealed at high temperatures (Co_3O_4 -CC) have low activity as compared to the catalysts annealed at comparatively lower temperatures (Co_3O_4 -SG, Co_3O_4 -TD and Co_3O_4 -HT). This may be due to the fact that at high temperatures, sintering of the catalyst occurs which makes the material less porous by deactivating the active sites. However, catalysts annealed at low temperatures retain their porous nature and hence activity. The study of the oxidation of formaldehyde establishes the concept of green chemistry as it is studied at mild temperature conditions and in aqueous medium. Being heterogeneous, the synthesized catalysts are easy to remove and reuse. The nanosize of the catalyst imparts high surface area for better contact. Thus the study reveals that the nano oxides of Cobalt are capable of oxidizing organic molecules as catalyst at mild temperature conditions. Fig. 4 clearly shows that out of all the catalysts synthesized, Co_3O_4 -TD and Co_3O_4 -HT have shown exceptionally high catalytic activity. Much literature is not available in this respect.

A general mechanism for the oxidation of formaldehyde on the surface of nano Co_3O_4 has also been proposed. Firstly, formaldehyde will adsorb on the surface of the nanocatalyst. The formaldehyde molecules orientate themselves on the nanosized cobalt oxide (Co_3O_4) catalyst having a surface with alternate Co^{2+} and Co^{3+} sites by making vander waals interactions between O of carbonyl (CO) and Co^{3+} whereas the C of methylene ($-CH_2$) remains free. This facilitates the attack of oxygen (O_2) on the C of methylene ($-CH_2$) and leading to its conversion in to CO_2 and H_2O as shown in Figure 5.

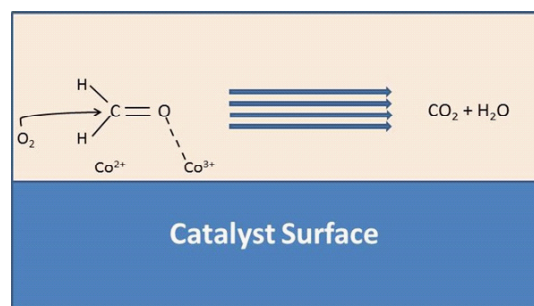


Fig. 5. Mechanism for the catalytic oxidation of formaldehyde on the surface of Co_3O_4 nano catalyst

Thus, the process is a continuous adsorption of formaldehyde and oxygen on the active surfaces of Co_3O_4 consisting of Co^{2+} and Co^{3+} sites and degradation of toxic formaldehyde to carbon dioxide and water molecules.

CONCLUSION

Low cost nano transition metal oxide of Co_3O_4 were synthesized via chemical combustion, sol-gel autocombustion, thermal decomposition and hydrothermal route; and were comparatively studied as catalyst for the oxidation of formaldehyde in aqueous medium and at moderate temperature

conditions (20-40 °C). These Co_3O_4 nanoparticles synthesized via thermal decomposition and hydrothermal route have shown good catalytic activity towards the oxidation of formaldehyde and hence they are found as useful catalysts for dynamic oxygen transfer reactions.

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