



CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY METAL EXCHANGED ZEOLITE- Y: A GREEN APPROACH

Nethravathi B P

Assistant Professor

PG Department of Chemistry

Vijaya College, R V Road, Bangalore – 560004, India.

Abstract : Here we report the catalytic behaviour of zeolite-Y exchanged with Cu(II), Co(II), Ni(II) and Zn(II) complexes represented as Z-Y-Cu, Z-Y-Co, Z-Y-Ni and Z-Y-Zn for the decomposition of 30% H₂O₂. The metal content was determined by ICP-AES method. These zeolite-Y based compounds are stable and recyclable under present reaction conditions. Amongst them, Z-Y-Cu showed higher catalytic activity (8 %) and Z-Y-Co showed least catalytic activity (3 %). The reaction condition was optimized by varying the different parameters, amount of catalyst, substrate and catalyst ratio, temperature, solvent and amount of H₂O₂. The order of decomposition of H₂O₂ is found to be as follow: Cu- Z-Y- > Ni-Z-Y > Zn- Z-Y > Co-Z-Y.

Keywords: Zeolite, H₂O₂, decomposition, catalyst, oxidation.

I. INTRODUCTION

Catalysis process is one of the greatest contributions of chemistry for the economic growth and environmental protection. Catalysis is considered in many organic synthesis via reduction, oxidation, substitution reactions etc. Oxidation reactions are an essential process, which can play an important role in giving the desired functionality to the intermediates of valuable compounds such as pharmaceuticals, agricultural chemicals and fine chemicals. The design and fabrication of inorganic porous materials, such as mesoporous and microporous zeolite based complexes as heterogeneous catalysts are used widely in industrial processes including organic synthesis [1]. The use of zeolite-Y entrapped transition metal complexes as catalysts over various oxidation reactions is reported by earlier authors [2-8].

As rightly said by R.A. Sheldon, "The chemical industry is under increasing pressure to minimize or preferably eliminate waste production in chemical manufacture" . The goal now is to synthesize catalysts that do not get deactivated and can be recovered with 100% efficiency. The ability of transition metals to exist in different oxidation states makes them excellent catalysts for many reactions. Molecular oxygen and air are attractive oxidants as they are inexpensive and yield no environmentally harmful side products. But since catalytic processes with these oxidants require elevated temperatures and pressures, oxidation is generally carried out using active oxygen reagents such as peroxides. Among the peroxides, hydrogen peroxide is one of the most readily available peroxide [9, 10].

Hydrogen peroxide is industrially and chemically important because of it is considered as a standard reaction for the determination of the catalytic activity of metal complexes [11]. The reaction can be catalyzed by several transition metal ions and transition metal complexes. [12].

In recent years the effects of chlorinated organic from bleach plant effluent on the environment have caused some concern. Consequently there has been great interest in adopting more environmentally friendly bleaching chemicals such as oxygen, ozone and hydrogen peroxide. Hydrogen peroxide in particular has been used by manufacturers of high yield mechanical pulps as the preferred bleaching chemical. For example, Australian Newsprint Mills Ltd operate a hydrogen peroxide refiner process bleaching radiata pine TMP at its Albury mill and peroxide tower bleaching at the Boyer mill processing eucalypt cold caustic soda pulp. Hydrogen peroxide bleaching requires alkaline conditions to form the active bleaching species OOH⁻. However, under these conditions hydrogen peroxide is very susceptible to transition metal ion catalysed decomposition. The metals manganese, iron and copper promote the greatest rate of peroxide decomposition.

Zeolites are aluminosilicates that have porous cage structures. They have a high internal surface area available for adsorption due to the channels and pores that uniformly penetrate the entire volume of the solid. There are many types of naturally occurring and synthetic zeolites, varying in aluminate to silicate ratio, water content, pore size and ion exchange capacity. They are used in a diverse range of applications such as molecular sieves catalysis, and ion exchange. Zeolites are also being used as water softeners in detergents to replace phosphates which can cause eutrophication in waterways. Zeolites containing transition-metal ions often show promising activity as heterogeneous catalysts in pollution abatement and selective oxidation reactions [13-15].

By considering the above factors, here with we reported the use of zeolite –Y exchanged with Cu(II), Co(II), Ni(II) and Zn(II) metal ions in the decomposition of 30% H₂O₂.

II. EXPERIMENTAL

Materials:

Zeolite-Y was purchased from Sud-Chemie, Mumbai, India. 30% H₂O₂ from Sd Fine Chemicals. Copper acetate, Cobalt acetate, Nickel acetate and Zinc acetate are of AR grade and purchased from Merck and they were used as purchased without any further purification.

Preparation of metal exchanged zeolite:

Metal ion exchange was carried out by the following procedure. Hydrogen form of zeolite- Y (H-Z-Y) was stirred in 100ml ethanol solution of metal salt at 80°C for 12 hours. Metal exchanged zeolite was washed with distilled water till the filtrate was free from metal ions. The metal exchanged zeolite was dried at 150°C for 3 hours. The metal content was determined by ICP-AES method. Colour and metal content of the metal exchanged zeolite-Y was observed and it is tabulated in Table 1.

Decomposition of hydrogen peroxide:

All the above catalysts were activated by heating to 120°C for two hours. 3.95ml of 30% H₂O₂ was added to 25mg of catalyst and it was stirred for 1 hour and 2 hour at room temperature respectively. The catalyst was then filtered and washed with distilled water. The filtrate containing partially decomposed H₂O₂ and the washing were collected in a 250 ml volumetric flask, and then made up to the mark with distilled water. Then 10 ml of this solution was titrated against a standard KMnO₄ (0.05N) solution to estimate the unreacted H₂O₂ [16]. The results were tabulated in Table 2 and represented in Figure 1.

Blank run

The decomposition reaction was studied under conditions identical with those of catalytic activity experiments without adding the catalysts. There was no measurable decomposition of hydrogen peroxide.

Recycle

The catalyst used for the reaction was washed with acetone and dried in the oven. Then decomposition reaction was studied after 1 hr for three times. No measurable changes were observed in the activity of the catalyst.

III. RESULTS AND DISCUSSION

Synthesis and characterization of catalysts

Synthesis of the metal exchanged compounds in the cages of H-Z-Y was carried out by using metal salts [17]. The percentage of metal content in the encapsulated complex was measured by using ICP instrument. The percentages of metal content along with the colour and formule of the complexes are given in Table 1. The data shows the appreciable amount of metal present in the zeolite.

Table 1: Percentage of metal and colour of the compounds

Sl. no.	Compound	Colour	Metal (wt%)
1	H-Z-Y	White	----
2	Cu-Z-Y	Light blue	3.91
3	Co-Z-Y	Light pink	1.63
4	Ni-Z-Y	Light green	0.20
5	Zn-Z-Y	Off white	2.00

Decomposition of H₂O₂

Encapsulated complexes were tested for their catalytic activity towards the decomposition of H₂O₂. The percentage of H₂O₂ that reacted and the turnover frequency (TOF) at two different time intervals (1 and 2 hr) were measured. The results showed that the decomposition of H₂O₂ is slow up to 1 h (0.60 to 2.39 %) in all the cases and increases after 2 h with different trends. The percentage decomposition of H₂O₂ and the turn over frequency (TOF) are tabulated in Table 2 and represented in Figure 1. The data indicate that the compounds requires a relatively longer time to attain maximum equilibrium. Hence, increasing time of reaction is a very effective method of carrying out the oxidation reaction, with H₂O₂ as the source of oxygen.

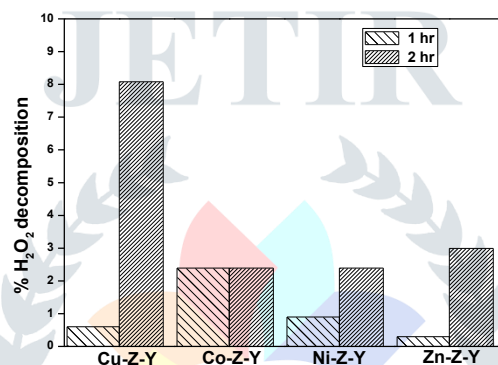
Table 2: Percentage decomposition of 30% H₂O₂ and TOF values

Sl.No.	Catalyst	H ₂ O ₂ Decomposition (%)		TOF* (h ⁻¹)	
		1 hr	2 hr	1 hr	2 hr
1	Cu-Z-Y	0.60	8.08	62.92	4247.1
2	Co-Z-Y	2.39	2.39	560.18	560.18
3	Ni-Z-Y	0.90	2.39	1703.72	2271.13
4	Zn-Z-Y	0.3	2.99	63.25	316.25

*TOF = Turn over frequency

Reaction condition: Amount of catalyst: 25 mg, Volume of 30% H₂O₂: 3.96 ml, Temperature: 30°C.

Figure 1: Percentage decomposition of H₂O₂ with time



Blank run

The decomposition reaction was studied under conditions identical with those of catalytic activity experiments carried out for the catalyst, without adding the catalysts. There was no measurable decomposition of hydrogen peroxide for up to 1 hr.

Effect of recycled catalysts

The catalysts once used were washed with acetone, and dried in oven at 120 °C for two hours. The recycled catalyst was characterized using XRD and IR. The recycled complexes are able to retain their catalytic activity and the XRD, IR and electronic spectra of the recycled complexes shows that the structure of the complex remains same as that of the fresh catalyst.

IV CONCLUSIONS

Hydrogen peroxide has diverse uses throughout a range of applications. The use of hydrogen peroxide in pulp, paper bleaching and in extraction of metals from their ores has increased significantly over the last decade due to environmental compatibility.

We have studied the decomposition of hydrogen peroxide using different reaction conditions. The decomposition reaction was studied by varying the amount of catalyst. When more amount of catalyst was used, there was a subsequent increase in the rate of decomposition of peroxide. By varying the volume of hydrogen peroxide also an increase in the rate of decomposition was observed. The addition of methanol shows a different observation. The addition of methanol was found to slow down the decomposition reaction. This was observed with all the three type of zeolite samples. Since methanol is of lower polarity than water, the decrease in reaction rate observed here may be because of the decrease in polarity. But pyridine helps in the increase in rate of decomposition of hydrogen peroxide.

Finally, the reaction was also carried out by using recycled catalysts. All the compounds retain their activity, which is confirmed by their XRD and IR studies. The retainment of catalytic activity indicates the stability of the zeolite encapsulated compounds. It can be concluded that under optimized conditions, 30% hydrogen peroxide can be used as an environmentally friendly oxidant for many reactions.

Acknowledgement: The author express their sincere gratitude to the UGC-MRP XII PLAN [Ref: 2030-MRP/15-16/KABA057/UGC-SWRO] for their financial support.

REFERENCES

- [1] Chetan K. Modi , Parthiv M. Trivedi, 2017, Zeolite-Y entrapped Ru(III) and Fe(III) complexes as heterogeneous catalysts for catalytic oxidation of cyclohexane reaction, *Arabian Journal of Chemistry*, 10 (S1452) : S1452-S1459.
- [2] S. L. Sharifi, M. H. Hosseini, A. Mirzaei and A. Salmani Oskuloo, 2015, Catalytic decomposition of hydrogen peroxide in the presence of synthesized iron-manganese oxide nanocomposites via different methods, *Int. J. Nanosci. Nanotechnol.*, 1 (4) : 233-240.
- [3] Mannar R Maurya, Priyanka Saini, Chanchal Haldar, Anil K Chandraka and Shri Chand, 2012, Oxidation of styrene and cyclohexene with TBHP catalyzed by copper (II) complex encapsulated in zeolite-Y, *Journal of Coordination Chemistry*, 65(16): 2903-2918.
- [4] Srinivasa Rao Amanchi, Anjali Patel and Amar K Das, 2014, Polyoxometalate coordinated transition metal complexes as catalysts: Oxidation of styrene to benzaldehyde/benzoic acid, *Journal of Chemical Sciences*, 126 (6):1641-1645.
- [5] Jie He, Xiaofang Yang, Bin Men, Dongsheng Wang, 2016, Interfacial mechanisms of heterogeneous Fenton reactions catalyzed by iron-based materials: A Review, *Journal Of Environmental Sciences*, 39: 97 – 109.
- [6] Fatemeh Rajabi, María Pinilla-De Dios And Rafael Luque, 2017, Highly ordered nanomaterial functionalized copper schiff base framework: synthesis, characterization, and hydrogen peroxide decomposition performance, *Catalysts*, 7(7): 216.
- [7] Massomeh Ghorbanloo, Somayeh Ghamari, Nahid Shahbakhsha and Seik Weng Ng, 2014, Diaquabis (L-phenylalaninato)nickel(II) encapsulated in zeolite: An efficient heterogeneous catalyst system for the oxidation of cyclohexene, toluene and ethyl benzene, *J. Braz. Chem. Soc.*, 25(11): 2073 – 2079.
- [8] B. P. Nethravathi and K. N. Mahendra, 2015, Efficient catalytic oxidation of primary and secondary alcohols using zeolite encapsulated complexes, *International Journal of Chemical Science and Technology*, 5(2): 394 -399.
- [9] R. A. Sheldon, Catalytic oxidation and fine chemicals, 1987, *Catalysis Today*, 1(3): 351-355.
- [10] Von S.P. Schirmann, S. Y. Delavarenne, 1980, Hydrogen Peroxide in Organic Chemistry, *Information Chimie*, Paris, 28(6):408.
- [11] E. Tsuchida and H. Nishide, 1977, Polymer-metal complexes and their catalytic activity advances in polymer science, 24 (1).
- [12] R. Sreekala and K. K. Mohammed Yusuff, 1995, Catalytic activity of five coordinate cobalt (II) complexes for the decomposition of hydrogen peroxide, *Indian Journal of Chemistry*, 34a : 994 – 996.
- [12] Priv.-Doz. H. Sigel, Catalase and peroxidase activity of Cu^{2+} complexes, 1969, *Angew. Chem. Int. Ed. Engl.*, 8(3): 167-177.
- [13] Ivo F. J. Vankelecom, Sacha Van den broeck, Edouard Merckx, Hilde Geerts, Piet Grobet, Jan B. Uytterhoeven, 1996, Silylation to improve incorporation of zeolites in polyimide films, *J. Phys. Chem.*, 100 (9): 3753 - 3758.
- [14] B. M. Choudary, M. L. Kantam, P. L. Santhi, 2000, New and ecofriendly options for the production of speciality and fine chemicals, *Catalysis Today*, 57(1-2) :17-32.
- [15] R. Raja and P. Ratnasamy, 1997, Direct conversion of methane to methanol, *Applied Catalysis. A: General*, 158 (L7- L15).
- [16] J. Bassett, R. C. Denney, G. H. Jeffery, J. Mendham, *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th edn. (Longman Scientific and Technical, London, 1978.
- [17] B. P. Nethravathi, P. Manjunathan and K. N. Mahendra, 2016, Copper complex of isatin schiff base encapsulated in zeolite as active heterogeneous catalyst: an efficient protocol for the acetylation reaction, *Journal of porous materials*, 23(5):1305-1310.