



Decomposition of Hydrogen Peroxide by Green Chemistry Approach

KEYWORDS

Green Chemistry, Spinel nanoparticles, Ferrites, Heterogeneous catalysts, Hydrogen peroxide and Decomposition.

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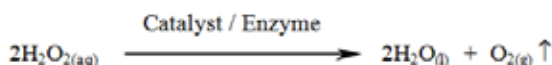
ABSTRACT *The role of some mixed-metal oxide spinel nanoparticles of nickel substituted copper ferrites as heterogeneous catalysts in the decomposition of hydrogen peroxide has been investigated by measuring the evolution of oxygen at different time intervals in the temperature range of 35-60°C. Enhanced catalytic activity is observed with $\text{Cu}_{0.2}\text{Ni}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles, while the lowest but considerable catalytic activity was observed with $\text{Cu}_{0.8}\text{Ni}_{0.2}\text{Fe}_2\text{O}_4$. The specific reaction rate, in general, is found to be increasing with increase in the temperature and the decrease in the sizes of the catalyst nanoparticles. The possible reaction mechanism for the decomposition of H_2O_2 over catalysts surface have been suggested.*

Introduction

Hydrogen peroxide is a widely used chemical now a days which has a promising future in improving the Green Chemistry aspects of the chemical processing industry. Hydrogen peroxide, being a versatile chemical, it is used in the processes of bleaching, chemical syntheses, environmental control, effluent treatment, sterilization, cleanser etc. The most important active constituent of H_2O_2 is the nascent oxygen that provides the utilization of H_2O_2 in the uses mentioned above. This active oxygen can be obtained by controlled decomposition of H_2O_2 with water as the bi-product. The activity of H_2O_2 can be controlled or enhanced using activators, co-reagents or catalysts.

The catalytic release of nascent oxygen from H_2O_2 , has also led to a number of proposed uses of H_2O_2 in blowing agents, preparation of foam rubber in polymer industry, military missiles and space craft propellant, as an oxidizing agent and an energy source, etc. Converse effects of production of H_2O_2 are that, in the development of fuel cells, H_2O_2 is formed as an undesirable side product during the reduction of oxygen. Therefore, it becomes a need of hour to synthesize an efficient catalyst for decomposition of H_2O_2 to obtain nascent oxygen i.e. [O] and water i.e. H_2O as bi-product.

In the surrounding environment, the superoxide radicals O_2^- and H_2O_2 generated are extremely harmful to the physiological processes if they accumulate in them. These superoxides and H_2O_2 are decomposed by the enzymes superoxide dismutase and catalase. In the living systems, catalase is the heme protein enzyme which controls H_2O_2 concentration by catalyzing its dismutation to water and molecular oxygen^{1,2}. The decomposition of hydrogen peroxide over a catalyst or an enzyme is represented by the following reaction.



Therefore, it stimulated the interest in the metal ion catalyzed disproportionation reaction of H_2O_2 . Several transition metal ions and metal complexes have been used to catalyse this reaction^{3,4}. Metal salts and complexes have also been employed^{5,6}. However, in most of the studies, it

has been observed that single salts, binary or ternary metal complexes species have been employed. In the present studies mixed-metal oxide spinel nanoparticles have been employed in the kinetic study of the catalytic decomposition of hydrogen peroxide. Our literature survey reveals that the compositions prepared in the present study have never been used for heterogeneous catalytic decomposition of hydrogen peroxide. This paper reports a sequential study of various compositions of nickel substituted copper ferrites nanoparticles for H_2O_2 decomposition.

Experimental Materials

All the chemicals used were of analytical reagent grade. Salts of copper nitrate, nickel nitrate, ferric nitrate, sodium hydroxide and hydrogen peroxide were purchased from Thomas Baker. Double distilled water was used throughout for the preparation of solutions and washings of the catalyst nanoparticles. All glasswares used were made up of Pyrex, Borosil or Corning glass were calibrated by the method described by Vogel⁷.

Preparation of the catalyst

Nanocrystalline powders of $\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were prepared^{8,9} by co-precipitation method. The metal nitrates were dissolved in double distilled water and the pH of the solution was increased gradually and adjusted to about 9.0-9.5 by 10%NaOH solution with the help of pH meter. The products so obtained were digested on a boiling water bath for three hours and oxidized by 75cm³ of 30% hydrogen peroxide solution and aged overnight over a heavy magnet. The supernatant solution was discarded and the precipitate was filtered through Whatman filter paper No.42 and washed several times with double distilled water. The precipitates were dried in an air drying oven at 110°C.

The prepared precursor powders were ground finely in agate mortar and pestle because of which uniform distribution of the elements resulting in a well-defined morphology and quite homogeneous particle size are obtained⁹. Since the synthesis of such spinels require a thermal treatment to lower the surface or bulk defects¹⁰ the samples were uniformly sintered in an Eurocon automated programmable furnace at the reaction temperatures determined

from the thermogravimetric analysis curves at the rate of 4°C per minute for three hours to get the final product. The catalyst compounds were characterised^{8,9,11} by various method like TG-DTA, X-ray diffraction, Energy Dispersive X-ray, Field Emission Gun-Scanning Electron Microscopy, FT-IR Spectroscopy.

Kinetic measurements

A known quantity of the catalyst was stirred continuously with 10cm³ of hydrogen peroxide solution (5 Vol. & 3 Vol.) in a closed reaction vessel kept in thermostated water bath and the volume of the oxygen evolved was measured¹² by using the gasometric technique. Experiments were carried out at three different temperatures in the range of 35-60°C. The effect of varying amount of catalyst used was studied at a constant concentration of hydrogen peroxide at 55°C using Cu_{0.0}Ni_{1.0}Fe₂O₄ as a model catalyst. The specific reaction rates 'k' were evaluated from the plot of log(a-x) against time 't' where 'a' is initial volume of H₂O₂ and 'x' is the volume of oxygen evolved after completion of H₂O₂ decomposition and at any time 't'. The activation energy 'E' was calculated from the Arrhenius plots.

Table 1 : Specific reaction rate and Activation energy for the decomposition of H₂O₂

Catalyst	Temp. (°C)	Specific Reaction Rate		Energy of Activation	
		k × 10 ⁻² (min ⁻¹)		E (E × 10 ⁻² J/mol/min/mol)	
		3 Volume	5 Volume	3 Volume	5 Volume
Cu _{1.0} Ni _{0.0} Fe ₂ O ₄	35	2.70	2.03	62.2	16.85
	50	4.08	3.89	80.8	32.30
	60	7.63	5.34	98.0	44.42
Cu _{0.8} Ni _{0.2} Fe ₂ O ₄	35	1.90	1.01	82.3	84.0
	50	2.35	2.86	195.3	237.4
	60	5.83	4.31	484.4	358.0
Cu _{0.6} Ni _{0.4} Fe ₂ O ₄	35	2.55	1.82	195.3	151.2
	50	3.73	3.68	310.1	306.3
	60	7.25	5.14	631.0	426.9
Cu _{0.4} Ni _{0.6} Fe ₂ O ₄	35	3.04	3.23	252.7	185.7
	50	4.42	4.10	367.6	340.8
	60	7.97	5.55	662.4	406.1
Cu _{0.2} Ni _{0.8} Fe ₂ O ₄	35	3.73	2.65	310.1	220.2
	50	5.14	4.51	426.9	375.2
	60	8.71	5.99	732.7	497.8
Cu _{0.0} Ni _{1.0} Fe ₂ O ₄	35	3.39	2.44	284.0	202.9
	50	4.77	4.31	396.5	358.0
	60	8.34	5.78	693.0	480.5

Amount of catalyst: 0.025 g; Volume of H₂O₂ = 10 cm³

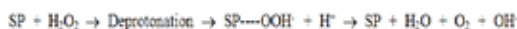
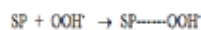
Results and discussion

All the nanoparticles prepared in the present study are non-hygroscopic, insoluble in water, hydrogen peroxide and many organic solvents like acetone, methanol, isopropyl alcohol; but forms fine suspension of the particles

in these liquids. Therefore, these nanoparticles could be used as heterogeneous catalysts for the decomposition of hydrogen peroxide.

The plots of log(a-x) versus time(t), where a = initial concentration of H₂O₂ and x = decrease in the concentration at time 't' are linear which clearly indicates that the decomposition of H₂O₂ in the presence of the catalysts under study follow first order kinetics. In the first order reactions the rate is directly proportional to the concentration of the reactant at that instant of time. Secondly, only one molecule is necessary for the reaction to proceed. In the present study, the linear regression in the value of log(a-x) with respect to the increase in time indicates that the decomposition of H₂O₂ in the presence of spinel nanoparticle catalysts follows first order kinetics rate law. At the constant amount of the catalyst and the value of k increase with the increase in the temperature and decrease in particle size.

According to the results obtained in the present study it is observed that the particle sizes of the nanoparticles is the important factor in the heterogeneous catalytic decomposition of hydrogen peroxide. Among all the various ferrite compositions of the compounds prepared Cu_{0.2}Ni_{0.8}Fe₂O₄ was found to cause maximum disproportion of hydrogen peroxide in present study. The mechanism proposed for the decomposition of H₂O₂ can be shown as below.



The separation of the catalyst was done simply by magnetic separation where sophisticated filtration and centrifugation techniques were not required; therefore, it becomes the user friendly catalyst for the decomposition reaction of the hydrogen peroxide. Therefore, the present nickel substituted spinel ferrites nanoparticles, provide a green chemistry route to decompose H₂O₂.

Conclusion

The nickel substituted mixed metal-oxide spinel ferrite nanoparticles in the present study provide simple, benign and eco-friendly route for the decomposition of the hydrogen peroxide in the optimized reaction conditions. Cu_{0.2}Ni_{0.8}Fe₂O₄ nanoparticles has an enhanced effect on the catalytic decomposition of H₂O₂ particularly at higher temperature. The nanoparticles acts as catalysts which has been proved by the fact that they remain intact after the reaction as they show identical XRD patterns after the reactions and can be used for several cycles.

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