

Use of mixed metal oxide as a catalyst in the decomposition of hydrogen peroxide

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ABSTRACT

The decomposition of hydrogen peroxide in presence of some metal oxides as a heterogeneous & heterogenized catalyst has been investigated by measuring the evolution of oxygen at different time intervals in the temperature range 30-60⁰C. The catalytic activity is increased, an increase in the amount of catalyst and pH. The variation of H₂O₂ at constant pH reveals that the values of k are nearly constant irrespective of H₂O₂. Various parameters have been calculated. The probable reaction mechanism have been suggested in which an intermediate surface complex is thought to be responsible for the enhancement of the decomposition of hydrogen peroxide. LaCrO₃ catalyst was characterized by XRD, TG/DTA, SEM, AFM.

Keywords: Catalyst, XRD, EDX, TG/DTA, SEM, AFM, H₂O₂ decomposition.

INTRODUCTION

Hydrogen peroxide and its solutions find use as antiseptic in medicine [1-2]. Hydrogen peroxide is environmentally benign oxidant, is expected to play an increasingly important role in the chemical industry, Other applications of H₂O₂ such as bleach in the textile & paper/pulp industry, in treatment of waste water ([3]. The sterilization of packages food, beverages, drugs etc, requires fast, reliable and inexpensive aseptic methods. The sterilization by hydrogen peroxide H₂O₂ vapour offers one distinct advantage over other chemical methods [4] like gaseous formaldehyde, glutaraldehyde and ethylene oxide, namely its harmless decomposition products of H₂O₂ and oxygen. On the other hand, in industrial applications H₂O₂ is mixed with ambient air and heated up to more than 200⁰C; yielding a gaseous H₂O₂ concentration varying between 1 to 10 vol. %. The controlled decomposition of H₂O₂ on oxides and mixed oxides has been studied

extensively by many researchers. [5-9]. Recently the literature survey reveals that mixed oxide catalyst is more active in the reaction of H₂O₂ decomposition. These catalysts have attracted much attention of the chemist due to their application as low cost fuel cells, their stability and highly activity. [10-11]. The catalytic activity of this catalyst depends on the preparative methods viz. Combustion method, Oxalate route, Co-Precipitation method, solid solution precursor wet Chemical method, Sol gel method, Microwave synthesis, Oxidation method, Spray dry etc. [12-19]. Out of these methods solution combustion method is important because catalyst is prepared within a minute, simple technique. LaCrO₃ is a spinel type structure and due to their chemical stability and highly oxidative nature, it is industrially important. In this paper the kinetics of H₂O₂ decomposition on LaMnO₃ mixed oxide at room temperature has been investigated. In present study reports the heterogeneous and heterogenized homogeneous catalysis using nanocrystalline LaCrO₃ prepared from combustion method.

MATERIALS AND METHODS

Experimental-

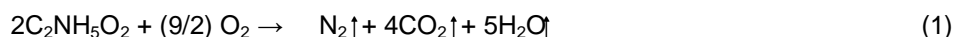
Polycrystalline LaCrO₃ was synthesized by the combustion synthesis method using glycine as fuel (organic fuel). All chemical reagents were analytical grade and used without further purification. Stoichiometric quantity of solid mixture of one mole reagents i.e. Lanthanum nitrate La (NO₃)₃.6H₂O, Cr (NO₃)₃.9H₂O and two mole of glycine were mixed together in a flat Pyrex disc. The solid were stirred for five minutes (clear solution was obtained). Solution formed was evaporated on hot plate in temperature range 80-90⁰ C gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range of 160-180⁰ C. The nanocrystalline LaCrO₃ powder was formed within five minutes.

Kinetic Measurement-

A weight quantity of the catalyst was shaken with 10 cm³ H₂O₂ (5 Vol) in a closed vessel kept in a thermostatic water bath and the volume of oxygen evolved was measured by using gasometric technique [20]. Experiment were carried out at three different temperatures (*T*) in the range 30-60⁰C. The effect of changing in the amount of catalyst was studied at constant concentration of H₂O₂ at 55⁰C. The specific reaction rates (*k*) were calculated from the plot of log (a-x) versus time *t*, where *a* and *x* are the volumes of oxygen evolved after completion of decomposition and at any time *t*, respectively. The ln *k* values were plotted against 1/*T* (Arrhenius plot). The slope of Straight line obtained is -*E*/*R*. Thus, the activation energy (*E*) was calculated from slope. The activation parameters, Δ*H*[#], Δ*S*[#], were calculated by Eyring equation (21).

RESULT AND DISCUSSION

When reactants were heated at 180⁰C the reaction proceeds by the mechanism indicated by equation number 1 and 2 give the final product LaCrO₃.



The TG curve recorded for thermal decomposition of LaCrO_3 is shown in Fig.1. The curve indicates that the slight weight loss in LaCrO_3 powder due to little loss of moisture, carbon dioxide and nitrogen gas. The DTA curve of LaCrO_3 recorded in static air, curve shows that LaCrO_3 did not decompose, but weight loss was due to dehydrogenation decarboxylation and denitration and yield final product at 775°C . This weight loss and weight gained was very negligible. This weight change was in the range of 0.02 % only. These indicate that the synthesized powder was almost stable from the beginning.

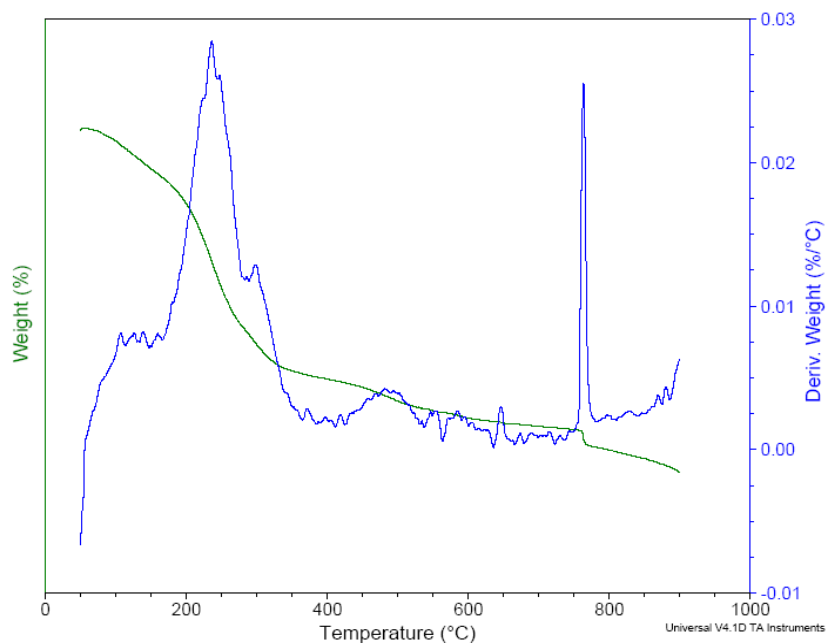


Fig. 1 TG - TDA curve of LaCrO_3 as synthesized powder.

X-ray diffraction XRD measurements were performed on Philips Analytic X-ray B.V. (PW-3710 Based Model) Advanced X-ray diffraction using $\text{Cu K}\alpha$ 1.54056, radiation. The XRD pattern shown in the fig.(2).The XRD pattern shows that the product is pure spinel oxide LaCrO_3 with an orthorhombic structure. The diffraction data are good agreement with JCPD card of LaFeO_3 (JCPDS No.24-1016) The average crystalline size of LaCrO_3 spinel powder was estimated with the help of Scherrer's equation $t = 0.9\lambda / \beta \cos\theta$ [22-23] where t is the thickness of the crystals (in angstroms), λ is the X-ray wavelength and θ is the Bragg angle β is the integral breadth that depends on the width of the most predominant peak at 100% intensity = 1.54056 \AA . The average particle size of nanocrystalline LaCrO_3 was ~16 nm. LaCrO_3 nanocrystals are more attractive in the field of catalytic application. Fig.3 shows Energy Dispersive X-ray (EDX) technique that allows the determination of chemical composition of LaCrO_3 Catalyst.

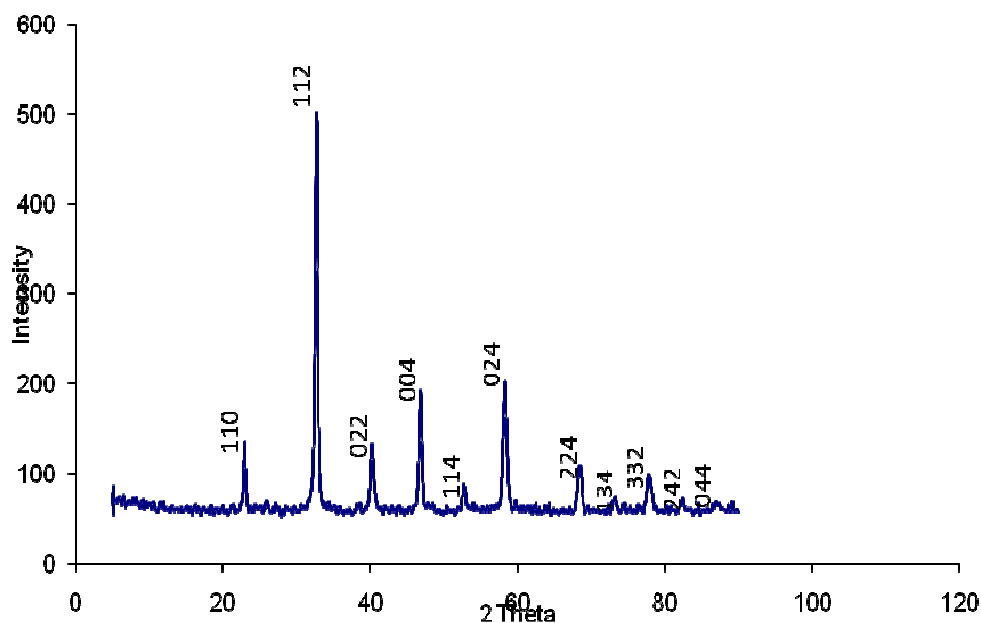


Fig. 2 X-ray diffraction patterns of LaCrO_3 as synthesized powder.

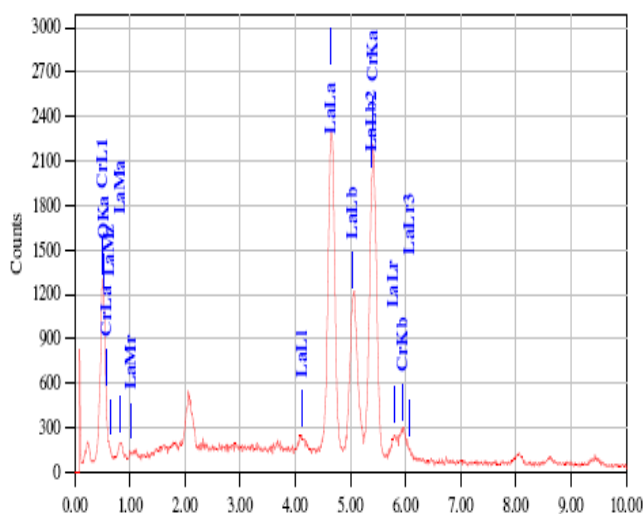


Fig.-3 Energy Dispersive X-ray (EDX) of LaCrO_3 Catalyst

The surface morphology was studied by using scanning electron microscopy (SEM) Model No. JEOL, JSM.6360. The SEM images of LaCrO_3 are shown in fig. (4). The SEM images reveal the product is a low density, loose and porous material that is favorable to a catalyst application. The BET surface areas were measured on a Benchman coulter SA 3100 plus instrument using nitrogen adsorption at 200°C . the surface area of the synthesized powder was $3.5\text{ m}^2/\text{g}$.

Scanning Electron Microscope (SEM) image of the LaCrO_3 powder prepared by combustion method at 180°C is presented in Fig.4. (a) and SEM images at 510°C and 1000°C are shown in

fig.4(b) and fig. 4(c) respectively. It shows that average particle size of LaCrO_3 formed is $\sim 16\text{nm}$. The particle size was also calculated from atomic force microscopy (AFM) recorded at 450°C and 1000°C temperatures. AFM images are shown in fig.5. Particle size increases as the temperature increases.

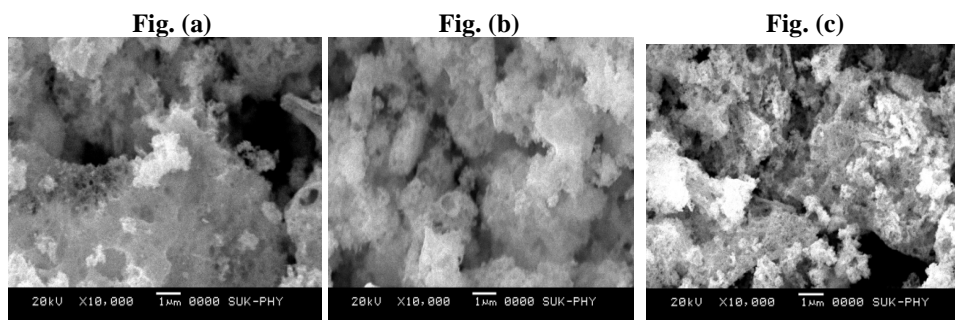


Fig.4 SEM images of LaCrO_3 Fig.4 (a) as synthesized powder, Fig.4 (b) at 510°C , Fig.2 (c) at 1000°C

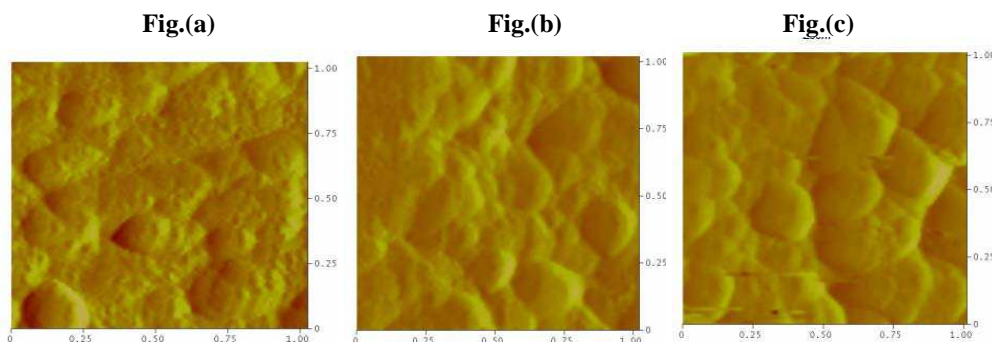


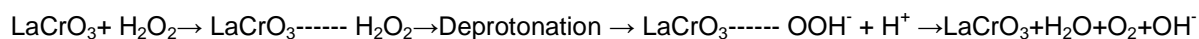
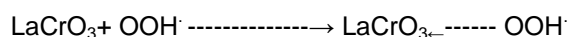
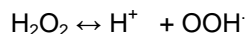
Fig.- 5: AFM images of LaCrO_3 Fig.(a) as synthesized powder , Fig.(b) heated at 450°C and Fig.(c) heated at 1000°C .

LaCrO_3 oxide as heterogeneous catalysts in decomposition of H_2O_2

In presence of LaCrO_3 in heterogeneous phase, the catalytic disproportionation is increased considerably. The results of the present study on kinetic of catalytic decomposition of H_2O_2 in presence of LaCrO_3 as a catalyst are also given in the table. The plot of \log of $(a-x)$ versus t for LaCrO_3 catalyst is linear indicating that the decomposition of H_2O_2 in present of catalyst follows first order kinetics. Keeping the quantity of catalyst and H_2O_2 constant and varying temperature in the range $30-60^\circ\text{C}$, the value of k increases with increase in temperature Table-1. It has been also observed that the rate of decomposition decreases with increase in H_2O_2 . It may be decrease in pH of the solution. It is noted that an increase in H_2O_2 from 3 to 5 vol changes the pH of the solution from 6.6 to 5.4. This is also the evident from the fact that an increase in the pH of the solution from 5.4 to 9.2 increases the k value by about 7 fold .the variation of H_2O_2 at constant pH 8.06 (controlled by phosphate buffer) Shows that the value of k are nearly constant irrespective of H_2O_2 . Keeping H_2O_2 and temperature constant, when the quantity of catalyst is varied in the range 0.01-0.05g, the value of k increases with increase in the quantity of catalyst Table-2. and Fig.7. The plot of \log of k versus \log of (amount of LaCrO_3) is linear with a slope of 1.1, indicating that the order of disproportionation reaction is almost unity. Fig-(6) The values of

ΔS^\ddagger are found to be negative in all the cases indicating that molecule in transition state are more ordered than the reactant in ground state[24] Mechanism proposed for decomposition of H_2O_2 catalyzed by $LaCrO_3$ is shown in scheme 1.

H_2O_2 auto ionizes as



The reaction is :

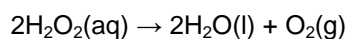


Table 1 Decomposition of hydrogen peroxide^a catalyzed by $LaCrO_3$ as heterogeneous catalyst^b

Metal oxide	T (°C)	K in (min ⁻¹)	E kJ/mol	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J.K ⁻¹ mol ⁻¹)
$LaCrO_3$	35	6.4×10^{-3}	66.466	62.977	-93.57
	45	1.3×10^{-2}			
	55	7.89×10^{-2}			

^aVolume of hydrogen peroxide: 10.0 cm³ (- 5 vol) , ^bwt.%,0.036

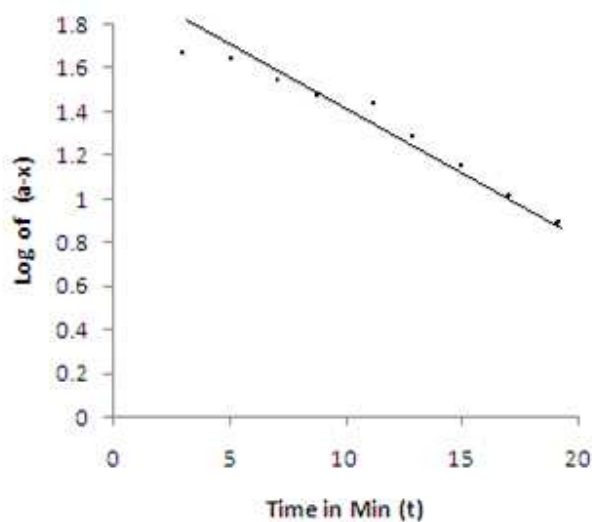


Fig. 6 plot of \log of (a-x) versus time in min (t)

Table 2- Influence of the amount of heterogeneous catalyst on the decomposition^a of hydrogen peroxide by $LaCrO_3$

Catalyst	Wt.%	Specific reaction rate k (min ⁻¹)	Order of reaction with respect to catalyst
$LaCrO_3$	0.09	0.0095	1.1
	0.18	0.0117	
	0.27	0.0146	
	0.36	0.0182	
	0.45	0.0213	

^aTemperature: 55°C Volume of hydrogen peroxide: 10.0 cm³ (- 5 vol)

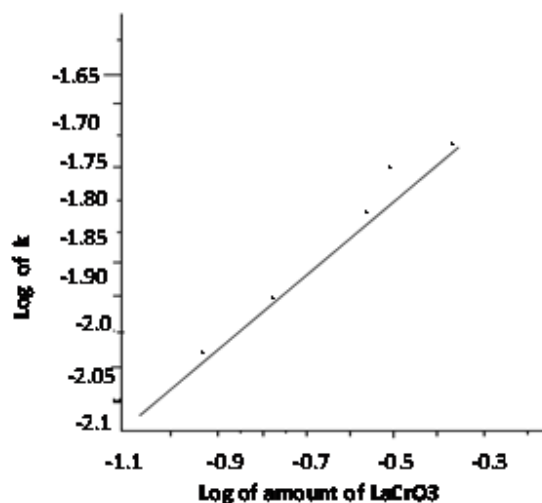


Fig.7 Log k versus log of amount of LaCrO₃ catalyst

4.1 Reuse of catalyst

LaCrO₃ was separated from the reaction mixture by using microcentrifuge machine at 16000 rpm (Model, Rm-12C DX). The separated LaCrO₃ was dried at 110⁰C for one hour. It was used for many times for the same purpose and it was found that similar activity of LaCrO₃ for decomposition of hydrogen peroxide. This is the green approach in chemistry.

CONCLUSION

The LaCrO₃ is prepared successfully by the combustion method. This method is simple, rapid. The reaction obeys the first order rate laws. The reaction generally proceeds through the formation of activated complex. LaCrO₃ has an enhanced effect on the catalytic decomposition of H₂O₂ especially at higher temperature. The role of LaCrO₃ as catalysts in the decomposition of H₂O₂ has been confirmed by the fact that they remain unchanged in amount and chemical composition at the end of reaction.

Acknowledgments

Sanjay M. Khetre is very much thankful to UGC for sanctioning FIP under XIth Plan. He is also thankful to Dr.Patanrao Kadam Mahavidyalaya Sangli for providing research facility.

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