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Short Communication

Comparative Study of Catalytic Activity of Ferrites and Commercial Fe-Mo Catalyst

Sachin J. Deshmukh*, P.Y.Patil and A. Venkatachalam

*Department of Chemistry, PAHER University, Udaipur, Rajasthan-313024, **INDIA**

Email: sachinjd@outlook.com

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ABSTRACT

The comparison of catalytic activity of ferrites with that of commercial Fe-Mo catalyst (New and Re-palletized) has been studied at different temperatures and timings using hydrogen peroxide which undergoes decomposition. It has been observed that at low temperatures there is a difference in activities of catalysts but as we increase the temperature the difference in the activities between new and re-palletized catalyst decreases to a large extent. The order of Catalytic activity at 343 K is New Catalyst > Re-palletized Catalyst > Ferrite Catalyst.

Keywords: Spinel ferrites, Ferro-Molybdenum Catalyst, Catalytic studies, H_2O_2 Decomposition.

INTRODUCTION

Ferrites and mixed metal oxides have been found to act as oxidation catalyst since very long time. Several workers [1-5] have reported the properties of spinels using various techniques. Transition metal oxides show good catalytic activity due to ability of showing variable oxidation states. Hydrogen peroxide is used as an oxidizing agent because it self decomposes to give oxygen. In this experiment we have studied the catalytic activity by using decomposition of hydrogen peroxide as a simple model reaction at various temperatures and at different timings. The need of an efficient catalyst for decomposition of H_2O_2 is of great demand, especially with the development of fuel cells in which hydrogen peroxide is formed as an undesirable side product during reduction of oxygen. With this view in mind, the study has been carried out from 313K to 343K at times intervals from 0 to 5h.

MATERIALS AND METHODS

The ferrite used in this study is $CuFe_{2-2x}Cr_xAl_xO_4$. This ferrite has been prepared by using co-precipitation technique [6]. In this technique an aqueous solution containing metal ions in molar proportion is prepared by dissolving respective salts in de-ionized water. The respective hydroxides are precipitated by adding sodium hydroxide solution maintaining the pH between 9 & 9.5. The precipitate is heated on water bath (90°C) for 3-4 h and oxidized by adding 75 mL 30% (100 vol.) H_2O_2 with constant stirring. The precipitate thus obtained is filtered, washed & dried at 80°C in vacuum cryostat. The precipitate is ground and heated at 900°C for 2 h to get single phase spinel. The compound formation is checked by XRD technique. XRD patterns for all the compositions have been taken using Cu Kα radiation with nickel filter. The XRD patterns for all the compositions are given in figure 1. The New Catalyst and re-palletized catalyst have been obtained from formaldehyde plant of a chemical industry.

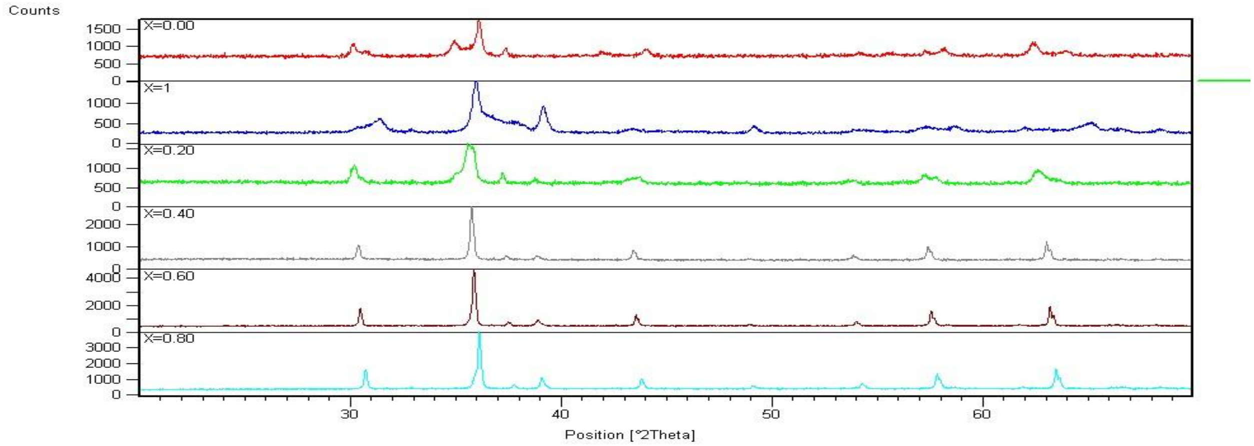

Fig.1: XRD Pattern for the System $CuFe_{2-2x}Cr_xAl_xO_4$

Experimental : All the compositions have been studied for their catalytic power using a model reaction of decomposition of H_2O_2 at temperatures between 303- 343K and at various timings viz. 1- 5 h. 100 mg of catalyst is added to a diluted 5 mL H_2O_2 solution (20 % /100 vol. of H_2O_2 is used). To this, one test tube of dilute H_2SO_4 is added and the solution is titrated against 0.1 N $KMnO_4$ used as titrant. The concentration of H_2O_2 at various timings can be calculated from the relation

1 mL of 0.1N KMnO4 = 0.00178 g of H_2O_2

From the initial and final concentration of H_2O_2 at different timings, the rate constant can be calculated using first order rate law,

$$K = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

Where, K = rate constant, t = Time, a & a-x = initial concentration and final concentration at time t.

From the rate constants at different temperature T_1 and T_2, the activation energies are calculated by using the relation,

$$Ea = 2.303 \times \log\left(\frac{K_1}{K_2} \times\right) R \times \frac{T_1 \times T_2}{T_2 - T_1}$$

Where, R (Factor) = 8.314 J., T_1& T_2 = Absolute temperatures, K_1& K_2 = Rate constants at T_1& T_2 respectively.

The catalytic power of ferrites is determined from the rate constants and the % decomposition of H_2O_2 at various timings and at various temperatures. Similar work has been reported in the literature for the catalytic study of ferrites [7-11]

RESULTS AND DISCUSSION

Commercial iron-molybdate catalysts have high activity and selectivity for the oxidation of methanol to formaldehyde, but in spite of the intense research effort developed during the last three decades, important deactivation problems persist. Usually, every 6–12 months the catalyst charge of industrial reactors must be replaced. The deactivation of the iron-molybdate catalysts is attributed to the loss of MoO_3 by volatilization. Hence there is need for the re-palletized catalyst to reduce the cost of production of formaldehyde.

As expected the new iron-molybdate catalyst exhibited greater catalytic power as it has been prepared to perform at commercial level. The re-palletized catalyst showed low catalytic activity since there is some deactivation due to the loss of MoO_3 by volatilization and which cannot be recovered by re-palletization. The catalytic activity of the ferrite $CuFe_{2-2x}Cr_xAl_xO_4$ at X=0.00 was taken into consideration since it was found to be most catalytically active during as per our findings [12].

The Catalytic activities of the three catalysts i.e. New Catalyst, Re-Palletized and Ferrite are given in tables 1 to 4. The comparative charts are shown in figures 2 to 5.

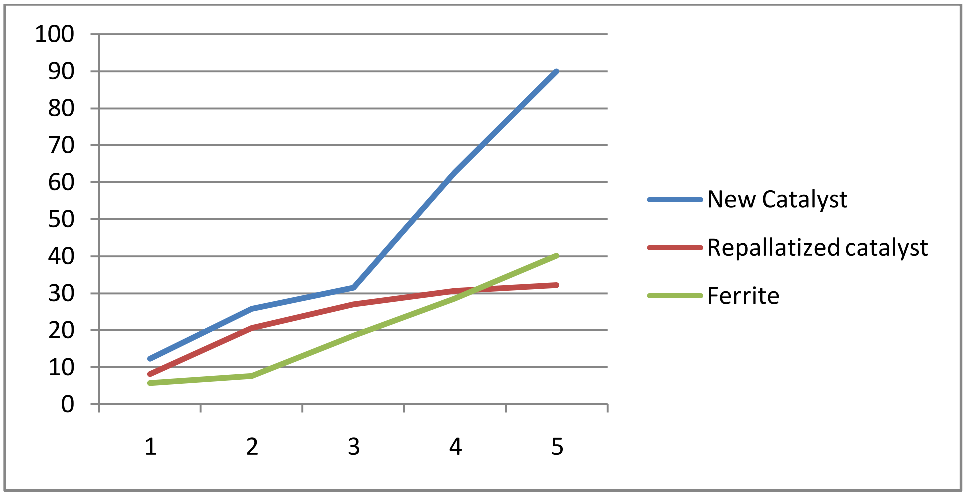

Fig.2: Comparison chart of New Catalyst, Re-palletized catalyst and Ferrites at 313K

Table 1: Catalytic activity of New catalyst, Re-palletized catalyst and Ferrites at 313K

Hours	% Decomposition New Catalyst	% Decomposition Re-palletized catalyst	% Decomposition Ferrite
1	12.28	8.04	5.72
2	25.75	20.48	7.62
3	31.58	26.91	18.43
4	62.72	30.51	28.62
5	90.00	32.12	40.12

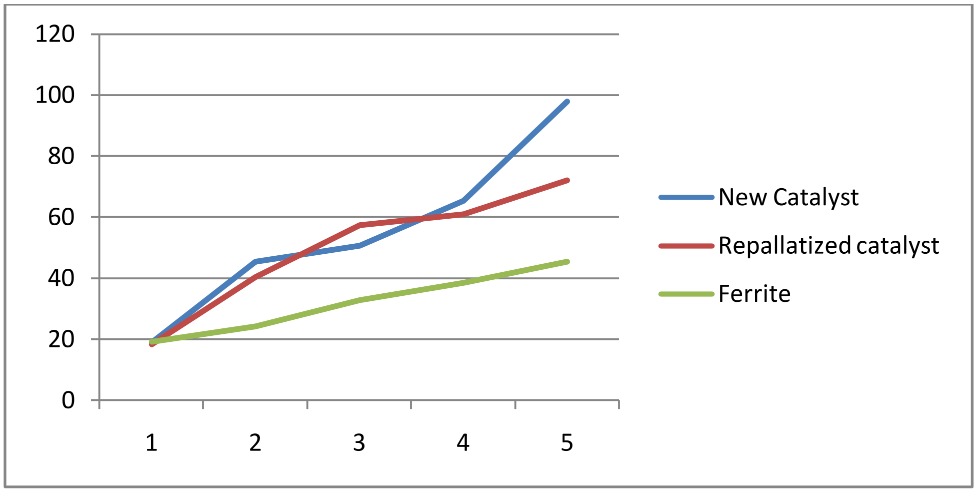

Fig.2: Comparison chart of New Catalyst, Re-palletized catalyst and Ferrites at 323K

Table 2: Catalytic activity of new catalyst. Re-palletized catalyst and Ferrites at 323K

Hours	% Decomposition New Catalyst	% Decomposition Re-palletized catalyst	% Decomposition Ferrite
1	19.09	18.42	19.22
2	45.45	40.46	24.20
3	50.85	57.28	32.75
4	65.45	60.85	38.44
5	97.97	72.04	45.36

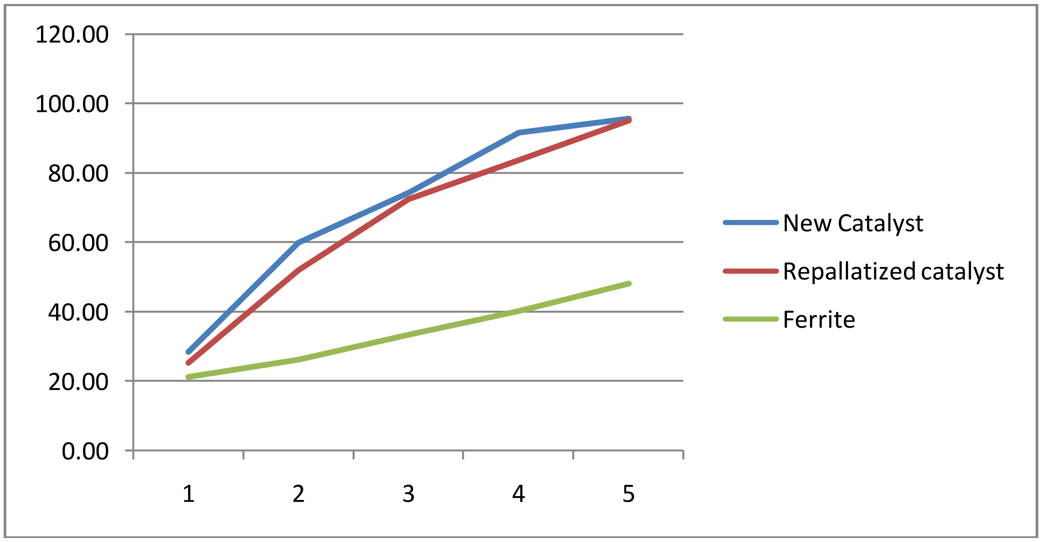

Fig.3: Comparison chart of New Catalyst, Re-palletized catalyst and Ferrites at 333K

Table 3: Catalytic activity of new catalyst. Re-palletized catalyst and Ferrites at 333K

Hours	% Decomposition New Catalyst	% Decomposition Re-palletized catalyst	% Decomposition Ferrite
1	28.45	25.32	21.26
2	60.00	51.93	26.31
3	74.25	72.43	33.48
4	91.57	83.69	40.22
5	95.71	95.11	48.21

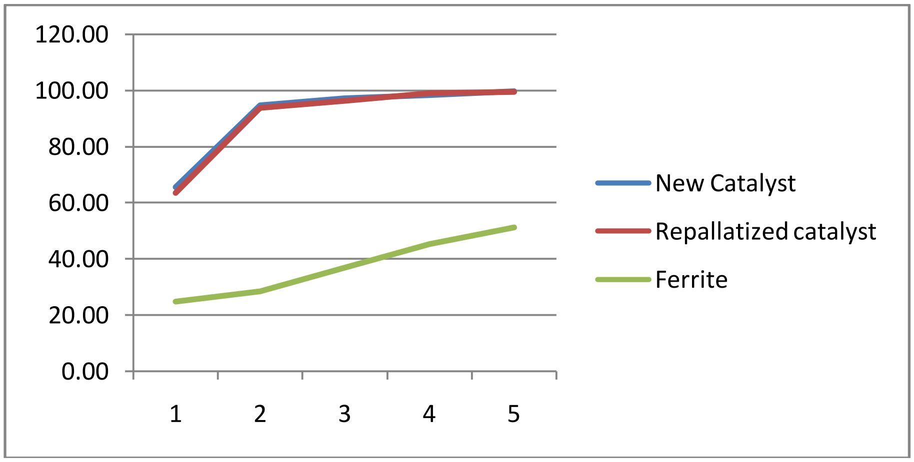

Fig.4: Comparison chart of New Catalyst, Re-palletized catalyst and Ferrites at 333K

Table 4: Catalytic activity of new catalyst. Re-palletized catalyst and Ferrites at 343K

Hours	% Decomposition New Catalyst	% Decomposition Re-palletized catalyst 1	% Decomposition Ferrite
1	65.53	63.53	24.68
2	94.68	93.75	28.32
3	97.22	96.35	36.88
4	98.42	98.95	45.20
5	99.71	99.48	51.22

APPLICATIONS

The study shows that spinel ferrites can be used as catalysts for some oxidation reactions like alcohol oxidation, CO –> CO_2 etc. which are used in industrial process. However the catalytic activity of ferrite was very poor compared to the catalytic activity of the new Fe-Mo catalyst and Re-Pelletized catalyst.

CONCLUSIONS

The present study reveals that

1. All the compositions of the system form a single cubic spinel phase.
2. The catalyst studies using decomposition of H_2O_2 also showed that the synthesized ferrite showed very poor catalytic activity compared to the catalytic activity of the new Fe-Mo catalyst and Re-Pelletized catalyst.
3. At low temperature (313K) the activity of the synthesized ferrite was comparable to the activity of re-pelletized catalyst .
4. At higher temperatures (343K) the activity of new catalyst and that of re-pelletized catalyst was almost the same. However even at this temperature the activity of ferrite was very low.
5. The order of Catalytic activity is New Catalyst > Re-palletized Catalyst > Ferrite Catalyst.

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