COPPER-LOADED DEALUMINATED HY ZEOLITE CATALYSTS

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Copper was incorporated into NaY and HY zeolites by impregnation and by ion-exchange methods. Zeolites with copper incorporated by impregnation have high catalytic activity. The influence of dealumination on the behaviour of these catalysts was also studied. The results demonstrate the catalytic activity can be attributed to small copper agglomerates in the zeolite pores and to larger copper crystallites outside the pores. The decomposition of hydrogen peroxide was used to measure the catalytic activity of the zeolites.

Key words: Zeolites, Cu-loaded catalysts, Dealumination.

INTRODUCTION

Small copper clusters or copper oxide particles encaged in the pore channel systems of zeolite supports [1-5] are attractive catalytically systems. In recent years, considerable attention has been given to methods in which zeolite surfaces can be chemically modified. The acidic as well as the hydrophobic or hydrophilic properties of zeolites depend considerably on their aluminium content, as does their catalytic properties. This present work aims at showing the effect of modification of zeolite Y by dealumination and cation exchange on its properties as a support for copper-loaded catalyst. The catalytic decomposition of hydrogen peroxide was used as a model for reactions carried out in solution.

EXPERIMENTAL

Reagents and materials. All reagents were of analytical grade, unless otherwise noted. Bidistilled water was used.

The sodium form of synthetic Y faujasite was obtained as a powder from Union Carbide (SK-40 Molecular Sieve type Y).

H_2O_2 *solution.* 30 % aqueous H_2O_2 (Merck, Medical Extra pure grade, density 1.11 kg dm^{-3} at 20°) was used.

Modified zeolites. The preparation of various types of these materials has been achieved by ion-exchange, decationation, dealumination and impregnation.

(i) *Cation-exchange.* 20 g powdered NaY was shaken thoroughly with 3M CuCl$_2$ and 3M NH$_4$Cl solution. The resulting suspension was filtered through a sintered glass funnel. During filtration the rest of 2 dm^3 solution of 3M-metal chloride was allowed to percolate through the zeolite

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bed. The ion-exchanged zeolite was washed several times with bidistilled water until the filtrate became free of chloride ions. The samples were dried at 120° for several hours and stored.

(ii) *Dealumination.* In order to prepare dealuminated zeolites, four samples (20 g each) were taken from the NH$_4$Y zeolite. Each sample was immersed in 300 cm^3 bidistilled water in a soxhlet boiling flask. Appropriate amounts of ethylenediamine tetraacetic acid (H$_4$EDTA) were added to the boiling flask. At least 24 hours were required for completing the addition of the complexing agent to the boiling flask. After filtration, the zeolite was washed, dried and stored. A subsequent ion-exchange was used to prepare dealuminated zeolites exchanged by Cu^{2+} ions.

(iii) *Impregnation.* Five samples were prepared by adding a known weight of the metal chloride solution (2.9 g) in an appropriate volume of water to the catalyst (10 g) at 90°. They were evaporated to dryness and stored.

Cu-loaded catalysts were prepared by reduction of the samples containing Cu^{2+} ions. The reduction was carried out in a stream of H$_2$ gas at 400° for 4 hours. For the copper impregnated samples, reduction was carried at 500° for 6 hours.

Chemical analysis of modified zeolites. Both sodium and copper contents were determined by using a Pye Unicam SP 90A atomic absorption spectrometer. Aluminium was determined gravimetrically using 8-hydroxyquinoline. The degree of dealumination was determined by the analysis of NH$_4$Y before and after extraction. The modified zeolites are designated Y$_x$-Z, x being the number of Al atoms per unit cell and Z being the percentage degree of Cu^{2+} ion-exchange.

Catalytic activity measurements. The decomposition of H_2O_2 was followed by measuring the volume of oxygen liberated at atmospheric pressure in a gas burette. The manometric liquid was water containing 5 % NaCl saturated with oxygen to prevent the dissolution of any liberated oxygen. The rate of decomposition was determined at four different temperatures in the range of 30-45°. The H_2O_2 concentration was determined from the following equation.

$C = C^o - PV_g/RT V_1$. C^o, C are the concentrations of H_2O_2 before and after evolution of the volume V_g of oxygen gas, P is the atmospheric pressure, R is the gas constant, and V_1 is the total volume of solution.

RESULTS AND DISCUSSION

Different chemically modified Y zeolites were obtained from the original NaY zeolite (53 Al atoms per unit cell) as follows:

(i) Dealuminated HY zeolites with 6 Na^+ ions per unit cell; HY_{53}, HY_{48}, HY_{42} and HY_{38}.

(ii) Cu(II) ion-exchanged zeolites of different percentages; Cu NaY-59, Cu NaY-67, and Cu NaY-76.

(iii) Cu(II) ion-exchanged dealuminated zeolites of nearly the same degree of ion-exchange (52.5 %); $CuHY_{53}$, $CuHY_{42}$ and $CuHY_{38}$.

(iv) Cu(II) ion-exchanged dealuminated zeolites of the same Al content and different percentages of ion-exchange; $CuHY_{38}$-29, $CuHY_{38}$-45, $CuHY_{38}$-52 and $CuHY_{38}$-57.

In addition, calcination of Cu(II) ion-exchanged zeolites for four hours at 400° in a stream of hydrogen was used to obtain zeolites containing copper (Cu) metal.

The effect of zeolite sample (NaY) and its modified forms was tested with respect to H_2O_2 solution. The effect of the pH of the H_2O_2 solution on the catalytic properties of the different zeolite series was studied at 30°. Fig. 1 includes representative curves. The optimum pH of the H_2O_2 solution chosen in this study is 6.8. At low pH ~ 1 the rate of decomposition was immeasurably slow. Kanungo *et al.* [6], showed that the rate is accelerated at higher pH values (11.3 − 12.0). In this study, the rate of decomposition was found to increase with increasing pH up to 6.8 while it decreases with further increase of pH. However, the decrease in catalytic activity observed at pH values higher than 6.8 may be due to the interaction between OH^- − groups and the acidic sites of the zeolite structure. All the tested catalysts showed the same trend regarding the effect of pH. Consequently, a H_2O_2 solution of pH 6.8 was used in all subsequent experiments and the initial rate of decomposition normalised to unit surface area of a zeolite is considered as a measure of catalytic activity

(cm^3 of O_2 liberated per unit surface area per second, $cm^3 m^{-2} s^{-1}$).

The decomposition of H_2O_2 in presence of the original NaY zeolite was found to be remarkably slow. On exchange of the sodium ions with Cu(II) ions, the decomposition was found to proceed with a measurable rate. Generally, the
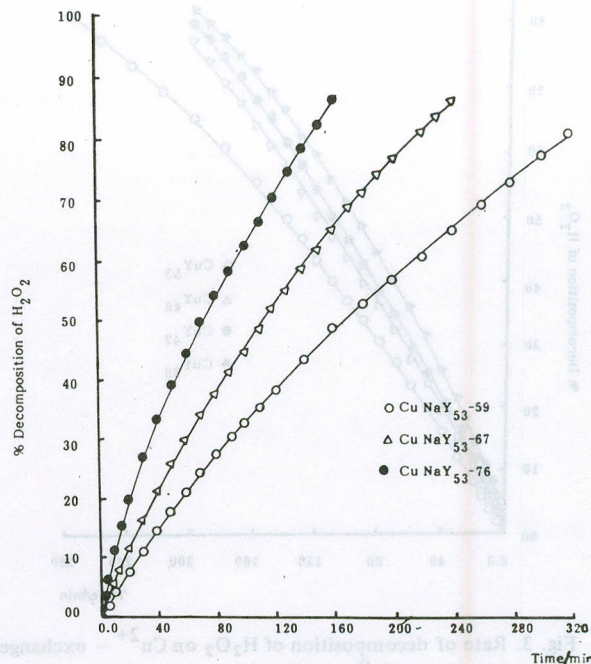

Fig. 1. Rate of decomposition of H_2O_2 on CuNaY zeolite catalysts at 30° and pH = 6.8.
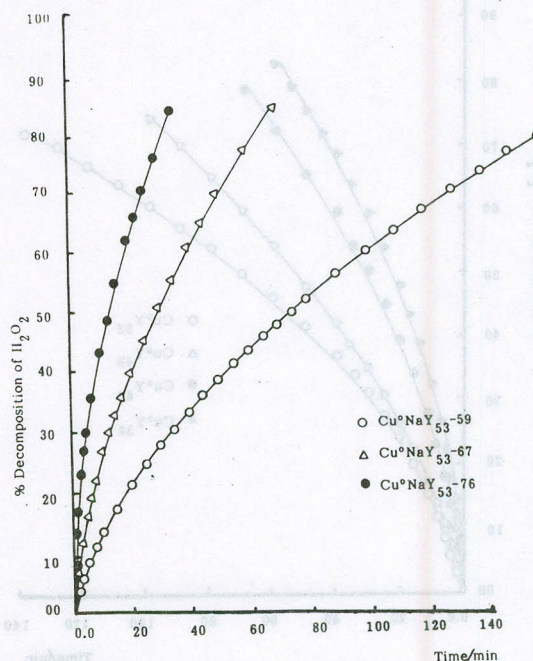

Fig. 2. Rate of decomposition of H_2O_2 on Cu^oNaY zeolite catalysts at 30° and pH = 6.8.

rate of reaction was found to increase as the percent of Cu(II) increases, whether this is performed in the original
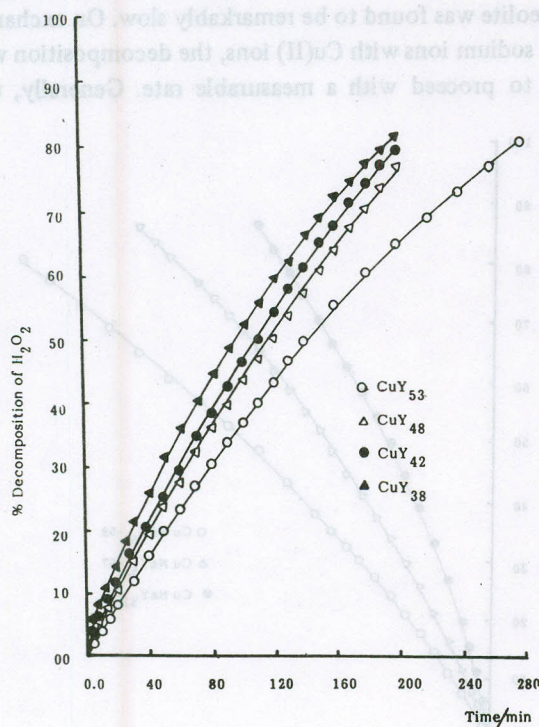
or dealuminated zeolites. The rate of reaction is highly increased using the corresponding Cu— zeolites (Table 1 and 2). This indicates that the rate of decomposition depends on the valence state of copper in the zeolite structure. It is well known that various mechanisms have been

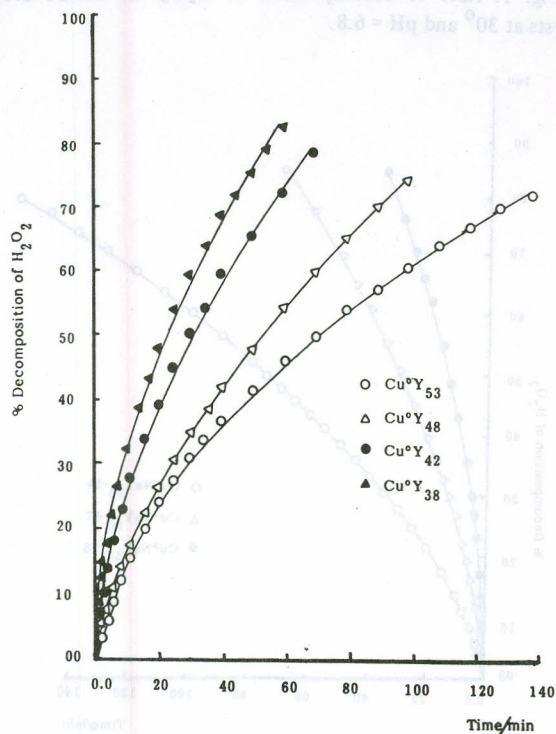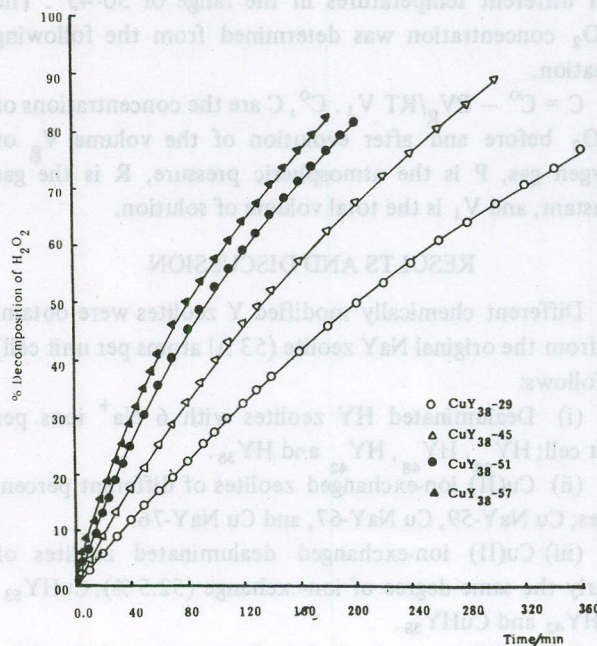Fig. 3. Rate of decomposition of H_2O_2 on Cu^{2+} – exchanged dealuminated zeolites at 30° and pH = 6.8.

Fig. 5. Rate of decomposition of H_2O_2 on CuY_{38} zeolite samples at 30° and pH = 6.8.

Fig. 4. Rate of decomposition of H_2O_2 on Cu° – exchanged dealuminated zeolites at 30° and pH = 6.8.
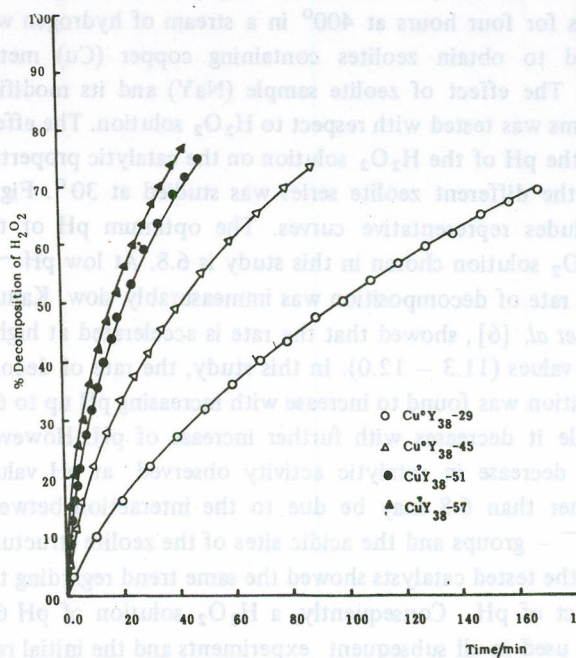

Fig. 6. Rate of decomposition of H_2O_2 on $Cu^{\circ}Y_{38}$ zeolite samples at 30° and pH = 6.8.

proposed for the heterogeneous decomposition of H_2O_2 over metal oxide catalysts containing metal ions of variable valence. However, it has been reported [7] that reduction of Cu(II)Y zeolite by hydrogen results in the formation of cuprous ions which is reversible, while reduction under more severe conditions (400°) results in the formation of copper agglomerates and crystallites.

The Cu(II) exchanged is reduced by passing a stream of H_2 gas at elevated temperature (400-500°). Fig. 1 and 2; 3 and 4; 5 and 6 shows greater reactivity after passing

Table 1. Initial rate of decomposition of H_2O_2 over Cu-exchanged Y zeolites at 30° and pH = 6.8.

Catalyst	ml of $O_2.10^3$ g s	ml of $O_2.10^5$ m^2 s	Catalyst	ml of $O_2.10^3$ g s	ml of $O_2.10^5$ m^2 s
CuNaY$_{53}$ – 59	8.0	0.64	Cu^{o}NaY$_{53}$-59	102.3	8.26
CuNaY$_{53}$ – 67	12.0	1.04	Cu^{o}NaY$_{53}$-67	160.0	13.60
CuNaY$_{53}$ – 76	24.5	2.11	Cu^{o}NaY$_{53}$-76	300.0	26.90

Table 2. Initial rate of decomposition of H_2O_2 over Cu-exchanged dealuminated zeaolites at 30° and pH=6.8.

Catalyst	ml of $O_2 \cdot 10^3$ g s	ml of $O_2.10^5$ m^2 s	Catalyst	ml of $O_2.10^3$ g s	ml of $O_2.10^5$ m^2 s
Cu Y$_{53}$	8.7	0.69	Cu^{o}Y$_{53}$	104	8.39
Cu Y$_{48}$	11.0	0.86	Cu^o Y$_{48}$	104	8.32
Cu Y$_{42}$	12.0	0.86	Cu^{o}Y$_{42}$	157	12.27
Cu Y$_{38}$	17.6	1.19	Cu^{o}Y$_{38}$	244	18.21

Table 3. Kinetic parameters of decomposition of H_2O_2 over Cu-exchanged dealuminated and non-dealuminated zeolites at 30° and pH = 6.8.

Cu^{2+} exchanged zeolite	$k(s^{-1})$ 10^3	Activ. energy kcal/mole	Cu^o-exchanged zeolite	$k(s^{-1})$ 10^3	Activ. energy kcal/mole
Cu Y$_{53}$	5.0	24.8	Cu^o Y$_{53}$	9.9	15.5
Cu Y$_{48}$	5,8	22.9	Cu^o Y$_{48}$	13.4	14.1
Cu Y$_{42}$	6.3	22.0	Cu^o Y$_{42}$	22.4	12.2
Cu Y$_{38}$ –29	3.5	27.1	Cu^o Y$_{38}$ –29	6.9	16.9
Cu Y$_{38}$ –45	6.1	23.3	Cu^o Y$_{38}$ –45	16.5	13.1
Cu Y$_{38}$ –51	7.5	21.3	Cu^o Y$_{38}$ –51	31.5	10.9
Cu Y$_{38}$ –57	8.7	20.0	Cu^o Y$_{38}$ –57	37.0	10.0
Cu NaY$_{53}$ –59	4.3	24.2	Cu^o N'aY$_{53}$ –59	9.3	15.6
Cu NaY$_{53}$ –67	6.2	21.3	Cu^o NaY$_{53}$ –67	23.9	11.7
Cu NaY$_{53}$ –76	9.9	19.4	Cu^{o}NaY$_{53}$ –76	53.5	8.7
			Cu/H Y$_{38}$	77.0	7.4
			Cu/H Y$_{53}$	49.5	10.3

H_2 gas. Moreover, the decrease of the number of Al atoms per unit cell from 53 down to 38 enhances greatly the activity of the zeolite catalyst (Fig. 3).

According to the recent adsorption studies [8,9], the dealumination is accompanied by significant changes in the acidic properties of zeolite Y. These properties are closely related to the composition and structural characteristics of the zeolites. The changes in total acidity with increasing dealumination is accompanied by a corresponding decrease in ionic exchange capacity of the zeolite, since the number of exchange sites is determined by the number of Al-atoms left in the framework. Thus on changing the degree of Cu^{2+}-ion-exchanged in the most active dealuminated zeolite (38-Al-atoms/unit cell), the decomposition rate of H_2O_2 increases remarkably with increasing Cu^{2+}-ion content from 29 to 57 % than the originally unexchanged form (Fig. 5). Furthermore, the treatment of the Cu-exchanged zeolites with H_2 gas at elevated temperatures enhances sharply their catalytic activity (Fig. 4 and 6).

Reduction of CuNaY zeolites (400-500°) results in hydrogen consumption which approaches the quantity required for complete reduction of Cu^{2+} to Cu^+ ions. It has been shown for highly exchanged CuNaY zeolites [4] that at 400° the reduction to metallic Cu is incomplete and some of the consumed hydrogen is held as a copper hydride moeity [8]. Therefore, we can conclude that the enhancement of the catalytic activity of zeolite Y containing Cu^{2+} ions by reduction is due to the Cu^+-ions formed in the zeolite structure and/or the metallic copper agglomerated outside the structure.

These results have established the significance of the use of different modification methos to develop the catalytic properties of the zeolite structure.

In conclusion, the influence of temperature on the decomposition of H_2O_2 was investigated overall the previously mentioned catalysts at 30°, 35°, 40° and 45° The rate of reaction is first order with respect of hydrogen peroxide. Table 3 summarizes the kinetic parameters obtained in this investigation with the lowest activation energy (7.4 kcal) on using Cu Y$_{38}$ which indicates its greatest activity among the zeolites mentioned and confirms the necessity of modifications in zeolites to enhance its catalytic reactivity.

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