

Efficiencies of the Copper(II) Adsorbed Zeolites in the H_2O_2 Disproportionation Reaction

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This work describes FT-IR studies results on adsorption of Cu(II) metal cation. Adsorption has been performed on 3A, 4A, 5A, AW-300, ammonium Y zeolite, organophilic, and molecular sieve zeolites using aqueous solution of the metal studied. Changes in intensities and positions of the pseudolattice bands corresponding to ring vibrations have been observed in the measured spectra. These changes are expected particularly in the pseudolattice bands connected with the presence of alumino- and silicoxygen tetrahedral rings in the zeolite structure. Also, Cu(II) adsorbed zeolites were each tested for their ability to catalyse the disproportionation of hydrogen peroxide in the presence of the added base imidazole. The Cu(II) adsorbed zeolites display efficiency in the disproportionation reactions of hydrogen peroxide, producing water and dioxygen.

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1. Introduction

Hydrogen peroxide is an ubiquitous metabolite in living systems, produced at increased levels in a variety of pathological situations. For the detoxification of H_2O_2 , and probably also for maintaining its regulatory function, nature has developed a family of highly effective enzymes, the catalases, which dismutate H_2O_2 according to Eq. (1) [1, 2]:



Catalase, one of the three major sensitive protective enzymes in living organisms, exists in almost all aerobically respiring organisms. It protects cells from the toxic effects of hydrogen peroxide (H_2O_2), the latter being linked to a variety of pathological consequences such as aging, diabetes, and cancer [1, 3, 4]. Therefore during the past decades a wide variety of complexes have been synthesized as models for their catalase-like activities. A variety of complexes containing manganese, copper, etc., have been used considering this purpose [5–7].

Because of the solubility problem of the zeolites in water, catalytic activity studies were performed in heterogeneous media. Although homogeneous catalysts exhibit excellent activity and selectivity, the technical problems encountered in their applications, such as the difficulty in product separation and the deactivation by self-aggregation of active sites, have slowed their industrial applications [8].

Encapsulation in microporous solids such as zeolite is an attractive technique for heterogenization and metal adsorbed zeolites are used for their catalytic activity properties in heterogeneous media [9–11]. Catalytic activities of metals and their complexes are usually ex-

plained in terms of either their redox potentials or structures [12, 13].

It is known that an adequate Cu(II)/Cu(I) redox potential for effective catalysis of superoxide radical must be required. Therefore the reason for the selection of copper is due to favorable redox potentials.

Herein we report the preparation of copper(II) adsorbed zeolites (3A, 4A, 5A, AW-300, ammonium Y zeolite, organophilic and molecular sieve). Furthermore the catalytic activities of the copper(II) adsorbed zeolites for the decomposition of hydrogen peroxide were investigated in the presence of imidazole.

2. Experimental

All the solvents and reagents were reagent grade and used as received. The IR spectra of the fresh and copper(II) adsorbed zeolites were measured using a Shimadzu IRPrestige-21 FT-IR spectrophotometer within the range $4000\text{--}400\text{ cm}^{-1}$, using KBr discs.

2.1. Adsorption studies

As a source of copper(II) ions, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was used for preparing of aqua solutions. For the adsorption of copper(II) ions from aqueous solutions on zeolites 3A, 4A, 5A, AW-300, ammonium Y zeolite, organophilic, molecular sieve, zeolites activated at 873 K for 2 h before contact copper(II) ions. Filtration process applied for the solution and metal adsorbed zeolites are dried in the oven.

2.2. H_2O_2 disproportionation reaction studies

Volumetric measurements of evolved dioxygen during the reactions of the copper(II) adsorbed zeolites (3A, 4A, 5A, AW-300, ammonium Y zeolite, organophilic, molecular sieve) with H_2O_2 were carried out as follows. A 50 cm^3 three-necked round-bottom flask containing

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0.025 g metal adsorbed zeolites in water (10 cm^3) was placed in a water bath (25°C). One of the necks was connected to a burette and the others were stoppered by a rubber septum. While the solution was stirring, H_2O_2 (1.33 mmol , 0.150 cm^3) was injected into it through the rubber septum using a microsyringe. Volumes of evolved dioxygen were measured at 1 min time intervals by volumetry. In cases where imidazole (50 mg) was added this was introduced into the reaction vessel before the addition of H_2O_2 (in the absence of the imidazole the metal adsorbed zeolites were either inactive or very weak catalysts for this reaction).

3. Results and discussion

IR spectra is one of the most suitable techniques to give enough information to elucidate the adsorption of metal ions on zeolites. Comparison of the spectra of the treated and untreated zeolites shows that there are significant differences between them (Fig. 1). The fresh zeolites showed the two well known main peaks about 3600 and 3700 cm^{-1} attributed to OH stretching of bridging Si-(OH)-Al groups located at the internal zeolite surface and OH stretching of the weakly acidic terminal silanol groups located at the external zeolite surface, respectively in the hydroxyl stretching vibration region of the infrared spectra [14, 15]. The bands near 3600 cm^{-1} are definitely decreased in intensity and shifted down to about 3580 cm^{-1} for copper(II) adsorbed zeolites. Also the band near 3700 cm^{-1} is a little weakened in the case of copper(II) adsorbed zeolites. The decrease of the intensity of the bands is very likely due to the exchange of the protons by Cu(II) ions [16].

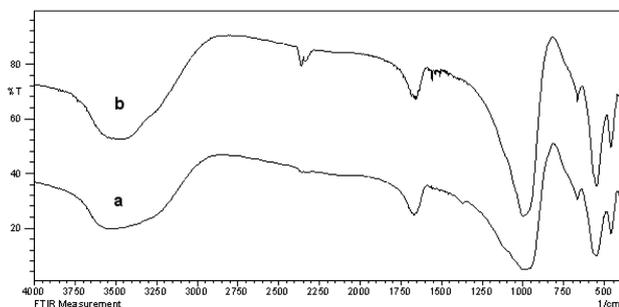


Fig. 1. FT-IR spectra of zeolite 3A (a) and Cu(II) adsorbed zeolite 3A (b).

Two weak bands near 1500 and 1450 cm^{-1} assigned to the Brønsted and Lewis acid sites of the fresh zeolites, respectively. The sorption of the Cu(II) ions by the fresh zeolites causes an increase in the Lewis acid sites and a decrease in the Brønsted acid sites. The increase in the number of Lewis acid sites was due to the function of the electron acceptors of transition metal cations as additional Lewis acid sites in a general sense. On the other hand, the reduction in the Brønsted acid sites is reasonable as these sites are replaced by metal ions. These results were also found by other researchers [17, 18]. These

expected changes in the infrared spectrum confirm that the adsorption reactions were completed.

The catalytic activities of the copper(II) adsorbed zeolites 3A, 4A, 5A, AW-300, ammonium Y zeolite, organophilic and molecular sieve to disproportionate H_2O_2 into H_2O and O_2 was examined in aqueous media at 25°C by volumetric measurements of evolved dioxygen. It was found that all the copper(II) adsorbed zeolites showed activity for the catalytic decomposition of H_2O_2 in the presence of added imidazole. Among them, the copper(II) adsorbed zeolite 3A is the most effective (Table). Experiments were repeated several times to ensure consistency of the results.

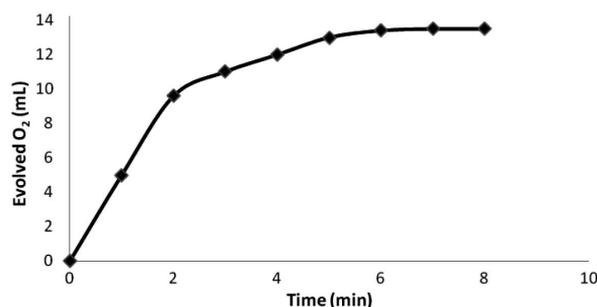


Fig. 2. Time courses of dioxygen evolution in the disproportionation of H_2O_2 by the Cu(II)-zeolite 3A: $[\text{Cu(II)-zeolite 3A}] = 0.025 \text{ g}$, $[\text{H}_2\text{O}_2] = 1.33 \text{ mmol}$, 298 K .

The time course of the O_2 evolution is shown in Fig. 2. The H_2O_2 disproportionation efficiency of the complexes in the presence imidazole follows the order: $1 > 3 > 6 > 7 > 2 > 4 > 5$. In the absence of heterocyclic base, the complex decomposes hydrogen peroxide slowly, but the decomposition of H_2O_2 is enhanced in the presence of a heterocyclic base such as 1-methylimidazole (1-MeimH), imidazole (imH), or pyridine (py) because of their strong *p*-donating ability. On the other hand, heterocyclic bases themselves cause only a very slight disproportionation of the peroxide.

The evolution profile in Fig. 2 for the copper(II) adsorbed zeolite 3A shows the involvement of a fast catalytic process occurring at the initial stage followed by a short slow period process to finish the reaction. It was suggested that these bases may be essential in the catalysis disproportionation of H_2O_2 by manganese catalase since they are known to be present in the vicinity of the active site of catalase and other manganese enzymes [19].

4. Conclusion

In view of the importance of catalytic decomposition of hydrogen peroxide, we have screened our copper(II) adsorbed zeolites to assess their catalytic activity towards decomposition reaction. For this purpose, firstly copper(II) was adsorbed on zeolite 3A, 4A, 5A, AW-300, ammonium Y zeolite, organophilic, and molecular sieve. As a result according to the FT-IR spectra the incorporation

of Cu(II) cation into the zeolite structures causes changes in the spectra. These changes are expected particularly in the pseudolattice bands connected with the presence of alumin- and silicoxygen tetrahedral rings in the zeolite structure. The catalytic activities of the copper(II) adsorbed zeolites for the decomposition of hydrogen peroxide were investigated in the presence of imidazole. As a result all copper(II) adsorbed zeolites disproportionate H_2O_2 into less harmful dioxygen and water but copper(II) adsorbed zeolite 3A exhibited the best catalytic efficiency for this reaction.

TABLE

Time courses of O_2 evolution (mL) from H_2O_2 disproportionated by the Cu(II) adsorbed zeolites 1-7 with added 1*H*-imidazole (im: 50 mg) at 25 °C (1: Cu(II)-zeolite 3A, 2: Cu(II)-zeolite4A, 3: Cu(II)-zeolite5A, 4: Cu(II)-AW-300, 5: Cu(II)-ammonium Y zeolite, 6: Cu(II)-organophilic, 7: Cu(II)-molecular sieve).

Time [min]	1	2	3	4	5	6	7
1	5.0±0.2	2.5±0.1	2.9±0.1	1.8±0.1	2.2±0.1	3.4±0.1	4.5±0.2
2	9.6±0.3	4.1±0.2	4.1±0.1	2.5±0.1	4.2±0.1	4.8±0.2	6.1±0.2
3	11.1±0.3	5.6±0.2	5.4±0.2	3.4±0.2	5.0±0.2	6.2±0.2	7.0±0.3
4	12.0±0.3	6.5±0.3	6.9±0.2	4.0±0.2	5.5±0.2	7.2±0.3	7.5±0.2
5	13.0±0.4	7.2±0.3	8.2±0.3	4.5±0.2	6.3±0.3	8.1±0.2	8.3±0.4
6	13.4±0.4	7.6±0.3	9.0±0.3	5.4±0.3	6.7±0.2	8.5±0.3	8.4±0.3
7	13.5±0.5	8.1±0.2	9.8±0.2	6.1±0.2	6.8±0.3	8.8±0.3	
8			10.4±0.5	6.7±0.4		9.1±0.3	
9				6.9±0.2		9.7±0.5	
10				7.0±0.3		9.8±0.4	

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