Influence of Different Preparation Methods of Copper Loading on Na-Y Zeolite for Green Gas Emission

Patcharin Worathanakul and Nattachar Rakpasert

***Abstract*—This research was focused on different preparation methods of copper loading on zeolite. Cu cation supported on Na-Y zeolite (Cu-Y) was prepared by aqueous solution ion exchange and incipient wetness impregnation methods. Different amounts of copper (II) were loaded in the Na-Y zeolite. The catalysis materials were characterized by X-ray diffraction, X-ray fluorescence and Brunauer-Emmett-Teller. The results show that Cu loading did not change the structure of Na-Y zeolite. The obtained Cu/Y has enlarged pore size and octahedral shaped crystal with approximately 0.19 ± 0.08 µm diameter. 5.5 wt. % Cu/Y with impregnation method clearly exhibits a higher BET surface area and a total pore volume than 5.5 wt. % solution ion exchanged.**

***Index Terms*—Na-Y zeolite, green gas emission, X-ray powder diffraction, scanning electron microscope (SEM).**

I. INTRODUCTION

The FAU-type zeolites, including FAU-X and FAU-Y, with a 3-dimensional pore structure have large channels, large surface area, high cation exchange capacity, high activity, possession of a highly catalytic center and high surface energy [1]. It has been found that the size of zeolite crystals could be a significant impact on the catalytic performance [2]. FAU-Y can be used for large molecules separating and it is also reported that FAU-Y with small particle size can improve catalytic cracking selectivity, reduce coke formation, increase the yield of diesel oil, faster diffusion and higher external surface area as well as easier cation exchange and template extraction, etc. [3], [4].

To reduce the greenhouse effect, caused by a substantial rise in CO_2 concentration in the atmosphere, the development of technologies for fixing and recycling CO_2 emissions is required [5], [6]. Crystalline microporous materials like zeolite have been found important industrial applications in processes such as catalysis, molecular sieving, gas separation and ion exchange. The major classes of microporous materials are represented by zeolites such as MOR, FAU and ZSM-5 [7]. Zeolite are said to have some advantages such as enrichment of reactants in a zeolite pore, ion-exchange ability, high dispersion of loaded metals and, thus, control of valence of the metals [8]. The sizes of intra-crystalline channel/pore and guest molecule are often one of the key parameters in zeolite diffusivity. Many researchers have reported that zeolite diffusivity can be correlated with the critical diameter of guest molecule [9].

FAU-Y or Na-Y zeolite can be also used for many applications such as pervaporation for dehydration, vapor permeation for organic/organic separation, gas separation such as CO_2/N_2 and NO reduction [10]-[19]. Different preparation methods have been utilized for the preparation of transition metal on zeolite support as conventional ion exchange in aqueous solution, solid-state ion-exchange, sublimation or chemical vapour deposition, the ex-framework and impregnation method. Ramirez and his co-workers [20] reported that the Fe-MFI prepared by ex-framework is more active towards direct N_2O decomposition than that obtained via SSIE methods. Li and his co-workers [21] reported that the Cu–TS-1/cordierite prepared with two methods as ion-exchange and impregnation exhibited similar high activities, the max NO_x conversion at 58%. Liu and his co-workers [22] reported that Cu/MCM-41 for selective catalytic NO reduction with NH_3 prepared from the template- and hydroxyl group-ion exchanges show high activities at low Cu contents, while a high Cu content was required for the impregnation method to reach a high activity. Moreover, the template-ion exchange was found to have the advantage in maintaining the physical of the support. The aim of this paper was to compare preparation methods of Cu (II) loading on Na-Y zeolite supported by aqueous solution ion exchange and incipient wetness impregnation methods. The obtained samples will with different metal loadings to further reduction of CO_2 and oxides of nitrogen.

II. MATERIALS AND METHODS

The material used for synthesize of Na-Y zeolite are as follow: Sodium hydroxide (NaOH 99 wt%, Merck) for sodium source, Sodium aluminate (Al_2O_3 50-56 %wt., Fe_2O_3 0.05 wt%., Na_2O 40-45 wt. %, Aldrich) for alumina source and Sodium silicate (Na_2O 18 %wt., SiO_2 63 %wt., Aldrich) for silica source and Copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$ 98 %wt., Merck) for Cu loading.

A. *Na-Y Synthesis*

Na-Y zeolite was prepared at Si/Al ratio 0.75 and divided into seed gel, feedstock gel and overall gel.

1) *Seed gel*

The preparation of seed gel comprises of 5% of the whole gel. Sodium silicate solution (S1) was prepared by mixed sodium hydroxide, distilled water and sodium silicate with

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stirring until dissolved. Sodium aluminate solution (S2) was prepared by mixed sodium hydroxide, distilled water and sodium aluminate stirring until dissolved. Then, sodium aluminate solution and sodium silicate solution were mixed together by stirring moderately and left at ambient temperature for 24 h. The mixed solution was called seed gel.

2) Feed stock gel

The preparation of feedstock gel comprises of 95% of the whole gel. The methodology is similar to the preparation of seed gel but large quantity of starting material. Then, sodium silicate solution (F1) and sodium aluminate solution (F2) were mixed together by stirring vigorously and left at ambient temperature for 1 night. The mixed solution was called feed stock gel.

3) Overall gel

The feedstock gel and seed gel were mixed as overall gel. The feedstock gel was started with stirring left them at ambient temperature for 1 night. After 5h, the gel was settled to the solid at the bottom, and a hazy supernatant liquid to the top. The samples were continued heated at 100 ^{0}C until the supernatant is clear. It should not be exceed 2h addition with complete crystallization. After that, the samples were aged at room temperature for 1 night and heat was added in crystallization step. The overall gel was filtered with distilled water until pH of filtrate is below 9 and dried at 110 ^{0}C overnight. The synthesized conditions were performed

B. Difference Copper Loading Methods

1) Incipient wetness impregnation of Na-Y zeolite

Copper (II) exchanged Na-Y zeolites (Cu/Y-IM) were prepared with different percentages of Cu loading (2.3 wt. % and 5.5wt. % by an incipient wetness impregnation method. It is necessary to keep the zeolite carrier completely wetted. Aqueous solution of metal-nitrate was added dropwise to the zeolite with continuous stirring. Finally, the zeolite was filtered and then dried at 120 ^{0}C overnight and calcined for 5 h at 600 ^{0}C in dry air.

2) Aqueous solution ion exchanged Na-Y zeolite

For an aqueous solution ion exchange method, the metal-nitrate aqueous solution with a solid-to-liquid ratio of 1 g/ 100 ml was carried out under vigorous stirring at room temperature for 24 h. The zeolite was filtered and dried at 120 ^{0}C overnight and calcined for 5 h at 600 ^{0}C in dry air. The exchanged samples as Cu/Y-IE were prepared at 2.3 wt. % and 5.5 wt% Cu loadings.

C. Physicochemical Characterization

The crystallinity of synthesized catalysts as Cu (II) on Na-Y zeolites were analyzed following:

1) X-ray powder diffraction (XRD)

(XRD) patterns using X-ray powder diffraction (Phillips PW 1830/40, Netherlands) with CuK$_\alpha$1 radiation (λ = 1.5406A°), generator tension 40 kV and generator current 30 mV.

2) Scanning electron microscope (SEM)

The crystal morphology and size of the obtained zeolite were determined via scanning electron microscopy (SEM) in the range of 5–70° (2θ). The sample was coated with a thin layer of gold using a sputter coater (Edwards Laboratories, Milpitas, CA) before scanning electron microscope (SEM).

3) BET N2-adsorption/desorption isotherm

Specific surface area, adsorption/desorption isotherms, pore size and pore size distribution of the prepared samples were determined using BET-N$_2$ adsorption (Quantachrome, Autosorb® -1-C) with microporous analysis (74 points N$_2$ adsorption/ desorption).

D. Catalytic Activity Test Procedure

Cu/FAU catalysts for nitric oxide (NO) with H$_2$ reducer was primary studied in a continuous flow system with a fixed bed stainless steel tube reactor containing 0.3 g of catalyst as shown the condition in Table I. The reaction gas, a mixture of NO, H$_2$ and O$_2$ with He balance was fed to the catalyst. The total flow is 200 cm^3 /min. Before the reaction was started, the catalysts were activated under helium flow at pre-treated temperature at 500 ^{0}C for 1 h. The temperature was then adjusted to reaction temperature at 600 ^{0}C. The outlet gas compositions were analyzed by combustion analyzer with measurement every 2 min for 1 h.

TABLE I: LIST OF THE STUDY CATALYTIC ACTIVITY

Metal loading	Copper (II) nitrate trihydrate
Metals loading method	5.5%Cu/FAU-IM 5.5%Cu/FAU-IE
Pretreated temperature	500 °C
Reaction temperature	600 °C

III. RESULTS AND DISCUSSION

XRD patterns of Cu/Y-IM and Cu/Y-IE are shown in Fig. 1 according to standard peak as shown 2θ at 6, 10, 15.8, 20.2, 23.5, 27 and 31.3 [19] and Cu/Y shown CuO peaks at 2θ = 35.5, 38.6, 58.3.

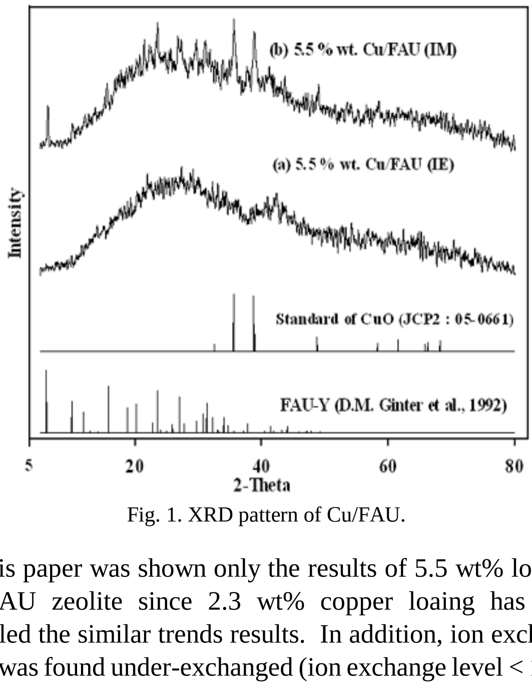

Fig. 1. XRD pattern of Cu/FAU.

This paper was shown only the results of 5.5 wt% loading on FAU zeolite since 2.3 wt% copper loaing has been revealed the similar trends results. In addition, ion exchange level was found under-exchanged (ion exchange level < 100%)

at 36.8 % and 33.0 % for Cu/Y-IM and Cu/Y-IM, respectively.

The pore size distribution shows diameter of both exhibit micropore (<2 nm) as shown in Fig. 2. The results reveal that it is potentially suitable uses for gas adsorption for environmental application.

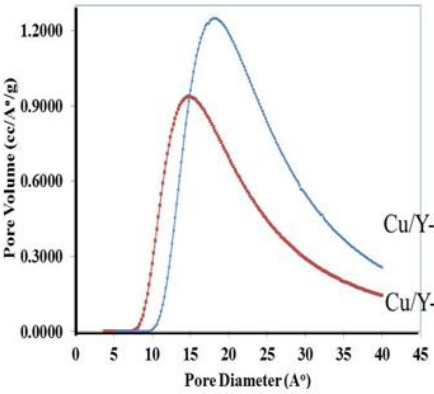

Fig. 2. Pore size distribution of Cu/Y-IM and Cu/Y-IE.

Specific surface area, pore volume and pore diameter of Cu/Y zeolites with different preparation methods were characterized by BET N_2-adsorption/desorption isotherms as shown in Table II. The results were shown that impregnation method with 5.5 wt. % Cu loading clearly exhibits a higher BET surface area and a total pore volume than 5.5 wt. % Cu loading with ion-exchanged method. The result can imply that higher BET surface area and high pore volume may reduce greenhouse gas emission for future application.

TABLE II: BET SURFACE AREA AND PORE VOLUME OF CATALYSTS

Physical properties	Metals loading (wt.%)	
	5.5% Cu/FAU-IM	5.5% Cu/FAU-IE
BET surface area[2] (m^2/g)	114.1	52.3
Micropore volume[1] (cm^3/g)	0.014	0.010
Total pore volume[2] (cm^3/g)	0.235	0.204
Pore diameter[3] (Å)	14.8	18.2

[1]t-plot micropore analysis method, [2]MP micropore analysis method at P/P_0 close to unity, [3]DA method micropore analysis

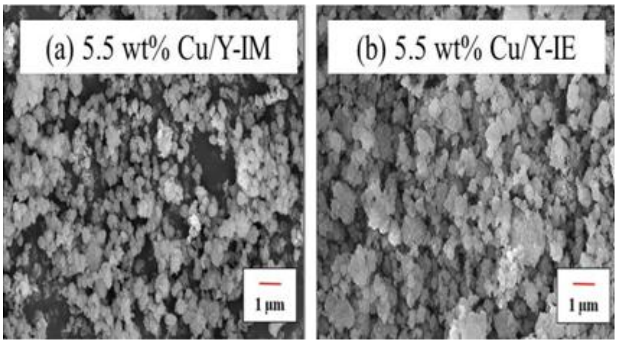

Fig. 3. SEM images of Cu/Y-IM and Cu/Y-IE for 5.5 wt% loading (a) 5.5 wt% Cu/Y-IM and (b) 5.5 wt % Cu/Y-IE.

Moreover, SEM images of Cu/Y-IM with incipient wetness impregnation exhibit that most of the octahedral shaped crystals, confirming the formation of Y zeolites (Fig. 3). Metal loading did not change the Y-zeolite structure. It was also found that Cu/Y crystals were approximately 0.19 ± 0.08 μm in diameter.

The catalysts from 5.5% Cu loading prepared by incipient wetness impregnation method were shown higher nitric oxide conversion than aqueous solution ion exchange method (Table III) at reaction temperature of 600 ^{0}C.

TABLE III: SUMMARIZE FOR NO CONVERSION OF 5.5 WT.% CU CATALYSTS

Type of catalysts	Nitric conversion (%)
5.5 wt.% Cu/Y-IM	38.86
5.5 wt.% Cu/Y- IE	32.67

IV. CONCLUSIONS

Different preparation methods of wet impregnation and ion exchanged have effect for various environmental applications such as nitric oxide reduction or carbon dioxide reduction. Cu loading on Na-Y zeolite did not change the structure of Cu-Y zeolite. The results can confirm that we can synthesize Na-Y zeolite and metal loading on zeolites successfully. The obtained zeolite can further study more about catalytic testing in the future.

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