

Different Preparation Methods of Ni-FAU(Y) Zeolite for Nitric Oxide Reduction

P. Worathanakul and N. Rakpasert

Abstract—The effect of Ni cation supported on FAU(Y) zeolite was prepared by aqueous solution ion exchange and incipient wetness impregnation methods in the selective catalytic reduction of nitric oxide using hydrogen as the reactant in packed bed reactor. 0.5 and 3.5 wt% of Ni (II) metals were loaded in the FAU(Y) zeolite. The samples were characterized by X-ray diffraction, X-ray fluorescence and scanning electron microscope. The obtained Ni/FAU has enlarged pore size of octahedral shaped crystals with approximately $0.22 \pm 0.085 \mu\text{m}$ diameter. Ni loading did not change the structure of FAU(Y) zeolite. Ni (II) loading with 3.5 wt% to FAU-Y zeolite by incipient wetness impregnation method was shown higher nitric oxide conversion than aqueous solution ion exchange method.

Index Terms—FAU (Y) zeolite, metal loading, nickel, nitric oxide reduction.

I. INTRODUCTION

Flue gases of many combustion processes are critical concerns of environmental pollutions with acid rains and smog. [1]. Nitric oxide (NO_x) is one of the most dangerous pollutants. At high concentrations nitric oxide is rapidly oxidized in air to form nitrogen dioxide, however, in fire gases, most of the nitric oxide remains unchanged. At high concentrations, it can affect in health and death. Excessive levels of nitric oxide in blood have been shown to cause low blood pressure. There are many researches to reduce nitric oxide. The catalytic reduction using metal-zeolites catalysts by hydrocarbons can be one method for reduction of NO_x dangerous pollutants [2]. Mosqueda-Jimenez and his co-workers [3] reported that the activity of Ni/ZSM-5 is the most active catalyst for the NO reduction with propane reducing agent. However, using propane as reducing agent catalysts was rapidly deactivated due to the acid site catalyzed formation of carbonaceous deposition. The formation of carbonaceous deposition will block the active sites. It can change the catalyst structure and remove Al from framework positions. These are primary reasons for the changes in the catalysts activity during NO reduction with hydrocarbons [4], [5].

Zeolites are aluminosilicate structures and crystalline

microporous materials. They have been used in many industrial applications such as catalysis, molecular sieving, gas separation and ion exchange. Zeolite with microporous materials has some advantages with enrichment of reactants in zeolite pore, metal loadings and control of valence of the metals [6], [7]. The key parameters in zeolite diffusivity are sizes of intracrystalline channel. Many researchers have reported that zeolite diffusivity can be correlated with the critical diameter of guest molecule [8]. Metal loading into zeolite makes the intrinsic reaction rate faster; therefore diffusivity of intracrystalline would have more significant influence on the catalysts performance [7].

FAU (Y) zeolite has a size of 7.4 \AA with faujasite family of zeolites that highly versatile molecular sieve including the three-dimensional pore structure and solid acidity. FAU (Y) is commonly prepared with aluminum and silicon content in low silicon and aluminum ratio.

Transition metals such as Cu, Co, Fe, and Ni have been used a wide range in combination with different zeolite structures [3], [4] and [9]-[11]. They were found to be active catalysts for NO reduction. FAU zeolite can be also used for many applications such as pervaporation for dehydration, vapor permeation for organic separation, gas separation such as CO_2/N_2 [12]-[14]. Wada and his co-workers [15] reported that the Pd-Ni-Y catalyst employed the highest activity toward the hydrocracking reaction of phenanthrene and pyrene.

NO_x reduction using H_2 as reducing agent is interesting. It is due to H_2 was very efficient in the catalytic conversion of NO into N_2 in the absence and in the presence of oxygen. Zero emissions of greenhouse gases are achieved and H_2 is evidenced in a wide temperature ranging and giving high cycle-average NO conversion [16], [17]. Moreover, the H_2 using as a reducing agent in selective catalytic reduction systems for NO_x elimination in passenger cars may provide the advantage in terms of low temperature NO_x reduction under lean conditions. The main interesting issue is to reduce NO_x at very low temperatures without producing large amounts of N_2O [18].

The aim of this paper was to compare the preparation methods of Ni (II) on FAU(Y) zeolite support by ion exchange and incipient wetness impregnation methods for NO reduction with packed bed reactor.

II. MATERIALS AND METHODS

A. Materials

The material used for FAU-Y zeolite synthesis are as follow: Sodium hydroxide (NaOH 99 %wt., Merck), sodium

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aluminate (Al_2O_3 50-56 %wt. Fe_2O_3 0.05 %wt. Na_2O 40-45 %wt., Aldrich) and sodium silicate (Na_2O 18 %wt. SiO_2 63 %wt., Aldrich) were used. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 98 %wt., Alpha) was used as material metal loading.

B. FAU (Y) Synthesis

FAU(Y) zeolite was prepared at 0.75 of Si:Al ratio. Sodium aluminate and sodium silicate solutions were mixed together by stirring moderately and left at ambient temperature for overnight. The mixed solution was called seed gel.

It was then prepared feedstock gel by mixing the sodium aluminate solution and sodium silicate solution with stirring vigorously. The seed gel with was then added to the feedstock gel slowly for 30 mins. It was left at ambient temperature for 5 h. The samples were continuing to heat at 100 °C for 2 h and left at ambient temperature again. The samples were then aged at room temperature and the overall gel was filtered. The product was obtained after drying at 110 °C overnight.

C. Ni Loading to FAU(Y) Zeolite

Ni (II) exchanged FAU (Y) zeolite was prepared with 0.5% wt. and 3.5% wt. of Ni loadings by incipient wetness impregnation and aqueous solution ion exchanged methods. For incipient wetness impregnation, it is necessary to keep the zeolite carrier completely wetted. Aqueous solution of metal-nitrate was added drop wise to the zeolite with continuous stirring.

Finally, the zeolite was filtered and dried at 120 °C overnight and calcined for 5 h at 600 °C in dry air [19]-[20]. For aqueous solution ion exchange, Ni (II) exchanged FAU(Y) zeolite was prepared with a solid-to-liquid ratio of 1 g/100 ml and carried out under vigorous stirring at room temperature for 24 h.

D. Catalytic Activity Test Procedure

0.3 g of Ni/FAU catalysts for NO reduction testing with H_2 as reducing agent were studied in a continuous flow system with a fixed bed stainless steel tube reactor.

The reaction gas, a mixture of NO 0.025 %vol., H_2 1%vol., O_2 10%vol. and He balance was fed to the catalysts. The space velocity was $6,351 \text{ h}^{-1}$ (total flow = $200 \text{ cm}^3 \text{ min}^{-1}$).

Before the reaction was started, the catalysts were activated under helium flow at 500 °C pretreated temperature for 1 h. The temperature was then reduced to reaction temperature at 450 °C. Table I was shown summary of conditions for nitric oxide testing.

TABLE I: SCHEME OF CATALYTIC ACTIVITY TEST FOR NITRIC OXIDE REDUCTION IN PACKED BED REACTOR

CATALYST	METALS/FAU (IM & IE)
METALS LOADING	0.3, 3.5 WT.% Ni/FAU
SAMPLE WEIGHT	0.3 G
REACTOR	0.7752 CM.ID. STAINLESS STEEL
	TUBE
BED LENGTH	4 CM
VOLUME REACTOR	1.89 CM3
SPACE VELOCITY	6356 H-1
PRETREATED TEMP.	500 °C
REACTION TEMP.	450 °C
PRESSURE	1 ATM

The outlet gas compositions were analyzed by combustion

analyzer with measurement every 2 min for 1 h. The scheme of catalytic activity test for nitric oxide reduction in packed bed reactor was shown in Fig. 1.

Nitric oxide conversion was calculated from the difference of inlet and outlet concentrations.

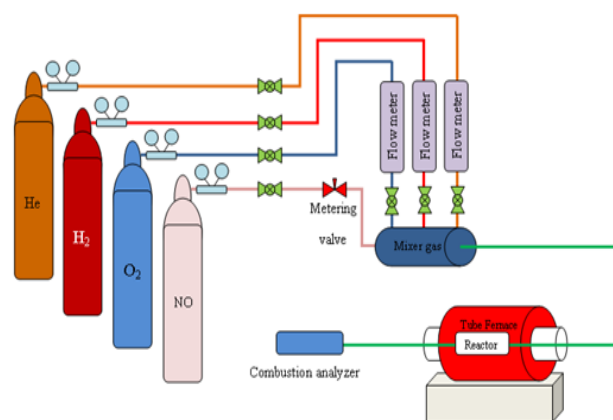


Fig. 1. Scheme of catalytic activity test for nitric oxide reduction in packed bed reactor.

E. Material Characterization

X-ray powder diffraction (XRD) The crystallinity of synthesized catalysts as Ni (II) on FAU(Y) zeolites was analyzed by powder X-ray diffraction (XRD) patterns with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), generator tension 40 kV and generator current 30 mV. (Phillips PW 1830/40, Netherlands)

X-ray fluorescence spectroscopy (XRF) The chemical analysis was determined using X-ray fluorescence spectroscopy (HORIBA, MESA-500 W, Japan). This analyzer is capable of extremely easily and accurately analyzing the amount of elements contained in powders.

Scanning electron microscope (SEM) The morphology of catalysts was determined by scanning electron microscope (Jeol, JSM-6301F, Japan).

The samples were coated with a thin layer of gold using a sputter coater (Edwards Laboratories, Milpitas, CA) before scanning images.

III. RESULTS AND DISCUSSION

A. Physicochemical Characterization

XRD patterns of 3.5% Ni/FAU(Y) zeolite with incipient wetness impregnation and aqueous solution ion exchanged methods were shown in Fig. 2. The XRD peaks are in line well with the diffraction standard of FAU-Y zeolite as shown 20 at 6, 15.8, 18.8, 23.5, 27 and 31.3 [21]. XRD patterns of Ni loading to FAU(Y) were compared with NiO peaks at 20 with 43.3 and 74.4.

The physicochemical of XRD characterization was confirmed that Ni loading did not change FAU (Y) zeolite structure.

The composition of 3.5 wt% Ni loading from XRF was summarized in Table II. The results were shown that catalysts have Si/Al ratios (by weight) with 1.38 and 1.62 for Ni/Al

and Na/Al, respectively. The result of Ni/Al ratio was lower than Na/Al ratio.

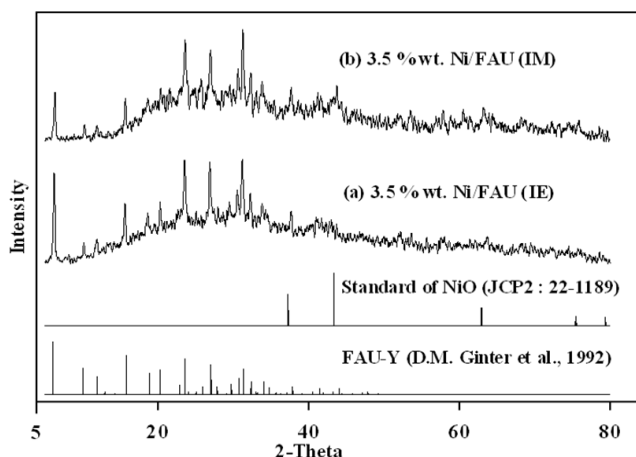


Fig. 2. XRD pattern of Ni/FAU zeolite.

According to the percentage of exchange of nickel, Ni/FAU zeolite of incipient wetness impregnation and aqueous solution ion exchanged methods was also found under-exchanged (ion exchange level < 100%), whereas the Ni/FAU with incipient wetness impregnation method exhibit higher ion exchange level than ion exchanged method.

The ion exchange level of 3.5 wt% Ni/FAU with incipient wetness impregnation method was 29.4%.

TABLE II: CHEMICAL COMPOSITION OF CATALYSTS DETERMINED BY XRF

CATALYSTS	Si/Al	Na/Al	Ni/Al	% EXCHANGE
3.5 wt.% Ni-IM	1.38	1.31	0.14	29.4
3.5 wt.% Ni-IE	1.62	1.06	0.13	26.0

Moreover, SEM images of Ni/FAU were prepared by incipient wetness impregnation and aqueous solution ion exchange are shown in Fig. 3a) and Fig. 3b). The images exhibit that the morphology of samples is the octahedral shaped crystals with confirming to the formation of FAU zeolites [22].

The crystal size of Ni/FAU structure was approximately $0.22 \pm 0.08 \mu\text{m}$ in diameter both incipient wetness impregnation and aqueous solution ion exchanged methods.

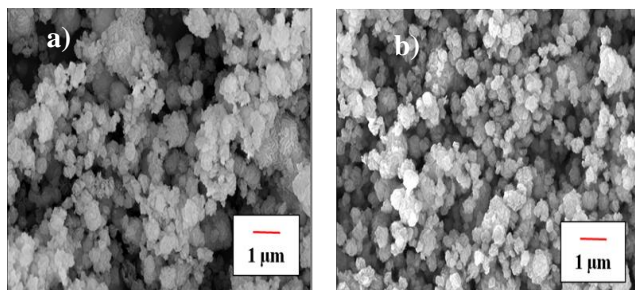


Fig. 3. SEM images of a) Ni/FAU (IM) and b) Ni/FAU (IE).

B. Effect of Ni/FAU Catalysts for Nitric Oxide Reduction

The nitric oxide conversion of Ni introduced into zeolite prepared by incipient wetness impregnation and aqueous solution ion exchange methods were shown in Fig. 3.

The results were shown that when increasing metal

contents, nitric oxide conversion was increased accordingly.

It was also found that Ni (II) loaded FAU-Y zeolite by incipient wetness impregnation method was higher NO_x conversion than aqueous solution ion exchange method. It is due to percentage of nickel exchange for impregnation having outstanding aluminum site more than ion exchange [23], [24].

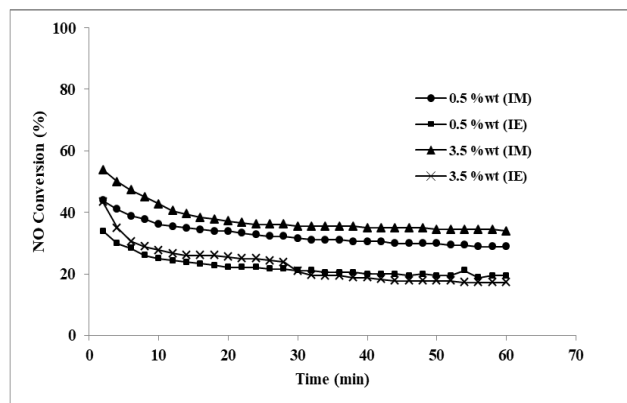


Fig. 3. Nitric oxide conversion of Ni/FAU catalysts.

IV. CONCLUSION

Ni/FAU(Y) zeolites were successfully synthesized with 0.5% and 3.5% nickel loadings. Ni (II) loaded FAU-Y zeolites by incipient wetness impregnation method gave the higher nitric oxide conversion than aqueous solution ion exchange method. 3.5 % wt. Ni/FAU(Y) prepared by impregnation method was found the highest nitric oxide conversion at 450°C reaction temperature in packed bed with space velocity was $6,351 \text{ h}^{-1}$.

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