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 ± 0.085 μm 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 pollutants with acid rains and smog. [1]. Nitric oxide (NOx) 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 NOx 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 Å 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 CO2/N2; [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.

NOx reduction using H2 as reducing agent is interesting. It is due to H2 was very efficient in the catalytic conversion of NO into N2 in the absence and in the presence of oxygen. Zero emissions of greenhouse gases are achieved and H2 is evidenced in a wide temperature ranging and giving high cycle-average NO conversion [16], [17]. Moreover, the H2 using as a reducing agent in selective catalytic reduction systems for NOx elimination in passenger cars may provide the advantage in terms of low temperature NOx reduction under lean conditions. The main interesting issue is to reduce NOx at very low temperatures without producing large amounts of N2O [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
aluminate (Al₂O₃ 50-56 %wt. Fe₂O₃ 0.05 %wt. Na₂O 40-45 %wt., Aldrich) and sodium silicate (Na₂O 18 %wt. SiO₂ 63 %wt., Aldrich) were used. Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O 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 H₂ 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., H₂ 1%vol., O₂ 10%vol. and He balance was fed to the catalysts. The space velocity was 6,351 h⁻¹ (total flow = 200 cm³ 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.

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 CuKα₁ radiation (λ = 1.5406Å), 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.

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%.

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±0.08 μm in diameter both incipient wetness impregnation and aqueous solution ion exchanged methods.

**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       |

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

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\textsubscript{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].

**IV. CONCLUSION**

Ni/FAU(Y) zeolites were successful synthesized with 05% 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 h\textsuperscript{-1}.

**ACKNOWLEDGMENT**

The authors would like to thank funding from King Mongkut’s University of Technology North Bangkok (KMUTNB) granting No.KMUTNB-GEN-59-06.

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P. Worathanakul was born in Bangkok, Thailand. She received a D.Eng. (chemical engineering) from the Kasetsart University, Bangkok, Thailand in 2008. She did her doctoral research collaboration with Washington University in Saint Louis, USA during 2006-2007. P. Worathanakul received a M.S. (chemical engineering) and B.S. (chemical engineering) from King Mongkut’s University of Technology Thonburi in 1999 and Kasetsart University in 1997, Thailand, respectively. She is now a faculty with an associate professor in the Department of Chemical Engineering, Faculty of Engineering, King Mongkut’s University of Technology North Bangkok, Bangkok, Thailand. She has worked related to chemical, environmental and energy fields as a position of project manager/research associate at Thailand Environmental Institute during 1999-2004. She has published some papers in nanostructured composite materials synthesis and their applications.

She is interested in catalytic properties of nanoparticles for environmental and chemical applications as well as nanotechnology, advanced materials properties and cleaner technology. Dr. Worathanakul has become a member of American Chemical Society (ACS) since in 2007 and Asia-Pacific Chemical, Biological & Environmental Engineering Society (CBEES) since in 2014.

She is the member of the Council of Engineers and the Thai Institute of Chemical Engineering and Applied Chemistry. She has worked for carbon footprint committee in Thailand. She has recognized award for oral technical presentation at the 17th National Chemical Engineering and Applied Chemistry Conference and honor award advisor of Master’s student year 2012.

N. Rakpasert lives in Pathumthani province, Thailand. She received a B.Sc. (industrial chemistry) in 2009 and a M.S. (chemical engineering) in 2012 from the King Mongkut’s University of Technology North Bangkok, Bangkok, Thailand. N. Rakpasert is now with the Thai Oil Group for Strategic Sourcing Coordinator position.