

A study of hydrogen storage in zirconium-containing NaY_{5.7} zeolite

F. Mulana

Chemical Engineering Department, Faculty of Engineering, Syiah Kuala University, Darussalam, Banda Aceh - 23111, Indonesia. Corresponding Author: farid.mulana@che.unsyiah.ac.id

Abstract. The inclusion of metals/alloys inside the pores of zeolite is of a great interest for developing composites with functional materials distributed in the intended fields. Zirconium-containing NaY_{5.7} zeolite samples with 1 wt% and 3 wt% metal loading were prepared using impregnation method. The starting material was commercial available NaY_{5.7} zeolite and zirconocene dichloride ((C₅H₅)₂ZrCl₂) as zirconium source and benzene as solvent. The characterization of samples was performed by X-ray diffraction (Rigaku RINT2000) using a Cu K α radiation, nitrogen adsorption isotherms, hydrogen sorption isotherms and heats of sorption by a twin-conduction-type calorimeter (Tokyo Riko Co., Japan) equipped with a volumetric adsorption system at 298 K. The X-ray diffraction pattern reveals that the framework structure of zeolite is retained in the calcination condition performed and the metallic form of zirconium exists on zeolite particles. The nitrogen adsorption isotherm for the zirconium-containing NaY_{5.7} zeolite was similar to that for the untreated zeolite which indicates that Zr-NaY sample retains its structure even after the heat treatment at higher temperature. The hydrogen sorption on Zr-NaY_{5.7} zeolite was brought about by a combination of formation of solid solution inside zeolite pores and hydridation of zirconium species. The inclusion of zirconium inside the framework of NaY_{5.7} zeolite has increased the amount of occluded hydrogen on all synthesized samples. NaY_{5.7} zeolite itself could occlude hydrogen approximately 0.097 mmol H₂/gr at low hydrogen pressure of 80 kPa. Zirconium-NaY_{5.7} zeolite system, which resided zirconium nanoparticles inside the pores of zeolite, could be one of alternative composites to be used for hydrogen sorbing materials providing water resistance.

Keywords: zirconium, zeolite, impregnation, hydrogen, sorption isotherms

Introduction

Except for cost, hydrogen seems like a perfect fuel. The byproducts of hydrogen combustion are electricity, water and heat. Although its low density makes efficient storage difficult, hydrogen has the largest energy of combustion per unit of mass. For decades, hydrogen universally accepted as the green fuel has been targeted as the utopian fuel of the future due to its abundance and environmental friendliness. Storage modes like, high pressure gaseous storage, liquid hydrogen, glass-microspheres and activated carbon adsorption, have been developed over the years. The one having the highest potential corresponds to reversible hydrogen storage in metal hydrides in solid phase.

The most common materials for hydrogen storage are metals and alloys that are based on transition metals. Metals and alloys intended to serve as hydrogen storage media must provide the hydriding/dehydriding procedure to be reversible and to occur at the hydrogen partial pressure as close as possible to atmospheric pressure. Up to now, there has been no metal or alloy which completely satisfies such a set of requirement. In most of these materials, hydrogen tends to occupy tetrahedral order sites. Among the variety of such compositions, much interest is devoted to systems in which zirconium is used as nanocrystal metal particle.

The incorporation of metals into the framework of zeolite has attracted the attention of many researchers. Numerous studies have been focused on the preparation, characterization and properties of metallic particles entrapped in zeolites. An aluminosilicate-type zeolite is a microporous material with framework anions and exchangeable cations in its structure and the anion-cation pairs form strong electrostatic fields (M. E. Davis 1991; R.M. Barrer. 1978) which strongly interact with polar adsorbates. Since Y-zeolite, NaY, has relatively large pores (entry aperture: 0.74 nm; diameter: 1.3 nm) than other zeolites, such as zeolite A (0.41 nm; 1.1 nm) and ZSM-5 (0.51-0.55 nm; 0.51- 0.55 nm) (D.W. Breck 1974), it can be modified through the incorporation of active species in the pores by various methods, for instance ion exchange and impregnation.

In this study the inclusion of zirconium inside the pores of zeolite was attempted in order to develop composites with functional materials. The inclusion of zirconium inside the pores of zeolite was undertaken due to the hydrophilic-hydrophobic field of zeolite can be precisely controlled and accurately evaluated (T. Kawai & K. Tsutsumi 1992; T. Kawai et al., 1994). In addition, in the fact that NaY zeolite system is well-characterized and has nanospace.

The aim of this work is to study the behavior of metal-exchanged zeolite for this application. In this study, the influence of the preparation method (calcinations, reduction, and metal loading) was investigated. The inclusion of zirconium with different loadings inside the pores of NaY_{5.7} zeolite was carried out by impregnation method.

Material and Methods

Zirconium-containing NaY_{5.7} zeolite samples with 1 wt% and 3 wt% metal loading were prepared using impregnation method. The starting material was a commercially available NaY_{5.7} zeolite and zirconocene dichloride ((C₅H₅)₂ZrCl₂) from Tokyo Chemical Industries, Japan was used as zirconium source and benzene (Kishida Chemical, Osaka, Japan) was used as solvent. A 0.79 g of zirconocene dichloride was well mixed in 20 ml of benzene while stirring until a clear solution was obtained. In the next step, 8.17 g of fresh NaY_{5.7} zeolite was added in solution and stirred at slow speed for about 3-4 h until the wet mixture gel was observed. The wet mixture gel was calcined in flowing Ar gas at a specific calcination temperature (T_c) (873 K to 1023 K) for about 4 - 8 h and finally, after being cooled to room temperature, the white obtained-sample was reduced under hydrogen atmosphere at 673 K (T_r) for 4 h. To prevent any contact with air, all the material handling (including weighing and loading) was performed in a glove box containing nitrogen with carefully controlled atmosphere.

After being calcined, reduced and cooled, the samples were subjected to analysis of XRD by Rigaku RINT2000 using a Cu K α radiation and scans were obtained in the 2 θ range of 15° - 50° with a scanning rate of 2 deg/min. The nitrogen adsorption isotherm was measured volumetrically at 77 K using a laboratory-made automatic adsorption apparatus equipped with two pressure transducers that read 10⁻¹ to 10⁵ Pa. Before each measurement the sample was outgassed at 673 K for 4 h.

Heats of adsorption versus hydrogen concentration and adsorption isotherms of hydrogen on the zirconium-containing NaY_{5.7} zeolite sample were measured simultaneously by a twin-conduction-type calorimeter (Tokyo Riko Co., Japan) equipped with a volumetric adsorption system at 298 K. The apparatus was equipped with two pressure gauges in the full ranges of 10 and 1000 Torr (Tsutsumi et al., 1993). Adsorption isotherms are generated along with heats of adsorption as a function of surface coverage by dosing consecutively a small amount of hydrogen gases.

Prior to measurement of adsorption isotherm and heats of adsorption, the samples were performed 4 times evacuating and 3 times hydriding cycles. The first evacuating of samples was regenerated under vacuum condition while heating from 298 K to 673 K for 3 h, keeping heating at 673 for 4 h, and then cooling to room temperature naturally. The second, the third and the fourth evacuating of samples were undergone on the same treatment. The hydriding of the samples was performed at 298 K under 100 kPa of hydrogen for 10 h to give the reproducible isotherm on hydriding. The adsorption isotherms and heat of adsorption measurement were measured at 298 K. In all cases, adsorption was carried out by introducing successive doses of adsorbate onto the sample located in the calorimeter cell. The heat evolved, the quantity of gas adsorbed and the equilibrium pressure were measured at the end of the interaction of each dose, i.e., when the calorimeter had returned to thermal equilibrium. Introduction of doses was repeated until the equilibrium pressure reached ca. 100 kPa.

Results and Discussion

X-ray diffraction pattern of the 3 wt% Zr-NaY_{5.7} zeolite together with fresh NaY_{5.7} zeolite is shown in Figure 1. The X-ray diffraction pattern reveals that the framework structure of zeolite is retained in the calcination condition performed. It closely resembles that of the starting material. However, the incorporation of a small amount of zirconium into NaY_{5.7} zeolite would cause a little distortion of the framework of zeolite. The X-ray diffraction pattern of samples also indicated that the metallic form of zirconium exists on zeolite particles. Nevertheless, the peak of zirconium at $2\theta = 35.72$ was still ambiguous whether it was due to zirconium metal or zeolite itself. The nitrogen adsorption isotherms at 77 K are presented in Figure 2. The figure expressed the nitrogen adsorption isotherm of all samples including fresh NaY as reference. The specific surface areas were determined from nitrogen adsorption at 77 K using B.E.T equation (Rouquerol et al., 1999; Gregg & Sing, 1967). It was observed that the specific surface areas of the Zr-NaY sample were similar to the fresh NaY_{5.7} zeolite. Therefore, it could be said that the nitrogen adsorption isotherm of samples after modification at 1023 K revealed no collapse of the structure of zeolite framework. This result shows that Zr-NaY sample retains its structure even after the heat treatment at higher temperature.

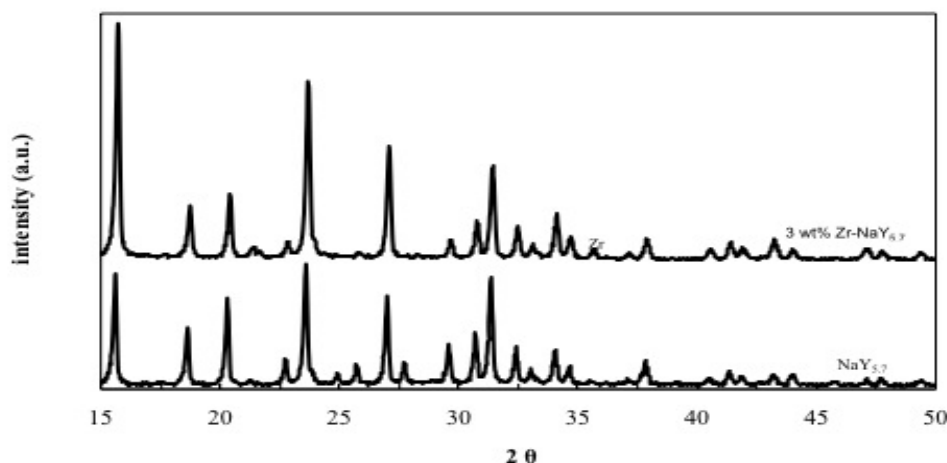


Figure 1. X-ray diffraction pattern of fresh NaY_{5.7} and 3 wt% Zr-NaY_{5.7} composite

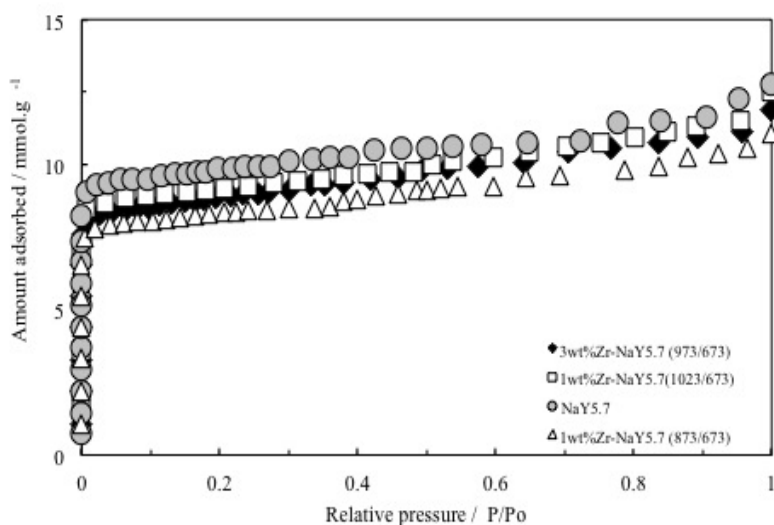


Figure 2. Adsorption isotherm of N₂ on fresh NaY_{5.7}, 1 wt% Zr-NaY_{5.7} (T_c=873 K /T_r=673 K), 1 wt% Zr-NaY_{5.7} (T_c=1023 K/T_r=673 K) and 3 wt% Zr-NaY_{5.7} (T_c=973 K/T_r=673 K)

The adsorption isotherms for all of the samples (1 wt% Zr-NaY_{5.7}, 3 wt% Zr-NaY_{5.7} and fresh NaY_{5.7} zeolite as comparison) were described in Figure 3. These figures demonstrated that the inclusion of zirconium inside the framework of NaY_{5.7} zeolite has slightly increased the amount of occluded hydrogen on all synthesized samples except 1 wt% Zr-NaY_{5.7} calcined at 1023 K.

Figure 3 was reconstructed in order to elucidate the ability of zirconium-containing NaY zeolite sample in occluding hydrogen and to understand the effect of its modification on various temperature calcinations and amount of zirconium loading in modifications treatment. It was observed on the figure that the ability of 3 wt% Zr-NaY_{5.7} zeolite to occlude hydrogen was higher than those of 1 wt% Zr-NaY_{5.7} zeolite calcined both at temperatures of 873 K and 1023 K. The amount of occluded hydrogen of 1 wt% Zr-NaY_{5.7} zeolite (T_c= 1023 K) at hydrogen pressure over 75 kPa decreased sharply even below occluded hydrogen amount of fresh NaY_{5.7} zeolite. The sharp decrease of it might be due to the high calcination temperature chosen. One might consider that the calcination of the sample at 1023 K collapsed part structures of zeolite framework. But the measurement of nitrogen adsorption isotherm of zirconium-containing NaY samples after modification at 1023 K revealed no collapse of the structure of zeolite framework. On the contrary, the data of the measurement of hydrogen adsorption isotherm revealed that any collapse of the structure of zeolite framework of 1 wt% Zr-NaY_{5.7} zeolite was observed. Another possibility is due to some unfavorable reaction of zirconium such as oxidation.

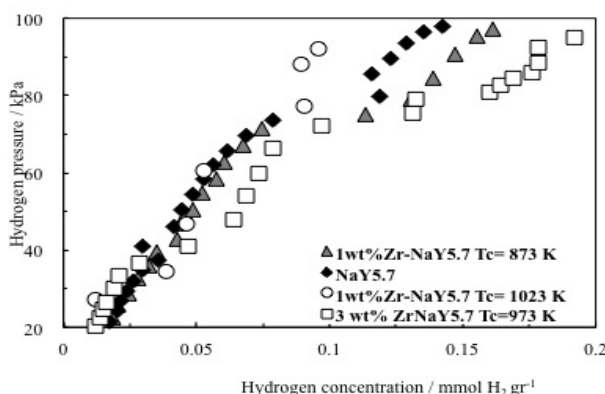


Figure 3. Comparison of P-C isotherm for hydrogen adsorption by zirconium-containing NaY_{5.7} zeolite and NaY_{5.7} zeolite

The measurement of heat of adsorption of hydrogen on 1 wt% Zr-NaY_{5.7} zeolite sample was revealed in Figure 4.

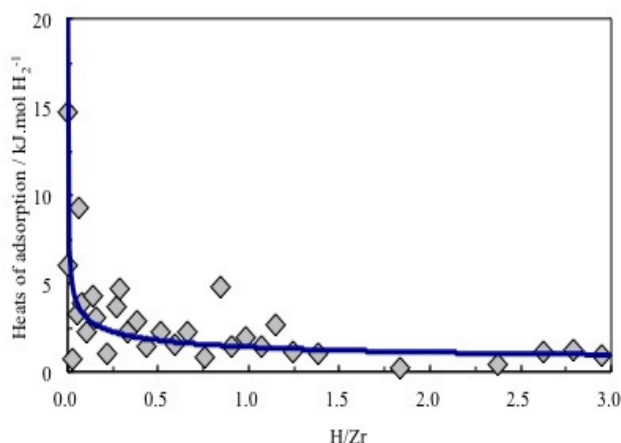


Figure 4. Heat of adsorption of hydrogen gas on 1 wt% Zr-NaY_{5.7} (T_c=873 K /T_r=673 K)

It was observed that the heat of adsorption of 1 wt% Zr-NaY_{5.7} zeolite sample was too small. The initial heat of adsorption of 1 wt% zirconium-containing NaY_{5.7} zeolite was around 15 kJ/mol H₂. However, the heat of adsorption of fresh NaY_{5.7} zeolite could not be observed in this experiment due to a small heat of adsorption released by the sample. Since the heat reached 170 KJ/mol H₂ or so for zirconium simplex (Mulana, 2002), zirconium species in the 1 wt% Zr-NaY_{5.7} zeolite would be active to hydrogen.

Figure 5 illustrates the amount of occluded hydrogen on zirconium-containing NaY zeolite system. The figure was constructed by subtracting the amount of hydrogen concentration of 1 wt% Zr-NaY_{5.7}, 3 wt% Zr-NaY_{5.7} zeolite to fresh NaY_{5.7} zeolite. It was observed from the figure that the occlusion of hydrogen on zirconium-containing NaY zeolite sample was initiated at hydrogen pressure around 30 kPa. With increase of hydrogen pressure. the difference of the amount of occluded hydrogen also became larger.

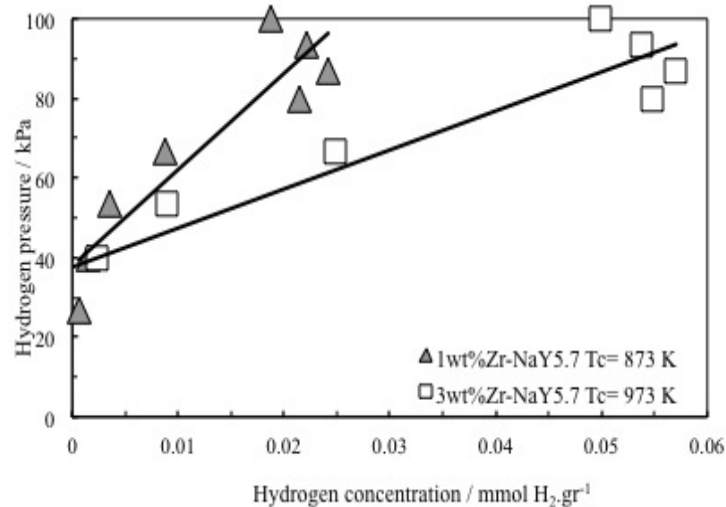


Figure 5. The amount occluded hydrogen by zirconium-containing NaY_{5.7} zeolite subtracted by NaY_{5.7} zeolite itself.

Figure 6 shows the comparison of occluded hydrogen amount on zirconium-containing NaY zeolite at 80 kPa. The figure was constructed in order to explain the effect of zirconium Na loading in increasing the amount of occluded hydrogen. It was observed at 80 kPa that the amount of occluded hydrogen on 3 wt% Zr-NaY_{5.7} zeolite was 0.15 mmol/gr and on 1 wt% Zr-NaY_{5.7} zeolite was 0.12 mmol/gr. In addition, fresh NaY_{5.7} zeolite itself can occlude hydrogen about 0.097 mmol/gr.

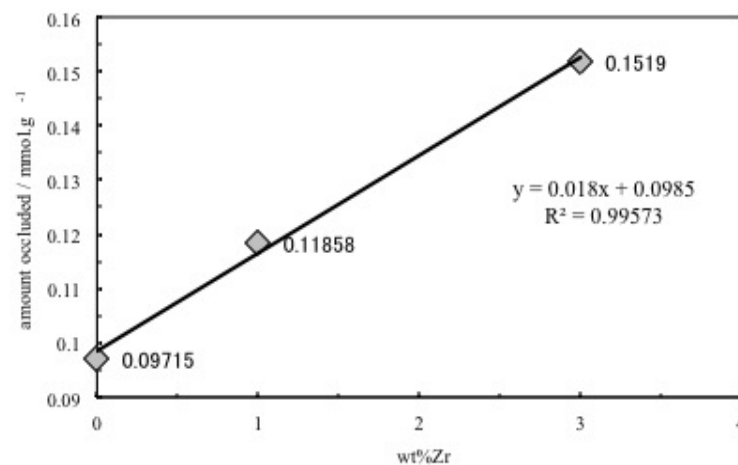


Figure 6. Comparison of occluded hydrogen amount by NaY_{5.7}, 1 wt% Zr-NaY_{5.7} composite and 3 wt% Zr-NaY_{5.7} composite at 80 kPa

Conclusions

The X-ray diffraction pattern reveals that the structure of zeolite framework is retained in the calcination condition and the metallic form of zirconium exists on zeolite particles. The specific surface areas of the Zr-NaY sample were similar to the fresh NaY_{5.7} zeolite and no collapse of the structure of zeolite framework was observed. The inclusion of zirconium inside the framework of NaY_{5.7} zeolite has increased the amount of occluded hydrogen on all synthesized samples. NaY_{5.7} zeolite itself could occlude hydrogen approximately 0.097 mmol H₂/gr at low hydrogen pressure of 80 kPa.

Acknowledgements

The author would like to thank to Toyohashi University of Technology, Japan and I am sincerely grateful to Professor Nobuyuki Nishimiya for his continued support and encouragement.

References

- Barrer R.M. 1978. Zeolite and Clay Mineral as Sorbent and Molecular Sieves, Academic Press, London.
- Breck D.W. 1974. Zeolite Molecular Sieves. Wiley & Sons, New York, USA.
- Davis M.E. 1991. Zeolites and molecular sieves: not just ordinary catalysts. *Ind. Eng. Chem. Res.* 30:1675.
- Kawai T. and Tsutsumi K. 1992. Evaluation of hydrophilic-hydrophobic character of zeolites by measurements of their immersional heats in water. *Colloid Polym. Sci.* 270:711.
- Kawai T. and Yanagihara T. and Tsutsumi K. 1994. Adsorption characteristics of chloroform on modified zeolites from gaseous phase as well as its aqueous solution. *Colloid Polym. Sci.* 272:1620.
- Gregg S.J. and Sing K.S.W. 1967. Adsorption, Surface Area and Porosity, 1st edition, Academic Press, London.
- Mulana F. 2002. Preparation and Characterization of Hydrogen Absorbing Composites. Master thesis, TuT, Toyohashi, Japan.
- Tsutsumi K., Matsushima Y. and Matsumoto A. 1993. Surface heterogeneity of modified active carbons. *Langmuir* 9: 2665.
- Rouquerol F., Rouquerol J. and Sing K.S.W. 1999. Adsorption by Powders and Porous Solid. Academic Press, London.