

GAS ADSORPTION CAPACITY OF METAL OXIDE MODIFIED ZEOLITE ADSORBENTS

Chieng Yu Yuan¹, Khairul Sozana Nor Kamarudin¹,
Halimatun Hamdan², Hanapi Mat¹

¹Advanced Process Engineering (APEN) Research Group, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81300 Skudai, Johor.

²Zeolite and Porous Material Group, Faculty of Science, Universiti Teknologi Malaysia, 81300 Skudai, Johor.

ABSTRACT

Advance developments in preparation, characterization and modification of zeolites and processes have leading to new insights in adsorbent property and performances. This research studies the modification of zeolite physicochemical properties and its gases (N₂, O₂ and CH₄) adsorptive characteristics by incorporating metal oxides into the zeolitic system using thermal monolayer dispersion method. The structures of the metal oxide modified zeolites were characterized by powder XRD; the physical features and gas adsorption capacity were analyzed using TGA and Quantachrome NOVA 1000. Results revealed that types of metal oxides, calcination temperature, metal oxide loading concentration and the modification techniques greatly affect the modified zeolite adsorbents structural properties and its gases adsorption capacity.

Keywords: Zeolites, Metal Oxides, Modification, Adsorption, Thermal Monolayer Dispersion.

1 INTRODUCTION

In the last two decades, the modification of zeolite to obtain interesting catalytic and adsorptive properties has been the object of intense research. Zeolites are microporous materials with very large internal surface areas, well-organized, regular systems of pores and cavities and uniform channels that suitable for gas adsorption. They are regenerable, physically sturdy, hydrothermal stable and resist harsh environment; they perform well over a broad spectrum of operating conditions (Frost & Sullivan, 2001).

Metal oxides are simple inorganic materials having well-defined chemical structure. In recent years, many applications have been found for them such as catalysts, magnetic materials, superconductor and semiconductor. The ability to adjust pore sizes and interlayer spacing also makes these nanostructure materials useful as molecular sieves for separation and sorption application (Benvenuti *et al.*, 1998). For example, metal oxides developed for industrial adsorbents include magnesium oxide, titanium oxide, zirconium oxide and cerium oxide (Suzuki, 1990).

Zeolites represent almost ideal matrices to host nanostructure materials. The regular pore structure of zeolite molecular sieves offers a suitable reaction or adsorption chamber for them. Many properties such as the composition, the internal surface area, the acidity, and the geometry of the system can be modified by the dispersion of oxides or salts on the surface of zeolite (Thoret *et al.*, 1997). Besides, the high thermal and chemical stability of zeolite matrices would afford the metal oxide to operate in a broad range of temperature, pressures and in various media for multiple applications in the field of catalysts, adsorbents and nanoparticles technology. In other words, this modification has opened a new route for the synthesis of novel nanostructure materials having unique physical and chemical characteristics. Various techniques have been employed for the confinement of a wide range of nanocrystalline materials, metal, metal oxide and semiconductors into or on the surfaces of ordered microporous and mesoporous structures: ion exchange, incipient wetness impregnation, chemical vapor deposition and spontaneous thermal monolayer dispersion (Kumar *et al.*, 2003). As compared with other techniques, the spontaneous

thermal monolayer dispersion as reported is relatively simple, low cost, easy control and good repeatability in preparation of metal oxide modified zeolite adsorbents. It also was shown to be very useful for obtaining modified samples with superior coke resistances, high activity, saving time, chemicals, and waste to be disposed – environmental friendly (Hagen *et al.*, 2003).

From literature investigation, most of the research works related to metal oxide-modified zeolite that prepared by various modification conditions are conducted mostly for catalysis application. Their studies do not identify the influences of different types of metal oxides to the changes of zeolite physicochemical properties and gas adsorptive characteristics in a systematic modification ways by varying and controlling the parameters (types of metal oxides, calcination temperature, metal oxides loading concentration and modification techniques) involved. The present paper reported below is a brief review of recent study in the modification and investigation of the zeolite- metal oxides that are widely applied by other researchers. Several types of gas which are industrial interest such as gas nitrogen, oxygen and gas methane adsorption capacity and characteristics onto metal oxide modified zeolite adsorbents also being investigated in order to gain a better understanding on the fundamental aspects of metal oxide-zeolite interaction and adsorbate-adsorbent interaction that might results in a novel process for the design of the special adsorbents in new era.

2 EXPERIMENTAL PROCEDURES

2.1 PREPARATION OF METAL OXIDE MODIFIED ZEOLITE SAMPLES

2.1.1 Thermal Monolayer Dispersion

2.0 g of commercial zeolite NaY is extensively mixed in a mortar with powdered metal oxide (NiO, CuO, ZnO, Ga₂O₃ and SnO) purchased from Acros, Malaysia, at a predetermined ratio corresponding to up to 5 metal oxides per unit cell NaY (290 µmol/g adsorbent). The resulting mixture is sieved to a particle size of 300 µm and consecutive calcined at elevated temperature with heating rates of 10 K/min to 873.15 K in a furnace for 24 hours.

2.1.2 Incipient Wetness Impregnation

Metal oxide modified zeolite adsorbent was prepared by impregnation of commercial zeolite NaY with equimolar amounts of metal oxide. For this study purpose, 0.1 M aqueous solution of Gallium (III) Nitrate Hydrate (10 ml) was stirred with 1.0 g of zeolite NaY at room temperature for 1 hour and after that the mixture was evaporated to dryness. Then, the sample was dried overnight at 373.15 K in oven and further calcined at 823.15 K for 5 hours leading to the transformation of the Gallium (III) Nitrate into Gallium (III) Oxide modified structure. The theoretical amount of Ga₂O₃ introduced in samples was 290µmol/g adsorbent or 5 Ga₂O₃/unit cell NaY.

2.2 ANALYTICAL PROCEDURES

In this research work, before and after metal oxide-zeolite NaY modification, the structures of modified samples were characterized by powder X-Ray Diffraction (XRD) with CuKα radiation ($\lambda = 1.5418 \text{ \AA}$) and 40 kV and 40 mA in the range of $2\theta = 2^\circ - 50^\circ$ at scanning speed of 0.05° per second. The physical features such as pore diameter, pore volume, micropore surface area and pore size distribution were determined by nitrogen gas adsorption method that carried out at 77 K using Quantachrome NOVA 1000. Meanwhile, the gases adsorption capacities were characterized using Perkin Elmer Thermogravimetric Analyzer Model TGA 7. The weight change of the adsorbent was used to determine the adsorption performance of the materials.

3 RESULTS AND DISCUSSIONS

3.1 EFFECT OF MODIFICATION PARAMETERS ON METAL OXIDE MODIFIED ZEOLITE

3.1.1 Types of Metal Oxide

A series of metal oxides (NiO, CuO, ZnO, Ga₂O₃ and SnO) were used as a guest to disperse into the zeolite NaY host matrix system. These 5 metal oxides/unit cell NaY samples were thermal monolayer dispersion prepared with the mechanical mixtures of NaY zeolites with different types of metal oxides, followed by heating at 873.15 K for 24 hours.

The XRD patterns of 5 metal oxides/unit cell NaY samples are shown in Figure 1. It is observed that the intensity of the XRD reflections slightly decreases after calcination process for 24 hours in furnace. This is accompanied by a slightly shift of XRD lines to higher 2θ values indicating a decrease in *d* spacing. It is suggested that the presence of metal oxide within the pores of the NaY zeolites thus reflected in the decrease of the intensities of XRD reflections.

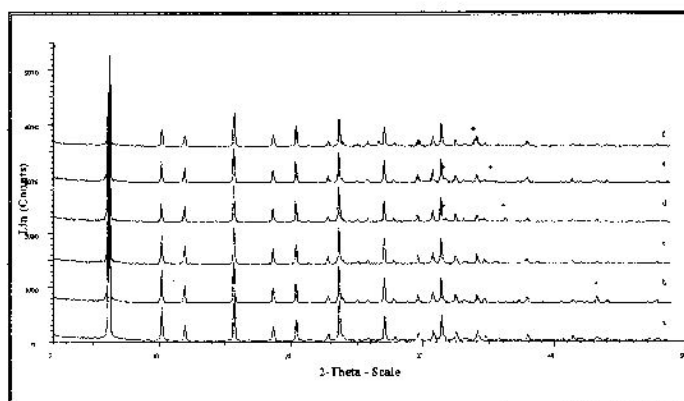


FIGURE 1. XRD Patterns of 5 Metal Oxide/Unit Cell NaY Samples. (a) NaY; (b) 5 NiO/UC (• - NiO); (c) 5 CuO/UC; (d) 5 ZnO/UC (* - ZnO); (e) 5 Ga₂O₃/UC (+ - Ga₂O₃); and (f) 5 SnO/UC (♦ - SnO₂).

The characteristic peaks of crystalline NiO, ZnO, and Ga₂O₃ with Tammann temperature of 1117 K, 1124 K and 1007 K respectively showed up clearly in their XRD patterns. However, no peaks corresponding to the crystalline phase of CuO (Tammann temperature at 800 K) and SnO (Tammann temperature at 677 K) were observed in the samples at the same loading concentration and modification condition. SnO modified zeolite NaY after heat treatment at 873.15K however was oxidized to some extent from SnO to SnO₂. The crystalline peaks of NiO, ZnO and Ga₂O₃ as expected might disappear and able to disperse well with a higher calcination temperature, which is between their Tammann temperature and melting point temperature. Different types of metal oxides could be dispersed spontaneously onto the surfaces of oxide support NaY after calcining the mixtures at a dispersive temperature with formation of a monolayer or submonolayer. In the calcination process, 3D bulk metal oxides are suggested to transformed into 2D species on the inner or outer surfaces of zeolite NaY. For these five types of metal oxide, it is clear that CuO and SnO are good pore modifiers to NaY zeolite at this dispersive temperature (600°C), which is suitable for zeolite structure stability.

The surface areas of the supports play an important role in the dispersion of metal oxides. Table 1 shows that the incorporation of metal oxide into zeolite NaY greatly diminished its specific surface area. Some pore blockage might have occurred due to high dispersion capacity of metal oxide loading. Before and after zeolite framework modification the micropore volumes and micropore surface areas decreased, which resulted from penetration of a small amount of metal oxide into the pores of the zeolite. It is interesting to found out that the average pore diameters of metal oxide modified zeolites

were broadened after modification. This enlargement of micropore diameter of NaY zeolites might due to the imbedding of metal oxides into the skeleton of NaY zeolite instead of incorporating into the pores system. These embedded metal cations might substitute the skeletal aluminium and make the pore diameter larger due to the bond length of Metal-O is shorter than Al-O. Meanwhile, the characteristic energy of the adsorption of N₂ over SnO modified NaY is the lowest compared with others metal oxide-supported zeolites, which is consistent with the result we obtained in the gas nitrogen adsorption characteristic.

TABLE 1. Physical Features of Metal Oxide-Modified Zeolite NaY Samples.

| Sample | Specific Surface Area (m ² /g) | Micropore Surface Area (m ² /g) | Micropore Volume (1×10 ⁻⁷ m ³ /g) | Average Pore Diameter (1×10 ⁻⁹ m) | Adsorption Energy, E ₀ (kJ/mol) |
|--------------------------------------|---|--|---|--|--|
| NaY | 793.33 | 847.35 | 2.99 | 1.56 | 16.28 |
| 5 NiO/UC | 364.75 | 394.78 | 1.39 | 1.68 | 16.07 |
| 5 CuO/UC | 401.37 | 439.15 | 1.55 | 1.92 | 14.94 |
| 5 ZnO/UC | 308.38 | 322.81 | 1.14 | 1.64 | 19.07 |
| 5 Ga ₂ O ₃ /UC | 216.09 | 210.14 | 0.74 | 1.78 | 16.40 |
| 5 SnO/UC | 621.06 | 710.31 | 2.51 | 1.71 | 9.81 |

3.1.2 Calcination Temperature

Apart from these, calcination temperature is one of the most important parameters that give effects on metal oxide modified zeolite physicochemical and gas adsorptive characteristics. XRD has been used to study the effect of calcination temperature on the interaction between SnO and NaY as shown in Figure 2. The results found out that the intensity of XRD pattern increased after the heat treatment at 673.15K compared with physically mixed sample, slight decrease in the diffraction peak intensity can be seen with the increase of calcination temperature. The characteristic peaks assigned to SnO disappear completely when the sample is heated at 688.15K; it means that SnO can disperse well at this optimum calcine temperature without showing any partial oxidation or residual crystalline SnO remains.

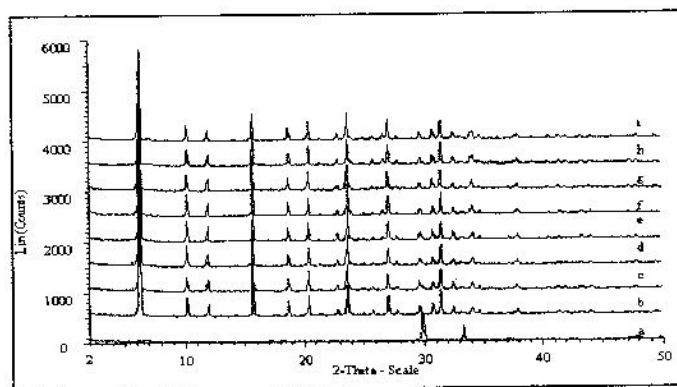


FIGURE 2. XRD Patterns of 5 SnO/NaY Samples Before and After Heat Treatment: (a) SnO; (b) NaY; (c) 5 SnO/NaY Physically Mixed; (d) 5 SnO/NaY at 673.15K; (e) 5 SnO/NaY at 688.15K; (f) 5 SnO/NaY at 723.15K; (g) 5 SnO/NaY at 773.15K; (h) 5 SnO/NaY at 873.15K; and (i) 5 SnO/NaY at 973.15K.

For samples calcined at temperature 673.15 K and below, the peaks of crystalline SnO are present, but with reduced intensity. It revealed that heating at this temperature only causes SnO to disperse onto the surface of NaY but not to diffuse into the bulk NaY. However, a high dispersion temperature could lead the SnO to oxidize to some extent. It is obvious that calcination process at 723.15K and above, SnO will oxidize to SnO₂. The calcination process at high temperature may result in the transport of metal oxide species out of pore the system and their subsequent deposition at the external surface, where they agglomerate finally to form larger size crystallites. When all the useable vacant sites are occupied, a close-packed capping O²⁻ layer is formed. This is in confirming with the XRD

data where the reflections of crystalline SnO_2 can be seen clearly and increased from 723.15K to 973.15K.

3.1.3 Metal Oxide Loading Concentration

A series of SnO/NaY samples were prepared with the mechanical mixtures of NaY zeolite with various SnO loadings (1 SnO/NaY , 3 SnO/NaY , 5 SnO/NaY , 7 SnO/NaY , 9 SnO/NaY) followed by heating at its optimum temperature 688.15 K for 24 hours. From Figure 3, we can observe that the peaks assigned to SnO crystal in the treated samples disappear completely after heating for 24 h at 688.15 K when the content of SnO is low. SnO is not known to undergo a reaction with NaY support and the transformation of SnO into amorphous phases is really impossible at the temperature of thermal treatment 688.15 K. The disappearance of the XRD peaks assigned to SnO can be interpreted as SnO spreading onto the surface of the support with the formation of a monolayer or sub-monolayer after heat treatment, 3D bulk SnO is transformed into 2D SnO species. When the content of SnO in the mixtures increases to 5 SnO/NaY and above, the peaks of crystalline SnO exist, but the relative intensities are markedly reduced after the heat treatment. The large fraction of SnO were located on the external surface of the zeolite crystals and led to a narrowing of the pore openings on the zeolite, which suppressed the further penetration of SnO into the pores of the zeolite.

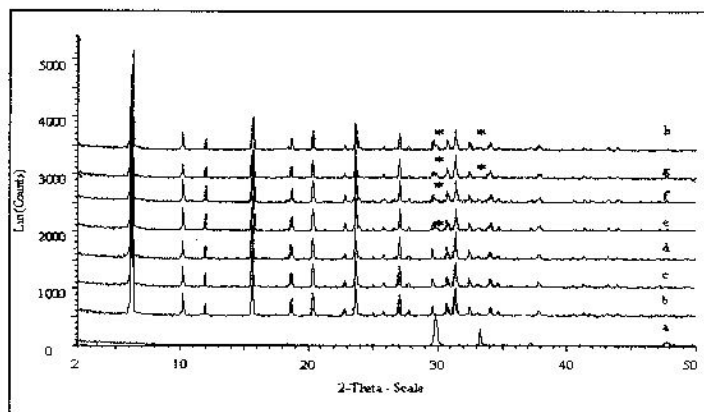


FIGURE 3. XRD Patterns of SnO/NaY Samples: (a) SnO ; (b) NaY ; (c) 1 SnO/NaY ; (d) 3 SnO/NaY ; (e) 5 SnO/NaY (* - SnO); (f) 7 SnO/NaY (* - SnO); and (g) 9 SnO/NaY (* - SnO).

There is always exist a critical dispersion capacity for each types of metal oxide content on the surfaces of supports. From the XRD patterns, we can estimate that the critical dispersion capacity of SnO onto the surface of NaY support is 5 SnO/NaY with weight ratio of about 3.9 wt%. The loading of metal oxide parameter easily influences the pore sizes of zeolite systems. Therefore, it is suggested that the pore size of zeolites can be designed to various degrees by dispersing various concentration loadings of metal oxide into zeolites, which is very important for the application on adsorbents by zeolites because different types of adsorbate required specific suitable pores of zeolites.

3.1.4 Modification Techniques

There are several types of modification techniques to disperse metal oxides on/into zeolite host matrix system. Gallium (III) oxide modified zeolite NaY adsorbents prepared by thermal monolayer dispersion method (TMD) and incipient wetness impregnation method (IWI) are compared in this work at the same loading concentration 5 $\text{Ga}_2\text{O}_3/\text{NaY}$. From the results presented in XRD pattern as shown in Figure 4, for both of the samples, as expected, Ga_2O_3 crystallites peaks showed slightly in the thermal dispersed sample but none of the sharp peaks characteristic of Ga_2O_3 crystallites is detected on the impregnated sample. These data suggest that the gallium (III) oxide is probably dispersed monolayer in or on the surface of the NaY support.

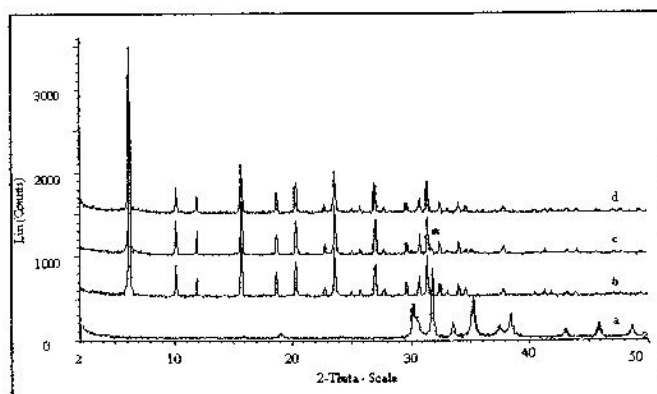


FIGURE 4. XRD Patterns of $\text{Ga}_2\text{O}_3/\text{NaY}$ Samples: (a) Ga_2O_3 ; (b) NaY ; (c) 5 $\text{Ga}_2\text{O}_3/\text{NaY}$ prepared by thermal monolayer dispersion technique (* - Ga_2O_3); and (d) 5 $\text{Ga}_2\text{O}_3/\text{NaY}$ prepared by incipient wetness impregnation technique.

In order to compare adsorption capacity of thermal monolayer dispersion with incipient wetness impregnation prepared samples, equilibrium adsorption for gas methane at 50°C and 1.3 bar using TGA Analyzer on both are shown in Figure 5. When compared both modified adsorbents, thermal dispersion modified adsorbent showed superior adsorptive capacity and higher initial adsorption rates with 21.7% and 61.5% respectively higher than the same adsorbent prepared by incipient wetness impregnation sample. When the surface areas were compared, no significant differences were encountered. In overall, adsorption rates to achieve 100% completion for both adsorbent were fast. These characteristics enable the adsorbents as good candidates for use with pressure swing adsorption process. Thus, modification techniques selection plays an important role in metal oxide modified zeolite gas adsorption capacity. These differences of modification techniques can be used to manipulate the adsorptive properties of adsorbents to suit a particular separation better.

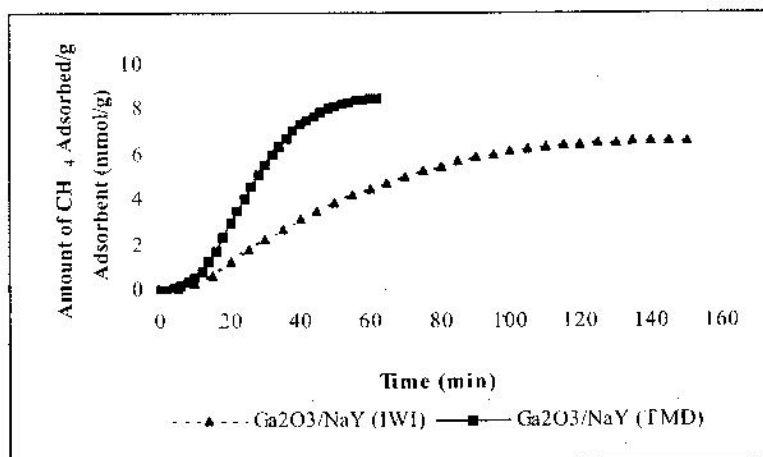


FIGURE 5. The CH_4 Adsorption Curve of Ga_2O_3 Modified Zeolite NaY .

3.2 GAS ADSORPTIVE CHARACTERISTICS OF METAL OXIDE MODIFIED ZEOLITE

Based on the characterization data presented in Figure 6, it is observed that the gas nitrogen and oxygen adsorption capacity decreased after metal oxide-zeolite modification. However, incorporation of CuO and Ga_2O_3 into zeolite NaY greatly enhanced gas methane adsorption capacity to 31.6% and 3.7% respectively. These data are not enough to explain the mechanism showing why the adsorptivity of gas CH_4 could be improved by mechanically mixing CuO with NaY materials. It is suggested that after calcining the CuO with NaY at a high temperature, some of the CuO might migrate and coated on the surface of NaY through solid-state reaction. The surface coating of CuO onto NaY may influence

the surface reactivity of CuO with gas CH₄. Result here revealed that no matter what the coexistence state of the metal oxide on NaY support is, the difference in adsorption capacity of different types of gases (N₂, O₂, and CH₄) into the pore structures of modified adsorbents give changes to the gases selectivity that is important and needed to be discover further.

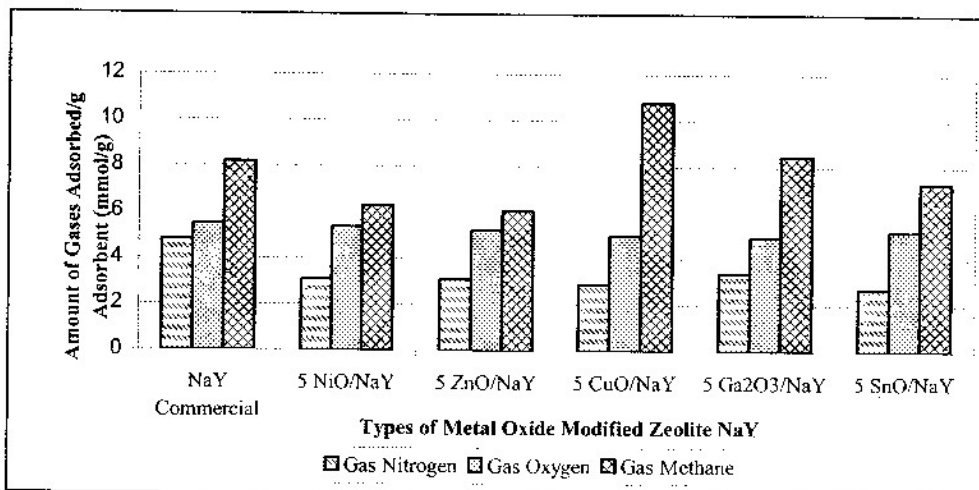


FIGURE 6. Gases Adsorption Characteristics of Metal Oxides Modified Zeolite NaY.

4 CONCLUSION

Metal oxide-zeolite modification parameters such as types of metal oxide or substrate, calcination temperature, metal oxide loading concentration and modification techniques will greatly influence the physicochemical properties of zeolite and its gas adsorptive characteristics. By controlling all of the parameters involved well, it is possible to get a new finding in designing zeolite system as special adsorbents in new era.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to the IRPA grant No. 74512 from the Ministry of Science, Technology and Environment, Malaysia, and National Science Foundation (NSF) Fellowship awarded to Chieng Yu Yuan.

REFERENCES

- Benvenuti, E. V., and Gushikem, Y. (1998). Comparative Study of Catalytic Oxidation of Ethanol to Acetaldehyde Using Fe(III) Dispersed On Sb₂O₃ Grafted On SiO₂ and On Untreated SiO₂ Surfaces, *J. Braz. Chem. Soc.*, 9, 469-472.
- Frost and Sullivan. (2001). *Zeolites: Industry Trends and Worldwide Markets In 2010*. New York: Technical Insights.
- Hagen, A., Schneider, E., Kleinert, A., and Roessner, F. (2003). Modification of Acid Supports by Solid-State Redox Reaction. Part I, Preparation and Characterization, *Journal of Catalysis*, *In Press*.
- Kumar, D., Bera, S., Tripathi, A. K., Dey, G. K., and Gupta, N. M. (2003). Uranium Oxide Nanoparticles Dispersed Inside The Mesopores of MCM-48: Synthesis and Characterization, *Microporous and Mesoporous Materials*, 66, 157-167.
- Suzuki, M. (1990). *Adsorption Engineering*. New York: Elsevier Science Publishing.
- Thoret, J., Man, P. P., and Fraissard, J. (1997). Solid-Solid Interaction and Reaction Between Antimony Oxide and NaY or LaNaY Zeolites. Comparison With V₂O₅ and MoO₃, *Zeolites*, 18, 152-161.