

ZEOLITE SYNTHESIS FOR METHANE ADSORBENT: EFFECT OF EXPERIMENTAL CONDITIONS ON STRUCTURAL FRAMEWORK FORMATION*

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ABSTRACT

Zeolites are seen as a potential adsorbent for methane due to the ability of the microporous structure to adsorb molecules selectively, depending upon the size of the pore window. The understanding of factors that affect the formation of zeolite framework is very important as it will affect the physical and chemical properties the zeolite. Therefore, in this research, zeolites have been hydrothermally synthesized in the laboratory with different SiO₂/Al₂O₃, crystallization time, and temperature. SiO₂/Al₂O₃ affects the crystallinity of zeolite sample without changing the structural framework formed. However, crystallization time and temperature affect the structural frameworks formed.

Keywords: zeolites; synthesis; adsorbent; structural framework.

INTRODUCTION

There are in principle many different shapes and dimensions of intracrystalline cavity and channel in zeolite topologies. The accessibility of the intracrystalline pores is governed by aperture or window made by linked tetrahedral. There are two types of structures: one provides an internal pore system comprised of interconnected cage-like voids; the second provides a system of uniform channel [1]. Faujasite type is the most open framework that has the biggest cavities and cavity entrances of any known zeolites. This zeolite can act as an adsorbent for gas molecules such as methane.

Zeolites can be synthesized from a wide range of batch composition and temperatures. It can also be made from a variety of alumina and silica sources. It involves a few elementary steps by which a mixture of Si and Al species, metal cations, and water are converted via an alkaline supersaturated solution into a microporous crystalline aluminosilicate [2]. It can be obtained under hydrothermal condition from Na₂O – SiO₂ – Al₂O₃- H₂O gels from commercial reagents. Hydrothermal synthesis of aluminosilicate zeolites involves a few elementary steps by which a mixture of Si and Al species, metal cations, organic molecules and water is converted via alkaline supersaturated solution into a microporous crystalline aluminosilicate. The complex processes involved in this transformation can be denoted as zeolitization. The process of zeolitization is thermally activated and usually takes place at elevated temperatures in order to achieve high yield of crystals in an acceptable period of time [3]. Zeolites that have been synthesized are of several types, namely zeolite A, aluminophosphate, zeolite beta, borosilicate, clinoptilolite, faujasite, ferrisilicate, gallosilicate, high silica, zeolite L, MCM, mordenite, sodalite, and zeolite omega. All the synthetic zeolites are distinguishable from each other

* Poster presentation at 'National Symposium of Science and Technology' Ministry of Science, Technology, and Environmental, Golden Horse Palace, Kuala Lumpur, 28 – 30 July, 2003.'

and from natural zeolites on the basis of composition, crystal structure and sorption characteristics [4]. Our studies aimed at the synthesis of zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, crystallization temperature and time.

EXPERIMENTAL PROCEDURE

The synthesis was carried out by using reactant mixture with the molar composition of $6.4\text{Na}_2\text{O}: 1\text{Al}_2\text{O}_3: x\text{SiO}_2: 180\text{H}_2\text{O}$ and the hydrothermal process was carried out in a temperature range of $100 - 200^\circ\text{C}$ at different crystallization time (24 hours – 30 days). In preparing gel composition, sodium aluminate anhydrous (Riedel-de Haën) was added into sodium hydroxide (MERCK) solution and heated under rigorous stirring until dissolved. Ludox was added into sodium hydroxide solution and heated under rigorous stirring until clear solution appeared. Both solutions were mixed and stirred for 2 hours to obtain a homogeneous mixture. Then, the mixture was transferred into a container (polyethylene bottle or Teflon lined autoclave) and heated in an oven at different temperature and time for crystallization. After that, the solids were recovered by filtration, washed with distilled water until $\text{pH} < 10$ and then dried overnight in the oven at 100°C . The parameter used and their respective values are in Table 1. The structure of synthesized zeolite was identified using X-ray diffractometer (Bruker) to determine the structural framework with $\text{CuK}\alpha_1$ radiation of $\lambda = 1.5418\text{\AA}$ at 40 kV and 20mA in the range of $2\theta = 5^\circ - 50^\circ$ at scanning speed of 0.05° per second.

Table 1: The experimental conditions used in this study.

Sample	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Temperature ($^\circ\text{C}$)	Time
Na-16	4	100	24 hours
Na-18	8	100	24 hours
Na-21	12	100	24 hours
Na-24	20	100	24 hours
Na-18(b)	8	100	10 days
Na-18(c)	8	100	15 days
Na-18(d)	8	100	21 days
Na-18(e)	8	100	30 days
Na-18(f)	8	150	24 hours
Na-18(g)	8	200	24 hours

RESULTS AND DISCUSSION

Different samples have been synthesized by varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the reactant mixture, time and temperature of crystallization. The powder XRD patterns of four zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ are shown in Fig. 1. The position and the relative intensities are in good agreement with those reported in the literature [5]. All samples have faujasite type of framework with different intensities (Fig.1). The crystallinity of the sample increases as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ increasing. However, amorphous phase was observed at low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Fig. 2 is a diffraction pattern of zeolites with different crystallization time. Faujasite transformed into gismondine as the time was extended from 24 hours to 30 days. This is due to the occurrence of successive phase transformation (Oswald's Rule) where the thermodynamically least favorable phase will crystallize first, and will be successfully replaced in time by more stable phases [2]. The crystallization temperature also influence the type of zeolite formed. At 100°C faujasite type of framework was formed, but at higher temperature (150°C and 200°C) analcime type of framework was formed (Fig.3).

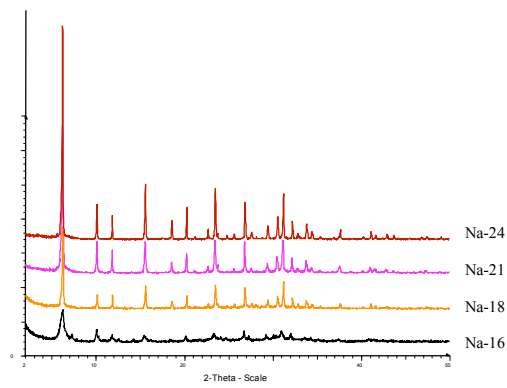


Fig. 1: Diffraction patterns of zeolites for different $\text{SiO}_2/\text{Al}_2\text{O}_3$.

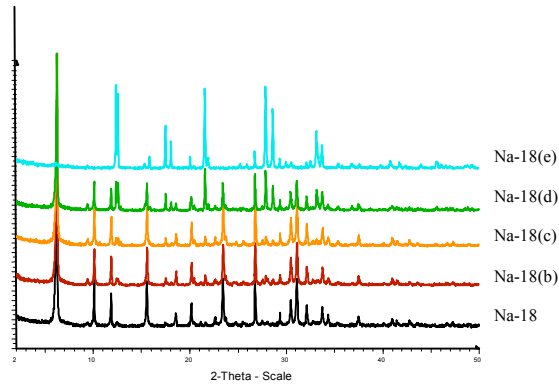


Fig. 2: Diffraction patterns of zeolites for different crystallization time.

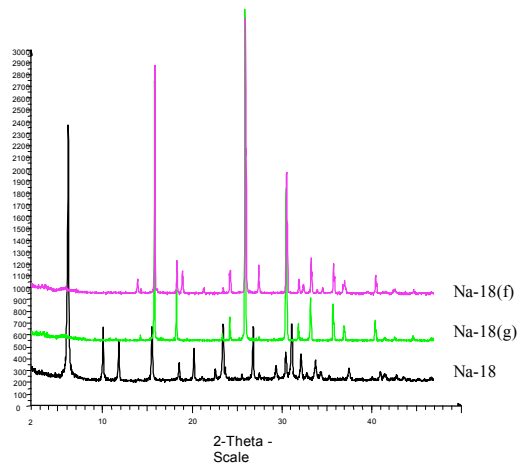


Fig. 3: Diffraction patterns of zeolites for different crystallization temperature.

Table 2: Structural framework of zeolites obtained for different experimental conditions.

Sample	Structural framework
Na-16	Faujasite
Na-18	Faujasite
Na-21	Faujasite
Na-24	Faujasite
Na-18(b)	Faujasite
Na-18(c)	Faujasite
Na-18(d)	Faujasite + gismondine
Na-18(e)	Gismondine
Na-18(f)	Analcime
Na-18(g)	Analcime

CONCLUSION

Our results suggest that $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio affects the crystallinity of zeolites but maintain faujasite structural framework. However, crystallization time and temperature affect the structural framework formation. Gismondine and analcime were formed when the crystallization time and temperature were altered respectively. Therefore, the formation of zeolite structural framework is influenced by the experimental condition such as $\text{SiO}_2/\text{Al}_2\text{O}_3$, crystallization time and temperature.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support from the Ministry of Science, Technology and Environment, Malaysia (IRPA grant No. 74512), and the Universiti Teknologi Malaysia for the scholarship awarded to Khairul Sozana Nor Kamarudin to make this study possible.

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