



# Synthesis of zeolite ZSM-48 from rice husk ash

H. Paul Wang<sup>\*</sup>, Kuen Song Lin, Y.J. Huang, M.C. Li, L.K. Tsaur

*Department of Environmental Engineering, Cheng Kung University, Tainan, Taiwan*

---

## Abstract

Zeolite ZSM-48 with a very high crystallinity (99%<sup>+</sup>) can be synthesized from a reaction mixture containing a silica source from rice husk gasification ash. The difference in the cracking behavior of *n*-hexane for zeolites ZSM-5 and ZSM-48 may be attributed to the unique two-dimensional channel structure for the ZSM-48. The ammonia desorption data also indicate that the influence of the channel system of ZSM-48 could play an important role in the molecular traffic control. © 1998 Elsevier Science B.V.

*Keywords:* ZSM-48; Zeolites; Rice husk; Recycling

---

## 1. Introduction

South and South East Asia account for over 90% of world's rice production [1]. Rice husk is a major by-product of the rice-milling industries and is abundantly available. However, rice husks have been considered as a waste, causing disposal problems. Like most other biomass materials, rice husk contains a high amount of organic volatiles. Thus, rice husk is recognized as a potential source of energy [2]. Gasification of rice husks has been known as one of the most effective technology options for the utilization of a renewable energy resource. Moreover, its 20% (approximately) ash content comprising of over 95% amorphous silica would make the rice husk utilization systems becoming very economically attractive [2].

Previous studies have indicated that oxidation of rice husks at > 973 K results in a physical structural transformation of silica from its original amorphous state to crystalline state thereby encapsulating residual carbons [2]. Once the structural changes of

---

<sup>\*</sup> Corresponding author. Tel.: +886 6 2757575 ext. 54551; fax: +886 6 2752790; e-mail: wanghp@mail.ncku.edu.tw

husk rice silica occur, the combined carbon becomes unavailable for further oxidation reactions even at higher temperatures. The carbonaceous ash has little utility except for landfill.

The advent of shape-selective catalysis, first discovered and reported by Weisz and Frilette [3] in the early 1960s, has created new opportunities to direct and control catalytic reactions involving hydrocarbons. A new zeolite designated ZSM-48 was synthesized in the early 1980s [4]. Zeolite ZSM-48, first found as an impurity phase in zeolite ZSM-39, has a framework based on the ferrierite sheet with linear non-interpenetrating 10-membered ring channels (ideal dimensions are  $5.3 \times 5.6 \text{ \AA}$  running perpendicular to the sheet) [5]. Schlenke et al. [6] have proposed that ZSM-48 has a structure that is based on ferrierite sheets linked via bridging oxygens located in a mirror plane.

Zeolite ZSM-48 can be prepared [7–10] from a reaction mixture containing a source of silica, optionally alumina, alkali metal oxides, water and an organic amine (RN) (RN is a  $C_1$ – $C_{20}$  organic compound having an amine functional group of  $pK \geq 7$ ). It has been recognized that ZSM-48 exhibits a high selectivity for olefins in the methanol conversion. The unique catalytic and shape selectivity properties of ZSM-48 have been attributed to its pore and channel structures [11]. Thus, the main objective of this work was to synthesize and characterize zeolite ZSM-48 utilizing the silica source found in the ash of rice husk gasification process (for power generation).

## 2. Experimental

Zeolite ZSM-48 was prepared from a reaction mixture containing a source of silica (rice husk ash), an organic compound ( $C_6$ DN) having an amine functional group with  $pK_a > 7$  and an alkali metal oxide (sodium oxide) and water. The composition ranges for the compounds comprising the reaction mixture are presented in Table 1 in terms of the mole ratios of the oxides. The mixture was maintained at 443 K in a stainless-steel autoclave until crystals of ZSM-48 were formed. The sodium-form ZSM-48 was subsequently exchanged three times with a 1 N ammonium nitrate solution at 298 K. The ammonium-form of ZSM-48 was heated for 16 h at 1023 K to obtain the hydrogen form of the catalyst.

The structures of the synthesized zeolites were investigated using X-ray diffraction spectroscopy (Rigaku D/Max X-ray Diffractometer). The morphology of the zeolites

Table 1  
Composition ranges in terms of mole ratios for the synthesis of ZSM-48

Reactants	Valyocsik's work [9]	This work
$Al_2O_3/SiO_2$	0–0.01	~ 0.002
$Na/SiO_2$	0.1–1.0	0.01–0.6
$RN/SiO_2$	0.05–1.0	0.1–0.3
$OH^-/SiO_2$	20–70	40

prepared in this investigation was examined by a Hitachi X-530 scanning electron microscope (SEM) equipped with an X-ray detector (Jeol JSMr840 SEM). A diffuse reflectance infrared cell was used in a Digilab FT-IR spectrometer (model FTS-40) to study the structural information of zeolite samples.

A microreactor/TPD (temperature programmed desorption) apparatus was used to study normal-hexane cracking ( $\alpha$ -test) and temperature-programmed ammonia desorption. The cracking of *n*-hexane provides a suitable test reaction for measuring the acidity of the zeolites since *n*-hexane is free of diffusion limitations for zeolite ZSM-48. Measurements were carried out with *n*-hexane in a continuous flow microreactor at temperatures at which the conversion is above 5%, for accuracy of measurement and below about 40% to avoid complications due to reactant and/or product transport limitations.

### 3. Results and discussion

Zeolite ZSM-48 was prepared from a reaction mixture containing a silica source from rice husk gasification ash. The effect of the crystallization time on the synthesis of ZSM-48 is shown in Fig. 1. The XRD spectra indicate that ZSM-48 with a high crystallinity could not be obtained within 30 h of crystallization time in the autoclave at 443 K. However, extending the crystallization time to, for instance, 78 h, a mixture of ZSM-5 and ZSM-48 was synthesized. The SEM micrograph indicates that zeolites ZSM-5 and ZSM-48 are not intergrowth crystals but rather physical mixtures of the two zeolites.

According to the Flanigen–Khatami–Szymanski correlation [12], the  $650\text{--}550\text{ cm}^{-1}$  band was empirically assigned to the presence of double-rings of tetrahedral in the framework of a zeolite. A band around  $500\text{ cm}^{-1}$ , which was not observed in silica, may be attributed to internal vibrations of ZSM-48. The optical density ratios of the A ( $\sim 600\text{ cm}^{-1}$ ) and B ( $\sim 500\text{ cm}^{-1}$ ) bands determined from normal coordinate calculations are presented in Table 2. It appears reasonable to use the optical density ratio, A/B, as a criterion for determining the structural characteristics of the zeolite frameworks since the ratio depends on the variety of the external vibrations of the zeolites. Thus, one may predict that the A/B ratio increases as the degree of the external vibrations, which are assigned to linkages of the  $\text{TO}_4$ -tetrahedral, increases. This is true for high crystallinity zeolites, the A/B ratio of ZSM-48 is equal to 0.25 and that of ZSM-5 is equal to 0.82.

The typical temperature-programmed desorption (TPD) profiles for ammonia desorption from HZSM-48 are shown in Fig. 2. At least four discrete features at 410, 480, 700 and 830–860 K were observed corresponding to adsorption in site I, site II, site III and site IV, respectively. Since the interactions between ammonia and sites I and II are weak for ZSM-48, they are attributed to physisorbed ammonia on ZSM-48 surfaces. It is believed that site III and site IV are the Brønsted acid sites and Lewis acid sites, respectively. The broadening of the desorption band in the temperature range assigned to type III sites may be due to the influence of the channel system of ZSM-48 which could

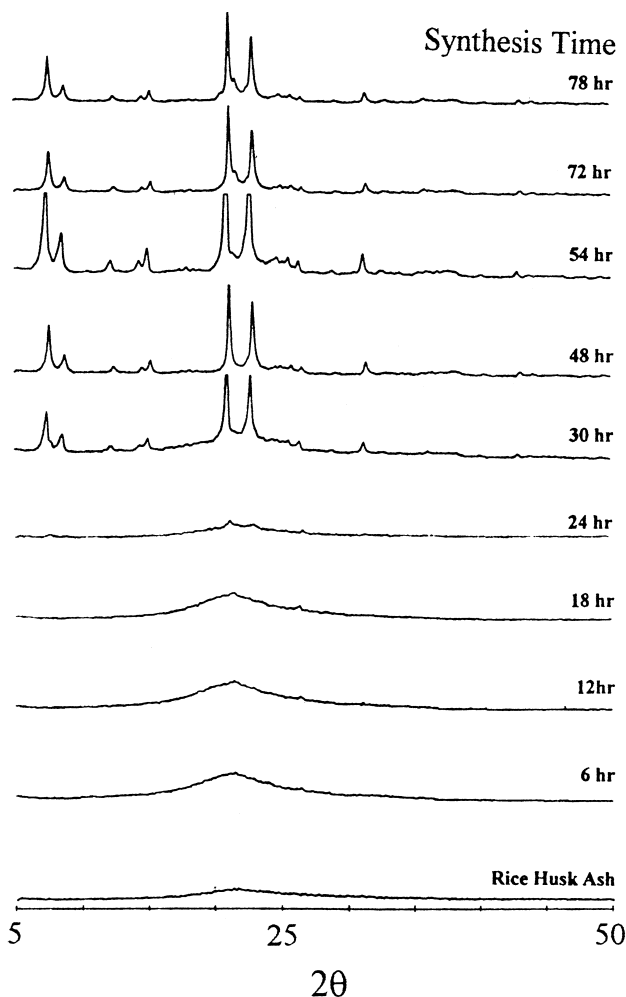


Fig. 1. X-ray diffraction patterns of synthesized ZSM-48—effect of crystallization time on zeolite crystallinity.

also play a role in molecular traffic control with desorbed ammonia. It should be noted that ZSM-48 has an intermediate pore diameter and a two-dimensional non-intersecting channel system [6].

Table 2  
Structural characteristics of the zeolite frameworks

Zeolites	SiO <sub>2</sub> source	Optical density ratio <sup>a</sup> , A/B	XRD crystallinity
HZSM-5	SiO <sub>2</sub>	0.82	99 <sup>+</sup>
HZSM-48	SiO <sub>2</sub>	0.25	99 <sup>+</sup>
HZSM-48	Rice husk ash	0.25	99 <sup>+</sup>

<sup>a</sup>Optical density ratio (A/B) is defined in the text.

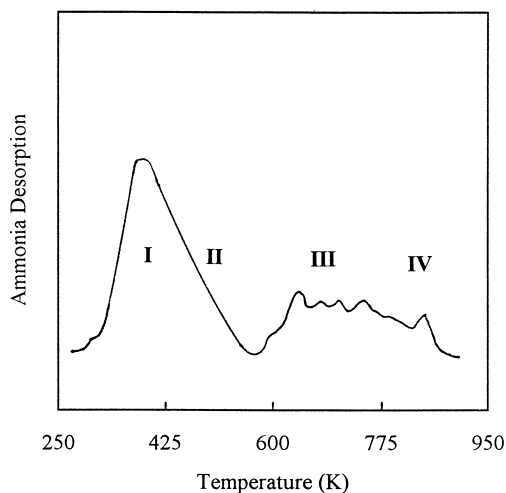


Fig. 2. Temperature-programmed desorption spectrum of ammonia on HZSM-48.

The cracking of *n*-hexane provides a suitable test reaction that is free of diffusion limitations for the intermediate pore size zeolite ZSM-48. The results of hexane cracking over crystalline aluminosilicates including ZSM-5 and ZSM-48 are presented in Fig. 3. Attainable levels of superactivity of the order of magnitude of  $\alpha > 10\,000$  (relative to amorphous silica–alumina,  $\alpha = 1$ ) were obtained for both ZSM-5 and ZSM-48. The zeolite ZSM-5 showed a normal apparent activation energy of 30 kcal/mol. Interestingly, a deviation in apparent activation energy from the generally prevailing behavior

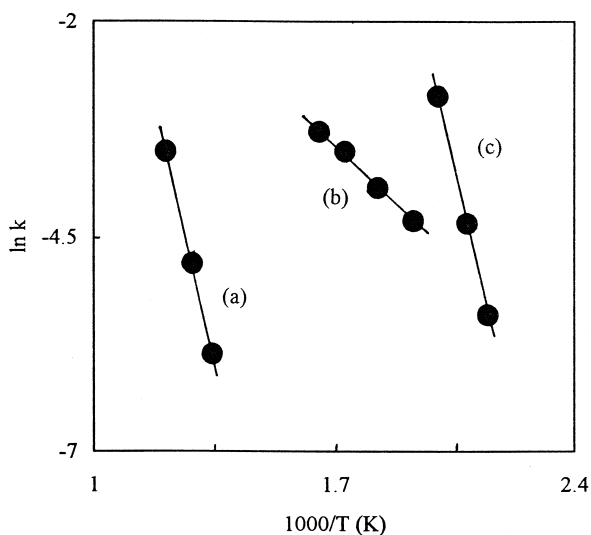


Fig. 3. Normal-hexane cracking activity with (a) aluminosilica and zeolites (b) HZSM-48 and (c) HZSM-5.

for the ZSM-48 type zeolites was found. This indicates that the true intrinsic rate constant of the ZSM-48 type zeolites was even greater than measured. The results may be attributed to the unique two-dimensional channel structure for the ZSM-48.

#### 4. Conclusions

Zeolite ZSM-48 with a high crystallinity can be synthesized from a reaction mixture containing a silica source from rice husk gasification ash. For high crystallinity zeolites, the optical density ratio, A/B (a criterion for determining the structural characteristics of the zeolite frameworks), for ZSM-48 is equal to 0.25. The difference in the cracking behavior of *n*-hexane for zeolites ZSM-5 and ZSM-48 may be attributed to the unique two-dimensional channel structure for the ZSM-48. The ammonia desorption data also indicate that the influence of the channel system of ZSM-48 could play an important role in the molecular traffic control.

#### Acknowledgements

The assistance of Professor F.V. Hanson of the University of Utah and the financial support of the National Science Council of Taiwan, R.O.C. (NSC86-2113-M-006-020 and NSC86-2621-P-006-003) are gratefully acknowledged.

#### References

- [1] T.B. Reed, Biomass Gasification Principles and Technology, Noyes Data, Park Ridge, NJ, 1981.
- [2] A. Kaupp, Gasification of Rice Hulls: Theory and Practices, Deutsches Zentrum Fuer Entwicklungs Technologies (GATE) Eschborn, 1984.
- [3] P.B. Weisz, V.J. Frilette, J. Phys. Chem. 64 (1960) 382.
- [4] C.D. Chang, C.T.W. Chu, P.D. Perkins, U.S. Patent 4,476,338 (1984).
- [5] P. Chu, U.S. Patent 4,397,827 (1981).
- [6] J.L. Schlenke, W.J. Rohrbaugh, P. Chu, E.W. Valyocsik, G.T. Kokotailo, Zeolites 5 (1985) 355.
- [7] L.D. Rollmann, E.W. Valyocsik, Eur. Pat. 15,132 (1980), U.S. Patent 4,423,021 (1983).
- [8] P. Chu, Eur. Patent 23,089 (1980), U.S. Patent 4,448,675 (1984), US Patent 4,397,827 (1983).
- [9] E.W. Valyocsik, U.S. Patents 4,585,747 and 4,568,654 (1986).
- [10] W. Fan, R. Li, B. Fan, J. Ma, J. Go, Appl. Catal. A 143 (1996) 299.
- [11] K.S. Lin, H.P. Wang, M.C. Li, Appl. Catal. B, submitted.
- [12] E.M. Flanigen, H.A. Szymanski, H. Khatami, Molecular sieve zeolite I, in: R.F. Gould (Ed.), Advances in Chemistry, ACS Series 101, Washington, DC, 1976, p. 206.