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catalyst

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# Surface structure of alkylsilylated HZSM-5 as phase-boundary catalyst

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**ABSTRACT** : The need for cleaner environment concerns motivates the development of more efficient catalytic system. Based on this consideration, recently a novel catalyst named "Phase-boundary catalyst", a bimodal amphiphilic solid catalyst, was proposed. It was demonstrated that the catalytic system containing phase-boundary catalyst required neither stirring to make an emulsion nor addition of a co-solvent to make a homogeneous solution to drive the reaction. The driving force that has prompted this paper is to investigate the surface structure of alkylsilylated HZSM-5 as phase-boundary catalyst. Temperature Programmed Desorption (TPD) of ammonia and,  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR spectroscopy were used to elucidate the surface structure of alkylsilylated HZSM-5. It is suggested the addition of small amount of water to the solid particles before alkylsilylation, as a recipe to make a bimodal amphiphilic particles, is desired to enhance the acidity of HZSM-5. The enhancement of acidity might be induced by polymeric octadecylsiloxane as elucidated by  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR spectroscopy.

**KEYWORDS** : HZSM-5; polymeric octadecylsiloxane; phase-boundary catalyst

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## 1 INTRODUCTION

Recently, a novel concept of "phase-boundary catalysis" (PBC) in order to utilize the immiscible liquid-liquid reaction system with solid catalysts was proposed [1-4]. In the PBC system, the bifunctional particles, containing both hydrophilic and hydrophobic regions, were placed at the phase boundary in order to catalyze the reaction without requiring an emulsion containing the catalyst by stirring. This system offers advantages in terms of ease of separation, the possibility of continuous supply of immiscible substrates and working effectively without co-solvent. Proposed model of catalyst for immiscible liquid-liquid reactions is shown in Fig. 1. The phenomenological aspects of catalytic functions in PBC and its correlation with bimodal amphiphilic character of the catalyst have been reported previously [1-6]. It was found that the highest catalytic activity under static conditions was observed when the catalyst was located at the phase boundary. We concluded that the location of catalysts in immiscible liquid-liquid system plays an important role in the reaction. However, in order to establish the PBC concept, the understanding the surface structure of phase-boundary catalyst is a conditional prerequisite and of utmost important. The emphasis of this ar-

title will therefore be to understand the surface structure of alkylsilylated HZSM-5 as a model of phase-boundary catalyst. The detail surface structures of catalyst particles is examined in more detail, focusing on clarification of the arrangement of alkylsilyl groups on the surface of particles by using Temperature Programmed Desorption (TPD) of ammonia,  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR spectroscopy.

## 2 EXPERIMENTAL

### 2.1 Catalyst preparation

HZSM-5 zeolite powder was supplied by Zeolyst International (CBV 8014) and used after treatment at 450 °C under nitrogen atmosphere. Modified HZSM-5 on which the external surface was partly covered with alkylsilane was prepared by attachment of *n*-octadecyltrichlorosilane (OTS). This preparation method is same as given in our recent papers [1-4]. In typical experiment, in order to modify HZSM-5 with alkylsilane, the HZSM-5 powder containing water (0.5 g per 1.0 g of HZSM-5) was immersed in 10 ml toluene containing 500  $\mu\text{mol}$  of *n*-octadecyltrichlorosilane (OTS, Aldrich) and the suspension was shaken for ca. 15 minutes at room temperature. Then, the solid was

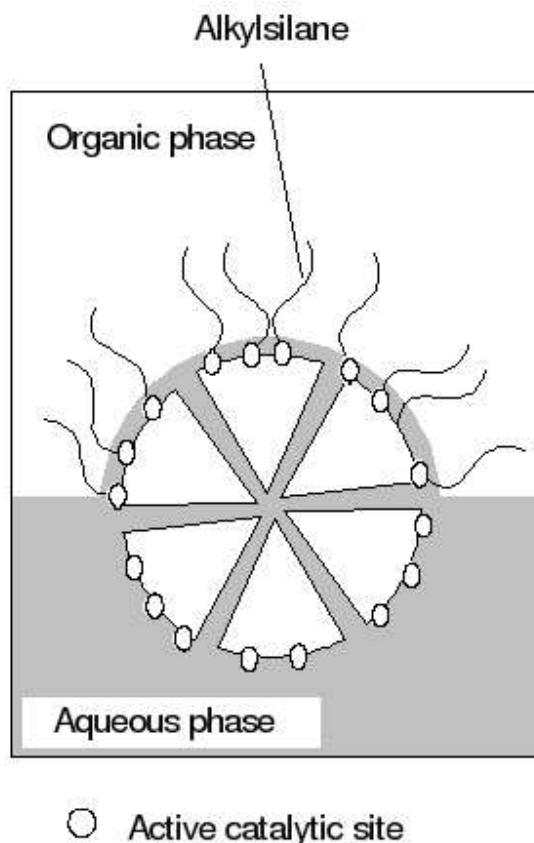


FIGURE 1: Proposed model of catalyst for immiscible liquid-liquid reactions.

collected by centrifugation and dried at 110 °C for overnight. Due to the hydrophilicity of the HZSM-5 surface, addition of a small amount of water led to aggregation owing to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates, in contact with organic phase can be modified with OTS. The partly modified sample was labeled *w/o*-HZSM-5. Fully modified HZSM-5 (*o*-HZSM-5) was prepared without addition of water.

## 2.2 Characterization of catalysts

A TPD/R/O 1100 ThermoFinnigan was used for the temperature programmed desorption (TPD) measurements. The sample was heated at 450 °C for 2 hours and cooled down to 80 °C before passing ammonia. After saturation with ammonia, the sample was flushed with  $N_2$  to remove the physically adsorbed  $NH_3$ . The temperature of desorption was increased at the rate of 10 °C/min. Due to the alkyldisilyl groups are decomposed at 500 ~ 700 °C and the desorption of ammonia also occurs at this range of temperatures,

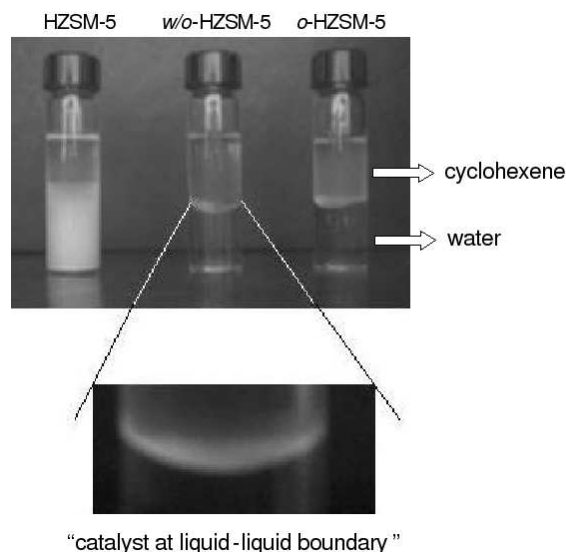


FIGURE 2: Photographs of modified HZSM-5 zeolite particles in a cyclohexene-water: (a) HZSM-5, (b) *w/o*-HZSM-5, (c) *o*-HZSM-5.

the peak of the desorption of ammonia is plotted by means of subtraction of the TPD curve of ammonia desorption with TPD curve without the presence of ammonia. The MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The  $^{29}Si$  MAS NMR spectra were recorded at 79.44 MHz using 5.5  $\mu s$  radio frequency pulses, a recycle delay of 20s and spinning rate of 7.0 kHz. The  $^{13}C$  NMR, spectra were collected by a Cross Polarization (CP) MAS method with a 1000  $\mu s$   $^{13}C$  pulse and 5 s recycle delay. Both  $^{29}Si$  and  $^{13}C$  NMR chemical shifts were referred to TMS at 0 ppm.

## 3 RESULTS AND DISCUSSION

As shown in Fig. 2, when the *w/o*-HZSM-5 particles were added to a mixture of cyclohexene and water, they were feasibly located just at the liquid-liquid phase boundary, whereas HZSM-5 and *o*-HZSM-5 were dispersed in aqueous and organic phases respectively. To gain an idea about the nature of the active sites present in the catalysts, TPD of ammonia analysis has been made. Results of the TPD of ammonia on HZSM-5, *w/o*-HZSM-5 and *o*-HZSM-5 are presented in Fig. 3. The ammonia TPD profiles of HZSM-5 and *o*-HZSM-5 samples consist of two peaks at 175 °C and 475 °C. It is evident that the peaks at 175 °C of *w/o*-HZSM-5 is shifted to a higher temperature, i.e., 280 °C; suggests that *w/o*-HZSM-5 possesses a stronger acidity. It was observed that the peak areas of *w/o*-HZSM-5 and *o*-HZSM-5 are similar than that

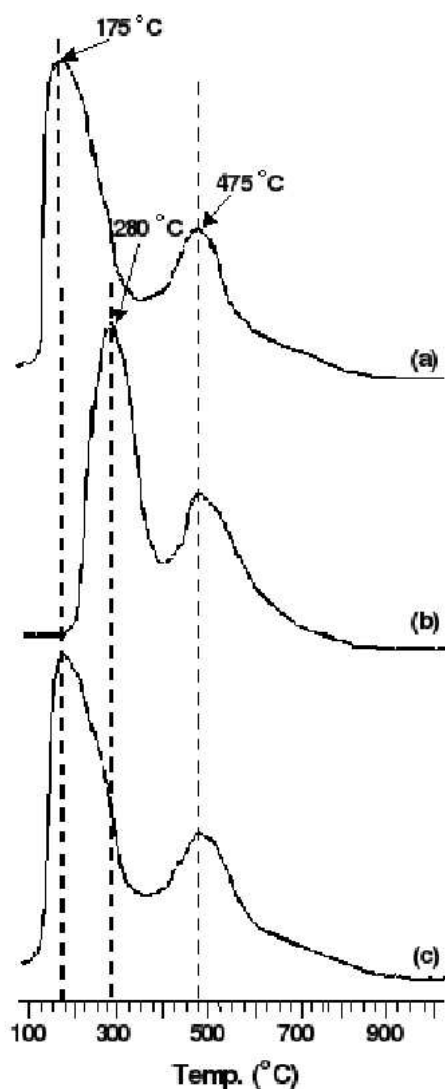


FIGURE 3: TPD curves of ammonia adsorbed of (a) HZSM-5, (b) *w/o*-HZSM-5 and (c) *o*-HZSM-5.

of original HZSM-5, suggesting the amount of acidity is similar. In order to explain why *w/o*-HZSM-5 possesses a stronger acidity, the local structure of the catalyst was elucidated by  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR. Fig. 4 shows the  $^{13}\text{C}$  CP/MAS NMR spectra of *w/o*-HZSM-5 and *o*-HZSM-5. The intense peak at 34 ppm corresponds to the well-oriented methylene carbons. The peak is characteristic of the  $^{13}\text{C}$  chemical shift for the crystallite methylene carbons of the alkane chains in the all-trans conformation. The peak at 32 ppm which appears as a shoulder in the spectrum correlated to the methylene chain. Thus, the chemical-shift position of the resonance associated with the internal methylene can be used to measure the degree of order in the amorphous phase

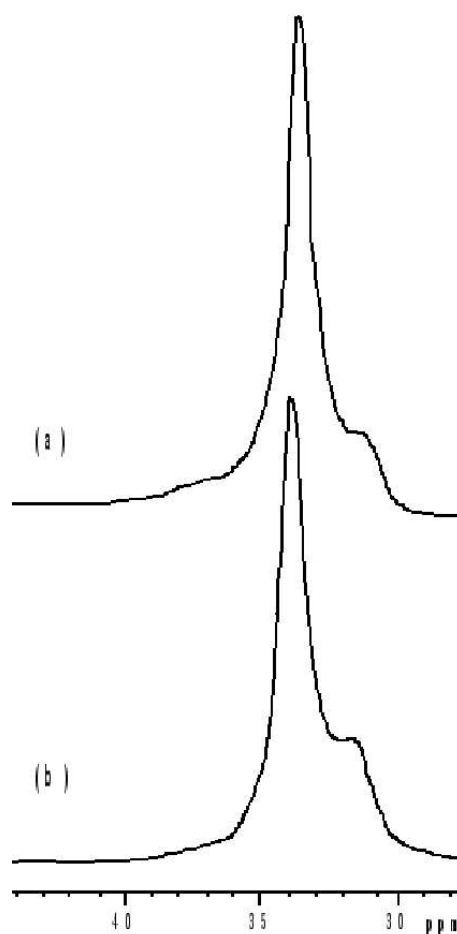


FIGURE 4:  $^{13}\text{C}$  CP/MAS NMR of (a) *o*-HZSM-5 and (b) *w/o*-HZSM-5.

with gauche conformation in the long-chain molecules. By comparison the peak at 34 ppm (highly ordered methylene chains) and 32 ppm (less ordered methylene chains), it was observed that the chain conformation of *o*-HZSM-5 is more symmetrical and compact packing compared to *w/o*-HZSM-5 which is more irregular and loosely packed.

The close-packed conformation of the carbon chains is also evident in  $^{29}\text{Si}$  MAS NMR results (Fig. 5). The intense peak at -110 ppm is from  $\text{Si}(3\text{SiO})$  in hydrolyzed OTS and from HZSM-5. In Fig. 5, three additional peaks from -50 to -80 ppm correspond to three different environments of the siloxane groups in the modified HZSM-5 [7]: (i) isolated groups that are not bound to any neighboring siloxanes (ii) terminal groups that are only bound to one neighbouring siloxane, and (iii) cross-linked groups that are bound to two neighbouring siloxane. Due to the presence of small amount of alkylsilane in *w/o*-HZSM-5, only peaks with low intensities were observed.

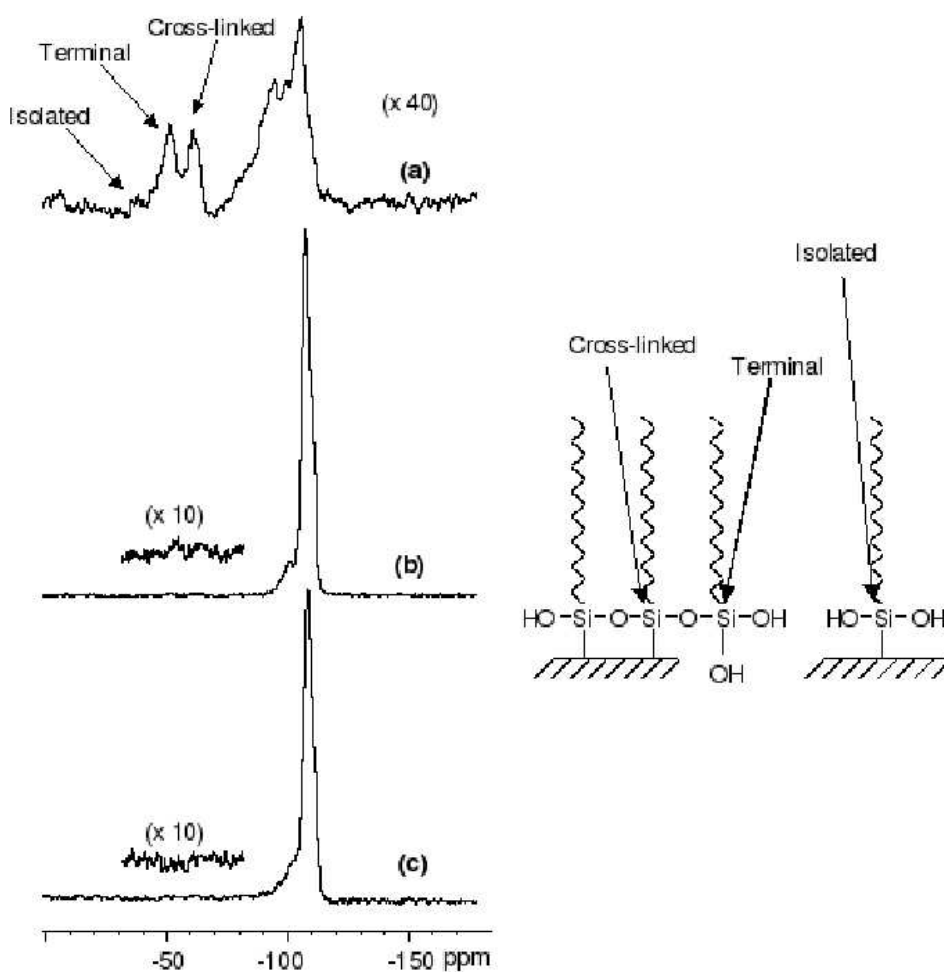


FIGURE 5:  $^{29}\text{Si}$  MAS NMR of (a) hydrolyzed OTS, (b) *w/o*-HZSM-5 and (c) *o*-HZSM-5.

Based on the above results, it is proposed that the polymeric octadecylsiloxane induced the acid strength of protonic species of HZSM-5. Note that the proton acidity could be enhanced by neighboring terminal Si-OH of polymeric octadecylsiloxane (see Fig. 5).

#### 4 CONCLUSIONS

The characterization of alkylsilylated HZSM-5 by using TPD of ammonia suggests that the addition of small amount of water to the solid particles before alkylsilylation, as a recipe to make a bimodal amphiphilic particles, is desired to enhance the acidity of HZSM-5. The enhancement of acidity might be induced by polymeric octadecylsiloxane as elucidated by  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR spectroscopy.

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#### REFERENCES

- [1] H. Nur, S. Ikeda and B. Ohtani, *Chem. Commun.* (2000) 2235.
- [2] H. Nur, S. Ikeda and B. Ohtani, *J. Catal.* **204** (2002) 402.
- [3] S. Ikeda, H. Nur, T. Sawadaishi, K. Ijiri, M. Shimomur and B. Ohtani, *Langmuir* **17** (2001) 7976.
- [4] S. Ikeda, H. Nur, P. Wu, T. Tatsumi and B. Ohtani, *Stud. Surf. Sci. Catal.* **45** (2003) 251.

- [5] H. Nur, S. Ikeda and B. Ohtani, *React. Kinet. Catal. Lett.* **82** (2004) 255.
- [6] H. Nur, S. Ikeda and B. Ohtani, *J. Braz. Chem. Soc.* **15** (2004) 719.
- [7] X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemmer, *Science* **276** (1997) 923.