

^{31}P , ^{27}Al , and ^{129}Xe NMR Study of Phosphorus-Impregnated HZSM-5 Zeolite Catalysts

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Received October 25, 1989; revised January 26, 1990

Phosphorus-impregnated HZSM-5 zeolite has been characterized by ^{31}P and ^{27}Al magic angle spinning NMR and ^{129}Xe NMR spectroscopy. All the NMR data clearly indicate that the phosphorus compound reacts initially with the framework aluminum, modifying the chemical environment of the internal zeolite surface. Excessive impregnation of phosphorus did not change the physicochemical environment of the channel any further, as the chemical shift in ^{129}Xe NMR indicated. This reaction of the phosphorus compound with the framework aluminum is responsible for changes in the adsorption and catalysis of the zeolite. © 1990 Academic Press, Inc.

INTRODUCTION

The conversion of methanol to gasoline (MTG) depends greatly on the characteristics of the catalyst (1). A suitable modification of the catalyst such as impregnation of phosphorus on HZSM-5 zeolite (2) can be effective in converting methanol to low olefins selectively. The selectivity for low olefins is high at low conversions or under the conditions favorable for cracking (3). The phosphorus-impregnated HZSM-5 (P/HZSM-5) also exhibits high selectivity for para-substitution in alkylations of toluene (5), and thus phosphorus is an interesting modifier of zeolite catalysts.

Previous studies on the P/HZSM-5 catalyst (4-8) generally agree that the impregnation of phosphorus increases olefin selectivity in the MTG conversion and para-selectivity in the alkylation of toluene, but there is controversy over the nature of the catalyst modification. For example, Kaeding and Butter (4) suggested that the phosphorus compound reacts with aluminum to lower the acidity of the zeolite. Vedrine *et al.* (6) suggested that the phos-

phorus compound, impregnated in the zeolite channel, decreases the channel size and poisons the acid site at the channel entrance. Nunan *et al.* (7) explained the effect of phosphorus impregnation by poisoning of strong acid sites on the external surface of zeolite. It is of great interest at this point to investigate whether the impregnated phosphorus is located on the external surface or within the zeolite channel. Furthermore, it is very important to determine whether the phosphorus compound, if it exists in the zeolite channel, reacts with zeolite framework elements modifying the chemisorptive and catalytic properties of the channel surface.

The ^{129}Xe NMR of xenon gas adsorbed on zeolites is known as a very useful probe to study the physicochemical environment inside the zeolite channel (9). The adsorbed xenon atoms can be more or less polarized by rapid collision or adsorption on the zeolite wall, other xenon atoms, and other adsorbed species in the zeolite channel. The magnitude of the xenon polarization is signaled by the chemical shift in ^{129}Xe NMR. Therefore, the ^{129}Xe NMR method will be most suitable for the determination of changes in the zeolite channel size and the chemical environment which may occur by

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the phosphorus impregnation. Magic angle spinning (MAS) ^{31}P and ^{27}Al NMR will also be very effective in studying the reaction of the impregnated phosphorus compound with framework aluminum (10). But ^{29}Si MAS NMR would detect such a change with difficulty because of a high Si/Al ratio of the HZSM-5 zeolite.

In this work, the chemical changes in the framework aluminum and the impregnated phosphorus were investigated by ^{27}Al and ^{31}P MAS NMR as a function of the phosphorus loading on HZSM-5 zeolite. The surface change within the zeolite channel was also monitored by ^{129}Xe NMR spectroscopy. The result of this multinuclear NMR approach was compared with the selectivity variation in the P/HZSM-5 catalyst in the MTG conversion reaction.

EXPERIMENTAL

A ZSM-5 zeolite sample was prepared by a hydrothermal reaction of a colloidal silica (Ludox HS-40, Du Pont) with sodium aluminate (Junsei) and tetrapropylammonium bromide (Fluka, 98%) (12). This sample was calcined at 823 K to remove organic cations and then stirred in an aqueous solution of ammonium nitrate (Wako, 98.5%) for 72 h at 353 K to produce $\text{NH}_4\text{ZSM-5}$ zeolite. Calcination of the $\text{NH}_4\text{ZSM-5}$ at 823 K gave a HZSM-5 zeolite. The crystal structure of the sample was confirmed by X-ray diffraction. Chemical analysis yielded a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 47.

Five samples of P/HZSM-5 were prepared by incipient wetness of the HZSM-5 sample with aqueous solutions of diammonium hydrogen phosphate (Sigma, 99.95%). The samples were then calcined with a flow of O_2 at 823 K. The phosphorus contents of these samples are 0.4, 0.8, 1.9, 2.9, and 7.1%, respectively. These samples are designated as P(0.2)/HZSM-5, P(0.4)/HZSM-5, P(0.9)/HZSM-5, P(1.4)/HZSM-5, and P(3.6)/HZSM-5 according to the P/Al ratios which are listed in parenthesis, respectively.

Temperature-programmed desorption (TPD) of ammonia was performed by flowing helium gas at 4.6 ml s^{-1} through a shallow bed of 0.2 g sample which was previously saturated with ammonia gas at 353 K. Heating rate was 0.15 K s^{-1} , and the desorption profile was obtained by a thermal conductivity detector. The surface area of samples was determined by the BET method. Gas adsorption isotherms were obtained at 296 K by a conventional volumetric adsorption apparatus. Propylene (Matheson, 99.0%), propane (Matheson, 99.0%), and xenon (Matheson, 99.995%) were used without further purification.

For the ^{129}Xe NMR experiment, samples were placed in conventional 10-mm NMR tubes jointed with specially designed vertical ground-glass stopcocks. The samples were then dehydrated under vacuum at 673 K before adsorption of xenon gas at 296 K. The ^{129}Xe NMR spectra were obtained at 296 K by a Bruker AM 300 instrument operating at 83.0 MHz for ^{129}Xe . At very low pressures, each ^{129}Xe NMR spectrum was obtained after acquiring up to 140,000 pulse transients with 0.5 s recycle delay. The chemical shift was referenced with respect to xenon gas extrapolated to zero pressure.

To obtain the ^{31}P and ^{27}Al magic angle spinning NMR spectra, the samples were evacuated overnight at 673 K and open to air only for a short time required for packing in Delin rotors. The spectra were obtained at 296 K by a Bruker AC 300 instrument without cross polarization or proton decoupling. The spinning speed was about 3.6 kHz. The resonance frequencies for ^{31}P and ^{27}Al were 121.5 and 78.2 MHz, and the recycle delay for the ^{31}P and the ^{27}Al NMR were 15.0 and 1.0 s, respectively. The chemical shifts were reported with respect to H_3PO_4 and $\text{Al}(\text{H}_2\text{O})_6^{3+}$, respectively.

RESULTS

The XRD patterns obtained from phosphorus-impregnated samples with P/Al ratios up to 0.9 were identical to that from HZSM-5. Thus, the impregnation of phos-

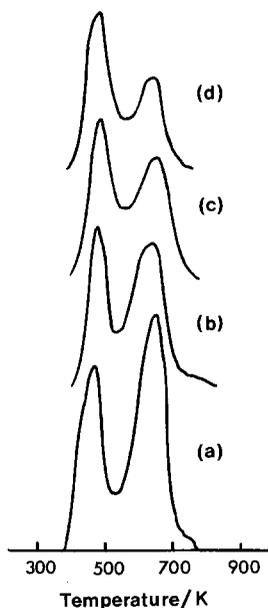


Fig. 1. Temperature-programmed desorption spectra of NH_3 from (a) HZSM-5, (b) P(0.2)/HZSM-5, (c) P(0.4)/HZSM-5, and (d) P(0.9)/HZSM-5 samples, where the number in parenthesis is the P/Al ratio. The sample weight, the heating rate, and the helium flow rate are 0.2 g, 1.5 K s^{-1} , and $4.7 \text{ cm}^3 \text{ s}^{-1}$, respectively.

phorus did not lower the zeolite crystallinity. The surface area of HZSM-5, as determined by the BET method, was $439 \text{ m}^2 \text{ g}^{-1}$. The P(0.2)/HZSM-5 and P(0.9)/HZSM-5 samples did not show a significant decrease in the surface area compared with the HZSM-5 zeolite.

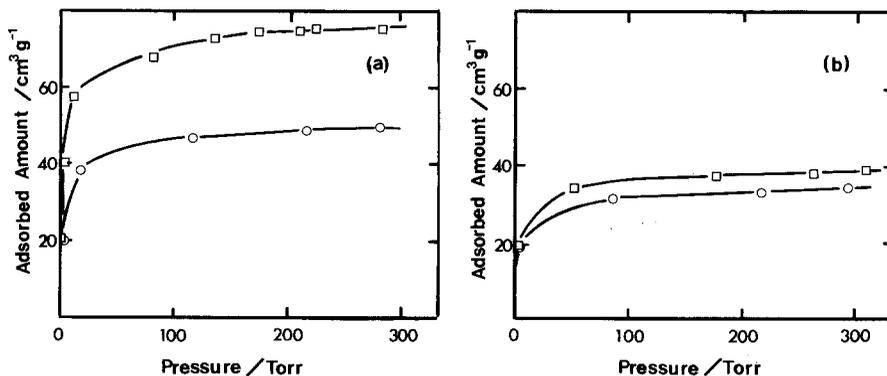


Fig. 2. Adsorption isotherms of (a) propylene and (b) propane for HZSM-5 (\square) and P(0.9)/HZSM-5 (\circ) at 296 K.

Figure 1 shows ammonia TPD spectra of HZSM-5 zeolite and its phosphorus-impregnated samples. All the TPD spectra show two well-resolved peaks with maximum intensities at about 470 and 650 K, respectively. The TPD peak appearing at 470 K did not change in intensity as the P/Al ratio was increased to 0.9, but the higher temperature peak decreased remarkably. The decrease in this higher temperature peak agrees with weakening acid-site strength by the phosphorus impregnation (4). Figure 2 shows the adsorption isotherms of propane and propylene obtained at 296 K from HZSM-5 and P(0.9)/HZSM-5. The adsorption of propylene, unlike the propane adsorption, decreased significantly after the phosphorus impregnation.

Figure 3 shows a change in the ^{27}Al MAS NMR spectrum of the P/HZSM-5 samples which occurred as the phosphorus loading was increased. The HZSM-5 zeolite gave only a single ^{27}Al NMR peak appearing at 60 ppm with respect to $\text{Al}(\text{H}_2\text{O})_6^{3+}$, confirming known tetrahedrally coordinated aluminum in the zeolite framework (10). As the P/Al ratio was raised to 0.9, this NMR peak decreased in intensity and a new peak increased. This change in the ^{27}Al NMR spectrum indicates that the tetrahedral aluminum changed to octahedrally coordinated aluminum by reaction with phosphorus.

Figure 4 illustrates ^{31}P MAS NMR spectra obtained from P/HZSM-5 samples.

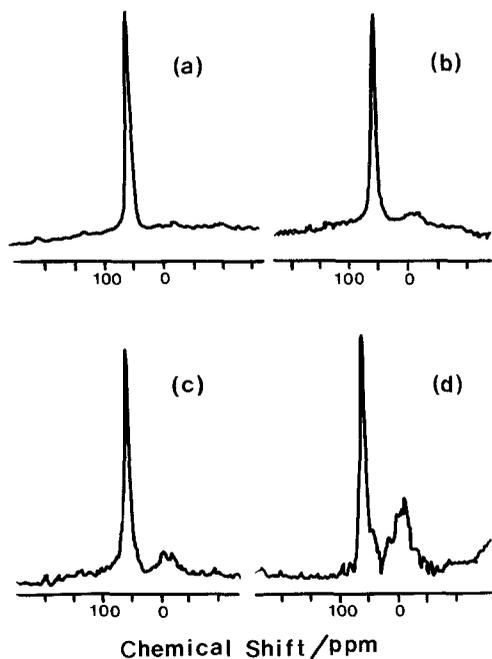


FIG. 3. ^{27}Al MAS NMR spectra obtained from (a) HZSM-5, (b) P(0.2)/HZSM-5, (c) P(0.4)/HZSM-5, and (d) P(0.9)/HZSM-5.

Spectrum (a) obtained from P(0.9)/HZSM-5 shows four resonance peaks with chemical shifts of 0, -6, -12, and -40 ppm with respect to 85% H_3PO_4 , respectively. Small peaks at about 24 and -27 ppm are the spinning side bands. Spectra (b) and (c) show that the ^{31}P NMR peak at 0 ppm continued to grow in intensity, relative to the other peak, as the amount of the impregnated phosphorus was increased up to 3.6 P/Al. Therefore, the 0 ppm peak is associated with the excess phosphorus compound which did not react with the framework aluminum. The intensity of the NMR peak at -40 ppm is very small, and therefore it may come from a small amount of phosphorus compound reacted with the strong xenon adsorption site which is discussed below. Two other peaks at -6 and -12 ppm are attributed to the phosphorus compound reacted with different aluminum sites. Integration of the NMR peak intensity revealed that about half the phosphorus impregnated

on this sample changed its chemical state by reacting with the zeolite framework. The rest of the phosphorus gave the same chemical shift as phosphates which could be produced by thermal decomposition of the impregnated $(\text{NH}_4)_2\text{HPO}_4$ during the calcination step. Figure 5 shows the xenon adsorption isotherms of the HZSM-5 zeolite and the P(0.9)/HZSM-5 sample. Here, the amount of adsorbed xenon is expressed in terms of xenon atoms per framework element for taking into account the sample weight change caused by the impregnation. The two adsorption isotherms are very similar in the given pressure range.

The ^{129}Xe NMR spectra obtained from the adsorbed xenon gas are illustrated in Fig. 6. All the samples gave only a single symmetrical NMR peak due to very rapid exchange of xenon (12-15). The chemical shifts obtained at 400 Torr xenon at 296 K are 141.1 (± 0.5) ppm for the HZSM-5 zeolite and 135.5 (± 0.5) ppm for the P(0.9)/

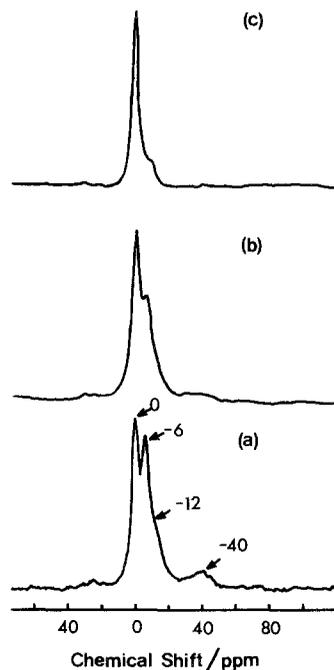


FIG. 4. ^{31}P MAS NMR spectra obtained from (a) P(0.9)/HZSM-5, (b) P(1.4)/HZSM-5, and (c) P(3.6)/HZSM-5.

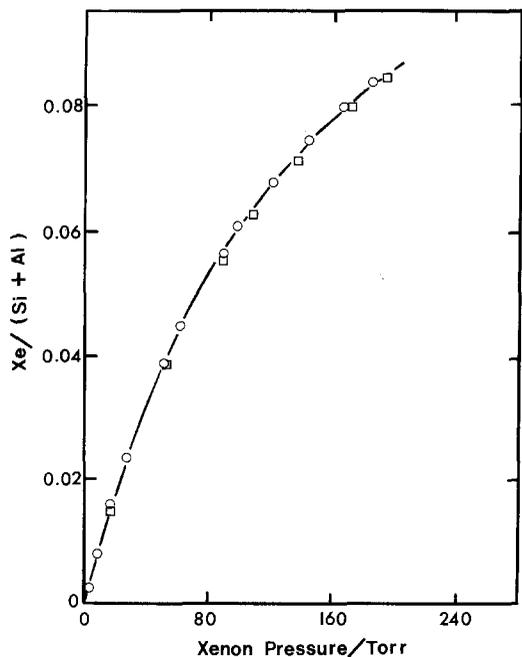


FIG. 5. Xenon adsorption isotherms for HZSM-5 (○) and P(0.9)/HZSM-5 (□) at 296 K.

HZSM-5 sample, respectively. Thus, the phosphorus impregnation corresponding to 0.9 P/Al resulted in a 5.6-ppm upfield chemical shift. Increasing the phosphorus load-

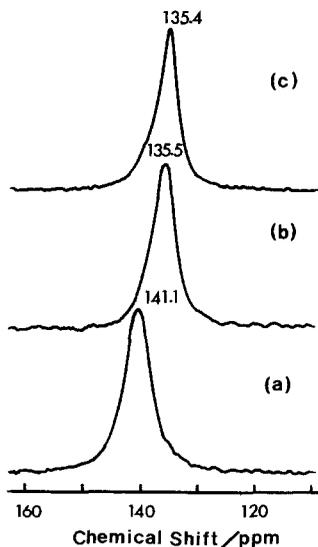


FIG. 6. ^{129}Xe NMR spectra obtained from (a) HZSM-5, (b) P(0.9)/HZSM-5, and (c) P(3.6)/HZSM-5 under 400 xenon at 296 K.

ing up to 3.6 P/Al did not change the chemical shift further.

Figure 7 illustrates the pressure dependence of the chemical shift in the ^{129}Xe NMR. The spectrum from HZSM-5 shows a sharp increase in the chemical shift as the xenon pressure decreased below 50 Torr. This result is due to a small amount of xenon adsorption site which may come from impurities or vacancies in the zeolite structure. Such an effect of strong adsorption site on the pressure-dependence of the ^{129}Xe chemical shift can be explained quantitatively by assuming very rapid xenon exchange between different sites (16). At high pressures, the amount of xenon saturated on the strong adsorption site is relatively so small that its effect on the chemical shift becomes negligible. The influence of this strong xenon adsorption site on the chemical shift may mislead the comparison of ^{129}Xe NMR chemical shifts between HZSM-5 and P(0.9)/HZSM-5. This can be avoided by comparing the two data at least above 100 Torr.

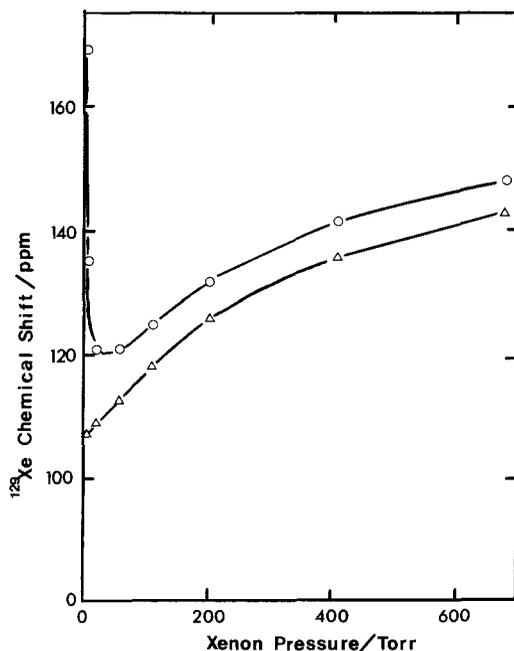


FIG. 7. The chemical shift in ^{129}Xe NMR for HZSM-5 (○) and P(0.9)/HZSM-5 (△) as a function of xenon pressure at 296 K.

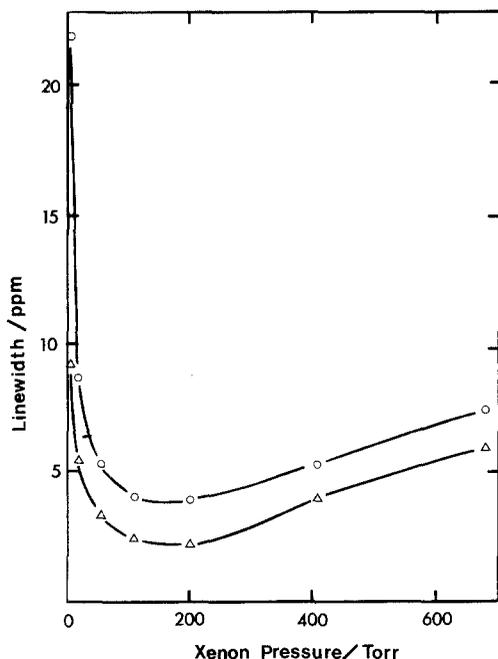


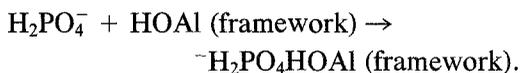
FIG. 8. The linewidth in ^{129}Xe NMR for HZSM-5 (\circ) and P(0.9)/HZSM-5 (\triangle) as a function of xenon pressure at 296 K.

A gradual increase in ^{129}Xe chemical shift above 100 Torr, as seen in Fig. 7, is due to the increasing collision frequency between xenon atoms in the zeolite channel. The contribution of the xenon-xenon collision to the chemical shift is approximately proportional to the adsorbed xenon density (12). As mentioned above, the xenon adsorption isotherms of HZSM-5 and P(0.9)/HZSM-5 are very similar. Thus, the xenon-xenon collision term does not explain a decrease of 5.6 ppm from HZSM-5 to P(0.9)/HZSM-5 unless the zeolite pore volume is increased due to the phosphorus impregnation, which is opposite to what can be expected. Therefore, the chemical shift decrease should be due to a modification of the zeolite wall by phosphorus compound which will further be discussed below. The linewidth variation in ^{129}Xe NMR, as Fig. 8 shows, is very similar to the chemical shift variation shown in Fig. 7.

DISCUSSION

It has been discussed above, based on our result of ^{31}P and ^{27}Al MAS NMR experiments, that about half the impregnated phosphate came to react with the framework Al as the phosphorus loading was increased up to 0.9 P/Al, above which the excessively impregnated phosphate underwent no chemical reactions with the framework Al. Thus, only about half the impregnated phosphate reacted effectively with the Al at 0.9 P/Al. This result can be due to low efficiency of our incipient wetness method for achieving uniform distribution of phosphorus into the HZSM-5 channel. The ^{27}Al NMR spectra in Fig. 3 indicate that about half the framework Al is reactive with the impregnated phosphate. The other half may not be reactive with or inaccessible to the impregnated phosphate. This reaction between 50% P and 50% Al at 0.9 P/Al gave a stoichiometry of approximately 1 P : 1 Al in agreement with a model proposed by Kaeding and Butter (4).

Neutralization of acid site which occurred due to the phosphorus impregnation will not only introduce phosphorus moiety into the zeolite channel but also change tetrahedral Al to octahedral as follows:



Such a change will certainly decrease the zeolite channel size, which will in turn change the catalyst's diffusive characteristics and thus its product selectivity (4-8). But physical methods such as X-ray diffraction and adsorption of inactive gases have failed to detect the physicochemical changes which occurred in the HZSM-5 channel due to the phosphorus impregnation up to 0.9 P/Al. Thus, the pore volume decrease due to the phosphorus impregnation up to 0.9 P/Al was too small to detect with conventional physical methods.

The physicochemical changes in the HZSM-5 channel have become clearer by our ^{129}Xe NMR data, i.e., the chemical shift

and the linewidth. We have obtained a 5.6-ppm decrease in the chemical shift at 400 Torr after phosphorus impregnation corresponding to 0.9 P/Al. This decrease is due to modified xenon-polarizing abilities of the zeolite wall. Phosphorus loadings above 0.9 P/Al on the HZSM-5 zeolite catalyst did not change the chemical shift any further. In this way, the chemical shift decrease due to phosphorus impregnation reached a limit at about 0.9 P/Al, but this result does not mean that all the impregnated phosphorus compound is located in the channel at 0.9 P/Al. The ^{31}P NMR spectra in Fig. 4 suggested that half the impregnated phosphorus compound reacted with the framework aluminum at 0.9 P/Al. The other half of the impregnated phosphorus may be located on the external zeolite surface. The additional phosphorus compound introduced above 0.9 P/Al may also exist as phosphate at the external surface or fill in the zeolite channel as an aggregate. In the former case, the chemical shift change will be negligible since the amount of xenon adsorbed inside the zeolite crystal is much greater than that experiencing collisions or adsorption on the external surface. In the latter case, xenon atoms would not be accessible to the region filled by the impregnated phosphorus.

The activity change in our P/HZSM-5 catalyst in the MTG conversion reaction (17) agrees with the results obtained in this NMR study. The olefin selectivity reached a maximum at 0.9 P/Al. Higher loadings above 0.9 P/Al did not increase the olefin selectivity further. Thus, the catalytic activity change is really in parallel with all the physicochemical changes shown by our NMR data. The decrease in the propylene adsorption by the phosphorus impregnation (shown in Fig. 2) can also be related to the olefin selectivity in the MTG conversion reaction. The olefin may be a reaction intermediate which is more easily desorbed from the active site by the phosphorus impregnation.

CONCLUSION

Application of multinuclear solid state NMR techniques combined with the ^{129}Xe NMR of adsorbed xenon gas was able to show clearly that the impregnation of phosphorus on HZSM-5 zeolite modifies the zeolite catalyst by direct reaction of the framework aluminum with phosphorus compound within the zeolite channel. This reaction of aluminum with the phosphorus compound is responsible for the increasing olefin selectivity of the catalyst in MTG conversion reaction.

ACKNOWLEDGMENTS

This work was financially supported by Korea Science and Engineering Foundation. We thank Hanyang Chemical Corp. Central Research Center for magic angle spinning NMR.

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