

## **$^{129}\text{Xe}$ NMR TO PROBE MICROSCOPIC MIXING STATE OF COMPOSITE CATALYSTS**

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$^{129}\text{Xe}$  NMR spectra obtained from microporous solid mixtures such as  $\text{NaY-Pt}/\text{NaY}$  and  $\text{NaY-Pt}/\text{Al}_2\text{O}_3$  have indicated that the NMR peak pattern can depend greatly on the mixing method.  $^{129}\text{Xe}$  NMR can thus be a very simple and useful technique to probe the physical mixing state of many composite catalysts.

### **1. Introduction**

Many modern industrial catalysts are composites associating several phases. For instance, hydrocracking catalysts usually comprise a zeolite and a noble metal supported on alumina [1]. High octane cracking catalysts containing both rare-earth exchanged Y zeolite (REY) and ZSM-5 have been described [2]. Mixtures of pillared clays, REY and amorphous matrix have also been reported for the cracking of heavy oils [3]. As reported earlier by Weisz [4], the catalytic properties of these bifunctional systems will depend on the distance separating the two functions, and therefore on the homogeneity of the distribution of the components.

It is indeed very difficult to determine the distribution of e.g. two different silico-aluminates in a grain of catalyst, and simple methods would be very useful for the characterization of composites.  $^{129}\text{Xe}$  NMR can be one of these methods,

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because the chemical shift of adsorbed xenon is very sensitive to the surface composition and porosity of the adsorbate [5–7], and furthermore the heterogeneity of the sample can cause splitting of the  $^{129}\text{Xe}$  NMR signal depending on the sample domain size over which the chemical shift is averaged [6,8–10]. Earlier papers on the subject of the  $^{129}\text{Xe}$  NMR line splitting by Fraissard and co-workers assumed that the domain size can be significantly smaller than the crystal of Y zeolite [6]. Later, Shoemaker and Apple [8] reported that mixing of Ru/NaY (ruthenium supported on NaY zeolite) and NaY can result in coalescence of the  $^{129}\text{Xe}$  NMR peaks. Ryoo *et al.* [10] also clarified that such  $^{129}\text{Xe}$ -NMR-line coalescence can be a general nature of Y-zeolite mixing at room temperature. We exemplify here the possibility of using  $^{129}\text{Xe}$  NMR for the characterization of composite catalysts by showing that the NMR signal differs in a predictable way as a function of the homogeneity of samples composed of NaY zeolite and Pt/NaY (platinum supported on NaY zeolite), as well as NaY and Pt/ $\text{Al}_2\text{O}_3$  (platinum supported on alumina).

## 2. Experimental section

A 5% Pt/NaY sample was prepared by the typical ion exchange method [11] using  $\text{Pt}(\text{NH}_3)_4^{2+}$ -exchange into a high-purity NaY zeolite (prepared here,  $\text{Si/Al} = 2.4$ , mean crystal size by SEM =  $0.6\ \mu\text{m}$ ), calcination at 573 K and reduction at 573 K. A 5% Pt/ $\text{Al}_2\text{O}_3$  was prepared by the typical impregnation method [12] using  $\text{H}_2\text{PtCl}_6$ -impregnation on  $\gamma$ -alumina (Strem, BET surface area =  $220\ \text{mg}^2\text{g}^{-1}$ , pore volume =  $0.25\ \text{cm}^3\ \text{g}^{-1}$ ), calcination at 773 K and reduction at 573 K.

All sample mixing was performed under atmospheric condition. Re-reduction of the samples was performed in a static way by repeated evacuation and  $\text{H}_2$ -introduction as the sample was heated to 573 K over 2 h in 10-mm-OD NMR tube which has specially designed small ground-glass stopcocks to fit in the 45-mm-bore superconducting magnet. The samples were subsequently evacuated at 673 K under  $1 \times 10^{-5}$  Torr. Xenon gas (Matheson, 99.995%) was then equilibrated with the sample at 400 Torr and 296 K.

$^{129}\text{Xe}$  NMR spectra were obtained at 296 K by a Bruker AM 300 instrument operating at 83.0 MHz for  $^{129}\text{Xe}$  with 0.5-s relaxation delay. The chemical shift was referenced with respect to xenon gas extrapolated to zero pressure.

## 3. Results and discussion

Fig. 1 shows  $^{129}\text{Xe}$  NMR spectra obtained, at 400 Torr and 296 K, after various mixing treatments of NaY and 5% Pt/NaY. As described in the experimental section, all the samples were re-reduced prior to xenon adsorption.

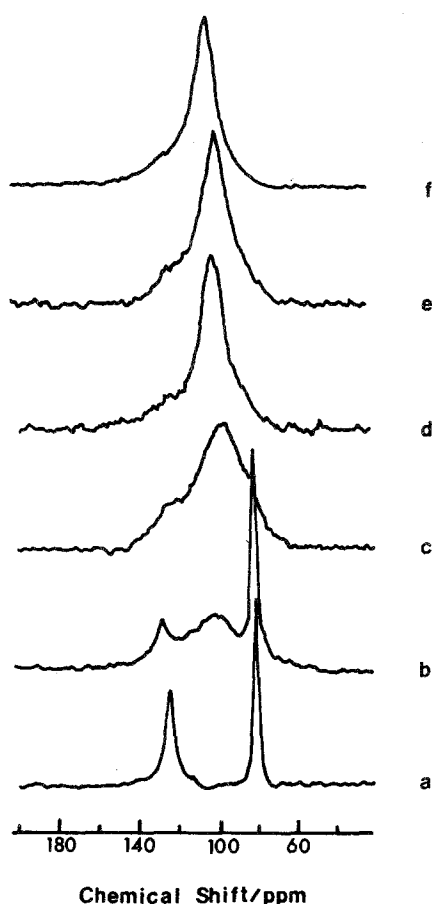


Fig. 1.  $^{129}\text{Xe}$  NMR spectra obtained from xenon adsorbed at 296 K and 400 Torr on a 1 : 1 mixture of NaY and Pt/NaY; (a) physically separated, (b) gently mixed by glass rod for 5 min, (c) slurried by magnetic stirrer for 30 min, (d) mixed in porcelain mortar for 30 min, (e) slurried by mechanical stirrer in ultrasonic cleaner for 30 min, and (f) same treatment as (e), except for 4 h, respectively.

Spectrum *a* was given when equal amounts of the two samples were placed in the upper and lower parts of an NMR tube separately. Two NMR signals appearing at 81.3 and 125.2 ppm came from xenon gas adsorbed on NaY and Pt/NaY, respectively [5]. Gently mixing the two samples in 1 : 1 weight ratio by glass rod for 5 min resulted in a decrease of the above two NMR peaks in intensity and appearance of a new broad signal between them, as spectrum *b* shows, which is due to the xenon exchanging rapidly between NaY and Pt/NaY in relatively well-mixed regions. Thus, such mixing by glass rod quite naturally results in a heterogeneous line-coalescence pattern in the  $^{129}\text{Xe}$  NMR spectrum. This is in contrast to the results of Shoemaker and Apple [8] who reported a rather homogeneous coalescence pattern from mixing of NaY and Ru/NaY, shifting two NMR peaks close together. Spectrum *c* was obtained after equal amounts of

NaY and Pt/NaY were slurried in distilled water at room temperature by magnetic stirrer for 30 min. Appearance of a broad coalescence peak indicates that the magnetic stirring gave much better homogeneity than the mixing by glass rod. However, the unsymmetrically broad pattern of the peak suggests that the sample can still become more uniform by another and better mixing method. This has been demonstrated: careful mixing by porcelain mortar and pestle (spectrum *d*) for 30 min or mechanical stirring in an ultrasonic cleaner (spectrum *e* after 30-min mixing, spectrum *f* after 4-h mixing) gave much better homogeneity. Among them, the mechanical stirring with ultrasonic wave for 4 h gave the best result. The two  $^{129}\text{Xe}$  NMR peaks in spectrum *a* in fig. 1 are separated by  $125 - 81 = 44$  ppm, and thus the diffusion time for xenon to give complete coalescence of the peaks in spectrum *f* is less than approximately  $t = (44 \times 83 \text{ Hz})^{-1} = 2.7 \times 10^{-4}$  s. During this time, the xenon diffusion distance would approximately be less than  $l = (6Dt)^{1/2}$  where  $D$  is the diffusivity of xenon in the sample [13]. Neglecting the void space between zeolite crystals, we may use an

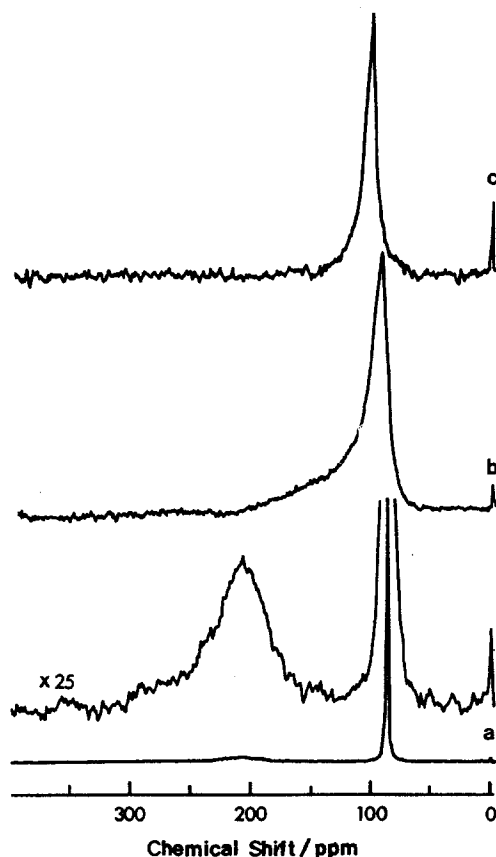


Fig. 2.  $^{129}\text{Xe}$  NMR spectra obtained from xenon adsorbed at 296 K and 400 Torr on a 3:1 mixture of Pt/ $\text{Al}_2\text{O}_3$  and NaY; (a) physically separated, (b) mixed in porcelain mortar for 5 min, and (c) slurried by mechanical stirrer in ultrasonic cleaner for 4 h, respectively.

intracrystalline diffusivity for  $D$ . Although the intracrystalline diffusivity depends on the structure and cation of the zeolite,  $D = 5 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ , which Karger et al. [14] obtained from NaX zeolite by the pulsed  $^{129}\text{Xe}$  NMR method, may be used for our approximate calculation. Then,  $l$  becomes  $2.9 \mu\text{m}$ , which suggests that Pt/NaY crystals and NaY crystals, after good mixing in an ultrasonic cleaner, are not separated by more than this distance. Therefore, comparison of spectra  $c$  and  $f$  in fig. 1 suggests that ultrasonic wave pulses broke large agglomerations of zeolite crystals whereas simple magnetic stirring did not.

Fig. 2 shows  $^{129}\text{Xe}$  NMR spectra obtained before or after various mixing treatments of 5% Pt/ $\text{Al}_2\text{O}_3$  and NaY in 3 : 1 weight ratio. Spectrum  $a$  was given from an NMR sample tube with the samples placed separately. NMR peaks at 207 and 85 ppm are from Pt/ $\text{Al}_2\text{O}_3$  and NaY, respectively. Pt/ $\text{Al}_2\text{O}_3$  seems to show a broad peak because alumina usually have distributions of porosity and particle size, compared with NaY. Mixing the two samples in a porcelain mortar for 5 min gave spectrum  $b$ , and good mixing by mechanical stirrer with ultrasonic wave gave spectrum  $c$  which shows a symmetrically coalesced NMR peak.

The results of this study are promising future applicability of  $^{129}\text{Xe}$  NMR in understanding the catalytic activity of many modern composite bifunctional or multifunctional catalysts as a function of mixing state.

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