

Xe NMR and Ar Quasi-Equilibrium Sorption of Coked H-Y Zeolite

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Acidic, H-Y zeolite was partially coked with propylene at 250 and 475°C. Standard micropore volume determination by N₂ physical sorption indicates that nearly all of the coke was confined to the micropores with little change in the larger mesopores. Xe NMR chemical shifts increased linearly with a decrease in the micropore volume for the coke samples. However, initial coke deposition on H-Y increased the Xe chemical shift beyond the changes predicted by the decrease in micropore volume. The increase in chemical shift due to coke was also found to be dependent on the aromaticity of the coke. Coke formation at 250°C (65% sp² carbon) increased the chemical shift by 6.5 ppm while coke formed at 475°C (>95% sp² carbon) increased the chemical shift by 8.5 ppm. The size of the pore apertures, i.e., the opening to the alpha cage, was determined by low-pressure Ar adsorption isotherms. As the level of coke increased, the size of the alpha cage aperture decreased by as much as 0.07 nm. A bimodal distribution in the pore apertures was clearly resolved on some catalysts at higher coke levels. One pore size was characteristic of apertures essentially free of coke (0.72 nm); while, the other, smaller aperture was more severely restricted due to coke deposits (0.58 nm). The inability of Xe NMR to detect two pore environments observed by Ar sorption may result from rapid exchange of Xe between the two sites. This implies that the distance between the two pore environments is small and that the two pore environments are uniformly distributed throughout the catalyst particle. © 1991 Academic Press, Inc.

INTRODUCTION

Progress in the synthesis (1, 2), modification (3), and application of zeolites has continued for over 30 years. Major advances have led to development of new processes in both the petroleum refining and chemical industries (4-6). New zeolites optimized for acidity, stability, pore size, or composition, etc., are being synthesized or modified by various post-synthesis treatment.

The characterization of zeolites has also experienced rapid development. Numerous techniques have been applied. Most common are infrared (IR) spectroscopy (3, 7-9), X-ray diffraction (XRD) (1, 10), X-ray photoelectron spectroscopy (XPS) (11), ²⁹Si and ²⁷Al NMR (12-15), NH₃ temperature-programmed desorption (16), and electron microscopy (TEM) (17, 19), among others. More recently, two dissimilar analytical techniques, ¹²⁹Xe NMR (20-25) and

quasiequilibrium sorption of Ar (26, 27), have been applied with success to the characterization of zeolites.

Xenon-129 has a spin ½ nucleus (no quadrupolar interactions), a natural abundance of 26%, a reasonable high-resonance frequency (83 MHz at 7.05 T), and a relative detectability that is 30 times that of carbon. The chemical shift, δ, of xenon in a particular molecular sieve is determined by a variety of factors related to its environment and collisions with other species. Fraissard represents this dependence in the form (20-24):

$$\delta = \delta_0 + \delta_s + \delta_E + \delta_{(Xe-Xe)} \cdot P_{Xe},$$

where δ₀ is the chemical shift of xenon gas at zero pressure, δ_s is the contribution due to collisions of xenon with the sieve walls, δ_E is caused by electric fields, and δ_(Xe-Xe) · P_{Xe} is a term due to collisions between excess xenon. By determination of the individual components which contribute to the chemical shift, information is obtained

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about the structural and chemical environment of the zeolite.

The use of gas sorption to characterize porous solids is well established, but previous procedures have been unable to accurately determine the pore size distribution for diameters of less than 2.0 nm since commonly used adsorbates, e.g., N_2 , liquify in zeolite pores even at very low partial pressures at the sorption temperature. The use of a noble gas, Ar, and the availability of new instrumentation enables isotherms to be obtained starting at relative pressures (P/P_0) as low as 10^{-6} (26). With the quasi-equilibrium Ar sorption technique, differences in pore size can now be determined for microporous solids (27).

In this study, Xe NMR and Ar sorption along with ^{13}C NMR and N_2 sorption, have been applied to a series of coke H-Y zeolite catalysts. Each technique offers unique information providing a better understanding of the deactivation process in zeolites.

EXPERIMENTAL

Catalyst Preparation

The H-Y zeolite was commercially obtained from Davison Chemical Company of W. R. Grace. The XRD crystallinity and the unit cell dimension were 86% and 2.452 nm, respectively. The zeolite had an Na content of 0.5 wt%. Approximately 5.0 g of catalyst was placed in a fixed-bed continuous flow, atmospheric reactor. The sample was heated to 450°C under flowing N_2 and cooled to room temperature. The gas flow was switched to 5% propylene/95% N_2 (100 ml/min) at room temperature. The flow was continued until the catalyst no longer adsorbed propylene. The propylene was discontinued, and N_2 flow was maintained for 15 min. The catalyst was heated under flowing N_2 to the coking temperature, either 250 or 475°C, and maintained at that temperature for 30 min. Adsorption of propylene at room temperature followed by heating under N_2 flow at elevated temperature was repeated up to four times. Additionally sev-

eral samples were coked by reacting a continuous flow of 5%, C_3H_6 /95% N_2 at either 250 or 475°C. The propylene was reacted until the propylene conversion decreased to less than 20%.

N_2 Physical Adsorption

Samples were analyzed on the Micromeritics Corporation ASAP 2400. Total surface area, mesoporosity, and its associated surface area, as well as micropore volumes derived from "t" plots. Micropore volumes, e.g., pores less than 1.0 nm, were determined by the amount of N_2 adsorbed at P/P_0 less than 0.1 (28). Mesopore volumes, pores from 1.0 to 50.0 nm, were calculated by standard procedures (29).

Xe Adsorption Isotherms

Samples were pretreated at 250°C under 25 mTorr overnight, cooled, backfilled with helium, reweighed (taking into account a buoyancy factor of 15.7 mg). Target Xe pressures were 50, 100, 150, 200, 300, 400, 470, and 740 mm. Equilibration times were typically 5 to 100 min. From each uptake, the xenon atoms per α cage were calculated at the given pressure. Measurements were made at room temperature on the Micromeritics ASAP 2400.

Quasi-Equilibrium Ar Sorption

Samples were analyzed on a Coulter Corporation, Omnisorb 100 CX. The samples were outgassed at 250°C and transferred under vacuum for the sorption studies. Sample size was approximately 100 mg and He and Ar flow rates into the sample chamber were 0.34 and 0.12 ml/min, respectively. (Helium was used to establish the volume of the sample chamber.) Once the volume of the sample chamber had been determined, the sample chamber was evacuated and Ar was introduced at a known flow rate. By monitoring the chamber pressure as a function of time, the isotherm could be generated. Data acquisition was started at $P/P_0 \approx 10^{-6}$ and ended at approximately 0.2. In order to better display the adsorp-

tion behavior in the microporous region, i.e., P/P_0 below approximately 10^{-2} , the isotherms are given as semilog (P/P_0) versus normalized sorption, W/W_0 . W_0 represents the maximum Ar adsorption. Further details of this procedure can be found elsewhere (26, 27).

^{13}C NMR

^{13}C CP MAS NMR spectra were obtained on a JOEL FX 60QS Fourier transform spectrometer equipped with a Chemagnetics solids accessory. Spectra were obtained using an $8\mu\text{s}$ ^1H 90° pulse, a 2-ms contact time, and a relaxation delay of 0.5 s. A spin rate of 2.4 kHz was employed, and chemical shifts were referenced to tetramethylsilane.

^{129}Xe NMR

Samples were prepared in special NMR tubes (Wilmad Corporation) equipped with a resealable valve suitable for attachment to a vacuum line. The tube was evacuated at room temperature and a dry weight was obtained. The sample was loaded as a powder to a height of about 10 mm, and a quartz wool plug was weighted and placed in the top of the tube to prevent catalyst loss during evacuation. The sample was evacuated (2 mTorr) for 1 h at ambient temperature, heated to 200°C under vacuum, and maintained overnight.

^{129}Xe NMR spectra were obtained on an NT300 spectrometer at a frequency of 83.0 MHz using a simple pulse-acquire-delay sequence. The spectral width was 16 kHz. Data were acquired into 1K blocks of memory, but were zero-filled to 4K to enhance digital resolution to 0.1 ppm. Delay times were 500 ms for zeolite samples and 10 s for pure gas samples. The T_1 measured for several zeolites was in the range of 40 to 300 ms, while the pure gas was between 10 and 20 s. Generally, 1200 scans were acquired for each sample. Referencing of chemical shifts was made relative to the gas at infinite dilution. ^{129}Xe NMR spectra were obtained at 50, 100, 150, 200, 300, 400, and 500 Torr Xe.

RESULTS AND DISCUSSION

^{13}C NMR

Propylene rapidly reacts on the surface of H-Y zeolite at 40°C (30–33). The reaction proceeds until the pores of the catalyst are completely filled, or blocked. At saturation, the catalyst contains 14.39 wt% C with an N_2 surface area of $6.8\text{ m}^2/\text{g}$ and no measurable micropore volume. The carbon species are strongly chemisorbed and cannot be removed even under high vacuum. The ^{13}C NMR spectrum of the chemisorbed species is shown in Fig. 1a and consists of sev-

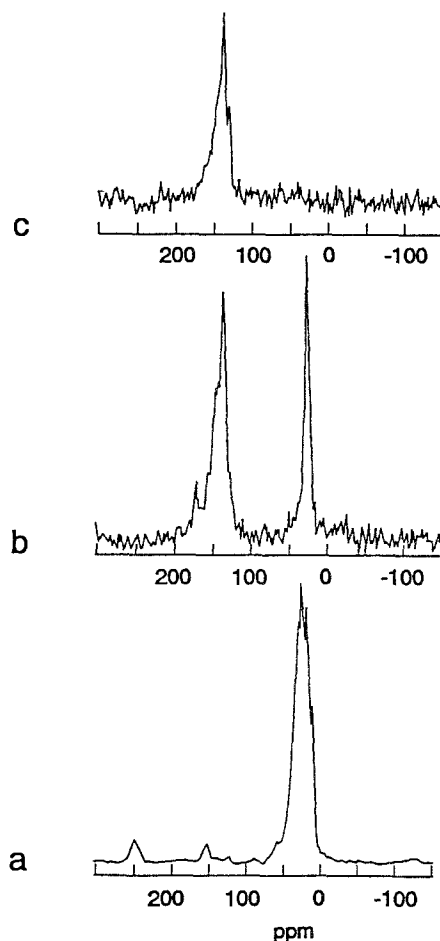


FIG. 1. ^{13}C NMR. a.) Catalyst A with propylene chemisorbed at 40°C . b.) Catalyst D (3.5 wt% C), propylene chemisorbed at 40°C and heated to 250°C in N_2 . c.) Catalyst F (7.4 wt% C), propylene chemisorbed at 40°C and heated to 475°C in N_2 .

TABLE I
 Physical Adsorption Properties

Catalyst	Coking conditions temp. °C (treatments)	Wt% C	N ₂ BET surface area (m ² /g)	N ₂ Micropore vol. (cc/g)	N ₂ Mesopore vol. (cc/g)	Ar Micropore vol. (cc/g)
A ^a	None	None	636	0.25	0.101	0.29
B	475 (1x)	2.44	578	0.23	0.093	0.22
C	250 ^b (1x)	2.51	566	0.22	0.096	0.19
D	250 (1x)	3.45	550	0.22	0.092	0.20
E	250 (2x)	5.60	463	0.19	0.090	0.17
F	475 (3x)	7.44	464	0.18	0.094	0.16
G	250 (3x)	8.06	420	0.16	0.090	0.16
H	250 (4x)	8.38	387	0.14	0.100	0.11
I	250 ^c	15.00	100	0.028	0.063	0.00
J	475 ^d	10.28	360	0.14	0.079	0.10
K	475 ^e	20.10	23	0.001	0.047	ND

^a XRD crystallinity is 86% (ucd = 2.454 nm).

^b Heated at 250°C at 10⁻⁶ Torr.

^c Coked with propylene continuously at 250°C.

^d Catalyst I heated to 475°C in flowing N₂.

^e Coked with propylene continuously at 475°C.

eral overlapping peaks from 10 to 50 ppm with two smaller peaks at 160 and 250 ppm. The peaks at 10–50 ppm are due to aliphatic carbons (sp³), while the peaks at 160 and 250 ppm have previously been assigned to carbon cations bound to the catalyst surface (33). These data indicate that the propylene is chemisorbed and rapidly transformed to an aliphatic polymer.

Coked zeolites were prepared by heating the zeolite saturated with the propylene polymer at the desired reaction temperature, either 250 or 475°C, in flowing N₂. As the catalyst was heated above 200°C, significant quantities of C₃ to C₈ paraffins were desorbed from the catalyst (33–35). Following heating at 250°C, for example, the catalyst contains 3.45 wt% C, and N₂ surface area and micropore volume have increased to 550 m²/g and 0.221 cc/g, respectively (Table 1, catalyst D). The ¹³C NMR spectrum of a catalyst heated to 250°C is shown in Fig. 1b and indicates that the carbon species have undergone a significant structural rearrangement (33, 35–37). The

spectrum consists of two resonances, a relatively sharp aliphatic resonance at 25 ppm and a broad resonance at 140 ppm due to unsaturated (sp²), and, probably, aromatic carbons. Aromatization of the surface carbon to form coke is occurring at reaction temperature near 200°C.

Further heating of the catalyst to 475°C produces only small additional amounts of desorbed hydrocarbons; however, these consist mainly of methane, ethane, and propane. The carbon on the catalyst has decreased to 2.44 wt%, and the N₂ surface area and micropore volume have increased to 578 m²/g and 0.231 cc/g, respectively. The ¹³C NMR spectrum of a catalyst heated to 475°C is shown in Fig. 1c. No saturated carbons (sp³) remain on the catalyst, and the carbon in the coke is completely aromatic at 475°C.

A series of catalysts with increasing coke was prepared by repeated saturation with propylene at 40°C followed by reaction at higher temperatures. The catalysts' physical properties are given in Table 1. The N₂

micropore volume continually decreases as the coke on the catalyst increases, indicating that much of the coke is deposited inside the zeolite pores. The N_2 mesopore volume, however, changes little as the coke content is increased, indicating that little coke has been deposited in the larger mesopores.

The H-Y zeolite was also coked by the continuous reaction of propylene at 250°C (catalyst I) and 475°C (catalyst K). At 250°C, for example, propylene is converted to C_3 to C_8 paraffins. These are the same products which were formed by heating the low-temperature propylene polymer to 250°C in N_2 . The flow of propylene was continued until the conversion dropped below 20%. At both 250 and 475°C, isothermal coking results in the near complete loss of surface area and micropore volume. The carbon distribution by ^{13}C NMR, given in Table 2 shows that the degree of aromatization (percentage sp^2) is determined mainly by the maximum reaction temperature of the catalyst, rather than by the availability of gas-phase propylene at a given temperature.

^{129}Xe NMR and Xe Sorption Isotherms

^{129}Xe NMR chemical shifts were obtained at Xe pressures from 50 to 500 Torr for each catalyst in Table 1. Xe adsorption isotherms (cc Xe/g catalyst) at 25°C were also obtained for each catalyst. The adsorption isotherms (cc/Xe/g catalyst) were converted to the number of Xe atoms/alpha cage assuming the H-Y zeolite unit cell contains 192 SiO_2 (MW = 11,520 g/mol) with eight alpha cages per unit cell. Accounting for the zeolite crystallinity of 86%, 3.6×10^{20} Xe atoms/g catalyst (0.078 g Xe/g catalyst) equals one Xe atom/alpha cage. Coked zeolites were additionally corrected for percent carbon. Each Xe isotherm (Xe/alpha cage vs Xe pressure) was fit to a second-order polynomial.

The plots of Xe chemical shift versus Xe/alpha cage were nearly linear for all catalysts. The contribution to the chemical shift

TABLE 2
Carbon Distribution by ^{13}C NMR^a

Catalyst	Wt% C	Coking temp. (°C)	% sp^2	% sp^3
B	2.44	475	0	100
D	3.45	250	40	60
E	5.60	250	37	63
F	7.44	475	0	100
G	8.06	250	31	69
H	8.38	250	28	72
I ^c	15.00	250	42	58
J ^b	10.28	475	0	100
K ^c	20.10	475	0	100

^a Precision of % sp^2 is 3%.

^b Sample J was obtained by heating sample I in N_2 at 475°C.

^c Coked continuously with propylene at the reaction temperature.

due to Xe collisions with the zeolite surface, i.e., zeolite wall and coke, was determined by linear extrapolation of the chemical shifts to zero Xe/alpha cage, i.e., zero Xe pressure. The zero-pressure chemical shift, δ_s , is given in Table 3. A plot of δ_s versus N_2 micropore volume reveals two families of curves, as shown in Fig. 2. At

TABLE 3

^{129}Xe NMR Chemical Shift at Zero Xe/Alpha Cage^a

Catalyst	Wt% C	N_2 MPV (cc/g)	δ_s (ppm)
A	None	0.25	62.3
B	2.44	0.23	73.9
C	2.51	0.22	71.5
D	3.45	0.22	73.3
E	5.60	0.19	77.1
F	7.44	0.18	80.4
G	8.06	0.16	83.0
H	8.38	0.14	83.7
J ^b	10.28	0.14	84.8
Mixture (A + F) ^c	—	—	61.8, 79.0

^a Precision of chemical shift, δ_s , is 0.5 ppm.

^b Catalyst I coked continuously with propylene at 250°C. Catalyst J prepared by heating catalyst I at 475°C in N_2 .

^c Mixture of 48.6% A + 51.4% F.

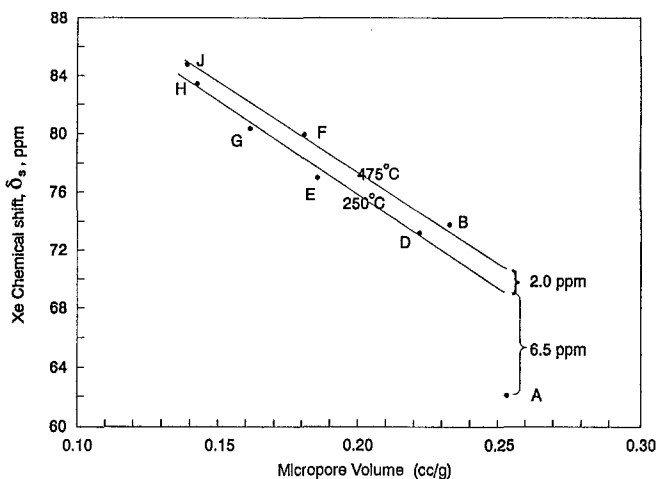


FIG. 2. Xe chemical shift (zero Xe/ α cage) vs. N_2 micropore volume.

each coking temperature, the chemical shift increases linearly with decreasing micropore volume. The samples coked at 475°C (>95% sp^2 carbon) had chemical shifts that were 2.0 ppm higher, at constant pore volume, than those of samples coked at 250°C (65% sp^2 carbon). The coke-free zeolite, catalyst A, is not on either curve. The interaction of the Xe with the coke surface results in an increase in the Xe chemical shift relative to the shift resulting from interaction with the coke-free zeolite walls.

At an equivalent pore volume, the 250°C coke is estimated to increase the chemical shift by 6.5 ppm, while the 475°C coke increases the chemical shift by 8.5 ppm. The Xe chemical shift, therefore, is affected by the coke composition, increasing slightly as the aromaticity of the coke increases.

Ar Physical Sorption at 87K

The 87K Ar adsorption isotherms for the coked Y zeolites are shown in Fig. 3. As the coke content on the zeolite increases, the

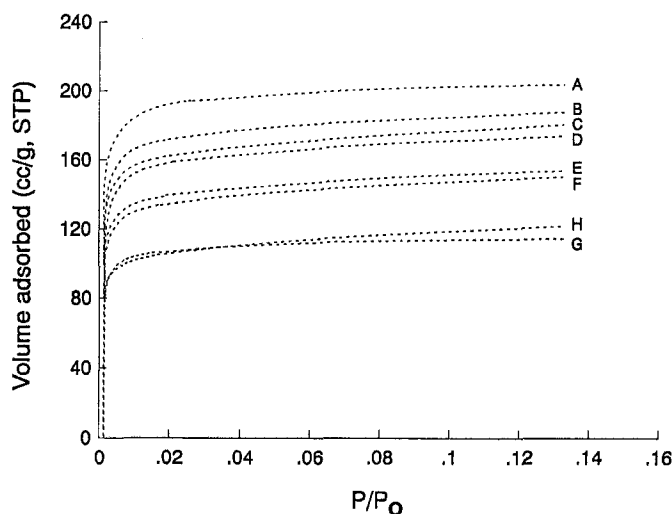


FIG. 3. Argon physical sorption isotherm at 87K. Catalyst: A (0.0 wt% C), B (2.4 wt% C), C (2.5 wt% C), D (3.5 wt% C), E (5.6 wt% C), F (7.4 wt% C), G (8.1 wt% C), H (8.4 wt% C).

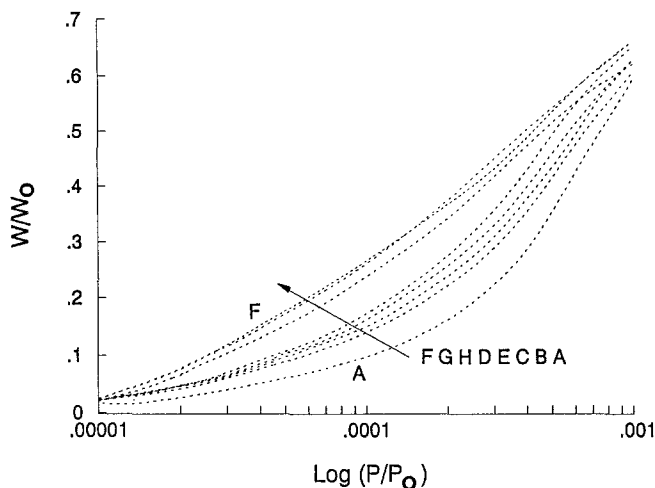


FIG. 4. Low pressure region of the Ar sorption isotherm at 87K. Catalyst: A (0.0 wt% C), B (2.4 wt% C), C (2.5 wt% C), D (3.5 wt% C), E (5.6 wt% C), F (7.4 wt% C), G (8.1 wt% C), H (8.4 wt% C).

Ar adsorption at saturation decreased. The Ar micropore volumes are given in Table 1 and are comparable to the N_2 micropore volumes. For microporous materials, there are two inflections in the 87K Ar adsorption isotherm, one at P/P_0 from 10^{-4} to 10^{-3} and a second at $P/P_0 > 10^{-3}$. The first inflection has been shown to reflect small changes in the pore size for molecular sieves (27). As the pore size is decreased, there is a shift to lower P/P_0 in the initial inflection point of the Ar isotherm. Figure 4 shows the normalized ($W/W_0 = 1$) Ar isotherms for the coked catalysts expanded to show the low-pressure inflections. The progressive shift to lower P/P_0 in the initial inflection point is indicative of a decrease in the pore size with increasing coke.

An effective pore size distribution was obtained from the Ar adsorption isotherm for pressures P/P_0 less than 10^{-3} by application of the Horvath-Kawazoe equation (38). The effective pore diameters are listed in Table 4, and representative pore size distributions are presented in Fig. 5. While the absolute values in Table 4 are affected by the specific choice of parameters in the Horvath-Kawazoe equation, the relative changes observed for the series are qualita-

tively correct. For the coke-free H-Y zeolite (Fig. 5a), one pore size 0.725 nm is observed. For catalyst with low coke levels, catalyst E (Fig. 5b), for example, the effec-

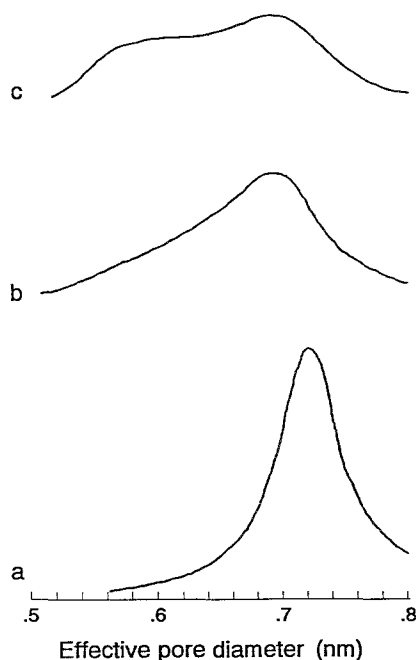


FIG. 5. Effective aperture diameter by Ar adsorption. a.) Catalyst A (0.0 wt% C). b.) Catalyst E (5.6 wt% C). c.) Catalyst F (7.4 wt% C).

TABLE 4

Effective Pore Diameter by Low Temperature Ar^a

Catalyst	Effective pore diameter (nm)
A	0.725
B	0.715
C	0.708
D	0.706
E	0.694
F	0.690 0.580
G	0.667 0.575
H	0.648 0.575
Mixture (A + F)	0.720 0.560

^a Precision of effective pore diameter is 0.01 nm.

tive pore diameter decreases to 0.694 nm. For catalysts with higher coke, e.g., catalyst F (Fig. 5c), a bimodal pore size distribution is observed, 0.690 and 0.580 nm. Catalyst F contains some pore apertures which are free, or nearly free, of coke (0.690 nm), while other apertures are partially restricted by coke deposits (0.580 nm). For the entire series, the number of coke-free apertures increases with increas-

ing coke on catalyst. Although it is likely that all coked catalysts have both types of pores, the bimodal distribution is clearly apparent at coke levels above 7 wt% C.

Mixtures of Catalysts

For catalysts with greater than 7 wt% carbon, catalysts F, G, and H, the effective pore size distribution by 87K Ar adsorption clearly indicates that there are two pore environments. ¹²⁹Xe NMR, however, gave evidence for only one pore environment. In order to resolve these discrepancies, physical mixtures of coke-free and coked zeolites were analyzed by each technique.

The ¹²⁹Xe NMR spectra for a mixture of catalyst A (0.0 wt% carbon) and catalyst F (7.4 wt% carbon) are given in Fig. 6. The catalyst particle size was approximately 0.5 to 1.0 mm, and the particles of the two catalyst were well mixed. In the mixture, the two chemical shifts are well resolved. In addition, both the pressure dependence of the observed chemical shift and the chemical shift at zero pressure, δ_s , for the two components in the mixture are equal to the

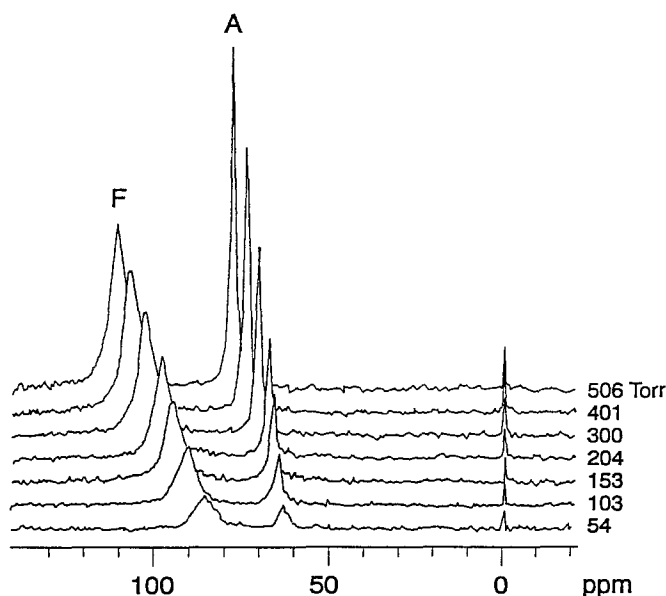


FIG. 6. ¹²⁹Xe chemical shift vs. pressure. Mixture of catalyst A (0.0 wt% C) and catalyst F (7.4 wt% C).

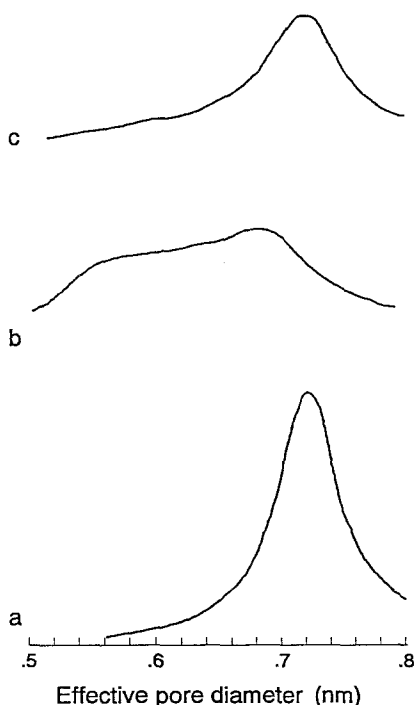


FIG. 7. Effective aperture diameter by Ar adsorption. a.) Catalyst A (0.0 wt% C). b.) Catalyst F (7.4 wt% C). c.) Mixture of Catalyst A and Catalyst F.

chemical shifts obtained for the individual catalysts, Table 4. ^{129}Xe NMR, therefore, can resolve separate pore (volume) environments, at least, when the different pore environments are separated by 0.5 nm, i.e., occur in separate macroscopic catalyst particles.

The Ar adsorption isotherm was obtained on the same mixture. A plot of the effective pore size distribution is given in Fig. 7. While two pore environments are clearly resolved in catalyst F, Fig. 7b, only one pore environment at 0.720 nm is prominent in the mixture of catalyst A and F, Fig. 7c. The smaller coked pores in catalyst F, 0.580 nm, appear as a shoulder at smaller diameter (0.56 nm) in the mixture of A and F, Fig. 7c. This is similar to the pore size distribution of catalyst E (7.4 wt% C), Fig. 5b. It is likely that in catalyst E, and all coked catalysts where one pore size is ob-

served, there are smaller, coke-restricted pores. As the number of coke-restricted pores increases with increasing coke, two pore environments are more easily resolved when the number of restricted pores are approximately equal to the number of coke-free pores.

The inability of ^{129}Xe NMR, even for spectra obtained at -125°C , to detect the two pore environments observed by Ar sorption may result from rapid exchange of Xe between the two sites (24, 39, 40). This would imply that distance between the two pore environments is small and that the two pore environments are uniformly distributed throughout the catalyst particle.

CONCLUSIONS

At room temperature, propylene is strongly chemisorbed, forming an aliphatic polymer which fills, or blocks, the available micropore volume in H-Y zeolite. Exposure of the aliphatic polymer to high temperature converts the carbon to aromatic coke with release of C_3 to C_8 (iso) paraffins. The aromaticity of the coke increases with increasing temperature and is determined by the highest reaction temperature. The coke is deposited in the micropores with little coke forming in the mesopores. For coked H-Y zeolites, ^{129}Xe NMR chemical shifts (at zero Xe pressure) increase linearly with decreasing micropore volume. At a constant pore volume, the Xe chemical shift is increased by 7 to 9 ppm relative to the coke-free zeolite at the same pore volume. The increase in the chemical shift due to coke is slightly dependent on the aromaticity of the coke. Low-temperature physical sorption of Ar is sensitive to the size of the pore aperture. As the coke content increases, the pore aperture decreases slightly. At high coke levels, two pore aperture environments, one aperture with deposited coke and one with little coke could be resolved. Since the two pore environments were not observed by ^{129}Xe NMR, it is likely that the two pore environments are

evenly distributed throughout the zeolite particle and the distance between the two pore environments is small. Each technique, ^{13}C and ^{129}Xe NMR, N_2 , Ar, and Xe physical adsorption, provides unique information necessary for the understanding of coke deposits and complements the information obtained by the other techniques.

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