Coke Formation on ZSM-5 Zeolites: Evidence from NMR Spectrometry of Sorbed Xenon Gas

CHIHJI TSIAO,*,[1] CECIL DYBOWSKI,*,[2] ANNE M. GAFFNEY,† AND JOHN A. SOFRANKO†

*Center for Catalytic Science and Technology and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716; and †ARCO Chemical Company, Newtown Square, Pennsylvania 19073

NMR spectrometry of xenon-129 adsorbed in coked samples of a totally protonated H-ZSM-5 zeolite and a Na,H-ZSM-5 zeolite acidified at the surfaces of the particles shows variations attributable to differences in coke distribution. © 1991 Academic Press, Inc.

INTRODUCTION

In petroleum refining and petrochemical production, catalyst deactivation by coke deposition is an important process that can limit the life of a catalyst. These carbonaceous deposits have been directly characterized by several experimental techniques (*1, 2, 3*). For zeolites, studies have shown that coke formation, like other reactions, is a shape-selective process that depends on the size and shape of the interconnecting pore and/or channel networks (*4, 5*). Recently Magnoux *et al.* (*6*) investigated the kinetics of coke formation over H-ZSM-5 zeolite and found that initial deactivation is due to coverage of acid sites by carbon residues. Above about 3 wt% coke, channel blockage obstructs access of reactant to part of the internal volume.

^{129}Xe NMR spectrometry is extremely useful for probing microporous materials. Ito *et al.* (*7*) demonstrated, for example, that NMR spectrometry of adsorbed xenon in coke-fouled H–Y zeolite could probe the deposits after coking and the nature of the internal surfaces after decoking. In this paper, we employ NMR spectrometry of ^{129}Xe gas sorbed in several samples produced by coking fully protonated and partially protonated ZSM-5 zeolites to explore the nature of acidification and coking in this catalyst. The NMR results are consistent with a distribution of coke restricted by size selectivity of the acidifying medium.

EXPERIMENTAL

Totally protonated H-ZSM-5 was prepared by the method given in U.S. patent 3,702,866, issued to Mobil. Na,H-ZSM-5 was prepared by heating Na-ZSM-5 zeolite with the protonated sterically hindered salt, (n-butyl)$_3$N · HCl, so that only cationic sites external to the zeolite channels undergo exchange. The modified Na,H-ZSM-5, therefore, has a much higher sodium content due to retention of sodium in the pores. Its constraint index number is significantly lower than that of the totally protonated H-ZSM-5, reflecting the external location of the acid sites.

For coking, approximately 0.8 g of either the H-ZSM-5 or Na,H-ZSM-5 zeolite was heated to 823 K, followed by exposure to 2-butene at 100 cm^3 min^{-1} for a specific time, as shown in Table 1, to obtain samples with varying degrees of coking. The samples were then stored at 298 K for later use in ^{129}Xe NMR or other measurements.

All coked and uncoked samples were pretreated for ^{129}Xe NMR spectrometry by the

---

[1] Present address: Department of Chemistry, State University of New York at Binghamton, Binghamton, NY.

[2] To whom correspondence should be addressed.

TABLE 1

Treatment and Coke Contents of Protonated
H-ZSM-5 and Modified Na,H-ZSM-5 Samples

Sample	Exposure to 2-butene (min)	Coke content (wt%)
A. Na,H-ZSM-5		
Fresh	0	0.
Slightly coked	1.6	1.
Heavily coked	48.	12.
B. H-ZSM-5		
Fresh	0	0.
Slightly coked	1.2	1.
Heavily coked	36.	12.

following procedure: Approximately 0.4 g of material was placed in an NMR tube with a resealable coaxial Teflon stopcock. The sample was outgassed to a pressure of 1.0×10^{-5} Torr at 295 K. It was slowly heated to 673 K over 6 h and maintained at that temperature for 12 h under dynamic vacuum. After cooling to 295 K, the sample was exposed to xenon gas (Air Products and Chemicals, 99.99%) for 15 min to allow equilibrium to be reached. Subsequently the tube was sealed and removed from the manifold. Xenon uptake isotherms were measured at 295 K during this successive adsorption process. They show Langmuir-type dependences of uptake on pressure in the range up to 700 Torr, as can be seen in Fig. 1.

^{129}Xe NMR spectra were recorded with a Bruker WM-250 NMR spectrometer at 69.19 MHz. Each spectrum is the accumulation of 500 transients with a relaxation delay of 0.5 s. The chemical shifts are reported with respect to bulk xenon gas extrapolated to $P = 0$, using a secondary standard of xenon adsorbed in Na–Y zeolite at 590 Torr (8). Positive chemical shifts are to higher frequency than the reference.

RESULTS

Figures 1A and 1B show the adsorption isotherms of xenon on the Na,H-ZSM-5 and

H-ZSM-5 zeolites, respectively. From the comparison, one sees that xenon uptake decreases slightly (about 10%) with coke content in the Na,H-ZSM-5 zeolite. However, it decreases greatly, even with a low (1%) coke content, on zeolite H-ZSM-5, and decreases only slightly more with heavy coking (12%).

Figures 2A and 2B give the xenon-129 chemical shift as a function of the uptake, ρ, of xenon per gram of dry zeolite for the Na,H-ZSM-5 and the H-ZSM-5 zeolites, respectively. One can see that the chemical shift in these materials obeys the truncated form of Fraissard's equation (9, 10):

$$\sigma(\rho) = \sigma_0 + \sigma_1\rho, \tag{1}$$

where $\sigma(\rho)$ is the observed ^{129}Xe chemical shift at a given uptake. σ_0 is the extrapolated chemical shift at infinitesimally low uptake, a term characteristic of the interactions be-
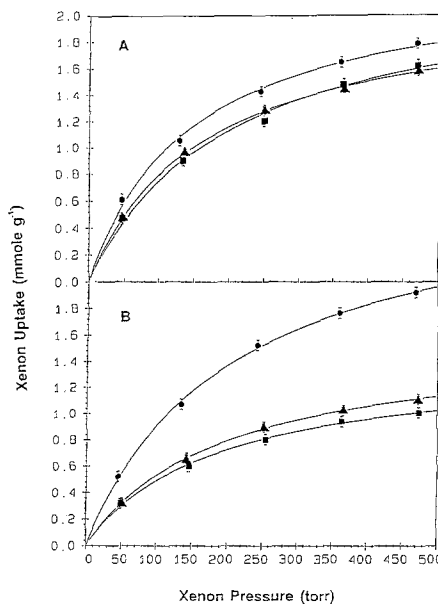

FIG. 1. (A) Xenon adsorption isotherms (at 297 K) of the size-selectively modified Na,H-ZSM-5 zeolites having different coke contents: ●—uncoked; ▲—1 wt% coke; ■—12 wt% coke. (B) Xenon adsorption isotherms (at 297 K) of fully protonated H-ZSM-5 zeolites having different coke contents: ●—uncoked; ▲—1 wt% coke; ■—12 wt% coke.
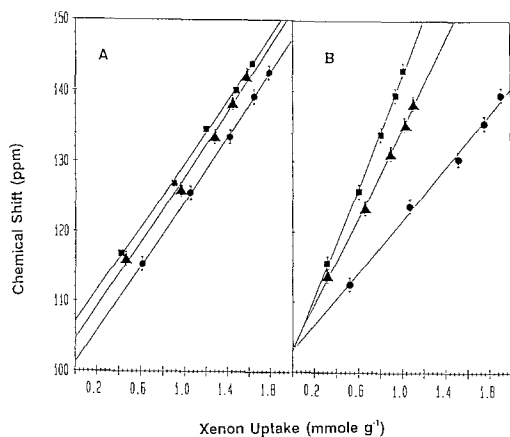
FIG. 2. (A) ^{129}Xenon chemical shift as a function of xenon uptake for the modified Na,H-ZSM-5 zeolites with different coke contents: ●—uncoked; ▲—1 wt% coke; ■—12 wt% coke. (B) Xenon chemical shift as a function of xenon uptake for fully protonated H-ZSM-5 zeolites having different coke contents: ●—uncoked; ▲—1 wt% coke; ■—12 wt% coke.

tween the xenon atom and the structure in which it is adsorbed. σ_1 is the first-order coefficient in a virial expansion of the chemical shift and is a measure of the effects of xenon–xenon interactions. From the graphs one obtains the Fraissard parameters for xenon under various conditions of treatment of the ZSM-5 zeolite; these are listed in Table 2. Figure 2A shows that, for the Na,H-ZSM-5 zeolite, the plots are nearly parallel, whatever the coke level. The intercepts, σ_0, do depend on the pretreatment conditions and increase with coke content. From Figure 2B, a much different picture emerges for xenon in H-ZSM-5. Again the plots obey Eq. (1). However, coking of H-ZSM-5 alters the slope of the profile, while leaving the intercept at low coverage nearly the same. (See Table 2.)

DISCUSSION

To understand the xenon chemical-shift profiles, one must remember that, because of relaxation-time differences, the NMR spectrum is that of xenon spending appreciable time in the zeolite channels. Demar-

quay and Fraissard (*11*) have shown that the intercept, σ_0, can be interpreted in terms of a "mean free path" of xenon in the zeolite and have related this NMR-derived mean free path to structural parameters such as channel diameter by a Monte Carlo simulation procedure. They empirically determined the intercept to depend on mean free path as

$$\sigma_0 = A/(B + \lambda), \qquad (2)$$

where λ is the mean free path in the structure. For an ideal infinitely long straight channel, λ is related to the channel diameter by the equation

$$\lambda = D_{\text{channel}} - D_{\text{xenon}}. \qquad (3)$$

Cheung and Fu (*12*) have derived an equation of similar form from a simple physical model. Recently, two of us have shown there is a relationship between the extrapolated chemical shift at low coverage, σ_0, and the average pore size of zeolites determined by argon uptake, as analyzed by the Horvath–Kawazoe method (*13*). Such derived parameters as the mean free path and average pore size seem to scale with other measures of the structure, but they do not necessarily correspond quantitatively to measures such as X-ray-derived interatomic distances. However, changes in σ_0 for

TABLE 2

Fraissard Parameter, Effective Channel Diameters, and Decrease of Void Volume for Samples after Various Treatments

Sample	σ_0 (ppm)	σ_1 (ppm-g/mmol)	D_{channel} (Å)[a]	V/V_0
A. Na,H-ZSM-5				
Fresh	101.3 ± 0.7	23.1 ± 0.5	7.3	—
Slightly coked	104.6 ± 1.3	23.2 ± 1.1	7.1	1.00[b]
Heavily coked	107.7 ± 0.6	23.5 ± 0.5	7.0	0.98[b]
B. H-ZSM-5				
Fresh	103.1 ± 1.1	18.7 ± 0.8	7.2	—
Slightly coked	103.4 ± 0.5	31.3 ± 0.6	7.2	0.60[b]
Heavily coked	102.9 ± 0.8	39.2 ± 1.0	7.2	0.48[b]

[a] Calculated using Eqs. (1) and (2), with $A = 499$, $B = 2.054$, and $D_{\text{xenon}} = 4.4$ Å.
[b] These quantities have associated uncertainties of ±0.05.

Na,H-ZSM-5 *do* indicate slight changes in structural features that affect the xenon NMR response. The data may be *interpreted,* for example, as a slight change in effective channel diameter. Using the A and B parameters of Demarquay and Fraissard, we estimate the effective channel diameters for the samples of ZSM-5 from Eq. (3). One must be cautious in overinterpreting these numbers as implying a *uniform* reduction of the channels; rather it represents an average description of the collisions experienced by a xenon atom.

As seen in Table 2, the effective channel diameter of the modified Na,H-ZSM-5 (as calculated from the ^{129}Xe NMR parameter, σ_0) is reduced by a few tenths of an Angstrom by deposition of coke even at the 1 wt% level. If one models the ZSM-5 structure as an infinite cylinder, a uniform reduction of the channel diameter by 5% (from 7.3 to 7.0 Å) is sufficient to account for a reduction of approximately 9–10% in volume. Coke surely does not deposit in such sub-Angstrom layers, but slight deposition in the interior is consistent with the reduction in uptake of xenon that we observe.

The channels available to xenon in coked H-ZSM-5 appear to be essentially of the same structure, no matter how heavy the coking, as indicated by the essentially constant value of σ_0 for these samples (and the similarly constant value of $D_{channel}$). Thus, the local environment of xenon atoms is, at most, only slightly changed by coking in this sample. This is in stark contrast to the 45% loss in uptake upon coking this sample, even at levels as low as 1 wt%. Perhaps the most startling observation in these experiments is the change in the slope, σ_1, of the curves for H-ZSM-5 with extent of coking. Ito *et al.* (7) observed similar changes in slope for coked H–Y zeolites.

Generally, σ_1 reflects the effects of two-body collisions between xenon atoms. The change in slope can be interpreted as a change in free volume upon coking. One may estimate effective relative internal vol-

ume accessible to xenon gas per gram of material from the slopes (7).

$$V/V_0 = \sigma_1^{\text{uncoked}}/\sigma_1^{\text{coked}}, \qquad (4)$$

where V is the internal volume of the coked sample and V_0 is the internal volume of the uncoked material. From the σ_1 values in Table 2B, one would conclude that H-ZSM-5 has lost about 40% of the internal volume per gram due to coking, even at 1 wt% coke. The isotherms for xenon uptake in Na,H-ZSM-5 show a 9–10% reduction in capacity not detectable in the slopes of the chemical-shift profiles (Table 2A).

For H-ZSM-5, we may estimate the expected loss of volume due only to channel filling by the coke, assuming a density of 1.8–2.1 g cm^{-3} for amorphous carbon^{14} and an internal volume for ZSM-5 in the range of 0.10–0.19 cm^3 g^{-1} (*15, 16*). For a 1 wt% loading the coke would occupy 2.5–5.7% of the internal volume, significantly less than the 45% loss observed. The fact that the loss in xenon-accessible volume calculated either from NMR parameters of Fig. 2 or from uptake measurements of Fig. 1 is larger than expected by a simple model of channel filling by coke indicates that much of the volume not accessible to xenon is not filled with coke in H-ZSM-5.

The internal Brønsted sites in protonated H-ZSM-5 zeolites have been proposed to be located at intersections between the straight and sinusoidal channels (*17*). Other investigators indicate that, at low coking, the carbonaceous material resides primarily on the external surfaces of crystallites, with each "coke molecule" covering one active site (*15*). At higher coking levels, highly alkylated aromatic material formed at the channel intersections block pores (*5*). The modified Na,H-ZSM-5 contains Brønsted sites only external to the channels. Carbonaceous residues will have formed primarily on the outer surfaces only and, perhaps near some channel mouths, as shown in Fig. 3. During coking the channels remain effectively accessible to xenon, as indicated by
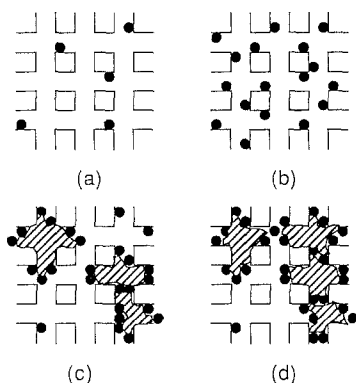
FIG. 3. Schematic depiction of coke distributions in zeolite ZSM-5. (a) Lightly coked Na,H-ZSM-5; (b) heavily coked Na,H-ZSM-5; (c) lightly coked H-ZSM-5; (d) heavily H-ZSM-5.

the NMR results, with a slight effective reduction of the channel size, *even at 12 wt% coke*. At this level of coking, a calculation similar to the one above would predict a blockage of 30–50% of the Na,H-ZSM-5 channels, if all the coke is formed inside the pores. We thus conclude that most of the coke resides on the external surfaces of the crystallites, with only a minor amount (about 10%) blocking channels in the material.

One difference between the xenon NMR results for coked Y-zeolites (7) and the results we present for ZSM-5 is the absence of resonances that would indicate the formation of mesopores in the latter material. Such resonances should be evident at chemical shifts nearer that of the bulk gas phase, and we see none. Thus, the deposition of coke on external surfaces must not have resulted in substantial amounts of the type of material found at the surfaces of the Y zeolites (7).

One model consistent with all these results is shown in Fig. 3, in which a few isolated, internal sites of Na,H-ZSM-5 are coked, but with no substantial blockage of large internal volumes, leaving most of the internal volume accessible to xenon. Most of the coke must, therefore, reside on the external surfaces of the Na,H-ZSM-5. For H-ZSM-5, on the other hand, substantial internal volume is blocked from access by the xenon, even at 1 wt% coking. The inaccessible volume is larger than the volume of coke deposited. Therefore, coke deposited in this material limits access of xenon to areas not filled with coke. Thus, the coke deposits in H-ZSM-5 occur in sufficiently large volumes to block off xenon movement. These deposits could be either (a) at the surface, (b) at intersections, or (c) in the channels. Comparison of the xenon results for this material to that of Na,H-ZSM-5, where the sites acidified are at the surface, leads one to conclude that the material is not totally deposited at the surface.

CONCLUSIONS

[129]Xenon NMR spectrometry uniquely gives information on the environment inside the ZSM-5 channels. As such, one may utilize it to investigate deposition of coke in active catalytic materials. For example, the deactivation of H-ZSM-5 upon deposition of coke results in channel blockage, which appears as a loss of void volume accessible to xenon in the NMR experiment and a reduction of sorption capacity. Treatment of ZSM-5 with the sterically hindered salt, (n-butyl)$_3$N · HCl, produces a material, Na,H-ZSM-5, which shows only slight blockage of channels, even at high coke levels. In both cases, it seems that the regions available to the xenon atoms are structurally similar, although one may interpret the results for Na,H-ZSM-5 in terms of a slight reduction of the effective channel diameter for this material. In particular, the Demarquay–Fraissard relation indicates that the regions available to xenon in H-ZSM-5 at the two coking levels examined are identical to those of the original material, as measured by xenon NMR spectrometry. These observations can be rationalized by a model in which deposition of coke in the channels or at intersections of H-ZSM-5 blocks xenon from accessing large internal volumes even

at low coking levels, whereas surface coking of the Na,H-ZSM-5 still permits access to most of the internal volume, even at high coking levels, with only a slight deposition of coke in the internal regions of this material.

REFERENCES

1. Butt, J. B., *Adv. Chem.* **24,** 259 (1972).
2. Wolf, E. E., and Alfani, F., *Catal. Rev.* **24,** 329 (1982).
3. Froment, G. F., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 1. Elsevier, Amsterdam, 1980.
4. Dejaifve, P., Auroux, A., Gravelle, P. C., Vedrine, J. C., Gabelica, Z., and Derouane, E. G., *J. Catal.* **70,** 123 (1981).
5. Guisnet, M., Magnoux, P., and Caneff, C., *in* "Proceedings, 7th International Zeolite Conference," p. 701. Kodasha, Tokyo, 1986.
6. Magnoux, P., Cartaud, P., Migrard, S., and Guisnet, M., *J. Catal.* **106,** 242 (1987).
7. Ito, T., Bonardet, J. L., Fraissard, J. P., Nagy, J. B., Andre, C., Gabelica, Z., Derouane, E. G., *Appl. Catal.* **43,** L5 (1988).
8. Scharpf, E. W., Crecely, R. W., Gates, B. C., and Dybowski, C., *J. Phys. Chem.* **90,** 9 (1986).
9. (a) Ito, T., and Fraissard, J. P., *J. Chem. Phys.* **76,** 5225 (1982); (b) Ito, T., and Fraissard, J. P., *Chem. Phys. Lett.* **111,** 271 (1984).
10. Tsiao, C., Corbin, D. R., and Dybowski, C., *J. Phys. Chem.,* **94,** 867 (1990).
11. Demarquay, J., and Fraissard, J. P., *Chem. Phys. Lett.* **136,** 314 (1987).
12. Cheung, T. T. P., and Fu, C. M., *J. Phys. Chem.* **93,** 3740 (1989).
13. Cotterman, R. L., Hickson, D. A., Cartlidge, S., Dybowski, C., and Tsiao, C., *Zeolites,* **11,** 27 (1991).
14. Weast, R. C., Ed., "CRC Handbook of Chemistry and Physics." CRC Press, Boca Raton, FL, 1982.
15. Breck, D. W., "Zeolite Molecular Sieves," p. 352. Krieger, Malabar, FL, 1984.
16. Flanigen, E. M., Bennett, J. M., Grose, R. W., Cohen, J. P., Patton, R. L., and Kirchner, R. M., *Nature* **271,** 512 (1978).
17. Derouane, E. G., and Vedrine, J. C., *J. Mol. Catal.* **4,** 479 (1980).