

STUDY OF COKE DISTRIBUTION IN HZSM-5 BY ^{129}Xe NMR*

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Received September 13, 1991

Accepted October 22, 1991

The location of coke formed during conversion of methanol or acetone on HZSM-5 zeolites has been examined using ^{129}Xe NMR spectroscopy. The results show that the type of reaction and the method of regeneration have great importance for the location of carbonaceous residues inside or outside the zeolite framework.

The deactivation of zeolites by coke deposition during cracking reactions is a crucial industrial problem. These coking phenomena have been studied by various techniques (^{13}C NMR, X-ray diffraction, IR, ESR)¹⁻³. Recently, the ^{129}Xe NMR technique, developed by Fraissard and Ito⁴, was successfully used to study coking in HY zeolites^{5,6}. The present paper emphasizes the influence of the reagents and the mode of coke destruction and removal on its location.

EXPERIMENTAL

We have studied two sets of HZSM-5 zeolites coked during methanol or acetone conversion. The first set consists of samples with low Al content ($\text{Si}/\text{Al} = 80$ before coking and 250 after coking) and pelletized with Al_2O_3 as a binder. Methanol conversion was carried out in a nitrogen or hydrogen stream. The reaction was stopped when the concentration of dimethyl ether exceeded 5%; the coke amounts were 7 and 14 wt. % under N_2 and H_2 atmosphere, respectively. The ratio of aromatic to aliphatic carbons in these two samples, prepared in the Section of Physics of Leipzig University, was the same⁷. The second set consists of samples with low Si/Al ratio (13.6). The fresh catalyst was prepared by acid treatment of NaZSM-5 supplied by the Research Institute for Oil and Hydrocarbon Gases, Czechoslovakia. Coke was produced during the acetone conversion and amounted to 10.7 wt. % when the catalyst was almost completely deactivated. Deposit removal of the 10.7 wt. % coke was realized either by pyrolysis at 873 K

* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis"*, Prague, September 8–13, 1991.

(resulting coke amount 9.2 wt. % or by gradual oxidation in a 20% oxygen-helium stream at 773 K (coke contents 9.7, 5.5 and 1.5 wt. %, respectively).

The xenon adsorption isotherms were measured in a classical volumetric apparatus at 300 K.

^{129}Xe NMR spectra were obtained at 300 K using a Bruker CXP 100 spectrometer operating at 24.9 MHz. The repetition time was 0.5 s and the number of scans was between 10^3 and $1 \cdot 10^5$. The zero ppm value for ^{129}Xe NMR is defined as that of Xe gas extrapolated to zero pressure.

RESULTS AND DISCUSSION

Xenon Adsorption Isotherms

In the case of samples with low Al content (Fig. 1A) the coking leads to a decrease by 30% of the void volume. However, for samples with 7 and 14 wt. % coke, the adsorption isotherms are superimposed, which means that a large portion of the coke, for samples with coke amount higher than 7 wt. % outside the crystallites.

For samples with low Si/Al ratio (Fig. 1B), adsorption isotherms show that the void volume within the framework is progressively restored during regeneration. Nevertheless, the removal of a small amount of the deposit by oxidation restores a large part of the internal volume. For the fresh catalyst and the catalyst with 1.5 wt. % of coke, the adsorption isotherms are exactly superimposed. Thus, the majority of the residual coke (doubtless with the most condensed components) is probably located outside the crystallites.

^{129}Xe NMR Results

Because of its high polarizability, the xenon atom is an ideal probe to investigate the porosity of microporous systems. The chemical shift δ of xenon adsorbed in such solids is given by the Fraissard equation⁴

$$\delta = \delta_s + \delta_{\text{Xe}} + (\delta_E + \delta_M) + \delta_{\text{ref}}$$

δ_s is the value of δ for $[\text{Xe}] = 0$ if there is neither electric ($\delta_E = 0$) nor magnetic ($\delta_M = 0$) effect, δ_{ref} represents the chemical shift of Xe at zero pressure taken as the reference. It depends on the mean free path of xenon imposed by the structure⁸. δ_{Xe} is due to Xe-Xe collisions; this term predominates at high concentration of xenon. In this case, the slope $d\delta/dn$ of the $\delta = f(n_{\text{Xe}})$ curve is proportional to the reciprocal of the void volume and thus provides information on the degree of the void intercrystalline volume filling⁴.

In the case of low Al content samples, we observe only one symmetrical signal, regardless of the xenon concentration and the coke content. For the fresh catalyst (Si/Al = 80), the $\delta = f(n_{\text{Xe}})$ curve has the shape reported by Fraissard and Ito⁴ with a break between $1 \cdot 10^{20}$ and $1 \cdot 10^{21}$ molecules Xe g^{-1} . For the two coked

samples (7 and 14 wt. %) the break disappears and the δ curves become straight lines, that are superimposed (Fig. 2A); this means that the remaining void volumes are the same. The ratio of the slopes $d\delta/dn$ between the coked and the fresh catalyst is 1.35, corresponding to a 27% decrease in the void volume, in good agreement with the xenon adsorption isotherms. The δ_s values for all the 3 samples are similar: at low concentration, xenon is mainly adsorbed in zones which are not influenced by the coke deposit; coke distribution within the zeolite framework is heterogeneous, as had been observed for HY zeolites in n-hexane and propylene conversions^{5,6}.

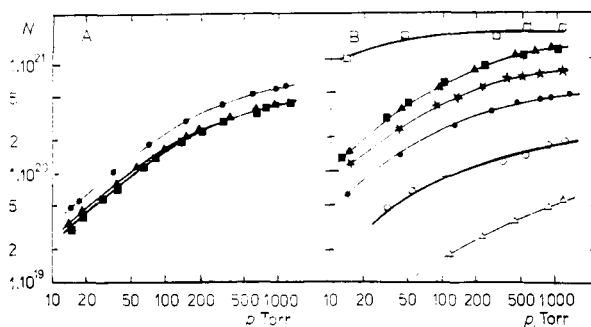


FIG. 1

Xenon adsorption isotherms at 300 K for fresh and coked HZSM-5 in methanol (A) and acetone (B) conversion. N means molecules g^{-1} . A: \bullet fresh catalyst ($\text{Si}/\text{Al} = 80$), \blacktriangle with 7 and \blacksquare with 14 wt. % of coke, respectively. B: \blacksquare fresh catalyst ($\text{Si}/\text{Al} = 13.6$), \square fresh catalyst at -50°C , \blacktriangle with 1.5, $*$ with 5.5, \bullet with 9.7, \circ with 9.2 (after pyrolysis of sample with 10.7 wt. % of coke) and Δ with 10.7 wt. % of coke

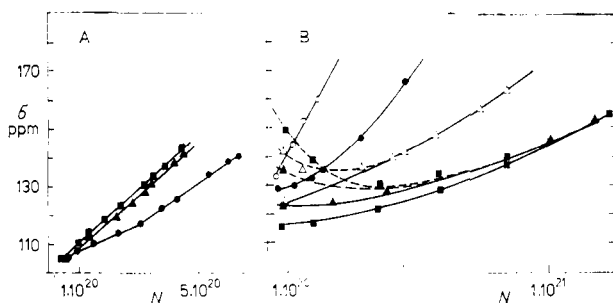


FIG. 2

^{129}Xe NMR shifts versus Xe concentration. A: \bullet fresh catalyst ($\text{Si}/\text{Al} = 80$), \blacktriangle with 7 and \blacksquare with 14 wt. % of coke, respectively. B: \blacksquare fresh catalyst ($\text{Si}/\text{Al} = 13.6$), \blacktriangle with 1.5, Δ with 5.5, \bullet with 9.7 and \circ with 9.2 wt. % of coke (after pyrolysis of the sample with 10.7 wt. % of coke)

For the high Al content samples, the ^{129}Xe NMR spectra are very different from the spectra described above. Some spectra are shown in Fig. 3. At high xenon concentrations, fresh and slightly coked samples (0–5.5%) exhibit only one NMR signal, which is symmetrical. However, when the xenon concentration decreases, two lines can be observed: one with a δ variation similar to that observed for pure HZSM-5 zeolites and the second, upfield, which shows an increase in δ and a strong broadening at low xenon pressure (Fig. 2B). This indicates that part of the extra-framework aluminium was not removed during the zeolite preparation and remains in the channels, acting as a strong adsorption site as in Ca, Mg or Ni zeolites^{4,9}. The same phenomenon was observed by Barrage et al.⁶ for partially dealuminated HY zeolites. When the coke content increases, this line tends to disappear. Therefore we can conclude that extraframework aluminium participates in the coke formation, either as an acid site or as its neighbour. The progressive disappearance of the 27-Al NMR line of hexacoordinated Al confirms this hypothesis¹⁰.

For the highest content of coke (10.7 wt. %), only one line is observed, which is pressure independent and weakly shifted (about 10 ppm). As was reported previously by Taro et al.⁵, this line can be attributed to xenon adsorbed in meso or macro cavities formed by intercrystalline coke. All the zeolite channels are then blocked or filled. Pyrolysis or oxidation removes a small part of the coke (about 10–15%), but, in agreement with the previous results¹¹, most of the changes occur in this region. For low and medium xenon concentrations, we observe only one

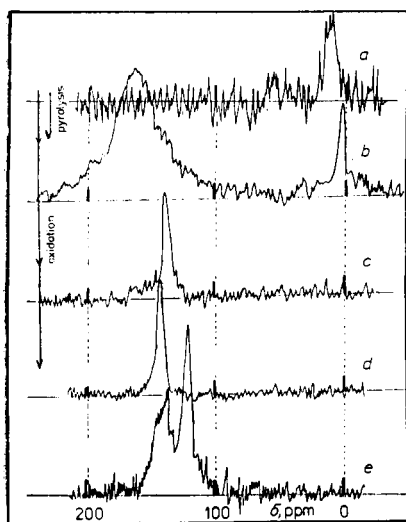


FIG. 3

^{129}Xe NMR spectra of xenon adsorbed on HZSM-5 (Si/Al = 13.6) with different coke amounts: a 10.7% coke, $5 \cdot 10^{19} \text{ Xe g}^{-1}$; b 9.2% coke, $2 \cdot 10^{20} \text{ Xe g}^{-1}$; c 5.5% coke, $5 \cdot 10^{20} \text{ Xe g}^{-1}$; d fresh catalyst, $4 \cdot 10^{20} \text{ Xe g}^{-1}$; e fresh catalyst, $4 \cdot 10^{20} \text{ Xe g}^{-1}$.

broad line, whose δ variation vs pressure is linear. It corresponds to xenon adsorbed in the restored void volume. The ratios of the slopes for pyrolyzed (9.2 wt. % of coke) and the fresh sample and for oxidized (9.7 wt. % of coke) and the fresh sample are 3.16 and 2.65, respectively. This means that about 32 and 38%, respectively, of the volume accessible to xenon is restored. Though a little lower, the latter value is comparable to that obtained in argon adsorption (43%) by Kubelková et al.¹². The former value is substantially higher than that measured for Ar and with TPD of benzene, ammonia and acetone³. The reason is not yet clear. Nevertheless, it follows from both types of measurements, that, although the oxidation removes a smaller amount of coke in the first step, it restores the inner volume to a higher extent than does the pyrolysis. For the pyrolyzed sample and at high concentration of xenon, a second, narrow and only very slightly shifted (2 ppm) line appears. It can be attributed to xenon in the remaining macrocavities of the coke or to xenon gas whose relaxation time is greatly shortened by the presence of the paramagnetic species. This line is not observed under the same conditions for the oxidized sample with 9.7 wt. % of coke.

These results support the assumption¹² that the partial oxidation begins by the reopening of the zeolite channels, removing primarily the lighter coke components; in contrast to the oxidation, the pyrolysis does not remove the polycondensed coke formed on the outer surface.

CONCLUSIONS

¹²⁹Xe NMR spectroscopy is an interesting tool for studying zeolite coking. First, it is able to detect the presence of extraframework aluminium remaining in the zeolite channels and show whether this species is incorporated in the coke within the framework. Second, it shows that the coking strongly depends on the reaction type and zeolite Si/Al ratio: with methanol (zeolite Si/Al = 80), only a third (even for 14 wt. % of coke) of the void volume is blocked or filled by coke a large part of which is located on the outer surface. With acetone (zeolite Si/Al = 13.6), all the channels are inaccessible when the amount of coke is 10.7 wt. %. Destruction of coke, either by pyrolysis or by oxidation, begins by the removal of the lighter coke components, however, the oxidation, in contrast to the pyrolysis, removes the polycondensed residue on the outer surface reopening thus the inner channels. The ¹²⁹Xe NMR spectra together with the previous results show that these two processes are different.

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