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Coking, Aging, and Regeneration of Zeolites

VII. Electron Microscopy and EELS Studies of External Coke Deposits on USHY, H–OFF, and H–ZSM-5 Zeolites

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External coke deposits produced by *n*-heptane cracking on USHY, H–OFF, and H–ZSM-5 zeolites have been located by a combination of transmission electron microscopic observations and electron energy loss spectroscopic (EELS) measurements performed with a field-emission gun scanning transmission electron microscope equipped with an electron spectrometer. The local structure of coke is determined from the fine structure at the high-energy side of the C_K EELS peak, in comparison with reference compounds such as graphite, coronene, and pentacene. In H–ZSM-5 and H–OFF the coke forms an external envelope around the zeolite crystal and stands as an empty mold after zeolite extraction. Its structure is similar to that of coronene (polyaromatic–pregraphitic). In USHY part of the coke is in the form of 1-nm-large carbon filaments protruding from the zeolite mesopores and micropores. Its structure is more like that of pentacene (linear polyaromatic). © 1988 Academic Press, Inc.

INTRODUCTION

The deactivation of acid catalysts during the conversion of organic compounds is due essentially to the formation of coke deposits which poison the acid sites and/or block the catalyst pores (*1*, *2*). As far as zeolites are concerned, coke could be located either in the microporous lattice or on the external surface depending upon the zeolite types and operating conditions (*3–7*). So far most of the studies on catalyst coking have been devoted to the kinetics of coke formation and catalyst deactivation; the few investigations on the chemical nature of coke are often limited to measurements of H/C ratios. Recently Guisnet *et al.* (*4–6*) have reported a solvent extraction technique based on the treatment with methylene chloride of coked zeolites previously leached with hydrofluoric acid. The soluble coke has a low polyaromatic character and corresponds essentially to coke deposited in the micropores. However, heavy hydrocarbons in large zeolite cages, in mesopores, or deposited on the outer surface might develop a high polyaromatic character and remain in the insoluble fraction.

Additional techniques are therefore required to better characterize the location and the structure of coke in zeolites. Physical techniques useful for this purpose have been reviewed by Bell (*8*). Electron energy loss spectroscopy (EELS) involving excitation of core electrons by primary electrons is potentially a well-suited technique giving analytical and structural information similar to that given by X-ray absorption spectroscopy. EELS spectra can be recorded either in a high-vacuum chamber equipped with an electron gun (100–2000 V) and CMA detector (*9*) or in an electron microscope (100–200 kV) equipped with an elec-

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tron spectrometer (*10*). The former equipment has been used to collect EELS data on a carbidic iron surface. Following the same procedure of data analysis of the fine structure (EXELFS) as that for EXAFS, it was shown that carbidic carbon can be differentiated from graphitic carbon on the basis of interatomic distances (*9*). On the other hand, recording EELS spectra with an electron spectrometer attached to a transmission electron microscope offers the additional advantage of having a high-resolution image of the specific zone analyzed (*10–11*). The spatial resolution of analysis can be as small as 1 nm^2 with a scanning transmission electron microscope (STEM) equipped with a field emission gun (FEG).

Until now there has been, to our knowledge, only a brief report (*12*) on the use of EELS coupled with electron microscopy to study the location and structure of carbon deposits on catalysts. Using this technique, we have started a series of studies on the location and structure of coke deposited in and on zeolites after catalytic reactions. In this first paper, the coke on the external surface of H–offretite, USHY, and H–ZSM-5 after *n*-heptane cracking has been characterized either on the coked zeolites or on the residual coke left after hydrofluoric acid and methylene chloride treatments. Their EELS spectra were compared to those of reference samples such as graphite, amorphous carbon, and polyaromatic molecules (pentacene and coronene).

EXPERIMENTAL

Materials and treatments. The ultrastable zeolite (USHY) and the proton-exchanged offretite (H–OFF) were supplied by Union Carbide and Grace-Davison, respectively. The H–ZSM-5 zeolite was synthesized according to Mobil patents (*13*). The compositions of the samples are given in Table 1.

TABLE 1

Composition of the Zeolites and Atomic H/C Ratio of Coke

Zeolites	Unit cell composition[a]	Total coke		Insoluble coke	
		%[b]	H/C[c]	%	H/C
USHY	$Na_{0.8}H_{47.7}Al_{48.5}Si_{143.5}O_{384}$	16	0.4	13	0.4[c]
H–OFF	$K_{0.4}H_{3.7}Al_{4.1}Si_{13.9}O_{36}$	13	0.5	7-8	0.5[c]
H–ZSM-5	$Na_{0.0015}H_{2.1}Al_{2.1}Si_{93.9}O_{192}$	7	0.65	4-5	0.5[d]

[a] From chemical analysis.

[b] Weight percent.

[c] Measured by oxidation.

[d] Estimated from the H/C ratio of the total and of the soluble cokes.

All the zeolites were pretreated at 500°C under flowing dry-nitrogen for 10 h and then coked at 450°C under flowing *n*-heptane as described in Ref. (*5*). Part of the coked zeolite was treated in a 40% hydrofluoric acid solution to dissolve the aluminosilicate lattice and then in methylene chloride at room temperature. The solid particles of the insoluble coke floating in the solvent were collected by decantation and kept for TEM and EELS studies. Table 1 gives the percentage of coke (total and insoluble) present in the coked zeolite as well as the ratios H/C determined by oxidation as described previously (*5*).

The reference samples for the EELS studies were a Lonza HSAG 12 graphite, amorphous carbons prepared by sputtering under vacuum, and pure coronene and pentacene obtained from Fluka.

Electron microscopy and EELS. The fresh zeolites, the coked zeolites, and the insoluble cokes were ultrasonically dispersed in water. A drop of the suspension was deposited on a copper grid coated with a holey carbon film. Some specimens were also prepared by sedimentation on the grid of an aerosol produced by a shock wave in a glass tube containing the sample. The final results were similar whatever the specimen preparation; however, the particles were more strongly held on the carbon film in the case of specimen prepared from the water suspension. Since our purpose was to study coke deposits on the external surface of the zeolite, no attempt has been made to cut the zeolite with an ultramicrotome which is required to study internal coke.

Transmission views of the specimen were taken with a Jeol 100C transmission electron microscope (TEM) equipped with high-resolution pole pieces. Analytical microscopy studies were performed with a Vacuum Generators HB-501 scanning transmission electron microscope. This dedicated STEM is equipped with a field-emission gun giving a very high current density electron beam. After demagnification by the objective lens the electron probe is as small as 0.5 nm on the specimen. The spatial resolution of analysis is such that 1 nm^2 of projected area of the sample can be analyzed selectively. Energy-dispersive X-ray emission spectroscopy (EDX) was performed with a Link solid-state detector fitting into the microscope column close to the specimen. Elements heavier than sodium are analyzed quantitatively with a standardless routine by a Tracor 5500 analyzer. EELS spectra were taken with a VG-ELS80 electron spectrometer attached to the microscope. Electrons transmitted through the sample were collected under a 2.5-mrad acceptance semiangle aperture and dispersed in energy by a magnetic prism. The electron spectrum was scanned sequentially through a linear acceptance slit facing the bright field electron detector. The sequential data acquisition, storage, and processing of the spectra were controlled by the Tracor analyzer.

During EELS data collection the image of the analyzed area on the sample was given by the annular dark-field detector. Slight corrections for specimen drift can be made to maintain the same area under the beam during data recording. The EELS spectra were recorded on an area of the sample lying over a hole in the carbon film. It is mandatory to avoid any contamination of the sample (building of carbon deposit under the electron beam) during analysis. Since the STEM column is in a high vacuum (10^{-8}–10^{-7} Pa) the main source of contamination is the specimen itself. Acid leaching of the copper grid before specimen preparation and treatment of the preparation at 100°C under 10^{-7} Pa in the airlock of the microscope were sometimes needed to avoid contamination. The spectra were not deconvoluted to remove plural scattering (*11*). However, the samples were sufficiently thin (<10 nm) to minimize this effect.

RESULTS AND DISCUSSION

1. Conventional TEM Study

TEM photographs were taken on the coked USHY, H–OFF and H–ZSM-5 zeolites as well as on the insoluble coke left after hydrofluoric acid and methylene chloride treatments. The images of the coked zeolites given in Figs. 1a, 2a, and 3a are compared to those of the insoluble cokes given in Figs. 1b, 2b, and 3b, respectively, at the same magnification.

The coked offretite (Fig. 2a) appears as rectangular platelets (0.2–1 μm width, 1–3 μm long). It has been checked that the offretite crystals before coking have the same habit. The image of the corresponding coke (Fig. 2b) is quite similar to that of the parent coked zeolite (Fig. 2a). Since the images are so similar (except that the coke is more transparent to electrons than the coked zeolite), it may be thought that the zeolite is not dissolved at all. To check this point, the composition of two platelets of similar habit, one from the coked zeolite and the other from the coke, have been analyzed by EDX. Figures 4a and 4b give the EDX spectra of the coked zeolite and of the coke, respectively. There is some silica left on the coke (Fig. 4b) but the intensity of the Si*Kα* emission peak is 250 times smaller than the signal recorded on the coked zeolite. Clearly, only traces of zeolite are left on this particular platelet so that Fig. 2b is very much the image of an almost pure coke.

The zeolite has been dissolved without any change of appearance, which means that there is a coating of coke around the zeolite platelet which is sufficiently rigid to

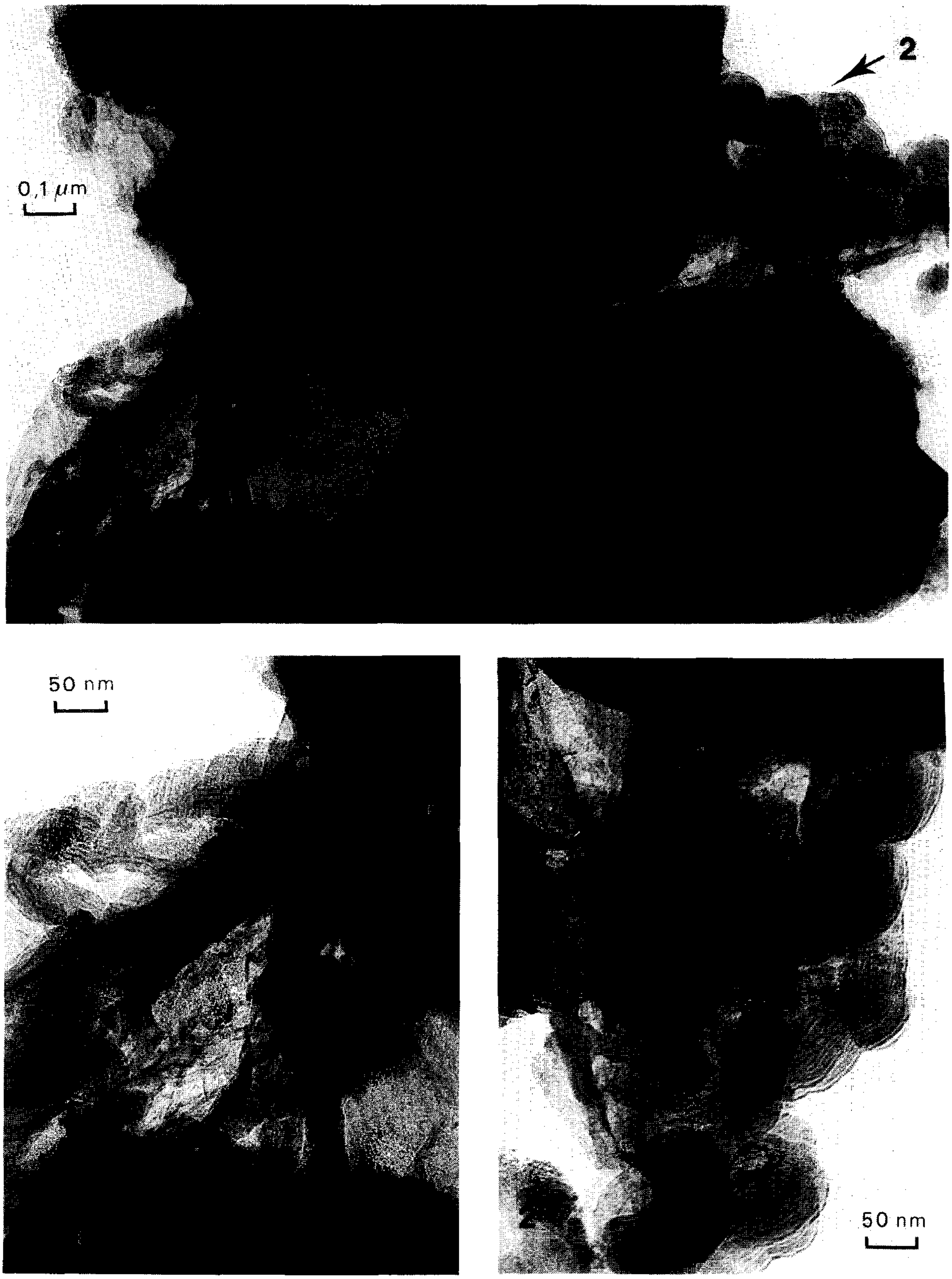

FIG. 1a. TEM view (× 75,000 magnification) of a coked USHY. The areas arrowed 1 and 2 are given at higher magnifications.

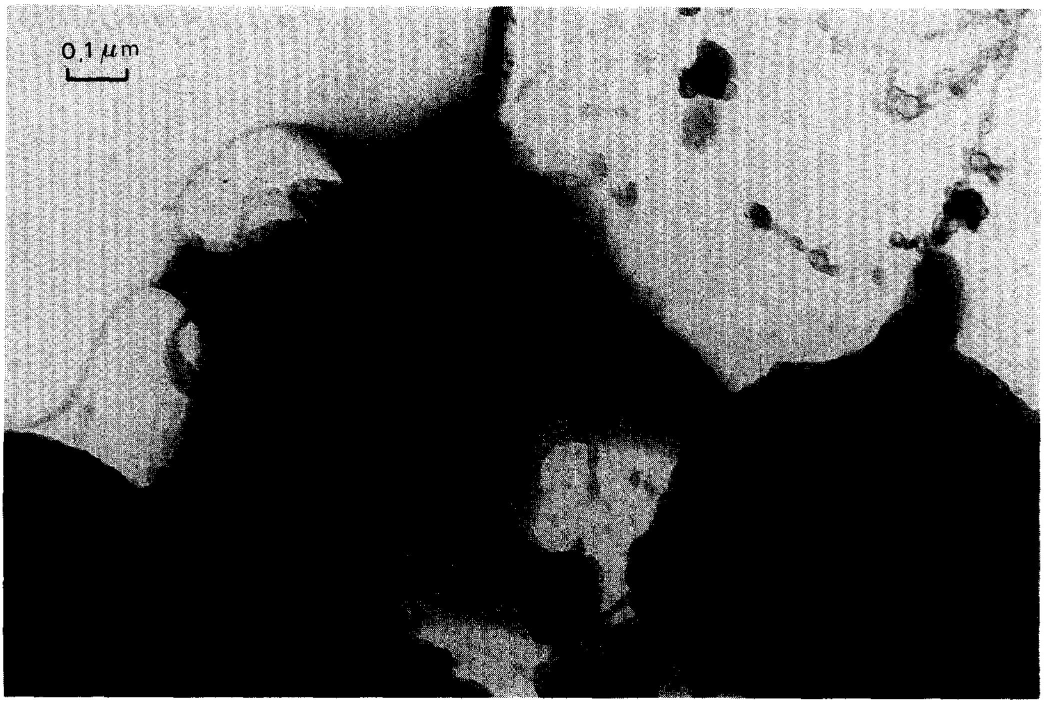

FIG. 1b. TEM view (× 75,000 magnification) of insoluble coke from USHY.

keep the external shape of the zeolite. The platelets of Fig. 2b can be described as empty shells or cocoons of coke.

The coked H–ZSM-5 zeolite (Fig. 3a) and the insoluble coke left after HF–CH_2Cl_2 treatments (Fig. 3b) also give similar images at the same magnification. A number of characteristic elongated hexagons are detected. It was checked again by EDX that the coke contains a very small amount of residual silica. Therefore, in this case too, the external coke is like a perfect replica of the parent zeolite.

The images of the coked USHY (Fig. 1a) and of the insoluble coke (Fig. 1b) bear strong similarities. The shape of the initial zeolite is kept by the coke but the coating is much less uniform than that in H–OFF and H–ZSM-5. In addition there are hairy carbon filaments present both in the coked zeolite and in the coke. It has been checked that these filaments were not present in USHY before coking. It seems that these filaments emerge from the zeolite grain (Fig. 1a) as if they were growing from the external surface, expecially from the mesopores present in USHY. Indeed, in a previous TEM study of USHY (*14*), it has been shown that the steaming process destroys part of the zeolite crystal leaving holes of 3 to 50 nm diameter partly filled with amorphous alumina and silica. These holes are evidenced on TEM photographs taken on ultramicrotome cuts; they are more difficult to see in Fig. 1a which is a direct view because the zeolite crystals are too thick. However, arrow 1 points to a zone on the edge of a zeolite crystal from which a bundle of coke filaments has issued. There are other places in Fig. 1a which suggest that coke filaments are protruding from the zeolite surface. On the other hand, arrow 2 points to a zone where nearly parallel filaments, about 1–2 nm thick, seem to have issued from the surface of the zeolite grain. This suggests that coke is produced inside the zeolite micropores fed by *n*-heptane cracking and then emerges from

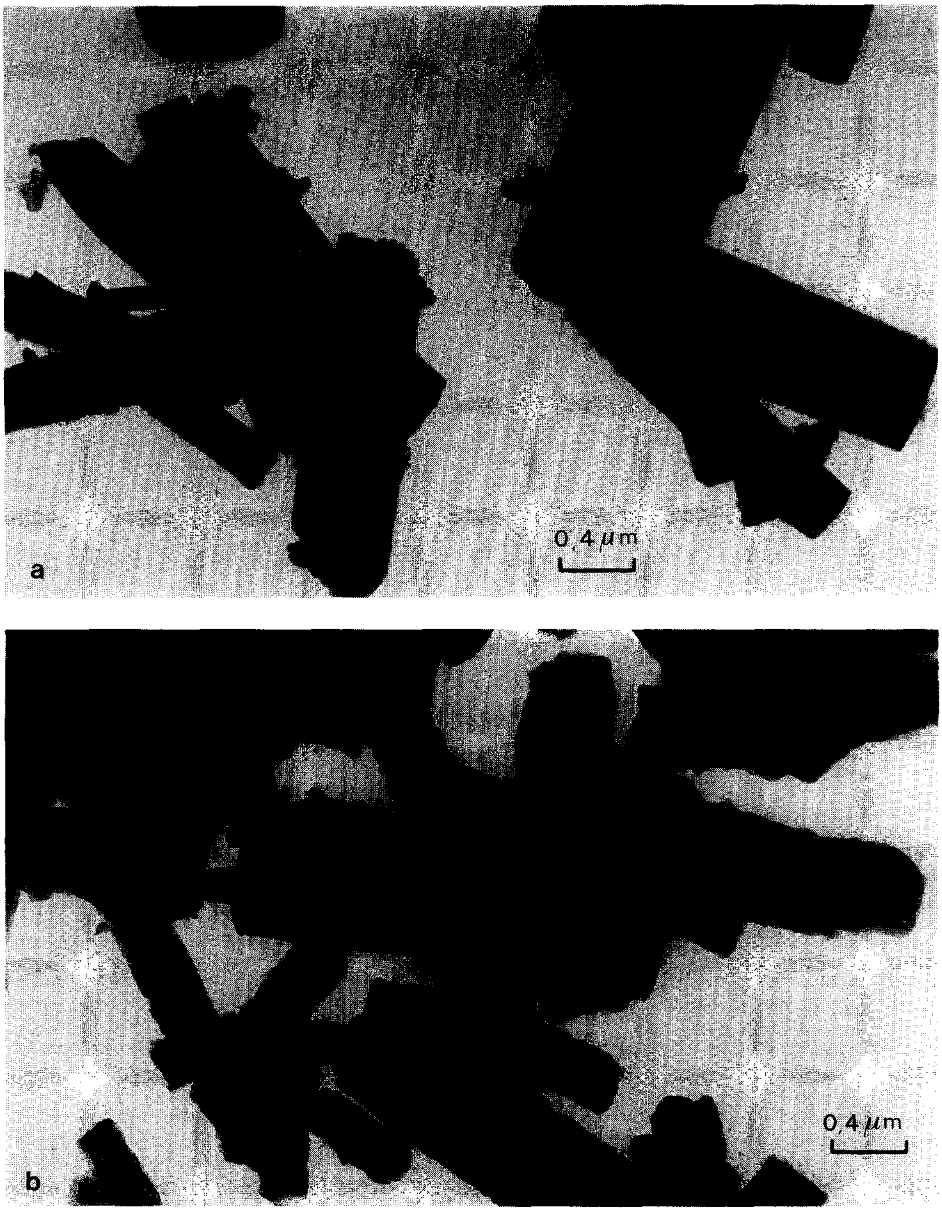

FIG. 2. TEM View (× 25,000 magnification). (a) Coked H-OFF; (b) insoluble coke from H-OFF.

zeolite like an extrudate from a nozzle. Figure 5 suggests two possible schemes of coke filament formation on USHY, corresponding to the images pointed out by arrows 1 and 2, respectively, in Fig. 1a.

2. EELS study of Coke Deposits

2.1. Location of coke on the zeolites. EELS measurements have been carried out on well-characterized areas of the zeolites imaged on the video of the STEM during data acquisition. Spectra were taken with different analysis windows (area scanned by the beam) ranging from 1 × 1 nm^2 area to whole zeolite grains (1000 × 1000 nm^2). A typical EELS spectrum, taken on an amorphous carbon film, is given in Fig. 6. In addition to the elastic peak there are two

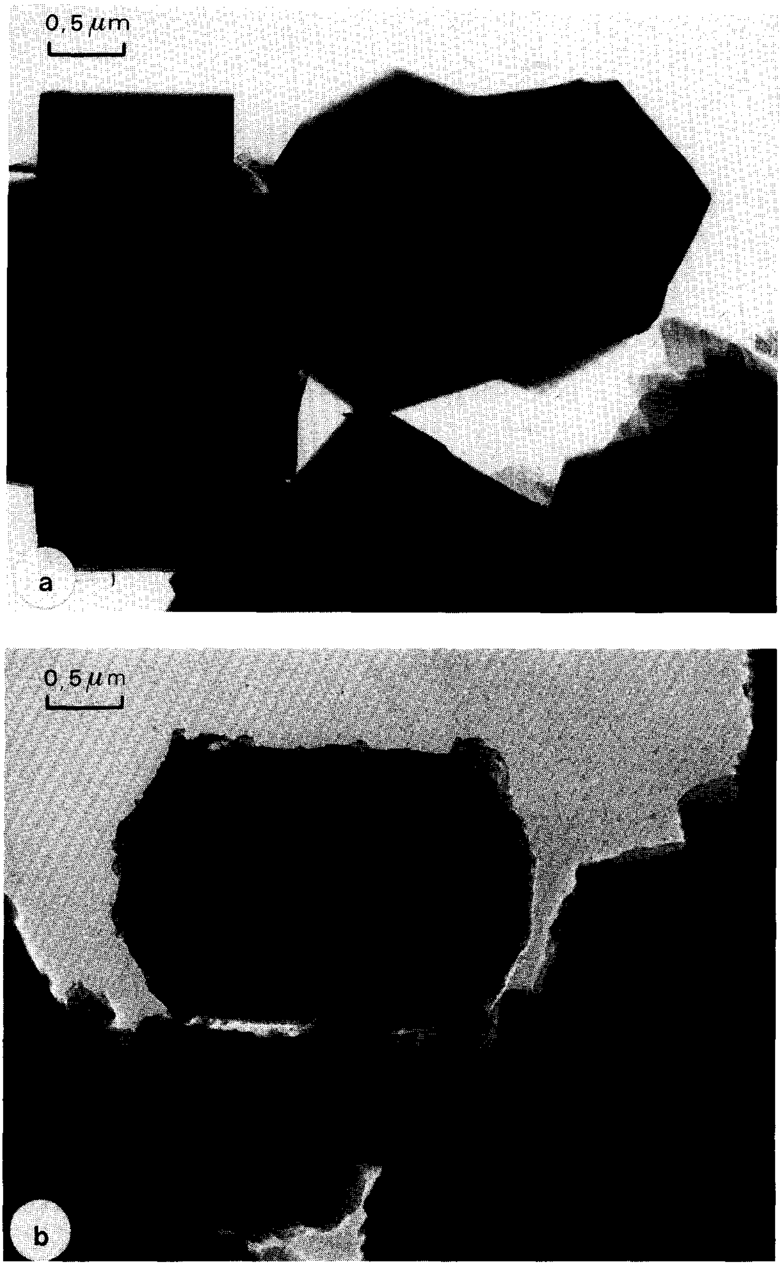

FIG. 3. TEM view (× 20,000 magnification). (a) Coked H–ZSM-5; (b) insoluble coke from H–ZSM-5.

noticeable features, namely a peak at 20–40 eV from the elastic peak which corresponds to excitation of valence band electrons (plasmon peak) and a much smaller peak at 285 eV corresponding to the excitation of the K electrons in the carbon atom. On thin samples, the intensity of the C_K edge is proportional to the amount of carbon atoms in the volume of sample scanned by the electron beam.

Using this technique it has been checked that the coke is present all around the

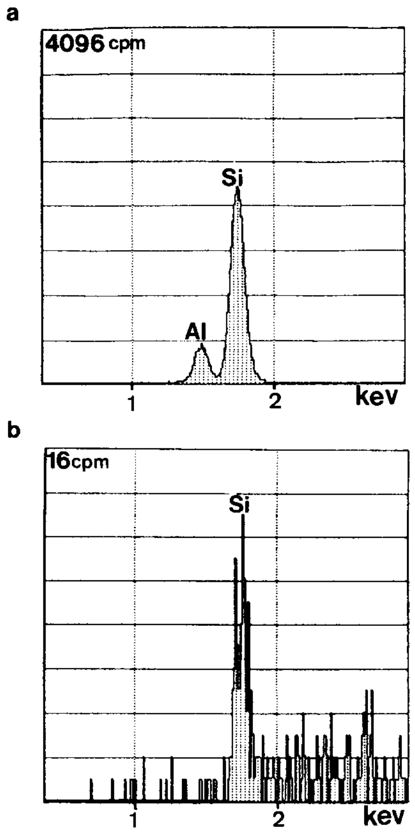

FIG. 4. EDX spectra taken with a FEG–STEM on 10 × 10-nm^2 areas. (a) Coked H-OFF (see Fig. 2a); (b) insoluble coke (see Fig. 2b).

grains of coked zeolites shown in Figs. 1a, 2a, and 3a and that the insoluble solids remaining after HF–CH_2Cl_2 treatments have carbon as the main component. This is not unexpected in view of the TEM study reported in the previous section. However, this technique to locate coke deposit is much more useful when it comes to locating internal coke. Thus we have been able to detect the presence of coke filling the mesopores of a dealuminated mordenite after dimethyl ether conversion (*15*).

2.2. Nature of the coke. From the fine structure past the edge of an EELS peak it is, in principle, possible to extract information similar to that given by XANES and EXAFS, i.e., the local coordination of atoms (distance and coordination number). However, the formulation of the multiple scattering theory of energy loss near edge structure (ELNES), the equivalent of XANES, is still in progress (*16*). The extended electron energy loss fine structure (EXELFS) technique has been applied previously (*17–20*) to calculate, with the same data processing as EXAFS (Fourier transform of 50–500 eV data), a radial distribution function giving interatomic distances in graphite (*17–20*). However, the present data, taken on small areas during a short period of time to minimize specimen drift and electron beam-induced damages, were too noisy to consider a data reduction process similar to EXAFS. Therefore no attempt has been made to perform a quantitative treatment of the EELS spectra. Instead we used a more qualitative approach which consists in comparing the EELS spectra taken on the coked zeolite (or on the insoluble coke) with the EELS spectra taken on reference carbon compounds of known structure.

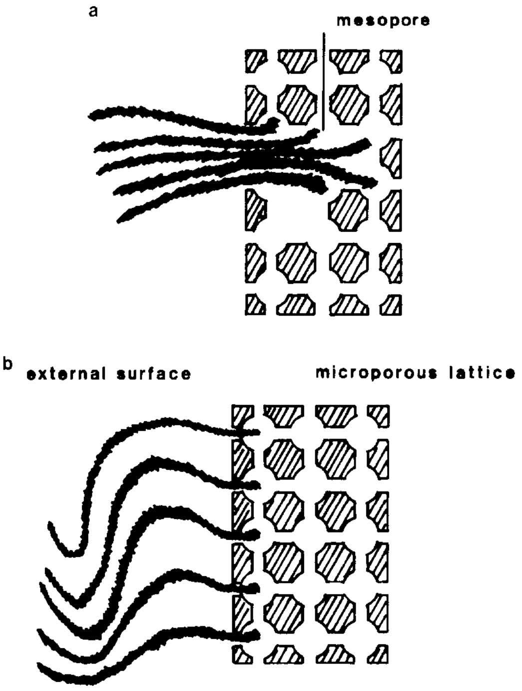

FIG. 5. Hypothetical schemes accounting for coke filament formation in USHY. (a) Zone arrowed 1 in Fig. 1a; (b) zone arrowed 2 in Fig. 1a.

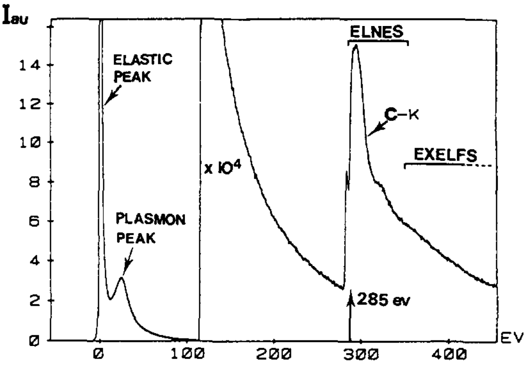

FIG. 6. Scheme of an EELS spectrum of amorphous carbon showing the different regions of interest.

EELS spectra of graphite (taken with the electron beam parallel to the [001] graphite axis), amorphous carbon, coronene, and pentacene are given in Figs. 7a–7d, respectively. The graphite spectrum shows two sharp peaks at 285 and 292 eV corresponding to the electron transitions from the K shell to the π^* and σ^* bands of graphite, respectively. The peak at 320 eV at the limit of the ELNES and EXELFS domains corresponds to an oscillation due to electron scattering–backscattering processes between the absorbing atoms and the neighbor atoms. This oscillation is especially high and sharp in graphite because of the crystal order of the atoms in the basal plane. In contrast, the EELS spectrum of amorphous carbon (Fig. 7b) exhibits no fine structure on the edge or past the edge (except a small shoulder on the edge onset) because the atoms are completely disordered. The EELS spectra of the polyaromatic molecules are intermediate between these two extreme cases. In contrast to graphite, coronene and pentacene are amorphous molecular compounds in random orientation; all the EELS spectra taken at different places were similar. The spectrum of coronene (Fig. 7c) does not exhibit marked π^* and σ^* transitions since the electronic structure of coronene is quite different from that of graphite. On the other hand the 320-eV ELNES–EXELFS peak is almost the same in graphite and coronene. This is not unexpected since coronene can be considered a small piece of graphite basal plane although it has only one ring with full sixfold coordination (Fig. 8a); therefore the local coordination of the carbon atoms is quite similar. By contrast, the 320-eV peak in the EELS spectrum of pentacene (Fig. 7d) is much broader than that in graphite and coronene indicating a less symmetrical coordination. Because of the linear arrangement of the aromatic rings (Fig. 8b), the molecule does not have the sixfold symmetry of graphite and coronene.

The EELS spectra of the coke derived from *n*-heptane cracking have been taken both on the coked zeolites and on the corresponding residual cokes. Because of the thickness of the zeolite crystal the spectra were recorded while the electron beam

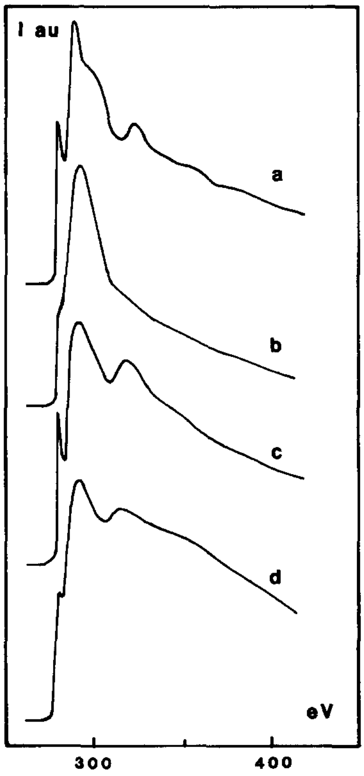

FIG. 7. EELS spectra taken on reference compounds with the EELS 80 electron spectrometer attached to the VG-HB501 STEM (background has been subtracted). (a) Graphite; (b) amorphous carbon; (c) coronene; (d) pentacene.

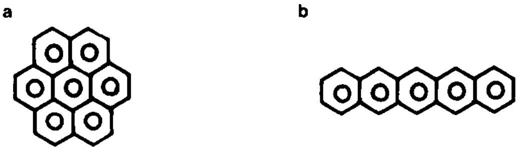

FIG. 8. Structural formulae. (a) Coronene; (b) pentacene.

was scanning 2- to 3-nm-large areas at the edge of the zeolite crystals. The spectra of insoluble coke were taken at different places with various analysis windows. These measurements show that the EELS spectra recorded on the coked zeolites and on the corresponding insoluble cokes are similar. Figures 9a, 9b, and 9c give the EELS spectra of the coke deposited on the external surface of USHY, H–OFF, and H–ZSM-5, respectively. The spectrum recorded on USHY (Fig. 9a) is different from those obtained on graphite (Fig. 7a) and coronene (Fig. 7c) since the 320-eV peak is much weaker. Since the peak reflects the local coordination one is led to conclude that the coke deposited on USHY does not have the sixfold symmetry typical of the coronene molecule or of the graphite basal plane. However, this does not mean that the coke is not polyaromatic since aromatic rings can form linear or branched chains. Indeed, the EELS spectrum bears some resemblance to that of pentacene (Fig. 7d) as far as the 320-eV peak is concerned. This result is in agreement with the TEM photograph (Fig. 1a) showing that coke filaments seem to emerge from the zeolite (see Section 1). Indeed, if the coke is formed in the zeolite micropores and grows from the inside to form protruding filaments, it cannot have the structure of the coronene molecule which is too bulky. On the other hand, polyaromatic molecules with a linear or partially branched configuration can creep along the micropores and emerge outside the zeolite crystal. The amorphous nature of the filaments was also checked by taking nanodiffraction patterns which exhibit only an amorphous ring.

By contrast, the coke formed on the external surface of H–ZSM-5 gives an EELS spectrum (Fig. 9c) not much different from that of coronene (Fig. 7c) which would indicate that the coke is built with graphite-like polyaromatic molecules. Obviously these molecules cannot originate from the micropores of H–ZSM-5, but must be formed by *n*-heptane cracking on the external surface or from a condensation of mono- or bi-aromatic products diffusing from the zeolite micropore where they are formed to the external surface.

As far as H–OFF is concerned, the EELS spectrum of the coke formed on the external surface (Fig. 9b) is intermediate between those on USHY and H–ZSM-5. Since the pore aperture in H–OFF is intermediate between those in Y-type and H–ZSM-5 zeolites, one can speculate that the structure of the coke is more heterogeneous, part of it protruding from the micro-

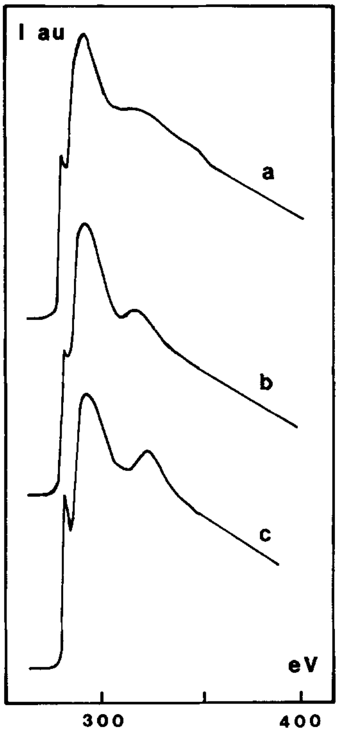

FIG. 9. EELS spectra of coke deposited on the external surface of zeolites. (a) USHY; (b) H–OFF; (c) H–ZSM-5.

pores as in USHY, the other part being formed as in H–ZSM-5.

CONCLUSION

It has been shown that a conventional TEM study conducted on coked zeolites can give detailed information on the coke morphology and its relation with the zeolite crystal. Thus the coke in H–OFF and H–ZSM-5 envelops the zeolite grain, forming an almost continuous shell which is sufficiently rigid to stand even if most of the zeolite has been dissolved by acid treatment. On the other hand, the coke on USHY exhibits a more heterogeneous morphology. The most striking features are the filaments of coke either bundled together at the mouth of mesopores or protruding individually out of zeolite as if the micropores were acting as nozzles. At any rate this strongly suggests that filamentous coke grows from the inside fed by the *n*-heptane cracking on the acid sites in the micropores.

This study shows for the first time that the attachment of an EELS spectrometer to a high-resolution STEM can be a powerful tool not only to locate carbon deposits on catalysts but also to obtain information on their structure. In this investigation the effort made on coke location was minimal since we focused our attention on the external coke which is easily detected. However, location of coke deposit at high spatial resolution is the most obvious use of the EELS–STEM technique and a forthcoming paper will show how useful it can be to detect a minute amount of coke filling mesopores (*15*).

The evaluation of the chemical nature of coke is less easy. The quality of the spectra is not sufficiently good to extract coordination numbers from the EXELFS. On the other hand, the ELNES portion of the spectra, i.e., that extending about 50 eV past the edge, can be recorded with a good signal-to-background ratio in a reasonable time; however, the ELNES theory is not yet routinely applicable. Nevertheless, a qualitative approach based on the comparison of the EELS spectra of the coked zeolites with those of reference compounds gives interesting results. Since the sixfold symmetry coronene molecule similar to graphite has an EELS spectrum different from the twofold symmetry of the pentacene molecule, it is possible to make a distinction between pregraphitic structure and linear polyaromatic structure. However, it should be kept in mind that many polyaromatic molecules that differ in size and configuration would have an ELNES spectrum almost similar to that of either coronene or pentacene. Thus it cannot be concluded from this study that pentacene is the main component of the coke formed on the external surface of USHY but it can be concluded that this coke is not coronene-like. This supports the fact that this coke is formed inside the micropores and emerges out the zeolite. On the other hand, the coke forming a cocoon around H–ZSM-5 has a marked polyaromatic pregraphitic character because it grows on the external surface.

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