JOURNAL OF CATALYSIS **116**, 164–170 (1989)

Location and Structure of Coke Deposits on Alumina-Supported Platinum Catalysts by EELS Associated with Electron Microscopy

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Received April 6, 1988; revised September 26, 1988

The location and structure of carbonaceous deposits formed upon coking Pt/Al_2O_3 catalysts with cyclopentane have been studied by conventional TEM and by electron energy loss spectroscopy (EELS) associated with high resolution scanning transmission electron microscopy. The TEM investigation shows patches of amorphous coke covering the support surrounding each metal particle. This is substantiated by EELS showing that the coke coverage can extend as far as 20 nm from a given particle. From the absence of fine structure on the EELS peak of carbon and from the comparison with reference compounds (graphite, coronene, and pentacene), it is concluded that the local structure of coke is not graphitic or pregraphitic but may consist in a disordered arrangement of polyaromatic molecules. After partial combustion at 563 K, the coke covering the metal particles is removed but the coke on the support is still present. This confirms previous temperature-programmed oxidation results.

INTRODUCTION

The chemistry and kinetics of catalyst deactivation by carbon deposition have been discussed thoroughly in several review papers (*1–4*). The literature on the structure of carbon deposits is comparatively scarce. Information can be obtained with various spectroscopic technique (*4, 5*) and even with diffraction techniques when the coke is graphitized (*6*). Analytical techniques such as chemical and chromatographic analyses of extracted coke (*7*) and temperature-programmed oxidation (TPO) are also very helpful. The latter has led to fruitful results on the location of coke on reforming catalysts (*8–10*). Thus TPO experiments performed on Pt/Al_2O_3 catalysts coked with cyclopentane show the presence of two peaks near 300 and 500°C corresponding to the combustion of the coke located on the metal and on the support respectively. The coke on the support is produced by the polymerization on the acidic sites of cyclopentadiene derived from the dehydrogenation of cyclopentane on platinum. How far from a given particle the coke builds up remains an open question. Also the structure of these coke deposits is not well established as yet. The best technique for probing the location and structure of carbonaceous deposits on a microscopic or nanoscopic scale is electron energy loss spectroscopy (EELS) combined with electron microscopy. Indeed, the attachment of an EELS spectrometer to a scanning transmission electron microscope (STEM) makes possible the recording of carbon EELS spectra on sample areas as small as a few square nanometers (*11*). We have shown in a previous study (*12*) that the location and local structure of coke on zeolites can be determined with this technique.

The first aim of the present paper is to determine the position and the structure of the coke formed on a Pt/Al_2O_3 catalyst coked with cyclopentane. The structure of this coke will be established in comparison with reference compounds of known structure. The second aim is to check previous TPO results showing that the coke deposited on platinum is eliminated after 300°C

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0021-9517/89 $3.00

heating in diluted oxygen while the carbon on alumina is untouched.

EXPERIMENTAL

Materials and Treatments

A homogeneous distribution of platinum particles was obtained by a multiple metal-loading technique described previously (*13*). In a first step, a homogeneous distribution of very small particles was obtained by ion exchange on γ-alumina followed by hydrogen reduction. The Pt/Al_2O_3 catalyst thus obtained was maintained for 1 h in a hydrochloric acid solution saturated with hydrogen. On replacing this solution by an oxygen-free chloroplatinic acid solution, the $PtCl_6^{2-}$ anions were reduced by dissociated hydrogen adsorbed on the small particles. This resulted in a deposit of platinum atoms on the particles. The entire process was repeated several times until the desired size of particle was obtained. The final catalyst contained 1 wt% platinum, with particle sizes in the range 3–6 nm, as confirmed by electron microscopy.

The Pt/Al_2O_3 catalyst was coked at 713 K for 4 h by cyclopentane. The percentage of carbon in the final catalyst, measured by TPO, was 4.3 wt%. To remove the coke deposit from the metal particles, the coked catalyst was heated for 30 min at 563 K in a mixture of 1% O_2–99% He.

Reference carbon compounds were a high surface area graphite from Lonza and pure coronene and pentacene from Fluka.

Electron Microscopy and EELS

Samples for the TEM and STEM studies were ultrasonically dispersed in water and the suspension was deposited on a copper grid coated with a holey carbon film. The conventional TEM study was carried out with a JEOL 100 CX microscope equipped with high resolution pole pieces. It has been checked that the (220) lattice planes of gold (d = 0.144 nm) can be imaged with this equipment. 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 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. EELS spectra were taken with a VG-ELS80 electron spectrometer attached to the microscope. Electrons transmitted through the sample were collected under a 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, storing, and processing of the spectra were controlled by a Tracor 5500 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 370 K 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. Location and Structure of Coke Deposits

A preliminary study was conducted on a real reforming catalyst. However, the particles were very small (<1 nm) and distributed all over the support. Since they were so close to each other it was impossible to check how far from a given particle the coke coverage was extending. Furthermore, they were too small to check if they were carbon covered and were sometimes very difficult to detect. Therefore, using the multiple-loading or refilling technique described previously (*13*), a 1 wt% Pt/Al_2O_3 has been prepared with Pt particles in a size range 3–6 nm so that the metal surface area remains high but the particles are large enough to be scanned individually by the electron probe in the STEM.

1.1. Conventional TEM study. It has been checked by taking successive photographs after different periods of time on a given area of the sample that the images are not changed, which indicates that the electron beam does not produce damage or contamination of the sample.

Figures 1a–1c give TEM photographs taken at two different magnifications. The preparation was successful since the particles are well separated from each other, and also no very large or very small particles are present. It can be noted that the Pt particles are sometimes faceted with a hexagonal outline. The images of the (111) lattice planes of alumina are clearly seen on thin sheets.

TEM views of the coked catalysts taken through the holes of the holey carbon film (Figs. 2a–2c) exhibit new contrasts. Indeed, around Pt particles the images are speckled as if a carbon film was present. The lattice images of alumina are difficult to detect except on areas far from any Pt particles. Thus, the lattice images of the platinum-free alumina sheet are still highly contrasted as in the area marked by the arrow A in Fig. 2a. In some cases (e.g., in Fig. 2b) the images of the Pt particles are also blurred, which could indicate that they are covered with coke. However, to be sure that this fuzziness is due to coke coverage rather than to a defocus, a through-focal series of pictures should have been taken in each case.

The speckled images were attributed to the presence of coke covering the support around the Pt particles. It was later checked by the EELS–STEM study that carbon is indeed present wherever the image is fuzzy. On thin edges of the sample the structure of the carbon can be imaged more distinctly. Thus, over the areas marked by the arrow B in Fig. 2a–2c, small curved chains packed together in a disordered manner are clearly observed. Neither regular graphite spacings nor fingerprint-like arrangements characteristic of graphitic structures were observed. Therefore, the coke deposited on the catalyst probably has a disordered structure.

It is noteworthy that the patches of coke surrounding Pt particles are not necessarily circular but may extend preferentially in a given direction. The coke spreads over alumina sheets supporting the Pt particles and sometimes spills over neighboring sheets.

1.2. STEM–EELS study. Most of the EELS spectra were taken on very small scanned areas, the typical analysis window being $(3 \times 4)\ nm^2$. In some cases the EELS spectra were recorded with the beam stopped on a given position; the area under analysis is then $(1 \times 1)\ nm^2$ but no image is available during the recording so that specimen drift cannot be compensated.

A first series of experiments was carried out on the fresh catalyst to check that no EELS peak at 285 eV characteristic of carbon was present. Several successive measurements on the same area were performed to check that there is no carbon building up under the beam due to contamination.

The coked catalyst was studied by performing STEM–EELS analysis at various distances from given particles. The carbon peak at 285 eV is easily detected; however, at most places, the coke and/or the support are too thick so that the fine structure near the edge (electron energy loss near edge structure (ELNES), the equivalent of XANES in X-ray adsorption spectroscopy) cannot be observed. It was found that coke

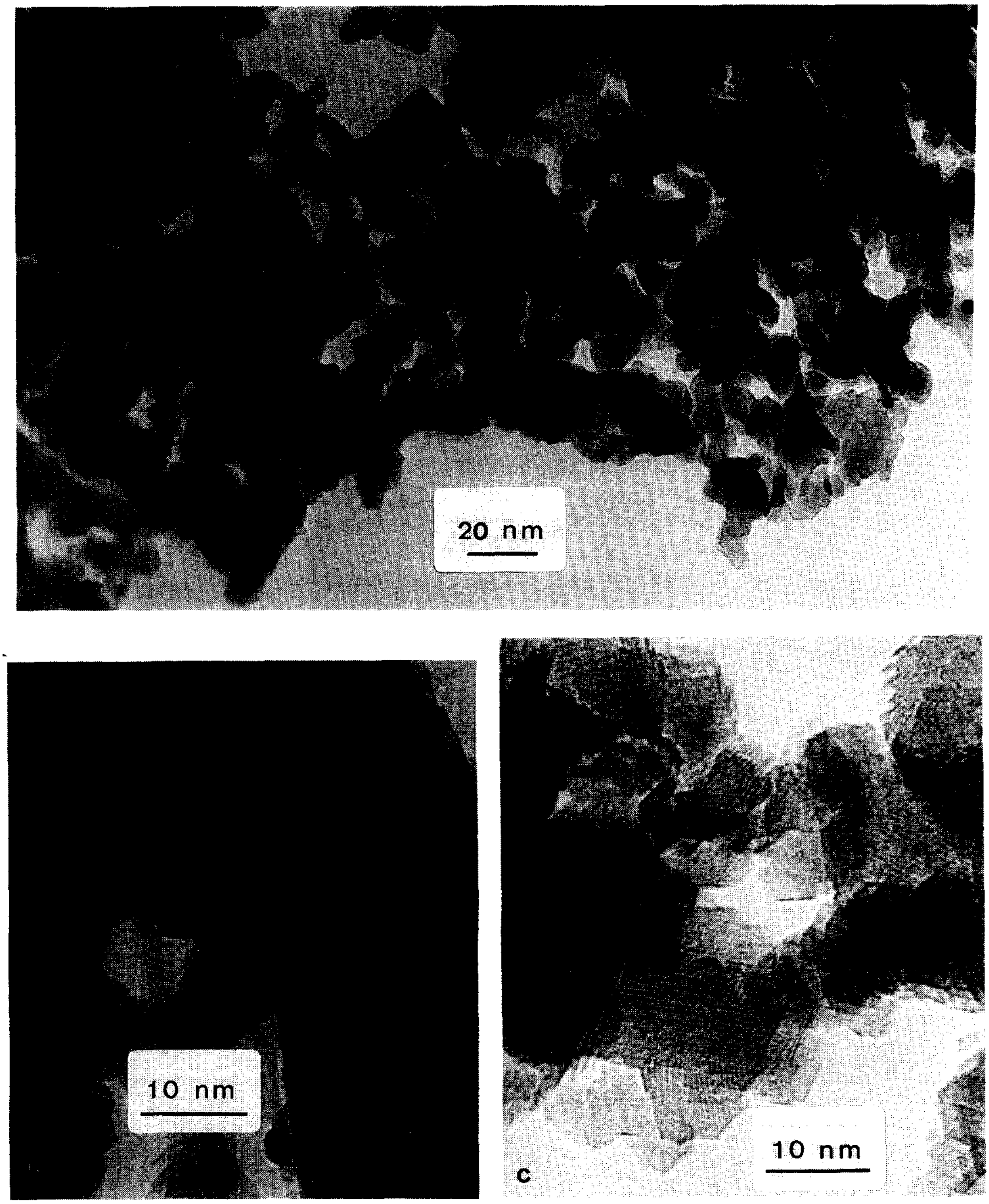

FIG. 1. TEM views of the fresh Pt/Al_2O_3 catalyst (a) at 6×10^5 magnification (b and c) at 1.5×10^6 magnification.

is always present on and around the platinum particles, but no carbon is detected at more than 20 nm from a given particle. This is in agreement with the size of the zones detected on TEM photographs where the images have a speckled contrast. The extent of coverage is often smaller, frequently being limited by the edge of the alumina

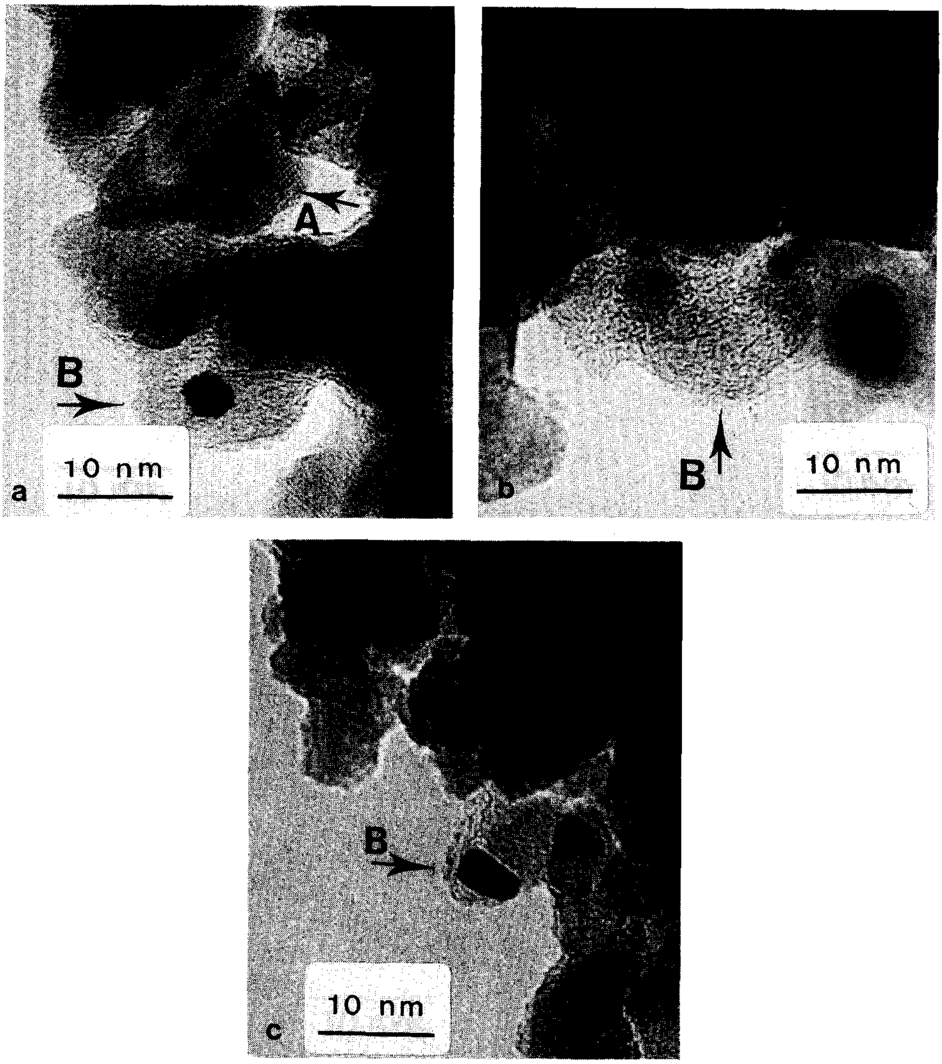

FIG. 2. (a, b, c) TEM views of the coked catalyst (1.5 × 10^6 magnification). Arrow A indicates carbon-free zones on platinum-free alumina sheets. Arrow B points to thin support areas where the carbon is better imaged.

sheet supporting the metal particle. The coke is always associated with the support, and there are no whiskers or filaments protruding from the support.

Under favorable conditions, i.e., when the carbon coating has an optimum thickness and on thin support areas giving little parasitic EELS scattering, the ELNES can be recorded with a good signal-to-noise ratio. Figure 3a gives the EELS peak of carbon after subtraction of the background. It has been recorded on an area similar to those marked by the arrows B in Figs. 2a–2c. The spectra taken on graphite, coronene and pentacene are given for comparison in Figs. 4a–4c. It is conspicuous that the spectrum of coke (Fig. 3a) is more comparable with that of amorphous carbon (Fig. 3b) than to any other reference compounds. The presence of graphite or pregraphitic carbon can be especially ruled out from the absence of the ELNES peak at

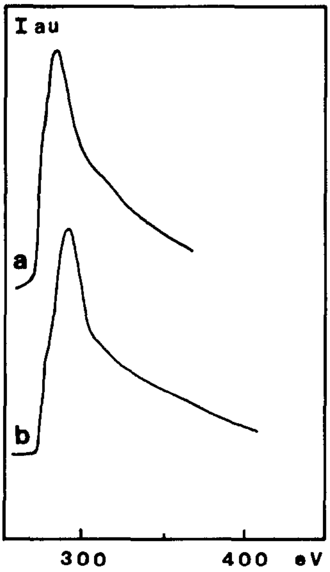

FIG. 3. EELS spectra (intensity in arbitrary units vs energy loss) taken with an electron spectrometer attached to a STEM (background has been subtracted): (a) EELS peak of carbon taken on a thin area of the coked catalyst and (b) EELS peak recorded on the amorphous holey carbon film supporting the specimen.

318–320 eV characteristic of the local structure of the graphite basal plane or of coronene which can be considered as a small piece of graphite basal plane. EELS spectra taken on the metal particles are similar to those taken on the support. This study shows that the coke deposited under the present coking conditions is essentially amorphous and forms patches around the platinum particles. However, a more organized coke structure and higher surface coverage could well exist under more severe coking conditions, e.g., at a higher temperature and pressure for a longer time on stream and for a larger coke accumulation.

2. *Localization of Coke after Partial Combustion*

The coked catalyst was heated at 563 K for 30 min in a 1% O_2–99% He mixture. The partially oxidized catalyst thus obtained was studied by STEM–EELS in the same way as previously described.

The EELS spectra taken on Pt particles with an analysis window smaller than the projected area of the particles do not show the presence of carbon except in a few cases. On the other hand, spectra taken in the immediate vicinity of the particles, or farther away, show that the coke is always present. Therefore, these results support previous TPO studies where it was assumed that the first peak on the TPO curve near 573 K corresponds to the combustion of the coke covering the metal particles while the coke on alumina is burned at higher temperatures (*8–10*).

CONCLUSION

EELS coupled with electron microscopy provides a unique tool to probe, on a nanometric scale, carbonaceous deposits on catalysts. It confirms previous results and gives new information on the location and structure of coke. Thus, previous investigations have shown that the mechanism of coke formation on Pt/Al_2O_3 catalysts involves as a first step the dehydrogenation of cyclopentane into cyclopentadiene cata-

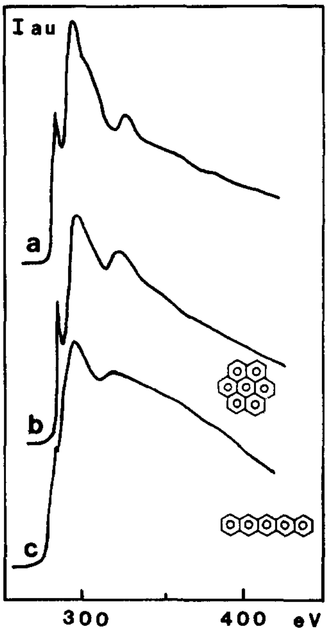

FIG. 4. EELS spectra of reference compounds (intensity in arbitrary units vs energy loss): (a) graphite, (b) coronene, and (c) pentacene.

lyzed by the metal particles. Then, the unsaturated molecules spill over to the support where they are converted to coke by a sequence of reactions catalyzed by the acidic sites of alumina. The present study confirms that coke builds up both on the metal and on the support. In addition it is shown that coke does not spread farther than ca. 20 nm from a given particle under the present coking conditions. The progression of coke is sometimes limited by the edges of the alumina sheets on which the metal particle sticks, but coke spilling onto neighboring alumina sheets occurs frequently. The coke formed either on the metal or on the support under the present coking conditions (low temperature and pressure) is essentially amorphous as shown by the combined TEM and STEM–EELS study. Finally, this study confirms previous TPO experiments showing that mild oxidation treatments can eliminate the coke on most of the Pt particles while it remains on the alumina support.

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