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NOTES

Carbon *K*-Edge X-ray Absorption Spectroscopy of Gas Oil Derived Coke Deposits in LZ-210 Zeolite

We have recently reported that fluorescence yield near-edge spectroscopy (FYNES) can be used for studies of the electronic structure of hydrocarbons adsorbed in zeolites (*1*). In this communication we show that FYNES can also be applied in studies of zeolitic "coke" deposits. Results for carbonaceous deposits produced in LZ-210 in simulated catalytic cracking experiments using naphthenic and aromatic gas oils clearly reveal the formation of polynuclear aromatic structures.

Coked zeolite materials were produced by impregnating dry, precalcined LZ-210 (Union Carbide, Si/Al = 4.6) with heptane solutions of aromatic or napthenic gas oils followed by drying at room temperature under nitrogen. Initial gas oil loadings were 25–30 wt%, and properties of these gas oils as determined by carbon NMR and HPLC are compared in Table 1. A major difference between these materials was the concentration of multiring aromatic hydrocarbons. Approximately 1.5-g samples of gas oil impregnated zeolite were then loaded in a tubular microreactor and quickly heated to 798 K under flowing nitrogen (heating rate ca. 500 K per min) and were held at 798 K for 1 min. The "coked" LZ-210 materials were subsequently cooled, discharged, and characterized using a variety of techniques including elemental analysis, x-ray photoemission (XPS), ^{13}C-MAS NMR, and carbon K-edge FYNES. The NMR measurements were carried out using a JEOL FX-60QS 15 MHz instrument operated with single pi pulse acquisition with decoupling gated on during acquisition. FYNES data were obtained at 1 eV resolution on the U-1 beamline at NSLS-Brookhaven National Laboratory using a grasshopper monochromator, high vacuum end station, and a novel thin window gas proportional counter for soft X-ray flourescence spectroscopy that was described previously (*1–3*). Prior to FYNES data collection, the coked zeolites were briefly outgassed by heating in vacuum to 573 K. FYNES data were collected in ca. 20-min. scans over the 270–330 eV photon energy range, and the results for coked zeolites were normalized relative to dehydrated, carbon-free LZ-210. Absorption energies were calibrated relative to Grafoil features in the output of the monochromator at 284.7 and 291.0 eV.

Normalized fluorescence yield X-ray absorption spectra recorded above the carbon *K*-edge for several materials are compared in Fig. 1. Coked LZ-210 containing 12 wt% carbon was produced using the aromatic gas oil, whereas the LZ-210 material with 4.5 wt% carbon was produced with the naphthenic feed. The reference compounds studied include 2,3-benzanthracene (linear 4-ring polynuclear aromatic), coronene (symmetric 7-ring PNA), a thin film of benzene condensed at 150 K, and highly oriented pyrolytic graphite (HOPG). All of the spectra display well resolved $1s \rightarrow \pi^*$ resonances for photon energies of about 283 to 290 eV, together with more poorly resolved σ^* resonances at higher photon energies. Table 2 summarizes energies for the major π^* resonances.

It is evident from Fig. 1 that the aromatic and napthenic gas oils produced coke deposits with very similar FYNES spectra. This comparison strongly implies that these de-

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TABLE 1

Properties of Naphthenic and Aromatic Gas Oils

	Gas oil	
	Naphthenic	Aromatic
API gravity	29.8	13.8
Avg boiling pt. (K)	768	764
Composition (wt%)		
Paraffins	7.8	4.8
Naphthenes	69.4	17.3
Total aromatics	22.9	77.9
3^+-Ring aromatics	0	32.5

posits are characterized by similar molecular structures, despite a large difference in feedstock composition. It is also very interesting that these lineshapes are nearly identical to that for linear benzanthracene, indicating at least a qualitative analogy with this "cata-condensed" PNA structure. By contrast, the other reference materials produced very different FYNES spectra suggesting little or no structural similarity for the coke deposits with graphite, "peri-condensed" coronene, or 1-ring aromatic compounds. While it appears reasonable to expect that the distribution of π* resonances could be altered by interactions with the zeolite framework, no evidence for these interactions could be detected in earlier studies of benzene adsorbed in Na–Y (*1*). Subtle differences in relative FYNES intensities for the coked zeolites in the region near 286–289 eV likely reflect differences in the distribution of multiring coke structures that are not understood at this time.

To a good approximation, FYNES π* resonances reflect the energies and degeneracies of antibonding orbitals that are accessible according to the dipole selection rule (*4*). In benzene, the lowest unoccupied e_{2u} orbital (LUMO) is doubly degenerate, whereas the next higher b_{2g} orbital is nondegenerate. The energies and relative intensities of the benzene π* resonances clearly

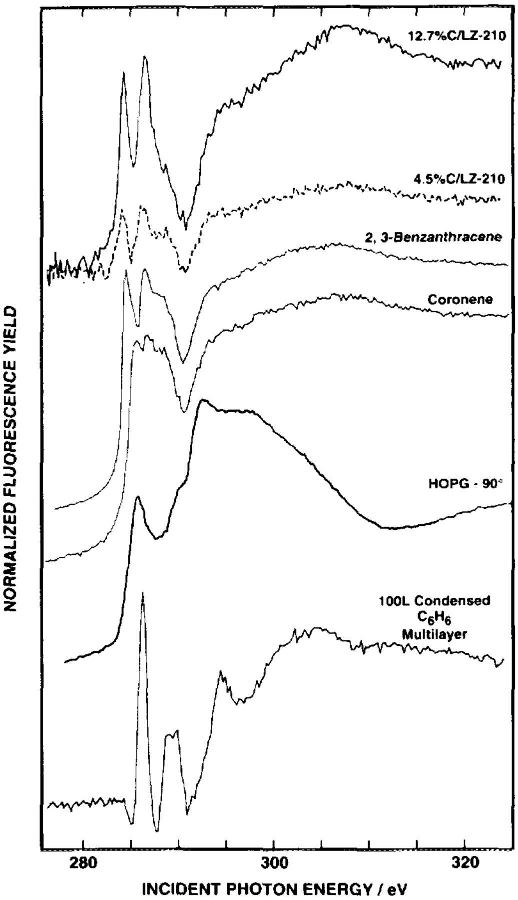

FIG. 1. FYNES data are compared for 4.5–12% coke on LZ-210, benzanthracene, coronene, benzene, and highly oriented graphite at 90° photon incidence. The LZ-210 spectra are displayed with the same fluorescence yield intensity scale. The benzene spectrum was obtained by condensing a 100-L (1 L = 10^{-6} torr sec) dose of C_6H_6 vapor onto a copper substrate at 150 K.

TABLE 2

Absolute Energies of π* Resonances

Material	Absorption energy (eV)
4.5% C/LZ-210	284.0, 286.4, 288.2
12% C/LZ-210	284.0, 286.7, 288.6
2,3-Benzanthracene	284.4, 286.3, 288.2
Coronene	285.4, 286.6, 288.3
Benzene	285.7, 288.5
Graphite	285.3

reflect transitions to these levels. Assignment of the π^* resonances in the larger molecules is more complicated due to the large number of π^* orbitals with different electron-hole interaction energies; e.g., final state screening becomes less efficient with electron delocalization in large multiatomic orbitals (*5*). However, it should be noted that the first π^* resonance in benzanthracene and the coke deposits occurred at a significantly lower energy (ca. 1 eV) as compared to any of the other materials. This behavior appears to reflect a low-lying LUMO, and it is well established from ultraviolet photoemission (UPS) studies (*6*) and molecular orbital calculations (*7, 8*) that linear PNAs have lower lying LUMOs relative to olefins and bent or peri-condensed PNA structures. Comparison of our FYNES results with NEXAFS, UPS, and inverse photoemission data for benzanthracene on Ag(111) reported by Koch and co-workers (*5, 9, 10*) shows a similar distribution of π^* resonances wherein the first resonance can be attributed to the b_{2g} LUMO. The next π^* resonance appears to arise from excitation to one or more of the next lowest b_{3g}, b_{1u}, a_u, and b_{2g} orbitals that are closely spaced 1.5–2.8 eV above the LUMO (*5*).

X-ray photoemission studies of the same coked LZ-210 materials indicated that the carbon deposits formed in the bulk micropores of the zeolite with little or no carbon enrichment at the external surface. Solid state, magic angle spinning carbon-13 NMR results displayed in Fig. 2 further indicate that the deposits are highly (ca. 90% or more) aromatic with little or no indication for sp^3 hybridized carbon. These data with the FYNES results appear consistent with most of the carbon being present as intrazeolitic, cata-condensed-type PNA structures. Due to the modest diameter (ca. 7.4 Å) of the faujasite 12-ring windows, more highly condensed, two-dimensional structures like coronene or graphitic carbon should be constrained to the external zeolite surface and would result in significant carbon surface enrichment as measured by XPS.

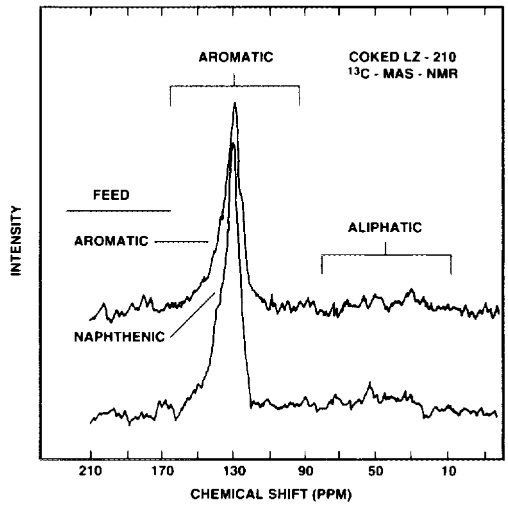

FIG. 2. ^{13}C-MAS NMR results are compared for coked LZ-210 produced using naphthenic and aromatic gas oils.

The higher coke yield detected with the aromatic feed appears consistent with FCC studies indicating that 3^+-ring aromatics contribute more strongly to coke make as compared to smaller aromatics and napthenoaromatic hydrocarbons (*11, 12*). Several processes including napthene dehydrogenation, carbocation hydrogen transfer/condensation, and strong adsorption of multiring aromatics reportedly contribute to FCC coke make (*13*). The concentration of 3^+-ring aromatics in the aromatic feed is almost adequate to account for the observed coke yield, so it is probable in this case that the observed FYNES spectra are influenced by unconverted, strongly adsorbed feed PNAs. However, with the napthenic feed, the observed coke yield largely exceeds the concentration of feed multiring aromatics. In this case, chemical reactions such as dehydrogenation, condensation, and/or hydrogen transfer must contribute to coke formation.

These results obtained using "*in situ*" spectroscopic probes compare favorably with earlier investigations by Guisnet *et al.* involving "*ex situ*" GC–MS analyses of residues obtained by chemical extraction of coked zeolites (12–16). Propylene polymerization in ultrastable-Y at 723 K, for example, produced 3- to 5-ring PNAs which were soluble in CH_2Cl_2, along with heavier insoluble residues (14). Similar PNAs formed during *n*-heptane cracking (15). Methylnaphthalene conversion over H–Y and Beta produced condensed ring structures at temperatures as low as 573 K (16).

It is worth noting that FYNES results can also be used for quantitative analysis provided that self-absorption effects are minimized by using samples that are thin compared to the absorption length of the photons (17). Specifically, for carbonaceous solids with similar scattering characteristics, the magnitude of the edge jump at energies above about 320 eV is proportional to carbon concentration. This is qualitatively reflected by the relative intensities indicated for the two coked zeolites in Fig. 1, despite the fact that no special procedures were used in this work to control sample thickness (ca. 100 μm).

In summary, these results indicate that the structure of coke deposits produced in LZ-210 in simulated gas oil cracking experiments shows little dependence on feed composition and is dominated by PNA structures. This work further demonstrates that FYNES offers excellent potential for studies of the electronic structure of hydrocarbons adsorbed on insulating catalytic materials. Extension of this work to other adsorbates and other types of fuels processing catalysts is planned.

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