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An Electron Spin Resonance Study of Coke Deposits on a Silica-Alumina Catalyst

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The coke deposited on a silica-alumina catalyst from the cracking of *n*-hexane, cyclohexane, *n*-hexene-1, benzene, thiophene, and pyridine was studied by electron spin resonance. Thiophene exhibited a different linear increase in spin concentration with carbon content and produced double the number of spins per deposited carbon atom as compared with the hydrocarbons. The number of carbon atoms was about 10^3 times the number of unpaired spins. In the absence of air the unpaired spins saturated easily, while the admission of air resulted in the adsorption of ogygen which rendered the spin system unsaturated. In addition, oxygen decreased the spin concentration by a factor of 3. These oxygen effects were reversible. The results of this study correlated well with the coke structure model proposed by Haldeman and Botty.

INTRODUCTION

When a chemical reaction involving organic compounds in the vapor phase is carried out over a catalyst at elevated temperatures, the catalyst gradually becomes coated with coke (*1–4*). Since the resulting coke is paramagnetic it is possible to study its unpaired spins by electron spin resonance (ESR). Singer (*5*) has reviewed the electron spin resonance results from various carbonaceous materials. Ingram *et al.* (*6, 7*) noted that low-temperature chars formed from a number of different carbonaceous materials produce ESR spectra with about the same spin concentration, linewidths, and *g* factors as those reported in this work.

In our case, coke was deposited on the surface of a silica-alumina catalyst by the cracking of *n*-hexane, *n*-hexane-1, cyclohexane, benzene, pyridine, and thiophene in the absence of air at 500°C. The ESR spectra were obtained at $g = 2.004$, and the number of unpaired spins was measured as a function of carbon content. The spin concentrations were compared for the different series of reactants, and the influence of exposure to air on the samples was determined. The electron spin resonance results were used to help elucidate the nature of the coke deposit.

EXPERIMENTAL

A diagram of the coking apparatus is presented in Fig. 1. Small glass reactors were packed in sand in each of the tubes of a five-tube electrically heated furnace. Each reactor contained 2.8 g (5 cc) of a commercial silica-alumina catalyst, Houdry S-46, having a surface area of 320 m^2/g. The catalyst was ground to 50–140 mesh size. The major impurities of the catalyst, in terms of per cent by weight, were: sodium, 0.17; iron, 0.037; sulfur, 0.013; and chlorine, 0.01. The furnace was mounted at an angle so that the charge

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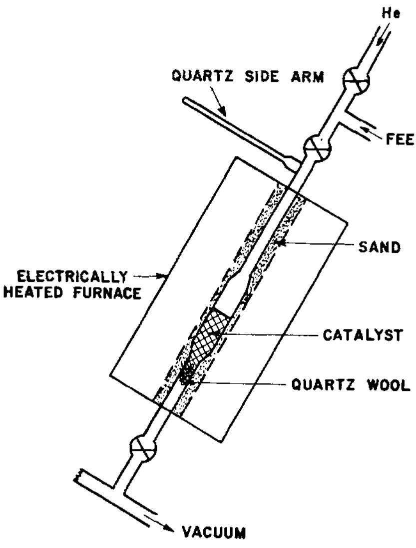

FIG. 1. Reactor. For simplicity, only one of the five reactors is shown. Manifolds were used on the inlet and outlet lines so that the reactors could be treated individually or collectively.

would not deposit in the quartz sidearm. After the furnace was equilibrated at 500° ± 15°C, the reactors were alternately flushed with helium for 5 min and evacuated to 10^{-3} mm Hg for ½ hr to remove all air from the system. This process was repeated three times. The coking was accomplished by pumping the charge through each reactor at a LHSV of 8 until the desired amount of coke had deposited on the catalyst. After all five catalyst samples had been coked, the reactors were flushed, evacuated, and cooled in helium to room temperature. The reactors were then capped and transferred to a high-vacuum system where they were evacuated at 500°C for 1 hr to a final pressure of about 10^{-4} mm Hg. A thoroughly mixed sample of each evacuated catalyst was sealed off in the sidearm tube and examined by ESR. After ESR examination the catalyst was removed from the quartz tube and analyzed for carbon and hydrogen by a microcombustion technique. Several samples were also analyzed for nitrogen or sulfur.

The following chemicals were used in the reactor to form the coke: Baker's reagent grade benzene, Phillip's pure grade hexene-1, Fisher's purified *n*-hexane, Eastman's Eastman grade thiophene, Phillip's pure grade cyclohexane, and Fisher's reagent grade pyridine. In each case the compound was purged with flowing hydrogen for 2 hr to remove dissolved gases and dried over molecular sieves prior to use.

The ESR measurements were made with a Varian V-4500 x-band spectrometer equipped with either a V-4007 6-inch magnet or a V-4012 12-inch magnet. The magnetic field was modulated at frequencies of 80 or 200 cps and at an amplitude of 0.9 gauss, which is considerably less than the observed linewidths. The spin concentrations and linewidths were measured relative to a solution of α,α-diphenyl-β-picrylhydrazyl in benzene. The measurements were made at a microwave power of approximately 1 mW where the spin system is only slightly saturated. To achieve this low power level without employing a low power bridge it was necessary to operate with a crystal current of about 4 μamp.

RESULTS

The spin concentrations obtained for the six series of coked silica-aluminas are shown in Fig. 2. The four hydrocarbons appear to fit one straight line and the two heterocyclics fit another. Unfortunately the pyridine data do not extend to a high enough coke content to determine their slope accurately. Each straight line has a different slope and intercept on the horizontal axis. There is about one unpaired spin for every thousand carbon atoms in the coke deposit. All of the coke samples had carbon/hydrogen ratios of 1.9 ± 0.3.

The power dependence of the ESR spectra was studied, and it was found that all of the samples are strongly saturated at a klystron power of 100 mW. The line shapes at 1 mW were approximately Lorentzian while the peak-to-peak first derivative full linewidths were all between 6 and 8 gauss, which corresponds to a spin–spin relaxation time, T_2, of 10^{-8} sec for a homogeneously broadened resonance. The saturation data were employed to estimate the spin–lattice

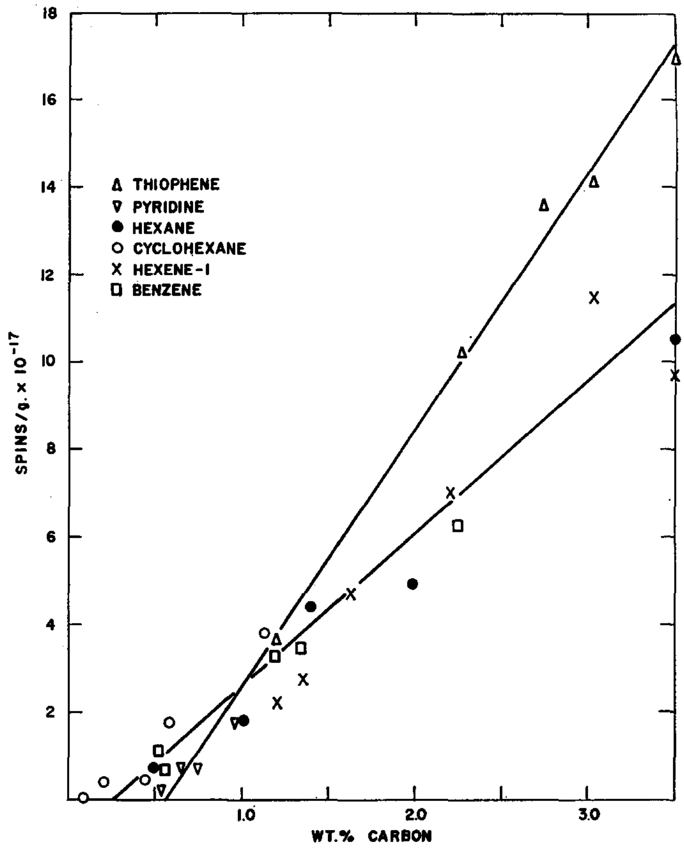

FIG. 2. Number of spins vs. wt % carbon for cokes from various sources formed on a silica-alumina catalyst at 500°C.

relaxation time T_1 which was found to be 4×10^{-4} sec for benzene coke. The linewidth was found to increase by 25% when the factor ($\gamma^2 H_1^2 T_1 T_2$) equaled 3, where γ is the gyromagnetic ratio and H_1 is the microwave magnetic field amplitude. This occurred when about 100 mW were incident on the resonant cavity. The linewidth increased slightly with increasing coke concentration.

When a coke sample was exposed to the air it became almost unsaturated at the highest microwave power available (about 100 mW incident on the resonant cavity) which indicated that the spin–lattice relaxation time T_1 had decreased by over an order of magnitude. At the same time the spin concentration decreased to about one-third of its initial value, and the linewidth increased slightly, indicative of a small decrease in T_2. The effect of oxygen on the saturation behavior was found to be reversible since a room temperature evacuation of the samples for 1.5 hr restored the original ESR behavior.

DISCUSSION

As can be seen in Fig. 2, it appears that for the two heterocyclic precursors it was necessary to lay down about 0.5 wt % coke on the surface before the ESR signal developed. This corresponds to about 2% of the surface covered with a single layer of a condensed ring system of the type postulated by others (*3*). However, scatter in the points at these low carbon concentrations, and the possibility that a very small amount of carbon is associated with the uncoked catalyst leave this point unresolved. It may be that the species of carbon initially deposited is not as susceptible to acquiring unpaired spins as the larger carbon crystallites formed later. It is also possible that early in the coking process the heterocyclics spread out more over the surface than the hydrocarbons before building up bulk coke crystallites. After the initial induction period the sulfur-containing coke produced twice as many spins per deposited carbon atom as the hydrocarbon coke.

The ESR resonant line was Lorentzian in shape and its width increased slightly with carbon content. When the sample was strongly saturated and the factor $\gamma^2 H_1^2 T_1 T_2$ equaled 3, the linewidth ΔH was found to increase by 25% over its unsaturated value ΔH_u. For homogeneous broadening the Bloch equations predict a factor of 2 increase in linewidth when $\gamma^2 H_1^2 T_1 T_2 = 3$ in accordance with the relation (*8*)

$$\Delta H = \Delta H_u (1 + \gamma^2 H_1^2 T_1 T_2)^{1/2} \qquad (1)$$

while no noticeable increase in linewidth is expected for an inhomogeneous broadening mechanism. The saturation behavior observed with the cokes indicates the presence of an intermediate case between homogeneous and inhomogeneous broadening.

When air was admitted to the sample it produced a factor of 3 decrease in the number of detected spins and an order of magnitude decrease in the spin–lattice relaxation time over the entire range of coke concentration. At the same time the line shape remained Lorentzian and the linewidth only increased slightly. No permanent change occurred because the process is reversible. This reversible effect of oxygen on unpaired spins has also been reported by de Ruiter (*9*) for fusain and petroleum coke. An adsorbed oxygen molecule may interact magnetically with adjacent unpaired spins on the surface, and thereby broaden them beyond detection. The second role played by the adsorbed oxygen is to provide a relaxation path between the unpaired spins and the lattice so that the spins can more rapidly dispose of their magnetic energy. The effectiveness of this energy transfer is given quantitatively by the decrease in T_1. The entire ESR resonance becomes unsaturated by the presence of adsorbed O_2, which means that all of the interior spins are effectively coupled to this oxygen. The ratio of surface to interior spins appears to be independent of coke concentration since the admission of oxygen always destroys the same fraction of the unpaired spins. The small increase in linewidth that results from exposure to the air may result from dipole–dipole broadening by the paramagnetic oxygen.

Haldeman and Botty (*2*) have shown that cracking catalyst coke deposits consist of small crystallites with dimensions of about 17 Å normal to the five condensed ring layers, and 10–12 Å in the plane of these layers. On the average each crystallite contains about 250 carbon atoms, which means that only one out of every four crystallites contains an unpaired spin. A similar figure was found by Collins *et al.* (*10*) from the ESR study of carbon blacks which also consist of small crystallites (*11*). If one assumes that the crystallite is laying flat on the catalyst surface then all of the carbon atoms on the top layer plus all of the edge carbon atoms of the four layers below are exposed. The exposed carbons constitute two-thirds of the total carbon atoms. It was mentioned above that adsorbed oxygen decreases the unpaired spin concentration to a third of its original value and renders the remaining spins unsaturated. Hence, both interior and surface carbon atoms are equally likely to be sites for unpaired electrons. When oxygen is adsorbed, it broadens beyond detection the two-thirds that are on the surface, and reacts magnetically with the remaining third. As a result only the latter are detected by ESR, and they are unsaturated because of the nearby paramagnetic oxygen molecules.

The observed carbon/hydrogen ratio of 1.9 ± 0.3 agreed with the value found by Haldeman and Botty (*2*). Klimenok *et al.* (*12*) found that the C/H ratio of a *n*-hexane coke prepared at 520°C on a silica-alumina catalyst increases with time, and that after 2 hr this ratio was 2.1, in good agreement with our findings. The carbon–hydrogen ratio should be about 3 for the proposed crystallite structure, and its closeness to 2 may result from the presence of aliphatic chains (*2*). One should not rule out the possibility that some unpaired spins may be associated with these aliphatic chains.

CONCLUSIONS

The electron spin resonance measurements showed that the number of unpaired spins in the coke increased linearly with the carbon concentration. The four hydrocarbon coke precursors behaved alike, while thiophene, and quite possibly pyridine coke, exhibited a different dependence on the carbon content. Exposure to oxygen destroyed some of the unpaired spins, and rendered the remainder less saturated. It is suggested that perhaps one out of every four coke crystallites contains an unpaired spin, and that two-thirds of these spins are on the surface and may be broadened beyond detection by adsorbed oxygen. The remaining one-third react magnetically with adsorbed oxygen and thereby decrease their spin–lattice relaxation time.

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