

ABSTRACTA NEW APPROACH TO CARBON SURFACE GROUP ANALYSIS

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Currently there are two opposing views concerning the nature of the surface groups which are responsible for the acidic properties of carbons. The first and most widely held view interprets the acidity in terms of contributions from varying amounts of surface carboxyl, lactone, hydroxyl, and quinone groups; however, there are significant discrepancies in the amounts of specific groups reported by various workers using different analytical methods on the same carbons. Unfortunately, critical comparisons are available only for a relatively few types of carbon blacks.

In another interpretation, the acidic properties of carbons are attributed to an adsorbed layer of carbon dioxide (CO_2 -complex) rather than to specific organic functional groups.

The present work has been undertaken in the hope of resolving these differences. Apart from classifications according to apparent acidity or reducibility, etc., chemical analyses alone are insufficient to unequivocally determine the nature and distribution of carbon surface groups. This is due as much to the variable effect of location and electronic surface environment on functional group properties as to the uncertainty in reactivity assumptions inherent in the chemical and electrochemical techniques.

For these reasons, this study has employed the parallel application of infrared spectrometry and a newly developed pyrolytic volatile analysis (PVA), in conjunction with selective neutralization measurements. Two representative channel blacks have been analyzed before and after neutralization with aqueous bicarbonate, carbonate and hydroxide solutions, as well as nonaqueous lithium t-butoxide in dimethyl sulfoxide and lithium aluminum hydride in diethyl carbitol.

Quantitative infrared measurements of functional groups on these blacks have been made using the KBr pellet technique. Spectra have been recorded in the region from 5000 to 400 cm^{-1} , with particular attention focused on the carbonyl-stretching regions.

The usual volatile products obtained from thermal decomposition of carbon surface groups are carbon oxides and hydrogen, with much lesser amounts of water, methane, and both sulfur and nitrogen oxides. At low pressures (≤ 5 torr), carbon monoxide and dioxide are shown to be primary decomposition products arising from functional groups containing one and two oxygen atoms, respectively. Hydrogen, water, and methane are produced by combination of a hydrogen atom with another hydrogen atom (C-H or O-H dissociation), an hydroxyl radical (C-OH dissociation), or a methyl radical.

Each type of surface group has a characteristic thermal stability producing a unique desorption temperature profile. This has not been fully appreciated in the past, since typical pyrolysis procedures involved large temperature increments and irreproducible heating rates.

The apparatus used in this work for vacuum devolatilization of carbon has a linear programmed heating rate of $1^{\circ}\text{C}/\text{minute}$ from room temperature to 1500°C . Evolved gases are continuously collected and automatically analyzed by gas chromatography at successive 20°C intervals. This chromatographic data is converted by computer into an integral curve of the evolved sum of each gas at every temperature, in addition to a differential devolatilization rate curve or thermogram. These thermograms reflect the characteristic surface group distribution of each carbon, and, in most cases, contain from 2 - 4 partially resolved individual functional group decomposition curves.

Resolved CO and CO₂ thermograms have been correlated with changes in the carbonyl-stretching region and quantitative base adsorption data. Application of these complementary techniques has led to a consistent description of the neutralization data.