

Carbonization of Walnut Shells and the Determination of Surface Acidity of Charcoal by Selective Neutralization Technique

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(Received 3rd June, 1987, Revised 20th March, 1988)

Summary: Charcoal obtained from walnut shells were studied for determining the acidic surface complexes by selective neutralization technique using bases of different strengths. Effect of time, benzene extraction and demineralization on the uptakes of various bases by charcoal were investigated and groups like carboxyl, lactone, phenolic, hydroxyl and keto-enol were thought to be present on the surface of charcoal. Uptakes of stronger bases sodium ethoxide and potassium isopropoxide were unexpectedly low, which were thought to be due to the bulky size of ethoxide and isopropoxide, which get access into the micropores with difficulty as compared to the small sized hydroxide.

Introduction

Surface acidity of carbon plays a prominent role in its applications such as adsorption, elastomer reinforcement etc. Work on determining the surface acidity of carbon has been extensively reported in the literature and surface acidity of carbon has been ascribed to various oxygen surface complexes i.e. carboxyl, lactone, phenol, keto-enol etc. Various techniques, such as, selective neutralization [1-3], potentiometric titration [4-7], infrared spectroscopy [8-14], derivative formation [15-18] etc. have been utilized for studying the structural characteristics of these acidic complexes.

The current work deals with elucidating the structure of various acidic complexes on the surface of walnut shell charcoal by selective neutralization method using bases of different strengths. The technique has been applied earlier by one of the author for structure elucidation

of the acidic complexes on the surface of carbon black [2] and charcoal [3].

Experimental

Preparation of charcoal:

Walnut shells were crushed into small pieces and were carbonized in pyrex glass tube placed in a tube furnace. The temperature was raised at the rate of 2°C per minute until the temperature reached to 450°C. The furnace was left at 450°C for one hour to complete carbonization. About 20 grams of walnut shells pieces were carbonized at a time. The furnace was cooled and the charcoal thus produced was ground. Several batches were mixed together and were passed through 120 mesh screen. The powdered charcoal was dried at 110°C in an oven for about one hour and then cooled in a dessicator, which was then stored in a bottle for further use.

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Extraction of Charcoal with Benzene:

Twenty grams of powdered charcoal prepared before, was taken in a thimble and extracted with benzene in a Soxhlet apparatus for two hours to extract the benzene soluble material from the Char. After extraction, the charcoal was first dried in a fume cupboard and then dried at 110°C in an oven for two hours. The loss in weight due to the extraction was then calculated.

Demineralization of Charcoal:

Portion of the benzene extracted sample as well as sample not extracted with benzene were demineralized with a mixture of H₂O, HNO₃, HCl and HF in a ratio of 10:5:1:1 respectively in a teflon beaker. The charcoal and acid suspension was heated on a water bath for 2 hours with occasional stirring. The suspension was then filtered through Watman filter paper and the residue was washed several times with hot distilled water until the filtrate became neutral. The residue was dried first in open atmosphere and then at 110°C in an oven. The loss in weight was then calculated. The acid extract and washings were evaporated in a teflon beaker on a water bath to remove the acids. The residue was dissolved in distilled water and was used for the determination of some of the trace elements.

Reaction of the Base with Charcoal:

The base solution preparation, its reaction with carbon and titration of the unreacted base solution has been described earlier [3].

Results and Discussion

The yield of walnut shells charcoal, its weight losses after benzene extraction and demineralization

are given in Table-1, indicating the presence of benzene soluble organic and acid soluble inorganic matters. However treatment of charcoal with oxidizing acids might also have resulted in loss due to oxidation of carbon to oxides of carbon. The trace elements determined in the acid extracts are shown in Table-2, which indicates that Ca and K are present in higher quantities in charcoal compared to other elements. Elements like Zn, Mn, Ni and Cr are present in quite trace quantities.

The uptakes of 0.1 M sodium bicarbonate by untreated and variously treated charcoal within different duration of time are shown in Fig.1. The figure shows that eventhough most of the sodium bicarbonate neutralizable acidic groups have reacted within one hour, a slight increase in the base uptake especially of the demineralized samples can be noticed even after six hours. This slow neutralization might either be due to microporosity of charcoal or due to the presence of weakly acidic carboxyl groups. The figure also shows that whereas benzene extraction has a negative effect on the acidity of charcoal, demineralization has quite a pronounced positive effect on the acidity of charcoal. This high increase in acidity of demineralized sample was thought to be due to surface oxidation of charcoal with HNO₃ in the acid mixture, which might have resulted in the formation of acidic groups on the surface of charcoal. Adsorption of acids during demineralization might also be one explanation for the high acidity of demineralized samples however in our later studies [19] of direct potentiometric titration of charcoal, no such break corresponding to strong acids adsorbed on the surface of charcoal was observed. The adsorbed acids have been completely removed during the repeated washing with warm water.

Table-1: Surface area and Weight loss of charcoal after various pretreatments.

Yield of charcoal	Surface area of charcoal (Untreated)	Percentage weight loss in charcoal after Benzene extraction	Percentage weight loss in charcoal after demineralization	Percentage weight loss after Benzene ext. + demineralization
39.175%	135.875 $M^2 g^{-1}$	4.11 %	5.70 %	7.12 %

Table-2

Amount of trace elements in charcoal ($\mu g g^{-1}$).

Elements	Amount ($\mu g g^{-1}$)
Calcium	57.250
Potassium	42.700
Magnesium	5.687
Sodium	1.757
Iron	1.565
Copper	0.288
Zinc	0.083
Manganese	0.064
Nickel	0.030
Chromium	0.008

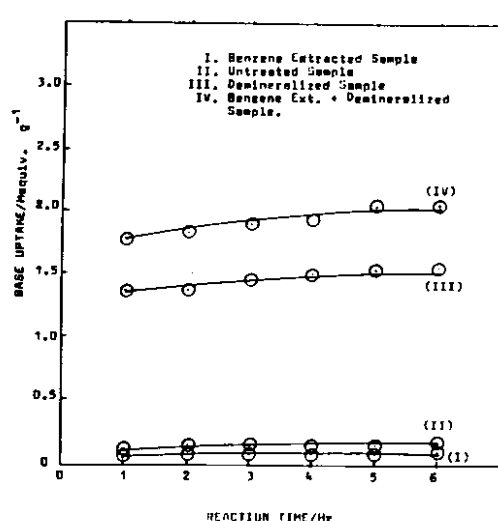


Fig.1: Uptakes of sodium bicarbonate at various reaction time by untreated and variously treated walnut charcoal.

Production of micropores in the structure of charcoal with the demineralizing acids might also have contributed to the increased acidity with demineralization. From the figure it is also apparent that charcoal sample extracted with benzene followed by demineralization have high uptakes of sodium bicarbonate compared to charcoal sample demineralized only. This was thought to be due to the solubility of disorganized organic matter in the coal structure with benzene, which might have resulted in an increase of accessible surface area to the acid mixture to perform surface oxidation and then have increased surface acidity of charcoal. Benzene extraction alone however have acidity of charcoal, which might be due to the slightly acidic nature of the benzene soluble compounds.

It has been established earlier by Boehm [1] that acidic groups which are neutralizable with sodium bicarbonate are carboxyl groups. It can thus be said that the sodium bicarbonate uptakes of our charcoal sample might also be due to the presence of carboxyl groups on the surface of charcoal. It can also be inferred from our results that demineralization with acid mixture has resulted in an appreciable increase of the carboxylic groups content on the surface of our charcoal sample.

The uptakes of aqueous sodium hydroxide by untreated and variously treated walnut charcoal within different duration of time are shown

in Fig-2. A slight increase in the uptake of sodium hydroxide with increase in the duration of time can be noticed especially in the case of demineralized samples similar to the uptakes of sodium bicarbonate. From the figure it is quite apparent that the uptakes of aqueous sodium hydroxide are considerably higher compared to aqueous sodium bicarbonate. It can also be seen that demineralization has resulted in an appreciable increase in the uptakes of sodium hydroxide similar to sodium bicarbonate, however increase in the uptakes of sodium hydroxide by demineralized sample are quite high compared to the uptakes of sodium bicarbonate. Extraction of charcoal with benzene alone has resulted in a decrease in the uptakes of sodium hydroxide, however extraction with benzene followed by demineralization has resulted in a considerable increase in acidity of charcoal, higher than sample demineralized alone similar to sodium bicarbonate. The higher uptakes of aqueous sodium hydroxide compared to sodium bicarbonate can be explained by suggesting the presence of weakly acidic groups like lactone and phenolic hydroxyl groups which are neutralizable with aqueous sodium hydroxide, but not with sodium bicarbonate.

The uptakes of stronger bases, sodium ethoxide and potassium isopropoxide by charcoal are given in Fig-3 & 4 respectively. The uptakes of these two stronger bases are considerably low compared to the uptakes of aqueous sodium hydroxide and even to sodium bicarbonate. Moreover the effects of various treatment of charcoal on the uptakes of these stronger bases are different from that of sodium bicarbonate and aqueous sodium hydroxide. The low uptakes of sodium ethoxide and potassium isopropoxide might be because of the

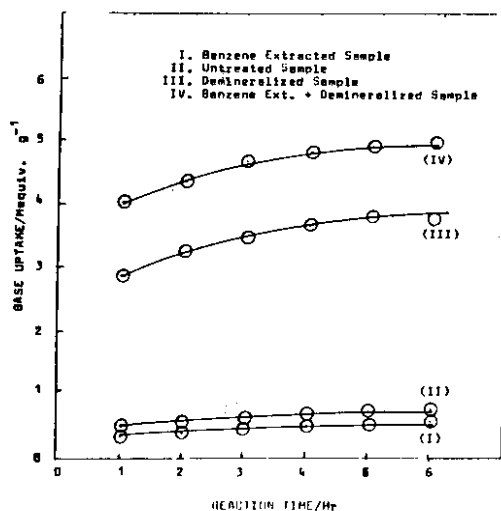


Fig.II: Uptakes of sodium hydroxide at various reaction time by untreated and variously treated walnut charcoal.

bulky nature of ethoxide and isopropoxide, which get access with difficulty into the micropores. Sodium ethoxide and potassium isopropoxide, stronger bases than aqueous sodium hydroxide, were thought to be capable of neutralizing some weaker acidic groups, not neutralizable with sodium hydroxide. Earlier workers [2,3] observed higher uptakes of sodium ethoxide compared to aqueous sodium hydroxide, which they thought to be due to the presence of some weaker acidic groups, not neutralizable with aqueous sodium hydroxide.

The uptakes of alcoholic potassium hydroxide by variously treated charcoal are shown in Fig-5. Increase in the uptakes of alcoholic potassium hydroxide with demineralization and benzene extraction followed by demineralization are quite pronounced. The uptakes of alcoholic potassium hydroxide are quite high compared to the uptakes of sodium bicarbonate, sodium hydroxide, sodium ethoxide and potassium isopropoxide.

The high uptakes of alcoholic potassium hydroxide compared to other bases might be due to small size of

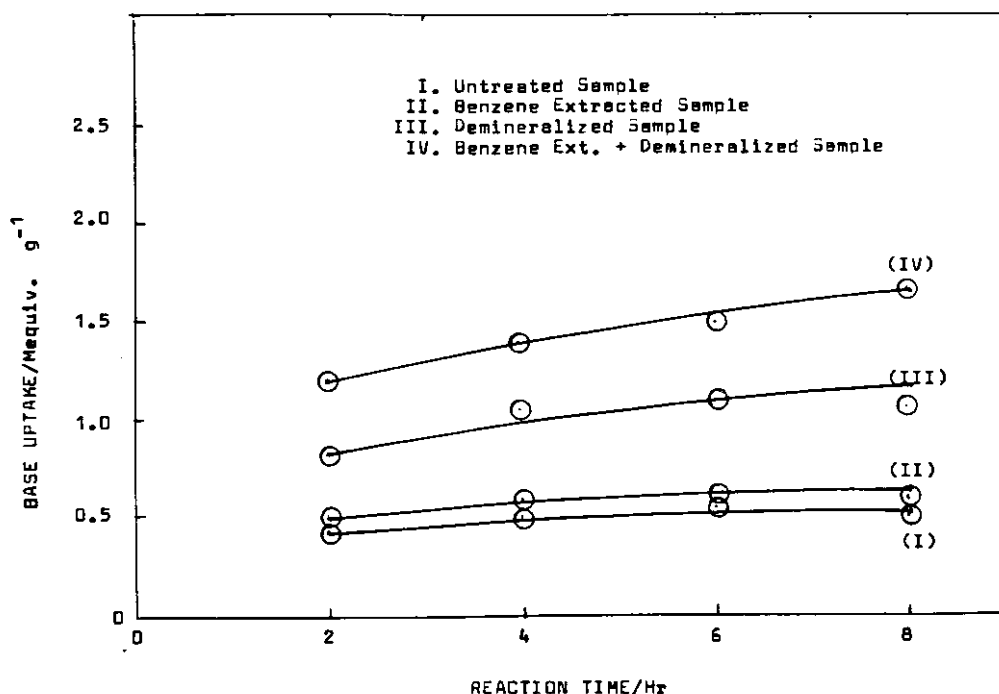


Fig.III: Uptakes of sodium ethoxide at various reaction time by untreated and variously treated walnut charcoal.

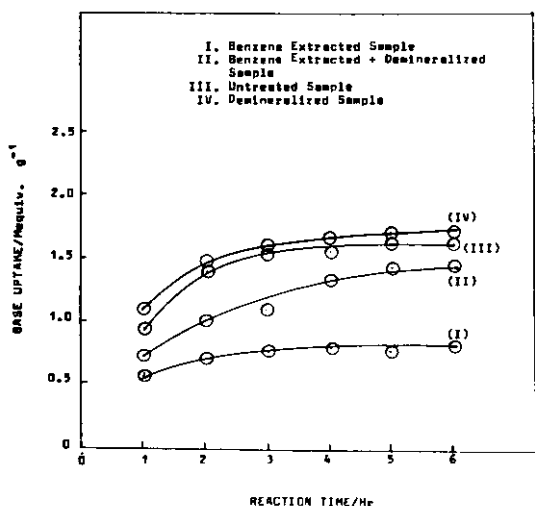


Fig.IV: Uptakes of potassium iso-prop oxide at various reaction time by untreated and variously treated walnut charcoal.

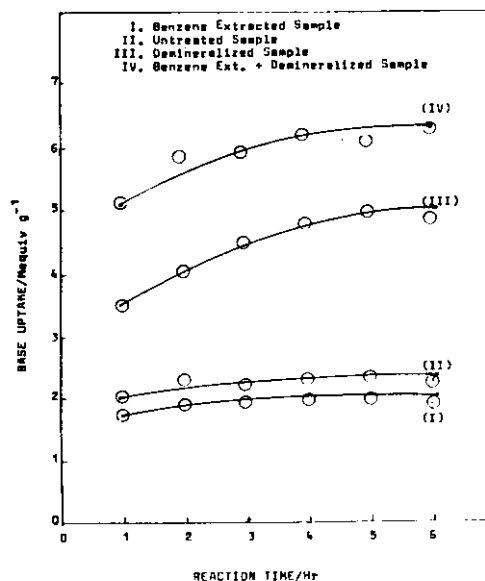


Fig.V: Uptakes of alcoholic potassium hydroxide at various reaction time by untreated and variously treated walnut charcoal.

the OH, because of which it can get an easy access into the pores in the structure of charcoal. Another contributing factor to the high uptakes of potassium hydroxide in alcoholic medium may be the presence of keto-

enol groups on the surface of charcoal in addition to other surface acidic groups. In keto-enol the tautomeric equilibrium shifts towards the more

acidic enol form in the non-aqueous medium and to the less acidic keto form in the aqueous medium [20]. Such types of groups have been reported earlier on the surface of carbon black and charcoal [2,3].

From the uptakes of the various bases, it can be easily inferred that carboxyl groups (neutralized with sodium bicarbonate), lactone and phenolic hydroxyl groups (neutralized with aqueous sodium hydroxide but not with sodium bicarbonate), and keto-enol (neutralized with potassium hydroxide in alcoholic medium but not with aqueous sodium hydroxide). Stronger bases such as sodium ethoxide and potassium isopropoxide, eventhough capable of neutralizing the weaker acidic keto-enol groups, but their comparative large sizes prevent them from getting access into the micropores to neutralize the acidic sites. It has thus to be pointed out that size of pores in the coal structure has quite an influence on determining its acidity with bases of different strengths and structure.

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