EFFECT OF CARBON-OXYGEN SURFACE COMPLEXES ON THE SURFACE AND CATALYST CARRIER PROPERTIES OF SUGAR CHARCOAL

by

T. SUDERSHAN RAO

Department of Chemistry

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ओं शं नो मित्रः शं वरुणः । शं नो भवत्वर्यमा । शं न इन्द्रो बृहस्पतिः । शं नो विष्णुरुरुक्रमः । नमो ब्रह्मणे । नमस्ते वायो । त्वमेव प्रत्यक्षं ब्रह्मासि । त्वामेव प्रत्यक्षं ब्रह्मवदिष्यामि । ऋृतं वदिष्यामि । सत्यं वदिष्यामि । तन्मामवतु । तद्वक्तारमवतु । अवतु माम् । अवतु वक्तारम् ।

ओं शान्तिः शान्तिः शान्तिः ॥ १ ॥

[इति प्रथमोऽनुवाकः]

May *Mitra* be propitious to us. May *Varuṇa* bless us. May the blessings of *Aryamā* be with us. May the grace of *Indra* and *Bṛhaspati* be upon us. May *Viṣṇu*, the All-pervading (widestriding) be propitious to us. Salutations to *Brahman*. Salutations to Thee, O *Vāyu!* Thou art the visible *Brahman*. Thee alone shall I consider as the visible *Brahman*. I shall declare: Thou art the 'Right'; Thou art the 'Good'. May *That* protect me; May *That* protect the speaker. Please protect me. Please protect the speaker.

Om Peace Peace Peace!

(End of Section One)

DEDICATED

TO MY FATHER AND MOTHER

AS TRIBUTE FOR THAT WHICH CANNOT BE REPAID

CERTIFICATE

This is to certify that the thesis entitled " **EFFECT OF CARBON-OXYGEN SURFACE COMPLEXES ON THE SURFACE AND CATALYST CARRIER PROPERTIES OF SUGAR CHARCOAL** " being submitted by Mr. T Sudershan Rao to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. T. Sudershan Rao has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

(N. K. SANDLE) N. K. Sandle

Professor

Department of Chemistry

Indian Institute of Technology, Delhi

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T Rao

(T. Sudershan Rao)

ABSTRACT

In the present work attempt has been made to study the effect of carbon-oxygen complexes present on the surface of sugar charcoals and catalyst carrier properties. Different charcoal samples having varying amounts of surface complexes were prepared by altering the conditions of preparation and activation. The original char was prepared by carbonizing the recrystallized sugar with concentrated sulphuric acid then it was washed thoroughly with distilled water, dried at 100^0C, in an air oven overnight, powdered, sieved and preserved under nitrogen environment for further use.

The original char was heat treated at 400^0C, 750^0C and 1000^0C in vacuum of the order of 10^{-2} torr. The 400-char and 750-char obtained after heat treatment were treated with nitric acid to reintroduce the carbon-oxygen complexes. Different types of chars thus obtained were impregnated with aqueous solution of chloroplatinic acid. The amounts of chloroplatinic acid taken was so adjusted that it would result in loading 2% platinum by weight on the charcoal sample.

The physico-chemical and surface properties for the different types of chars and Pt-coated chars were studied. The properties reported are: elemental analysis, surface area, base adsorption capacity, barium acetate reaction, FTIR, selective adsorption, SEM, ESCA and chemisorption of hydrogen.

Investigation of textural properties for the above chars and Pt-chars are based on the estimation of surface areas by BET single point method using nitrogen as adsorbate at liquid nitrogen temperature. A slight decrease in the surface area is observed with the increase in the heat treatment temperature. Surface acidities were estimated by barium hydroxide and n-butylamine titration. The effect of heat treatment in altering the surface acidity is observed. Surface reaction with $Ba(CH_3COO)_2$ was studied to estimate the carboxylic groups on the surface. It is seen that in the case of original and 400 chars the amounts of carboxyl groups is lesser than the total surface acidity. Reoxidation of 400 char and 750 char with 1 M nitric acid increased the carboxylic content on the surface of the chars. It is also found that the reoxidised chars showed similar amount of carboxylic content when compared with those of platinum coated reoxidised chars showing that the process of platinum loading does not alter the carbon-oxygen surface complexes. Structural analysis of the surface functional groups has been made by assigning the peaks of the Fourier Transform Infrared Spectra.

Evaluation of adsorption behaviour is based on the selective or preferential adsorption of polar or non-polar liquids by the chars from the four binary liquid mixtures, they are ethanol-cyclohexane, n-propanol-cyclohexane, benzene-carbon tetrachloride and benzene-cyclohexane. These mixtures were chosen keeping their nature of polarity and molecular size in view. The influence of surface oxygen complexes on the preferential adsorption is clearly demonstrated.

Pore size distribution and surface morphology was studied by Scanning Electron Microscopy. Average platinum crystallite size and distribution of platinum on the char surface has been estimated and the influence of surface oxygen complexes on the distribution and size of the platinum particles have been demonstrated. ESCA has been used to estimate elemental composition and chemical analysis of the surface. A comparison between the ESCA and Elemental Analysis has been made. The results obtained are comparable. Hydrogen chemisorption has been used to study the percent dispersion of the platinum metal and hence to demonstrate the effect of surface carbon-oxygen complexes in altering the dispersion of platinum on char surfaces..

The catalytic activity of the platinum coated char samples has been studied by the hydrogenation of cyclohexene to cyclohexane in carbon tetrachloride medium, in a stirred tank reactor.

It is observed that the catalytic activity has no linear relationship with any of the properties investigated. Although there is evidence from the physico-chemical properties that the presence of acidic type of carbon-oxygen complexes, giving rise to higher surface acidity and carboxyl content play an important role in controlling the dispersion of platinum on the char surface and thus lowers the activation energy of the hydrogenation reaction of cyclohexene to cyclohexane. The analysis of the kinetic data show that hydrogenation of cyclohexene is found to follow first order kinetics. The mechanism of the reaction is similar to the one described earlier by Horiuti and Polanyi [333].

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