

CHARACTERIZATION OF BIMETALLIC Pt-Sn CATALYSTS SUPPORTED ON UNMODIFIED AND MODIFIED ACTIVATED CARBON

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Introduction

The use of carbon as a support material for metallic catalysts enables the exploitation of the unique properties of carbon namely the possibility to modify the surface chemical properties of the support by changing the surface groups through different pretreatment conditions and, as a consequence, the possibility to modify the nature of the (generally weak) metal/support interaction. (1,2).

In this work a commercial activated carbon (NORIT ROX) was used as catalyst support either in its original form or after oxidation. Two different oxidation procedures were applied, namely direct oxidation with HNO₃ or air oxidation. The supports were characterised by nitrogen adsorption and TPD measurements. Three series of monometallic (Pt) and bimetallic (Pt-Sn) catalysts were prepared on these treated and untreated carbon supports. TPR, XPS, SEM-EDX, XRD measurements and benzene hydrogenation were performed on the catalysts to investigate the effects of changes in support properties, impregnation strategy and Pt:Sn ratio on the distribution of metal, its activity as well as the oxidation state of the metal phases.

Experimental

Preparation and characterization of AC supports

The activated carbon (AC) was ground and sieved to 200-300 µm particle size. Then the following pretreatment procedures were applied: (i) AC was washed with 2N HCl solution for 12 h under reflux with the aim of removing sulfur and some ash, and then washed with distilled water under reflux for 6 h. These were followed by an overnight drying at 383 K (AC1). HCl washed activated carbons were used as such and also taken as the base for the subsequent oxidation treatments; (ii) AC1 was oxidized in 5 % O₂-95 % N₂ mixture at 723 K for 10 h (AC2) and (iii) AC1 was directly oxidized in 5 N HNO₃ solution for 3 h and washed with boiling distilled water till the pH of the rinsed solution reached 5.5. These were followed by an overnight drying at 383 K (AC3).

Total surface area, micropore volume and mesoporous surface area of all samples were determined (Coulter Omnisorp 100 CX). With the aim of determining the oxygen-bearing surface groups, TPD tests were performed on all samples. In TPD tests, the temperature was increased at a rate of 5K/min up to 1373 K.

Preparation and characterization of catalysts

Three sets of catalysts were prepared on AC1, AC2 and AC3. For each set, (i) a monometallic 1 wt% Pt/AC was prepared by pore volume impregnation of aqueous solution of hexachloroplatinic acid, (ii) two Pt-Sn/AC bimetallic catalysts were prepared by coimpregnation of the ethanolic precursor solutions of hexachloroplatinic acid and tin chloride prepared for the fixed Pt load of 1 wt% and Sn loads of 0.25 and 0.5 wt% and (iii) two Pt-Sn/AC catalysts with the same metal loadings as coimpregnated samples were prepared by sequential impregnation (Sn+Pt) in which impregnation of acidic aqueous tin chloride solutions was followed by heat treatment under He flow at 673 K and then by impregnation of aqueous hexachloroplatinic acid precursors. All 15 catalysts prepared were tested in benzene hydrogenation at 393K with H₂:C₆H₆ molar ratio of 11, and 17 µL/min C₆H₆ flow in the feed. All gas flows were controlled by using mass flow controllers and the flow of benzene was controlled by an HPLC pump connected to an Autoclave Engineers' BTRS reactor. Prior to reaction, a reduction procedure was applied to the catalysts: He pretreatment at 673 K for 2 hours followed by 14 hours of reduction under flow of H₂ at 623 K. A representative group of three catalysts from each set have been selected (1 wt% Pt/AC, 1 wt% Pt-0.5 wt% Sn/AC prepared by coimpregnation and 1 wt% Pt-0.5 wt% Sn/AC prepared by sequential impregnation) and all these 9 samples were characterised by TPR and XPS (Escalab 200 A-VG). In TPR measurement, a heating rate of 5 K/min under the flow of 1% H₂-99% He (v/v) mixture was used. XPS tests were made on both fresh and reduced samples. Reduced monometallic samples of each set were observed in SEM-EDX (JEOL JSM 6301F). 0.5 wt % Sn loaded samples prepared by coimpregnation from all sets were also tested by XRD.

Results and Discussion

Characterization of activated carbon supports

The physical characterisation measurements on both untreated (AC1) and oxidised (AC2 and AC3) supports indicate that air oxidation increases the total surface area (BET), micropore volume (W_0) and mesoporous surface area (S_{meso}) relative to AC1. After air oxidation (to a burn off of 20%), the increase in mesoporous surface area is around 60% and the S_{meso} /BET ratio rises from 11.5% to 15%. The increase in micropore volume is around 15%. The increase in the S_{meso} /BET ratio of the support indicates that the texture of AC is enhanced by the air treatment. The nitric acid oxidation treatment led to a slight (7%) decrease in BET surface area. The total micropore volume, W_0 remained practically the same for the support as well as the S_{meso} /BET ratio. All the results that were obtained indicate that the direct liquid phase oxidation does not affect the texture of the support to a great extent. The TPD curves reveal that both air oxidation and direct liquid phase oxidation increase drastically the amounts of oxygen bearing groups that release CO. Compared to AC1, this increase is four times for AC2 and six times for AC3. Air oxidation did not lead to a significant increase in CO₂-releasing groups, whereas a very pronounced increase was observed for the HNO₃ oxidised sample, AC3. The air oxidised sample does not present carboxylic acid groups but has anhydride groups which are represented by a high temperature CO₂ peak. Carboxylic groups show a drastic increase for the HNO₃ oxidised sample. Both oxidation treatments led to phenol, carbonyl, ether and quinone groups on the surface of the support especially for the HNO₃ oxidised sample AC3. Air oxidation increases the ratio CO/CO₂ released compared to AC1 due to the sharp increase in oxygen bearing groups which release CO. This ratio drops for AC3 compared to AC1 but the absolute amounts of both types of groups are very high compared to the untreated sample.

Characterization of Pt/AC catalysts

Monometallic catalysts from each set were tested in SEM-EDX. Backscattered composition images of the samples indicated well distributed Pt particles with smaller size for both Pt/AC2 and Pt/AC3 compared to Pt/AC1. When compared to Pt/AC1, both Pt/AC2 and Pt/AC3 showed increased activity for benzene hydrogenation (six and sevenfold, respectively). This is considered as a structure insensitive reaction, and therefore the results indicate a sharp increase in Pt dispersion when surface groups were introduced.

A comparison of XPS measurements validates these findings and also indicates the migration of Pt from the

surface to the pores with the reduction and also higher atomic concentration of reduced Pt (Pt⁰) on the surface for catalysts supported on oxidised carbons.

Characterization of Pt-Sn/AC catalysts

Benzene hydrogenation tests on bimetallic samples revealed a decrease in benzene hydrogenation activity with the addition of tin, which corresponds to the decrease in the availability of active metallic Pt sites. Coprecipitated samples with 0.5 wt% and 0.25 wt% Sn for all sets gave zero activity and very low activities, respectively. XPS measurements revealed very small decrease of PtII for coprecipitated samples compared to that of the others. These results as well as the shifts in H₂ consumption peaks in TPR and XRD spectra indicate strong Pt-Sn interaction and the formation of SnPt and SnPt₃ alloys for coprecipitated samples. In sequentially impregnated bimetallic catalysts, the activities dropped by the addition of 0.25 wt% Sn for all sets. On AC3, the 0.25 wt% Sn loaded sample prepared by sequential impregnation has one fifth of the activity of Pt/AC3. A similar comparison indicates less pronounced activity losses for the catalysts supported on AC1 and AC2 which are 30% and 50%, respectively. The very sharp activity decrease of sequentially impregnated samples prepared on AC3 indicates the enhanced interaction between Pt and Sn as a result of the dominance of carboxylic groups in HNO₃ oxidized supports (AC3). As a consequence, samples prepared by sequential impregnation on AC2 have the highest benzene hydrogenation activities compared to those on AC1 and AC3, since AC2 does not present carboxylic groups.

Conclusions

The catalytic properties of activated carbon supported Pt and Pt-Sn catalysts are directly affected by changes in support pretreatment, catalyst preparation method and Pt:Sn ratio.

References

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