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SYNTHESIS AND CHARACTERIZATION OF CARBON-BASED BIFUNCTIONAL CATALYST

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Abstract

The current synthesis of carbon-based bifunctional catalyst is energy extensive as it requires high heat treatment whereas the use of amorphous carbon as support is not well understood. This paper reports the study of bifunctional catalyst synthesis using an amorphous carbon with polycyclic aromatic structure as support. Initially, the support precursor pyrolyzed under nitrogen atmosphere, followed by functionalization with fuming sulphuric acid. The functionalized char was deposited with hexachloroplatinic acid as the metal precursor at 0.5% Pt (wt%). The impregnated solution was reduced with formaldehyde to reduce the hexachloroplatinum complex to platinum. FTIR analysis has shown noticeable peaks necessary for $-SO_3H$, -COOH and –OH acidic groups while the structure of the samples was identified as amourphous as the XRD analysis spectrum shows broad band peaks. Platinum deposition was successful as observed from the XRD spectrum & EDX result which is visible through SEM magnification as white bright spots. Total acidity decreased 13.5% after impregnation of platinum suggesting that acidic groups replaced by metal particles. The newly created sugar catalyst with platinum has potential to be a bifunctional catalyst for the synthesis of branched paraffin via isomerization of paraffin as a cleaner fuel additive alternative compared to MTBE.

Keywords: Bifunctional, Functionalization, Sulfonation, Sugar Catalyst, Platinum.

1. Introduction

With the concern of environment and health, a cleaner alternatives gasoline additive has taken much interest to replace the widely used methyl-t-butyl ether (MTBE). In particular, boosting the octane quality of a gasoline fraction by increasing the degree of branching of alkanes is an environmentally more acceptable alternative compared with other technologies such as blending with

Abbreviations

EDX	Energy-dispersive X-ray microanalysis
FTIR	Fourier Transform Infrared Spectrometry
MTBE	Methyl-t-butyl Ether
PtC	Platinum Impregnated Catalyst
SC	Sugar Catalyst
SEM	Scanning Electron Microscope
USEPA	United States Environmental Protection Agency
XRD	X-ray Diffraction (XRD)

oxygenates and aromatics [1]. Thus, skeletal isomerization of alkanes into the corresponding branched isomers has attracted much attention as a reaction to produce clean fuel with high octane quality. Bifunctional catalysts with acid functions balanced by metal functions have shown high efficiency in the isomerization of alkane and traditionally, users of paraffin isomerization technology had the choice between robust zeolite based catalysts and chlorided alumina based systems [1].

Among most important physico-chemical features, ideal properties that bifunctional catalyst should exhibit are: a proper balance between acid and metallic function, high dispersion of metal on the catalyst surface, medium pore size, mild acidity and strength of the acid sites [2]. Busto et al. [3] concluded in their findings that Pt provides the most convenient metal function because it produces more active and stable catalysts.

Based on Toebes et al. [4], oxygen containing surface group is the most important groups influencing the surface characteristics and adsorption behaviour of a carbon and several of these surface-oxygen groups can be distinguished such as carboxylic group (-COOH) and phenol group (-OH). These characteristics can be introduced to the carbon surface via oxidative treatments and the treatment known to act as an anchoring point for the metal nanoparticles [5]. Yu et al. [6] oxidized carbon nanotubes by refluxing H_2SO_4-HNO_3 as its acid precursor thus resulted in functionalized carbon nanotubes with sulfonic -SO_3H, -COOH and –OH group onto its surface. Upon introduction of metal ions into the system, the ions interact with and attach to the surface functional groups by ion-exchange or coordination reaction and serve as nucleation precursors. Toda et al. [7] produced an amorphous sugar catalyst functionalized by refluxing fuming sulfuric acid and this also introduced –SO_3H, -COOH and –OH functional groups onto the surface of the carbon.

Yu et al. [6] demonstrates platinum deposition on carbon nanotubes via oxidation technique of H_2SO_4-HNO_3. The structure of the carbon material was modified by introducing functional groups [6] on the surface of the precursor and by reducing through redox reaction of $PtCl_2$, nucleation of the deposition of the metals starts and the result yields platinum deposition on the surface of the nanotube [6].

A more popular platinum precursor which has been researched by Jia et al. [8] and Fraga et al., [9] by using Hexachloroplatinic acid (H_2PtCl_6). Wang et al. [10] discovered the effect of metal-acid balance in pt-loading on zeolite support bifunctional catalyst. By using H_2PtCl_6 as their platinum precursor, they concluded their finding that the hydrogenation of benzene in terms of catalytic activity and the yield of cyclohexane increase drastically with the raise of Pt load on a given support at low Pt loads, but catalytic activity increase very slowly when Pt loads are higher than 0.5% pt wt%. They also proposed that over noble metal/acid bifunctional catalysts, the hydrogenation reaction could take place on metal sites as well as on acid sites.

Heat treatment such as calcination is usually done after metal impregnation on the support. Wang et al. [10] calcinated platinum impregnated carbon under N_2 flow of 12 $Lh^{-1}g^{-1}$ at 400°C for 2 h to allow the decomposition of the Pt precursor. Sinnathamb [11] discussed that the main function of calcination is the redistribution of metal complex functional group over the catalyst surface and into the channels or pores of the support which causes stronger interaction between metal species and the support. However according to Janaun [12], it was discovered that sugar catalyst functionalized with fuming sulphuric acid is only stable up to 240°C. Hence, this shows that an alternative method to induce the process at or lower than 240°C should be done to ensure the stability of the acidic functional group.

The reduction of platinum complex is important in order to obtain samples with the metal in neutral state [2]. Reduction process functions to reduce Pt(II) complex into Pt(0) [13]. Reduction of Pt/C catalyst with H_2 environment at high temperature (400°C) shows that the stability of acidic functional groups on sugar catalyst is weak in accordance to Janaun [12].

Hexachloroplatinic complex was also reduced using various carboxylic acid which are Formic, Ascorbic and Acetic acid as agent for the metal complex [14]. It was shown that Formic acid reduced the platinum precursor without any additional thermal treatment, whereas for ascorbic and acetic acids, it was necessary to heat the substrate with the platinum precursor up to 100 and 200°C, respectively, to obtain metallic platinum. Nevertheless, this process significantly lowered the temperature of the reduction from 500 to 200°C and platinum metal was obtained without the need for calcinations. They also found out that the crystallites sized for formic, ascorbic and acetic acid is 25, 15 and 15 nm respectively. The small size of the metal particles ensures good distribution and dispersion of them throughout the surface of the support.

Therefore, this paper reports the study of bifunctional catalyst with platinum as metal site and acidic site synthesized using an amorphous carbon with polycyclic aromatic structure as support.

2. Preparation of Bifunctional Catalyst

2.1. Preparation of carbon support

D-glucose monohydrate (System) was pyrolysed at 400°C for 4 hours under nitrogen atmosphere at the flow rate of 100 mL/min. Then, the resultant was grinded and sieved.

2.2. Sulfonation of carbon

The carbon char was then oxidized by refluxing fuming sulfuric acid H_2SO_4 (Acros Organics, 20-30% free SO_3) at 150°C for 12 hours under nitrogen atmosphere at the flow rate of 50 mL/min. The resultants were then washed with warm distilled water until it reached constant pH and until no sulfate ion detected in the washed water. The detection of sulfate ions was done by the precipitation of barium sulfate where 50 mL of the washed water sample heated and gently stirred until it boils. 1-2 mL of HCl was added during the heating process and then barium chloride added into the solution until no precipitation was observed. The oxidized char is denoted as sugar catalyst (SC). The samples were then dried at 100°C.

2.3. Platinum impregnation/deposition

The SC sample was then soaked with the appropriate amount of H_2PtCl_6 (Aldrich, >99.9% Pt) in a 100 mL of distilled water solution to obtain Pt load of about 0.5wt%. The solution was heated and stirred until 100°C for 1 hour 30 minutes in a reflux situation. Then 3 mL of formaldehyde (MercK, 37wt%) solution was added to the suspension to induce reduction of the Pt precursor at 100°C for 3 hours. The resulted samples were filtered, washed with distilled water and dried at 100°C. The impregnated sample is denoted as PtC.

2.4. Characterization

The catalyst samples were tested for their chemical and physical properties. The catalyst total acidity was measured using acid (0.02M HCl)-base (0.01M NaOH) back-titration method (Table 1). The functional groups of the char were determined by using Fourier Transform Infrared Spectrometry (FTIR). The catalyst was scanned at a range from 650 cm^{-1} to 4000 cm^{-1} on Perkin Elmer spectrum 100. The surface morphology analysis was determined by using Hitachi S-3400N Scanning Electron Microscope (SEM). Energy-dispersive X-ray microanalysis (EDX) (Bruker Quantax Esprit 1.0) was installed to the SEM to determine the composition of the features in the SEM image. The analysis molecular structure and Pt content were determined using Philip Expert pro X-ray diffraction (XRD) (Philips Expert Pro pw3040) analysis using Cu-Kα radiation source.

Table 1. Total Acidity of Carbon-Based Catalysts.

Samples	Total Acidity (mmol/g)
SC	3.35
PtC	2.90

3. Results and Discussion

The FTIR spectra of PtC and SC are represented in Fig. 1. Strong band at 1729 cm^{-1} and peak at 1052 cm^{-1} for both samples can be assigned to the SO_3H group [15]. Both samples showed peaks at 1611 cm^{-1} due to C=C stretching [16] while band at 1207 cm^{-1} for the carbon-based catalysts represents aryl-hydroxyl (Ar-OH) [17]. Furthermore, the overlapping band near 1700 cm^{-1} can be assigned to the carboxylic acid stretching [18]. Other than that, it can be seen that there are peaks at ~3600 cm^{-1} wavelength and based on [19] and known as the OH stretching at 3200 to 3700 cm^{-1}. The overall FTIR analysis shows that the SC and PtC samples contains -SO_3H, -COOH and -OH groups which is in agreement with [7, 12, 20-22] for successfully functionalizing these acidic groups onto the carbon surface.

Figure 2 shows the XRD diffraction patterns of SC and PtC of carbon catalyst samples. Both samples clearly showed broad diffraction peak from 20 – 30° (2θ) angle which is highly attributable to the amorphous carbon structure of the samples [23]. Furthermore, a weak distinguishable peak can be observed at peak angle of 39.8° (2θ) between sample PtC and SC. This peak is only observable at sample PtC and this shows the characteristic peak of face-centered cubic crystalline Pt metal [14]. Jia et al. [8] also deposited metal on the surface of carbon blacks by using 30% H_2O_2 and 65% HNO_3 as oxidative treatments and H_2PtCl_6 as platinum precursor also shows platinum peak at that particular angle namely Pt(111). The peak confirms the metal deposition of Pt on the surface of the carbon support from the result of Pt impregnation modification onto the SC sample.

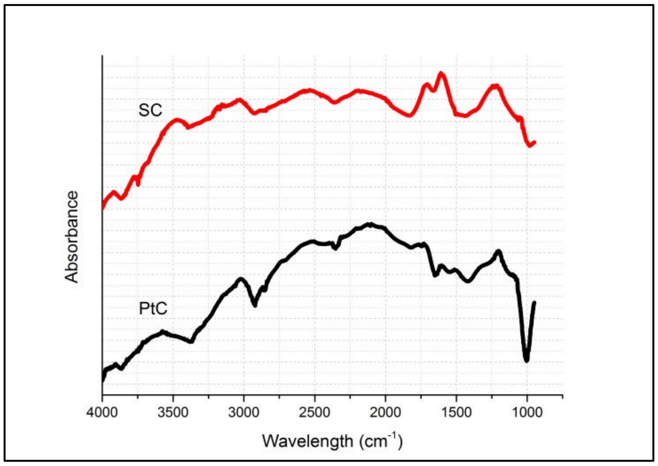


Fig. 1. FTIR Spectra of SC and PtC Samples.

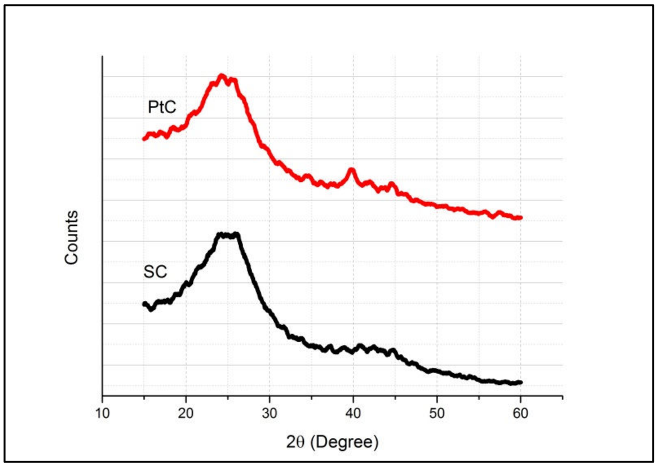
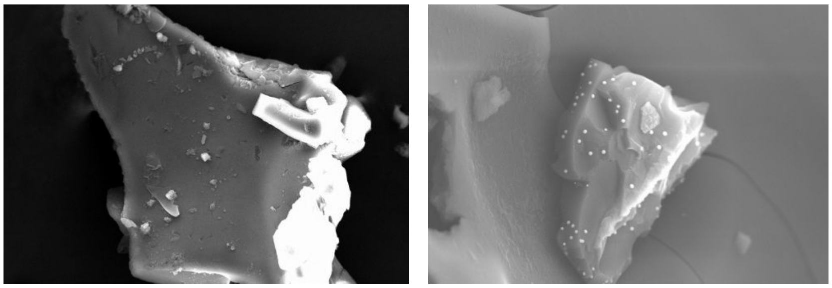


Fig. 2. XRD Patterns for SC and PtC Samples.

The acidity of the sample is due to the introduction of the acidic functional groups to the carbon support which are -COOH, -OH, and $-SO_3H$ as identified by FT-IR. The total acidity of SC sample is 3.35 mmol/g and the value decrease to 2.90 mmol/g with PtC sample; a decrement of 13.5% of total acidity after the Pt impregnation to the SC sample. This may be due to the acidic site replaced and reduced by metal precursor during the deposition. Yu et al. [6] deposited platinum on carbon nanotubes by chemical modification of H_2SO_4-HNO_3 and showed that the sulfate groups were removed after the deposition of platinum by using XPS as a medium of the analysis. This implies that the incorporation of Pt ions promoted the hydrolysis of sulfate [6].

Figure 3 shows the SEM images for both SC and PtC samples at 4500x magnification. Noticeable difference for these images is that sample PtC (Fig. 3(b)) shows round small white spots attached onto a carbon particle while the white spots could not be found on sample SC on Fig. 3(a). This might suggest that these spots are platinum deposited on the surface of the support particles and this occurrence is the same with Qu and Dai [24] findings where small platinum spots are observable through SEM whereas the sample before deposition (SC) has no spots. Similar occasion can be seen from [8] and [14] via TEM as magnification medium where the black spots can be observed on the support of the metal support.



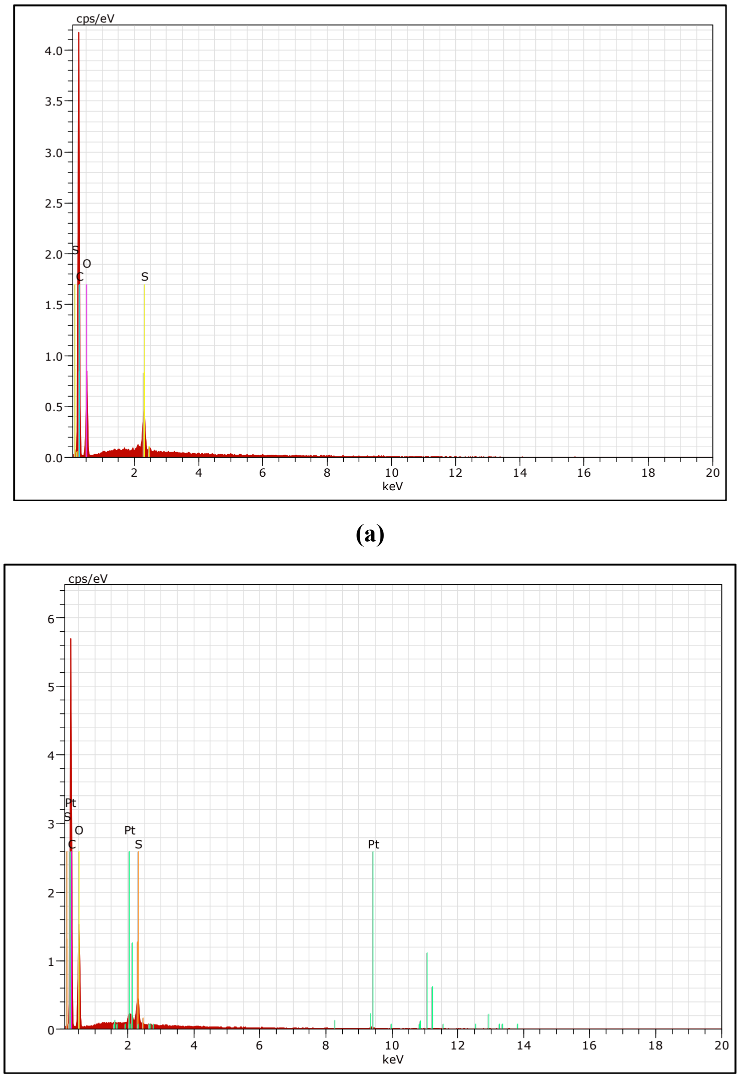
(a) **(b)**

Fig. 3. SEM images of (a) SC and (b) PtC at 4500x

The EDX analysis of SC and PtC are shown in Fig. 4 for both SC (a) and PtC (b) sample. Figure 4(a) for SC shows strong peak of C, O and S element that are available on the sample. This further confirms the introduction of –SO_3H acidic group from the FTIR analysis onto the surface of the carbon support via sulfonation due to the presence of S element. Pt peak is visible in Fig. 4(b) showing that the deposition of the metal onto the surface of SC was successful in agreement with the XRD analysis which shows the existence of platinum on angle 39.8^o (2θ). The EDX elemental analysis in terms of wt% is shown in table 2 and the percentage of platinum on PtC has increased to 3.07 wt% from none in SC sample. Based on Foronda et al. [25], the bright particles are observed on the SEM analysis of their platinum impregnated support which could easily be assigned to platinum on the composite as verified by energy dispersed X-ray (EDX) analysis. Therefore, through this statement and from both SEM and EDX analyses, it is said that the platinum was safely deposited on the carbon support.

Table 2: EDX Analysis of SC and PtC

Samples	**Elemental Composition (wt%)**			
	C	**O**	**S**	**Pt**
SC	67.64	30.35	2.01	0.00
PtC	61.37	33.27	2.29	3.07



(a)

(b)

Fig. 4. EDX spectrum of (a) SC and (b) PtC

4. Conclusion

An amorphous carbon-based support was prepared by low temperature incomplete carbonization of D-Glucose. The structure of the support was determined by the XRD analysis as it shown an obvious broad peak as opposed to sharp peak assigned to graphitic structure. Rich $–SO_3H$, -COOH and –OH acidic group was identified by using FTIR and EDX mainly due to the functionalization of the support via sulfonation using fuming sulphuric acid onto the surface of the support. Platinum metals were successfully deposited onto the support and this can be seen from the XRD and EDX analysis which clearly shown Pt deposition attainment. The platinum particles were also observable under SEM magnification as bright white spots can be seen. Through the total acidity analysis, the acidity of SC sample decreased after the impregnation of Pt as can be seen on the total acidity of PtC sample and due to that, it is said that the acidic groups are important to be used and as an anchor point for the deposition of metal. The newly created sugar catalyst with platinum has potential to be a bifunctional catalyst for the synthesis of branched paraffin via isomerization of paraffin.

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