

Thermally Activated Palm Kernel Based Carbon as a Support for Edible Oil Hydrogenation Catalyst

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Abstract— Activated carbon has distinctive properties as a support for hydrogenation catalysts. Thermally activated carbon has been prepared from palm kernel shell at 1073 K and placed under nitrogen flow for 2 h. It was impregnated by palladium using toluene solution of Pd (acac)₂. The Pd/C was reduced using a water solution of potassium borohydride (KBH₄). The Pd-B/C was characterized by the Brunauer-Emmett-Teller surface area analysis (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and inductively-coupled plasma mass spectrometry (ICP-MS). Pd-B/C was applied for sunflower oil hydrogenation at a temperature of 373 K, hydrogen pressure of 413.5 kPa and agitation of 1400 rpm for 1 h. Pd-B/C noticeably exhibited a higher overall catalyst activity in comparison to some recently published palladium catalysts.

Keywords— Activated Carbon; Palladium; Hydrogenation.

I. INTRODUCTION

Carbon has wide applications as a catalyst support due to its distinctive properties including inertness, stability, low cost, high surface area and the possibility to recover the active precious metals [1], [2]. It is usually produced by the carbonization of woody materials at high temperature and inert atmosphere which provides an opportunity to utilize part of the low value bio-waste materials [3], [4]. As such, the palm oil industry in Malaysia produces around 4.3 million tonnes waste of palm kernel shell annually [5]. From this quantity, most are burned to produce energy for the industrial applications. It may be seen as inefficient to utilize this waste material due to low economical yield and high degree of pollution [6]. Meanwhile, the production of activated carbon from the waste palm kernel shell can increase the return of this waste material to around 450 US\$ /ton [7]. The activated carbon was prepared by carbonization at around 1073 K in nitrogen and activation by steam at 1273 K, followed by chemical activated by KOH [4], [8], [9]. This carbon is reported to have excellent absorption ability that results from its unique attributes in terms of the surface area and pore specification [4].

The activated carbon's physical properties are enhanced by physical and chemical activation using KOH and CO₂ agents [10]. Phosphoric acid and Zinc chloride are also used as agents for the chemical activation process [11], [12].

In the field of vegetable oil hydrogenations, the Pd/C catalytic activity and trans-isomerization selectivity are correlated with the activated carbon structure [1], [13]. The latter has been influenced by the method and conditions of activated carbon preparation.

II. EXPERIMENTAL

A. Materials

The palm kernel shell used for activated carbon preparation was supplied by united oil palm industries (Sdn Bhd, Malaysia). Pd (acac)₂ (Johnson Matthey, USA) was used as a Pd precursor. The chemical reduction agent was potassium borohydride (KBH₄; Acros Organics, USA) and the alkaline agent was potassium hydroxide (KOH; Merck Schuchardt OHG, Germany). Sunflower oil (Yemen Company for Ghee and Soap Industry, Yemen) was used for catalyst testing. The composition (%) of the sunflower oil was C18: 0 = 3.23, C18: 1 = 30.74, C18: 2 = 56.78 and C18: 3 = 0.1, where the first number indicates the total carbon number of the fatty acid and the second number indicates the total number of C = C double bonds. Hydrogen (99.999%, chromatographic grade) from the local market was used for hydrogenation tests. The de-ionized water used for all stages of catalyst preparation and washing was provided by laboratories of the National University of Malaysia (UKM).

B. Methods

1) *Preparation of Activated Carbon:* A single preparation process was conducted to prepare the activated carbon. It included the washing of palm kernel shell and drying at 393 K for 5 h. Then it was carbonized at 1073 K under a flow of nitrogen for 2 h. Finally the carbonized shell was cooled down, grinded and sieved to a particle size of 0.5–1.5 mm [2].

2) *Preparation Pd-B/C catalyst:* The Pd/C was prepared through the wet impregnation method. Before impregnation, carbon powder was dried at 393 K for 2 h. Then, it was impregnated by a Pd (Acac)₂ toluene solution at 298 K for 24 h. Then, the catalyst was dried at 393 K for 2 h and heated at 623 K for 2 h in air.

The Pd-B/C catalyst sample was prepared through a chemical reduction process for Pd/C using an aqueous solution containing 0.2 M KBH₄ in the presence of KOH. The KBH₄/Pd⁺² molar ratio was equal to 3 for the purpose of the total reduction of palladium oxide [14]. The KBH₄ solution was added slowly to the catalyst precursor at a low temperature and with gentle agitation. Pd-B/C was washed using demineralized water and then ethanol [14]. Then the Pd-B/C was dried at 393 K.

3) *Catalyst Characterization:* The surface morphology was observed using the scanning electron microscopy (SEM) with INCAx-sight-7353 (Oxford Instruments, UK). The transmission electron microscopy (TEM) was performed using a CM12 transmission electron microscope (Philips, Netherlands). Inductively coupled plasma mass spectrometry (ICP-MS) tests were performed using a spectrometer-ELAN 9000 (Perkin Elmer SCIEX, USA) for analysing the catalyst content of the palladium and boron elements.

4) *Catalyst Testing:* The hydrogenation test of the prepared catalyst sample was performed in a batch reactor equipped with temperature, pressure and agitation controllers. The batch consisted of 150 g of refined sunflower oil. Prior to the hydrogen injection, the reactor was flushed with nitrogen gas to remove the air and dissolved oxygen. Hydrogenation was performed using Pd-B/C at 373 K, a hydrogen pressure of 413.5 kPa and an agitation of 1400 rpm for 1 h.

5) *Analytical and calculation procedures:* The analyses of the fatty acid composition, trans-fatty acids content and IV were performed using the corresponding American Oil Chemists' Society test methods [15]. The AOCS Ce 1k-09 method was used to determine the fatty acid composition and trans-fatty acid content of the unhydrogenated and hydrogenated samples via gas chromatography (GC). The AOCS Cd 1-25 test method was used to determine the iodine value (IV). The hydrogenation conversion was calculated according to the methods previously reported in [16].

The catalyst's overall activity and hydrogenation rate constant were calculated using the method previously followed by [1] as shown in Equation 1.

$$\ln (IV_o/IV_f) = m \cdot k_r \cdot t \quad (1)$$

where IV_o and IV_f are the IV at t = 0 and t = t respectively, m is the catalyst dose in the oil (ppm), k_r is the hydrogenation rate constant and t is the reaction time.

The trans-isomerization selectivity as a measure of the catalyst's tendency to form the trans-fatty acid was calculated by the following equation as in [17].

$$S_i = \Delta (\% \text{ trans fats}) / \Delta (\% \text{ conversion}) \quad (2)$$

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

The result of the BET surface area has shown that the carbon has 290 m²/g which was reduced to 230 m²/g for Pd-B/C as a result of impregnation and chemical reduction. The surface area seems small, compared with the corresponding surface area of activated carbon prepared from the palm kernel shell using a different method than that followed in this work, but it is useful to judge according to the performance of the catalyst. The pore diameter, however, decreased from 24.4 nm for carbon to 22.2 nm for Pd-B/C. This decline can be attributed to the deposition of Pd and B during impregnation and chemical reduction processes [18]. The pore diameter of Pd-B/C was considered to be suitable for oil hydrogenation according to the Coenen classification, in which the triglyceride molecule easily enters and exits a slot of the support's pore [19]. On the contrary, the pore size of the method of steam gasification [9] at high temperature had produced a pore size of lower dimension (0.53- 5.71 nm) than that required for vegetable oil hydrogenation (7-8 nm) [20].

The morphological structure of the carbon and Pd-B/C catalyst was studied by the SEM. The surface structure exhibited well-distributed macropores on the catalyst surface as shown in Fig. 1.

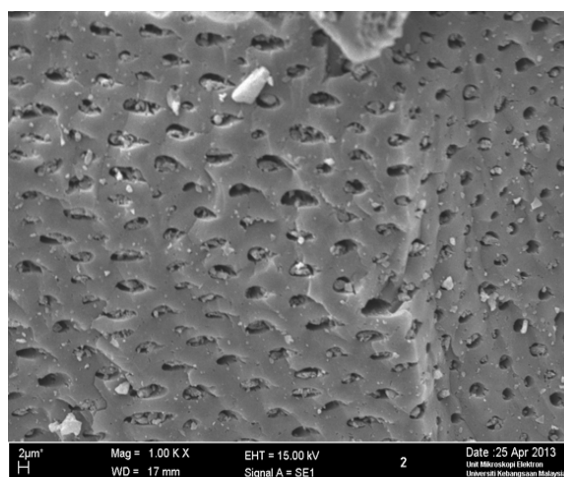


Fig. 1 SEM image for Pd-B/C catalyst

However, the development for the pores can be achieved via the post-thermal process using steam to perform a cleaning process for the pores in order to remove the remnants from the carbonization process as can be noticed in Fig. 1. This

development can increase the surface area and the catalyst activity.

Fig. 2 shows the TEM image of Pd-B/C, where the average particle size of Pd-B/C was 5.0 nm which was reported to have a positive influence on the catalyst activity and selectivity [21]. The TEM image and average particle size indicate the absence of sintering and aggregation.

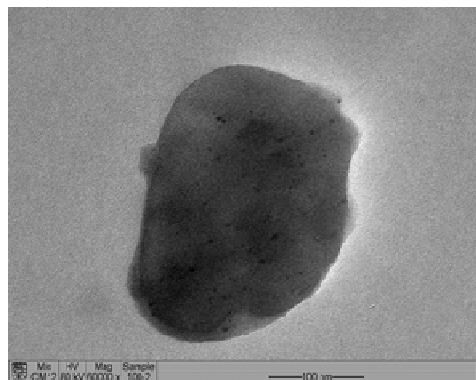


Fig. 2 TEM image of Pd-B/C catalyst.

The ICP results for the catalyst content showed 0.215 % for Pd and 0.022 % for B.

A. Catalyst Testing

The hydrogenation of sunflower oil on Pd-B/ C prepared catalyst showed the conversion of 22.6 % under the conditions previously mentioned. However, the overall catalyst activity ($m.k_r$) and reaction rate content (k_r) were calculated using Equation (1) for Pd-B/C and compared with that reported for Pd/ γ -(N) in [22]. As shown in Fig. 3, the Pd-B/C overall catalyst activity was noticeably higher than that for Pd/ γ -(N) under similar conditions.

The tendency for the Pd-B/C catalyst was reported as a trans-isomerization selectivity which was calculated using Equation (2).

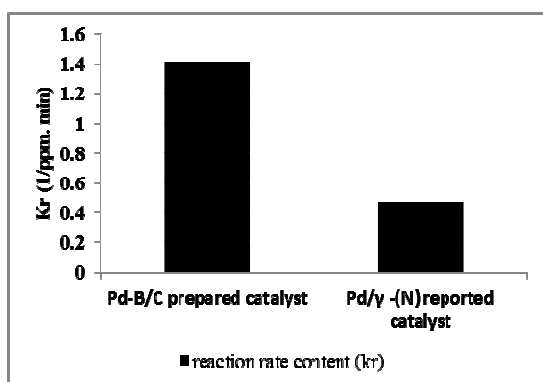


Fig. 3 Hydrogenation rate constant (k_r) for Pd-B/C prepared catalyst and Pd/ γ -(N) reported catalyst

Fig.4 demonstrates a lower tendency for the Pd-B/C catalyst to produce TFAs than Pd/ γ -(N). The higher Pd-B/C activity was attributed to its high capability for hydrogen adsorption and higher concentration of active sites resulting from the nature of the Pd-B alloy [23], [24]. However, the lower Si of Pd-B/C may correlate with the effect of the

metalloid element (boron) as an electron donor that changes the electron density of the Pd atom [25]. In addition, the support physical properties, especially the meso-structured pores may positively affect the reactants and products transportation from and to the catalyst active sites. This leads to the enhancement of the catalyst activity and selectivity [26].

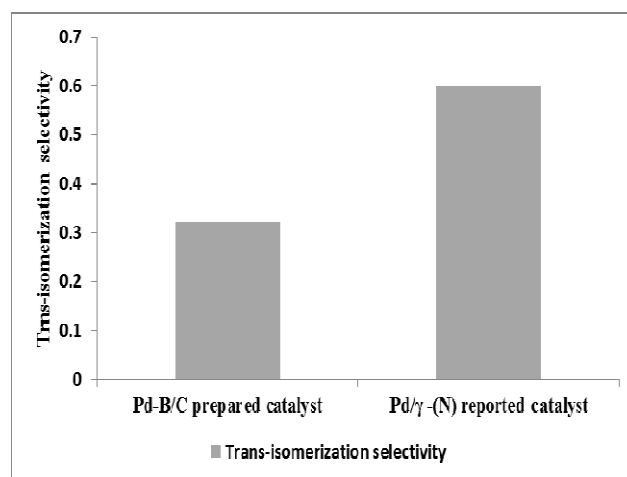


Fig. 4 Trans-isomerization selectivity for Pd-B/C prepared catalyst and Pd/ γ -(N) reported catalyst

III. CONCLUSIONS

Activated carbon was prepared from the palm kernel shell using a single thermal carbonization process. Despite low surface area, the activated carbon exhibited a good distribution of the macrostructure pores suitable for molecule transportation during sunflower oil hydrogenation.

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