RASĀYAN *J. Chem.*
Vol. 5 | No.4 | 463-467 | October-December | 2012
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

PALLADIUM-BORON CATALYST FOR VEGETABLE OILS HYDROGENATION

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ABSTRACT

Modification of a palladium-supported catalyst was performed in order to improve its activity and trans-isomerisation selectivity (S_i) for palm oil hydrogenation. A $Pd\text{-}B/\gamma\text{-}Al_2O_3$ amorphous alloy was prepared by wet impregnation of Pd $(acac)_2$ on $\gamma\text{-}Al_2O_3$ followed by chemical reduction using KBH_4. The catalyst was thermally treated at 573 K before hydrogenation and was characterised by the Brunauer-Emmett-Teller surface areas (BET), scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). A conventional hydrogenation for palm oil was performed using 0.12 % catalyst at 393 K, 500 kPa and 500 rpm for 1 h. The $Pd\text{-}B/\gamma\text{-}Al_2O_3$ catalyst exhibited significantly better catalytic activity and trans selectivity comparing to the corresponding $Pd/\gamma\text{-}Al_2O_3$ and commercial catalysts.

Keywords: Amorphous materials, sintering, trans fatty acids.

INTRODUCTION

Partial hydrogenation of edible oils is an important process of producing fats with desirable properties for food and nonfood aplications[1,2]. It is used to modify the color, odor, thermal behavior and oxidation resistance of oils[3]. Hydrogenation is conventionly performed at 413-503 K and 300 kPa hydrogen pressure using nickel supported on silica or alumina. Despite the benefits of using nickel as a catalyst, its major disadvantage is the significant isomerization[4,5].

Trans fatty acids TFAs have been reported as a harmful fats for human health[6]. As a result of that, the customer' awareness of hydrogenated oils has increased. The issues with TFAs have increased the impetus to discover viable alternatives that can be accessed through catalyst development[6]. Palladium (Pd) exhibits unique features for hydrogenation due to its high conversion under moderate temperature and the possibility to alter its performance through the addition of modifiers[7]. Modified Pd can introduce moderation of performance between the catalyst activity and trans selectivity[8]. Recently, amorphous materials have been widely studied as new catalysts for many reactions, and especially for hydrogenation. Amorphous materials have different chemical and physical properties than their corollary crystalline alloys[9]. These properties can provide for more active and selective catalytic performance[9, 10]. Amorphous Pd was scarcely reported in the field of hydrogenation. A $Pd\text{-}B/SiO_2$ amorphous catalyst was prepared and used for nitrobenzene hydrogenation first time in 2000[11], and $Pd\text{-}B/\gamma\text{-}Al_2O_3$ was used for anthraquinone hydrogenation in 2003[12]. While, a literature search found no reports using $Pd\text{-}B/\gamma\text{-}Al_2O_3$ catalysts in the field of edible oil hydrogenation.

EXPRIMENTAL

Catalyst preparation

The Pd/γ-Al_2O_3 catalyst was prepared by wet impregnation of palladium on alumina (γ-Al_2O_3) by a similar method previously used [3]. A γ-Al_2O_3 (Alfa Aesar, 60 mesh powder, 150 m^2/g) was dried at 423 K for 2 h. Then it was impregnated with a toluene solution of Pd (Acac) $_2$ (Johnson Matthey) at room temperature under agitation for 24 h. The catalyst was dried at 423 K for 2 h and then calcined at 773 K for 2 h. Unlike the previous preparation method, the drying and calcination were performed in absence of inert gases. The Pd-B/γ-Al_2O_3 catalyst was prepared by the chemical reduction of Pd/γ-Al_2O_3 using aqueous solution contain 0.2 MKBH_4 (Acros organics) and 0.96 M KOH. The KBH_4/Pd^{+2} molar ratio was equal to 3 for total reduction of palladium oxide. The KBH_4 solution was added slowly to the catalyst precursor at low temperature and well agitation. Pd-B/γ-Al_2O_3 was carefully washed using distilled water and subsequently with ethanol[13]. The Pd-B/γ-Al_2O_3 was dried and then annealed at 573 K for 2 h under air atmosphere. Unlike other oil hydrogenation catalysts, this catalyst is high stable against oxidation and does not need to keep in high saturated fat for long time storage.

Catalyst characterisation

The Brunauer-Emmett-Teller (BET, Micromeritics ASAP 2020) surface area was determined using a similar method reported by Fernandez et al[6]. Surface morphology was observed by scanning electron microscopy (SEM, INCAx-sight-7353-Oxford instruments), including the energy-dispersive X-ray spectroscopy (EDX) application for catalyst metal content measurement. Transmission electron microscopy (TEM) was performed on a CM12 transmission electron microscope (Philips).

Catalyst activity measurements

The hydrogenation tests were performed in a 400 ml batch reactor equipped with devices for controlling the temperature, pressure and agitation. The batch consisted of 250 g of refined, bleached and deodorised palm oil supplied by the Yemen Company for Ghee and Soap Industry (YCGSI). The hydrogenation was performed using 0.12 % catalyst at 393 K, 500 kPa and 500 rpm for 1 h. The composition (%) of the palm oil samples applied for hydrogenation was C18:0 = 6.0, C18:1 = 40.75, C18:2 = 7.75 and C18:3 = 0.1. The reactor was supplied with hydrogen (chromatographic grade) at a constant pressure as required for each test. The tests were performed using the catalysts shown in Table-1. Pd/γ-Al_2O_3 and Escat were used for the purpose of comparison, where Escat is a commercial Pd/γ-Al_2O_3 catalyst supplied by (BASF, Netherlands).

Analytical and calculation methods

The analyses of fatty acids, trans fatty acids and iodine values were performed using the corresponding American Oil Chemists' Society (AOCS) test methods[14].

Calculation of catalyst activity, trans selectivity and C = C conversion were performed by the methods used in literatures previously.[15-17]

Table-1: The metallic composition of the catalyst samples.

Catalyst	Pd content[a] (%)	Catalyst loading[b] (mg_{Pd}/g_{oil}) x10^3
Pd/γ-Al_2O_3	0.73	8.8
Pd-B/γ-Al_2O_3	0.73	8.8
Pd/γ-Al_2O_3 (Escat)	5	12

[a] Palladium content in the catalyst. [b] palladium metal concentration in the oil.

RESULTS AND DISCUSSION

Catalyst characterization

The BET surface area for Pd/γ-Al_2O_3 was 164.3 m^2/g. However, it was reduced to 121.3 m^2/g for Pd-B/γ-Al_2O_3. This reduction in surface area could be attributed to (1) an increase in the metal loading resulted from chemical reduction, or (2) thermal treatment at 573 K that could cause the Pd-B alloy particles sintering and gathering[18]. Pore diameter, however, was increased slightly from 5.71 nm for Pd/γ-Al_2O_3 to 5.84 nm for Pd-B/γ-Al_2O_3.This increase can be attributed to the thermal treatment performed for Pd-B/γ-Al_2O_3. The pore diameter of both Pd/γ-Al_2O_3 and Pd-B/γ-$Al_2O_3$is considered to be suitable for oil and fat hydrogenation according to the Coenen classification[19].

The morphology of Pd-B/γ-Al_2O_3 was confirmed by means of SEM. There were pure, clean, and small particles appeared on the surface of Pd/γ-Al_2O_3 as shown in Fig. 1A. However, Pd-B/γ-Al_2O_3 exhibited a "cotton-like" porous morphology in which the support was covered by fine white coating of Pd-B amorphous alloy as shown in Fig. 1B [20].

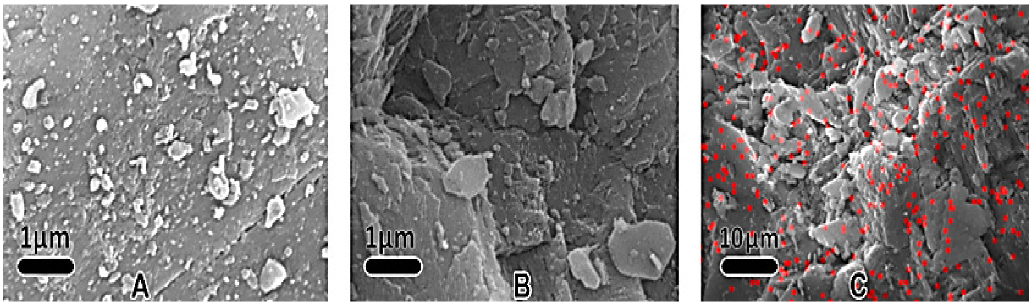

Fig.-1: The SEM images of: (A) Pd/γ-Al_2O_3 (annealed at 773 K), (B) Pd-B/γ-Al_2O_3 (annealed at 573 K) and (C) palladium distribution on the alumina support.

Pd-B/γ-Al_2O_3 exhibited a good distribution of Pd sites on the alumina support as shown in Fig. 1C. The EDX analysis detected both Pd and B, confirming the existence of Pd-B alloys on the catalyst particles and confirming that the average palladium content was 0.73% as shown in Fig. 2.

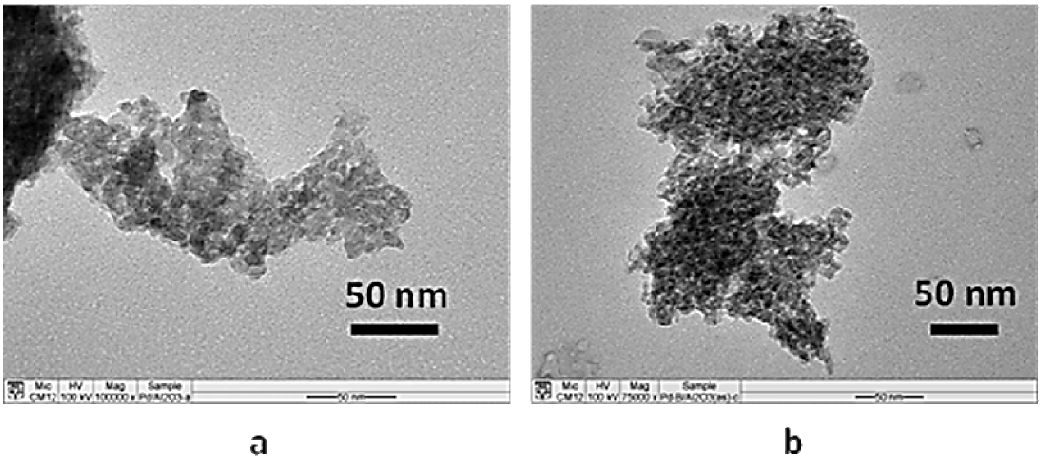

Fig.-2: The TEM images of: (a) Pd/γ-Al_2O_3 and (b) Pd-B/γ-Al_2O_3.

Fig. 3 shows the TEM images of the prepared catalysts. The average particle size was 5.8 nm and 6.9 nm for Pd/γ-Al_2O_3 and Pd-B/γ-Al_2O_3 respectively. The bigger size of Pd-B/γ-Al_2O_3 can be attributed to the aggregation and growth of metal particles during chemical reduction and thermal treatment for the Pd-B/γ-Al_2O_3 catalyst.

Catalyst activity measurement

The C = C saturation conversion for Pd-B/γ-Al_2O_3 was 7.82 % compared to 5.31 and 4.50 % for Escat and Pd/γ-Al_2O_3 catalyst samples respectively. This result was compatible with the catalyst activity of Pd-B/γ-Al_2O_3 which is higher than both the Pd/γ-Al_2O_3 and Escat samples as shown in Fig. 4.

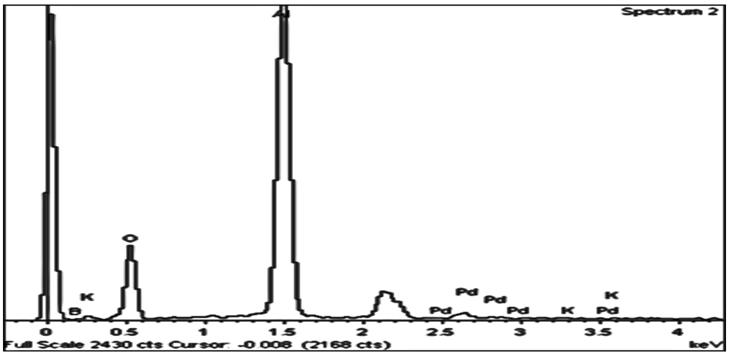

Fig.-3: EDX result for metallic content of Pd-B/γ-Al_2O_3 catalyst sample.

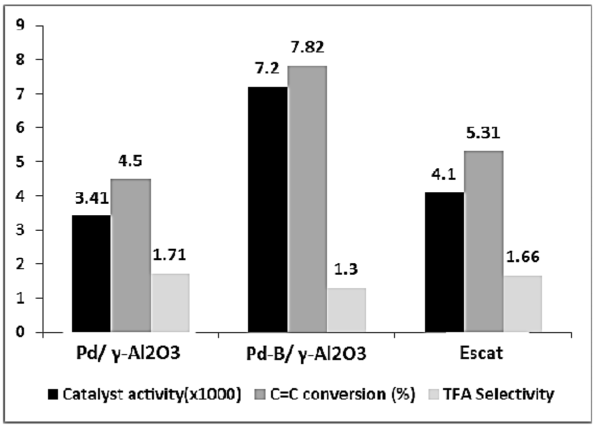

Fig.-4: Hydrogenation of palm oil. T = 393 K, P = 500 kPa, agitation = 500 rpm, reaction time = 1 h and catalyst loading 8.8 ppm for Pd/γ-Al_2O_3 and Pd-B/γ-Al_2O_3but 12 ppm for Escat.

The higher activity of Pd-B/γ-Al_2O_3 was attributed to a stronger capability for hydrogen adsorption as well as higher concentration of active sites[20, 21]. These results were in agreement with those previously reported of using similar catalyst for the hydrogenation of different hydrocarbons[13, 20, 21].

A reduction in the trans selectivity (S_i) was also noticed from 1.71 for Pd/γ-Al_2O_3 to 1.66 for Escat and 1.3 for Pd-B/γ-Al_2O_3catalyst. This reduction in selectivity may be correlated with the effect of the metalloid element (boron) as an electron donor that changes the electron density of the Pd atom[12]. Unlike the previous results of oil hydrogenation using palladium modified catalyst[3], it is worthwhile to emphasise that the reduction in trans isomerisation selectivity (S_i) for Pd-B/γ-Al_2O_3 was not correlated with decline in catalyst activity.

CONCLUSION

An amorphous alloy catalyst, Pd-B/γ-Al_2O_3, was prepared by impregnation and chemical reduction. Analysis showed that chemical reduction has clear effect on the catalyst behaviour. Pd-B/γ-Al_2O_3 exhibited higher activity and better trans selectivity than Pd/γ-Al_2O_3 and Escat catalysts. The results suggest that the catalyst morphology can be considered as a factor affecting on the hydrogenation activity and trans isomerisation selectivity.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support provided by Universiti Kebangsaan Malaysia (UKM) by the fund (MOSTI 03-01-02-SF0696), Yemen Company for Ghee and soap industry (YCGSI) and Food Technology and Nutrition Unit-Malaysian Palm Oil Board (MPOB).

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[RJC-983/2012]