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Synthesis of silica/carbon composite from agricultural waste as heterogeneous acid catalysts to produce dioxolane moieties from a biodiesel-derived waste compound

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Abstract

Silica/carbon composites from the carbonization of rice husk have been employed to act as heterogeneous Brønsted acid catalysts. These composites have been used to catalyze the acetalization of phenylacetaldehyde, vanillin, and 2-acetonaphthone with propylene glycol to produce hyacinth, vanilla, and orange blossom scent fragrances. As the carbonization temperatures affect the physicochemical properties and hence their catalytic activity, several characterization techniques and data manipulation have been performed to understand the correlations. Acid density and hydrophilicity has been proved to play a crucial part to obtain an optimized yield of desired products.

1. INTRODUCTION

Carbonyl groups are sensitive in organic synthesis reactions. Thus, various protection techniques have been demonstrated. One of the viable strategies to protect carbonyl groups is acetalization process to produce acetals. Acetals are not only acted as protecting groups, but their applications in cosmetics, food additives, detergents, and fragrances have been explored as well (Bauer et al., 1998). This acetalization reaction is accomplished by reacting carbonyl compounds with alcohol with the aid of acid catalysts. Furthermore, the formation of dioxolane moieties could enhance their resistance towards bases, metal hydrides, oxidants, bromination, and esterification, and Grignard reagents. The use of a solid acid catalyst is preferable due to facile separation and reduces the formation of salt that originated from neutralization (Kaneda et al., 2006).

Climent et al., (2004) had employed zeolite to produce phenylacetaldehyde glycerol acetals, vanillin propylene glycol acetal, and 2-acetonaphthone propylene glycol acetal which resulting hyacinth, vanilla, and orange blossom scent fragrance, respectively. However, the synthesis of zeolite materials requires intricate preparation and using expensive silica precursor. Very recently, the use of activated carbon has been demonstrated by Silva et al., (2016). Oxidized and sulfonated-activated carbons were tested in the catalytic conversion of glycerol by acetalization reactions. The best catalyst for the reaction of glycerol acetalization with phenylacetaldehyde was fuming sulphuric acid-treated activated carbon with a phenylacetaldehyde conversion of 95% after 90 min at 383 K and selectivity of 88% and 12%, respectively, to dioxolane and dioxane.

In this paper, we explore the potential of rice husk as silica/carbon (SiO2/C) precursor to be employed as a solid acid catalyst. An example of silica/carbon-supported metal oxide composite from rice husk has been published very recently (Al-Amsyar et al., 2017). Rice husk is one of the most abundant agriculture wastes in Malaysia. It consists of lignocellulosic components and also silica (Wang et al., 2011). The controlled-carbonization process transforms lignocellulosic components into graphitic carbon. This step creates a moderate Brønsted acid site which acts as active site while silica provides thermal stability to these composites.

These composites have been used to catalyze the reaction between phenylacetaldehyde (PA), vanillin (VN), and 2-acetonaphthone (AN) with propylene glycol (PG) to produce phenylacetaldehyde propylene glycol acetal (PAPGA), vanillin propylene glycol acetal (VAPGA), and 2-acetonaphthone propylene glycol acetal (ANPGA), as shown in Figure 1. Interestingly, PG could be obtained from the hydrogenolysis of glycerol, a by-product of biodiesel manufacturing (Dasari et al., 2005). Biodiesel production is one of the strategies to reduce the dependency on fossil fuel (Schmidt, 2007). As the biodiesel manufacturing is expected to soar in the near future, so does the glycerin production. Thus, this work demonstrates how agriculture waste could be utilized as a composite precursor to convert PG, a derivative of by-product from biodiesel production to produce the value-added compound in the chemical industry (Pagliaro et al., 2007).

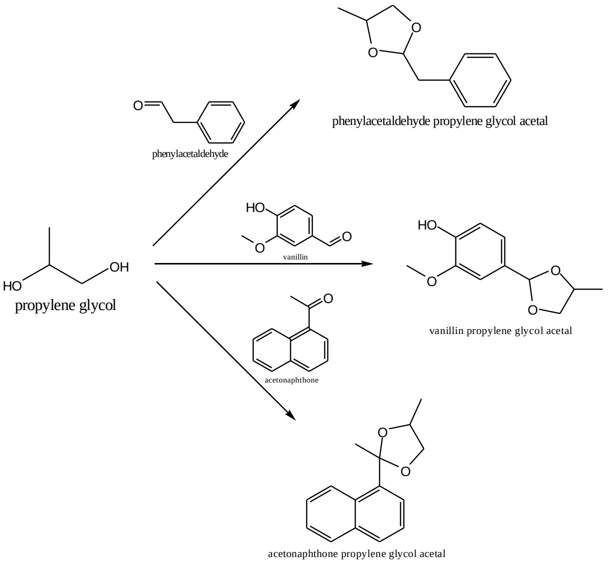

Figure 1: The reaction scheme of the formation of phenylacetaldehyde propylene glycol acetal (PAPGA), vanillin propylene glycol acetal (VAPGA), and 2-acetonaphthone propylene glycol acetal (ANPGA) from propylene glycol (PG).

2. MATERIALS AND METHODS

2.1. Raw materials and synthesis of the catalyst

Rice husk was obtained from rice milling factory in Kelantan. In general, the rice husk was washed thoroughly with tap water to remove dirt and then rinsed with distilled water. It was dried in an oven overnight before it was stirred at room temperature for 24 hours in 1.0 M HNO3 solution. After that, it was filtered and rinsed with distilled water, followed by drying in the oven.

The synthesis of SiO2/C catalysts was performed according to the literature without the sulfonation step (Al-Amsyar, 2018). In general, The RH was placed in a stainless-steel boat and placed inside the muffle furnace. The sample was heated from room temperature (30 °C) to reach the desired carbonization temperature (350, 400, and 450 °C) at a heating rate of 5 °C/minute under air atmosphere. The desired carbonization temperature was maintained for another 1 hour. The sample was ground into fine powder by using mortar and pestle. These composites were labelled as SiO2/C-X where X is the carbonization temperature.

2.2. Characterizations

The measurement of -COOH, and –OH functional groups was carried out by titration of 25 mL of 0.1M sodium bicarbonate (NaHCO3) with hydrochloric acid of 0.01M using methyl orange as indicator. Lastly, the 25 mL of 0.05 M sodium carbonate (Na2CO3) was used to measure the –COOH functional groups and using phenolphthalein as an indicator. For each titration test, 0.2 g of catalyst was added to a basic solution that was prepared before.

TGA was performed by using oxygen as the gas flow at the rate of 25 mL/min. In this study, the range temperature was set from 30 °C to 900 °C, and the heating rate was set at 10 K min-1.

2.3. Catalytic procedure

For catalytic reaction, 50 mg of SiO_2/C catalyst was added with PA/VN/AN (1.0 mmol), PG (2 mmol) and toluene (3 mL) in the pressure tube. The Ace pressure tube was placed in a silicone oil bath with a magnetic stirrer at a designated duration and temperature. After that, the catalyst was separated by centrifugation and analyzed by GC-MS to calculate the percentage conversion and yield/selectivity using the internal standard technique.

3. RESULTS AND DISCUSSION

At first, the SiO2/C composites were tested in the synthesis of PAPGA (Figure 2). SiO2/C-350 catalyst showed the best activity resulting in 70% conversion and 67% selectivity. Similar conversion (64%) was obtained, but significant dropped of yield (38%) was produced when SiO2/C-400 was utilized. This trend was clearly observed in the case of SiO2/C-450 in which 65% conversion and 17% selectivity were achieved.

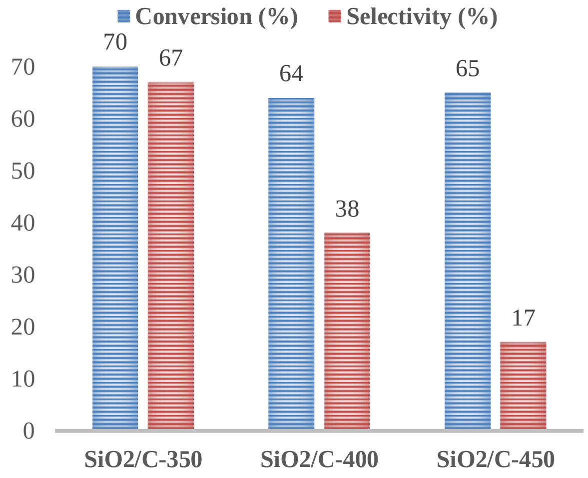

Figure 2: The catalytic reaction of PA and PG to produce PAPGA.

Next, these composites were employed in the synthesis of VAPGA (Figure 3). Again, the SiO2/C-350 showed the best performance to yield 69% conversion and 22% selectivity. The conversion and selectivity were decreased to 53% and 17% respectively when SiO2/C-400 was used. The usage of SiO2/C-450 had resulting almost similar percentage conversion and selectivity (56% and 16%).

The results from FTIR revealed that as the carbonization temperature increase, the higher polycyclic aromatic carbon consisting of phenolic and carboxylic acid group were available relatively (Figure 4). These functional groups act as Brønsted acid sites which is vital to catalyze this reaction.

To corroborate this claim, the amount and type of acid site were quantified by using base titration technique (Table 1). It is clearly seen that SiO_2/C-350 had the highest total acid site (8.900 mmol/g) compared to SiO_2/C-400 (8.825 mmol/g) and SiO_2/C-450 (8.800 mmol/g). Although SiO_2/C-350 had a similar amount of phenolic group with SiO_2/C-400, the density of carboxylic group was higher.

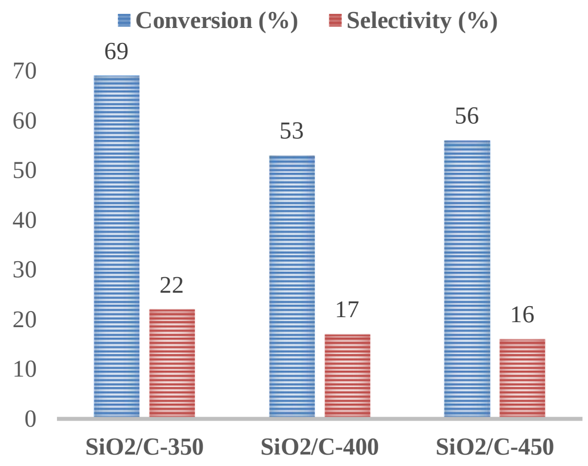

Figure 3: The catalytic reaction of VN and PG to produce VAPGA.

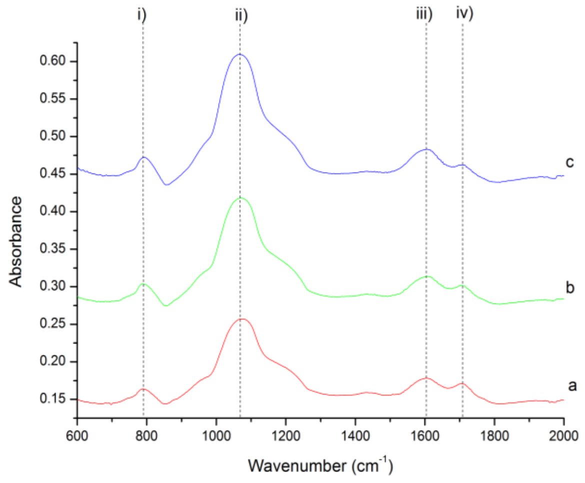

Figure 4: FTIR Spectra for a) SiO_2/C-350, SiO_2/C-400 and SiO_2/C-450. The functional groups are i) Si-O-Si bending, ii) Si-O-Si stretching, iii) C=C aromatic and iv) C=O carbonyl.

The applicability of SiO_2/C composites was further explored in the synthesis ANPGA (Figure 5). In all cases, comparable conversions were obtained (67% to 71%). However, unlike the previous synthesis, SiO_2/C-400 demonstrated the highest selectivity of ANPGA (52%). Lowering (SiO_2/C-350) or increasing (SiO_2/C-450) the carbonization temperature had decreased the selectivity of the desired product (36% and 38%).

Table 1. The amount and type of acid site for the SiO_2/C catalyst at different carbonization temperature.

Catalyst	The acid density of the functional group (mmol/g)		
	Total acid site	COOH	OH
SiO_2/C-350	8.900	4.500	4.400
SiO_2/C-400	8.825	4.425	4.400
SiO_2/C-450	8.800	4.415	4.385

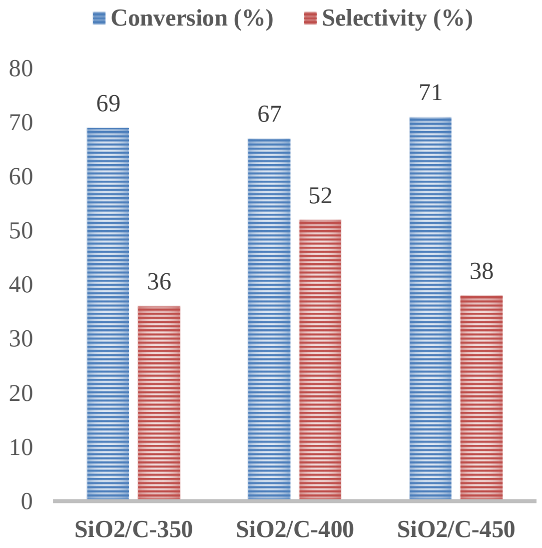

Figure 5: The catalytic reaction of AN and PG to produce ANPGA.

Since these composites consist of hydrophilic (silica) and hydrophobic (carbon), TGA analysis was performed to determine the silica and carbon content. In addition, to evaluate the catalytic performance of each catalyst, the comparative study must be taken into consideration. Thus, TON (mmol of product/mmol of the acid site) values were calculated to make the comparison (Figure 6).

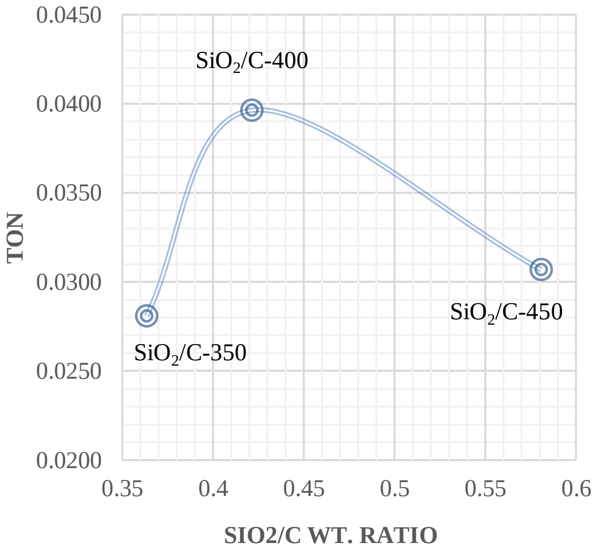

Figure 6: The correlation between silica-to-carbon weight % ratio and TON for each catalyst.

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The SiO_2/C-400 displayed the highest TON in this reaction compared to SiO_2/C-350 (most hydrophobic) and SiO_2/C-450 (most hydrophilic) in this catalysis system. It is might due to balanced hydrophilic/hydrophobic in the catalyst structure that allows better adsorption of substrates and faster desorption of the desired product from the catalyst surface (Karimi and Mirzaei, 2013).

4. CONCLUSION

An effortless and green method to fabricate SiO_2/C catalysts from rice husk has been demonstrated. These composited were able to catalyze the synthesis of PAPGA, VAPGA, and ANPGA from PG in moderate yield. The selection of carbonization temperatures is crucial since it affects the acid density and hydrophobic/hydrophilic nature of the catalysts. Parameter studies are currently being carried out to obtain an optimized yield of the fragrances. Noteworthy, this work shows very promising advantageous in term of economical and environmental as well.

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