PREPARATION OF MESOPOROUS SUGAR CATALYST

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Introduction

Since the discovery of sugar catalyst [1], also known as sulfonated carbon catalyst [2], the progress of carbon-based catalysts development has increased rapidly, especially for biodiesel production. A sugar catalyst is prepared by the incomplete carbonization of sugar, followed by sulfonation. Sugar catalyst has reactivities comparable to sulfuric acid in esterification of oleic acid [3], and are more reactive than sulfated zirconia, Amberlyst-15 and niobic acid in transesterification of waste vegetable oil [4].

Sugar catalyst is non-porous and has a very low surface area (<1 m^2/g). It is anticipated that the reactivity and application of sugar catalyst can be enhanced if its physical properties can be changed to a mesoporous and high surface area. In this paper, we report the preparation of mesoporous sugar catalysts using the silica template method via the confined activation process. The role of the silica templates on the effectiveness of sulfonation process in the synthesis of mesoporous sugar catalysts was investigated. The resulting catalyst characterized by the surface area, porosity, total acidity, and sulfur content was tested for the reactivity on esterification of oleic acid.

Experimental

Mesoporous sugar char was prepared with modification of the confined activation process [8]. D-glucose was used as carbon precursor with the molar ratio of phosphoric acid to tetraethyl orthosilicate (P/Si) as 0.31 pyrolyzed at 673 K under nitrogen for 4 h. The resultant black solids were divided into two: one was washed with 20% HF and deionized water to remove silica and phosphoric components, followed by sulfonation with the loading of 323 mmol fuming sulfuric acid (20 wt% free SO_3) in 1 g washed char (CMK-w) at 423 K under nitrogen for 15 h - denoted as CMK-w-SO_3H; and the half was sulfonated (similar procedure to the preparation of CMK-w-SO_3H), followed by the removal of silica and phosphoric components - denoted as CMK-SO_3H-w. The sugar catalyst was prepared according to the procedure reported by Toda et al. [1], with the sulfonation procedure similar to the preparation of CMK-w-SO_3H and CMK-SO_3H-w. The surface area, pore size, and pore size distribution of the sugar-based catalysts were analyzed based on the nitrogen adsorption isotherm at 77 K (Micromertics ASAP2020). Total acidity was measured using acid-base back titration method. Sulfur content was determined by elemental analysis performed by Canadian Microanalytical Service Ltd. (Delta, British Columbia). Infrared (IR) spectra were recorded using the Varian FTIR spectrometer equipped with ATR (Pike Inst.).

The reactivity of the carbon-based catalysts and sulfuric acid towards esterification of oleic acid by methanol was tested in a batch reactor at 80 ^{o}C under reflux, stirred at 800 rpm. The molar ratio of methanol to oleic acid was 10 to 1, and the amount of catalyst was 7 wt% based on oleic acid. Samples were analyzed on a gas chromatography (Hewlatt Packard 5890 Model II) using a DB-5 column equipped with FID.

Results and discussion

The porosity of the char and the sugar-based catalysts were analyzed using the Barrett-Joyner-Halenda (BJH) method. CMK-w, CMK-w-SO_3H, and CMK-SO_3H-w showed mesoporous characteristics with the average pore size ranging from 4 to 7 nm. The sugar catalyst did not show any porosity, suggesting that the sugar catalyst was a non-porous material. The average pore diameter of CMK-w-SO_3H and CMK-SO_3H-w increased by 1.8 nm and 0.5 nm, respectively, relative to the average pore diameter of CMK-w (Table 1). The pore volume of CMK-w-SO_3H and CMK-SO_3H-w decreased 94% and 33%, respectively, compared with the CMK-w. Higher pore diameter, low pore volume, and low surface area of the CMK-w-SO_3H indicated that the internal wall pores of the char collapsed during sulphonation.

Table 1. Characteristics and catalytic activity of the catalysts.

Sample	N$_2$ adsorption[a]			Total acidity[b]	Sulfur content[c]	Methyl oleate yield[d]
	S.A	P.D.	P.V.	mmol/g	ppm	%
CMK–w	880	4.8	1.24	0	-	-
CMK-w-SO$_3$H	70	6.6	0.07	4.23	4.13	73.0
CMK-SO$_3$H-w	588	5.3	0.83	2.52	1.71	44.0
Sugar Catalyst	<1			3.89	4.17	58.0
H$_2$SO$_4$	-	-	-			72.5

[a] BET surface area (S.A.) in m^2/g; pore diameter (P.D.) in nm; pore volume (P.V.) in cm^3/g.
[b] By acid-base back-titration.
[c] Quantified by elemental analysis.
[d] Experiments were run in duplicate.

As shown in Fig. 1, the FTIR analysis of CMK-w-SO_3H, sugar catalyst and CMK-SO_3H-w showed peaks at 1742 cm^{-1} and 1032 cm^{-1}, which can be assigned to the -SO_3H groups [3, 9]. These peaks were also detected in CMK-SO_3H-w but

weaker on 1032 cm^{-1}. All samples showed a strong band at around ~ 1600 cm^{-1} due to C=C stretching [6]. CMK-SO₃H-w showed a strong band at 1260 cm^{-1} over the CMK-w-SO₃H and sugar catalyst, which can be assigned to Ar-OH stretching [6].
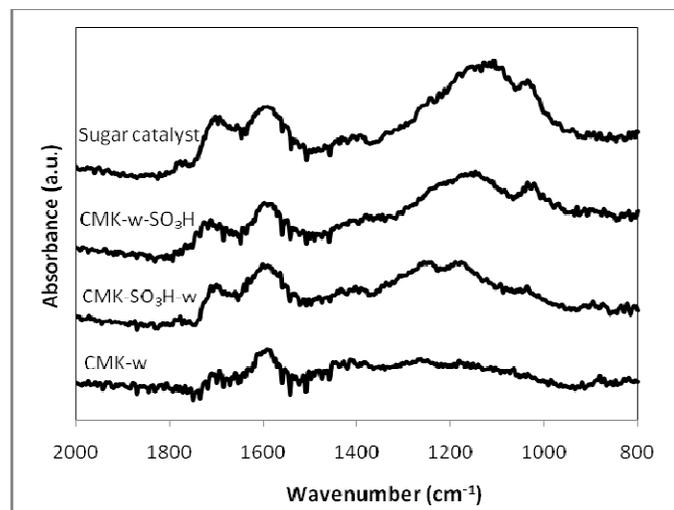
Fig. 1 FT-IR spectra of char and the sugar-based catalysts.

The total acidity and sulfur content of CMK-w-SO₃H were higher than CMK-SO₃H-w despite the higher surface area of CMK-SO₃H-w. In addition, sugar catalyst showed a high total acidity and sulfur content while having very low surface area. The surface area and total acidity of sugar catalyst in this study were comparable to those reported by Mo et al. [2], and Peng et al. [7]. In comparison, though CMK-w-SO₃H lost its internal porosity, it yielded a high total acidity and sulfur content suggesting that functionalization by the -SO₃H groups occurred on the outer surface of the char. This was further confirmed by a large total acidity and sulfur content of the sugar catalyst even though it was a non-porous material.

CMK-SO₃H-w showed the lowest yield despite of having the largest surface area. This observation can be explained from the total acidity and sulfur content of CMK-SO₃H-w. The total acidity of CMK-w-SO₃H and sugar catalyst mainly comes from the –SO₃H groups, whereas the total acidity of CMK-SO₃H-w comes from –OH, -COOH, and -SO₃H groups. CMK-SO₃H-w has a lower reactivity because –OH and –COOH groups do not catalyze esterification reaction [3, 9]. Peng et al. [7] suggested that pore size played more significant role than the density of SO₃H in catalyst reactivity. Our results suggest that catalytic activity for the esterification of oleic acid is independent of the specific surface area and dependent on total acidity. This observation was also reported by Kitano et al. [5] for the esterification of acetic acid by sulfonated porous carbon catalyst.

The reactivity of a catalyst depends on the accessibility of the reactants to the active group on the catalyst surface. We speculate that -SO₃H groups in our catalysts grafted on the outer surface of the catalyst, contrary to the observation of Mo et al. [2] where –SO₃H groups are in the bulk of the catalysts.

Conclusions

The preparation of mesoporous sugar catalysts has been investigated. The roles of silica templates in the preparation of mesoporous sugar catalysts were evaluated based on the surface area, pore size, pore volume, total acidity, sulfur content, and esterification of oleic acid. The silica templates method via the confined activation process technique produced mesoporous sugar char at low pyrolysis temperature (673 K). Sulfonation before removing the silica templates retained 67% of the surface area, increased by 0.5 nm in average pore diameter, and decreased 33% in pore volume relative to the sugar char. Whereas, sulfonation after removing the silica templates lost 92% of the surface area, increased by 1.8 nm in average pore diameter, and decreased 94% in pore volume relative to the sugar char. Silica templates provided support to the internal porosity of the char, but prevented sulfuric acid from effectively reaching the internal surface during the sulfonation process. The esterification of oleic acid was dependent on total acidity but independent of surface area. The amount of accessible –SO₃H groups was the crucial factor for a reactive catalysts.

References
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