Synthesis of Superacid Catalysts for Biodiesel Production

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Introduction

Biodiesel, an alternative energy source produced from renewable sources by transesterification, is becoming more popular due to the environmental benefits and its potential as a substitute for petroleum-based diesel fuels. Since catalysis plays an important role in biodiesel production via transesterification reaction, there are many different types of catalysts employed: NaOH, KOH and H_2SO_4. However, the use of these catalysts creates some undesirable consequences which cause problems during the production and separation stages.[1-3]

In the last decade, numerous heterogeneous solid acid catalysts have been developed for this reaction. Sulfated zirconia has attracted the attention due to its extremely high acidity.[4] However, the non-uniformity of pore size and relatively low surface area of sulfated zirconia limits its applications for catalyzing the bulky molecules such as oil molecule.[5] Using mesoporous material as a catalyst support for sulfated zirconia can tremendously expand the catalytic property and capability of the catalyst since the uniform pore opening and high surface area can assist diffusion of bulky molecules and reduce diffusion hindrance.[6]

Therefore, the objective of this study is to develop new solid superacid acid catalysts with high catalytic performance for transesterification of vegetable oil with methanol.

Materials and Methods

The solid acid catalysts of sulfated zirconium incorporated SBA-15 have been synthesized using different synthesis methods: post synthesis and direct synthesis. For the post synthesis catalyst, SBA-15, which was prepared according to literature [7], was dispersed into a solution containing n-hexane and zirconium (IV) n-propoxide, followed by sulfation with H_2SO_4 and finally by calcination. For the direct-synthesis catalyst, $ZrCl_4$ was directly added to the solution mixture during the synthesis of SBA-15. All catalysts were characterized by XRD, ICP, TEM, N_2 adsorption-desorption and ion-exchange titration. To study the catalytic activity, transesterification was performed in a reflux system with samples periodically collected for chemical analysis. Upon completion of each reaction, the product was mixed with n-hexane and centrifuged. The upper layer was collected and analysed by Agilent 6890 GC.

Results and Discussion

Sulfated Zr incorporated SBA-15 was successfully synthesized using post synthesis and direct synthesis methods. It is clear that both synthesis methods can preserve the ordered mesoporous structure of the catalysts. However, Table 1 shows that the post-synthesis catalysts provide higher acidity due to the high dispersion of Zr on the surface of SBA-15, resulting in the tremendous interaction between Zr and sulfate groups.

Table 1. Textural properties and acidity of catalysts

Sample ID	Si/Zr molar ratio	BET surface area m^2g^{-1}	Pore Volume cm^3g^{-1}	Acidity by titration µmol/g catalyst
SBA-15	∞	910.5	1.39	-
SSBA (sulfated SBA)	∞	645.2	1.14	40.2
SZS-P (sulfated Zr on SBA-15 by post synthesis)	6.7	587.4	0.80	572.3
SZS-D (sulfated Zr on SBA-15 by direct synthesis)	6.7	599.7	1.11	325.4
SZ (sulfated zirconia)	0	79	0.12	278.4

Figure 1 shows that both synthesized catalysts (SZS-P and SZS-D) perform good catalytic activity as compared with the conventional sulfated zirconia (SZ) for the same amount of catalyst used in the reaction. However, since the amount of Zr on SZSP and SZSD is much less than SZ, the sulfated Zr catalytic site of either SZS-P or SZS-P is much more active than those of SZ, showing that the dispersion of sulfated of Zr catalytic site on the on the large surface-area of SBA-15 is important to enhance the activity of the sulfated Zr catalytic site.

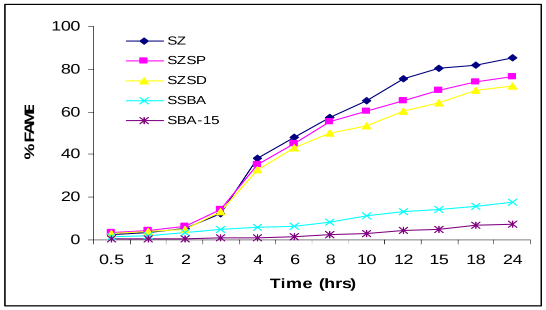

Figure 1. Conversion of palm oil on different catalysts: SZ, SZSP, SZSD, SSBA (sulfated SBA-15) and unsulfated SBA-15.

Significance

Sulfated Zr-incorporated SBA-15 has sulfated Zr catalytic site which is much more active than those found on the conventional sulfated Zr, showing that sulfated Zr-incorporated SBA-15 has the potential to be developed as commercial catalysts for biodiesel production.

References

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