Esterification and Transesterification Using Sulfonated Carbon Catalysts

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Introduction

The synthesis of biodiesel from vegetable oils and animal fats by transesterification of triglycerides (TGs) and esterification of free fat acids (FFAs) has drawn intense interest due to energy and environmental concerns.[1] Many of the heterogeneous acid catalysts studied to date for trans/esterification, such as zeolites, MCM-41, sulfated zirconia, Amberlyst-15 and Nafion present particular problems including low acid strength, microporosity and active site leaching that make them unsuitable for this type of reaction.[2] Recently, sulfonated carbons derived from carbonization of simple sugars were reported to show interesting activities in the esterification of fatty acids.[3] These catalysts can be prepared using a two-step procedure: first, natural products such as sugar, starch or cellulose are pyrolysized in N_2, resulting in a 'soft' material composed of polycyclic aromatic hydrocarbons; second, the hydrocarbon precursor is sulfonated to generate a stable solid with high density of sulfonic sites, which leads to their high catalytic performance in liquid-phase acid-catalyzed reactions.

Though the preparation, physical properties and catalytic activity of the sulfonated carbon catalysts for esterification have been reported, no studies on activity for transesterification and gas-phase esterification are available. Deactivation studies on these materials are also limited. Moreover, due to the low surface area ($< 2\ m^2/g$) of the carbon catalysts, the active sites are likely crowded and some of them become inactive for reactions involving large reactants, causing relatively lower performance. Utilization of a support with suitable porosity, acidity and hydrophobility should improve the performance of these carbon catalysts. The present work provides a comprehensive evaluation of the catalytic nature of these novel carbon catalysts and reports the preparation and characterization of supported carbon catalysts.

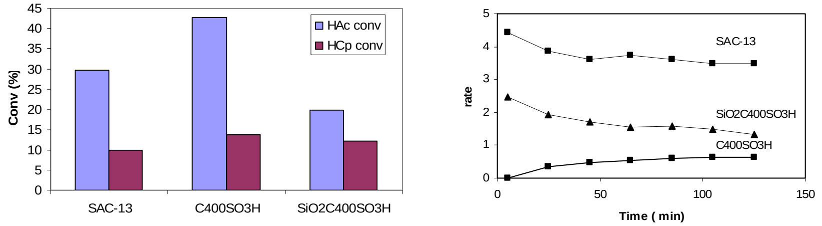
Materials and Methods

Carbon catalysts were prepared according to the procedure described by Toda [3]. Supported carbon catalysts were prepared by incorporating a carbon precursor, usually glucose, into a porous supporter by incipient wetness followed by pyrolysis and sulfonation. BET, XRD, FTIR and TGA were applied to characterize the as-prepared catalysts.

The catalytic activities were examined for the esterification of model compounds like acetic acid with methanol both in the liquid and gas phase. In addition, catalyst activity was studied for the transesterification of model compounds for triglycerides, such as triacetin and tricaprylin, as well as soybean oil with methanol in the liquid phase. Nafion$^{@}$SAC-13 (Nafion resin supported on a porous silica matrix) was employed for activity comparison purposes.

Results and Discussion

Comparing to Nafion@SAC-13, the sulfonated carbon catalysts exhibited higher bulk activity but lower initial TOF. Swelling was found to be critical for the activity of sulfonated carbon catalysts and may be affected by the polarity of reactants. For instance, the presence of an induction period and poor performance of the carbon catalysts in the gas phase esterification of acetic acid could be attributed to poor swelling. On the other hand, deactivation studies indicated that the activity of the carbon catalysts decreased in the initial cycles and then remained stable. Solvent washing experiments, NMR spectra, and elemental analysis suggested that the observed catalyst deactivation was caused by the leaching of polycyclic aromatic hydrocarbon containing SO_3H groups. The carbon catalysts supported on silica exhibited higher initial TOF but quicker deactivation.



(a) (b)

Figure 1. (a) Reagent conversions for $C400SO_3H$ and SAC-13 at 60 °C in the liquid phase (a) for esterification of acetic acid and caprylic acid ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M; catalyst loading = 0.025 g/ml; 1 h) (b) Conversion rate of acetic acid at 100 °C in gas phase for esterification of acetic acid with methanol catalyzed by $C400SO_3H$ and SAC-13 (total flow rate of 120 cc/min, P_{HAc}= 0.0085 atm, P_{MeOH}= 0.0085 atm).

Significance

Supported sulfonated carbon catalyst can be easily prepared using common, inexpensive precursors and presents all the characteristics required for a solid acid catalyst to be highly efficient in biodiesel synthesis: strong acid strength, mesoporosity, and surface hydrophobicity. This type of material offers possibilities for making biodiesel production more efficient, economic and clean.

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References

1. (a) Huber, G. W., S. Iborra, S., and Corma, A. *Chem. Rev. 106*, 4044(2006); (b) Lotero, E., Goodwin, J. G. Jr., Bruce, D. A., Suwannakarn, K., Liu, Y., and D. E. Lopez, *Catalysis*, 19, 41(2006).
2. (a) Corma, A. *Chem. Rev.* 97, 2373(1997); (b) Perez-Pariente, J., Diaz, I., Mohino, F., and Sastre, E. *Appl. Catal. A-Gen*. 254, 173(2003); (c) Yadav, G. D. and Murkute, A. D. *J. Catal.* 224, 218(200); (d) Bozek-Winkler, E.and Gmehling, J. *Ind. Eng. Chem. Res.* 45, 6648(2006).
3. (a)Toda, M., Takagaki, A., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K.and Hara, M. *Nature* 438, 178(2005); (b) Takagaki, A., Toda, M., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K. and M. Hara, *Catal. Today* 116, 157(2006).