

Bifunctional Co₃O₄/ZSM-5 Mesoporous Catalysts for Biodiesel Production via Esterification of Unsaturated Omega-9 Oleic Acid

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1. Textural properties of parent ZSM-5-A and ZSM-5-B

The N₂ adsorption-desorption isotherms of the bared ZSM-5-A and ZSM-5-B were measured for analyzing their microporosity. The loops of N₂ adsorption-desorption isotherms are presented as Figure S1 and Figure S2. These loops belong to type IV according to the clasification of the International Union of Pure and Applied Chemistry. Both ZSM-5-A and ZSM-5-B show typical mesoporous characters. The sharp step in the low p/p_0 region ($p/p_0 = 0.01-0.1$) was not observed, indicting that these two mesoporous ZSM-5 samples contain insignificant microporosity. The mean pore diameter is 0.87 nm for ZSM-5-A and 0.76 nm for ZSM-5-B, respectively. The micropore volume is lower than 0.055 cm³/g, which is much smaller in comparison with the values of total pore volume (0.76 cm³/g for ZSM-5-A and 0.83 cm³/g for ZSM-5-B).

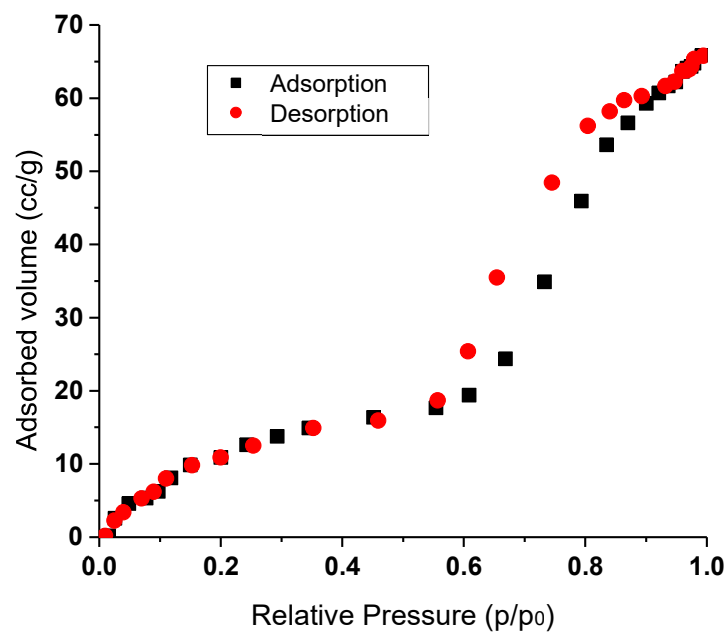


Figure S1. Loop of N₂ adsorption-desorption isotherms of ZSM-5-A zeolite

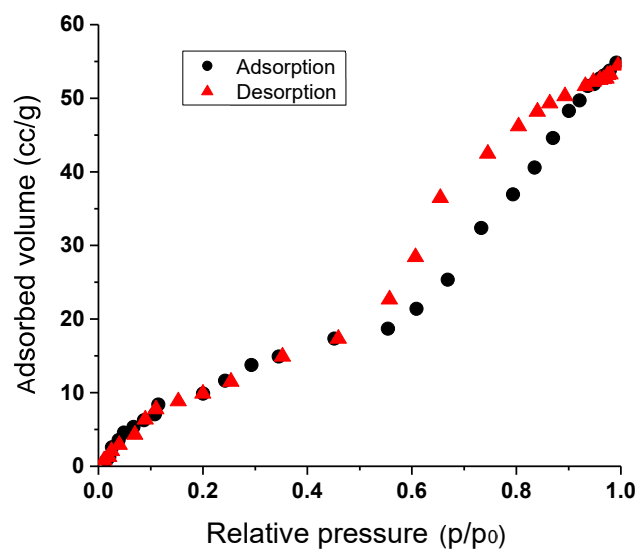


Figure S2. Loop of N₂ adsorption-desorption isotherms of ZSM-5-B zeolite.

2. Resuability of 10Co/ZSM-5-B catalyst

The reusability of the most active 10Co/ZSM-5-B catalyst was performed by 6 cycles under the optimal reaction conditions (methanol/oleic acid molar ratio of 30:1, catalyst concentration 2 wt%; reaction temperature of 160 °C, and reaction time of 3h). After each 3 h of reaction, the catalyst sample was filtered and washed, it was then calcined at 550 °C for 3 h in air before reuse for catalytic evaluation. The recycled results are shown in Figure S3 in the Supplementary Materials.

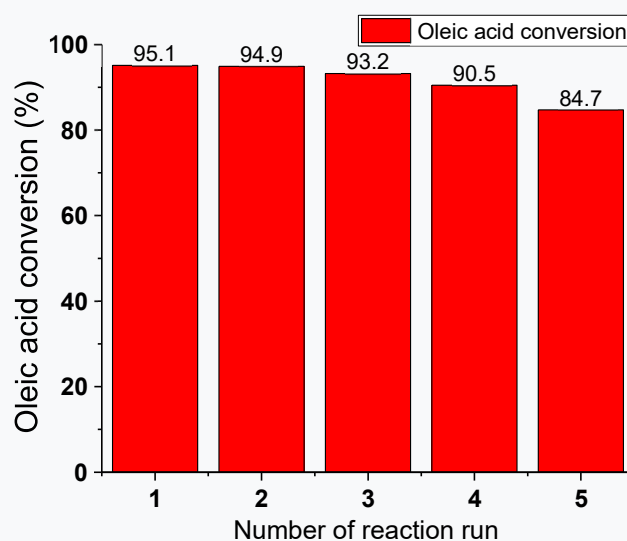


Figure S3. Reusability test of 10Co/ZSM-5-B catalyst under the optimal condition.

For the fresh catalyst, approximately 95% oil conversion was obtained. However, oleic acid conversion gradually decreased after the third reaction run. In the fifth run, oleic acid conversion dropped to 84.7%. It was found that catalyst mass was partly lost during the filtration and washing operations. Therefore, we believed that the catalyst activity deterioration principally resulted from the loss of catalyst mass during the operation procedure.

However, after several reaction runs, the possibility of the active sites blocking and surface acidity loss cannot be ruled out, they may be the other reasons of the catalyst deactivation. In the future, catalyst deactivation investigation will be performed by focusing the influence of the changes in textural properties and surface acidity on the catalytic activity.