Metallic Fe Nanoparticles Encapsulated into Ordered Mesoporous SiO_2 for Hydrodeoxygenation of Oleic Acid

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Abstract:

Metallic iron nanoparticles encapsulated in ordered mesoporous silica MCM-41 (Fe^0/MCM-41) and SBA-15 (Fe^0/SBA-15) were synthesized with different percentages of Fe^0 loadings and used as catalysts for hydrotreating of oleic acid. The most composition in the liquid product was C-18 alkane. The formation of intermediates suggests that the reaction proceeded initially by fast hydrogenation of C=C, followed by reduction of the COOH group to alcohol through hydrodeoxygenation process. The effect of pore size of silica and the stability of Fe^0 nanoparticles played a vital role in the product yield. The degree of oxidation of Fe in the catalyst determines the ratio of hydrodeoxygenation to decarbonylation. The highest yield of C-18 alkane was obtained at the 85% for Fe^0/SBA-15 catalyst with 5% Fe^0 loading, at reaction time 6 h, 300ºC and 30 bar of H_2 pressure.

Keywords: Hydrodeoxygenation, Oleic acid, Fe^0 nanoparticle encapsulated on silica.

1. Introduction

A major concern with limited fossil fuel resources and with global warming have prompted a worldwide search for alternative and sustainable energy sources. Green diesel produced from vegetable oil has emerged as an important biofuel to replace petroleum diesel. Green diesel production is commonly prepared under high pressure of hydrogen gas which known as hydrodeoxygenation reaction. The reaction requires a bifunctional solid catalyst for hydrogenation of double bonds of the side chains and the removal of oxygen during catalytic hydrotreating. The has been known that hydrotreating reaction using conventional transition metal sulfide such Ni Co and Mo sulfide and noble metal catalysts such as Pt and Pd supported on metal oxides. Noble metal catalysts are costlier than transition metal sulfide while slow desulfurization reduces the activity of metal sulfide and contaminate the fuels. There is an effort in establishing more economical sulfur-free catalysts to upgrade renewable oils. The success of using reduced catalysts on acidic metal oxide support such as $NiMo/Al_2O_3$, $Co\text{-}Mo/Al_2O_3$ stimulates the exploration of an inexpensive transition metal as catalysts. Iron is one of the most interesting candidates due to its low reduction properties and high national abundance. There is interesting reported on using iron nanoparticles supported on mesoporous silica nanoparticles for the hydrotreating process. This work, Fe^0 nanoparticles encapsulated into MCM-41, and SBA-15 ordered mesoporous silica was tested as hydrodeoxygenation catalyst for green diesel production.

2. Experimental

Synthesis of Metallic Fe Nanoparticles Encapsulated in Mesoporous Silica ($Fe^0/mSiO_2$)

MCM-41 and SBA-15 were synthesized following the literature procedures [1,2]. Fe^0-encapsulated in mesoporous SiO_2 nanoparticles was prepared by wet impregnation using $NaBH_4$ as reducing agent. In a typical experiment, the prepared mesoporous silica was dispersed in 10 ml of distilled water. Then 10 mL of 0.01 M $FeCl_3$ aqueous solution was slowly added to the colloidal suspension. The suspension was heated at 60ºC to evaporate water until nearly dry. The obtained powder was dispersed in 25.0 ml of water. Then, 20 mL of 4.0 M $NaBH_4$ aqueous solution was added dropwise under N_2 atmosphere and stirred at room temperature for 4 h. The obtained $Fe^0/mSiO_2$ nanoparticles were separated by centrifugation, and washed several times with distilled water and ethanol. The obtained samples were characterization by TEM, BET, XRD and XPS techniques.

Catalytic Testing

The catalytic reactions were performed in 50 mL batch reactor (Parr Instrument). In a typical experiment, the prepared catalysts and 30 mL of 5mM oleic acid solution in dodecane were added to the reactor. Then, the reactor was purged with hydrogen for 3 times and was pressurized with H2 at room temperature. The reaction was heated at different reaction temperature for different reaction time under stirring. The reaction was allowed to cool to room temperature, and the catalyst was separated. The reaction products were analyzed by gas chromatography. The percentage of hydrodeoxygenation and decarbonylation/decarboxylation (DCO/DCO2) reactions were calculated based on the total mole of n-alkanes with an odd number (HDO) or even number (DCO/DCO2) of carbon atoms in the product. The effect of reaction parameters on the conversion was investigated; temperature 250-300ºC, pressure 30-35 bar, reaction time 1-6 h and 1-10 mole % of the catalyst.

3. Results and discussion

Synthesis and characterization of Metallic Fe Nanoparticles Encapsulated in Mesoporous Silica ($Fe^0/mSiO_2$)

Metallic Fe^0 nanoparticles encapsulated in MCM-41 (Fe^0/MCM-41) and SBA-15 (Fe^0/SBA-15) was successfully synthesized with different % of Fe loadings (1, 3, 5 and 10%). MCM-41 with spherical and ordered porous structure were produced with the average particle size of MCM-41 68±8 nm. The surface areas and pore diameter analysis from BET were 1109 m^2/g^2 and 3.5 nm respectively. SBA-15 showed lower surface area (895 m^2/g^2) and large pore size (7.4 nm) than MCM-41. For MCM-41, there is more than 80% of pore volume decrease by 3% Fe^0/MCM-41. Formation of Fe nanoparticles led to decrease in the surface area and pore volume of the support. At higher Fe loading, TEM images and X-Ray diffraction pattern showed the partial destruction of silica crystal into an amorphous phase. Similar results were obtained found with Fe^0/SBA-15 sample. XPS analysis, The XPS analysis revealed the presence of some hydroxide/oxide species on the surface while no oxide peaks in the XRD pattern.

Catalytic hydrotreating of oleic acid with $Fe^0/mSiO_2$

Fe^0/MCM-41 and Fe^0/SBA-15 are effective catalysts for hydrotreating of oleic acid to hydrocarbon. At high temperature and H_2 pressure, no oleic acid was detected after 1 h, steric acid, n-octadecanal, and n-octadecanol were found as intermediates. No steric acid was observed in 2h. The yield of n-octadecane (C-18) increased with increasing of reaction time. At longer reaction time, there is an increase in a ratio of n-heptane. This indicates that the reaction proceeded initially by fast hydrogenation of C=C, followed by reduction of the COOH group to alcohol through hydrodeoxygenation which C-18 is the major reaction product. At low temperature, alkene was observed. The highest yield of C-18 alkane was obtained at the 85% for Fe^0/SBA-15 catalyst with 5% Fe0 loading, at reaction time 6 h, 300ºC and 30 bar of H_2 pressure.

4. Conclusions

$Fe_0/mSiO_2$ nanoparticles are effective catalysts for converting oleic acid to green diesel. Fe^0 nanoparticles encapsulated in SBA-15 showed much higher activity and selectivity in hydrodeoxygenation of oleic acid than encapsulated in MCM-41 silica. The effect of pore size of silica and the Stability of Fe0 nanoparticles play played an important role in the product yield. The degree of oxidation of Fe in the catalyst determine the ratio of hydrodeoxygenation to decarbonylation.

References

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