Synthesis and Characterization of Organosulfonic Acid Functionalized Mesoporous Silica as Catalyst Support for the Deoxygenation of Vegetable Oil to Hydorcarbon Fuels

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Introduction

The shortfall and current high prices of petroleum based fuel has sparked growing interest in research on alternative fuel production from sustainable sources. In this respect, conversion of vegetable oil into more compatible form of fuel hold the potential of reducing the dependency in the use of petroleum based fuel. However, this process has been limited due to high raw materials and production costs. Then, a careful selection of process conditions is fundamental to make the process economically viable.

The discovery of large pores sizes and large surface areas mesoporous materials (1) has sparked interest among researchers to the potential applications of these materials as catalysts . In addition, the ability to functionalize these materials by the introduction of different active groups in to the mesoporous framework allows them to be excellent as alternative catalysts and support.

This paper reports on the preparation and of metal supported organosulfonic acid functionalized mesoporous silica s catalyst for the deoxygenation of vegetable oil into liquid hydrocarbon fuels.

Experimental

The mesoporous materials were synthesized using a sol gel technique. 4 gram of Pluronic acid 123 was dissolved while stirring in 120 ml of 2M HCl at room temperature. The molar ratio of MPTMS/[MPTMS+TEOS] of 5, 10, 15 and 20% were used. A sample with higher acid concentration was also synthesized. The original mesoporous silica synthesized with tri-block copolymers P123 was called SBA-15, then materials functionalized were abbreviated as MS meaning MPTMS-SBA-15. Then, Pt, Pd and Ni metals were loaded in to the functionalized mesoporous support by wet impregnation. Another batch of metals were introduced by co-precipitation.

The catalyst compositions were characterized by ICP, BET, XRD, SEM, TEM. The catalytic deoxygenation experiments were performed in 300 ml semi-batch reactor coupled to condenser and heating jacket with liquid phase volume of 100m as described elsewhere (2).

Results and Discussion

The XRD patterns of functionalized mesoporous support (Figure 1A) show that sample with MPTMS/[MPTMS+TEOS] molar ratio below 0.10 have a typical pattern of hexagoanal SBa-15. However, a gradual decrease of the $d_{spacing}$ was observed at high MPTMS concentrations. Isotherms of adsorption (Figure 1B) shows a slightly derecase in hysteresis loop as higher MPTMS concentrations. It was also found that introducing metals by either wet impregnation or co-precipitation will impact in the structure and adsorption properties of the mesoporous materials. Surface area and pore size still are in the range of mesoporisty as shown in Table 1.

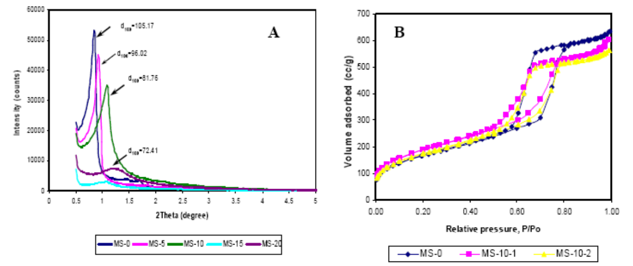

Figure 1. (**A**) X-ray diffraction patterns of functionalized mesoporous silica in various MPTMS/[MPTMS+TEOS] molar ratio; (**B**). N_2 adsorption-desorption isotherm of functionalized mesoporous silica in higher concentration of H_2O_2.

Table 1. Textural properties of the functionalized mesoporous silica

Sample	*Ratio molar MPTMS/[MPTMS+TEOS]*	*[H_2O_2] (mol)*	$d_{spacing}$ (A)	S_{BET} m^2/g)	Dp_{BJH} (nm)	Vp_{BJH} (cc/g)
MS-0*	-	-	105.17	687.50	11.2	0.80
MS-10-1	0.10	0.0369	98.16	669.50	7.7	0.78
MS-10-2	0.10	0.0738	100.38	620.12	8.9	0.73
MS-20-1	0.20	0.0123	72.41	635.03	3.1	0.37
MS-20-1	0.20	0.0738	84.94	597.54	4.5	0.60

*sample synthesized without add MPTMS and H_2O_2 (unfunctionalised mesoporous silica)

From the catalytic tests it was found that acidity and the way the metal is introduced plays an important role in the breaking of the molecule of vegetable oil into hydrocarbon entities. Controlling acidity give the possibility to break into gasoline or diesel range hydrocarbons. The interaction of Pd or Pt with Ni gives the shaping of the hydrocarbon molecule.

Significance

Metal incorporated organosulfonic acid functionalized mesoporous silica with high surface area and pore size and controlled acidity were synthesized. These materials has the potential to deoxygenated large molecules of vegetable oil into shorter hydrocarbon of gasoline or diesel range composition.

References

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