Catalytic upgrading of lignin model compound into transportation fuel by using Ti-MCM-41 mesoporous supported Cu-Ni catalyst

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Abstract:

The present study focus on the synthesis of MCM-41 and Ti-MCM supported bimetallic Cu-Ni catalysts for the hydrodeoxygenation of guaiacol into the transportation fuels. Catalysts characterization indicated that the Ti species are well-dispersed within the MCM-41 framework by a tetrahedral coordination. In additional, incorporation of Ti into the MCM-41 framework generates large amounts of acidic sites as well as enhances the dispersion of CuO and NiO species on the surface of Ti-MCM-41 support. The catalytic study revealed that the CuNi/Ti-MCM-41 catalyst exhibits a higher guaiacol conversion (90.49%) and superior selectivity to cyclohexane (50.09%) as compared to CuNi/MCM-41 catalyst.

Keywords: Hydrodeoxygenation, Guaiacol, cyclohexane.

1. Introduction (11-point boldface)

An efficient hydrodeoxygenation (HDO) process require appropriate catalyst systems to remove the chemically bonded oxygen from lignin-derived oil. However, the direct application of catalysts in the HDO of lignin is associated with many challenges due to the complex nature of its oxygenated aromatic components, such as guaiacol, anisole, methyl anisole, furan, benzofuran, dibenzofuran, phenols, and catechol [1]. It has been reported that heterogeneous catalysts composed of metal functions for the hydrogenation of aromatic ring and acidic support for deoxygenation are the most suitable catalysts for HDO reactions. Various non-noble transition metals, such as Co, Ni, Fe, Cu, and Ni have been tested, and it was found that Ni-Cu catalysts exhibit better activity in hydrodeoxygenation reaction [2]. In addition, mesoporous materials have suitable pore dimensions which facilitate the diffusion of the substrates to the active site [3]. Thus, the present study investigates the synthesis, characterization and the catalytic application of bimetallic Cu-Ni catalyst supported on Ti-MCM-41 for the hydrodeoxygenation of guaiacol. For comparison, the Cu-Ni catalyst supported on pure MCM-41 was also synthesized and compared its catalytic efficiency. The catalytic experiments were performed in an autoclave reactor at 260 °C, 10 MPa and 6 h.

2. Experimental (or Theoretical)

A co-impregnation method was used to prepare of Cu-Ni (3:1) supported on Ti-MCM-41 and MCM-41. In this procedure, the required quantities of $Ni(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}{}_3H_2O$ were dissolved in deionized water in a 250 ml beaker. In a separate beaker, the Ti-MCM-41 support was dispersed in 100 ml of deionized water and sonicated for 30 min to ensure efficient dispersion of the support. The support solution was impregnated with the metal precursor solution, stirred at 250 rpm and aged at 70 °C for 6 h to obtain a viscous liquid. The obtained sample was oven-dried at 90 °C for 18 h and subsequently calcined in air at 600 °C for 4 h as recommended by TGA measurements.

3. Results and discussion

Characterization results reveal that the Ti-MCM-41 support contains tetrahedral coordination of incorporated titanium species into the structural frame work of MCM-41, resulting in the generation of strong acid sites as evidence by NH_3-TPD studies. The Ti-MCM-41 displays an appreciable surface area of 705m^2/g although smaller than MCM-41 (983m^2/g) due to incorporated titanium species but larger average pore size than MCM-41. The incorporated titanium species were also found to enhance the dispersion of CuO-NiO on Ti-MCM-41. The investigated catalytic activity studies reveal that the CuNi/Ti-MCM-41 catalyst shows a high catalytic performance in guaiacol conversion and cyclohexane selectivity compared with that of CuNi/MCM-41 catalyst. The higher activity of CuNi/ Ti-MCM-41 catalyst was due to the cooperative function of larger surface area, medium size mesopores, hexagonal pore geometry, abundant acidic sites and superior redox properties. The catalytic experiments revealed that the CuNi/Ti-MCM-41 catalyst exhibits a higher guaiacol conversion (~90.49%) and superior selectivity to cyclohexane (~50.09%) than the CuNi/MCM-41 catalyst which exhibits only ~10.57% cyclohexane selectivity with a guaiacol conversion of ~37.03% (Fig. 1). The guaiacol conversion and cyclohexane selectivity were found to increase with the increase of reaction pressure from 40 to 100 bar for CuNi/Ti-MCM-41 catalyst. It has been demonstrated that the HDO of guaiacol proceeds via demethoxylation (CAR-OCH_3 cleavage) over the CuNi/Ti-MCM-41 catalyst and both demethylation (CARO-CH_3 cleavage) and demethoxylation (CAR-OCH_3 cleavage) pathways are possible over the CuNi/MCM-41 catalyst in HDO of guaiacol.

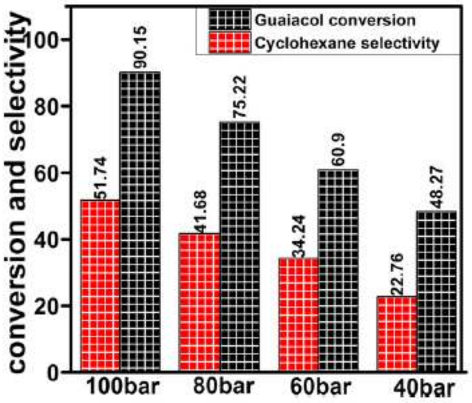

Fig. 1. Guaiacol conversion and cyclohexane selectivity at various pressure, 260 °C and 6h over NiCu/Ti-MCM-41.

4. Conclusions

The higher activity of CuNi/Ti-MCM-41 catalyst was due to the cooperative function of larger surface area, medium size mesopores, hexagonal pore geometry, abundant acidic sites and superior redox properties. Therefore, Ti-MCM-41 is an effective catalyst support for the hydrodeoxygenation of oxygenated compounds to saturated hydrocarbons. It can also be concluded that, higher hydrogen pressure greatly improves the guaiacol conversion and selectivity of the oxygenate compounds to hydrocarbon over Ti-MCM-41 supported CuNi catalyst. Based on the product distribution, it was proposed that HDO of guaiacol proceeds by hydrogenolysis pathway through demethoxylation via CAR-OCH_3 cleavage over CuNi/Ti-MCM-41.

References

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