Hydrodeoxygenation of Ni-W bimetallic catalysts for the conversion of jatropha oil into high-quality fuel

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Abstract: The production of fuel from the hydrodeoxygenation of vegetable oils has been studied due to the decline of fossil fuels and increase of environmental problems. Much work had focused on the conversion of vegetable oil into hydrocarbons by Ni-W catalysts. However, the intrinsic synergies effect of Ni and W have not been revealed. Here we synthesized a series of Ni-W catalysts, the jet fuel yield reached 64wt.% over 10%Ni-10%W/MCM-41 catalyst. XRD, XPS and TEM results suggested that the introduction of W would affect the particle size of $Ni_{17}W_3$ active phase, accordingly, thus plays an important role in jet fuel yield.
Keywords: Hydrodeoxygenation, Heterogeneous catalysis, Bio-oil.

1. Introduction

The exhaustion of traditional fossil fuels and the deterioration of ecological environment have arouse the development of biomass conversion technology to obtain alternative products for petroleum-based fuels. Typical feedstocks for renewable fuels were vegetable oils, especially, non-edible ones such as jatropha, algae oil or rapeseed etc. Unfortunately, the application of unmodified vegetable oils as the fuels is limited due to rich oxygenated molecules[1]. Richard H. Moore[1] reported the use of biofuel derived from the catalytic conversion of camelina oil to aircraft engines, which reduced particle number and mass emissions[2].

Catalytic hydrodeoxygenation has been emerged to upgrade vegetable oils using heterogeneous catalysts. Recently, Ni-W catalysts have been considered as prospective materials employed in deoxygenation process. However, the related studies concentrated mainly on the deoxygenation pathways and the interaction between Ni and W was still not clear[3,4]. In this work, high jet fuel yield (64wt.%) was obtained on 10%Ni-10%W/MCM-41 catalyst at 360℃ and 3MPa without solvents. We disclosed that 10%Ni-10%W/MCM-41 catalyst showed a good HDO performance originated from the transforming of electrons from Ni to W.

2. Experimental

2.1 Catalyst preparation and activity test

All catalysts were prepared by conventional co-impregnation method. First, MCM-41 was impregnated with proper amount of a mixture solution of ammonia metatungstate (AMT) and nickle nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$). Then impregnated supports were dried, calcined and reduced. The activities of the catalysts were evaluated in a fixed-bed reactor at 360 ℃ and overall pressure of 3 MPa.

2.2 Catalyst characterization and product analysis

Powder X-ray diffraction (XRD) was performed on a LabX XRD-6100. XPS spectra were taken by an AXIS Ultra DLD (KRATOS) spectrometer. Transmission electron microscopy (TEM) image was obtained on an FEI Tecnai G2 20 TWIN instrument. The liquid products were analyzed using gas chromatography-mass spectrometry(GC－MS, Agilent 5973) with a capillary column.

3. Results and discussion

3.1 Activity of the catalysts

The activity results suggested that the jatropha oil could be completely converted into jet fuel on all catalysts. The liquid yields on 10%Ni/MCM-41 and 10%W/MCM-41 catalysts were 19wt.% and 12wt.%

respectively, while the highest yield of 64wt.% was obtained on 10%Ni-10%W/MCM-41. Hence, the jet fuel yield of bimetallic catalysts was higher than that of monometallic ones. Nevertheless, when increasing the content of W to 15%, the oil yield decreased to 29wt.%.

3.2 Catalyst characterization

In Figure 1, the powder XRD patterns of catalysts showed that the diffraction peaks at 43.9˚,51.2˚and 74.9˚attributed to $Ni_{17}W_3$ alloy phase appeared with the increase of W loading, which might be the main active phase. As shown in Figure 2, the $Ni_{2p3/2}$ signal shifted from 852.2 eV to 853.1 eV, and W_{4f} doublets at 38.5 eV and 36.1 eV decreased to 37.9 eV and 35.8 eV,respectively,which caused by the formation of $Ni_{17}W_3$ alloy phase[5]. As displayed in Figure 3, when the W loading was 2.5%, the particle size of Ni mainly distributed over the range of 19-23 nm. With the content of W increasing to 10% and 15%, the particle size of $Ni_{17}W_3$ alloy phase was 7-9 nm and 20-24 nm, respectively.

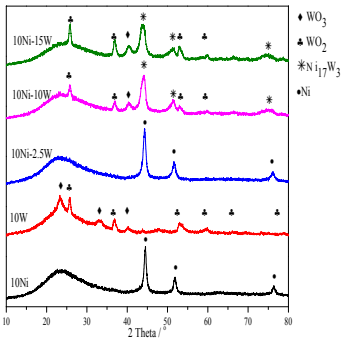

Figure 1. XRD patterns of catalysts

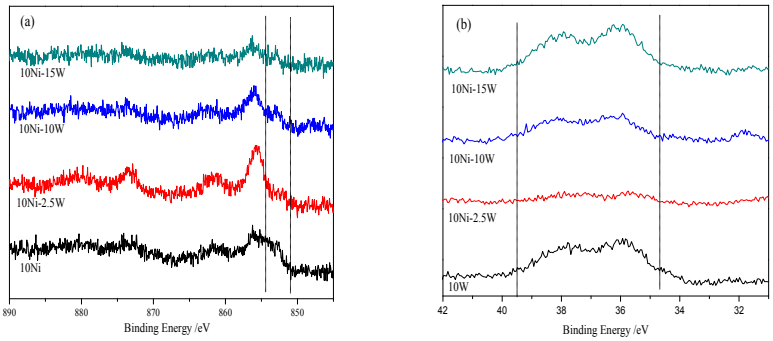

Figure 2. XPS patterns of catalysts. (a) Ni_{2p} (b) W_{4f}

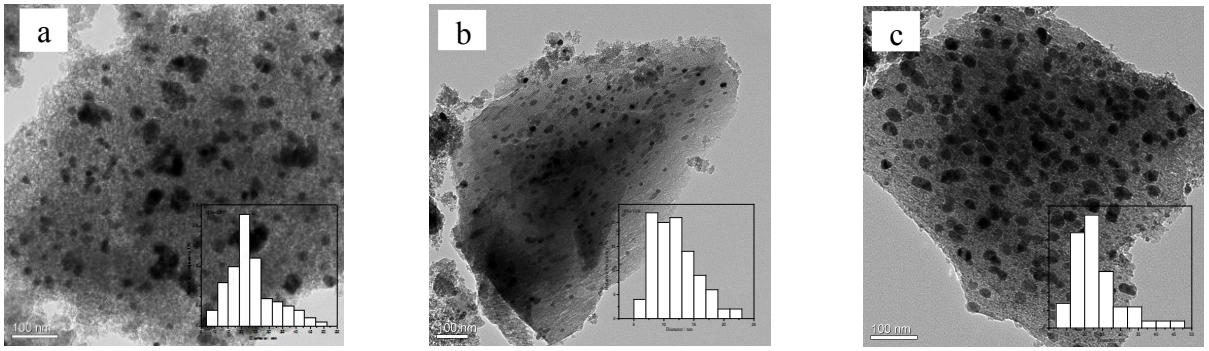

Figure 3.TEM images of catalysts. (a)10Ni-2.5W; (b)10Ni-10W; (c)10Ni-15W

4. Conclusions

In this study, Ni-W/MCM-41 catalysts realized the complete conversion of jatropha oil. Compared with monometallic catalysts, 10%Ni-10%W/MCM-41 bimetallic catalyst exhibited the best catalytic performance, with the jet fuel yield as high as 64wt.%. The interaction between Ni and W induced the formation of $Ni_{17}W_3$ alloy phase, which was proposed to be the main active phase. Excessive W loading would increase $Ni_{17}W_3$ alloy particle size and decrease the jet fuel yield.

References

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