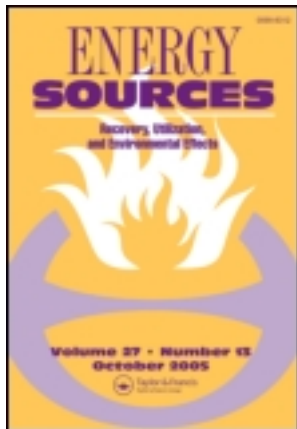


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# Hydrotreatment of Heavy Oil from Direct Coal Liquefaction on a Sulfided Ni-W/AC Catalyst

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**Abstract** *Ni-W catalysts supported on activated carbon and Al<sub>2</sub>O<sub>3</sub> were prepared by an incipient wetness impregnation method and characterized by x-ray diffraction and temperature programmed reduction. Heavy oil (distillation temperature: 320–340°C) derived from the direct coal liquefaction process using Shengli coal were hydrotreated using sulfided Ni-W catalysts at 400°C and 5.0 MPa initial H<sub>2</sub> pressure. The results showed that the support had a significant influence on the reducibility of metal oxides, hydrodenitrogenation, and hydrodearomatization activities of coal-derived heavy oil. Ni-W/activated carbon exhibited higher decolor performance and hydrodearomatization activities for upgrading the coal-derived heavy oil than the Ni-W/Al<sub>2</sub>O<sub>3</sub> catalyst.*

**Keywords** direct coal liquefaction, heavy oil, hydrodearomatization, hydrodenitrogenation

## 1. Introduction

With fast increasing demand of liquid transportation fuels and limited petroleum resources, production of transportation fuels from direct coal liquefaction (DCL) technologies has been an important option to lessen the deficiency in petroleum supply, especially for China—a fast developing country with limited petroleum reserves (Liu et al., 2010). But the liquid product obtained from the DCL process has a low hydrogen to carbon ratio and contains a considerable amount of heteroatom compounds that may cause many troubles, such as instability of fuel during its transportation or storage.

The challenge for product upgrading in DCL is to design a better catalyst, especially for feeds of high aromatic and nitrogen contents (Liu et al., 2010). Nitrogen compounds are certainly an inhibitor in hydrotreatment and cracking processes, and they lead the catalysts used in the downstream secondary processing (such as fluid catalytic cracking and hydrocracking) of these stocks to deactivate faster. Such a product must be upgraded to become a feedstock for the existing refineries through extensive removal of heteroatom contained molecules—principally N, S, and O in aromatic rings, over sulfided Ni-Mo,

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Co-Mo, or Ni-W catalysts to the acceptable levels in petroleum refining. Also, its refined products must satisfy the various requirements to be sold in the market, such as cetane index, aromatic content, and sulfur content. Thus, the higher content of nitrogen compounds present in the coal-derived heavy oil should be removed prior to further processing.

The aromatic nature of DCL products is another challenge. Advanced refinery technologies, such as hydrodearomatization (HDA), must be implemented in order to fulfill the limits for aromatic contents. The Cetane number can also be increased by the HDA process. The hydrogenation of polyaromatics is the main issue in the upgrading of coal-derived liquid. But hydrogenation of aromatics is more difficult than hydrodesulfurization and hydrodenitrogenation (HDN) due to the various types and amounts of aromatic species present in the oil as well as the complexity of the reactions.

Numerous studies have been conducted to investigate the hydrotreatment of coal-derived product on various catalysts (Liaw et al., 1994; Sumbogo Murti et al., 2005) and the effect of feed composition (Liaw et al., 1998). In recent years, in order to improve the activity of hydrotreating catalysts, many approaches, such as (i) different preparation method, (ii) support modification, and (iii) altering the active component, have been followed. Among these approaches, variation of support is an important one. Alumina is the most widely used support material for commercial Co or Ni promoted molybdenum hydrotreating catalysts. Notable features of alumina supports are their ability to provide high dispersion of the active metal phase and good mechanical properties. However, the results of intensive research (Patnasamy and Sivasanker, 1980) have shown that in the final oxidic or precursor state numerous chemical interactions exist between the amorphous alumina and the transition metal oxides. Some of the species formed are very stable and resist complete sulfidation. The dispersion of the catalytic metal-sulfide on alumina-supported CoMo or NiMo-sulfide is difficult to enhance due to the strong polarity and the limited surface area of the alumina support.

In recent years, carbon has received much attention as a support for hydrodesulfurization catalysts as high HDS activities that are superior to that of the alumina-supported counterparts have been reported (Sakanishi et al., 2000; Xu et al., 2007; Farag et al., 2000; Farag, 2008; Hussain and Ihm, 2009), which may be due to more favorable support/catalytic species interactions. The carbon support, such as active carbon or carbon black, has been reported to have some potential for enhancing the dispersion of the catalytic metal-sulfide because of the weak polarity and the larger surface area. The weak polarity reduces interaction between the active component and the supporting material, and the larger surface area provides much more anchor sites for the active component. In addition, carbons have many other additional advantageous features, such as high surface areas with controlled pore volume and pore size, reduced coking propensity, resistance to nitrogen compounds, the ease of recovery of metal component, and controllable surface functionality. Thus, carbon possesses the characteristics of a potential support for the preparation of a commercial coal-derived heavy oil upgrading catalyst with high activity. However, to the best of our knowledge, no report is available on the hydrotreating of coal-derived liquid from a pilot plant on the carbon supported catalysts, especially on hydrodenitrogenation (HDN) and hydrodearomatization (HDA) activities.

In this investigation, the activated carbon (AC) was used as support to prepare Ni-W catalysts with 15 wt% W and 5 wt% Ni. The hydrotreating activities (HDN and HDA) of AC supported Ni-W catalysts (Ni-W/AC) was evaluated for upgrading of DCL heavy oil at simulated industrial conditions and the results were compared with those of a Ni-W/Al<sub>2</sub>O<sub>3</sub> catalyst.

## 2. Experimental Section

### 2.1. Samples

The coal-derived heavy oil (HO) used was generated from direct liquefaction of Shengli coal in a 0.1 ton/day continuous unit at China Coal Research Institute, Beijing. The DCL reactor was operated at 455°C and 19 MPa in the presence of Shenhua Fe-based catalyst (1 wt% Fe loading on daf coal basis). The catalyst is highly dispersed ultra-fine FeOOH prepared by a procedure reported in the literature. The DCL products were separated through high-temperature and low-temperature separators, followed by atmospheric and vacuum distillations. The HO used in this study was the narrow fraction of Shengli coal-derived liquid, in which the distillation temperature was in the range of 320–340°C.

The support material, AC and Al<sub>2</sub>O<sub>3</sub>, were provided by Xingguang Active Carbon Co. (BET surface area of 1,100 m<sup>2</sup> g<sup>-1</sup>) and Fushun Petrochemical Co. (BET surface area of 185 m<sup>2</sup> g<sup>-1</sup>), respectively.

### 2.2. Catalyst Preparation

The loading of Ni-W was carried out by incipient wetness impregnation of the support using mixed solutions of ammonium metatungstate and nickel (II) citrate. The impregnated samples supported on AC and Al<sub>2</sub>O<sub>3</sub> were dried and then calcined at 500 and 400°C in Ar for 3 h, respectively. These calcined precursors were then sulfided at 400°C with a CS<sub>2</sub>/H<sub>2</sub> gas (10/90%, 60 ml/min) for 2 h followed by outgassing at the same temperature in stream of H<sub>2</sub> for 1 h. The sample was then cooled to room temperature and passivated in stream of N<sub>2</sub> for 6 h. The prepared Ni-W or Ni-Mo catalyst contains 5 wt% Ni and 15 wt% W.

### 2.3. Catalyst Characterization

**2.3.1. Powder X-ray Diffraction (XRD).** XRD patterns of sulfided catalysts were obtained on a Rigaku computer-controlled D/max 2500× using Cu-Kα as the radiation source. During the analysis, catalysts were scanned from 10 to 80° at a speed of 4°/min.

**2.3.2. Temperature Programmed Reduction (H<sub>2</sub>-TPR).** TPR experiments were carried out in a smaller fixed-bed quartz reactor (2 mm i.d.) coupled with a mass spectrometer. The transfer line between the fixed-bed reactor and the mass spectrometer was kept at 120°C. Samples, in the amount of 30 mg, were heated from room temperature to 800°C at a rate of 10°C/min under a flow of 10% H<sub>2</sub>/Ar (50 ml/min). The evolution of H<sub>2</sub>O was analyzed by mass spectrometer.

### 2.4. Catalyst Performance Test

The hydrogenation experiments of Shengli coal-derived heavy oil were carried out batchwise in a 30-ml tubing reactor shaken vertically. Then 3.0 g of heavy oil was charged into the reactor together with 0.15 g of sulfided catalyst, which simulates typical online hydrotreating conditions for heavy liquids in DCL with an initial H<sub>2</sub> pressure of 5 MPa and a temperature of 400°C. After loading the sample, the reactor was sealed and flushed three times with hydrogen followed by turning the system to the desired initial pressure of 5 MPa H<sub>2</sub>. The reactor, agitated vertically at 120 rpm, was submerged into a eutectic

salt bath, which had been heated to the desired temperature and maintained for 60 min. After the reaction, the reactor was quenched to ambient temperature in a water bath before the overhead pressure in the reactor was released slowly. The liquid and catalyst in the reactor were removed and separated by centrifuge.

## 2.5. Products Analyses

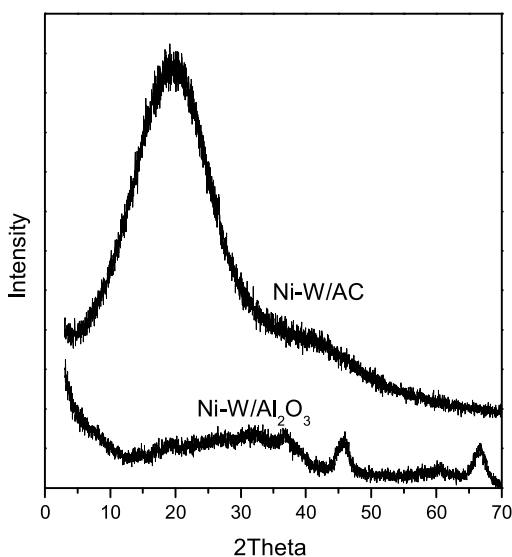
Nitrogen analysis was performed using an Elementar Vario EL III. The liquid samples in elemental analysis were sealed in the capsule. Air in the capsule was forced out the capsule via a gas stream of oxygen. The mean blank values of several samples were subtracted for evaluation.

Aromatic distribution analysis was carried out on a Shimadzu LC-2000 high performance liquid chromatography with an UV detector ( $\lambda = 254$  nm). A Sepax NH<sub>2</sub> (30 cm length; 0.8 cm i.d.) separation column was operated isothermally at 25°C. Hexane was used as the mobile phase with a flow rate of 1.2 ml/min. The identification of aromatic components (biaromatic and triaromatic) was carried out by the retention time of selected representative components of the mono-, di-, and triaromatic groups (toluene, naphthalene, anthracene, and phenanthrene).

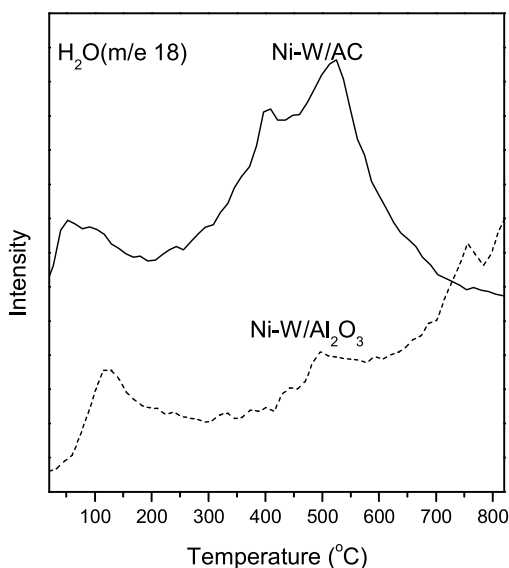
## 3. Results and Discussion

### 3.1. Catalyst Characteristics

3.1.1. XRD. Figure 1 shows the X-ray diffraction patterns of the sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts. The XRD patterns of two sulfided catalysts display only broad XRD peaks of the AC or alumina support, and there are no characteristic peaks of NiS<sub>2</sub>, WS<sub>2</sub> phases, NiO, and WO<sub>3</sub>, metallic nickel/tungsten phase to be observed. It indicates that the Ni and W domains species in the supports were either completely amorphous



**Figure 1.** X-ray diffraction patterns of sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts.



**Figure 2.** H<sub>2</sub>-TPR profiles for calcined Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts.

or composed of crystallites smaller than 4 nm. Then Ni and W species were considered to be uniformly distributed on the surface of the AC/Al<sub>2</sub>O<sub>3</sub> support under preparation conditions. Also, the absence of diffraction lines of nickel or tungsten sulfide could indicate that these phases have a very small particle size or that they are inserted into the structure of WS<sub>2</sub>, forming a well dispersed Ni-W-S solid solution (Rodríguez-Castellón et al., 2008).

**3.1.2. TPR.** TPR characterization gives a good indication of the degree of interaction of Ni-W with the supports. Figure 2 shows the TPR profiles of the calcined Ni-W catalysts on different supports. The evolution peak of H<sub>2</sub>O in the temperature range of 200–800°C is due to the reaction of Ni and W oxides with H<sub>2</sub>. It can be seen that the two samples showed quite different behaviors in H<sub>2</sub>O evolution profiles. The reduction of Ni-W catalysts supported on AC occurs in the temperature range of 200–700°C. The Ni-W/AC catalyst has two H<sub>2</sub>O evolution peaks at 400 and 500°C, respectively. But for Ni-W catalysts supported on Al<sub>2</sub>O<sub>3</sub>, the reduction is not complete even at 800°C, due to the reduction of highly dispersed Ni and W oxide species strongly interacting with the alumina support. The high temperature reduction peak has been frequently observed for alumina-supported catalyst systems and has been ascribed to the strong interaction between the small precursor species and the alumina support (Jacobs et al., 2002; Borg et al., 2007). Clearly, alumina presents a much stronger interaction compared with AC. The AC-supported catalyst is significantly easier to reduce than the Al<sub>2</sub>O<sub>3</sub>-supported one. It has been reported previously that there is a good correspondence of the reducibility of the metal oxides and their HDS activity (Shang et al., 2004). Also, the activity differences between carbon- and alumina-supported catalysts are ascribed to differences in active phase-support interaction. This is because the sulfiding process of a catalyst is combined with the reduction of the oxides by hydrogen. The whole process is usually done in excess of both the reducing and sulfiding agents, and a catalyst that is easily reduced

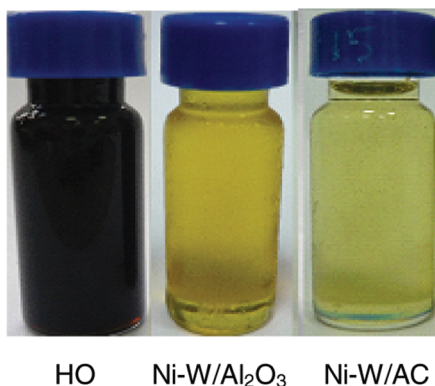
also easily undergoes sulfidation at the same conditions, resulting in a higher percentage of active species and higher activity of the catalysts.

### 3.2. Activity Evaluation

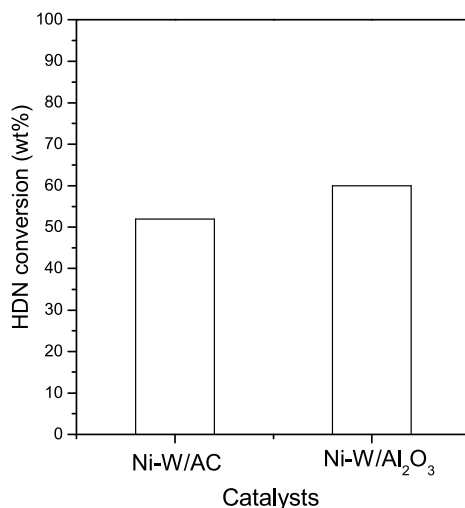
3.2.1. *The Change of Color of Heavy Oil.* The HO used in this experiment, which is characterized by high aromatic content and high nitrogen content, is a typical coal-derived liquid feed stock for hydrotreatment. Figure 3 shows the change of color of heavy oil after hydrogenation. The color of HO as received is black, which indicates that the HO has a high content of nitrogen and aromatic compounds. After hydrogenation, the color of HO turns from black to yellow. The extent of decolor has a significant difference for the two sulfide catalysts. The decolor performance was more pronounced in the Ni-W/AC catalyst, which displayed a light-yellow color.

3.2.2. *HDN.* Figure 4 shows the HDN activities of the two sulfided catalysts. It shows that the HDN conversion of the sulfided Ni-W/AC catalyst was 52%, which indicates that the nitrogen of HO is difficult to remove. Compared with the sulfided Ni-W/AC catalyst, the sulfided Ni-W/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited a slightly higher HDN activity. The HDN activities of sulfided Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts increased by 8% compared to that of Ni-W/AC. This result indicates that the type of support significantly affects HDN activity. Higher HDN activities toward coal-derived heavy oil hydrogenation were found on the Al<sub>2</sub>O<sub>3</sub> than on the AC supported catalysts.

3.2.3. *HDA.* Figure 5 shows the aromatic distribution of the feedstock (HO) and its hydrogenation products on the two sulfided catalysts. The percentile decrease of aromatic content was determined and defined as HDA activity and calculated by the difference of the peak area of aromatic hydrocarbons before and after the hydrotreatment. It shows that the aromatic of HO mainly contained biaromatics (naphthalene and its derivatives) and triaromatics (anthracene and phenanthrene). After hydrogenation, the amounts of aromatic significantly decreased on the two catalysts. Table 1 shows the HDA activities of two sulfided catalysts. It shows that the HDA activities of sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts were 64 and 58%, respectively. For sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub>,

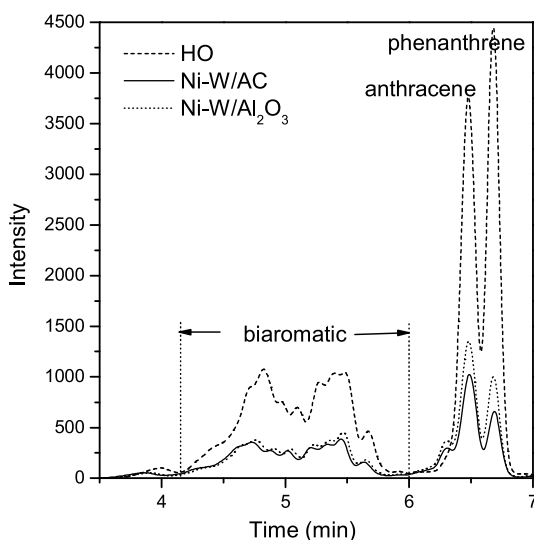


**Figure 3.** Photos of heavy oil (HO) and its hydrogenation products by sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts. (color figure available online)



**Figure 4.** HDN conversion of HO over sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts.

the HDA activities of triaromatics were higher than that of biaromatics. But for sulfided Ni-W/AC catalysts, the difference of HDA activities between triaromatics and that of biaromatics was higher (by 5%) than that of Ni-W/Al<sub>2</sub>O<sub>3</sub>. This result indicates that AC support can increase HDA activities compared with that of Ni-W/Al<sub>2</sub>O<sub>3</sub>. In order to gain some insight into the reactivity of HO, the HDA activity of triaromatic (anthracene and phenanthrene) were calculated in Table 1. It can be seen that hydrogenation of HO on the sulfided Ni-W/AC resulted in a 65 and 82% decrease of anthracene and phenanthrene, respectively. In the presence of Ni-W/Al<sub>2</sub>O<sub>3</sub>, the conversions of anthracene and phenanthrene were 55 and 74%, respectively. These results indicate that AC support



**Figure 5.** Aromatic distributions of the HO and its hydrogenation products on sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts.



**Table 1**  
HDA activities of two sulfided Ni-W/AC and Ni-W/Al<sub>2</sub>O<sub>3</sub> catalysts

|                                    | HDA,<br>% | HDA<br>(bi), % | HDA (tri),<br>% | HDA<br>(anthracene),<br>% | HDA<br>(phenanthrene),<br>% |
|------------------------------------|-----------|----------------|-----------------|---------------------------|-----------------------------|
| NiW/AC                             | 64        | 59             | 69              | 65                        | 82                          |
| NiW/Al <sub>2</sub> O <sub>3</sub> | 58        | 56             | 61              | 55                        | 74                          |

can significantly increase the hydrogenation of anthracene and phenanthrene for about 10 and 8% compared to that of Al<sub>2</sub>O<sub>3</sub>-supported catalyst. This might owe to different properties (e.g., acidity and surface structures) of the support materials (Al<sub>2</sub>O<sub>3</sub> and AC) or different metal-support interactions in the supported catalysts (Xu et al., 2007).

#### 4. Conclusions

HO derived from the direct coal liquefaction process of Shengli coal was hydrotreated in the presence of AC supported Ni-W sulfided catalyst at simulated industrial conditions (400°C and initial 5 MPa H<sub>2</sub>). The results show that the supports significantly affect the reducibility of the active phase, the HDN and HDA activities. The AC-supported catalyst was easier to reduce than the Al<sub>2</sub>O<sub>3</sub> catalysts, due to the weak interaction between the AC support and the metal particles. The HDN and HDA activities of sulfided Ni-W/AC were about 52 and 64%, respectively. The AC-supported sulfided Ni-W catalysts had higher hydrogenating activity (the decolor performance and HDA activities) than that of Al<sub>2</sub>O<sub>3</sub>-supported sulfided Ni-W catalysts, although the HDN activity was slightly lower than that of the Al<sub>2</sub>O<sub>3</sub>-supported sulfided Ni-W catalysts.

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