



## Full Length Article

# Multi-metal catalysts for slurry-phase hydrocracking of coal-tar vacuum residue: Impact of inherent inorganic minerals

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## ABSTRACT

Multi-metal catalysts for slurry-phase hydrocracking of coal-tar vacuum residue were investigated. The multi-metal catalysts system consisted of pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) transformed from inherent inorganic minerals in coal-tar vacuum residue and mixed molybdenum (Mo)–nickel (Ni) sulfide catalysts. The inherent inorganic minerals included iron oxide (hematite- $\text{Fe}_2\text{O}_3$ , goethite- $\text{FeO}(\text{OH})$ ) and other minerals. The formed pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) was acting as an active phase for hydrocracking. Mo naphthenate and Ni naphthenate were used as precursors to the dispersed Mo–Ni sulfide catalysts. The multi-metal sulfide catalysts were confirmed to form and well dispersed across the toluene insoluble sample by XRD, XPS and EDS analysis during hydrocracking. Comparative reaction tests revealed that the inherent inorganic minerals, as Mo–Ni catalyst carrier and coke carrier, enhanced the dispersion of Mo–Ni catalysts and induced less coke formation. Compared with only the Mo–Ni catalysts or inherent inorganic minerals, the multi-metal catalysts system promoted the thermal decomposition of CTVR feedstock at a low temperature, and suppressed coke formation, increased the liquid yield and improved hydrodeheteroatom at a high temperature, which resulted from the synergistic effects between the Mo–Ni sulfides and the inherent inorganic minerals.

## 1. Introduction

The heavy oil upgrading is of significant interest to oil refineries [1,2]. As the heaviest components of heavy oil, vacuum residues are difficult to process, and cause environmental pollution [3]. The conversion of vacuum residue to low-boiling products and their further processing to valuable products, is of importance [4]. Several processes that convert heavy oil into lighter products have been proposed, such as coking, visbreaking, catalytic cracking and hydrocracking [5]. Among the hydrocracking processes, much research is being conducted on slurry-phase hydrocracking, which is an alternative technique for vacuum residue processing [6,7].

Catalysts for slurry-phase hydrocracking include mainly solid-powder dispersed catalysts and oil-soluble dispersed catalysts [8]. Solid-powder dispersed catalysts have been used widely in slurry-phase hydrocracking [9,10]. Among them, inorganic minerals have been used as hydrogenation catalysts and coke carriers in slurry-phase hydrocracking. Although the use of fine inorganic minerals as low-cost catalysts is attractive to researchers, their homogeneous dispersion is the restricting factor in slurry-phase hydrocracking [11]. Studies have

found that iron oxide in red mud is transformed into iron sulfide by sulfur in the feedstock [12], and iron sulfide is an active phase for vacuum-residue hydrocracking [13,14]. In previous studies, fine inorganic minerals were used as coke-carriers [15,16], and could inhibit phase separation, prolong the growth and coalescence of the coke precursor, and reduce coke formation during thermal cracking and hydrocracking of heavy oil [17].

Oil-soluble dispersed catalysts (such as Mo, Ni, Co, W, and Fe salt) are applied as precursors to dispersed sulfide catalysts. Active metals (Ni, Mo, Co, W or Fe) help to moderate the rate of free-radical propagation via  $\beta$ -scission reactions by incorporating hydrogen into cracked active hydrocarbon fragments during heavy oil upgrading [18,19]. In general, molybdenite crystallites are more active than those of other sulfides [20]. Fe-based catalysts are active in the dealkylation of alkyl aromatics [21] and suppress the addition reaction [22]. Mixed phase Fe–Ni–S can provide the required hydrogen to promote bond cleavage and stabilize fragmental radicals in coal liquefaction [23,24]. The NiMoS phase showed a slight synergistic effect in the deoxygenation and hydrodesulfurization reaction over FeMoS [25,26]. However, relatively few studies have been devoted to the development of a multi-

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**Table 1**  
Properties of CTVR (480 °C+) and CTVR-NoTI.

Parameter	Unit	CTVR	CTVR-NoTI
Weight percent in coal tar	wt%	10.25	8.07
Density (20 °C)	g mL <sup>-1</sup>	1.096	1.027
Toluene insoluble (TI)	wt%	21.27	0
Microcarbon residue (MCR)	wt%	23.01	10.37
Ash	wt%	3.32	0.02
<i>Elemental component</i>			
C	wt%	85.19	86.96
H	wt%	6.30	6.51
S	wt%	0.36	0.38
N	wt%	2.88	2.21
O <sup>diff</sup>	wt%	5.27	3.94

metal catalyst system, which consists of oil-soluble and solid powder catalysts. Hence, it is essential to understand the detailed character of the multi-metal catalyst system to establish efficient methods for residue oil utilization.

There is a strong requirement to understand multi-metal catalysts for the slurry-phase hydrocracking of coal-tar vacuum residue, and in particular, the impact of inherent inorganic minerals. In this paper, a vacuum residue of coal tar was used to study and understand the formation of multi-metal catalyst and its characteristic in CTVR slurry-phase hydrocracking. In particular, the impact of inherent inorganic minerals from residue oil and its joint effect with Mo-Ni catalysts were systematically analyzed by designed experiments. Advanced analytical methods, including XRD, XPS and EDS analysis, have applied to identify the formed multi-metal sulfide catalysts and their dispersion. The significant synergistic effect of multi-metal catalysts was interpreted by using the comparative reaction tests, which suppressed coke formation, increased the liquid yield and improved deoxidation and desulfurization.

## 2. Experimental section

### 2.1. Materials

CTVR feedstock (480 °C+, CTVR) was obtained from low/middle-temperature coal tar in Shanxi Province, China. The coal tar was derived from Yulin lignite pyrolysis. Its properties are shown in Table 1.

As shown in Fig. 1, toluene insoluble was obtained from the CTVR feedstock via toluene extraction, and was defined as native toluene insoluble (NTI). Feedstock CTVR-NoTI was obtained from the toluene-

soluble fractions of feedstock CTVR, as shown in Table 1. Inherent inorganic minerals were extracted from NTI by using chloroform under ultrasonic oscillations until colorless. The sample was centrifuged and dried in a vacuum at 100 °C for 2 h. The inherent inorganic mineral yield was 3.05 wt%, which is close to the ash content (3.32 wt%) in CTVR feedstock.

### 2.2. CTVR hydrocracking experiment

The CTVR hydrocracking experiments were performed in a 500-mL batch stirred reactor at 9.0 MPa H<sub>2</sub> (initial pressure) for 20 min from 330 to 430 °C and with a 750-rpm stirring speed. The stirred reactor of FYXD series, equipped with measuring and control systems of pressure (0–30 MPa), temperature (0–480 °C), and stirring speed (0–1000 rpm). A mixture of molybdenum naphthenate and nickel naphthenate (made by our laboratory), at the specific metal-mass ratio of Mo to Ni (3:2), was applied as a precursor of the dispersed sulfide catalysts during slurry-phase hydrocracking. The autoclave was loaded with 150 g CTVR, with 300 µg g<sup>-1</sup> catalyst expressed as a metal mass, and 1200 µg g<sup>-1</sup> sulfur was added as the sulfurizing agent. The catalyst and sulfur were mixed with the CTVR by heating and stirring before reaction. The reaction without catalyst (blank test) was studied for comparison. Then, the reactor under vigorous stirring was heated up to different reaction temperatures for 60 min by temperature programmed. And the reactor was hold under different reaction temperatures (330 to 430 °C) for 20 min. Finally, the reactor was rapidly cooled down to 180 °C in 5 min by cold water after reaction. As shown in Fig. 2, the gas yield was obtained by the difference between the hydrocracked residue product after exhaust and the feedstock. The naphtha (Nap, < 180 °C), diesel (180–360 °C), vacuum gas oil (VGO, 360–480 °C) and vacuum residue (VR, > 480 °C) were separated from the hydrocracked products by atmospheric and vacuum distillation. The toluene-insoluble from the hydrocracked CTVR was identified as TI. TI was obtained from the hydrocracked vacuum residue via toluene extraction, the TI precipitate was washed by toluene solvent until the solvent became colorless, and the TI samples was dried in a vacuum at 100 °C for 2 h. According to our previous study, TI samples from hydrocracking products would normally consist of coke, catalyst, and inorganic matter [27]. Finally, three parallel hydrocracking experiments at 360 °C and 430 °C were conducted and the average results of product distribution to be described later. The CTVR conversion and the liquid yield were calculated by the following equations:

$$\text{Liquid yield (wt\%)} = [\text{naphtha yield (wt\%)}] + [\text{diesel yield (wt\%)}] + [\text{vacuum gasoil yield (wt\%)}]$$

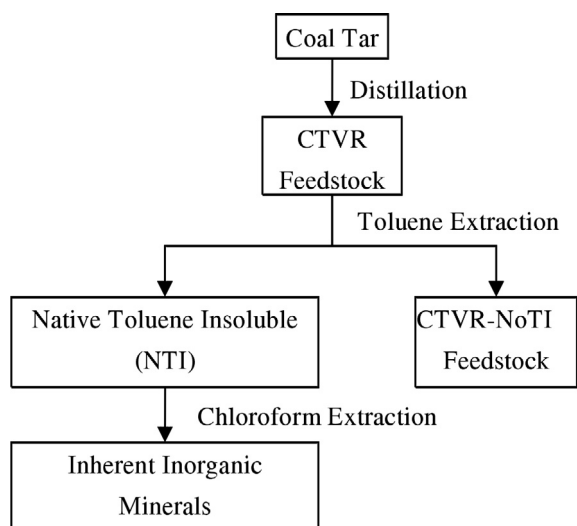


Fig. 1. Extraction scheme for samples.

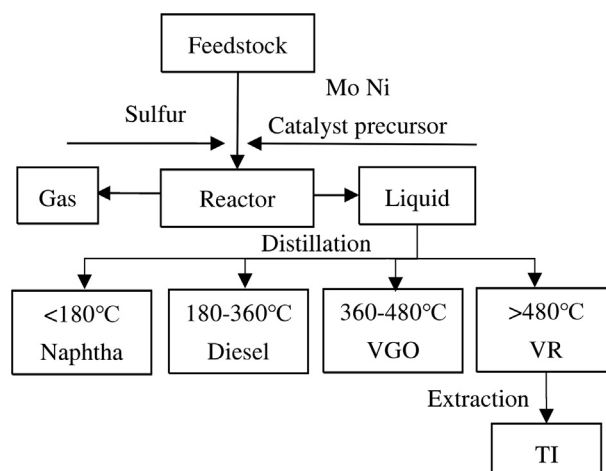


Fig. 2. Scheme of the operation procedure of hydrocracking experiments.

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