



Characterization and analysis of vanadium and nickel species in atmospheric residues



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HIGHLIGHTS

- HT-GC-AED successfully identified V and Ni species in as-received ARs.
- HT-GC-AED of oils after HDM provided evidence of a demetallisation mechanism.
- Such a mechanism contributes to the enhancement of HDM based on the staged reactions.

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ABSTRACT

Metal species (Ni and V) in as-received atmospheric residues (ARs) were characterized through conventional analysis methods as well as through gas chromatography-atomic emission detection (GC-AED) assembled with a high-temperature injector system (HT-GC-AED). The vanadium concentration in all ARs could be successfully measured by electron spin resonance (ESR) corrected with inductively coupled plasma-mass spectroscopy (ICP-MS). HT-GC-AED was attempted to confirm the characteristics of V and Ni species, from which at least five species of vanadium and six species of nickel in as-received ARs were identified, together with several shoulder peaks. In addition, HT-GC-AED analysis of product oils after hydrodemetallization (HDM) of ARs was investigated over both oxide and sulfide catalysts. This analysis provided evidence of a demetallization mechanism for the cracking of the alkyl group attached to the metal porphyrin structure over oxide catalysts. This mechanism contributes to the enhancement of HDM based on the staged reaction over the oxide (1st stage)-sulfide (2nd stage) catalytic system.

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1. Introduction

Recent trends in the worldwide supply of crude oil indicate a decline in the availability of conventional crude. This trend has been offset by the increasing production and use of heavy crude. For heavy crude, the yield of distillate fractions can be increased by upgrading distillation residues. However, heavy oils are very difficult to utilize because of their inherently poor qualities such as high viscosity and large molecular weight fractions. In addition, the quality of heavy oils suffers from hetero-atoms and metals, both of which are costly to treat with most conversion processes and unacceptable in clean refinery products for environmental reasons.

To overcome these problems, a number of thermal processes (e.g. visbreaking, delayed coking, fluid coking, flexicoking), as well as the so-called carbon-rejecting processes of asphaltene/metal separation (e.g. deasphalting), have been used on a commercial scale for several decades [1,2]. Heavy feeds can also be upgraded by hydroprocessing, which is known as the hydrogen addition option [3,4]. Of the processes above, hydroprocessing operations are more flexible, giving higher yields of liquid fractions.

Effective hydroprocessing of heavy feeds can be attained by the removal of metal species such as vanadium and nickel at the initial step, owing to a rather complex set of reactions and events as was demonstrated in several studies [5–8] focusing primarily on hydrodemetallization (HDM) with the batch and continuous reactor systems [9].

Metal species (V and Ni) tend to accumulate in the residuum during distillation and affect its properties adversely. Some organometallic compounds may also volatilize at the refinery

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distillation temperatures in the higher-boiling distillates. The presence of metal contaminants in fluid catalytic cracking (FCC) process feeds is known to be a potentially more serious problem. Although sulfur can be converted to gaseous forms that can be readily treated in an FCC unit, the nonvolatile metal contaminants tend to accumulate in the unit during the cracking process and are ultimately deposited on the catalyst together with the coke. Given that both nickel and vanadium exhibit dehydrogenation activity, their presence on the catalyst particles tends to promote dehydrogenation reactions during the cracking sequence, which in turn results in increasing the amounts of coke and light gases at the expense of gasoline production. The above problems can act as an inhibitor of further hydrotreating catalysis such as hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Earlier researches showed direct evidences on the catalyst poisoning and deactivation during HDM [10–12]. Ledoux et al. reported HDS activities over the NiMo catalyst poisoned by vanadyl and nickel porphyrins in HDM step where the nature and the structure of the poison in the catalyst were correlated to HDS activities [10]. Dejonghe et al. represented toluene hydrogenation over Mo and NiMo supported on γ -alumina, as well as γ -alumina alone modified by vanadium deposited through HDM of the vanadyl porphyrin [11]. The catalyst (HDS) poisoning by metal-free, vanadium and nickel etio- and tetraphenyl porphyrins, as well as the binding and reactivity of the porphyrins on oxide and sulfided surfaces had been also discussed by Mitchell and Scott [12]. Therefore, residues similar to heavy feed should be preferentially demetallized to avoid these problems before upgrading by HDS and HDN [13].

In the HDM process, the development of an effective analytical method has always been issued for heavy feeds. Such a method should be established for the effective design of the catalytic system and evaluation of its performance [14]. The methods that have been used traditionally in the evaluation of hydroprocessing catalysts for light feed applications cannot be applied directly to heavy feeds without necessary modifications. Thus far, the feed analysis as well as the catalytic performance of HDM have been mainly evaluated by the concentration of metals (inductively coupled plasma-mass spectrometry: ICP-MS), sulfur (X-ray fluorescence: XRF), and C, H, N (elementary analysis). In addition, various spectroscopic instruments such as Electron Spin Resonance (ESR), Solid-State Nuclear Magnetic Resonance (NMR), Ultra Violet–Visible Diffuse Reflectance Spectroscopy (UV–DRS) had been studied for demetal mechanism over the metal catalyst as well as support catalyst alone [10–12,15,16]. Recently, it has become possible to investigate detailed information of metal species over FT-ICR-MS [17]. However, this technique appears to be quit costly and time consuming. Another effective technique is needed to support conventional analytical methods.

For the analysis of light oils from petroleum and their catalytic performances, atomic emission detection (AED) coupled with gas chromatography (GC) has been used routinely because of its element-selective properties; it allows, in principle, the detection of all elements except for helium [18–29]. However, its use for the analysis of heavy oils has been limited owing to the lower vaporizing temperature around 320 °C in the injector part. This limitation can be overcome by assembling a programmable high-temperature (around 500 °C) vaporization injector. In fact, atmospheric residues (ARs) cut at 360 °C+ can be analyzed up to a range of 700 °C without problems. This implies that the more detailed catalytic behavior of hydroprocessing, in particular HDM, can be evaluated along with an effective analysis of heavy feeds.

In the present study, we describe feeds characterization with analytical results of metals in ARs by using HT-GC-AED. The product oil evaluation for catalytic performance over the oxide (as-received alumina and silica-alumina samples) and sulfide catalyst (commercial catalyst) are also described, as well as the staged

catalytic system. From these results, we expect to be able to make contributions to the development of an effective HDM process to achieve improved upgrading of heavy oil. In addition to the expectation, the limitation in the application is handled to improve further the analytic methods than present status.

2. Experimental

2.1. Analysis of feeds and products oil

Three kinds of ARs (KWT-, ARH-, NAP-) were supplied by SK Innovation Co. Ltd. The carbon, hydrogen, and nitrogen contents over all feeds were determined using an elemental analyzer (CE Instruments model EA 1110). The sulfur contents were measured by XRF (Horiba, XGT-1700WR). The separations of maltene, asphaltene, and coke were carried out using the standard methods of ASTM D4124-97.

The concentration of metals in oil samples was analyzed with ICP-MS spectrometer (Agilent 7700 series, Agilent Technologies, USA) with 1.5 mm diameter injector and 0.3 mm diameter tube line. The refrigerator was kept at -5 °C (G1879B heat exchanger, Agilent Technologies, USA). Oxygen was added at the injector entrance to minimize carbon fraction in the plasma. Pure THF solvent was flowed for overnight to clean and stabilized. Calibration was carried out using the V (2000 ppm) and Ni (500 ppm) standard samples from Japan Petroleum Society (JPS), in which the standard samples was diluted by several ppm level (V: 10, 20, 40, 80, 120, 150, 200, 300 ppm, and Ni: 10, 20, 40, 80, 120 ppm). All calibration data showed linear plots (R^2 of at least 0.997). Based on the ICP-MS calibration results, all ARs have been able to calculate their metal concentration.

The electron spin resonance (ESR) measurements were performed on samples that were transferred to the ESR quartz tube (5-mm o.d., 4-mm i.d.). The spectra were recorded on a JES-FA200 ESR spectrometer with an X-band Bridge by using standard 100-kHz field modulation and a nominal frequency of 9.4 GHz utilizing a cylindrical TE cavity. Magnetic field calibration was performed with the standard. Signal intensities (proportional to the VO^{2+} —P concentration) were calculated by integration of the first derivative V hyperfine ($m_l = 5/2$) line [30]. Real AR samples (from ARH-AR) have been diluted with solvent (THF) to correct V concentration with ICP-MS.

GC-AED was performed on an Agilent 7890 gas chromatography in combination with a JAS 2390AA atomic emission detector. A methyl silicone column (J&W DB-1) was used for the separations. The gas chromatograph was equipped with a programmable high-temperature vaporization (PTV) inlet. A transfer line was maintained at a high temperature (450 °C) to effectively and stably transport the elutes from the GC column to the detector. For heavy oil samples, the inlet was programmed to increase from 50 to 500 °C in 9 min. The inlet was held at constant pressure and the column flow rate was 12 ml/min at 30 °C. The oven was programmed to increase from 30 to 450 °C at 30 °C/min. The transfer line between the GC and the AED was 450 °C and cavity temperature was 430 °C. The standard C species (C_{18} – C_{74} , WemeasureIt Inc., USA) have been obtained for simulated distillation. V and Ni-ethioporphyrins (Sigma–Aldrich), as well as 5, 10, 15, 20-tetraphenyl porphyrinato V and Ni (Wako) were used as metal elution standard. Each AR samples have been diluted by 20 wt% in solvent (DCM) to syringe and inject smoothly.

2.2. Catalysts and HDM reaction

Various oxide catalysts (supports only) such as alumina (6275, 6276, 6175), silica-alumina (SIRA 30, 69155), and a commercial

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