



Promotion effects with dispersed catalysts for residue slurry hydroconversion



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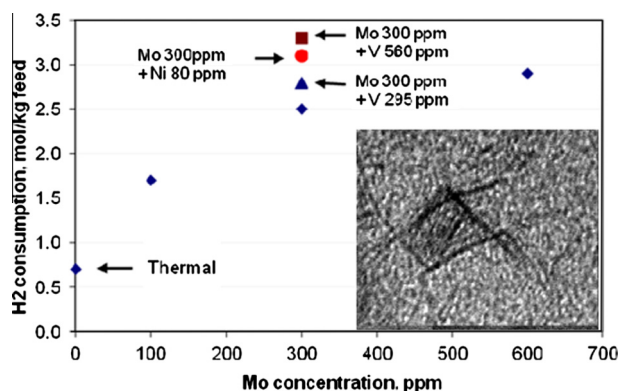
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HIGHLIGHTS

- Hydroconversion of atmospheric residue with dispersed sulfide catalysts.
- Dispersed catalysts characterized by HRTEM and XAS.
- Reverse synergy between Ni and Mo dispersed sulfides.
- V and Mo sulfide combination leading to additive effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydroconversion of an atmospheric residue (AR) was performed in an autoclave with Mo, Ni, V compounds applied as precursors of the dispersed sulfide catalysts. The reaction was conducted at 450 °C, residence time 1 h and the catalyst concentration in the range of 300–900 ppm. AR conversions were compared for the reaction carried out in the presence of sole metals and for the mixtures of two metals. By mixing of the Ni and Mo precursor salts together, improvement in the total conversion and hydrodesulfurization (HDS) degree of the AR was observed, indicating on a significant synergy between Ni and Mo dispersed sulfides. By contrast, in the case of V and Mo precursors mixture the total activity was just a sum of the contributions from two respective metals. With the support provides by high resolution microscopy (HRTEM) and core-hole X-ray absorption spectroscopy (XAS) it was concluded that in the case of mixed Ni–Mo catalyst, MoS₂ slabs were deposited on the surface of Ni₃S₂ crystallites, providing a reverse synergistic effect.

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1. Introduction

World oil demand is expected to be continuously increasing in the near future, at a rate of about 1.5% per year, with a growth of

transportation fuels and a relatively flat heavy oil demand [1]. Furthermore, the available crudes are getting heavier while the demand for light and clean fuels is steadily increasing, compelling the refiners to expand their residue upgrading capacity [2,3]. As the price differential between the light crudes and the heavy crudes is widening, a trend of processing heavier crudes is catching up fast in the refineries. As a result, refiners are getting burdened with

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heavy residues that are subsequently obtained by processing of heavy crudes. Several processes that convert these heavy feeds into lighter ones using different types of technologies are proposed [4–8]. An industrial plant using the slurry technology is at the start up phase (Eni Slurry Technology, 23,000 bpd, Sannazarro, Italy). Slurry technology using dispersed catalysts offers the advantage of an intimate mixing of the catalyst with the feed at low content of the active phase [9,10]. Slurry technologies can provide a solution for the conversion of “bottom of the barrel” residue, they are currently considered as the most adapted process for the treatment of the heaviest feedstocks. The slurry dispersed catalysts are used in the concentration range of hundreds of ppm and usually contain water-soluble or oil-soluble precursors [11–13]. The precursors are activated ex-situ or during the process to form dispersed sulfide hydrotreating catalysts. Oil soluble precursors are the most efficient ones. Among these precursors, Mo naphthenate is often considered as the benchmarking reference and as the most efficient one [11]. Similarly to conventional hydrotreating catalysis, synergistic or cooperative effects might be observed when the precursors of different metals are combined. Thus, NiMo and CoMo combinations have been evaluated starting from Mo, Ni and Co naphthenates [10,14] or phosphonic precursors [11] and slight synergy effects (or almost no effects [7]) were observed noticeably in terms of hydrodesulfurization or hydroconversion. Mo oil soluble precursor combined with a Fe water soluble precursor also exhibited some synergy effects [15]. By analogy with HDT catalysis, the origin of these effects can be assigned to the formation of so-called CoMoS (or NiMoS) promoted phase corresponding to the decoration of MoS₂ slabs by atomically dispersed Co(Ni) atoms. However, no characterizations were able to support this assumption in the case of slurry catalysts. Thus, the purpose of the present study is to investigate the cooperative or synergetic effects of the combination of Mo with V and Ni oil-soluble precursors and to clarify the origin of such promoting effects. An atmospheric residue was used as feed in order to prevent, as much as possible, any artifact coming from the Ni and V sulfides formed during the reaction by the conversion of asphaltenes. Rezaei and Smith observed by XRD the presence of both nickel and vanadium sulfides, deposited on coke, after processing a Cold Lake vacuum residue with a Mo based catalyst [16]. Using the combination of Ni and Mo precursors, Belussi et al. [7] characterized on the used catalyst by TEM large particles of Ni_xS_y particles acting as supports of MoS₂ slabs.

2. Experimental

2.1. Catalytic tests

The feed used for the hydroconversion experiments was an atmospheric residue (AR) and its characterizations are described in Table 1. Hydroconversion was performed in the presence of dispersed catalysts, produced in situ from the precursors including molybdenum naphthenate (MoNaph), nickel octoate (NiOcto), (supplied from Shepherd Chemical Co.), vanadium acetylacetonate (Vacac) (Sigma–Aldrich). The mixtures of catalysts are characterized by the *r* factor equal to the to the M/(M + Mo) ratio (M = V, Ni).

The reactions were conducted in a 250 cm³ autoclave (batch mode) equipped with a magnetically driven impeller (Autoclave PARR). In a typical experiment, about 100 g of feed was loaded and the catalyst precursor was introduced into the heavy oil and 100 μl of DMDS (Merck) was added in order to sulfide the precursors. After purging, the reactor was pressurized with H₂ up to 9 MPa. Slow stirring was applied (100 rpm) from 70 °C and increased up to 600 rpm when reaction temperature was reached after 25–30 min. These conditions ensured an effective mixing of gas and liquid. In the high temperature part; it took 5 min from

Table 1
Characterization of AR feed.

| Characterization | AR feed | |
|--|---------|------|
| <i>d</i> ₁₅ , g/cm ³ | 0.9576 | |
| API | 16 | |
| Sulfur, wt% | 2.84 | |
| Nitrogen, ppm | 1960 | |
| Nickel, ppm | 17.1 | |
| Vanadium, ppm | 45.7 | |
| Asphaltenes, C7 insol., (wt%) | 2.1 | |
| Conradson Carbon, wt% | 8.2 | |
| H/C (atomic ratio) | 1.59 | |
| State physique (at 25 °C) | Liquid | |
| Cut point | | |
| IBP – 350 °C | wt% | 7.5 |
| 350–510 °C | wt% | 41.8 |
| 510 ⁺ | wt% | 50.6 |

390 °C to reach the reaction temperature of 450 °C. At this reaction temperature for AR conversion, the total pressure was 16 MPa. During a run, pressure and temperature were continuously monitored as illustrated by Figs. 2 and 3 for the various catalysts composition; the reaction time after reaching the target temperature was 1 h. The gases were analyzed by a micro-GC using two modules PoraPLOTU (8 m × 0.32 mm ID) and OV1 (8 m × 0.15 mm ID). The liquid products from each experiment were analyzed by simulated distillation (D-6352 ASTM) which was used to estimate the boiling point distribution of the oil samples and to measure a conversion of C₅₁₀₊ compounds into C₅₁₀₋, considering the mass of liquid recovered [17]. The mass balance reaches typically 97%. The feed and the liquid products were defined as follows: gases, naphtha (IBP; 200 °C), distillates (200–350 °C), VGO (350–510 °C), and unconverted residue (510 °C +). Coke/sediment located inside the reactor and on the impeller was collected and weighted. A spot test performed (ASTM D4740-02) evidenced the stability of the sediments in the liquids except of Ni catalyst. In that case, 3 wt% of coke was obtained by contrast to the 0.1–0.2 wt% for the other catalysts. The catalytic properties of the various catalysts are summarized in Tables 2 and 3.

Considering the mass balance, the conversion of the heavy part of the feed was expressed as:

$$R_{510^+} = \frac{(m_{510^+ \text{ feed}} - m_{510^+ \text{ liquid product}})}{m_{510^+ \text{ feed}}} \times 100$$

where *m*₅₁₀₊ (feed) and *m*₅₁₀₊ (liquid product) are the fractions (wt%) with boiling points above 510 °C of the feed and the reaction product, respectively. Hydrodesulfurization (HDS) was evaluated

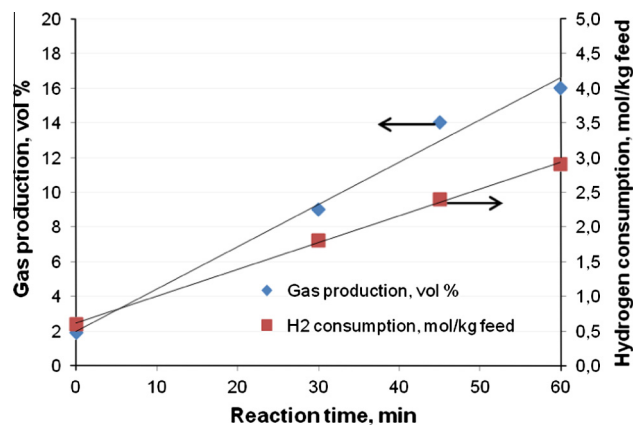


Fig. 1. Hydrogen consumption and gas production versus reaction time at 450 °C for the conversion of an AR with 600 ppm Mo catalyst.

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