Catalytic hydropyrolysis of El-Lajjun and Julia Creek shale oils using flow-through and sealed autoclaves

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ABSTRACT

High-sulfur shale oils from two marine oil shales, El-Lajjun (Jordan) and Julia Creek (Australia) were subjected to hydropyrolysis using NiMo catalysts deposited on Al-SBA-15 with Si/Al ratios ranging from 10 to 75, *i.e.* with decreasing acidity, both in a flow-through system at 0.1 MPa H_2 pressure and in sealed autoclaves at varying H_2 pressure (1–6 MPa (cold, *i.e.*, at room temperature)). For autoclave pyrolysis of El-Lajjun shale oil catalysed by NiMo-Al-SBA-15 (Si:Al = 10:1), sulfur content of oil decreased with H_2 pressure, catalyst:oil ratio and temperature, pyrolysis time having little effect. Coking decreased with increasing H_2 pressure, but increased with increasing temperature and catalyst:oil ratio. Time had little effect on coking. The conditions finally adopted were 400 °C, 6 MPa (cold) H_2 pressure, 30 min pyrolysis time and (0.1:1.0) catalyst:oil ratio. Lower Si/Al ratios (≤50) all gave the same hydrodesulphurization (HDS) activity, but coking declined with decreasing Si/Al ratio, so that the optimum ratio was 10. The Julia Creek shale oil also showed good HDS, but was more susceptible to coking at high Si/Al ratio. The oil obtained in catalysed pyrolysis contained almost no thiophenes or benzothiophenes and had more high-boiling point material than oil from non-catalysed pyrolysis. The catalyst was successfully regenerated after use and was also effective in HDS of both raw oil shales. For the flow-through experiments, no significant hydrodesulphurization (HDS) was observed for either shale oil, but some hydrodenitrogenation (HDN) occurred for the Julia Creek shale oils.

1. Introduction

Crude shale oil, particularly that from high-sulfur marine oil shales, usually contains large amounts of heteroatoms such as sulfur and nitrogen [1,2], which have to be decreased for the shale oil to be useful *e.g.* as a transport fuel. Apart from reducing the sulfur content of the original shale before pyrolysis [3] or altering pyrolysis conditions to reduce the heteroatom content of the resulting oil [4], most prior work has concentrated on reducing the heteroatom content of the shale oil as obtained. Sulfur and nitrogen have, for example, been removed with supercritical fluids [5] preliminary complexation with $CuCl_2.2H_2O$ [6] and other methods [7]. However, most upgrading, both commercial and experimental, has removed sulfur (HDS) and nitrogen (HDN) by hydropyrolysis. The first experiments were carried out in the 1930's using CoS_2/pumice [8], MoS_2, CoS and CoS/Al_2O_3 [9], bog iron ore and Fe-Cr [10] and Ni-Mo-S/acid clay [11]. For low-sulfur (< ca. 1 wt %), shale oils, conventional Mo and W catalysts, with Ni or Co promoters, are usually sufficient to lower the S and N content to a relatively low level, provided the temperature, hydrogen pressure and residence time

are suitably chosen [7,12]. However, for high-S shale oils, the conventional catalysts on supports such as γ-Al_2O_3 are insufficient. For example, NiMo/ γ-Al_2O_3 only reduced the S content of Israeli shale oil from 7.3 to 2.0 wt % [13] and NiMo + CoMo/ γ-Al_2O_3 of asphalted Timhadit (Morocco) shale oil from 7.5 to 1.8 wt % [14]. Better results (0.3-0.4 wt % S) were obtained for related distillation fractions of a similar oil, but other fractions coked the catalyst completely [15]. Better catalysts or promoters do not appear to have been reported, so that the path to improvement may lie in changing the supports. Landau et al [13] obtained S contents in the first stage of only 0.1–0.2 wt % rather than 2.0 wt % by substituting a special-large-pore Al_2O_3 for conventional γ-Al_2O_3.

A candidate support that has given promising results for other high-S substrates is SBA-15, a two-dimensional hexagonally ordered framework silicate with large pore diameter (˜10 nm) and high surface area (ca. 1000 m^2/g) [16,17]. The large pore size implies that SBA-15 can be used in hydrotreating reactions of bulky molecules [18]. At least in some circumstances, *e.g.* HDS of thiophene, SBA-15 was superior to γ-Al_2O_3 as a support for NiMo catalyst [19]. Altering the acidity of the

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SBA-15 by incorporating Al in the network has also been found to be beneficial, not only for model compounds, but also for bitumen-derived light gas oil (1.60 wt% S) [20].

Therefore, a series of pyrolyses was carried out in which high-S shale oils, not deasphalted or distilled, were hydropyrolysed after being mixed with NiMo deposited on Al-SBA-15 of different Si/Al ratios in flow-through and autoclave experiments, to explore whether this support would be useful in HDS of high-sulfur shale oil under appropriately chosen pyrolysis conditions (temperature, H_2 pressure, time, catalyst:oil ratio). These catalysts are also useful in HDN so this effect was also investigated. Two shale oils from shales with sulfur in different forms, organic (El-Lajjun) and half inorganic-half organic (Julia Creek) were studied [21], to see whether this made any difference to the results.

2. Materials and methods

2.1. Materials

Oil shale from the El-Lajjun deposit in the Karak region in Jordan was obtained from Jordan Energy and Mining and oil shale from the Julia Creek deposit, Queensland, Australia was provided by Extract Oil (Global Oil Shale).

H_2 and N_2 were supplied by BOC. HPLC grade tetrahydrofuran (THF) was purchased from Fischer Chemical.

For catalyst support (Al-SBA-15) synthesis, non-ionic triblock poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) copolymer ($EO_{20}PO_{70}EO_{20}$, PEG- PPG-PEG, Pluronic (P_{123}) Aldrich, average molecular weight ca. 5800 g/mole) was the templating agent. Analytical grade tetraethyl orthosilicate (TEOS) and aluminium isopropoxide from Aldrich were the silica and aluminium sources respectively. Dilute HCl solutions were mixtures of deionized H_2O and analytical grade 32% HCl sourced from Ajax Finechem Pty Ltd. For catalyst (NiMo-Al-SBA-15) synthesis, ammonium heptamolybdate was provided by Merck and nickel acetate was purchased from Sigma-Aldrich.

2.1.1. Support and catalyst preparation

2.1.1.1. Preparation of Al-SBA-15 supports. Approximately 33.6 g of TEOS and variable amounts of aluminium isopropoxide (depending on the Si/Al ratio required) were dissolved in 80 mL of dilute aqueous HCl solution (3.3 mL concentrated HCl in 1 L deionised H_2O) and the pH value of the solution was changed to 1.5 with the dilute HCl. The solution was stirred for 3 h. This solution was then added dropwise to another solution containing 16.0 g of P_{123} dissolved in 600 mL of dilute (0.03 M) HCl solution. The pH of the mixed solution was adjusted to 1.5 with the dilute HCl and the mixture stirred at 40 °C for 20 h. The solution was then aged in a sealed container for 48 h at 100 °C under N_2. The final mixture was then filtered, washed with ultrapure water, left to stand overnight in air to dry and then heated in air at 600 °C for 5 h to burn off the organic template [2,22,23].

2.1.1.2. Preparation of NiMo-Al-SBA-15 catalysts. The wet impregnation method was used to introduce NiMo into Al-SBA-15. 0.2 g of nickel acetate ($Ni(CH_3CO_2)_2$·4 H_2O) and 0.35 g of ammonium heptamolybdate (($NH_4)_6Mo_7O_{24}$. $4H_2O$) were dissolved in 20 mL deionised water and the resulting solution was added to 1.5 g of calcined Al-SBA-15. The final mixture was left to stir about 12 h at ambient temperature. After stirring, water was removed firstly in a stream of N_2 at ambient temperature and secondly by oven drying at 105 °C under N_2. The solid remaining was heated in air at 500 °C for 5 h. The resulting catalyst containing 3 wt% Ni and 12 wt% Mo was kept in a sealed container and dried at 105 °C under N_2 immediately before each experiment [23].

2.1.2. Support and catalyst analysis

X-ray diffraction (XRD) measurements for the NiMo-Al-SBA-15 catalysts with different Si/Al ratios utilized a Bruker D8 apparatus operating at 40 kV and 40 mA with Cu Kα (Λ = 1.54060 Å) radiation. XRD patterns were collected at a scanning speed of 0.02°/s, step size of 0.01°/s over a 2θ range of 5-80° using a coupled 2θ/θ scan type.

Small angle X-ray scattering (SAXS) patterns for Al-SBA-15 supports and NiMo-Al-SBA-15 catalysts with different Si/Al ratios were recorded using a Bruker N8 SAXS instrument operating at 50 kV and 1.0 mA with Cu Kα (Λ = 1.54060 Å) radiation over a 2θ range of 0.22–5.2° using the 2θ scan type. Structural parameters were calculated from the SAXS patterns by the method of Gommes [24] and also from N_2 take up at 77 K [25].

2.2. Production of raw shale oil

The raw shale oil (THF soluble fraction) was produced by pyrolysis of El-Lajjun or Julia Creek oil shale using a 100 mL sealed autoclave. The autoclave was charged with 20.0 g of < 0.180 mm representative, ground and dried (105 °C, N_2) sample. The autoclave was sealed, evacuated and pressurized with 3 MPa N_2 (cold). The autoclave was immersed in a sand bath which had been heated to 400 °C. The autoclave temperature could be measured by a thermocouple inserted into a thermal well in the cap. The autoclave was shaken for one hour, then removed from the bath and cooled to ambient temperature. The sample was washed out of the autoclave with THF and suspended in an ultrasonication bath for 10 min. The liquid THF soluble products were filtered off and ultrasonication/filtration repeated till nearly all soluble material had been extracted. The THF soluble fraction was used in the catalytic and non-catalytic hydropyrolysis experiments using flow-through and sealed autoclave techniques.

2.3. Catalytic hydropyrolysis using a flow-through system

In flow-through hydropyrolyses, 1.5 g of Al-SBA-15 support or NiMo-Al-SBA-15 catalyst was mixed with 1.0 g of shale oil and then placed inside a 40 mL stainless steel cage supplied with a fritted top and bottom to permit a sweep gas to flow through the oil/catalyst mixture. The stainless steel cage was placed inside a 70 mL Inconel autoclave with an inlet sweep gas line connected to the bottom. The sweep gas, at room pressure, was controlled by mass flow controllers which could manage gas flow rates from 10 to 500 mL/min. The autoclave inlet line at the bottom was connected to two valve-controlled gas flow lines, each for a specific gas. The outlet at the top of the autoclave was joined to a line covered with heating tape whose temperature was set by a controller at 10–15 °C above the autoclave temperature. The volatile product passed through this outlet line with the sweep gas into three glass condensers in series, each cooled by a dry ice-acetone bath. After the third condenser, the non-condensed gas was exhausted and vented to a fume cupboard.

Prior to the reaction, the autoclave was connected to the lines and moved to be above the sand bath, which had been preheated to obtain the required reaction temperature. The sweep gas began to pass through the autoclave. Heating of the outlet line began 30 min before the reaction was due to start. After the sand bath and the outlet line had reached their pre-assigned temperatures, the autoclave was moved down into the sand bath. The autoclave was heated to the reaction temperature in 10 min and was held at temperature to the end of the reaction (The difference between autoclave and sand bath temperature had been determined by preliminary experiments). The sweep gas flow rate was gradually raised as the autoclave was heated; the sweep gas flow rate, initially 100 mL/min, was lowered to 50 mL/min when the autoclave temperature had climbed to 250 °C, and to 25 mL/min when the autoclave was at 350 °C. The flow rate was then kept constant as long as flow continued. After 1 h, the autoclave was moved up clear of the sand bath and allowed to cool to ambient temperature. Sweep gas flow and outlet line heating were maintained until the temperature of the autoclave was only 100 °C. The three condensers were taken out from the lines and weighed and the residues in the flow through lines