

学 位 論 文 の 要 旨

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学位論文題目	Efficiently catalytic hydrotreatment of shale oil and its process design (シェールオイルの水素化処理触媒の性能向上とそのプロセス設計)		
<p>学位論文要旨</p> <p>With the massive consumption of petroleum and other fossil energy, crude oil shortage becomes an unprecedented challenge worldwide. Heavy oils generated from the unconventional energy resources such as biomass, oil shale and oil sand as the potentially alternative “new blood” are expected to solve the current dilemma owing to the abundant reserves and wide sources of raw materials in the world. Especially, the shale oil, which exists in many parts of the world. However, high viscosity, low heating value and high content of heteroatomic compounds seriously hinder its direct application as feedstocks/blend stocks for many existing crude oil refinery plants. Therefore, it is necessary to upgrade those low-quality feedstocks to meet refinery specifications. This study mainly focuses on the upgrading process design and preparation of novel catalysts for upgrading of shale oil by hydrotreatment.</p> <p>Firstly, a Ni-Mo/Al₂O₃ catalyst was sulfided and used for the continuous catalytic hydrotreatment of shale oil for its upgrading in a fixed bed reactor. With the hydrodesulfurization (HDS), the shale oil got an obvious improvement in its heating value and viscosity, and at the same time, 84.6% of sulfur was removed from the shale oil with a yield of upgraded oil as high as 96.2% under the optimal catalytic HDS conditions at a liquid hourly space velocity (LHSV) of 4 h⁻¹, a temperature of 380 °C, an H₂/oil volume ratio of 600:1, and a pressure of 4 MPa. After 5 times of recycling, the spent catalyst still maintained good activity. The upgraded shale oil met the quality requirement of national standard for Marine fuel oil requiring sulfur content below 0.5 wt%. In an attempt to investigate the influence of reaction media, the H₂ gas stream was mixed with N₂/CO₂ as an inert carrier gas for the hydrotreatment reaction. The results suggested that with the increase of CO₂ concentration in the gas feed from 5 to 20%, the sulfur removal ratio was stable. A conceptual process was finally proposed by coupling a high-pressure operation methanol reforming unit and the tested high-pressure HDS upgrading reactor, which can provide low-cost hydrogen source for industrial upgrading processes.</p> <p>Then, a two-stage system by coupling methanol steam reforming (MSR) for on-line hydrogen production and HDS of shale oil as shown in Figure 1(a) was proposed. In the first stage,</p>			

methanol-water mixture was pumped into a MSR reactor with Cu-Zn/Al₂O₃ catalyst for producing compressed H₂-rich gas. Then, the generated gas without purification was transported into the second stage to participate the following HDS process with Ni-Mo/Al₂O₃ catalyst. The MSR over a commercial Cu-Zn/Al₂O₃ catalyst reached a conversion over 95% with H₂ selectivity of 100% under a volumetric space velocity (liquid) of 1.0 h⁻¹, a temperature of 360 °C and a pressure of 4 MPa, and enabled a wide operation window to match the downstream hydrotreatment of shale oil. As a result, in the upgraded shale oil, the sulfur content was reduced to about 4200 ppm in the presence of the sulfided catalyst Ni-Mo/Al₂O₃, which met the requirement of the national standard of Marine fuel oil. A long-term continuous operation of the integrated process at a laboratory level verified its technical feasibility. This direct coupling technology not only simplifies the process to achieve high energy efficiency but also increases the process safety by avoiding transportation and storage of H₂, which can lead a fundamental new process for shale oil upgrading.

Finally, two Ni-Mo/Al₂O₃ catalysts with the identical Ni-Mo component composition were prepared in this study for shale oil HDS by calcining the same wet-impregnated catalyst precursor using different heating modes. One is by fast heating of infrared radiation and another is via slow heating in a conventional electric heater (Figure 1(b)). The catalytic performances of the catalysts were compared at various reaction conditions of temperatures varying from 320 to 400 °C, pressures from 1.0 to 4.0 MPa, H₂/oil (v/v) ratio from 200:1 to 600:1 and LHSV from 1 to 4 h⁻¹. Under all tested conditions, the catalyst prepared by using the infrared heating method always yielded a product oil having the lower sulfur content than the catalyst prepared by heating with the conventional furnace. At the optimal condition of T = 380 °C, P = 4 MPa, H₂/oil (v/v) = 600:1 and LHSV = 4 h⁻¹, the infrared-heating catalyst enabled the oil to decrease its sulfur content to 2600 ppm, which thus met the national Marine fuel oil standard. Characterizations of the fresh, sulfided and spent catalysts showed that the catalyst prepared with the infrared heating had the higher BET surface area, smaller and narrower size distribution of metal particles, higher binding energy between Mo and S, and more oxygen-deficient sites in comparison with the catalyst prepared using conventional electric heating.

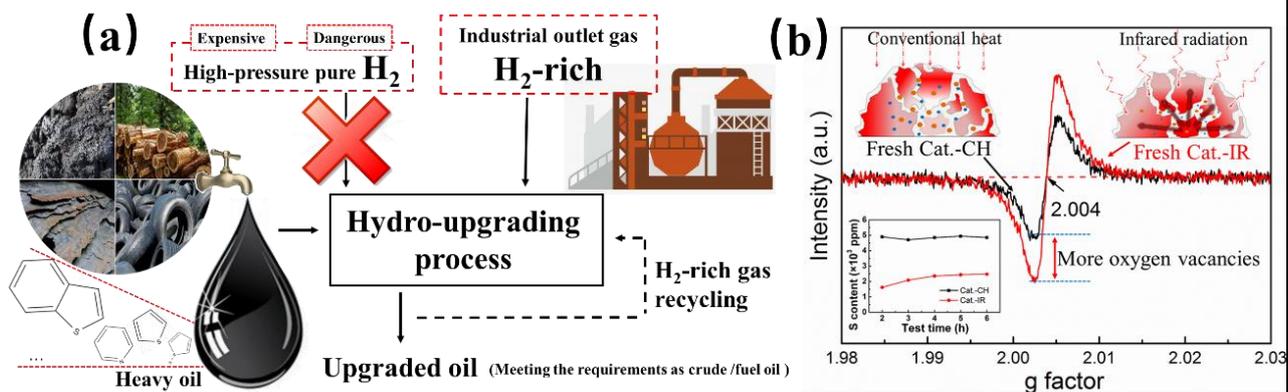


Figure 1 Schematic diagram of (a) implementation of heavy oil upgrading with CO₂-H₂ gas and (b) conventional and infrared radiation heating for fresh Cat.-CH/IR