

Catalytic desulfurization of residual oil through partial oxidation in supercritical water

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Abstract

Catalytic desulfurization of a model sulfur-containing compound benzothiophene (BT) through partial oxidation in supercritical water (SCW) was investigated in a bomb reactor at 623–723 K and 30–40 MPa over sulfided $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$. Vacuum residuum was used to confirm the desulfurization rate and efficiency, and the desulfurization mechanism of vacuum residuum was determined by the pyrolysis temperature (T_R) of the vacuum residuum (VR). For $T > T_R$, obvious reduction of sulfides up to 67% was obtained. The thermodynamic equilibrium of in situ H_2 generation was a controlling factor of the desulfurization pathway.

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1. Introduction

As a cheap and environmentally benign medium for organic reactions, supercritical water (SCW) has been paid with high attention in the field of chemical reaction engineering, as has been surveyed by Savage in his excellent review [1]. In the recent years, much work has been done focusing SCW with application into the field of energy and fuel processing [2,3]. Among these studies, pyrolysis of residual oil in SCW has been regarded as an example of one of the most promising attempts which is in comply with the increasing demand for light fuel and also with the inevitable trend of processing low-grade crude oil [4–6].

NMR measurement shows that when high molecular weight hydrocarbons crack in SCW, the hydrogen originated from the water may be donated to the cracking products [7–9]. Therefore, the H/C ratio of the cracking reaction is balanced and coke generation is suppressed. Kishita and Takahashi [10] performed bitumen pyrolysis in SCW to obtain a high yield of light oil up to 85%, and coking was evidently restrained. After pyrolysis in SCW, the light products of residual oil are more suitable for the FCC feedstock due to their reasonable

H/C ratio and viscosity. However, there exist a large variety of sulfides (mainly homologues of thiophene) in the residual oil, and the reduction of these refractory sulfides by SCW alone is marginal [11]. When these light products are fed into the FCC unit, massive sulfides go together into the cracked oils, so to make downstream hydrotreatment of cracked oils inevitable. Therefore, when conducting residual oil pyrolysis in SCW, it is strongly desirable that most sulfides need to be removed simultaneously. Adschiri and co-workers [12,13] introduced O_2 into the SCW/hydrocarbon system, and found that dibenzothiophene (DBT) could be removed effectively in the presence of $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ as the catalyst. The desulfurization mechanism implying partial oxidation of hydrocarbons, followed by water–gas shift (WGS) reaction and hydrogenation of sulfide (HDS) was also suggested [12]. The pathway described in Adschiri's work provides a helpful idea of coupled pyrolysis and desulfurization of residual oil in SCW.

To distinguish the difference in desulfurization rate and reaction mechanism between a model compound benzothiophene (BT) and a real sample of vacuum residuum (VR), a benzothiophene (10 wt.%)–heptane solution and a vacuum residuum were used in this work. Experiments were carried out under an SCW oxidation (SCWO) environment in the presence of $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

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2. Experimental

2.1. Apparatus and reaction runs

A bomb reactor with a capacity of 10 ml was used in the batch operations. The main body of the reactor was 11.5 mm i.d. and constructed of 316L stainless steel. A needle valve was connected at one side. A molten salt bath of a temperature control precision of ± 0.2 K was used to heat the reactor.

Experiments were conducted within a temperature range of 623–723 K and pressure range of 30–40 MPa. The catalyst and reactants were loaded into reactor in turn, and then the reactor was sealed and submerged into the molten salt bath. When a preset reaction time was reached, the reactor was quenched in a water bath to remove products by washing with chloroform (for BT) or toluene (for VR). The loaded catalyst for each run was 1 g, and was placed at the middle of the reactor. The P – V – T properties of mixed reactants under high temperature and pressure were predicted through a flash process using *Aspen Plus* 11.1. The PR-BM equation of state was applied for the prediction.

Benzothiophene of 95 wt.% purity was purchased from Fluka Chemie Co. The vacuum residuum of 2.3 wt.% sulfur content was obtained from SINOPEC Shanghai Petrochemical Company Limited, with a distillation range of 623–803 K. CoMo supported on γ -Al₂O₃ was prepared by impregnation. Before each run, the catalyst was sulfided in a CS₂ (5 vol.%)–heptane–H₂ gas stream at a total flow rate of 50 Nml/min in a temperature range of 463–623 K and under the atmospheric pressure.

2.2. Analytical procedures

For experiments of BT runs, components contained in the liquid product were determined by MS-GC (Micromass GCT CA055), and their concentrations were analyzed by GC-FID (HP 6890). The conversion of BT was determined on benzene structure basis. For experiments of VR runs, a microcoulometric detector (WK-2D) was employed to determine the total sulfur content in the product. Both fresh and spent catalysts were characterized through XRD (Rigaku D/max 2550 VB/PC) and BET analysis (Micromeritics Instrument Corp., ASAP 2010).

3. Results and discussion

Prior to desulfurization, the stability of catalyst in an SCWO environment was examined. It was found that γ -Al₂O₃ transformed into boehmite rapidly in the pure SCW, and its surface area and average pore diameter changed by one or two orders of magnitude within 1 h. Such a situation was improved only when the SCW/hydrocarbon ratio was reduced to a certain value. At the SCW/hydrocarbon ratio applied in this work, the crystal structure of γ -Al₂O₃ was maintained. Because of the exposure to oxidation environ-

ment in the initial reaction stage, some complex compounds such as CoMoO₄ and CoMoS_{2.96}O_{0.25} were detected after 1 h desulfurization, indicating loss of catalyst activity.

3.1. Desulfurization of the model compound

Hydrogen peroxide forms in the SCWO environment [14], so direct oxidation of thiophene ring into sulfoxide using hydrogen peroxide and carboxylic acid can be another desulfurization method. The possibility of direct oxidation of BT was carefully checked under all the experimental conditions, but only ethyl benzene (EB) and toluene were detected in the liquid products after desulfurization. No sulfoxide compound, even in a trace amount was found. Evidently, BT was reduced through hydrogenation, therefore direct oxidation mechanism was not considered hereafter.

3.1.1. Effect of reaction temperature

Fig. 1 shows that the reaction temperature played an important role in desulfurization kinetics. BT conversion versus reaction time presented some autocatalytic property. At 623 K, reduction of BT remained almost negligible. However, with elevation of the reaction temperature, particularly at 723 K, the BT conversion increased rapidly along with reaction time.

According to the reaction pathway suggested by Adschiri et al. [12], the desulfurization of hydrocarbons through catalytic SCWO consists of two consecutive steps: in situ H₂ generation and HDS (Fig. 2).

The hydrogenation kinetics of BT or DBT is usually expressed in Langmuir–Hinshelwood type rate equations [15,16]. Despite the different postulates about inhibiting effects on HDS rate are made, the developed rate equations are similar. Ishihara and co-workers [17,18] reported that, for HDS the adsorption heat of sulfides was significantly af-

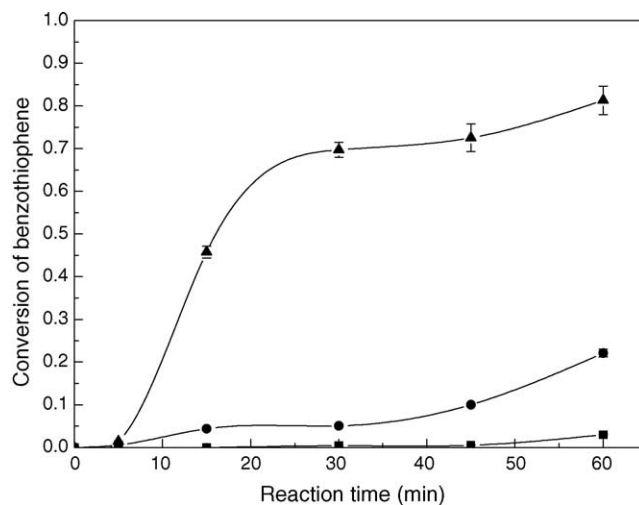


Fig. 1. BT conversion vs. reaction time at different reaction temperatures; $p = 40$ MPa, $C_7H_{16}:H_2O:O_2 = 1:12.1:0.7$ (mol), CoMo/ γ -Al₂O₃; reaction temperatures: (■) 623 K, (●) 673 K and (▲) 723 K.

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