

Catalytic denitrogenation of hydrocarbons through partial oxidation in supercritical water

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Abstract

In this work, the denitrogenation of hydrocarbons under supercritical water oxidation environment was investigated in a rotated bomb reactor at 623–723 K and 25–35 MPa over sulfided NiMo catalyst. Quinoline was used as a model nitrogen-containing compound. A high reduction of total nitrogen up to about 85% was obtained. The denitrogenation pathway is composed of two consecutive steps: in situ H₂ generation and the hydrogenation of quinoline. The hydrogenation mechanism of quinoline varies with reaction temperature because of the participation of supercritical water in HDN step. The strong adsorption of quinoline and its hydrogenation intermediates on catalyst surface has an adverse influence on total nitrogen reduction rate.

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1. Introduction

As an environmentally benign solvent for organic reactions, the application of supercritical water (SCW) in the field of chemical engineering has been emphasized for many years. However, most studies relating to SCW still focus on the fundamental aspects, only very limited industrial practice has been touched. In recent years, the application of SCW into residual oil process becomes a promising attempt which complies with the strict environmental protection requirement and the increasing demand for light oil consumption [1–3].

Water may act as a hydrogen donor in its supercritical region. When conducting hydrocarbons pyrolysis in SCW, the hydrogen originated from H₂O will participate in the pyrolysis reaction [4,5]. In a way, the H/C ratio of pyrolysis is balanced and the coke generation is suppressed. Kishita and Takahashi [6] performed bitumen pyrolysis in SCW to obtain a high yield of light oil up to 85%, with effectively suppressed coking. After pyrolysis in SCW, the cracked residual oil possessing reasonable H/C ratio and viscosity is

more suitable as the feedstock for FCC unit. However, the majority of heteroatom-containing compounds of crude oil, especially nitrogen-containing compounds, still exist in the residual oil. They are harmful not only to the acid FCC catalyst, but also to the stability of cracked oil. It is strongly desired that most nitrogen-containing compounds be removed when processing residual oil in SCW, but the reduction of refractory heteroatom-containing compounds through SCW process is marginal [7].

Adschiri and co-workers introduced O₂ into the SCW/hydrocarbons system, and found that dibenzothio-*phene* was removed effectively in the presence of sulfided NiMo/ γ -Al₂O₃ [8]. The desulfurization pathway was suggested to be partial oxidation of hydrocarbons, a water-gas shift (WGS) reaction and hydrogenation of sulfides (HDS) in series. Following this method, a reduction of sulfur-containing compounds up to 67% in residual oil was obtained in authors' previous work [9]. Difficult though the hydrodenitrogenation (HDN) is, the authors supposed that the same technique may be valid to the removal of nitrogen-containing compounds in hydrocarbons. With the simultaneous reduction of heteroatom-containing compounds, it is more feasible to process residual oil in SCW.

This paper focuses on the characteristic of denitrogenation of model nitrogen-containing hydrocarbons through catalytic SCW oxidation (SCWO), trying to provide some fundamental

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information for the further research on processing real residual oil sample in continuous operation mode.

2. Experimental

2.1. Materials and methods

The experiments were conducted in the range of temperatures 623–723 K and pressures 25–35 MPa over sulfided NiMo/ γ -Al₂O₃. A bomb reactor constructed of 316 L stainless steel with a capacity of 10 ml was used in the batch operations. An adjustable speed motor was used to drive the reactor within which two previously placed stainless steel balls served as the agitator. After loading the catalyst and reactants, the reactor was sealed and submerged into a molten salt bath controlled at a precision of ± 0.2 K. During experiment, the reactor rotated with a given speed. At the very moment of preset reaction time, the reactor was quenched in a water bath and the liquid products were flushed out using chloroform.

The model nitrogen-containing hydrocarbons used in denitrogenation were a mixture of quinoline/benzene/heptane in a fixed mole ratio of 1.0/4.5/8.1, and part of heptane was oxidized in denitrogenation. Quinoline of analytical purity was obtained from Shanghai Tingxin Chemical Reagent Plant. 1,2,3,4-tetrahydroquinoline of 98 wt% purity and 5,6,7,8-tetrahydroquinoline of 95 wt% purity for analytical standard were purchased from Acros Organics and Tokyo Kasei Kogyo Co. Ltd, respectively.

The *P-V-T* properties of reactants were predicted by a phase equilibrium calculation using the Peng-Robinson EOS, which suggested the proper operation conditions for the experiment to be carried out in a single phase. Table 1 lists the loadings of reactants in experiments.

2.2. Catalyst preparation

NiMo/ γ -Al₂O₃ containing 12 wt% MoO₃ and 2.2 wt% NiO was prepared by sequential impregnation. Before using, the catalyst was sulfided in a CS₂ (5 vol%)-

heptane-H₂ gas stream at a total flow rate of 50 Nml/min in a range of temperatures 463–623 K and at atmospheric pressure.

2.3. Analytical procedures

Components in liquid product were determined by MS-GC (Micromass GCT CA055), and their concentrations were analyzed by GC-FID (HP 6890). Both fresh and spent catalysts were characterized by XRD (Rigaku D/max 2550 VB/PC), BET (Micromeritics Instrument Corp, ASAP 2010) and ICP-AES analysis (Baird PS-6). Since quinoline and its hydrogenation intermediate tetrahydroquinoline are main precursors resulting in instability of hydrocarbons, the evaluation of denitrogenation efficiency was based on the total nitrogen reduction as well as quinoline reduction, their definitions are as follows:

Quinoline reduction

$$= \left(1 - \frac{\text{recovered amount of quinoline (mol)}}{\text{loaded amount of quinoline (mol)}} \right) \times 100[\%] \quad (1)$$

Total nitrogen reduction

$$= \left(1 - \frac{\text{recovered amount of quinoline and tetrahydroquinoline (mol)}}{\text{loaded amount of quinoline (mol)}} \right) \times 100[\%] \quad (2)$$

3. Results and discussion

3.1. Denitrogenation pathway

Quinoline and its hydrogenation intermediates can be easily hydrogenated with hydrogen radicals formed through hydrocarbons reforming in SCW; in addition, they may be reduced by the pyrolysis as well as direct oxidation under SCWO environment. In order to evaluate the contribution of above three factors to the denitrogenation, blank experiments employing quinoline-containing hydrocarbons and deoxygenated water, and blank experiments employing quinoline-containing hydrocarbons, water and oxygen were conducted respectively at 723 K and 35 MPa. After 1 h reaction, only small quantities of intermediates of quinoline hydrogenation appeared in the liquid products, and the quinoline reduction in each blank run was always less than 5%. Since the blank experiments covered the most critical reaction conditions of the following denitrogenation, the contribution of hydrocarbons reforming, pyrolysis and direct oxidation to the denitrogenation under SCWO environment was hereby neglected.

For the denitrogenation method performed in this work, nearly all the intermediates of quinoline hydrogenation in

Table 1
Loadings of reactants in experiments

No.	Reaction conditions		Loadings of reactants	
	<i>T</i> (K)	<i>p</i> (MPa)	$\rho_{\text{H}_2\text{O}}$ (g/cm ³)	C ₇ H ₁₆ /O ₂ (mol)
1	623	35	0.256	1.00/0.55
2	673	35	0.185	1.00/0.55
3	723	35	0.140	1.00/0.55
4	673	35	0.193	1.00/0.28
5	673	35	0.177	1.00/0.83
6	698	25	0.103	1.00/0.55
7	698	35	0.159	1.00/0.55

The mole ratio of quinoline/benzene/heptane/water was fixed at 1.0/4.5/8.1/142.1.

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