

Hydrodenitrogenation of Carbazole and Quinoline over a Nano-Dispersed Mo Sulfide Catalyst Using *In Situ* Hydrogen

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Introduction

Bitumen derived from oil sands is becoming an important resource of energy and transportation fuels due to the depletion of conventional oil resources. Canada has large reserves of bitumen and heavy oil which play an increasingly important role in supplying the need for transportation fuels. However, bitumen and heavy oils have a low H/C ratio and contain a large percentage of S- and N-heterocyclic compounds. For producing environmentally friendly transportation fuels, the maximum amount of sulfur is legislated to be as low as 50 ppm in diesel fuel in 2005 and will probably be reduced further by 2010 [1]. At the level of deep desulfurization, aromatic polynuclear molecules, especially N-containing heterocyclic compounds, exhibit strong inhibiting effect on HDS due to competitive adsorption on active sites of the catalyst [2,3]. Therefore, removal of N-heterocyclic compounds from the feedstocks will help to achieve ultra low S specification for transportation fuels. We have developed a process for upgrading heavy oil and bitumen emulsions using the water gas shift reaction to generate *in situ* hydrogen via nano dispersed Mo sulphide catalysts [4]. We recently found that the nano dispersed Mo sulfide catalyst was effective in the hydrodesulfurization (HDS) of refractory sulphur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) in the presence of benzothiophene (DBT), however, nitrogen compounds such as quinoline and carbazole are found to be strong inhibitors for the HDS reactions. The present study will focus on the hydrodenitrogenation (HDN) activity of the nano dispersed Mo sulfide using *in situ* H₂ generated via the water gas shift reaction.

Materials and Methods

The HDN experiments using the dispersed Mo sulfide catalyst with *in situ* H₂ were carried out in a 300 ml SS batch Autoclave reactor at 380°C. The model compound, basic quinoline or non-basic carbazole, was dissolved in toluene, and the Mo precursor was dissolved in de-ionized water. After these solutions were transferred into the reactor vessel, the reactor was sealed and purged three times with N₂ to remove O₂ from the solution, and then was purged three times with the reactant gas CO. 600 psi of the reactant gas mixture of H₂S/CO (1.7mol% of H₂S) was introduced into the reactor vessel, and then the reactor was heated up to the designated temperature at a rate of 2~3 °C/min. The reaction system was maintained at the reaction temperature for a certain time. After the reaction, the HDN products were identified by a Varian GC-MS and the quantitative analysis was carried out with a GC (Varian CP-3800) equipped FID and S (PFPD) and N (TSD) specific detectors

Results and Discussion

The reaction network for HDN of quinoline using supported Mo catalysts has been established [5], wherein quinoline was denitrogenated to produce propylcyclohexane, propylbenzene, propylcyclohexene via hydrogenation of the aromatic ring and the

heteroatomic ring. We also found similar HDN products in our reaction system [6] suggesting similar mechanism for HDN of quinoline as that reported for the supported Mo catalysts.

The mechanism for HDN of carbazole was less well documented in the literature. The HDN products of carbazole found in our reaction are shown in Fig.1, wherein dicyclohexyl (DCH), cyclohexylbenzene (CHB), hexylcyclohexane (HCH), and hexylcyclohexene (HCHE) were identified by GC-MS and quantitatively analyzed by GC. The results indicated that the ring-opened products, HCHE and HCH, were predominant over the two-ring products, DCH and CHB. A proposed HDN reaction network for carbazole in our reaction is shown in Fig. 2.

Interestingly, different effects of the refractory sulfur compounds, DBT and 4,6-DMDBT, on N-removal from the basic quinoline and non-basic carbazole were observed. The denitrogenation of quinoline was increased by 5 mol% in the presence of DBT and 4,6-DMDBT, while the N-removal from carbazole was slightly inhibited by 4,6-DMDBT. The preliminary experiment results also indicated that the presence of 4,6-DMDBT increased the selectivity of ring-opened products obtained from HDN of carbazole. This paper will discuss the kinetics and mechanism for HDN of carbazole and quinoline and the effect of the refractory sulfur compounds on HDN using the dispersed Mo sulfide catalyst and *in situ* H₂.

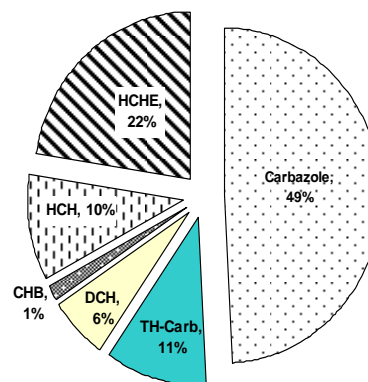


Figure 1. HDN product distribution of carbazole

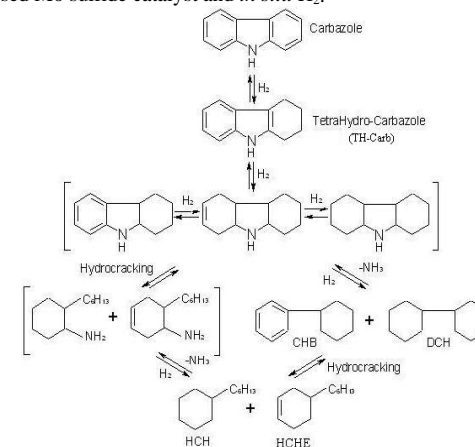


Figure 2. Proposed HDN reaction network of Carbazole

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