

# Development of $\text{FeN}_4/\text{C}$ And $\text{FeN}_2/\text{C}$ Catalysts for Hydrodesulfurization and Hydrodearomatization of Model Compounds of Heavy Oil

Chaojie Song, Lianhui Ding, Craig Fairbridge, Hansan Liu, Rob Hui, JiuJun Zhang

**Abstract**—Two novel hydrodesulfurization (HDS) catalysts:  $\text{FeN}_4/\text{C}$  and  $\text{FeN}_2/\text{C}$ , were prepared using an impregnation-pyrolysis method. The two materials were investigated as catalysts for hydrodesulfurization (HDS) and hydrodearomatization (HDA) of model compounds. The turnover frequency of the two FeN catalysts is comparable to ( $\text{FeN}_4/\text{C}$ ) or even higher ( $\text{FeN}_2/\text{C}$ ) than that of  $\text{MoNi}/\text{Al}_2\text{O}_3$ . The  $\text{FeN}_4/\text{C}$  catalyst also exhibited catalytic activity toward HDA.

**Keywords**—catalyst,  $\text{FeN}_2/\text{C}$ ,  $\text{FeN}_4/\text{C}$ , HDS, HDA

## I. INTRODUCTION

BECAUSE of the high sulphur and aromatics contents of petroleum derived from Canadian oil sands, high conversion upgrading and refining processes are required. Standard hydrotreating catalysts such as  $\text{NiMo}/\text{Al}_2\text{O}_3$  are designed for light to medium crude oils. These catalysts could have critical limitations, such as low selectivity, when operated at more severe reaction conditions leading to higher energy consumption. Thus, new catalysts with higher activity, selectivity, and stability are needed to produce fuels from future crude petroleum supplies as the average crude sulphur content, density and viscosity increase over the next decades.

Iron based catalysts have been used for coal liquefaction [1]. Due to the similarities between chemical reactions in coal liquefaction and heavy oil upgrading, iron-based catalysts might be suitable for heavy oil upgrading. The commonly studied iron catalysts include iron oxides, iron sulphide and iron carbonyl [1]-[3]. These low cost, Fe-based catalysts are more feasible than Mo based catalysts for coal liquefaction. However, their catalytic activity is lower and they are often used as small particles in slurry reactors requiring separation and disposal downstream. Clark reported the use of an iron

aqueous solution for bitumen upgrading, which minimized the formation of insoluble products and lowered the viscosity to give a product suitable for direct pipeline transportation [4]. Further upgrading is necessary. Ovalles *et al.* used a dispersed iron catalyst for extra heavy oil upgrading; the sulfur content was reduced by 14%, and the crude oil viscosity was reduced by two orders of magnitude, but, a significant amount of coke was formed [5].

$\text{FeN}_4/\text{C}$  and  $\text{FeN}_2/\text{C}$  catalysts, usually prepared by an impregnation-pyrolysis method, are well known non-noble metal catalysts for fuel cells [6],[7]. The exact structure of these materials is not clear, it is dependent on the heat treatment temperature.  $\text{FeN}_4/\text{C}$  is usually considered to form below  $700^\circ\text{C}$ , and  $\text{FeN}_2/\text{C}$  above  $700^\circ\text{C}$  [7]. To the best of our knowledge, the use of these FeN/C catalysts as hydrotreating catalysts has never been reported. It is therefore worthwhile to investigate the catalytic activity of these FeN/C catalysts toward upgrading reactions.

In this work, iron phthalocyanine, a catalyst known to be active toward the oxygen reduction reaction, was selected as the FeN precursor, and Vulcan carbon XC-72, a widely used support in fuel cell catalysts, was selected as the support. The iron phthalocyanine was loaded onto the carbon using a wet impregnation method followed by heat treatment at  $700$  and  $900^\circ\text{C}$  for preparation of the  $\text{FeN}_4$  and  $\text{FeN}_2$  samples, respectively. Physical characterization techniques, including scanning electron micrograph (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and specific surface area, were used for materials characterization. Their catalytic activities toward HDS and HDA were evaluated using model compounds.

## II. EXPERIMENTAL

### A. Materials

Vulcan carbon XC-72 was purchased from Cabot. A commercial  $\text{MoNi}/\text{Al}_2\text{O}_3$  catalyst was used for comparison. Iron phthalocyanine and all other chemicals were purchased from Aldrich. All materials were used as received.

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### B. Preparation of FeN/C catalysts

The FeN/C catalysts were prepared as described in the literature [8]. Typically, 10 g of Vulcan carbon was dispersed in 200 mL tetrahydrofuran (THF) under stirring followed by ultrasonication for 1 h. Then 25 mL THF solution containing 1 g of iron phthalocyanine, corresponding to a Fe:C weight ratio of 1:100, was added to the suspension, and the mixture was stirred overnight. The solvent was removed by evaporation at room temperature, resulting in a dry powder that was then divided into two parts for heat-treatment (5.5 g each).

Dry powder (5.5 g) was heat-treated at 700°C (or 900°C) in a horizontal alumina tube under a continuous flow of nitrogen (Praxair, purity: 99.9999%, flow rate: 140 mL/min) for 2 h. Prior to heat-treatment, the tube was flushed with N<sub>2</sub> for 1 h to remove air. The heating rate was 5°C/min. After the tube furnace cooled down to room temperature in flowing nitrogen, the sample was removed, and subjected to physical characterization and model compound testing. The samples prepared by the impregnation-pyrolysis method are designated as FeN<sub>4</sub>-C-7 (pyrolyzed at 700°C), and FeN<sub>2</sub>-C-9 (pyrolyzed at 900°C).

### C. Physical characterization of the samples

The morphologies of these samples were observed with a scanning electron microscope (SEM, Hitachi S-3500N) operated at 20 kV. EDX was conducted using an Oxford EDX system. The X-ray diffraction (XRD) measurements were carried out with a Bruker D8 X-ray diffractometer equipped with a graphite monochromator and a vertical goniometer, using Cu-K $\alpha$  radiation. Specific surface area measurement was carried out using the BET method in a surface area analyzer (SA3100, Beckman Coulter).

### D. Catalytic activity tests

The FeN<sub>4</sub>-C-7 and FeN<sub>2</sub>-C-9 catalysts were evaluated in a 300mL autoclave reactor (PP-11). Before testing, the catalysts (1 g) were sulfided with dimethyl disulfide (DMDS) (5 mL) at 350 °C for 1 h according to a procedure described in the literature [9]. Then 100 g solution containing the model compound was loaded into the autoclave under N<sub>2</sub> protection. After purging with N<sub>2</sub> and H<sub>2</sub>, the reactor was pressurized with H<sub>2</sub> to 500 psi. Under stirring at 600 rpm, the reactor was heated to 300°C and kept there for 1h; then cooled down to room temperature. The liquid sample was analyzed by gas chromatography–mass spectrometry. For comparison, a commercially available MoNi/Al<sub>2</sub>O<sub>3</sub> was also tested.

## III. RESULTS AND DISCUSSION

### A. Physical characterization of the FeN/C catalysts

Fig. 1 shows SEM micrographs of FeN<sub>4</sub>-C-7. The particles are irregularly shaped, and present a wide size distribution (Fig. 1A). The surface of the particles is not smooth: a significant number of pores with a diameter of ~150 nm were observed (Fig. 1B). Similar morphologies were also observed

for FeN<sub>2</sub>-C-9.

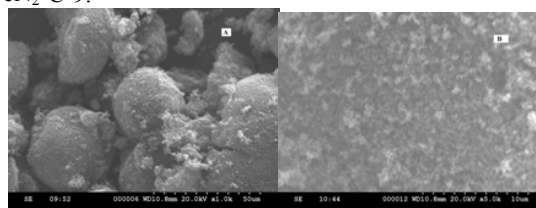


Fig. 1 SEM micrographs of FeN<sub>4</sub>-C-7 pyrolyzed at 700°C (A) 1000x magnification, and (B) 5000x magnification

EDX results showed that the Fe content for the two samples was about 1%, the same amount as the initial impregnation, but the Fe was not uniformly distributed.

Fig. 2 shows the XRD patterns of the FeN<sub>4</sub>-C-7 and FeN<sub>2</sub>-C-9. For comparison, the XRD pattern of Vulcan carbon is also given. A wide diffraction peak centered at 25°, attributed to carbon, was observed for all samples. The XRD pattern of FeN<sub>4</sub>-C-7 is exactly the same as that of Vulcan carbon, indicating that no new phases were formed during pyrolysis at 700°C. However, two extra peaks at 2 $\theta$  of 43.8° and 51° were observed for FeN<sub>2</sub>-C-9. The diffraction peak at 43.8 is likely attributable to  $\gamma$ -Fe; the peak at 51° can be attributed to either  $\gamma$ -Fe or FeC, indicating that high temperature pyrolysis resulted in the formation of metallic iron [10].

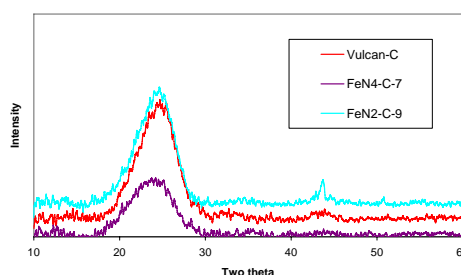


Fig. 2 XRD patterns of Vulcan carbon, FeN<sub>4</sub>-C-7 and FeN<sub>2</sub>-C-9

Table I summarizes the BET surface area of the as-prepared samples. It is clear that compared with Vulcan carbon, the FeN-carbon samples showed a significant decrease in BET surface area, with FeN<sub>2</sub>-C-9 exhibiting a slightly higher surface area than FeN<sub>4</sub>-C-7. Pyrolysis at 700°C did not fully decompose the organic compounds, leading to a lower surface area, whereas pyrolysis at 900°C might cause a more pronounced loss of organic compounds, freeing some parts of the surface.

TABLE I  
BET SURFACE AREAS OF THE AS-PREPARED SAMPLES

| Samples               | BET surface area (m <sup>2</sup> /g) |
|-----------------------|--------------------------------------|
| Vulcan carbon         | 236.6                                |
| FeN <sub>4</sub> -C-7 | 124.8                                |
| FeN <sub>2</sub> -C-9 | 138.2                                |

### B. Catalytic activity tests

Table II summarizes the activity evaluation results for FeN<sub>4</sub>-C-7 and FeN<sub>2</sub>-C-9 using model compounds. The FeN<sub>2</sub>-C-9 catalyst showed slightly higher activity than FeN<sub>4</sub>-C-7.

For example, after evaluation, the sulfur content in the liquid was 0.262% for FeN<sub>2</sub>-C-9, and 0.274% for FeN<sub>4</sub>-C-7. This might have been due to the absence of free coordination sites in the FeN<sub>4</sub>-C-7 catalyst, as Fe was coordinated with 4 N. Another explanation might be the presence of metallic Fe in FeN<sub>2</sub> as reviewed by the XRD pattern. This metallic Fe might be more active toward desulfurization.

Compared to the commercially available MoNi/Al<sub>2</sub>O<sub>3</sub> catalyst, the FeN/C catalysts showed significantly lower HDS activity. For the commercial catalyst, the HDS efficiency was 76.34% (i.e., 76.34% of the sulphur was removed in the process), while for the FeN/C catalysts, the efficiency was less than 18% (< 18% of sulphur was removed). This result indicates that MoNi/Al<sub>2</sub>O<sub>3</sub> had a higher activity toward HDS than the FeN/C catalysts. This difference was not due to the surface area. The BET surface area of MoNi/Al<sub>2</sub>O<sub>3</sub> was 150–350 m<sup>2</sup>/g, close to that of the FeN/C catalysts. However, the catalytic activity difference might have been due to the different catalyst loadings. In MoNi/Al<sub>2</sub>O<sub>3</sub>, the Mo loading was 10% and the Ni loading was 4%, while in the FeN/C catalysts, Fe loading is only ~ 1%. Since the metal is the active site for HDS, low metal loading yields low catalytic activity.

To make a fair comparison, the turnover frequency (TOF) for the three catalysts toward HDS was calculated based on the metal loading according to equation (1).

$$TOF = \frac{S_{feed} - S_{product}}{32M_m t} \quad (1)$$

where S<sub>feed</sub> is the sulphur content in the feed, S<sub>product</sub> is the sulphur content after testing, M<sub>m</sub> is moles of metal in the catalyst (moles of Fe in FeN/C catalysts, and the sum of moles of Mo and Ni in MoNi/Al<sub>2</sub>O<sub>3</sub>), and t is the reaction time (in this work, 1 h). The TOF unit is mol(sulfur)/mol (metal).s, and it was simplified as s<sup>-1</sup>.

FeN<sub>2</sub>/C shows higher TOF than MoNi/Al<sub>2</sub>O<sub>3</sub>, while the TOF obtained for FeN<sub>4</sub>/C is comparable to that of MoNi/Al<sub>2</sub>O<sub>3</sub>. The highest TOF was obtained with FeN<sub>2</sub>/C-9 catalyst, at a value of 2.7x10<sup>-3</sup> s<sup>-1</sup>.

Neither MoNi/Al<sub>2</sub>O<sub>3</sub> nor FeN<sub>2</sub>/C-7 could catalyze the HDA of toluene. However, FeN<sub>4</sub>/C-7 showed catalytic activity toward the HDA reaction. After testing, the toluene content had decreased from 15% to 14%, corresponding to a 6.7% reduction. This indicates that the FeN<sub>4</sub>/C and FeN<sub>2</sub>/C might have different catalytic mechanisms. Further studies are underway.

TABLE II  
AUTOCLAVE EVALUATION RESULTS

| Catalyst           |                        | Ref.<br>MoNi/Al <sub>2</sub> O <sub>3</sub> | FeN <sub>4</sub> /C-7 | FeN <sub>2</sub> /C-9 |
|--------------------|------------------------|---|-----------------------|-----------------------|
| Liquid analysis    | Feed                   |   |                       |                       |
| Sulfur, wt%        | 0.317                  | 0.075                                       | 0.274                 | 0.262                 |
| Toluene, wt%       | 15.0                   | 15.1  | 14.0                  | 14.9                  |
| HDS                | %                      | 76.34                                       | 13.57                 | 17.35                 |
|                    | TOF (s <sup>-1</sup> ) | 2.0x10 <sup>-3</sup>                        | 2.1x10 <sup>-3</sup>  | 2.7x10 <sup>-3</sup>  |
| HDA, %             |                        | 0   | 6.7                   | 0                     |
| Liquid yields, wt% |                        | 93  | 94                    | 94                    |

#### IV. CONCLUSION

FeN<sub>4</sub>/C and FeN<sub>2</sub>/C catalysts were prepared using a wet impregnation-pyrolysis method. Metallic Fe was observed in the FeN<sub>2</sub>/C, while no specific phase was observed in the FeN<sub>4</sub>/C. With respect to the HDS conversion efficiency, the catalytic activities of FeN<sub>4</sub>/C and FeN<sub>2</sub>/C were lower than that of MoNi/Al<sub>2</sub>O<sub>3</sub>. However, when the metal loading is considered, the FeN<sub>2</sub>/C catalyst had the highest TOF toward HDS, while TOF values for the FeN<sub>4</sub>/C and MoNi/Al<sub>2</sub>O<sub>3</sub> were similar. FeN<sub>4</sub>/C could catalyze toluene HDA, while neither MoNi/Al<sub>2</sub>O<sub>3</sub> nor FeN<sub>2</sub>/C could. The catalytic mechanism of the FeN catalysts is not clear at this stage, and further studies are in progress to also examine the catalysts for cracking potential to reduce the density and viscosity of heavy oil.

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