

Development of FeN₄/C And FeN₂/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: FeN₄/C and FeN₂/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 (FeN₄/C) or even higher (FeN₂/C) than that of MoNi/Al₂O₃. The FeN₄/C catalyst also exhibited catalytic activity toward HDA.

Keywords—catalyst, FeN₂/C, FeN₄/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 NiMo/Al₂O₃ 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].

FeN₄/C and FeN₂/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. FeN₄/C is usually considered to form below 700°C, and FeN₂/C above 700°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°C for preparation of the FeN₄ and FeN₂ 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 MoNi/Al₂O₃ 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 N₂ 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 FeN₄-C-7 (pyrolyzed at 700°C), and FeN₂-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 α 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 FeN₄-C-7 and FeN₂-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 N₂ protection. After purging with N₂ and H₂, the reactor was pressurized with H₂ 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/Al₂O₃ was also tested.

III. RESULTS AND DISCUSSION

A. Physical characterization of the FeN/C catalysts

Fig. 1 shows SEM micrographs of FeN₄-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 FeN₂-C-9.

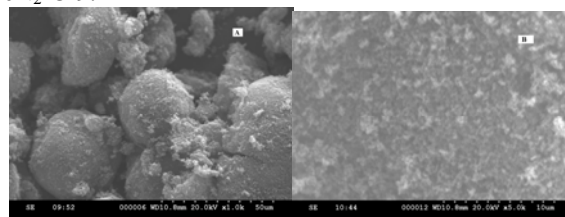


Fig. 1 SEM micrographs of FeN₄-C-7 pyrolyzed at 700°C (A) 1000x magnification, and (B) 5000x magnification

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 FeN₄-C-7 and FeN₂-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 FeN₄-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 θ of 43.8° and 51° were observed for FeN₂-C-9. The diffraction peak at 43.8 is likely attributable to γ -Fe; the peak at 51° can be attributed to either γ -Fe or FeC, indicating that high temperature pyrolysis resulted in the formation of metallic iron [10].

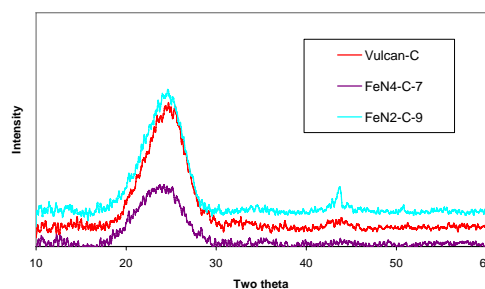


Fig. 2 XRD patterns of Vulcan carbon, FeN₄-C-7 and FeN₂-C-9

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 FeN₂-C-9 exhibiting a slightly higher surface area than FeN₄-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 ² /g) |
|-----------------------|--------------------------------------|
| Vulcan carbon | 236.6 |
| FeN ₄ -C-7 | 124.8 |
| FeN ₂ -C-9 | 138.2 |

B. Catalytic activity tests

Table II summarizes the activity evaluation results for FeN₄-C-7 and FeN₂-C-9 using model compounds. The FeN₂-C-9 catalyst showed slightly higher activity than FeN₄-C-7.

For example, after evaluation, the sulfur content in the liquid was 0.262% for FeN₂-C-9, and 0.274% for FeN₄-C-7. This might have been due to the absence of free coordination sites in the FeN₄-C-7 catalyst, as Fe was coordinated with 4 N. Another explanation might be the presence of metallic Fe in FeN₂ as reviewed by the XRD pattern. This metallic Fe might be more active toward desulfurization.

Compared to the commercially available MoNi/Al₂O₃ 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/Al₂O₃ 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/Al₂O₃ was 150–350 m²/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/Al₂O₃, 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_{feed} is the sulphur content in the feed, S_{product} is the sulphur content after testing, M_m 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/Al₂O₃), 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⁻¹.

FeN₂/C shows higher TOF than MoNi/Al₂O₃, while the TOF obtained for FeN₄/C is comparable to that of MoNi/Al₂O₃. The highest TOF was obtained with FeN₂/C-9 catalyst, at a value of 2.7x10⁻³ s⁻¹.

Neither MoNi/Al₂O₃ nor FeN₂/C-7 could catalyze the HDA of toluene. However, FeN₄/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 FeN₄/C and FeN₂/C might have different catalytic mechanisms. Further studies are underway.

TABLE II
AUTOCLAVE EVALUATION RESULTS

| Catalyst | | Ref. MoNi/Al ₂ O ₃ | FeN ₄ /C-7 | FeN ₂ /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 ⁻¹) | 2.0x10 ⁻³ | 2.1x10 ⁻³ | 2.7x10 ⁻³ |
| HDA, % | | 0 | 6.7 | 0 |
| Liquid yields, wt% | | 93 | 94 | 94 |

IV. CONCLUSION

FeN₄/C and FeN₂/C catalysts were prepared using a wet impregnation-pyrolysis method. Metallic Fe was observed in the FeN₂/C, while no specific phase was observed in the FeN₄/C. With respect to the HDS conversion efficiency, the catalytic activities of FeN₄/C and FeN₂/C were lower than that of MoNi/Al₂O₃. However, when the metal loading is considered, the FeN₂/C catalyst had the highest TOF toward HDS, while TOF values for the FeN₄/C and MoNi/Al₂O₃ were similar. FeN₄/C could catalyze toluene HDA, while neither MoNi/Al₂O₃ nor FeN₂/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.

ACKNOWLEDGEMENT

Partial funding for this work has been provided by the Canadian Program for Energy Research and Development, the Institute for Fuel Cell Innovation, and CanmetENERGY Natural Resources Canada.

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