Supporting Information

Synthesis of NiW catalysts supported on hierarchically meso/microporous KIT-5/Beta composites and their hydrodenitrogenation performance of quinoline

Xing Liu[a,b], Shaoqing Guo[c], HaitaoCui[a], Zhenrong Li[a], Zhenhui Liang[a,b], Xin Li[a], Jiantao Zhao[a,*], Lijing Yuan[a,*], Liangfu Zhao[a,*]

[a] *Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China*

[b]*University of Chinese Academy of Sciences, Beijing 100049, China*

[c] *School of Environmental Science and Engineering, Taiyuan University of Science and Technology, Taiyuan, Shanxi 030024, P. R. China*

*Corresponding Author

phone: +86-134-8536-2851; e-mail: lfzhao@sxicc.ac.cn

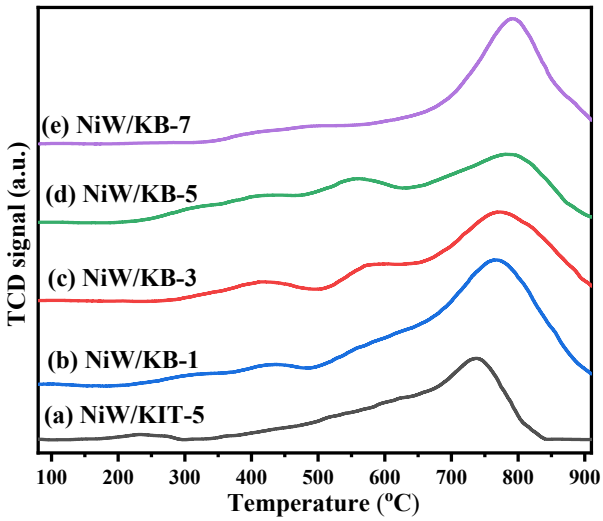

Figure S1. H_2-TPR of the oxided catalysts.

H_2-TPR techniques were employed to investigate the metal−support interaction andthe reducibility of the oxided catalysts over different supports. And the results are shown in **Figure S1**. Due to the complex reduction of W^{6+} oxide species (W^{6+} species firstly reduced to W^{5+} and then to W^{4+} phase), the exact attribution of TPR signals over NiW catalysts is always complicated[1,2]. The first peak of all the samples located at 300~500℃ is attributed to the reduction of NiO species[1]. The peak at 500~650℃ belongs to the superimposed reduction of polymeric octahedral W species and Ni octahedral species[2]. The peak at 650~730℃ can be assigned to further reduction of W^{5+} species to W^{4+} and the peak at higher temperatures (>800℃) corresponds to the reduction of tetrahedrally coordinated W^{4+} species to W^0. **Figure S1** shows that the peak positions of the catalysts shift toward higher temperature with the increase of the Beta content in the composite support, confirming that NiW/KIT-5 has the easier reducibility compared with NiW/KB-x catalysts due to the weaker interaction with KIT-5 support[3,4]. Therefore, the addition of Beta is beneficial to tuning the metal-support interactions.

1. M. Shao, H. Cui, S. Guo, L. Zhao and Y. Tan, RSC Advances, 2016, 6, 61747-61757.

2. P. A. Nikulshin, P. P. Minaev, A. V. Mozhaev, K. I. Maslakov, M. S. Kulikova and A. A. Pimerzin, Applied Catalysis B: Environmental, 2015, 176-177, 374-384.

3. J. N. Díaz de León, T. A. Zepeda, G. Alonso-Nuñez, D. H. Galván, B. Pawelec and S. Fuentes,

JOURNAL OF CATALYSIS, 2015, 321, 51-61.

4. X. Tao, Y. Zhou, Q. Wei, G. Yu, Q. Cui, J. Liu and T. Liu, FUEL PROCESSING TECHNOLOGY, 2014, 118, 200-207.

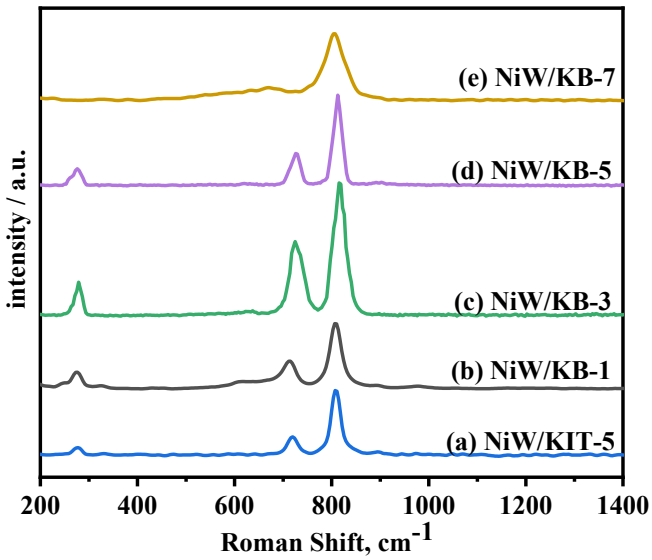

Figure S2. Raman spectra of oxided catalysts.

The Roman spectra of the oxided catalysts in the region of 200-1400 cm^{-1} are displayed in **Figure S2**. According to the literatures[1-3], the standard octahedral crystalline WO_3 presents the Raman bands at 804, 714 and 274 cm^{-1}. The octahedral crystalline WO_3 is easily sulfided to form active phases in the presulfiding process. The bands of the octahedral crystalline WO_3 are observed for all the catalysts and the intensity of these bands increase first and then decreases with the increase of the beta content in the composite support. The peak intensity of NiW/KB-3 is the highest, showing that NiW/KB-3 catalyst has more active species that are easily sulfide to form active phases of WS_2[2], which is beneficial for the HDN reactions[3].

1. F. Guo, S. Guo, X.-X. Wei, X. Wang, H. Xiang, Z. Qiu and L. Zhao, CATALYSIS LETTERS, 2014, 144, 1584-1593.

2. A. Ramanathan, R. Maheswari, B. P. Grady, D. S. Moore, D. H. Barich and B. Subramaniam, MICROPOROUS AND MESOPOROUS MATERIALS, 2013, 175, 43-49.

3. P. Blanchard, C. Lamonier, A. Griboval and E. Payen, Applied Catalysis A: General, 2007, 322, 33-45.

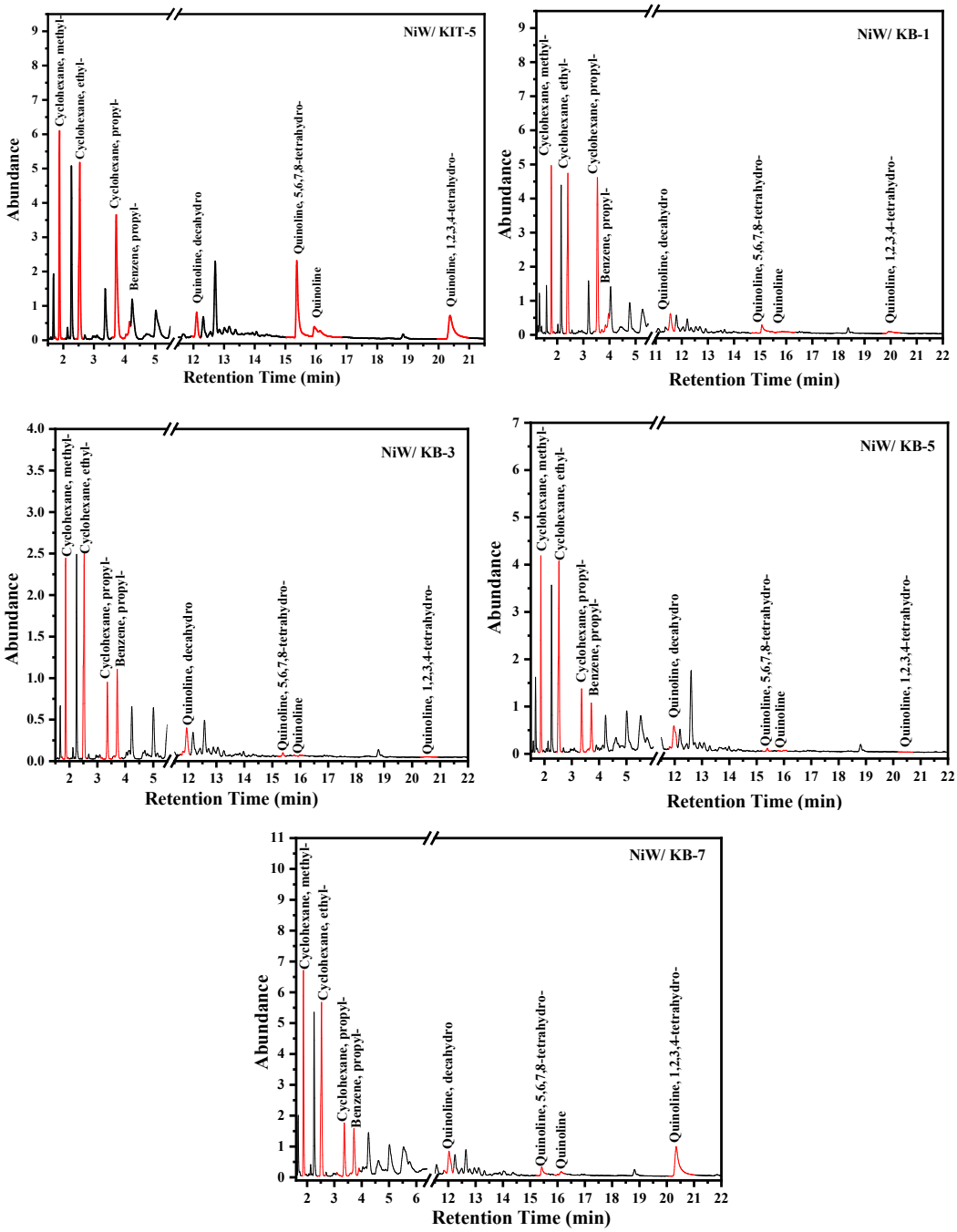

Figure S3. The product distribution spectra from GC-MS

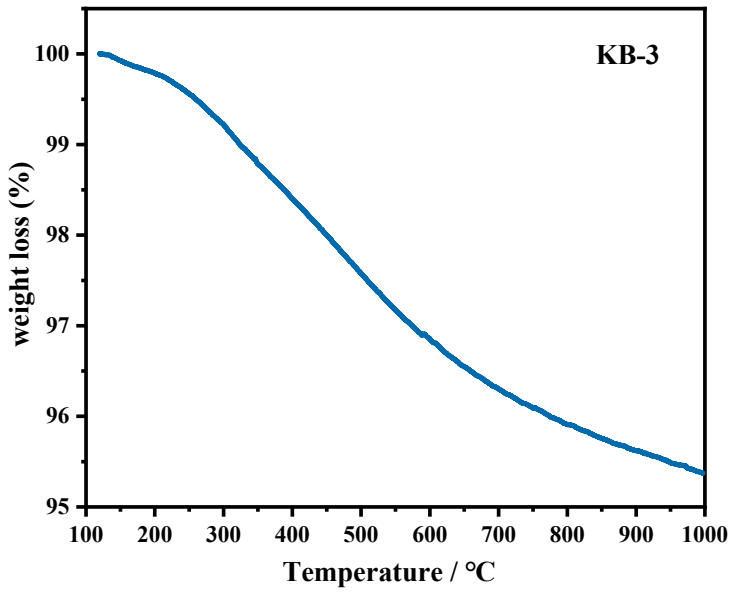

Figure S4. TGA pattern of KB-3

The thermal stability of the synthesized compounds was evaluated by thermogravimetric analysis (TGA) in which weight loss is observed upon heating the catalyst samples to 1000℃. The TGA pattern of the composite material (KB-3 as an example) is displayed in **Figure S4**. A slight decrease(4.5%) of the compounds weight between 120 and 1000℃ is observed, which indicates that the surfactant added to KB-3 during the synthesis process has been completely removed after calcination. Meanwhile, it is demonstrated that the KB-3 composite possess higher hydrothermal stability up to 1000℃.