Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Synthesis of novel hierarchically porous NiMo/ZSM-5-KIT-5 catalysts and the superior performance for hydrodenitrogenation of quinoline

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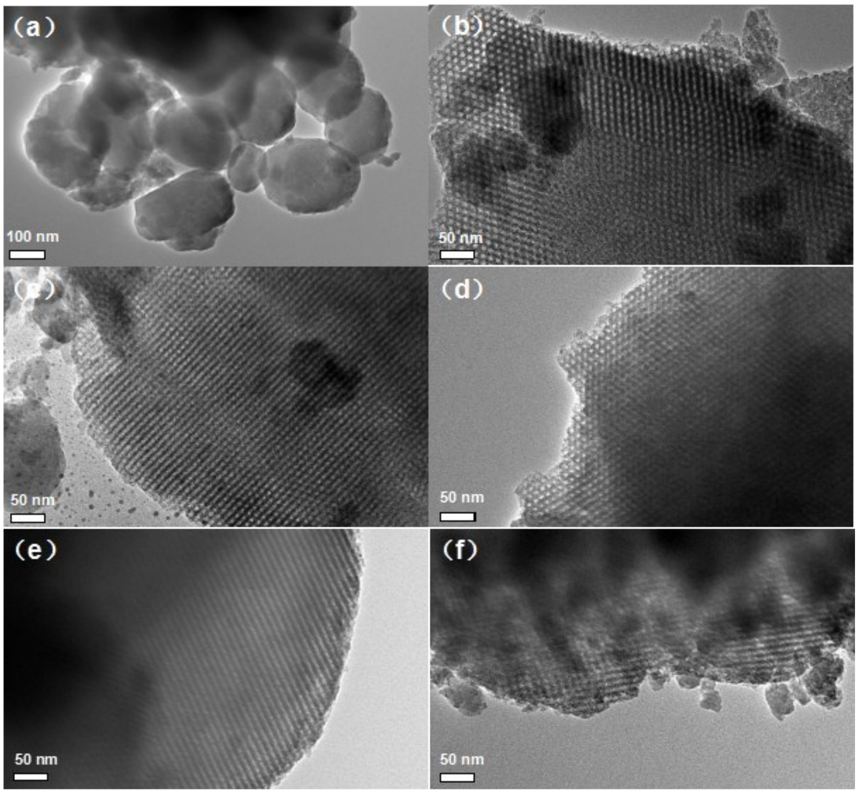

Figure S1. TEM images of the calcined supports: (a) ZSM-5, (b) KIT-5, (c) Zk-2, (d) Zk-3, (e) Zk-4, (f) Zk-6

Table S1 Amounts of L and B acid sites of NiMo/Zk-x catalysts tested by pyridine

Catalysts	Acid amount (200 °C)/mmol·g^{-1}				Acid amount (350 °C)/mmol·g^{-1}			
	L	B	L+B	B/L	L	B	L+B	B/L
NiMo/KIT-5	155	0	155	0	34	0	34	0
NiMo/Zk-2	177	7	184	0.037	41	0	41	0
NiMo/Zk-3	230	14	244	0.061	51	0	51	0
NiMo/Zk-4	370	16	386	0.043	62	0	62	0
NiMo/Zk-6	416	17	433	0.041	73	0	73	0
NiMo/ZSM-5	399	32	431	0.080	92	10	102	0.109

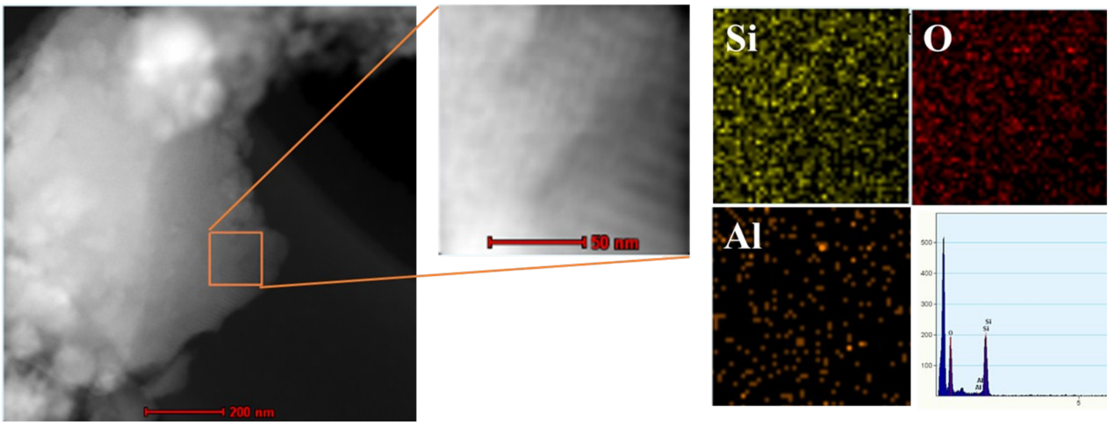

Figure S2. HAADF-STEM and EDX elemental mapping images of Zk-3.

The Al mapping image of Zk-3 material were showed in Figure S2. It can be seen, the Al element were widely distributed in Zk-3 composite material.

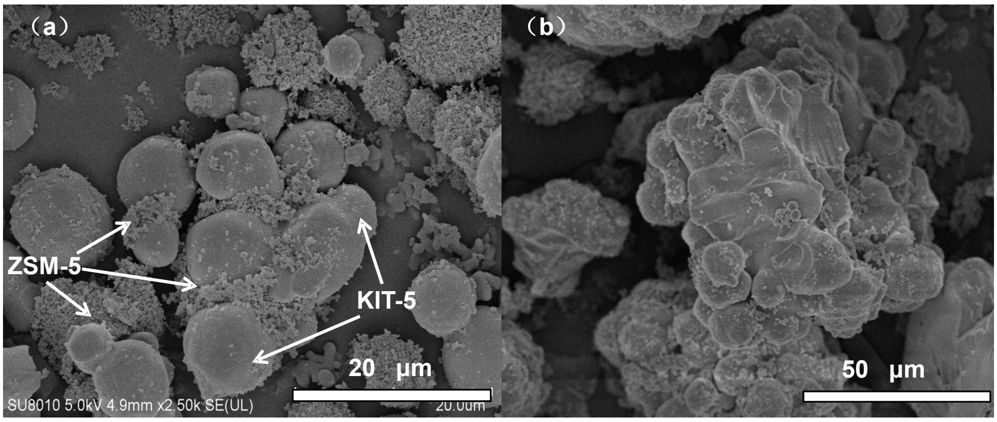

Figure S3. SEM images of: (a) PZK, (b) Zk-3.

In order to study the morphologies of PZK (mechanical mixing) and Zk-3 supports, the SEM spectra are performed and shown in Figure S3. From Figure S3 (a), the PZK mixture possesses two separated phases, which is ZSM-5 and KIT-5 materials respectively. The Zk-3 material in Figure S3 (b) exhibits no isolated ZSM-5 crystals and contains homogeneous dispersed phases.

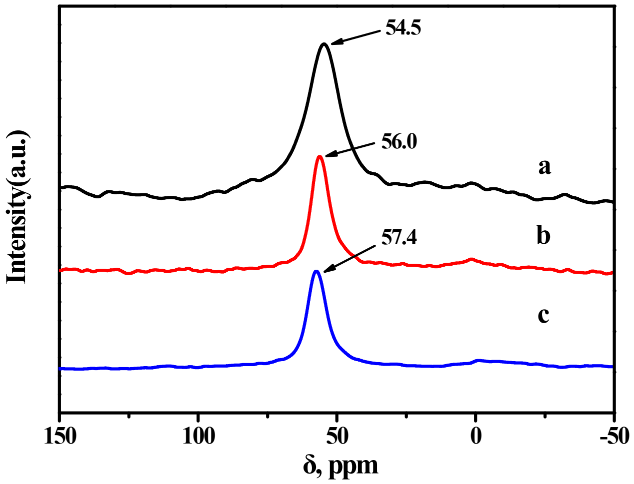

Figure S4. ^{27}Al NMR spectra of the series materials: (a) Al-KIT-5. (b) Zk-3, (c) PZK

The coordination information of Al atoms are studied by ^{27}Al MAS NMR spectra, and shown in Figure S4. The peak ascribed to the tetrahedral (framework Al species) coordinated aluminum atoms is observed at 54.5 ppm[1]. As shown in Figure S4, the peak centered at 54.5 ppm could be assigned to the Al atoms incorporated into the framework of KIT-5; while the signal centered at 57.4 ppm is ascribed to the Al atoms existing in the form of TO_4 in the ZSM-5 material. For the Zk-3 composite material, the chemical shift of Al species is at 56.0 ppm, different with 54.5 ppm and 57.4 ppm, indicating that partial Al species are embedded into the framework of KIT-5 support and formed the micro-mesoporous structure[2]. The above discussion confirms that the as-synthesized Zk-3 materials are the composites of ZSM-5 nanocrystals fabricated into the frameworks of mesoporous KIT-5 materials.

[1] I Hannus, Z Kónya, JB Nagy, P Lentz, I Kiricsi. Solid state MAS NMR investigation of Y-type zeolites reacted with chlorofluorocarbons[J]. Applied Catalysis B: Environmental, 1998, 17(1-2): 157-166.

[2] XL Wang, JL Mei, Z Zhao, P Zheng, ZT Chen, DW Gao, JY Fu, JY Fan, AJ Duan, CM Xu.. Self-assembly of hierarchically porous ZSM-5/SBA-16 with different morphologies and its high isomerization performance for hydrodesulfurization of dibenzothiophene and 4, 6-dimethyldibenzothiophene[J]. ACS Catalysis, 2018, 8(3): 1891-1902.

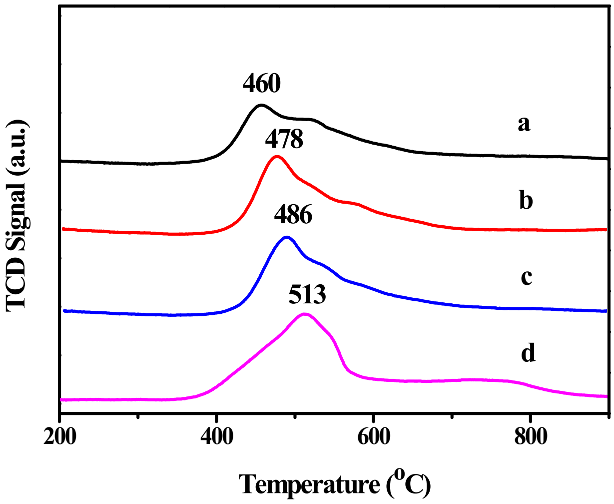

Figure S5. H_2-TPR of various catalysts: (a) NiMo/KIT-5, (b) NiMo/Zk-3, (c) NiMo/Zk-4. (d) NiMo/ZSM-5.

The H_2-TPR spectra of various NiMo/Zk-x catalysts are tested to investigate the metal-support interaction (MSI) and the reducibility of the oxide phases; and the results are displayed in Figure S5. All the catalysts show the low-temperature characteristic signal in the range of 400-600 °C and the high-temperature characterization signal in the range of 700-900 °C, which are ascribed to the reduction of polymeric octahedral coordination Mo species ($Mo^{6+} + 2e^- \rightarrow Mo^{4+}$) and the deep reduction of tetrahedrally coordination monomeric Mo species ($Mo^{4+} + 2e^- \rightarrow Mo^0$)[1-2]. For all the catalysts, the low reduction temperatures are in accordance with the following order: NiMo/KIT-5 (460 °C) < NiMo/Zk-3 (478 °C) < NiMo/Zk-4 (486 °C) < NiMo/ZSM-5 (513 °C). It can be deduced that the NiMo/Zk-x catalysts have the stronger MSI than NiMo/KIT-5.

[1] XL Wang, JL Mei, Z Zhao, P Zheng, ZT Chen, DW Gao, JY Fu, JY Fan, AJ Duan,

CM Xu.. Self-assembly of hierarchically porous ZSM-5/SBA-16 with different morphologies and its high isomerization performance for hydrodesulfurization of dibenzothiophene and 4, 6-dimethyldibenzothiophene[J]. ACS Catalysis, 2018, 8(3): 1891-1902.

[2] B Wang, ST Song, LN Han, AJ Duan, CM Xu, ZT Chen, Q Meng, XG Chen, JM Li, D Wang. Synthesis of Zirconium Modified Spherical Mesostructured Cellular Silica Foams and Its Hydrodesulfurization Performance for FCC Diesel[J]. Energy & Fuels, 2017, 31(5): 5448-5460.

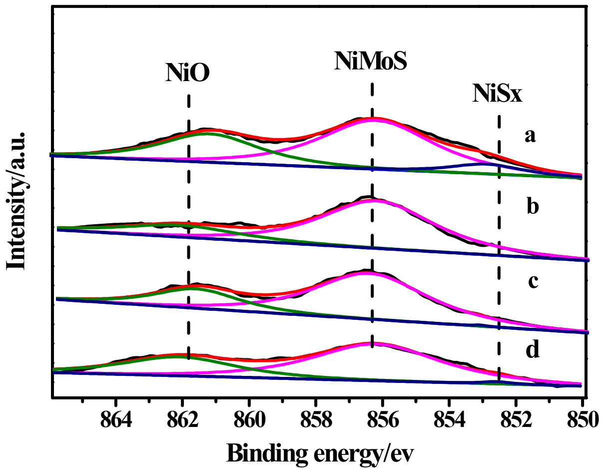

Figure S6. Ni2p XPS Spectra of the sulfided catalysts: (a) NiMo/ZSM-5, (b) NiMo/Zk-3, (c) NiMo/Zk-4, (d) NiMo/KIT-5.

Table S2 XPS fitting results of Ni 2p spectra of the sulfided catalysts

Catalysts	NiMoS ar.%	NiS$_x$ ar.%	NiO ar.%	Ni$_{sulfidity}$ ar.% [a]
NiMo/ZSM-5	61.3	7.6	31.1	68.9
NiMo/Zk-3	79.9	0.1	20.0	80.0
NiMo/Zk-4	75.7	0.2	24.1	75.9
NiMo/KIT-5	68.0	0.9	31.0	68.9

[a] $Ni_{sulfidity} = (NiMoS + NiS_x)/Ni_{total}$

Figure S6 displays the Ni 2p XPS spectra of the various sulfided NiMo/Zk-x, NiMo/ZSM-5 and NiMo/KIT-5 catalysts. And the Ni 2p orbit consists of three peaks at 856.4 ± 0.1 eV, 862.3 ± 0.1 eV and 853.1 ± 0.1 eV, corresponding to NiMoS, NiO and NiS_x, respectively[1-2]. The detailed fitting results are displayed in Table S2. It can be observed from Table S2, the amounts of NiMoS phase follow the order: NiMo/Zk-3 > NiMo/Zk-4 > NiMo/KIT-5 > NiMo/ZSM-5. Furthermore, the NiMo/Zk-3 catalyst has the highest sulfidity degree of Ni species.

[1] WK Lai, WJ Song, LP Pang, ZF Wu, N Zheng, JJ Li, JB Zheng, XD Yi, WP Fang. The effect of starch addition on combustion synthesis of NiMo–Al_2O_3 catalysts for hydrodesulfurization[J]. Journal of catalysis, 2013, 303: 80-91.

[2] B Wang, ST Song, LN Han, AJ Duan, CM Xu, ZT Chen, Q Meng, XG Chen, JM Li, D Wang. Synthesis of Zirconium Modified Spherical Mesostructured Cellular Silica Foams and Its Hydrodesulfurization Performance for FCC Diesel[J]. Energy & Fuels, 2017, 31(5): 5448-5460.

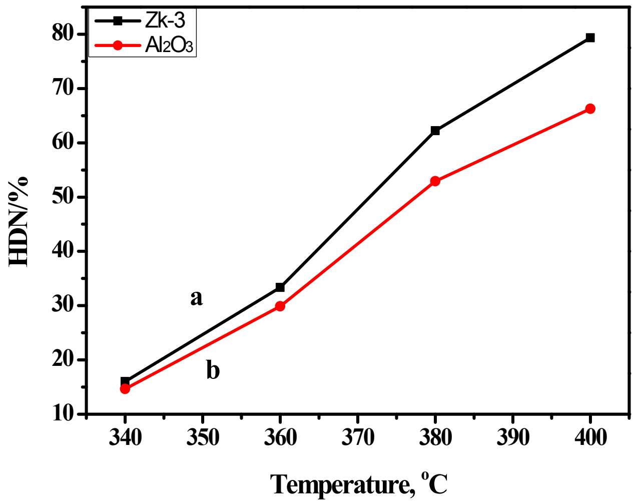

Figure S7. Quinoline HDN results at different temperatures (10 h^{-1}, 4 MPa, 400 ml/ml).

The commercial Al_2O_3 catalysts were obtained from Aluminum Corporation of China Limited. The catalytic activities of NiMo/Zk-3 and NiMo/γ-Al_2O_3 are shown in Figure S7. It is observed, the NiMo/Zk-3 catalyst exhibits higher activities than NiMo/γ-Al_2O_3 at different reaction temperatures.

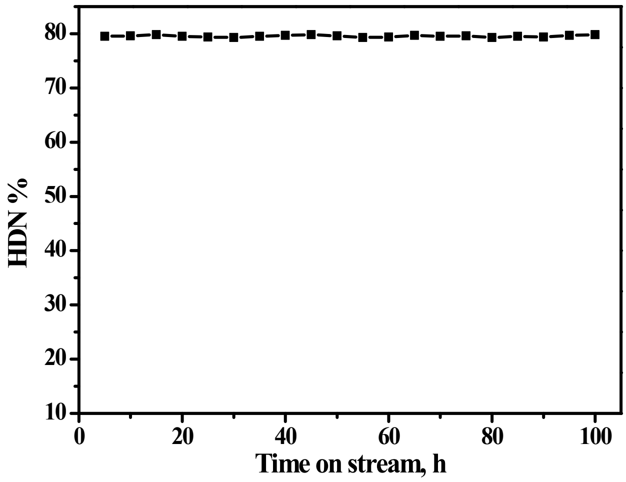

Figure S8. Quinoline HDN result with time on stream over NiMo/Zk-3(400 °C, 4.0 MPa, 400 ml/ml and 10 h^{-1})

The long-period (100 h) quinoline HDN reactive experiment over NiMo/Zk-3 catalyst (400 °C, 4.0 MPa, 400 ml/ml and 10 h^{-1}) was tested, and the results are displayed in Figure S8. It can be observed from Figure S8 that the quinoline HDN efficiencies are maintained to 79.6 % at 100 h time on stream, indicating that the NiMo/Zk-3 catalyst possesses good catalytic stabilities.

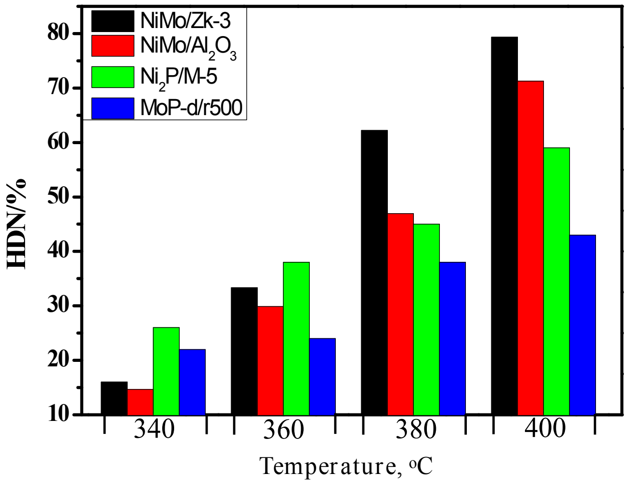

Figure S9. Quinoline HDN performance over various catalysts at different temperatures

The role of the support is complex due to the metal-support interaction (MSI). The NiMoS structure is present as either type I or type II depending on the MSI. The

Al_2O_3 support possesses the strong MSI, however, the silica support has the relatively weak MSI. In order to study the effect of supports, different supports are prepared catalysts for quinoline HDN reaction. The commercial Al_2O_3 catalysts were obtained from Aluminum Corporation of China Limited. The Ni_2P and MoP catalysts supported on the commercial silica were evaluated catalytic activities according to the literature[1-2]. From Figure S9, the Ni_2P/M-5 and MoP-d/r500 catalysts show higher catalytic activities than NiMo/Zk-3 and NiMo/Al_2O_3 at 340 °C, and with the temperature increasing, the NiMo/Zk-3 and NiMo/Al_2O_3 display the higher catalytic activities than Ni_2P/M-5 and MoP-d/r500 catalysts.

[1] A Infantes-Molina, JA Cecilia, B Pawelec, JLG Fierro, E Rodríguez-Castellón, A Jiménez-López. Ni_2P and CoP catalysts prepared from phosphite-type precursors for HDS–HDN competitive reactions[J]. Applied Catalysis A: General, 2010, 390(1-2): 253-263.

[2] A Infantes-Molina, C Moreno-León, B Pawelec, JLG Fierro, E Rodríguez-Castellón, A Jiménez-López. Simultaneous hydrodesulfurization and hydrodenitrogenation on MoP/SiO_2 catalysts: Effect of catalyst preparation method[J]. Applied Catalysis B: Environmental, 2012, 113: 87-99.