

Design and synthesis of KIT-5/Beta composites under varied hydrothermal temperatures and evaluation of their hydrodenitrogenation performance

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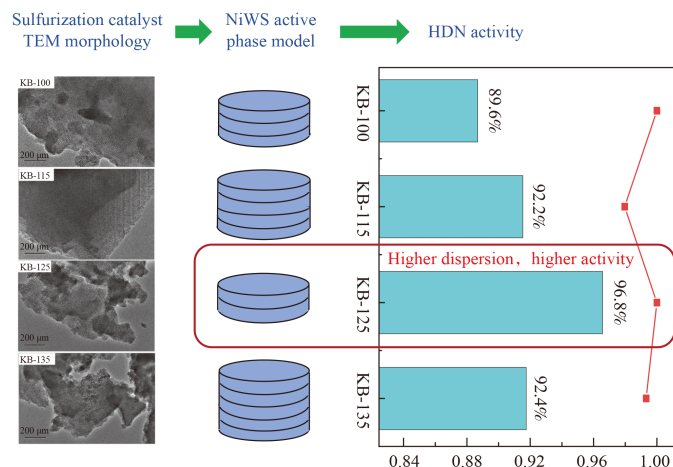
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Abstract: KIT-5/Beta composite supports were synthesized using an *in situ* self-assembly hydrothermal method, and NiW/KIT-5/Beta catalysts were prepared by impregnation. A series of characterization techniques were utilized to evaluate the influence of varying hydrothermal synthesis temperatures on the physicochemical properties of both the KIT-5/Beta supports and the resulting catalysts. The catalytic performances of catalysts were evaluated under reaction conditions of 320 °C, 4 MPa H₂ pressure, and a weight hourly space velocity (WHSV) of 4.8 h⁻¹ for hydrodenitrogenation (HDN) of quinoline. The results indicated that the specific surface area and pore structure of the materials could be effectively regulated by adjusting the hydrothermal synthesis temperature, which in turn influenced the number of active sites on the catalyst. The NiW/KB-125 catalyst, synthesized at 125 °C, presented the highest quinoline HDN efficiency (96.8%), which can be attributed to its favorable pore channel structure, greater Brønsted acid number, higher degree of metal sulfidation (80.12%) and appropriate metal-support interaction (MSI).

Key words: mesoporous-microporous material; KIT-5/Beta composite; NiWS; quinoline; hydrodenitrogenation



In China, coal is a key energy resource and forms the backbone of the country's energy system. Coal tar, a major by-product of the clean conversion and utilization of coal, has seen steady growth in production. It can be processed into valuable chemical materials like phenolic, pyridine anthracene and asphalt or converted into clean fuel oil through hydrotreatment^[1]. Despite its high output and economic potential, less than 50% of coal tar is utilized effectively. Notably, most of the medium- and low-

temperature coal tar, along with a minor portion of high-temperature coal tar, is directly utilized as fuel for extensive combustion.

Coal tar contains a significant quantity of aromatic heterocyclic compounds (e.g., sulfur-, nitrogen-, and oxygen-containing species), which generate substantial emissions of SO_x and NO_x during combustion. These emissions not only cause corrosion and damage to equipment but also lead to severe environmental

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pollution^[2–6]. Among these compounds, nitrogen-containing substances are particularly challenging to remove, as they require more stringent conditions—such as higher hydrogen pressure and temperature—to achieve effective elimination. Furthermore, residual nitrogen compounds may lead to the deactivation of downstream hydrocracking and hydrotreating catalysts^[7–8]. Given these challenges, hydrodenitrogenation (HDN) has emerged as a critical technology for the efficient and resourceful utilization of coal tar.

To achieve deep HDN of coal tar, it is essential to develop catalysts that exhibit high activity, selectivity, and stability^[9–10]. Traditional HDN catalysts are typically based on bimetallic NiW or NiMo sulfides supported on various materials. A wide range of supports has been employed for HDN catalysts, including Al_2O_3 , TiO_2 , SiO_2 , composite oxides, molecular sieves and activated carbon^[11–16]. Among these, Al_2O_3 is the most utilized support for HDN catalysts. However, the strong interaction between the Al_2O_3 support and the active metal hinders the complete sulfidation of the active metal, thereby significantly restricting the catalytic activity of the catalysts^[14–18]. Considering this, the development of more suitable supports for HDN has become a key focus of ongoing research.

In recent years, composite zeolites have emerged as promising catalyst supports, demonstrating extensive application potential in the field of hydrogenation catalysis^[19–24]. Wu et al.^[19] synthesized the composite material ZSM-5/KIT-6 (ZK-W) using a two-step hydrothermal crystallization method and evaluated its performance in the hydrodesulfurization (HDS) of 4,6-dimethyl dibenzothiophene (DBT). The results showed that the NiMo/ZK catalyst exhibited superior catalytic performance compared to the conventional NiMo/ Al_2O_3 , which can be attributed to its enhanced diffusion properties and the presence of suitable Brønsted acidic sites. Li et al.^[20] successfully synthesized the ZSM-5-FDU-12 (ZF) composite materials via an *in situ* assembly crystallization method and evaluated their performance in HDS and HDN. The results indicated that all NiMo/ZF-T catalysts, except NiMo/ZF-140 °C, presented improved hydrotreating performance relative to the commercial NiMo/ Al_2O_3 catalyst. This enhancement was primarily attributed to the synergistic effects of their larger specific surface area, appropriate acidity, favorable metal dispersion and higher sulfidation degree. Meng et al.^[21] synthesized the novel ZSM-5-KIT-5 (Zk) composite materials and used them as the supports to prepare the corresponding HDN catalysts. The experimental results revealed that NiMo/Zk-3 exhibited the highest HDN efficiency and propyl-cyclohexane selectivity, due to its open 3D channel structure, higher specific surface area and pore volume, the highest sulfidation degree and appropriate stacking of MoS_2 . Fan et al.^[24] synthesized a novel W-MCM-41 micro/mesoporous composite material through self-assembly of the W zeolite nanocrystal precursor and prepared the corresponding CoMo supported catalysts. The results indicated that the CoMo/WMA catalyst exhibited the highest HDS activity

(93.4%) and the excellent octane number ($\Delta\text{RON} = -1.3$ unit), which could be attributed to its favorable support structure, moderate metal-support interaction and the highest degree of the active phase sulfidation.

To date, numerous studies have been conducted on the development of composite zeolite supports with diverse structures; however, limited research has been reported in the field of HDN applications. In our previous work, it was found that the KIT-5 zeolite possessed a unique Fm3m three-dimensional mesoporous structure, which facilitated the dispersion of active metals and the diffusion of macromolecule^[25]. However, the KIT-5 material was a pure silicon-based zeolite, and its HDN performance was significantly constrained by its weak acidity and limited thermal stability. Therefore, the current research mainly focuses on rationally matching and modulating the micro/mesoporous composite zeolites and using them as supports. In this paper, we selected the Beta zeolite^[25] with the three-dimensional twelve-membered ring pore structure, and leveraged its unique topological structure, strong acidity and stability to construct a composite material with KIT-5 zeolite. The aim was to modulate the structure and surface acidity of the composite material and investigate its HDN performance. A series of KIT-5/Beta micro/mesoporous composite materials were successfully synthesized using an *in situ* self-assembly hydrothermal method under varying hydrothermal temperature conditions and were designated as KB samples.

Simultaneously, the corresponding NiW/KIT-5/Beta catalysts for the HDN reaction were prepared and systematically characterized using a variety of analytical techniques, including XRD, FT-IR, TEM, Py-FTIR, XPS, and HRTEM, to investigate the correlations between hydrothermal temperature and the structural properties, acidity, and active phase composition of both the support and the catalyst. Moreover, quinoline was utilized as probe molecule to evaluate the HDN performance of the catalysts. Finally, the HDN reaction mechanisms and pathways over different catalysts were thoroughly analyzed.

1 Experimental section

1.1 Preparation of the supports and catalysts

1.1.1 Synthesis of the KIT-5/Beta-*t* supports

The KIT-5/Beta-*t* (KB-*t*) composite materials were synthesized by *in situ* self-assembly of Beta aluminosilicate nanocrystalline precursor under the presence of triblock copolymer $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ (F127) micella. The specific preparation steps were as follows: Firstly, 5 g of F127 micella was added into 250 mL of 0.5 mol/L HCl solution and kept stirring at 45 °C for 4 h. Secondly, 25 g of tetraethyl orthosilicate (TEOS, 98%) was slowly added in the above solution and stirred for another 12 h at 45 °C. Subsequently, 3 g of H-type Beta zeolite ($\text{Si}/\text{Al} = 30$) was

added to the above mixture and kept stirring at 45 °C for 24 h. Thirdly, the resulting solution was added into a 500 mL Teflon-lined stainless-steel autoclave and heated for 24 h at different hydrothermal temperatures of 100, 115, 125 and 135 °C for 24 h to obtain the composite materials designated as KB-*t* (*t* = 100, 115, 125 and 135 °C). Finally, the as-synthesized samples of KB-*t* materials were filtered, dried at 100 °C for 12 h and calcined at 550 °C for 6 h to remove the organic template. The process flow chart for the preparation of KIT-5/Beta samples is shown in Figure 1.

1.1.2 Preparation of NiW oxidation catalysts

The series of NiW catalysts were prepared by a one-step incipient-wetness co-impregnation method using KB-*t* as the supports. Then a certain amount of nickel nitrate and ammonium metatungstate was weighed and simultaneously dissolved in deionized water. Afterwards, the above solution was evenly dripped into the well-weighed support while stirring. The mixture was then subjected to a drying process at 120 °C for 12 h, followed by calcination at 550 °C for 6 h.

The nominal loadings of WO₃ and NiO were 20% and 3%, respectively. Finally, the catalysts were tableted and sieved to obtain particles (20–40 mesh) for activity evaluation. The obtained oxidation catalysts were designated as NiW/KB-*t*, where “*t*” denoted the hydrothermal synthesis temperature (100, 115, 125 or 135 °C).

1.2 Characterization of the supports and catalysts

1.2.1 The crystal structure of the supports and catalysts

The phase composition and crystal structure of the supports and catalysts were analyzed by X-ray diffraction (XRD) on the D8 Advance A25 diffractometer (German Bruker Company), equipped with Cu K α radiation (λ = 0.154 nm). The tube current and tube voltage are 40 mA and 40 kV respectively. Besides, the wide-angle (2θ = 5°–90°) scanning rate and the small-angle (2θ = 0.3°–5°) scanning rate are 2(°)/min and 0.2(°)/min, respectively.

1.2.2 The textural properties of the supports

The specific surface area, pore volume and pore size

distribution of the supports were determined by the Tristar 3020 N₂ adsorption-desorption analyzer (MAC Instruments Corporation of the United States). The supports were heated in a vacuum environment for 5 h to remove the free water and other impurities adsorbed by the samples. Then the supports were cooled in liquid nitrogen to –196 °C for N₂ adsorption and desorption tests and the relevant data were automatically collected by a computer.

1.2.3 The morphological characteristics of the supports and catalysts

The surface microstructure of the samples was observed by scanning electron microscopy (SEM, JEM-7001F microscope) under the condition of 10 kV. The microscopic morphology of the active metals on the surface of the catalyst was observed using the transmission electron microscopy (TEM, JEM-2100F microscope). The samples were thoroughly milled and ultrasonically dispersed in ethanol solution for 10 min. Then, a drop of suspension was added on an ultrathin carbon-support film and allowed to dry naturally before testing.

The average stacking length ($\bar{L}$, nm) and stacking layer number ($\bar{N}$) of WS₂ slabs are summarized by 200 slabs in different parts of each catalyst according to the Equation (1)–(3).

$$\bar{L} = \frac{\sum_{i=1}^t (n_i l_i)}{\sum_{i=1}^t n_i} \quad (1)$$

$$\bar{N} = \frac{\sum_{i=1}^t (n_i N_i)}{\sum_{i=1}^t n_i} \quad (2)$$

where N_i , l_i and n_i refers to the layer number, the lengths and the number of the WS₂ slabs, respectively;

$$f_w = \frac{W_{\text{edge}}}{W_{\text{total}}} = \frac{\sum_{i=1}^t (6n_i - 6)}{\sum_{i=1}^t (3n_i^2 - 3n_i + 1)} \quad (3)$$

f_w is denoted as the dispersion degree of *W* species over the sulfided catalysts; $\frac{W_{\text{edge}}}{W_{\text{total}}}$ represents the ratio of the number of active *W* atoms at the edge to the total number of *W* atoms; n_i represents the number of *W* atoms along the side of WS₂ slab, which is determined by its length ($L = 3.2(2n_i - 1) \text{ \AA}$).

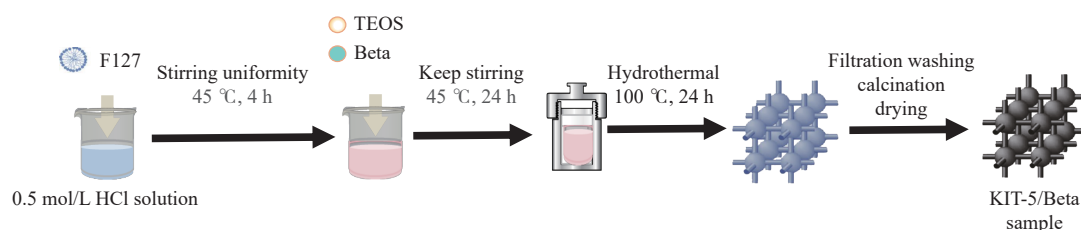


Fig. 1 The process flow chart for the preparation of KIT-5/Beta samples

1.2.4 The chemical state of elements on the catalysts surface

The chemical state and sulfidation degree of active metals in sulfided catalyst were determined by the Escalab 250Xi X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific, USA) using Al K α radiation under the condition of 15 kV. The test samples were in powder form following sulfidation. The binding energies of all the elements were calibrated using contaminated the C 1s spectrum at 284.8 eV, and the peak fitting was performed using XPS-PEAK software.

1.2.5 The reducing property of active metal species in the catalysts

H₂ temperature-programmed reduction (H₂-TPR) characterization of the catalysts was carried out on the Auto-Chem II 2920 analyzer (Micromeritics, USA). The specific operation was as follows: First, 100 mg of the sample was weighed and placed in a U-shaped quartz tube and dried at 300 °C under Ar atmosphere for 2 h before the measurement. Then, 10% H₂/Ar mixture (50 mL/min) was introduced after the temperature was reduced to 50 °C. After the baseline stabilized, the temperature was raised to 900 °C at a rate of 10 °C/min for desorption. Meanwhile, the change curve of the reduction gas was recorded using the thermal conductivity detector TCD.

1.2.6 The acidity of the catalysts

The Pyridine-FTIR spectroscopy (Py-FTIR) were recorded by a Nicolet 380 FT-IR spectrometer connected with a vacuum system and an *in situ* quartz cell for quantitative analysis of different acidic sites on the surface of the catalyst. The scanning range, the number of scans and the resolution were 400–4000 cm⁻¹, 32 times and 4 cm⁻¹, respectively. Before the test, 10 mg of the sample was first pressed into a thin sheet with a diameter of 13 mm and placed in an infrared cell. Then, it was pretreated in a high vacuum environment at 300 °C for 2 h and cooled to room temperature for pyridine adsorption. Finally, the infrared spectra were recorded during the pyridine desorption process at 100, 200 and 300 °C, respectively.

The acidic property of the catalyst surface was determined by the temperature-programmed desorption of NH₃ (NH₃-TPD). 0.1g of the catalysts were pretreated at 400 °C under He flow (50 mL/min) for 1 h and then cooled down to 100 °C for NH₃ adsorption. Afterwards, the reduction spectra were recorded under the mixture of 3% NH₃/He during the NH₃ desorption process at 700 °C.

1.3 Catalytic activity evaluation and product analysis

1.3.1 Catalytic activity evaluation

The quinoline was selected as a model compound to

evaluate the HDN performance of different catalysts. The HDN reaction was carried out in a continuous fixed-bed reactor using a stainless-steel tube (inner diameter 6 mm, outer diameter 14 mm and length 60 cm). Prior to the HDN reaction, 1 mL catalyst (20–40 mesh) diluted with equal amount of quartz sand, was loaded into the constant temperature zone of the reaction tube, which was subsequently installed in a fixed-bed reactor. The reaction solution was introduced into the pipeline by a high-performance liquid phase infusion pump. H₂ was transported into the stainless-steel reaction tube mixed with liquid raw materials through the mass flowmeter and pressure regulators.

The HDN activity evaluation was performed with 3% quinoline in the decalin as the feed at 320 °C, 4.0 MPa, an H₂/oil volume ratio of 1000/1 and a WHSV of 4.8 h⁻¹. After the reaction was completed, the product was separated by a cold trap to obtain gas product and liquid product for sampling and analysis. Figure 2 shows the scheme of apparatus for catalytic activity test.

It should be noted that the catalyst needs to be presulfided before the HDN reaction. The presulfided experiment was carried out with 3% CS₂ in the decalin as the feed under the condition of 4.0 MPa, an H₂/oil volume ratio of 1000/1 and a weight hourly space velocity (WHSV) of 2.4 h⁻¹ by temperature-programmed method. The temperature profile included three stages: heating from room temperature to 170 °C over 2 h and holding for 1 h; further heating to 220 °C over 3 h and holding for 1 h; and final heating to 320 °C over 3 h, followed by a 1 h hold.

1.3.2 Product analysis and data processing

The products over different catalysts were analyzed by an Agilent 7890A-5975 gas chromatography coupled with a mass spectrometer (GC-MS), which was equipped with a hydrogen flame ionization detector and employed a HP-5MS quartz capillary column (0.32 mm × 30 m × 0.25 μm).

According to the analysis results of GC-MS, the HDN conversion (HDNc) of quinoline was calculated based on Equation (4), in which the nitrogen contents of the products and feedstock were defined as N_p and N_f , respectively.

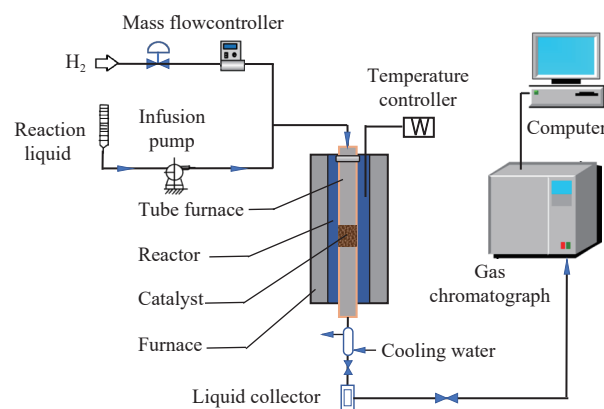


Fig. 2 Scheme of apparatus for catalytic activity test

$$\text{HDNc}(\%) = \frac{N_t - N_p}{N_t} \quad (4)$$

2 Results and discussion

2.1 Crystal structure of the KB-*t* materials

Figure 3 shows the small-angle XRD patterns of the KB-*t* composite materials prepared by different hydrothermal temperatures. It can be observed from Figure 3 that the KB-*t* composite materials exhibit the same characteristic peak of KIT-5 zeolite in the region of $2\theta = 0.5^\circ$ – 1.1° , indicating that the composite materials retain the 3D face-centered cubic symmetry structure (Fm3m) of mesoporous materials^[25]. The characteristic peak of the composite materials gradually shifts to the left with the rise of the hydrothermal temperature, which is attributed to the change in the unit cell parameters of the composite materials^[26]. At the same time, the peak intensity increases with the rise of the hydrothermal temperature, indicating that the increase in hydrothermal temperature is conducive to further improving and enhancing the orderliness of the mesoporous structure.

The results of wide-angle XRD patterns of the KB-*t* composite materials are displayed in Figure 4.

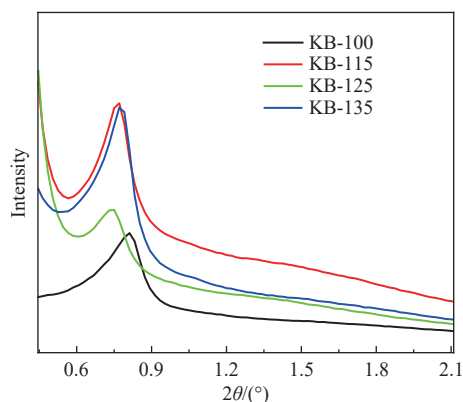


Fig. 3 Small-angle XRD patterns of different KB-*t* composite materials

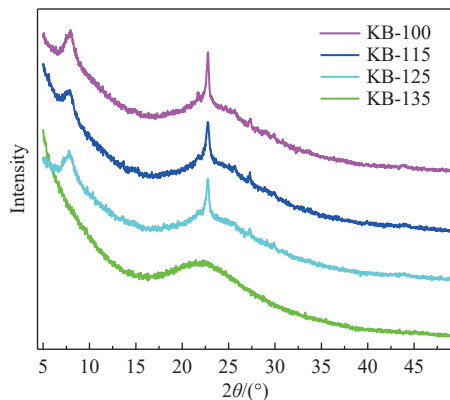


Fig. 4 Wide-angle XRD patterns of different KB-*t* composite materials

From the Figure 4, the characteristic diffraction peaks ($2\theta = 7.7^\circ$ and 22.4°) belonging to the BEA microporous structure of zeolite Beta appears in the KB-100, KB-115 and KB-125 composite materials (except KB-135), which indicated that the crystal structure of the Beta zeolite could remain constant when the hydrothermal temperature is lower than 135°C ^[27]. The significant broadening of the characteristic peak of KB-135 material demonstrates that the microporous structure of Beta zeolite has been damaged to a certain extent. The above results indicate that, except for KB-135 material, other composite materials simultaneously possess structural characteristics of both KIT-5 and Beta materials.

2.2 Physical structural properties of KB-*t* materials

The N_2 adsorption-desorption patterns and pore diameter distribution patterns of the composite materials are shown in Figure 5 and Figure 6. As shown in Figure 5, all the KB-*t* composite materials show type IV isothermal curves at the relative pressure range of 0.4–0.8 with obvious H2 hysteresis loops, which indicates that the KB-*t* series materials possess face-centered cubic structures (Fm3m) and the cage mesoporous structure. From the Figure 6, the pore size distribution curves of the KB-*t* composite materials are concentrated between 5 and 9 nm.

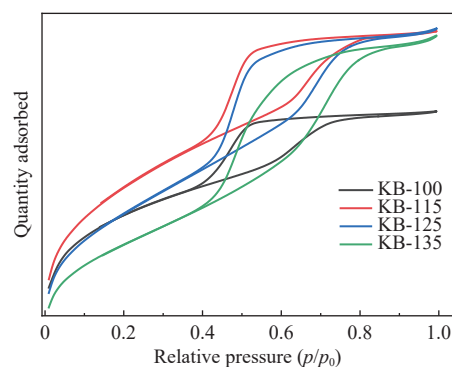


Fig. 5 N_2 adsorption-desorption isotherms of different KB-*t* composite materials

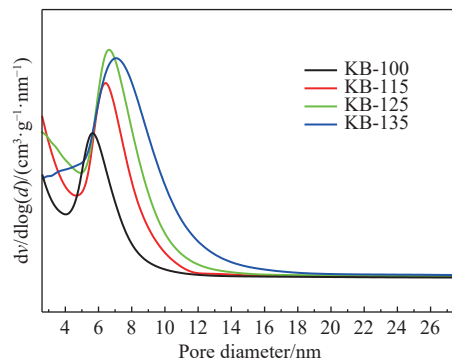


Fig. 6 Pore size distribution curves of different KB-*t* composite materials

The textural properties of the KB-*t* composite materials, including specific surface area (S_{BET}), pore size (d_p) and pore volume (v_p) are presented in Table 1. As shown in Table 1, the specific surface areas and pore volume of the KB-*t* series materials show firstly increase and then decrease with the increase of hydrothermal temperature. Among them, KB-115 has the highest specific surface area (1004 m²/g) and KB-125 has the largest pore volume (0.77 cm³/g). And the pore size exhibit increases tendencies with the increase of hydrothermal temperature, which indicates that high hydrothermal temperature is conducive to form relatively large pore size.

2.3 Morphology characteristics of KB-*t* materials

The morphology images of the series of different composite materials were characterized by SEM, as shown in Figure 7. The KB-100 material possesses smooth-surfaced spherical shape and its diameter is approximately 2 μm. However, the particles of the KB-*t* series materials (except for the KB-100 material) gradually grow larger and aggregate with the increase of hydrothermal temperature, which indicates that the higher hydrothermal temperature is conducive to accelerating the growth rate of particle^[20].

The TEM images are presented in Figure 8 to observe the pore microstructures of all samples. It can be clearly noted that KB-100 and KB-115 exhibit highly ordered honeycomb-like pore structures, and the pore size is uniform (about 6 nm) which is consistent with the BET results. However, the KB-125 and the KB-135 materials possess worm-like mesoporous structures, which presents an absolutely different morphology from the KB-100 and KB-115 material.

Table 1 Textural properties of different supports

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	d_p/nm	$v_p/(\text{cm}^3 \cdot \text{g}^{-1})$
KB-100	893	5.5	0.59
KB-115	1004	6.3	0.75
KB-125	883	6.5	0.77
KB-135	735	7.8	0.74

This is due to the change in the assembly behavior of the template agent, leading to the small angle distortion of the channel. Meanwhile, the KB-135 material exhibits the lattice fringes (1.15 nm) of Beta in the partial enlarged drawing, corresponding to the crystal plane (320). This result is consistent with the XRD analysis result.

2.4 The acidity of NIW/KB-*t* series catalysts

The Py-FTIR spectra of different catalyst samples are shown in Figure 9. The peaks at around 100, 200 and 300 °C respectively correspond to the weak acid, medium-strong acid and strong acid of KB-*t* series catalysts^[26]. The characteristic absorption peaks at the wavenumbers of 1610 and 1450 cm⁻¹ are ascribed to the absorbed pyridine on Lewis (L) acid sites. The absorption peak at the wavenumbers of 1540 cm⁻¹ is assigned to the absorbed pyridine on Brønsted acid site. And the absorption peak at around 1490 cm⁻¹ is attributed to the combination of L and B acid sites^[25–26]. It can be seen from the Figure 9, the spectral peaks corresponding to the acidic sites of different catalysts show significant differences; indicating that the change of hydrothermal temperature of composite material can effectively regulate the amounts of different acid sites of the catalyst.

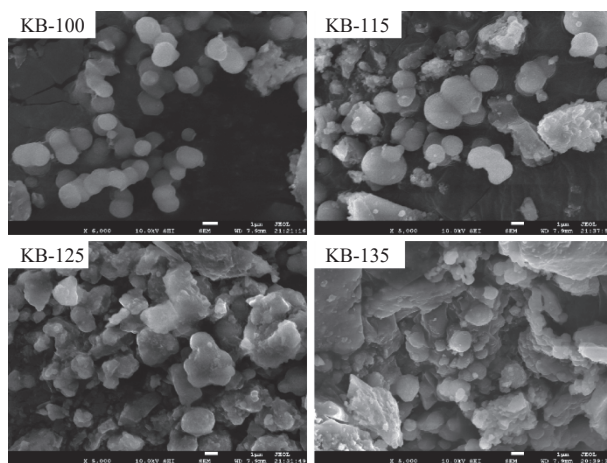


Fig. 7 SEM images of different KB-*t* materials

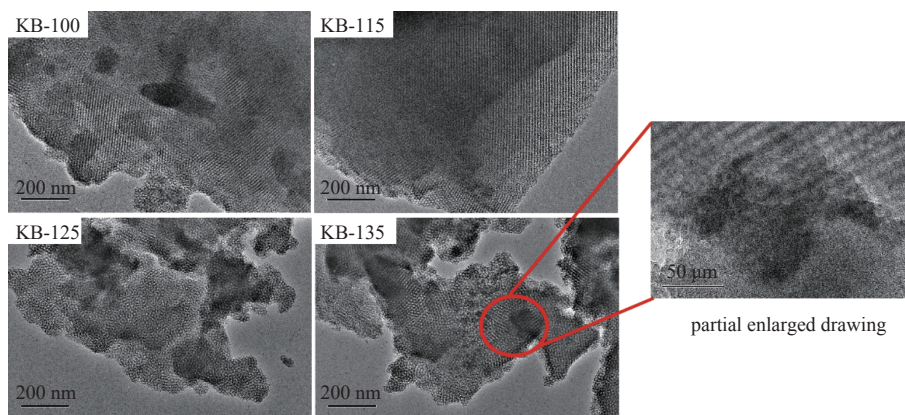


Fig. 8 TEM images of different KB-*t* materials

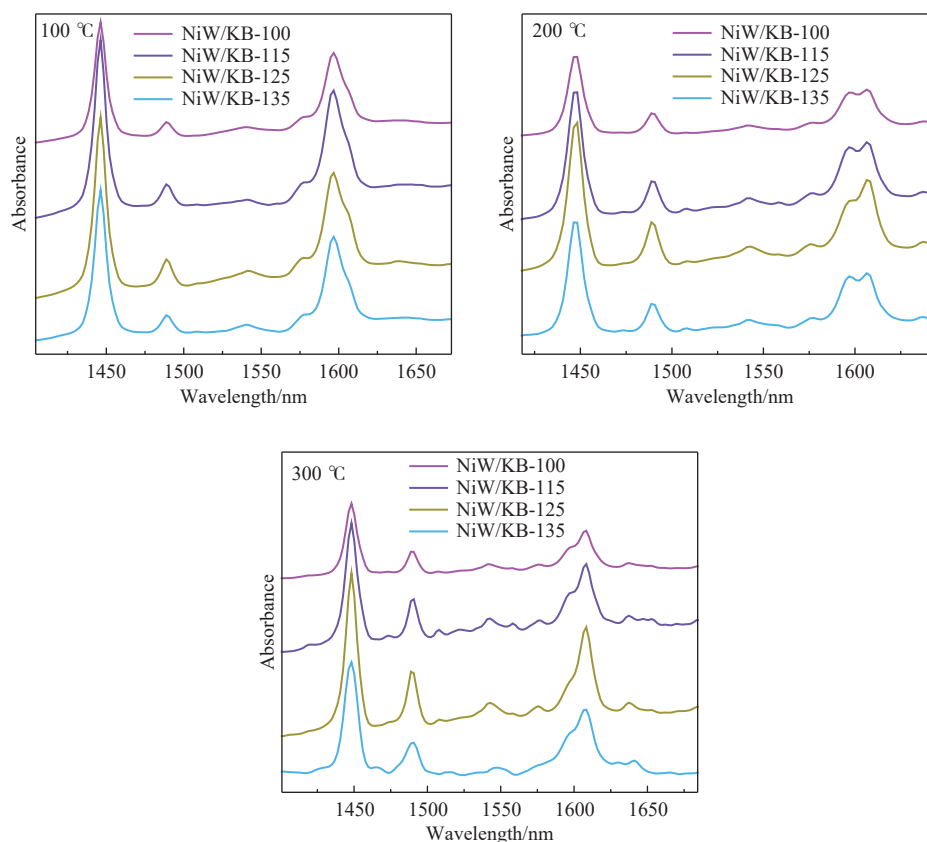


Fig. 9 Pyridine FT-IR spectra of various catalysts

The quantitative calculation data of weak acid sites, medium acid sites and strong acid sites of NiW/KB-*t* series catalysts are listed in Table 2. The higher L acid amount of NiW/KB-*t* series catalysts mainly result from the addition of zeolite Beta. The B acid amount of the series catalysts follow the order of NiW/KB-125 > NiW/KB-115 > NiW/KB-135 > NiW/KB-100. When the hydrothermal temperature is 125 °C, the amounts of weak, medium and strong B acid sites of NiW/KB-125 catalyst reach the highest value of 13.68, 7.10 and 4.89 $\mu\text{mol/g}$, which are obviously higher than those of other NiW/KB-*t* catalysts.

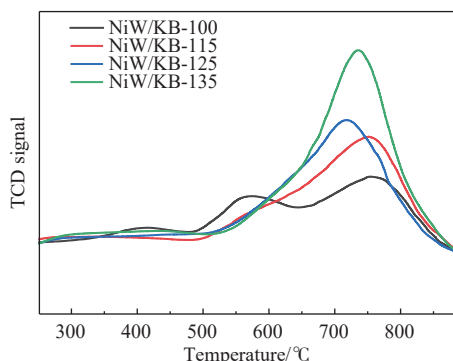
2.5 The reducibility of NiW/KB-*t* series catalysts

To investigate the reduction performance and the metal-support interaction of oxidized catalysts, H_2 -TPR experiment was carried out, as shown in Figure 10. The H_2 -TPR curves of all catalysts show obviously three reduction peaks within the temperature ranges of 300–500 °C (L zone), 500–650 °C (M zone), and 650–800 °C (H zone). Due to the complex reduction process of the NiW oxidized catalyst, the

exact attribution of the TPR signal becomes extremely difficult. According to the literature, the W^{6+} species are first reduced to W^{5+} , then to W^{4+} phase, and finally to W^0 . The reduction peak of octahedrally coordinated (Oh) W^{6+} species is located at 300–600 °C, while tetrahedrally coordinated isolated or dimeric (Td) W^{6+} is more difficult to be reduced due to its strong interaction with alumina, requiring a temperature of about 900–1000 °C^[28]. For nickel species, there are three types of reduction peak: the reduction temperature of bulk NiO is less than 400 °C; the reduction temperature of the Ni^{2+} oct interacting with alumina is 450–690 °C; the reduction temperature of Ni^{2+} incorporated into alumina to form NiAl_2O_4 spinel is higher than 700 °C^[28]. For the NiW/KB-100 catalyst, the reduction peaks in the L region and the M region belong to the reduction of Ni^{2+} species and W^{6+} species, respectively. The NiW/KB-*t* series catalysts show a reduction peak in the H region and the temperature of the reduction peaks decrease in the order of NiW/KB-100 > NiW/KB-115 > NiW/KB-135 > NiW/KB-125.

Table 2 The acidity of different catalysts determined by Py-FTIR spectra

Sample	Brønsted acidity/ $(\mu\text{mol} \cdot \text{g}^{-1})$			Lewis acidity/ $(\mu\text{mol} \cdot \text{g}^{-1})$		
	100 °C	200 °C	300 °C	100 °C	200 °C	300 °C
NiW/KB-100	9.74	4.60	2.61	88.88	31.97	16.15
NiW/KB-115	8.67	4.82	2.72	126.66	50.66	28.44
NiW/KB-125	13.68	7.10	4.89	128.47	56.48	34.36
NiW/KB-135	11.29	6.53	3.89	110.31	45.13	25.76


 Fig. 10 H₂-TPR profiles of the oxidized catalysts

It is demonstrated that the NiW/KB-125 catalyst possesses weakened metal-support interaction and is more readily sulfided in the HDN reaction.

2.6 The microstructure of the active phase of the NiW/KB-*t* series catalysts

In order to observe the microstructure of the WS₂ active phase on the catalyst surface, the series sulfided NiW/KB-*t* series catalysts were characterized by HRTEM technique. The representative HRTEM images of different sulfided catalysts are presented in Figure 11. From the figure, the lattice fringes with 0.64 nm interplanar distances of the different catalysts can be clearly observed, which matches the basal planes (002) of the WS₂ crystal^[26]. The results can be further proved by XPS characterization.

The average stacking length ($\bar{L}$, nm) and stacking layer number ($\bar{N}$) of WS₂ slabs are summarized by 200 slabs in different parts of each catalyst and the corresponding statistical data are listed in Table 3.

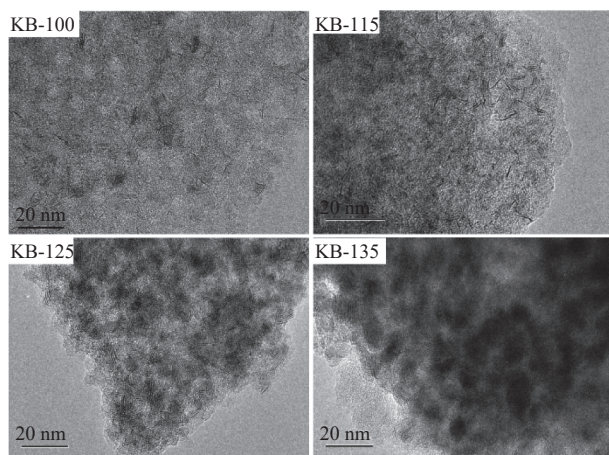


Fig. 11 HRTEM images of different sulfided catalysts

 Table 3 Average length ($\bar{L}$), average number ($\bar{N}$) and dispersity (f_w) of WS₂ slabs

Catalyst	$\bar{L}/\text{nm}$	$\bar{N}$	f_w
NiW/KB-100	4.89	3.12	0.22
NiW/KB-115	4.54	3.62	0.25
NiW/KB-125	3.92	2.60	0.28
NiW/KB-135	4.67	4.88	0.24

It can be seen from Table 3, the average lengths of WS₂ slabs follows the order of NiW/KB-100 > NiW/KB-115 > NiW/KB-135 > NiW/KB-125. The average layer numbers of WS₂ slabs are in the order of NiW/KB-135 > NiW/KB-115 > NiW/KB-100 > NiW/KB-125. It can be observed that NiW/KB-125 possesses the lowest average layer number and the shortest average lengths of WS₂ slabs, which can be attributed to the strong interaction between active metal and support and is stay in step with the H₂-TPR result. f_w is also an important parameter for evaluating the microstructure of the WS₂ active phase, and the variation law is different from that of the other two parameters ($\bar{L}$ and $\bar{N}$). f_w values follow the order of NiW/KB-125 > NiW/KB-115 > NiW/KB-135 > NiW/KB-100. The results show that NiW/KB-125 possesses the highest dispersion degree of the active phase WS₂ (0.28), which is beneficial for improving the HDN catalytic activity.

2.7 The chemical states of surface elements of the NiW/ KB-*t* series catalysts

The XPS characterization was utilized to test the chemical states of surface elements of the NiW/KB-*t* series catalysts. W 4f XPS spectra are fitted by the XPS-PEAK software and presented in Figure 12. The W 4f spectrum is composed of W⁴⁺ (WS₂), W⁵⁺ (WS_xO_y) and W⁶⁺ (WO₃ or NiWO₄). The deconvolution peaks with binding energies of 32.1 and 34.3 eV ascribe to W 4f_{7/2} and W 4f_{5/2} levels for W⁴⁺ species of WS₂ phase; the peaks with binding energies of 33.2 and 35.2 eV are assigned to W 4f_{7/2} and W 4f_{5/2} levels for W⁵⁺ species of WS_xO_y phase; the peaks with binding energies of 35.9 and 37.9 eV are attribute to W⁶⁺ species of the WO₃ or NiWO₄ phase^[29]. It is particularly worth noting that the peak at 38.0 eV belongs to 5p_{3/2} for W⁴⁺ species. Table 4 demonstrates the XPS fitting results of W species over the sulfided NiW catalysts using the deconvolution method, and the sulfidation degree of W species is calculated as the ratio of W⁴⁺ species to all the W species based on the decomposition peak area.

It can be seen from the Table 4 that the sulfidation degree of W species follows the order of NiW/KB-125 > NiW/KB-135 > NiW/KB-115 > NiW/KB-100, indicating that the appropriate increase in hydrothermal synthesis temperature is beneficial to improve the sulfidation degrees of the W species. Meanwhile, the NiW/KB-125 catalyst has the highest sulfidation degree (80.12%), which can be attributed to its moderate interaction between active metals and supports as well as the highest dispersion degree of active metals. This result is consistent with the results of HRTEM and H₂-TPR.

3 HDN catalytic performance evaluation

The HDN performances of the NiW/KB-*t* series catalysts are evaluated under the conditions of the pressure of 4 MPa, the reaction temperature of 320 °C, the H₂/oil volume ratio of 1000/1 and the WHSV of 4.8 h⁻¹, respectively.

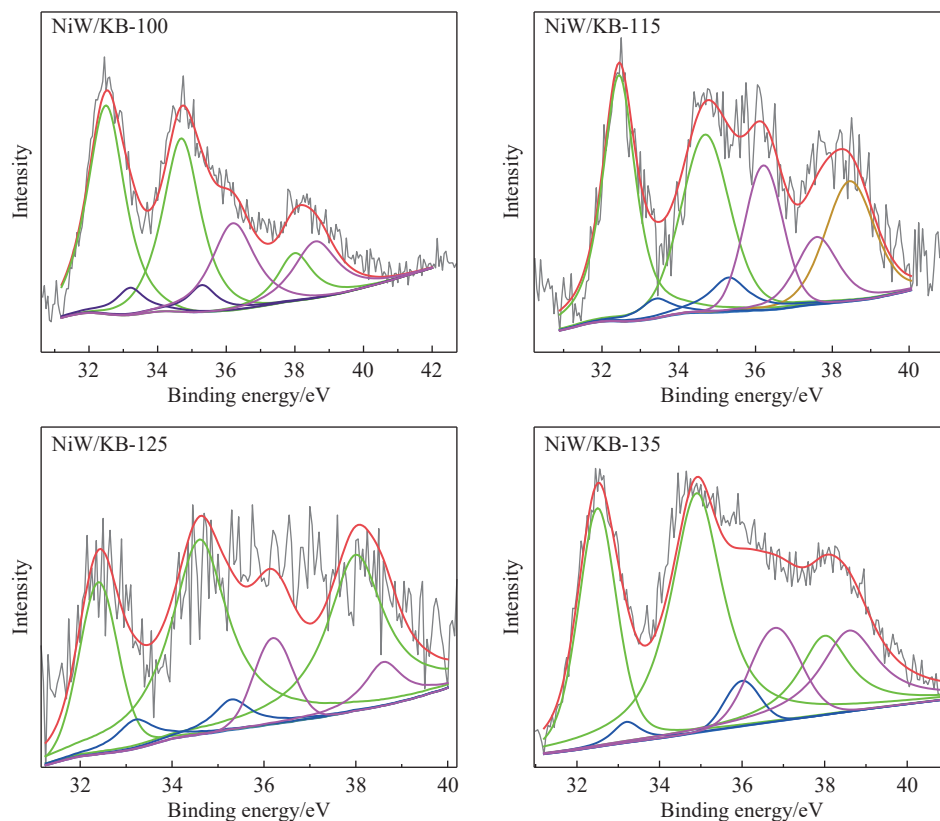


Fig. 12 XPS spectra of various sulfided catalysts

Table 4 XPS fitting results of W 4f spectra of various sulfided catalysts

Catalyst	W ⁴⁺ /%	W ⁵⁺ /%	W ⁶⁺ /%
NiW/KB-100	65.98	8.25	25.77
NiW/KB-115	69.00	7.47	23.53
NiW/KB-125	80.12	7.34	12.55
NiW/KB-135	70.51	4.91	24.57

Quinoline (600×10^{-4} , N) was selected as probe for the HDN evaluation to verify the relationship between the HDN performances and the properties of the catalysts. Figure 13 shows the HDN rates and the conversion rates of the quinoline over different catalysts. As shown in Figure 13, the conversion rates of all the catalysts are relatively similar and all approach 100%. The HDN rates of the NiW/KB-*t* series catalysts follow the order of NiW/KB-125 > NiW/KB-135 > NiW/KB-115 > NiW/KB-100. The NiW/KB-125 catalyst exhibits the highest HDN activity (96.8%), This is mainly due to its higher specific surface area and pore volume, which promote the dispersion of active metals and the diffusion of reactants. Additionally, the increased number of acidic sites facilitate the adsorption of reactant molecules, thereby reducing the contact time between active sites and reactants^[30].

The product distributions of quinoline HDN over the NiW/KB-*t* series catalysts are presented in Table 5. According to the product distributions and the previous researches^[8,15,28], the Q-HDN proceeds through two reaction

pathways. One reaction pathway is partial hydrogenation route: Q → 1,2,3,4-tetrahydro-quinoline (THQ1) → *o*-propyl-aniline (OPA) → propyl-benzene (PB); the other reaction pathway is complete hydrogenation: Q → THQ1/5,6,7,8-tetrahydro-quinoline (THQ5) → decahydro-quinoline (DHQ) → propyl-cyclohexylamine (PCHA) → propyl-cyclohexene (PCHE) → propyl-cyclohexane (PCH). Among them, THQ1, THQ4, OPA, DHQ and PCHA belong to hydrogenation intermediate products (HYD intermediate products); PB, PCHE and PCH belong to denitrification products (DC). Furthermore, we found hydrocracking products (HC) of PB and PCH including ethyl-cyclohexane (ECH), methyl-cyclohexane (MCH) and cyclohexane (CH), which is different from other studies. The detailed Q-HDN reaction network is displayed in Figure 14.

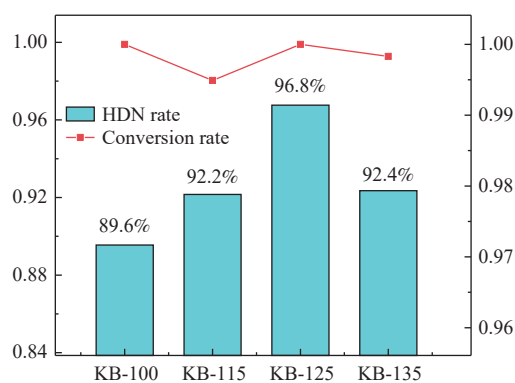
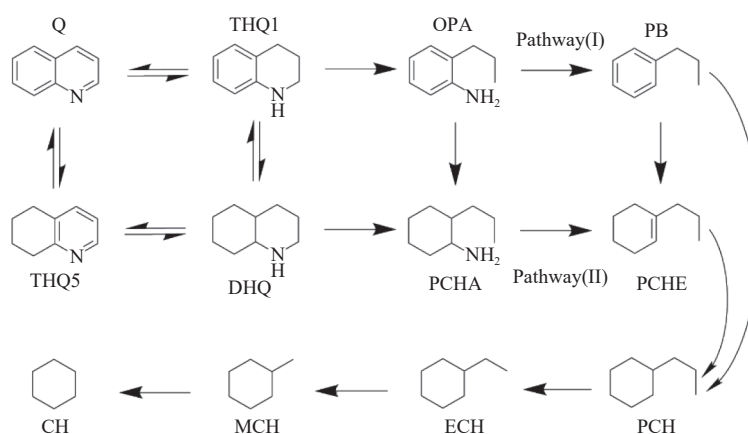


Fig. 13 Catalytic activity results of the quinoline HDN over different catalysts

Table 5 Product distribution of quinoline hydrogenation over different catalysts

Catalyst	Product selectivity/%											DN (PCH+PB+PCHE)	HC (CH+MCH+ECH)	HDN
	PCH	PCHE	PB	CH	MCH	ECH	DHQ	THQ5	Q	OPA	THQ1			
NiW/KB-100	15.9	0.0	0.0	9.1	28.2	36.4	0.0	0.0	0.0	3.6	6.8	15.9	73.6	89.6
NiW/KB-115	13.7	19.7	0.0	6.5	21.4	30.9	3.4	0.0	0.5	0.8	3.1	33.4	58.7	92.2
NiW/KB-125	13.9	21.5	0.0	8.1	22.7	30.6	1.8	0.0	0.0	0.0	1.4	35.3	61.4	96.8
NiW/KB-135	14.3	0.0	21.6	6.4	20.4	29.6	5.3	0.0	0.2	0.0	2.2	35.9	56.5	92.3



Q: quinoline; THQ1: 1,2,3,4-tetrahydro-quinoline; OPA: *o*-propyl-aniline; PB: propyl-benzene; THQ5: 5,6,7,8-tetrahydro-quinoline; DHQ: decahydroquinoline; PCHA: propyl-cyclohexylamine; PCHE: propyl-cyclohexene; PCH: propyl-cyclohexane; ECH: ethyl-cyclohexane, MCH: methyl-cyclohexane, CH: cyclohexane.

Fig. 14 The reaction network of quinoline HDN

It can be seen from Table 5 that PB was not detected in NiW/KB-100, NiW/KB-115 and NiW/KB-125 catalysts, indicating that the reaction path is mainly complete hydrogenation route. There may be two reasons for this phenomenon. On the one hand, the nitrogen atom with a lone pair of electrons in aniline can form conjugated structure with the benzene ring, enhancing the stability of aniline; On the other hand, quinoline and its hydrogenation products exhibit a strong competitive adsorption effect toward OPA, which hinders the direct cleavage of the C–N bond in OPA. In addition, the HYD intermediate products and the DN products possess only DHQ, THQ1, PCHE and PCH for the NiW/KB-125 catalysts. This result indicates that the NiW/KB-125 catalyst has excellent hydrogenation and cracking capacity, thereby possessing the best HDN performance (96.8%).

4 Discussion

The series of KB-*t* composite materials combining the advantageous properties of mesoporous and microporous materials were prepared under different hydrothermal synthesis temperature by the *in situ* assembly method. The effect of the synthetic conditions on quinoline HDN performance of the corresponding NiW catalysts were systematically discussed, and the physicochemical properties of the supports and catalysts were also analyzed by various characterization methods.

The hydrothermal synthesis temperature has significant effects on the structural properties of the series KB-*t* materials, thereby altering the HDN activity and selectivity of the catalyst. The higher hydrothermal synthesis temperature is conducive to form relatively large total pore volume, mesopore volume and pore size. Among them, KB-125 material possesses higher specific surface area (883 cm²/g), the largest pore volume (0.77 cm³/g), and the concentrated pore size distribution (6.5 nm). Its excellent textural properties facilitate the dispersion of W and Ni on the support surface and the diffusion of reactants and products, thereby enhancing the catalytic activity of the catalyst in HDN reactions.

Factors such as the metal-support interaction (MSI), the sulfidation degree of the active metal and the morphology of the active phase are also closely related to catalytic activity. The H₂-TPR results indicated that NiW/KB-125 catalyst have the moderate MSI, which is conducive to the formation of the highly active NiWS catalyst. The results of HRTEM and XPS also verify that the NiW/KB-125 catalyst exhibits the highest degree of sulfidation (80.12%) and the lowest average stacking length and stacking layer number of WS₂ slabs.

The type and the amount of acid sites in the catalyst can also affect the HDN reaction activity of the catalyst. The B acid site amount of the NiW/KB-125 catalyst is significantly higher than that of other catalysts, which is conducive to enhance the hydrogenation active sites and cracking active sites of the catalyst, and further improves

the HDN activity.

5 Conclusion

A series of KB-*t* composite materials were successfully fabricated through *in situ* self-assembly method. The influence of different hydrothermal synthesis temperatures on the physicochemical properties of the materials and the HDN activity of the supported NiWS catalysts was studied. The KB-*t* composite materials and the corresponding NiWS/KB-*t* catalysts were characterized by various characterization techniques such as XRD, BET, SEM, FT-IR, XPS and TEM. The results show that the KB-*t* composite materials exhibit satisfying pore structure, specific surface area and pore volume. Among them, the NiW/KB-125 catalyst has the best HDN activity, which is attributed to the synergistic results of its larger surface area, the abundant B acid sites, the optimal dispersion degree and the sulfidation degree of active metals, the appropriate microstructure of WS₂ slabs and the moderate MSI. In terms of the products selectivity, the reaction path of the NiW/KB-125 catalyst is the complete hydrogenation path due to its strong hydrogenation and hydrogenolysis capabilities.

Declaration of Competing Interest

The authors declare no conflict of interest.

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不同水热温度下 KIT-5/Beta 复合材料的设计合成及其加氢脱氮性能研究

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摘 要: 以原位自组装水热合成法制备的 KIT-5/Beta 复合材料为载体, 采用等体积浸渍法制备 NiW/KIT-5/Beta 催化剂。通过 XRD, SEM, TEM, py-FTIR, H₂-TPR, XPS 等表征方法研究了不同水热温度对复合载体及相应催化剂理化性质的影响。以喹啉为模型反应物, 在温度 320 °C, 压力 4 MPa, WHSV 为 4.8 h⁻¹ 的反应条件下, 考察了不同催化剂的加氢脱氮性能。结果表明, 通过改变水热合成温度可以调控分子筛的比表面积和孔道结构, 进而调控催化剂的活性位点数量。当水热合成温度为 125 °C 时, NiW/KB-125 催化剂表现出最佳的喹啉脱氮率 96.8%, 这主要归因于 NiW/KB-125 催化剂优异的孔道结构, 较大的比表面积(883 m²/g)和孔容(0.77 cm³/g), 较多的 B 酸位点、较高的金属硫化度(80.12%)和适宜的金属载体相互作用力(MSI)。

关键词: 介孔材料; KIT-5/Beta 复合分子筛; NiWS; 喹啉; 加氢脱氮

中图分类号: TQ519

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