

The Research of Nano Self-assemble Catalyst Used for Residue HDN

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Abstract: The properties and compositions of feedstock have great impact on reaction performances in residue hydrotreating and hydrocracking. The deactivation of residue hydrotreating and hydrocracking catalysts are mainly due to the high content of sulfur and nitrogen in residue. The removal rate of sulfur and nitrogen is an important parameter for the stability and life of catalyst. The primary objective of the present work is to prepare highly efficient denitrification catalyst. According to the mechanism of nano self-assembly, a series of Mo-Ni nano self-assemble catalysts were prepared by the method of forward and reverse micelles. The results shown that refining catalysts with the Mo and Ni ratio of 6:1, the theory loading is 30%, the denitrification rate was 56.2%; While the Mo and Ni ratio of cracking catalyst is 6:1, the theory loading is 25%, the Mo-Ni nano self-assemble catalysts will reach the best performance at the denitrification rate of 58.3%. For further studies grading the high activity of hydrotreating catalyst SS-1 and hydrocracking catalyst SS-2 in a fixed bed microreactor to investigate the denitrification rate with different process by orthogonal experiments. The result shown that when pressure arrived 14MPa, LVSH is 0.2h^{-1} , reaction temperature is 390°C , hydrogen/oil ratio 850:1 is the final investigation result, at this point HDN = 79.20%.

Keywords: Nano Self-assembly, Hydrotreating, Hydrocracking, Denitrification Rate

1. Introduction

With extensive exploitation of petroleum, worldwide crude oil is becoming heavier and declining in quality. As demand for oil remains strong around the world, while residue oil hold about 30%~50% percent of crude oil, having eighty percent of nitrogenous compounds and some other poisonous inclusions. These poisonous inclusions have serious influence on environment and catalysts. Because of the requirement for light fuels, many researches have been performed upon converting the residue to clean light fuels efficiently and economically. [1-3]

Nowadays, there are many residue upgrading processes. [4] Among them, the residue hydrotreating process attracts more attention because of its high liquid product yields, good product quality, high production flexibility, and good environmental protection. [5] Nitrogenous compounds in the residue can be strongly adsorbed on the catalyst surface, especially basic nitrides in raw materials. [6] Acid

neutralization leads to decrease in the catalytic activity, oil stability will also decreased because of the neutral N-compounds enter into the cracking products. The influencing factors on the residue hydrotreating reaction are temperature, pressure, liquid hourly space velocity (LHSV), hydrogen/oil ratio (H/O), catalyst, feedstock properties, etc. [7].

In order to remove nitrogen compounds from residues the catalyst needs to be active and stable, so the Mo-Ni catalyst was prepared based on the mechanism of nano self-assembly. The object of this paper is to elucidate the influence factors on the residue hydrotreating reaction to remove the nitrogen compounds contained in residual oil. The reactive metal content and mass ratio when the denitrogenation rate have the best performance was studied, we also studied the denitrogenation rate when the hydrotreating and hydrocracking nano assembled catalysts graded. which was

28.94% higher than that of domestic FZC catalyst [8].

2. Materials and Methods

2.1. Drugs and Reagents

Tween-80(AR), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR), 150HVI(Industrial goods), Mo-Ni-P active component solution, Urea(AR), Deionized water(electrical conductivity was less than $5.0\mu\text{S}/\text{cm}$ when 25°C).

2.2. Preparation of Nano Self-assemble Catalyst

2.2.1. The Mechanism of Nano Self-assembly

According to the principle of micelle solubilization, the surfactant with volume balance value >1 or $<<1$ is dissolved in the impregnating solution or hydrocarbon oil containing surfactant components. The forward micelle and reverse micelle impregnating solutions were prepared by solubilizing active components in micelles in the form of micelles. In the impregnating solution, the weak interaction force between micelles and micelles is integrated into a certain form. When the catalyst is loaded, the micelle interacts with the surface of the support, so nano self-assembly is carried out on the surface of the catalyst to construct a three-dimensional structure which is prominent on the surface of the support.

2.2.2. Reverse Micelle Method

In order to prepare the solution, the reaction temperature was controlled in the range of $120\text{--}170^\circ\text{C}$. Deionized water, MoO_3 , $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and H_3PO_4 were mixed in a certain mass and then refluxed for 3-5 hours. Then the solution was cooled to 80°C and added to the mixture of stirred surfactant and 150HVI slowly to prepare homogeneous Mo-Ni-P supersolubilized micelles. After diluted with an organic solvent, the reverse micelle organic immersion solution was obtained. The carrier Al_2O_3 was uniformly impregnated with the impregnating solution. After drying at 100°C and roasting at 400°C , the reverse micelle macroporous nano self-assembly catalyst was obtained.

2.2.3. Forward Micelle Method

In order to prepare the solution, the reaction temperature was controlled in the range of $120\text{--}170^\circ\text{C}$. Deionized water, MoO_3 , $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and H_3PO_4 were mixed in a certain mass and then refluxed for 3-5 hours. Then the co impregnation agent (Tween-80) was added to the solution to prepare homogeneous Mo-Ni-P supersolubilized forward micelle solution. the carrier Al_2O_3 was uniformly impregnated with the forward micelle solution. After dring at 100°C and roasting at 400°C , the forward micelle macroporous nano self-assembly catalyst was obtained.

2.3. Properties of Residue and Conditions of Catalyst Vulcanization

The performance of catalysts for hydrodenitrogenation was carried out in a fixed-bed micro-reactor with a catalyst loading of 20 mL (by volume). The catalyst was pre-vulcanized with 2%

sulfur oil at 230°C for 3h and 340°C for 5h. The basic properties of the residue are shown in Table 1.

Table 1. Properties of residue.

Project	Data
Carbon residue/%	4.78
Alkaline nitrogen/ $(\mu\text{g} \cdot \text{g}^{-1})$	2110
Saturated mass fraction/%	50.90
Aromatic mass fraction/%	3.07
Adhesive mass fraction/%	3.07
Asphaltene mass fraction/%	0.27

3. Results and Discussion

3.1. Preliminary Screening of Catalysts

A series of Mo-Ni nano-self-assembled catalysts were prepared by forward micelle method and reverse micelle method in order to investigate the effects of different proportion of active components and different content of active components on the hydrodenitrogenation of residue. When the residue hydrodenitrogenation is the best, the proportion of active components and the content of active components were selected.

3.1.1. Effect of the Ratio of Mo and Ni on the Hydrodenitrogenation Rate

According to the study of Zhang Y X et al. [9-11] Based on the Mo content at the Mo-Ni mass ratio of 6:1, the impregnating solution with the Mo-Ni mass ratio of 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1 was prepared, and the carrier was $\gamma\text{-Al}_2\text{O}_3$. A series of self-assembled Mo-Ni catalysts were prepared to investigate the effect of nano self-assembled catalysts with different active component ratios on residue hydrodenitrification efficiency. Catalysts with different Mo to Ni rates for the performance of HDN are shown in Figure 1.

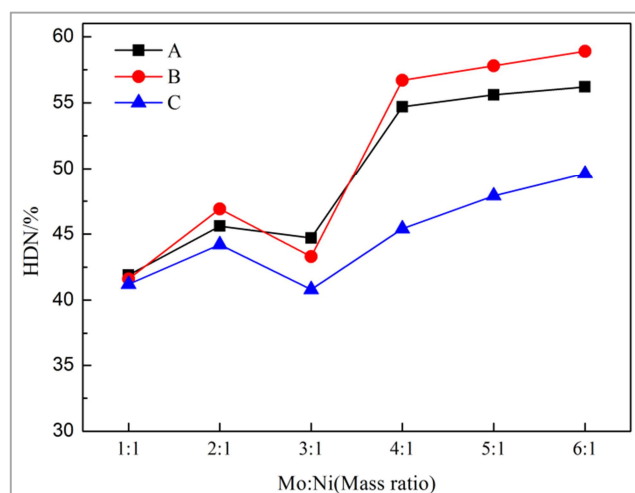


Figure 1. Catalyst with different ratio of Mo and Ni for the performance of HDN.

A. Hydrotreating catalyst by the method of forward micelle; B. Hydrocracking catalyst by the method of forward micelle; C. Hydrotreating catalyst by the method of reverse micelle.

As shown in Figure 1, the denitrification rate increased with the decrease of Ni content in active components. When the mass ratio of Mo to Ni reaches 6:1, the catalysts prepared by the forward micelle method achieves the best hydrodenitrogenation performance. The hydrodenitrification rate of the refined catalyst prepared by the forward micelle method was 56.2% and that of the cracking catalyst was 58.9%, The hydrodenitrification rate of refined catalyst prepared by reverse micelle method was 49.6% and that of cracking catalyst was 51.5%. The result shown that the nano self-assembled catalyst can achieve better hydrodenitrification activity when the ratio of Mo to Ni is 4.82~6.41.

3.1.2. Effect of Active Component Content on Hydrodenitrogenation Rate

According to the 3.1.1, When the molybdenum-nickel mass ratio is 6:1, the impregnating solution with 5%, 20%, 25%, 30%, 35% and 40% active components is prepared respectively.[12] $\gamma\text{-Al}_2\text{O}_3$ was used as carrier for impregnation. A series of Mo-Ni nano self-assembled catalysts with different active component contents were prepared to investigate the effect of nano self-assembled catalysts with different active component contents on nitrogen removal rate in residue. The results of hydrodenitrogenation of nano self-assembled catalysts with different active component contents are shown in Figure 2.

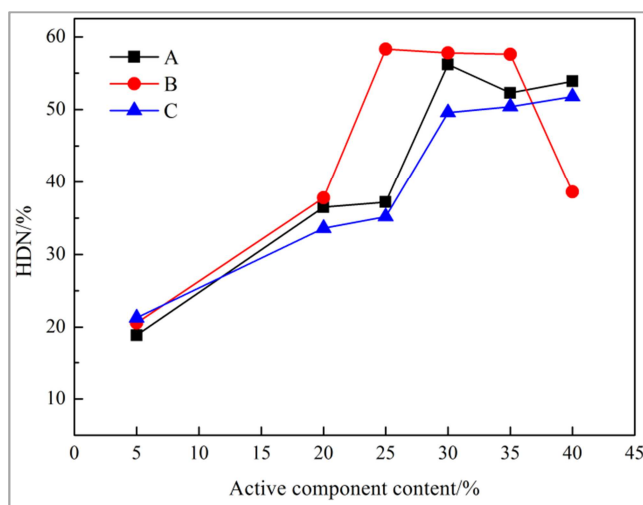


Figure 2. Catalyst with different contents of active components for the performance of HDN.

A. Hydrotreating catalyst by the method of forward micelle; B. Hydrocracking catalyst by the method of forward micelle; C. Hydrotreating catalyst by the method of reverse micelle.

From Figure 2, we can see that with the increase of active component content in the nano self assembled catalyst, the hydrodenitrogenation rate is obviously improved. When the content of active components increased from 25% to 30%, the hydrodenitrification rate of the catalyst prepared by forward micelle method increased from 51.1% to 56.2%, the denitrification rate of the refined catalyst prepared by reverse micelle method increased from 40.9% to 49.6%. However, when the content of active components exceeded 30%, the

hydrodenitrogenation rate basically unchanged and decreased. While the cracking catalyst prepared by forward micelle method, When the content of active component increased from 20% to 25%, the hydrodenitrification rate increased from 54.2% to 58.3%, and when the content of active component exceeded 25%, the hydrodenitrification rate remained unchanged or even decreased.

In summary, the nano self-assembled catalysts SS-1 and SS-3 with 30% theoretical content of active components; SS-2 with 25% theoretical content of active components with cracking function were prepared by forward micelle method and reverse micelle method with 6:1 mass ratio of active components. Then the effects of the dispersions of active components and the gradation of hydrotreating catalyst and hydrocracking catalyst on the residue hydrodenitrification rate were also investigated.

3.2. Analysis of the Dispersion Properties of Active Components in Catalyst

Catalysts SS-1 and SS-2 were prepared by the method of forward micelles, SS-3 was prepared by the method of reverse micelles. The active components were Mo and Ni, the carrier is $\gamma\text{-Al}_2\text{O}_3$. For supported catalysts, the dispersion of active components on the surface of the supports has an important effect on the hydrogenation performance of the catalysts. Therefore, the rational and fully use these active components will be helpful to enhance of the hydrogenation activity of the catalysts. [13]

In this paper, the dispersion of Mo and Ni on the pore and surface of support ($\gamma\text{-Al}_2\text{O}_3$) in catalysts has been analyzed by using the calculated value of NSA (active component dispersion parameter). The dispersion of NSA (active component dispersion parameter) is different from that in general sense. [14, 15] The formula is shown in the next.

$$\text{NSA} = S_{\text{BET, catalyst}} / (S_{\text{BET, support}} \times \omega_{\text{support}})$$

Type: $S_{\text{BET, catalyst}}$ ——Specific surface area of catalyst, $\text{m}^2 \cdot \text{g}^{-1}$

$S_{\text{BET, support}}$ ——Specific surface area of carrier, $\text{m}^2 \cdot \text{g}^{-1}$

ω_{support} ——Mass fraction of carrier, %

According to the nature of NSA,[16] When $\text{NSA} > 1$, some metal active components form small or similar clusters in the pore of the carrier. Besides the pore wall of carrier can provide specific surface for the catalyst, the active metal particles can also provide specific surface for the catalyst; When $\text{NSA} < 1$, the metal active component agglomerated, and the particle size is larger than the carrier pore, thus blocking the carrier pore, so the specific surface area of the catalyst will be greatly reduced. When $\text{NSA} \approx 1$, the contribution of the pore wall of carrier to the specific surface area of the catalyst is almost no loss, and the active metal component is monolayer dispersed in the carrier pore. [17] The calculation results of NSA (active component dispersion parameter) are shown in Table 2.

Table 2. The NSA of SS-1, SS-2 and SS-3.

Catalyst	SBET/(m ² ·g ⁻¹)		Vp/(mL·g ⁻¹)		ω(Active Component)/%	NSA
	Carrier	Catalyst	Carrier	Catalyst		
SS-1	207.34	159.6	0.59	0.28	28.32	1.07
SS-2	337.94	276.5	0.58	0.31	22.38	1.05
SS-3	207.34	128.41	0.59	0.29	26.84	0.87

According to Table 2, The NSA values of the catalysts SS-1 and SS-2 are approximately equal to 1, indicating that Mo and Ni are monolayer dispersed and the loading amounts of Mo and Ni are lower than the threshold values. the contribution of the pore wall to the surface area of carrier γ -Al₂O₃ remained unchanged, and the hydrogenation effect of the catalyst is better. The NSA of catalyst SS-3 is $0.87 < 1$, indicated that the active component is not monolayer dispersed but accumulated. The particle size of catalyst is larger than that of carrier pore, thus blocking the carrier pore, so the specific surface area of catalyst SS-3 will be greatly reduced.

3.3. Comparison of the Hydrotreating Performance of SS-1 and SS-3

The active components of nano self-assembled catalyst SS-1 prepared by forward micelle method is monolayer dispersed, while the nano self-assembled catalyst SS-3 prepared by reverse micelle method is multilayer dispersed, and both of them are catalysts with hydrotreating function. The nitrogen in residue can

be removed during hydrotreating. The catalysts SS-1 and SS-3 were evaluated at reaction pressure of 14 MPa, LVSH of 0.25 h⁻¹, reaction temperature of 370°C and hydrogen/oil ratio of 758:1 in order to investigate the hydrodenitrification rate of the active components in the catalyst under different dispersion conditions. The hydrogenation performance evaluation results of catalysts SS-1 and SS-3 are shown in Table 3.

According to table 3, the denitrification rate of catalyst SS-1 prepared by forward micelle method is 56.2%. The denitrification rate of catalyst SS-3 prepared by reverse micelle method is 49.6%. The denitrification rate of catalyst SS-1 is 1.13 times than that of SS-3. This is due to the fact that the active component of multilayer dispersion has little dispersion and weak interaction with the carrier, which can not provide enough acidic sites, which makes the hydrogenation activity of the catalyst SS-3 inferior to that of SS-1. which accords with Topsoe et al.[18, 19] provided, Co-Mo-S-II catalyst has low dispersion and weak interaction with the support, and its hydrogenation activity is not very high.

Table 3. Performance evaluation of SS-1 and SS-3.

Catalyst	Most probable aperture/nm	HDN/%
SS-1	13.25	56.2
SS-3	13.76	49.6

In order to further investigate the hydrodenitrification rate of the catalyst, the high activity nano self-assembled catalysts SS-1 and SS-2 were graded, and orthogonal test was designed to investigate the hydrodenitrification rate of the catalyst under different process conditions.

3.4. Research of Denitrification Performance by Graded Nano Self-assembled Catalyst SS-1 and SS-2

3.4.1. Grading Test of Nano Self-assembled Catalyst SS-1 and SS-2

The higher activity of hydrotreating catalyst SS-1 and hydrocracking catalyst SS-2 are graded in a fixed bed microreactor to investigate the hydrodenitrification rate of the catalyst under different process conditions by Orthogonal experiment. Temperature, Pressure, Hydrogen/oil ratio and LVSH as four factors of the process. The results are shown in Table 4.

Table 4. Result of orthorhombic experiment.

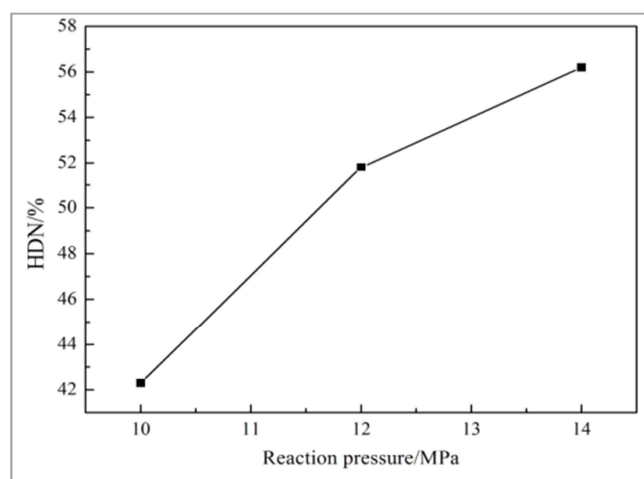
Sequence	Factor	A	B	C	D	Result
		Pressure/MPa	LVSH/h ⁻¹	Temperature/°C	Hydrogen/oil ratio/v·v ⁻¹	HDN/%
1		1	1	3	2	37.63
2		1	2	1	1	47.16
3		1	3	2	3	42.23
4		2	1	2	1	52.42
5		2	2	3	3	57.06
6		2	3	1	2	45.78
7		3	1	1	3	76.59
8		3	2	2	2	42.21
9		3	3	3	1	49.72

3.4.2. Effect of Temperature, Pressure, Hydrogen/Oil Ratio and LVSH on HDN

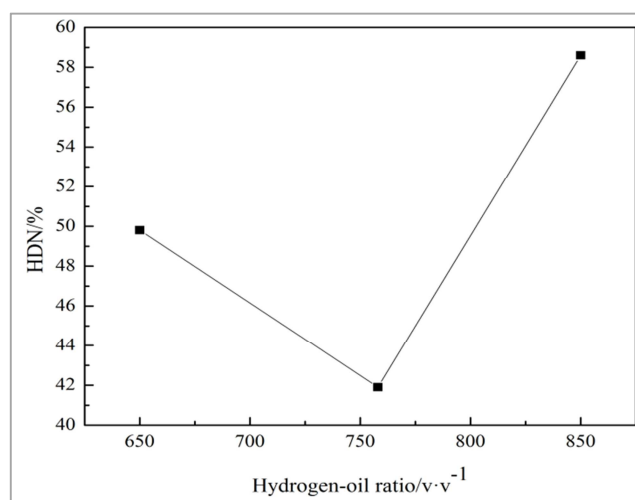
The effects of various factors (temperature, pressure,

Hydrogen/oil ratio and LVSH) on HDN of residue were discussed by range analysis of orthogonal experiment. The curves of the effects of reaction factors (temperature, pressure, Hydrogen/oil ratio and LVSH) on hydrodenitrification rate are

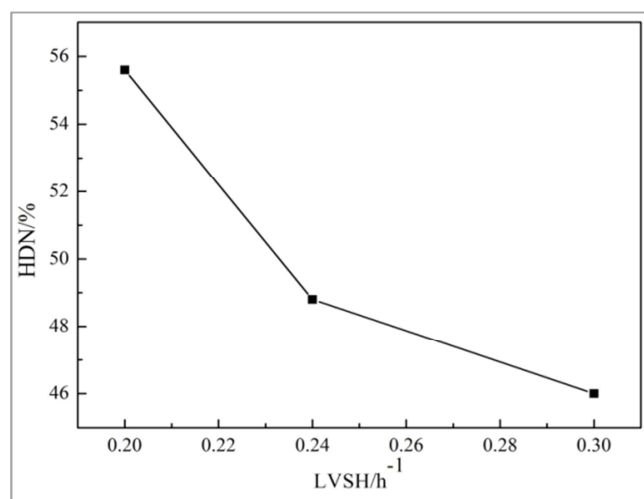
shown in Figure 3.



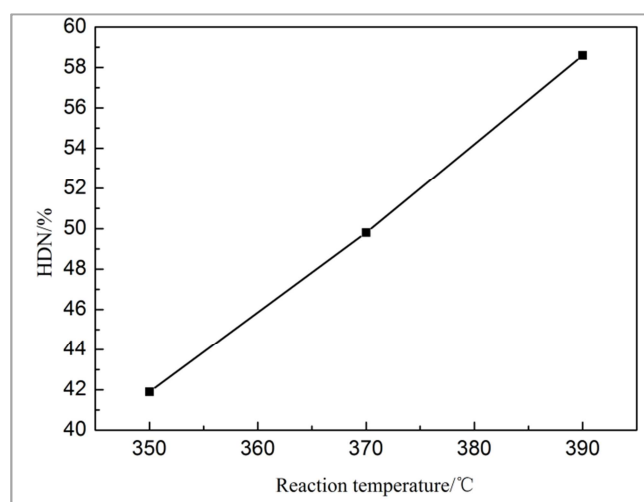
(a)



(d)



(b)



(c)

Figure 3. Reaction pressure, LVSH, Reaction temperature and hydrogen/oil for the effect of residue hydrogenation.

According to Figure 3(a), the residue denitrification rate (HDN) is proportional to the reaction pressure, That is, the rate of hydrodenitrogenation increases with the increase of reaction pressure, and the maximum hydrodenitrification rate is 56.2% at 14Mpa. According to Figure 3(b), the rate of hydrodenitrification decreases with the increase of LVSH. For heavy oil hydrodenitrification process with high nitrogen content, LVSH has a very important influence on the reaction process. And hydrodenitrification is the slowest link in the process of heavy oil hydrogenation, so considering the requirement of HDN reaction on reaction depth, it is suitable at high pressure and low LVSH for heavy oil hydrogenation. In Figure 3(c), the hydrodenitrification rate (HDN) of residue increases with the increase of reaction temperature, and the denitrification rate is approximately linear with the reaction temperature. Because the effect of reaction temperature on the reaction rate of hydrodenitrification follows the Arrhenius equation, the reaction rate constant will be increased and the reaction rate will be accelerated by increasing temperature. According to Figure 3(d), with the increase of the hydrogen/oil ratio, the rate of hydrodenitrification first decreases and then rises. When the hydrogen/oil ratio is 850:1, the highest denitrification rate is 58.6%. No matter high, low reaction temperature or high and low LVSH, the rate of hydrodenitrogenation has a maximum value. From the direct range analysis, the hydrogen/oil ratio has the greatest influence on the hydrodenitrification rate, followed by the reaction pressure, followed by the reaction temperature, and the LVSH has the least influence on the hydrodenitrogenation rate. The optimum technological conditions are $A_3B_1C_3D_3$.

4. Conclusion

The results show that the best hydrodenitrification effect can be obtained when the mass ratio of active component of nano

self-assembled catalyst is 6:1, the theoretical load of active component of hydrofining catalyst is 30%, and the theoretical load of active component of hydrocracking catalyst is 25%. the denitrification rate is 56.2% and 58.3% respectively. According to the gradation of high activity hydrofining catalyst SS-1 and hydrocracking catalyst SS-2 in a fixed bed, the optimum technological conditions are $A_3B_1C_3D_3$, i.e. the reaction pressure is 14Mpa, LVSH is $0.2h^{-1}$, reaction temperature is $390^{\circ}C$, hydrogen/oil ratio is 850:1. According to this condition, the experiment of the orthogonal table does not appear in the nine experiments, through the supplementary experiment, the hydrodenitrification rate under this condition was 79.20%, which was 28.94% higher than that of domestic FZC catalyst.

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