Hydrodenitrogenation Kinetics of Diesel Oil and Catalyst Stacking Simulation

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ABSTRACT

The kinetics of hydrodenitrogenation (HDN) was systematically studied in an isothermally high-throughput reactor over three kinds of catalysts (CoMo, NiMo, NiMoW) to produce clean diesel meeting latest national standard of China. The influences of reaction temperature, reaction pressure, volume ratio of H_2 to oil and space time on hydrodenitrogenation were investigated to obtain kinetic parameters. Two-lump kinetic model considering the influence of self-inhibition was selected for the HDN reaction of diesel oil after the comparison with one-lump kinetic model. The model could well predict the evolution of nitrogen-containing compounds concentration along the axial length of reactor. Based on the two-lump kinetic model, the simulation on the HDN activity of various catalyst stacking-schemes is close to the experimental data, which proves the model is applicable for the simulation of catalyst stacking system. And the concentration of nitrogen-containing compounds was predicted for the catalyst gradation model of different loading sequences.

Key words: hydrodenitrogenation; diesel oil; reaction kinetics; model; catalyst stacking.

Introduction

Diesel oil is an important vehicle fuel, which occupies a large proportion in fuel oil. Nitrogen-containing compounds in diesel oil will be converted to harmful substances in the combustion process, such as NO_x. These substances are harmful to human body and pollute the environment, leading to the environmental problems. Furthermore, nitrogen-containing compounds causes discoloration and colloid in

diesel fuel and affect the stability of diesel oil.[1] In general, all nitrogen-containing compounds in diesel oils can be divided into two groups: basic and non-basic nitrogen-containing compounds. During the procedure of diesel oil hydrofining, basic nitrogen-containing compounds primarily affect acid sites of the catalyst and non-basic nitrogen-containing compounds primarily affect metal active sites of the catalyst.[2] As well as, competing adsorption of nitrogen-containing compounds could inhibit other reactions during the procedure of diesel oil hydrofining, such as hydrodesulfurization and hydrodearomatization.

In recent years, because of the stricter environmental legislation, it's necessary to reduce vehicle exhaust pollution.[3] According to the National VI emission standard of China, sulfur content in diesel oil must be lower than 10 ppm and mass fraction of polycyclic aromatic hydrocarbons in diesel oil must be lower than 7%. There are no clear limits on the nitrogen-containing compounds of diesel oil, but there are strict limits on nitrogen oxides emissions. NO_x release limit of World Harmonized Transient Cycle (WHTC) of the past few years is showed in Table 1. NO_x release limit of National VI emission standard of China is 600 mg/kWh, which is far less than that of National IV and National V emission standards of China. One of the effective measures to meet new emission standard is deep hydrofining of diesel oil. However, the quality of crude oil is getting worse and worse and the contents of heteroatoms (S, N, O, etc.) in crude oil are increasing. In order to obtain high quality products, the operating conditions of hydrofining might be changed, including increased hydrogen partial pressure, increased reaction temperature and longer residence time. But the most cost-effective way is to increase the quality of the catalyst, including the higher selectivity, activity, and stability.[4]

Table 1. NOx release limit of WHTC

Emissions	National IV	National V	National VI
NOx, mg/kWh	4200	2800	460

The hydrodenitrogenation of diesel oil usually occurs in the diesel oil hydrofining system. Hydrodenitrogenation could convert the organic nitrogen species to the corresponding hydrocarbons and NH_3. The traditional catalysts for hydrotreating are $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and $Ni(Mo)W/Al_2O_3$ catalysts.[5]

The production of clean fuel is closely related to high performance hydrofining catalysts and catalyst stacking systems. Catalyst stacking technology is an important technology for producing clean fuel. It is of great significance for catalyst stacking to clarify the evolution of nitrogen-containing compounds concentration along the axial length of reactor with reaction kinetics. Therefore, it is necessary to study the hydrodenitrogenation kinetics since nitrogen compounds has an important effect on diesel oil hydrofining system. Different molecules in the oil have competitive adsorption phenomenon on the active centers of catalyst. For the same reactions, different catalysts have different selectivity and different reaction depths. The use of catalyst stacking technology can make different catalysts complement each other in performance and give full play to catalyst performance.

Reaction kinetic model can be used to optimize and design technological process. It's a cheaper and faster tool which can estimate the impacts of changes in variables, such as operating conditions on system performances.[6] Establishment of kinetic model can avoid running expensive experiments in a laboratory or pilot plant but it is a difficult task considering the complexity of reaction system.[7,8]

Many studies on the kinetics of diesel hydrodenitrogenation are concerned with model compound kinetics. Machida et al.[9] investigated individual and simultaneous HDN of aniline and pyridine over Ni–Mo–P/alumina catalyst and established kinetics of HDN. Their kinetic model considered that HDN of aniline was inhibited by pyridine and both individual and simultaneous reactions of aniline and pyridine were quantitatively predicted by Langmuir-Hinshelwood equations. Dai et al.[10] investigated shale oil

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hydrogenation in a two-stage fixed bed reactors. Their kinetic model could accurately predict the nitrogen-containing compounds removal ratios and desired product yields in shale oil hydrogenation at different catalyst stacking-schemes with ultra-low nitrogen-containing compounds. Nguyen et al.[11] investigated a kinetic study of the hydrodenitrogenation of quinoline over a $NiMo(P)/\gamma-Al_2O_3$ sulfide catalyst in a batch reactor. Liquid−vapor mass transfer is considered in the reactor model, and the self-inhibition effect due to competitive adsorption of nitrogen-containing compounds was confirmed. The kinetic model was able to predict for HDN of model molecule under different reaction conditions. Besides the kinetic model for specific nitrogen-containing compounds, lumping kinetic models of hydrodenitrogenation are also reported in the literatures. Tang et al.[12] investigated shale oil hydrogenation in miniature fixed bed reactor. Nitrogen compounds was divided into 2, 3, 4 or 5 lumps and four models of hydrodenitrogenation were established. All the four kinetic models have obtained satisfactory results, among which the 5-lump kinetic model had the best fitting effect.

In the present work, HDN kinetics of three catalysts (CoMo, NiMo, NiMoW) and their combinations in diesel oil was systematically investigated in high-throughput reactor. Two-lump kinetic model for diesel oil HDN was proposed, and its kinetic parameters were estimated through fitting experimental data of diesel oil hydrogenation at various levels of reaction pressure, volume ratio of H_2 to oil, temperature and liquid hourly space velocity (LHSV). The agreement between experimental data and model fit appears to be rather satisfactory in all tested conditions. Experimental data of catalyst stacking was used to validate the model. The prediction application of the catalyst stacking model is also presented.

Mechanism of hydrodenitrogenation

For six-membered N-Rings nitrogen compounds and five-membered N-Rings nitrogen compounds, it is generally believed that the aromatic ring is saturated first and then the C-N bond is broken.[13,14] The

hydrogenation of aromatic rings is generally regarded as ring by ring. Sun et al.[15] investigated the chemistry of (N-ethyl) carbazole hydrogenation over Raney-Ni catalyst, and proposed that the reaction was a stepwise hydrogenation process and the first H_2 was added to the C1=C10 double bond in the hydrogenation. According to the literature,[16-18] pyridine was first hydrogenated and saturated with aromatic ring into piperidine. Then denitrogenating went via piperidine ring opening to pentyl amine followed by nitrogen removal, producing C5 hydrocarbons and ammonia as end products. Quinoline was first hydrogenated and saturated with aromatic ring one by one. Then nitrogen was removed via ring opening, converting to corresponding hydrocarbons and ammonia as end products. [11] In the paper of Bunch et al. [19], the reaction steps for OEA (o-ethylaniline) and OECHA (o-ethylcyclohexylamine) are respectively expected to be similar to that of o-propylaniline and o-propylcyclohexylamine.

For amine nitrogen compounds, there are generally two reaction paths for HDN: one is aromatics hydrogenation followed by hydrogenolysis of C-N bond, and the other is hydrogenolysis of C-N bond followed by aromatics hydrogenation. [20] But C–N bond of aniline is sp^2 hybridization with higher energy barrier, and it is difficult to deaminate directly. [21] According to Bachrach et al.[22], most anilines are converted to cyclohexylamine through hydrogenation saturation reaction, and then break C(sp3)-N bond.

Reaction network of typical nitrogen compounds were shown in Table 2.

Mechanism of carbon–nitrogen bond cleavage

Rupturing the C-N bond is the last step in hydrodenitrogenation. [23] There are two mechanisms for C-N bond cleavage[4,23-25]: Hoffmann E (E_1, E_2) elimination and nucleophilic S_N (S_N1, S_N2) substitution. For E_2 reaction mechanism, the final products were alkene and NH_3. For S_N2 reaction mechanism, the cation reacts with base B^- converted to NH_3 and thiol, and then converted to an alkene and alkane. The protonated amine releases NH_3 to form a carbocation, which then reacts with B^- or SH^- to give either thiol (S_N1) or an alkene

$(E_1)^3$. Prins et al. carry out a detailed investigation of the HDN of alkylamines over sulfided NiMo/Al$_2$O$_3$ and they concluded that the removal of the nitrogen heteroatom from alkylamines occurs mainly by a nucleophilic substitution of the alkylamine to an alkanethiol, which subsequently produces an alkene or alkane and H$_2$S. [26] They also proposed that the mechanism of the HDN of amines is governed by the type of carbon to which the amino group is attached.

Table 2. Reaction network of typical organonitrogen heterocycles

Typical nitrogen compounds	Reaction network
Pyridine[16]	
Quinoline[11]	
Indole[19]	
Ortho-propylaniline[22]	

Cattenot et al.[24] investigated the HDN of several amines on noble metal sulfides and MoS$_2$. The difference in reactivity was due to the different numbers of hydrogens attached to the α and β carbons of the amine. Reactivities of amines depending on different HDN mechanism are shown in Table 3.

Table 3. Reactivities of amines depending on HDN mechanism

reactant	Mechanism of C-N cleavage

	S_N1	S_N2	E_1	E_2
n-pentylamine	Very low	High	Very low	Medium high
tert-pentylamine	High	Very low	Very high	High
neo-pentylamine	Very low	Very low	None	None

Experimental

The properties of diesel oil used in the investigation are shown in Table 4. Compositions of nitrogen compounds in two kinds of diesel oil are shown in Table 5, in which the other nitrogen compounds include indole derivative and quinoline derivative. The properties of catalysts for the reaction were shown in Table 6.

Table 4. Properties of two diesel fuels

Properties	Feedstock 1	Feedstock 2
Density, $g \cdot cm^{-3}$	0.8509	0.8823
w (Sulfur), $\mu g \cdot g^{-1}$	12000	8560.8
w (Nitrogen), $\mu g \cdot g^{-1}$	220	419.85
w (paraffin), %	43.2	28.8
w (naphthenic hydrocarbon), %	20.8	18.0
w (mono-aromatics), %	16.4	19.6
w (di-aromatics), %	17.4	29.9
w (tri-aromatics), %	2.2	4.2
w (total aromatics), %	36.0	53.7

Table 5. Types and percentage of organonitrogen heterocycles in the diesel oil

Organonitrogen heterocycles	Feedstock 1, $mg \cdot kg^{-1}$	Feedstock 2, $mg \cdot kg^{-1}$
Methyl carbazole	28.78	53.18
Dimethyl carbazole	44.95	50.03
Trimethyl carbazole	63.03	104.84

Tetramethyl carbazole	33.36	101.15
Pentamethyl carbazole	33.60	52.94
Carbazole	3.59	8.04
Other nitrogen compounds	12.68	49.68

Table 6. Properties of catalysts

Catalyst	specific surface, $m^2 \cdot g^{-1}$	pore volume, $cm^2 \cdot g^{-1}$	average particle diameter, mm
CoMo	228	0.31	0.365
NiMo	146	0.28	0.365
NiMoW	139	0.26	0.365

The HDN kinetic experiments of diesel oil were carried out in a the high-throughput fixed bed device. This system was equipped with 16 parallel reactors, which can perform the HDN reaction at the same conditions (reaction pressure, reaction temperature, flow of the feed, volume ratio of H_2 to oil). The deviations of control parameters for these reactors were lower than 3%. The detailed information of the equipment can be found elsewhere.[35]

Table 7. Loading schemes of catalysts and their combinations in 1-16 reactors

Loading quantity	Reaction tube number							
	1	2	3	4	5	6	7	8
1/4	CoMo	CoMo	CoMo	CoMo	NiMo	NiMo	NiMo	NiMo
2/4		CoMo	CoMo	CoMo		NiMo	NiMo	NiMo
3/4			CoMo	CoMo			NiMo	NiMo
4/4				CoMo				NiMo

Loading quantity	Reaction tube number							
	9	10	11	12	13	14	15	16
1/4	NiMoW	NiMoW	NiMoW	NiMoW	NiMoW	NiMoW	CoMo	NiMo

2/4	NiMoW	NiMoW	NiMoW	NiMoW	NiMoW	NiMo	NiMo
3/4		NiMoW	NiMoW	CoMo	NiMo	NiMo	NiMo
4/4			NiMoW	CoMo	NiMo	NiMo	CoMo

Table 8. Reaction conditions of experiment scheme of high-throughput reactor

Operating conditions	Reaction conditions						
	1	2	3	4	5	6	7
Space velocity, h^{-1}	1.5	1.5	3	2.5	1.5	0.75	1.5
Reaction temperature, °C	300	320	340	340	340	340	360
Reaction pressure, MPa	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Volume ratio of H$_2$ to Oil	300	300	300	300	300	300	300
Operating conditions	Reaction conditions						
	8	9	10	11	12	13	14
Space velocity, h^{-1}	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Reaction temperature, °C	340	340	340	340	340	340	340
Reaction pressure, MPa	4.4	5.4	6.4	6.4	6.4	6.4	7.4
Volume ratio of H$_2$ to Oil	300	300	800	500	300	200	300

Three kinds of catalysts (CoMo, NiMo, NiMoW) were investigated in the kinetic experiments. The ranges of reaction temperature, reaction pressure, liquid hourly space velocity, volume ratio of hydrogen/oil were 300-360°C, 4.4-7.4MPa (gage reaction pressure), 0.75-3h^{-1}, 200-800v/v, respectively, which is close to that of commercial hydrofining installations. As show in Table 7, proper amount of catalysts and their combinations were respectively loaded in 16 reactors for investigating the influence of space velocity and catalyst type. The catalysts were sulfided with a solution of 2 wt% CS$_2$ in kerosene under 6.4MPa of hydrogen reaction pressure at 250°C (ramp of 25°C/h) for 6 h and at 320°C (ramp of 15°C/h) for 4h. After the sulfidation, the catalysts were activated by hydrogenated diesel (S content: 685 mg·kg^{-1}) for 24h at 325°C. Afterwards, the diesel oil was fed to the reactors. A variety of conditions were performed for kinetic reaction

investigation by varying reaction temperature, reaction pressure, volume ratio of H_2 to oil, and flow of feed, which were shown in Table 8. For each condition, the time on stream was maintained for 72h. During the experiment, the properties of products were checked every 24h. It was showed that the N content for every three days did not show obvious variation. The general deviation of N contents in 72h days were less than 3mg·kg^{-1}. Even at more severe conditions, no change in the catalyst activity was observed. The results suggested that the deactivation of the catalyst was not significant during the reaction. Sulfur and nitrogen contents in the products were measured by S and N analyzer. The compositions of diesel were quantitatively analyzed by near-infrared spectroscopy method on spectrometer Antaris II from Thermo Scientific equipped with InGaAs detector.[36] The type and percentage of nitrogen-containing compounds in the feed and products were analyzed by gas chromatography method.

Experiment results

In the present investigation, effects of space time, reaction temperature, reaction pressure, and volume ratio of H_2 to oil on the reaction were systematically investigated. For each catalyst, 68 groups of experimental data under different experimental conditions were used to estimate the hydrodenitrogenation kinetic parameters of diesel oil. The experimental data with trace amount of total organonitrogen in the product was excluded (N < 0.5 mg/kg). In fact, 49-60 groups of experimental data under different conditions were used to estimate the kinetic parameters for each catalyst. Furthermore, 48 groups of experimental data with four cases of catalyst stacking-schemes at various reaction temperature and reaction pressure were used to confirm the accuracy of hydrodenitrogenation two-lump kinetic model for all three catalysts.

*Effect of reaction temperature on HDN of diesel oil*
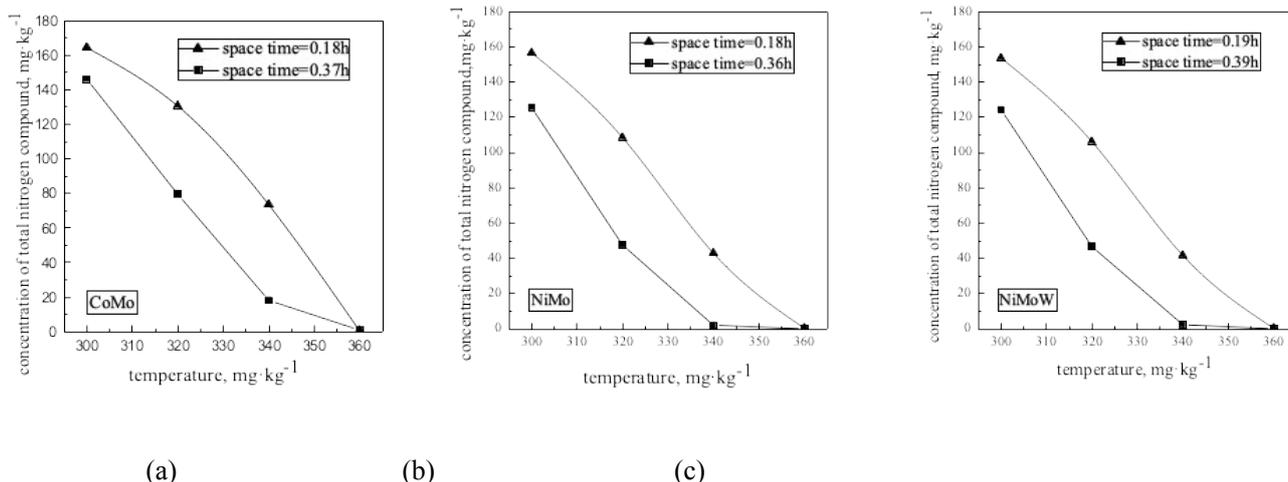
Figure 1. Effect of reaction temperature on HDN of diesel oil on CoMo(a), NiMo(b) or NiMoW(c) catalyst
P=6.4MPa, H$_2$/Oil=300v/v

In general, from a perspective of reaction kinetics, with the increase of reaction temperature, the rate of reaction increases. In this study, the effect of reaction temperature on HDN reactions is shown in Figure 1. Within the scope of investigation, the influence of reaction temperature on hydrodenitrogenation reaction is consistent with CoMo, NiMo or NiMoW catalysts. With increasing reaction temperature from 300 °C to 360 °C, the diesel nitrogen content decreases gradually. This means that, under the experimental conditions of this study, the rise of reaction temperature is favorable for HDN reaction on three kinds of hydrogenation catalysts. The comparison between the HDN results on three catalysts also showed that the influence of reaction temperature on HDN reaction with CoMo catalyst is less than that with NiMo or NiMoW catalyst.

Effect of reaction pressure on HDN of diesel oil

It is generally believed that the influence of reaction pressure on hydrogenation reaction is mainly reflected by hydrogen partial pressure. From the perspective of kinetics, increasing the reaction pressure means increasing the concentration of HDN reactant, and the reactants' adsorption ratio of active site on the surface of solid catalyst increases, which is conducive to increase the reaction rate. However, the reaction pressure should not be too high because of the operating cost and the limitation of reactor materials should be considered. Therefore, it is important to choose the proper reaction pressure in the hydrofining process.

In this study, the influences of reaction pressure on hydrodenitrogenation are shown in Figure 2. Within the scope of investigation, on CoMo, NiMo or NiMoW catalyst, the influence of reaction pressure on hydrodenitrogenation reaction is consistent, namely with increasing reaction pressure from 4.4 MPa to 7.4MPa, the nitrogen content decreases gradually. This means that, under the experimental conditions of this study, the rise of reaction pressure is favorable for HDN reaction on three kinds of hydrogenation catalysts.

(a)   (b)   (c)
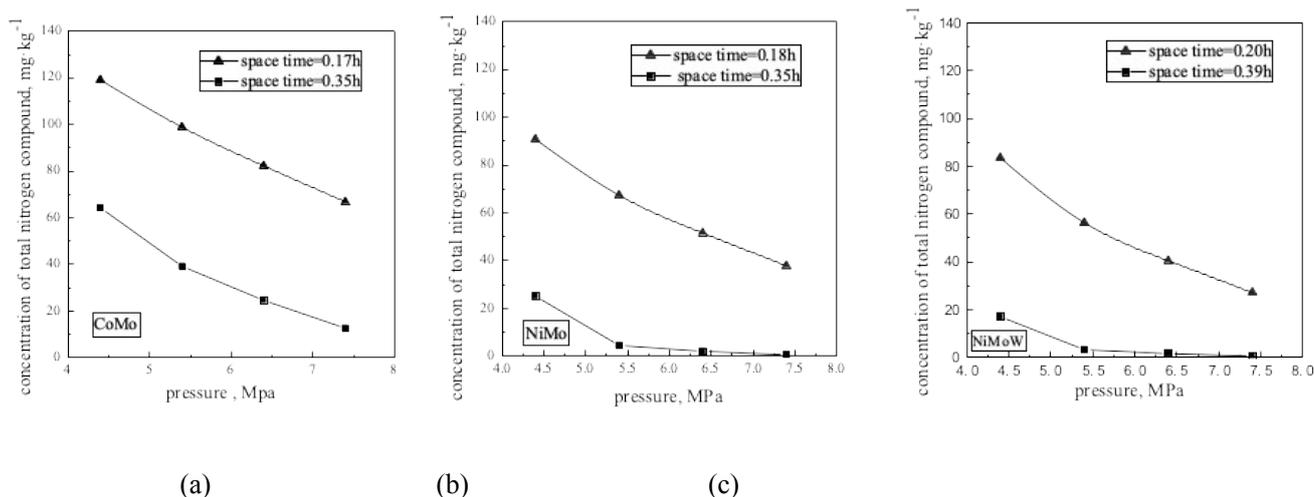
Figure 2. Effect of reaction pressure on HDN of diesel oil on CoMo(a), NiMo(b) or NiMoW(c) catalyst
T=340°C, H_2/Oil=300v/v

Effect of volume ratio of H_2 to oil on HDN of diesel oil

The volume ratio of H_2 to oil is usually defined as the ratio of the gas and feed flow into the unit. The increase of volume ratio of H_2 to oil is helpful to inhibit the dehydrogenation and condensation reaction of the coking precursor and reduce the carbon content of the catalyst surface area, which can not only maintain the high activity of the catalyst surface, but also extend the service life of the catalyst.[27]
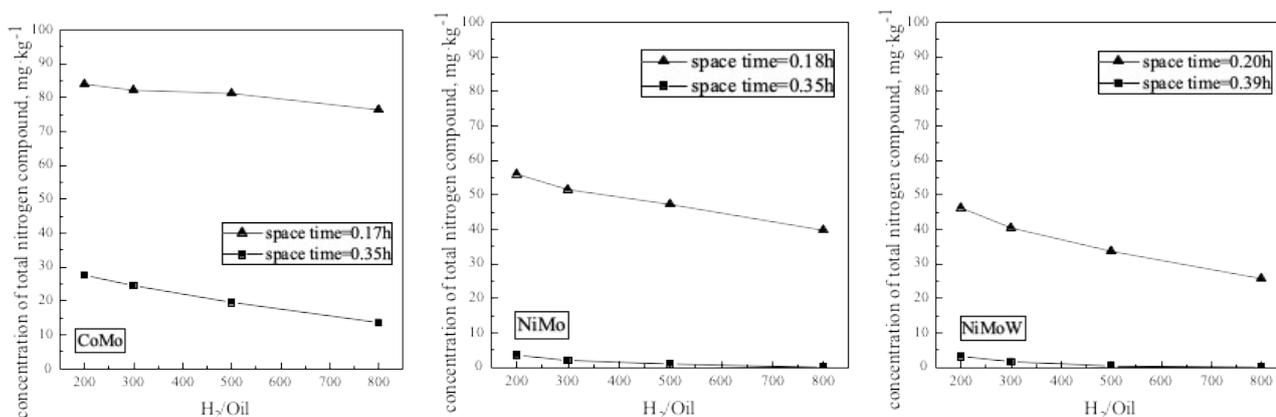
Figure 3. Effect of volume ratio of H_2 to oil on HDN of diesel oil on CoMo(a), NiMo(b) or NiMoW(c) catalyst
P=6.4MPa, T=340°C

In this study, the influences of volume ratio of H_2 to oil on hydrodenitrogenation are shown in Figure 3. Within the scope of investigation, on CoMo, NiMo or NiMoW catalyst, the influence of volume ratio of H_2 to oil on hydrodenitrogenation reaction is consistent, with increasing volume ratio of H_2 to oil from 200 v/v to 800 v/v, the nitrogen content of product decreases gradually.

Effect of space time on HDN of diesel oil

(a)   (b)   (c)
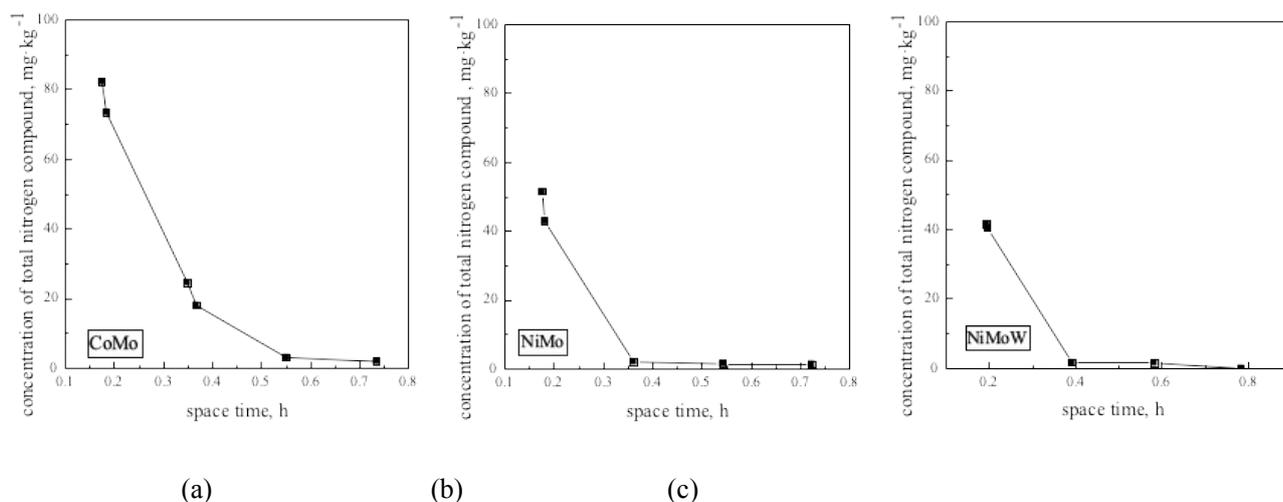
Figure 4. Effect of space time on HDN of diesel oil on CoMo(a), NiMo(b) or NiMoW(c) catalyst
P=6.4MPa, T=340°C, H_2/Oil=300v/v

Space time is the reciprocal of space velocity. Space time is an important indicator of the processing capacity of the device.[28] Effect of space time on HDN on three catalysts is shown in Figure 4. Within the scope of investigation, on CoMo, NiMo or NiMoW catalyst, the influence of space time on hydrodenitrogenation reaction is consistent, namely with increasing space time, the organonitrogen content decreases gradually. Hydrodenitrogenation reactions are not simple order reactions according to the trend in Figure 4. It is worthwhile to determine the HDN reaction orders for the three catalysts.

***Effect of linear velocity on HDN of diesel oil***

(a)   (b)   (c)
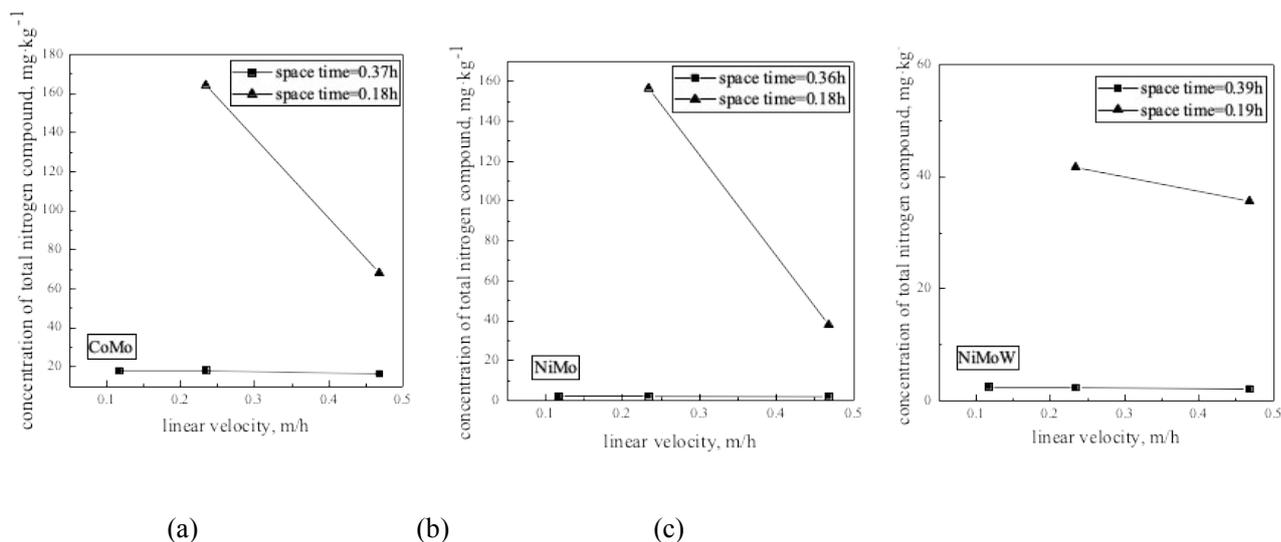
Figure 5. Effect of linear velocity on HDN of diesel oil on CoMo(a), NiMo(b) or NiMoW(c) catalyst

P=6.4MPa, T=340°C, H_2/Oil=300v/v

As shown in Figure 5, in some cases there is certain diffusion effect on hydrodenitrogenation reaction. With the increase of linear velocity, the influence of external diffusion on the reaction decreases, and the nitrogen content of product decreases. The effects of external diffusion cannot be excluded.

Model approach

In this study, two apparent kinetic models instead of intrinsic kinetic models were proposed for diesel oil hydrodenitrogenation: one-lump kinetic model and the two-lump kinetic model.

Yan et al.[34] used the first-order kinetic equation to calculate the reaction rate constants of carbazole derivatives, and the difference between them is very small. Based on some experimental results in this study, the concentration changes of various nitrogen content with space time are shown in Figure 6. As shown in Figure 6, carbazoles with branched chain have similar reaction curves. So, in this study, nitrogen-containing compounds in diesel were divided into two lumps according to the difference of their reaction characteristics. The carbazoles with branched chain are categorized into lump 1, while carbazole and other nitrogen compounds are categorized into lump 2.
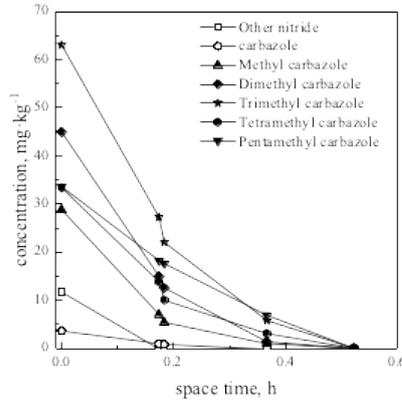
Figure 6. The concentration changes of various nitrogen content with space time on CoMo catalyst
P=6.4MPa, T=340°C, H₂/Oil=300v/v

Model assumption

(a) The reactor operates isothermally under isobaric and steady-state conditions. No catalyst deactivation happens during the hydrogenation reaction.

(b) The reactor behaves like a plug-flow reactor with pseudo-homogeneous reaction assumption.

(c) The vaporization of diesel oil during reaction is neglected.

(d) The reaction pressure is constant during hydrogenation, and the reaction pressure is equal to the hydrogen partial pressure.

(e) There is no mutual conversion reaction between different lumps for two-lump kinetic model.

Taking the nitrogen compounds in diesel oil as a lump, and considering the hydrodenitrogenation reaction of reaction temperature, reaction pressure, hydrogen oil ratio, space time and linear velocity, the following one-lump kinetic model of hydrodenitrogenation reaction was established：

$$\frac{d w_N}{d \tau} = -k_N e^{\left(\frac{-E a_N}{RT}\right)} w_N{}^{n_N} P_{H_2}{}^{\alpha_N} \left(\frac{H_2}{oil}\right)^{\beta_N} \eta_N{}^{ed} \tag{1}$$

$$\eta_N{}^{ed} = \tanh\left(parp_N * v\right) \tag{2}$$

The kinetic model of HDN is not a simple first order reaction or simple second order, and the expression for the effect of external diffusion on the reaction can hardly be deduced. For the better practical

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application, a simplified empirical function was chosen for describing the influence of external diffusion. After trying various forms, formula (2) with good fitting effect was finally chosen. Function of tanh (tangent hyperbolic) corresponds to the trend of the linear velocity on the hydrodenitrogenation. When the x-axis is bigger than 0, the range of y is 0 to 1. The correlation coefficient is determined by experimental data. When the linear velocity is relatively small, it has a certain effect on the reaction. When the linear velocity is large enough, it has no effect on the reaction.

Ho[29] found that HDN of organonitrogen heterocycles is self-inhibited. Therefore, the self-inhibition of nitrogen compounds was considered in the establishment of the two-lump kinetic model. Considering the influence of self-inhibition of nitrogen compounds, reaction temperature, reaction pressure, external diffusion and volume ratio of hydrogen/oil, the following two-lump kinetic model of hydrodenitrogenation reaction was established :

$$\frac{d\,w_{N1}}{d\,\tau}=\frac{-k_{N,1}\,w_{N1}{}^{n_{N1}}\,P_{H_2}{}^{\alpha_{N1}}\left(\frac{H_2}{oil}\right)^{\beta_N}\eta_N{}^{ed}}{\left(1+f_{N1}\times w_{N1}+f_{N1}\times w_{N2}\right)} \tag{3}$$

$$\frac{d\,w_{N2}}{d\,\tau}=\frac{-k_{N,2}\,w_{N2}{}^{n_{N2}}\,P_{H_2}{}^{\alpha_{N2}}\left(\frac{H_2}{oil}\right)^{\beta_N}\eta_N{}^{ed}}{\left(1+f_{N2}\times w_{N1}+f_{N2}\times w_{N2}\right)} \tag{4}$$

$$\eta_N{}^{ed}=\tanh\left(parp_N*v\right) \tag{5}$$

Model parameters

Multivariate function Levenberg-Marquardt[32,33] was used to optimize the model parameters and variable step-size adaptive Runge-Kutta method was adopted to solve the ordinary differential equations of two-lump kinetic model.

Considering the demand of actual industrial installations, it is sufficient to predict the concentration trend of total nitrogen compounds. For the raw diesel oil, the total nitrogen detection and analysis data are accurate and the ratio of different nitrogen compounds morphological data be measured accurately too. As

the reaction product of hydrofining, under certain conditions of deep hydrodenitrogenation, the concentration of total nitrogen compounds in diesel oil can be detected and analyzed, but the morphology of nitrogen compounds can't be detected and analyzed. In order to make full use of experimental results under different reaction conditions, the concentration of total nitrogen compound was taken as the optimization objective function for the parameter estimation of two-lump model.

The following optimization objective function is the sum of the relative deviation between the experimental data and calculated values of mass percentage of each product. The experimental concentration of total nitrogen compounds and calculated values which are the sum of two lumps were used in the optimization objective function,

$$Q=\sum_{a=1}^{n} \frac{\left|\left(W_{N,a,\exp}-W_{N,a,cal}\right)\right|}{W_{N,a,\exp}} \tag{6}$$

Where a=1~n means there are n groups of experimental data; $W_{N,a,cal}$ is the sum of two lumps; $W_{N,a,\exp}$ is the experimental value of total nitrogen compounds.

Experimental data of different lumps under same reaction temperature were used to estimate the reaction rate constants. The effect of reaction temperature on reactions follows the Arrhenius equation:

$$k_{N,i}=k_{0,i}e^{\left(\frac{-Ea_i}{RT}\right)} \tag{7}$$

where $k_{0,i}$ is the pre-exponential factor, E_{ai} (kJ/mol) is the activation energy of the reaction, T (K) is the reaction temperature.

The influence of reaction temperature on the adsorption-equilibrium constant can be described by the Hoff equation[30]:

$$f_i=f_{i0}e^{\frac{\Delta H_{ads}}{RT}} \tag{8}$$

where f_{i0} is the pre-exponential factor, ΔH_{ads} (kJ/mol) is the influence factor of reaction temperature on adsorption.

One-lump kinetic model parameters of hydrodenitrogenation on three is showed in Table 9. The

reliability of the one-lump kinetic model is showed in Figure 7 by the comparison of experimental and predicted values.

Table 9 One-lump kinetic model parameters of hydrodenitrogenation on three catalysts

| Catalysts	CoMo	NiMo	NiMoW
$k_{0,N} \, min^{-1} \cdot (mg/kg)^{-n_{N1}}$	6.77×10^9	3.92×10^{10}	3.35×10^{10}
$Ea_1(kJ/mol)$	1.25×10^2	1.29×10^2	1.29×10^2
n_1	0.94	0.80	0.83
α	1.42	1.40	1.36
β	0.037	0.035	0.15
$parp(min/m)$	4.4×10^3	8.9×10^2	7.2×10^2

(a)   (b)   (c)
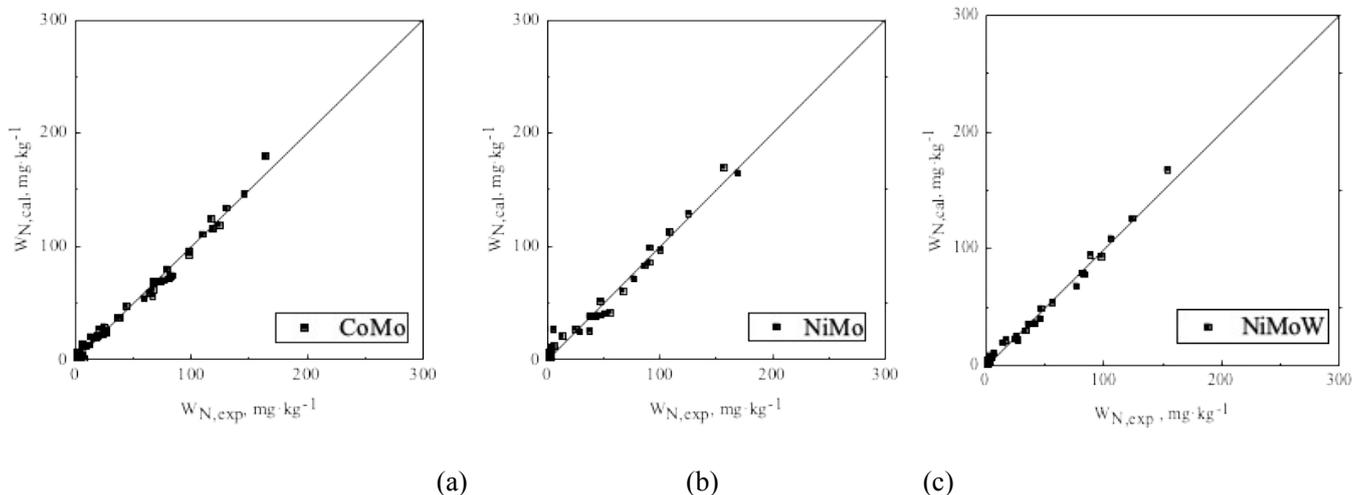
Figure 7. Comparison between experimental and predicted values of total nitrogen compounds lumped model on three

catalysts（CoMo, NiMo, NiMoW）

P=6.4MPa, T=340°C, H_2/oil=300v/v

The average absolute error of the total nitrogen compounds hydrodenitrogenation kinetic model on three catalysts (CoMo, NiMo, NiMoW) were 5.07 mg/kg, 4.28 mg/kg and 3.45 mg/kg, respectively.

The reliability of the two-lump kinetic model is showed in Figure 8 by the comparison of experimental and predicted values which is the sum of two lumps.

The average absolute error of the hydrodenitrogenation two-lump kinetic model on three catalysts (CoMo, NiMo, NiMoW) were 3.93mg/kg, 4.37 mg/kg, and 3.06 mg/kg, respectively. The two-lump kinetic model parameters were listed in Table 10.

Table 10. The two-lump kinetic model parameters

| Parameters	CoMo	NiMo	NiMoW
$k_{0,N_1}, min^{-1} \cdot (mg/kg)^{-n_{N1}}$	6.84×10^{9}	4.14×10^{10}	3.49×10^{10}
$k_{0,N_2}, min^{-1} \cdot (mg/kg)^{-n_{N2}}$	4.72×10^{9}	1.24×10^{9}	2.11×10^{9}
Ea_{N1}, kJ/mol	1.20×10^{2}	1.25×10^{2}	1.26×10^{2}
Ea_{N2}, kJ/mol	1.29×10^{2}	1.17×10^{2}	1.27×10^{2}
n_{N1}	0.71	0.62	0.65
n_{N2}	1.89	1.32	1.78
α_{N1}	1.32	1.25	1.25
α_{N2}	1.24	1.54	1.54
β_N	0.06	0.06	0.06
f_{10}	7.75×10^{-10}	3.60×10^{-6}	1.70×10^{-8}
f_{20}	4.66×10^{-5}	1.92×10^{-5}	5.06×10^{-7}
ΔH_{ads1}, kJ/mol	13.81	8.48	11.29
ΔH_{ads2}, kJ/mol	24.80	30.00	30.00
$parp_N, min/m$	4.4×10^{3}	8.8×10^{2}	9.3×10^{2}

(a)   (b)   (c)
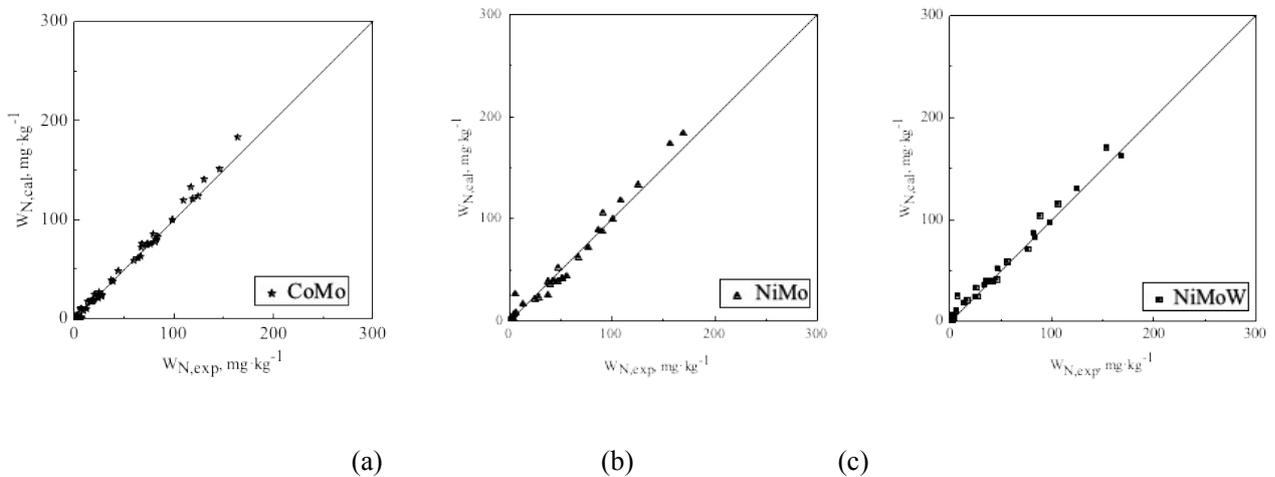
Figure 8. Comparison between experimental and predicted values on three catalysts（CoMo, NiMo, NiMoW）
P=6.4MPa, T=340°C, H$_2$/Oil=300v/v

The two-lump model is established to better adapt to the characteristics of different diesel oils. From the view point of fitting effect, the two-lump kinetic model is better than the one-lump kinetic model. The mean absolute error of two-lump kinetic model for both CoMo and NiMoW catalysts is smaller than that of the one-lump kinetic model. The mean absolute error of two-lump kinetic model for NiMo catalyst is

As shown in Table 10, the parameters of the two-lump kinetic model are different for three catalysts, which means the different lumps have different reaction characteristics on different catalysts. The reaction order of lump 2 on three catalysts is bigger than the reaction order of lump 1, where the reaction order of lump 2 is bigger than 1 and the reaction order of lump 1 is smaller than 1. When concentration of reactants is very small, the reaction rate of reaction order bigger than 1 is slower than the reaction rate of reaction order smaller than 1. This means that the reaction rate of lump 1 is faster than that of lump 2 for deep hydrodenitrogenation. Reaction pressure had obvious effect on the hydrogenation reaction of diesel oil for three catalyst. According to the assumptions in this article, the reaction pressure is equal to the hydrogen partial pressure. Increased pressure means more hydrogen as the reactants, so it has a significant effect on the reaction. The pressure influence factors of the three catalysts are relatively close, which indicates that the sensitivity of the three catalysts to pressure change is similar. However, the influence factor of volume ratio of H_2 to oil was the smaller one for three catalysts, which means hydrogen/oil had little effect on the HDN reaction of diesel oil under the present experimental conditions. Under preconditions of constant pressure, the change in the volume ratio of H_2 to oil does not produce a significant change in the number of reactants. So, the effect of volume ratio of H_2 to oil on reaction was not significant. For the CoMo catalyst the external

diffusion correlation coefficient is relatively large. According to the formula $\eta_N{}^{ed} = \tanh\left(parp_N * v\right)$, when v

is the same, $\eta_N{}^{ed}$ for CoMo catalyst is closer to 1 which is higher than that of other two catalysts , which

means external diffusion has smaller effect on CoMo catalyst than the other two catalysts. The activation energy values of the three catalysts are also within a reasonable range. The activation energy is much larger than the adsorption energy, which agrees with Hans Korsten[29]. There is no significant difference in activation energy between the three catalysts, which means that the activity of three catalysts are similarly sensitive to temperature.

Table 11. Reaction rate constant of each lump on three catalysts

Temperature, °C	$k_{N,1}$			$k_{N,2}$		
	CoMo min^{-1}· $(mg/kg)^{-0.71}$	NiMo min^{-1}· $(mg/kg)^{-0.62}$	NiMoW min^{-1}· $(mg/kg)^{-0.65}$	CoMo min^{-1}· $(mg/kg)^{-1.89}$	NiMo min^{-1}· $(mg/kg)^{-1.32}$	NiMoW min^{-1}· $(mg/kg)^{-1.78}$
300	0.073	0.165	0.126	0.007	0.024	0.005
320	0.172	0.399	0.307	0.017	0.056	0.013
340	0.380	0.912	0.705	0.040	0.121	0.030
360	0.802	1.980	1.535	0.089	0.251	0.066

Reaction rate constants of each lump on three catalysts were shown in Table 11. Rate constant of lump 1 of HDN on three catalysts were all bigger than that of lump 2, which means the reaction rate of lump 1 is faster. With the increase of temperature, the reaction rate constants keep increasing. NiMo catalyst has the highest reaction rate and CoMo catalyst has the lowest reaction rate, which means among the three catalysts, NiMo catalyst has the fastest hydrodenitrogenation rate and CoMo catalyst has the slowest hydrodenitrogenation rate.

Table 12. Adsorption constants of each lump for three catalysts

Temperature, °C	f_{N1}			f_{N2}		
	CoMo	NiMo	NiMoW	CoMo	NiMo	NiMoW
300	2.91×10^{-8}	2.13×10^{-5}	1.82×10^{-7}	1.03×10^{-2}	1.04×10^{-2}	2.74×10^{-4}

320	2.79×10^{-8}	2.01×10^{-5}	1.68×10^{-7}	8.65×10^{-3}	8.42×10^{-3}	2.22×10^{-4}
340	2.67×10^{-8}	1.90×10^{-5}	1.56×10^{-7}	7.34×10^{-3}	6.90×10^{-3}	1.82×10^{-4}
360	2.57×10^{-8}	1.80×10^{-5}	1.45×10^{-7}	6.3×10^{-3}	5.73×10^{-3}	1.51×10^{-4}

Adsorption constants of each lump on three catalysts were shown in Table 12. The adsorption capacity of different nitrogen compounds lumps on the surface of CoMo, NiMo and NiMoW catalysts is different, and the adsorption capacity of lump 2 on the three catalysts is larger than that of lump 1. This is consistent with Laredo el 's result that self-inhibition of carbazole and indole in lump 2 is stronger.[31] The adsorption constant decreases with the increase of temperature, but the variation range is very small. This means that the adsorption of nitrogen-containing compounds is not very sensitive to the change in temperature.

Model validation

Table 13. Catalyst stacking-schemes of experiments

Scheme	Catalyst1	Catalyst2	Ratio
1	NiMoW	CoMo	1:1
2	NiMoW	NiMo	1:1
3	CoMo	NiMo	1:3
4	NiMo	CoMo	3:1

Independent sets of data obtained with four types of catalyst stacking-schemes at various reaction temperature and reaction pressure were used to validate the established two-lump kinetic model. The ratio of catalyst stacking-schemes for validation experiments were shown in Table 13. The reaction conditions of validation experiments for each catalyst stacking-scheme were shown in Table 14.

Table 14. Reaction conditions of catalyst stacking experiments

LHSV, h^{-1}	T, °C	P_{H_2}, MPa	$\left(\dfrac{H_2}{Oil}\right)$, $v \cdot v^{-1}$
0.75	340	6.4	300
1.5	340	6.4	300
2.5	340	6.4	300

|			
3.0	340	6.4	300
1.5	300	6.4	300
1.5	320	6.4	300
1.5	340	6.4	300
1.5	360	6.4	300
1.5	340	4.4	300
1.5	340	5.4	300
1.5	340	6.4	300
1.5	340	7.4	300
1.5	340	6.4	200
1.5	340	6.4	300
1.5	340	6.4	500
1.5	340	6.4	800
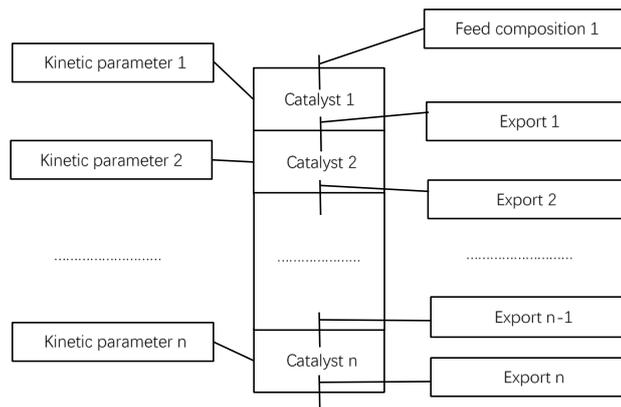
Figure 9. Schematic diagram of catalyst stacking loading model

The catalyst stacking kinetic model is shown in the Figure 9. According to feed composition of export n-1 and the reaction kinetics parameters of the catalyst at n stage, the composition of export n can be calculated. In this way, the whole catalyst stacking system could be simulated based on the kinetic model for individual catalysts.
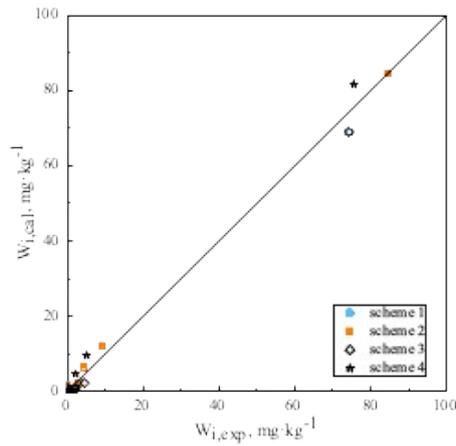
Figure 10. Comparison between experimental and simulated results of HDN product distribution
P=6.4MPa, T=340°C, H_2/Oil=300v/v

The HDN reaction process of different schemes in the gradation experiment was calculated, and the corresponding experimental data were compared. The specific comparison results were given in Figure 10. The diagonals represent that the values of experimental results and the values of calculated via the model are equal. The points are basically distributed on both sides of the diagonals, and the distance of the points from the line is small. The result of gradation verification proves that the model is reasonable.

Prediction of gradation model

Diesel oil hydrofining process mainly includes three reactions: hydrodenitrogenation, hydrodesulfurization and hydrodearomatization. The final optimal stacking-scheme should consider the all three types of hydrofining reactions, not just hydrodenitrogenation. The three catalysts have their own characters: CoMo catalyst has relatively good desulfurization activity, but not good in deep desulfurization. The aromatics saturation capacity of CoMo catalyst is weak; NiMo catalyst has moderate hydrodesulfurization and hydrodenitrogenation activity; NiMoW catalyst has a good performance on deep desulfurization as well as good capability of hydrodearomatization and hydrodenitrogenation. The main objective to consider three catalysts is to show the application of the kinetic model developed in this work. The combination of three catalysts also has the potential application because CoMo, NiMo and NiMoW are

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After obtaining the gradation kinetic model of HDN reaction in isothermal reactor, nitrogen-containing compounds of each lump for different stacking-schemes can be predicted. The following prediction was designed for different loading sequences of the three catalysts (CoMo, NiMo, NiMoW) and the same loading ratio was shown in Table 15.

Table 15. Catalyst stacking-schemes

scheme	catalyst stacking	ratio
1	CoMo NiMo NiMoW	1:1:1
2	CoMo NiMoW NiMo	1:1:1
3	NiMo CoMo NiMoW	1:1:1
4	NiMo NiMoW CoMo	1:1:1
5	NiMoW CoMo NiMo	1:1:1
6	NiMoW NiMo CoMo	1:1:1

The concentration trend prediction of the two lumps of different stacking-scheme is shown in Figure 11 – Figure 12. NiMoW/NiMo/CoMo scheme is the one with the least total time to remove the first lump. At a space time of 0.66h, the NiMoW/CoMo/NiMo scheme give deepest hydrodenitrogenation of second lump. Under the conditions we predicted, the best stacking-schemes for lump 1 is NiMoW/NiMo/CoMo scheme, and the best stacking-schemes for lump 2 is NiMoW/CoMo/NiMo.
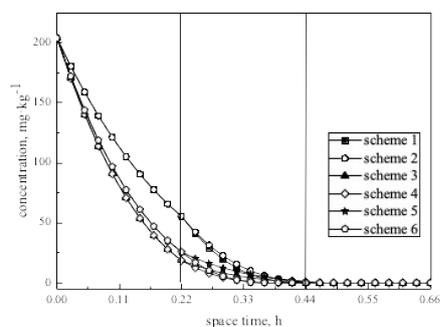
Figure 11. Lump 1 product distribution of different stacking-schemes
P=6.4MPa, T=340°C, H$_2$/Oil=300v/v
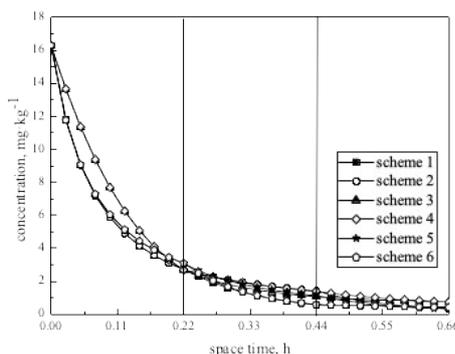
Figure 12. Lump 2 product distribution of different stacking-schemes
P=6.4MPa, T=340°C, H$_2$/Oil=300v/v

Conclusion

Based on the experimental data of diesel oil HDN in high-throughput reactor, the effects of reaction temperature, volume ratio of hydrogen/oil and reaction pressure on diesel oil hydrofining were investigated systematically. In this paper, the one-lump kinetic model of diesel oil and the two-lump kinetic model of diesel oil HDN were established. The influence of self-inhibition of nitrogen compounds, reaction temperature, reaction pressure, external diffusion, and volume ratio of hydrogen/oil was considered in two-lump kinetic model for the HDN reaction of diesel oil. After comprehensive consideration, the two- lump model is chosen finally. The two-lump kinetic model in this paper is reliable. The average absolute error of two-lump kinetic model for hydrodenitrogenation on three catalysts (CoMo, NiMo, NiMoW) were 3.93mg/kg, 4.37 mg/kg and 3.06 mg/kg, respectively. Based on the HDN kinetics of single catalyst, the catalyst stacking model was established. The model was verified by the experimental data of catalyst

stacking. The concentration of nitrogen-containing compounds was predicted for the catalyst stacking model of six loading sequences. The best stacking-schemes for lump 1 is NiMoW/NiMo/CoMo scheme, while the best stacking-schemes for lump 2 is NiMoW/CoMo/NiMo. The optimal catalyst stacking model will be combined with the subsequent hydrodearomatization model and hydrodesulfurization model.

Notation

α_N = the influence factors of reaction pressure of total nitrogen compounds

α_i = the influence factors of reaction pressure of lump i

β_N = the influence index of volume ratio of H_2 to oil

$\eta_N{}^{ed}$ = external diffusion influencing factor

τ = the space time, min

a=1~n means there are n groups of experimental data

E_{aij} = the activation energy of the reaction, kJ/mol

f_{i0} = the pre-exponential factor

f_i = adsorption equilibrium constant of lump i

$\dfrac{H_2}{Oil}$ = volume ratio of hydrogen/oil to the base volume ratio of hydrogen/oil (300v/v)

ΔH_{ads} = the influence factor of reaction temperature on adsorption, kJ/mol

$k_{N,i}$ = the reaction rate constant of lump i, $min^{-1}\cdot (mg/kg)^{-n_i}$

$k_{0,Э i i}$ = the pre-exponential factor, $min^{-1}\cdot (mg/kg)^{-n_i}$

n_N = the reaction order

P_{H_2} = the ratio of reaction pressure to the base reaction pressure

$parp_N$ = correlation coefficient

T = the reaction temperature, K

v = linear velocity, m/min

w_i = the content of lump i, mg·kg^{-1}

$W_{N,a,cal}$ = the sum of two lumps, mg·kg^{-1}

$W_{N,a,\exp}$ = the experimental value of total nitrogen compounds, mg·kg^{-1}

Acknowledgements

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