

Self-catalysed hydrogenation of heavy oil and coal mixtures

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Coal liquefaction and heavy oil processing have become the urgent need for national energy strategic technology reserves in China. However, the inactivation of solid catalysts in these processes is an inevitable problem. Therefore, a self-catalysed method was proposed. The properties of raw oil could be changed by adding a modifier, as it has the function of self-catalysis, and the additional catalyst is no longer needed. The effect of 200 ppm modifier on the hydrogenation of heavy oil and 500 ppm on the hydrogenation of coal and oil were investigated. The results showed that modifiers could be miscible with heavy oil at 50–100 °C and could change the properties of oil. When the temperature exceeded 250 °C, the sulfur element in the heavy oil combined with the metal element brought in by the modifier to form a particle with the size of 2–8 nm, which could interact with the hydrogen molecule to activate the hydrogen molecule. Activated hydrogen atoms further formed the complexes with nickel, vanadium, calcium, iron, and other elements in heavy oil to achieve the purpose of purifying and lightening the oil phase. Therefore, the self-catalysed method could be widely used in oil refining and would greatly promote the development of the oil refining and catalysis industry.

Keywords: self-catalysed; heavy oil; hydrogenation; coal liquefaction; co-processing technology.

INTRODUCTION

It is reported that the world's total crude oil reserves are between 900 million to 1.3 billion barrels, of which conventional oil accounts for only 30 percent. The majority of the rest oil reserves are heavy oil, ultra-heavy oil, and petroleum bitumen¹. With the rapid development of the economy and the increasing demand for light oil, the deep processing technology of heavy oil is being paid more and more attention. Clean fuel made from heavy oil by catalytic hydrogenation has a very large market and is of great strategic significance to ease the increasingly limited oil supply in China². However, heavy oil contains a large number of asphaltene and heteroatom compounds such as sulfur, nitrogen, metal, etc. When the traditional fixed-bed hydrocracking unit is used for processing, the supported catalyst is easy to block the pore due to coking. At the same time, the metal deposition would also lead to catalyst deactivation, which would affect the long-term stable operation of the processing unit^{3–6}.

The slurry bed residue hydrogenation process is an alternative process for heavy oil hydrogenation, and the dispersed catalyst is used to solve the problems effectively such as the diffusion limitation in the pore of the traditionally supported catalyst and the deactivation of the catalyst caused by coke blockage^{7, 8}. Generally, metal sulfides formed in the process of hydrocracking are the main catalytic active species, and metal sulfide catalysts are prepared by *in situ* prevulcanization of metal precursors in the feed⁹. The precursors of catalysts are classified into water-soluble and oil-soluble precursors. Both types of catalyst precursors usually contain metals such as Mo, Co, Cr, Ni, etc. In addition, the precursor of Mo-based oil-soluble catalyst has high catalytic hydrogenation activity and is considered to be the most popular candidate catalyst^{8, 10, 11}.

Direct coal liquefaction (DCL) technology is one of the ways of clean and efficient utilization of coal. As a derivative technology of DCL, the co-processing of crude oil and coal is to couple DCL with heavy oil suspension bed hydrogenation technology to achieve coal and heavy oil co-hydrogenation liquefaction. The co-processing technology of crude oil and coal can not only solve the problem of insufficient circulating solvents in DCL, but also improve the quality of heavy oil and improve the operation efficiency of the plant¹². At the same time, the introduction of inferior raw materials also leads to greater catalyst consumption and solid residue waste production. Hence high efficiency catalyst is the focus of the development of this technology^{13, 14}. In recent years, dispersed transition metal sulfides have been widely used as hydrogenation catalysts in slurry bed reactors for the hydrogenation of coal and heavy oil. However, their disposable characteristics limit the recycling of catalytic active components, resulting in high costs^{15–17}.

This study modified the liquid which needs chemical reaction by catalyst, so that it had the function of self-catalysis. The modifier was a type of metal organic compound, which can be miscible with oil at any ratio under 50–180 °C. In the hydrogenation process, no catalyst was needed in the reactors that could improve the catalysis largely and avoid the negative effects by using the solid catalyst such as insufficient contact surface with liquid and easy to be deactivated by liquid. Regardless of the density, quality and viscosity of liquid, the process of liquid self-catalysis is adopted, which could avoid the requirement of a solid catalyst on liquid quality and maximize the catalytic effect to promote the reaction.

EXPERIMENTAL METHODS

In this study, the modified agent was used to modify the heavy oil by analyzing the molecular morphology of heavy oil and modifiers. Finally, the modified heavy oil

reacted with hydrogen to occur hydrogenation reaction that could verify the modified effect.

Materials

Properties of Heavy oil

The crude oil from Gudao block of Shengli oil field, China was distilled to 300 °C, and the distilled heavy oil was used as experimental oil in this study. Its properties are shown in Table 1.

Properties of modifier

Molybdenum naphthenate and nickel naphthenate are used as modifiers. As naphthenic acid is a mononic acid, its basic structures are shown in Figs. 1, 2, and 3 respectively.

Molybdenum naphthenate and nickel naphthenate were obtained by the chelation of Mo and nickel ions to the carboxyl group, which was analyzed by an inductively coupled plasma atomic emission spectrometer (ICAP6300). The results showed that the content of Mo in molybdenum naphthenate was 4.87 wt%, and the content of Ni in nickel naphthenate was 6.85 wt%.

Table 1. Properties of the Heavy oil

Description		Properties
Elemental analysis (daf, wt%)	C	84.83
	H	11.16
	S	2.93
	N	0.77
	Ni	42.20
	V	4.40
	Ca	18.40
	Fe	8.60
	H/C	1.58
Saturates, wt%		15.70
Aromatics, wt%		33.00
Resin, wt%		45.80
Asphaltene, wt%		14.10
Aromatic carbon ratio (<i>fa</i>)		0.29
Naphthenic carbon ratio (<i>fn</i>)		0.23
Alkyl carbon ratio (<i>fp</i>)		0.48
Total ring number (<i>ft</i>)		9.20
Number of aromatic rings (<i>Ra</i>)		4.90
The number of naphthenic ring (<i>Rn</i>)		4.30
Ra/Rn		1.10

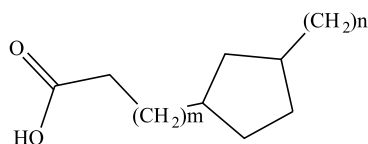


Figure 1. The structure of naphthenic acid

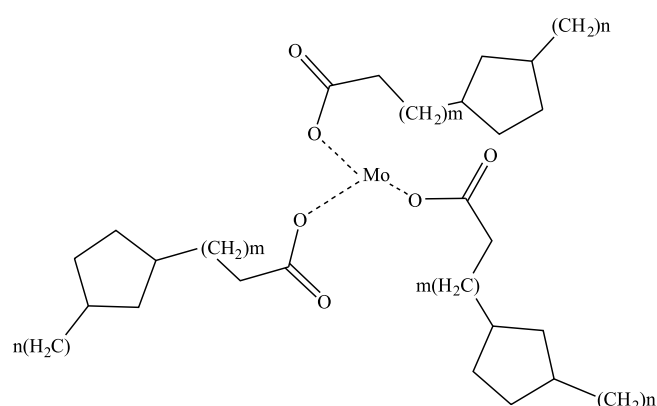


Figure 2. The structure of molybdenum naphthenate

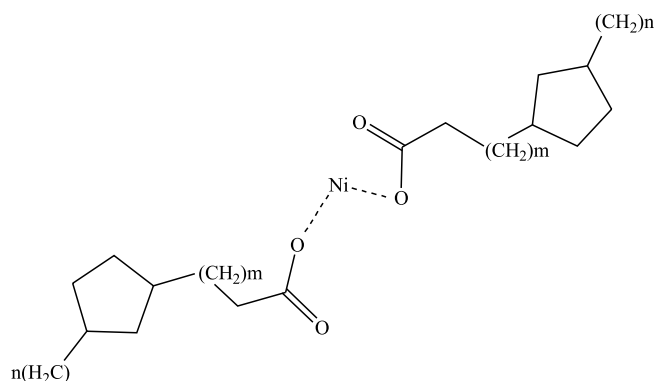


Figure 3. The structure of nickel naphthenate

Experimental set-up

The autoclave test facility was a volume of 2 L, with an experimental pressure of 20 MPa, an experimental temperature not exceeding 500 °C, and a feeding capacity of 250 kg/d. The slurry bed hydrogenation pilot unit was operated under an experimental pressure of 20 MPa and an experimental temperature of about 440 °C.

The modification process of heavy oil

The modifier was mixed with heavy oil at 100 °C, and they were completely miscible to form one single solution, as shown in Fig. 4.

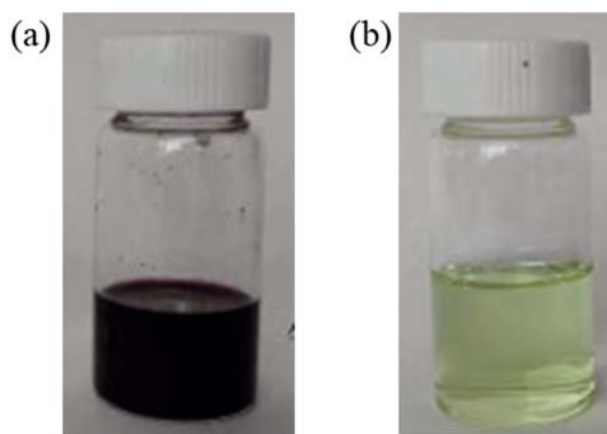


Figure 4. Mixture of heavy oil with (a) Mo-containing modifier and (b) Ni-containing modifier

The intermolecular space between the modifier and the heavy oil molecules is maintained by Van der Waals' force. The modifier reacted with the trace element sulfur in the heavy oil and formed a metal-organic sulfide chelate after the temperature reached 250 °C. The pattern is shown in Fig. 5 (SEM image). It can be seen from the SEM images that the particle size of the chelate was between 2–8 nm and individual units in the unit volume were numerous. The chelate was centered under the presence of hydrogen, and the groups of oxygen, nitrogen, nickel, vanadium, calcium, and iron in the heavy oil molecules reacted with the active hydrogen atoms. The asphaltene and colloid groups with larger molecular weights were also decomposed into small molecules under the action of sulfide chelates. The hydrogenation of heavy oil and a mixture of oil and coal with the modifier were taken as examples, respectively.

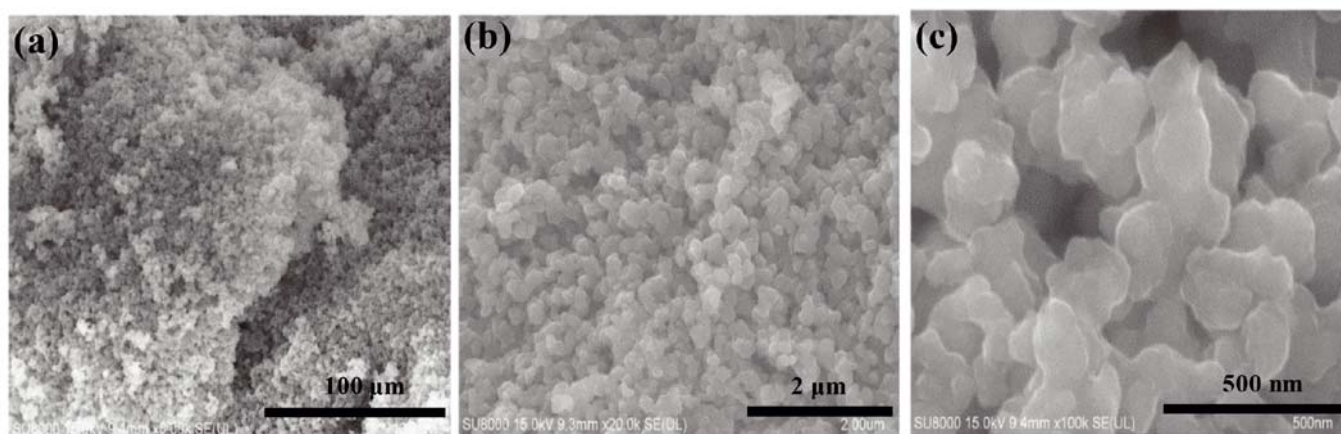


Figure 5. SEM images after the reaction of modifier and heavy oil with the resolution of (a) 100 μm , (b) 2 μm , and (c) 500 nm

Fig. 5 SEM images after the reaction of modifier and heavy oil with the resolution of (a) 100 μm , (b) 2 μm , and (c) 500 nm

Validation of the modified effect

At 100 $^{\circ}\text{C}$, the modifier with Mo / Ni mass ratio of 5:1 was added to the heavy oil as shown in Table 1, and the additional amount was 200 ppm. After the two were fully mixed, they were mixed with hydrogen. The heavy oil could be hydrogenated deeply by running continuously in a slurry bed hydrogenation unit for 1000 h. To make the oil and coal slurry have good fluidity, the wax oil produced was added into the oil-coal slurry, and the wax oil accounts for 20 wt% of the feed. Besides, the reaction temperature was 445 $^{\circ}\text{C}$, and the reaction pressure was 19 MPa. After the shutdown, the inspection of the slurry bed hydrogenation unit found that there were no obvious signs of coking and wear on the static equipment, pumps, valves, and pipe fittings. The changes in the properties of heavy oil after the addition of modifiers are shown in Table 2, and the results indicated that the macromolecular content of colloid and asphaltene decreased from 45.8% and 14.1% to 3.51% and 1.26%, respectively. The content of oxygen, sulfur, nitrogen, nickel, vanadium, calcium and iron also decreased greatly. The H/C ratio increased from 1.58 to 1.68, and the saturation was improved significantly.

Table 2. Properties of heavy oil after the addition of modifiers

Description	Properties	
Elemental analysis (daf, wt%)	C	84.83
	H	12.06
	S	0.88
	N	0.36
	Ni	0.08
	V ppmt	0.04
	Ca ppmt	0.13
	Fe ppmt	0.06
H/C	1.62	
Saturates, wt%	71.51	
Aromatics, wt%	23.72	
Resin, wt%	3.51	
Asphaltene, wt%	1.26	
Aromatic carbon ratio (f_a)	0.21	
Naphthenic carbon ratio (f_n)	0.48	
Alkyl carbon ratio (f_p)	0.51	
Total ring number (f_t)	2.80	
Number of aromatic rings (R_a)	1.90	
The number of naphthenic ring (R_n)	1.60	
R_a/R_n	1.20	

Although the absence of catalyst, a good hydrogenation effect was achieved.

To verify the purpose of the application for the self-catalysed method and the effective scope of the modifier. The mass ratio of molybdenum and nickel modifier added to heavy oil was 5:1 at 100 $^{\circ}\text{C}$, and then they were mixed with pulverized coal. The mass ratio of oil and coal was 1:1, and the added amount was 500 ppm. To make the oil and coal slurry have good fluidity, the wax oil produced was added into the oil-coal slurry, and the wax oil was 20 wt% of the feed. The reaction temperatures were 445 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$, and the reaction pressure was 19 MPa. There were no obvious signs of coking and wear in static equipment, pumps, valves, and pipes of the slurry bed hydrogenation unit after the shutdown. The properties of the oil and coal mixture used in the process of co-hydrogenation are shown in Tables 1 and 3, and the result data are shown in Table 4.

Table 3. Main properties of coal powders

Description		Properties
Industry analysis (wt%)	Mad	10.02
	Ad	5.03
	Vdaf	52.38
	FCdaf	47.62
Elemental analysis (daf, wt%)	C	75.03
	H	5.76
	N	0.73
	S	0.29
	O	18.19
	H/C	0.92
Coal Powders properties	Water content, wt%	3.80
	Ash content, wt%	4.80
	Bulk density t/m^3	0.47
	Particle size	$\leq 200 \mu\text{m}$

RESULTS AND DISCUSSION

The self-catalysed method and validation

The modifier was used to modify the mixture of heavy oil and the mixture of oil and coal. Their hydrogenation reaction had a relatively good effect without the addition of catalyst, and there was little coking substance, which indicated that the condensation reaction hardly occurred. It can be proven that the heavy oil had the ability of self-catalytic, which further verified the self-catalyzed method valid.

The properties of heavy oil changed after the modifier and heavy oil were completely miscible, and the metal

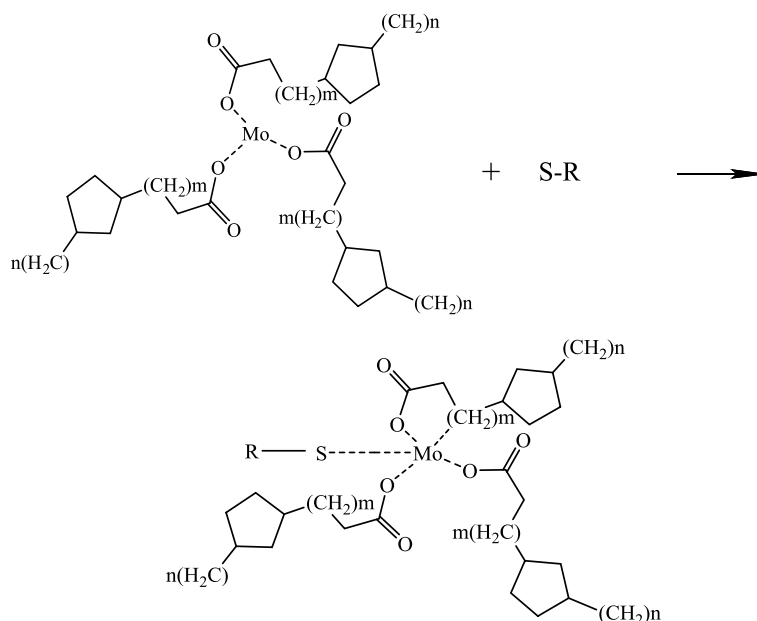
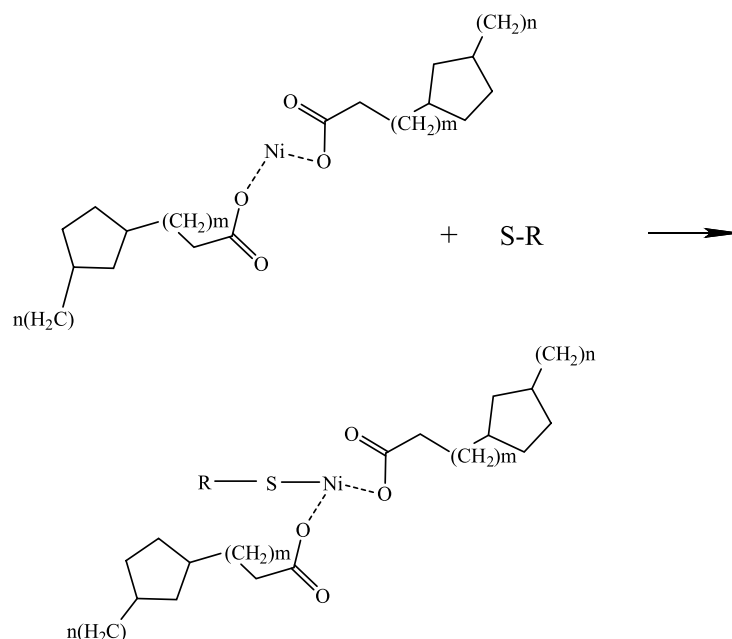
Table 4. Summary of test results with pulverized coal

Description	Properties		Description	Properties	
	450 °C			450 °C	
<170 °C, %	12.58		Residue yield, %	24.36	
170~370 °C, %	42.60		Hydrogen consumption, %	3.35	
<370 °C, %	55.18		Coal conversion rate, %	98.46	
370~500 °C, %	19.93		Gas yield, %	6.47	
<500 °C, %	75.11		C1	1.50	
Elemental analysis wt%	C	85.14	C2	1.10	
	H	13.13	C3	0.97	
	S	0.39	C4	0.49	
	N	0.32	C5	0.17	
	Ni	0.02	CO	0.96	
	V	0.002	CO ₂	1.26	
Water yield, %	7.05		H ₂ S	0.32	
Liquid yield, %	82.36		NH ₃	0.20	

elements in the modifier and the sulfur elements in heavy oil were acted upon at the temperature above 250 °C, and the metal organic sulfide chelates were formed and the dispersed evenly in the heavy oil. The procedures are shown in Figs 6 and 7.

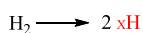
Lighting process of heavy oil

The hydrogen molecules attached to the chelates and were activated to the activated hydrogen atom at high temperature and high pressure, as one step activated hydrogen atom, which had a high concentration of electron

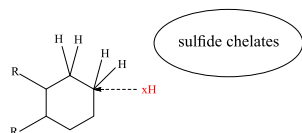
**Figure 6.** Schematic procedure of interaction process between Mo modifier and sulfur element**Figure 7.** Schematic procedure of interaction process between Ni modifier and sulfur element

cloud with the outer atom of the residual naphthenic hydrocarbon and the aromatics less than 3 of the ring number, and the high concentration of the electron cloud near the beta bit C-H. The covalent electron cloud dissolves the H- of C-H and forms two activation hydrogen atoms; while the two activation hydrogen atom is in a stronger activation state and carries a higher activation energy, which can be hydrogenated with the larger molecules, such as asphaltenes and the molecules of the asphaltene, which are activated by these macromolecules to induce their own cracking and become small molecules. During the continuous hydrogen transfer process, these small molecules achieve their own cracking when the rate of activation hydrogen is greater than that of the activated hydrogen. The modifier was removed from the reactor along with the reaction product after the reaction was completed, and there was no catalyst deactivation issue. The reaction process is shown in Fig. 8.

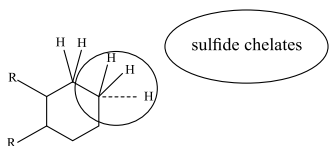
During the hydrogenation, deactivation is either due to the metal or coke deposition¹⁸⁻²³. The deactivation at the initial stage in which carbon deposition may occur due to the acid sites while at the later stage, deactivation is due to the hard coke or sediments formation²⁴⁻²⁹.



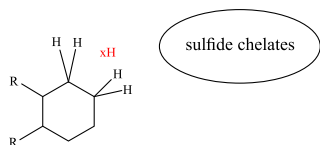
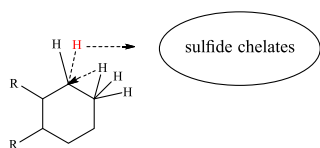
① The hydrogen molecule is activated to hydrogen atoms



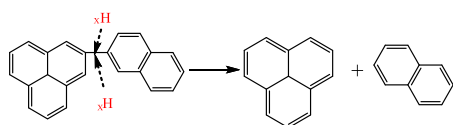
② The activated hydrogen atom has an affinity interaction with the outer electron of the residual oil molecular atoms



③ High concentration of electron cloud is formed



④ The C-H bond located at β is radiated by the strong electron cloud and turned to activated atoms



⑤ The asphaltene molecule is hydrocracked to small molecules by accepting the activated hydrogen atoms

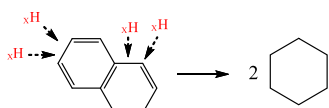


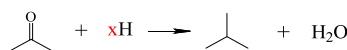
Figure 8. Schematic diagram of Heavy oil hydrocracking

In fixed bed units catalyst is deactivated by a progressive increase in bed temperature. Each degree increase in temperature would add to the severity of the process condition. Therefore, the deactivation is due to three main reasons: carbon laydown (step I), slow metal deposition on the active phase (step II), and diffusion limitation into the pores (step III). The coke/metal deposition is associated with the loss of activity, due to the decrease in catalytic sites as well as textural properties^{30, 31}.

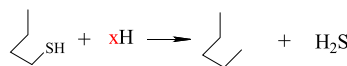
Reaction process of heavy oil hydrogenation

The modified heavy oil contains hydrogen, sulfur, nitrogen, vanadium, nickel, calcium, iron and other elements react with hydrogen under the action of sulfide chelates:

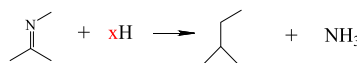
Reaction of oxygen group with hydrogen:



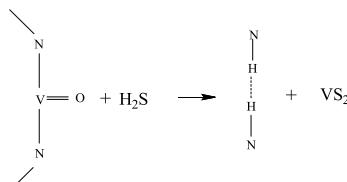
Reaction of sulfur containing groups with hydrogen:



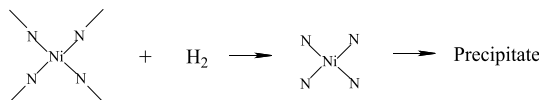
Reaction of nitrogen group with hydrogen:



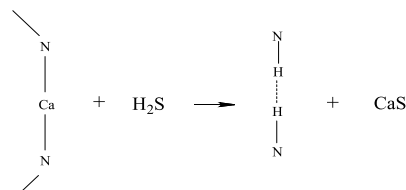
Reaction of Va containing groups with hydrogen:



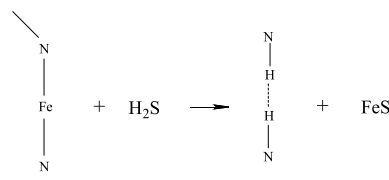
Reaction of Ni containing groups with hydrogen:



Reaction of Ca containing groups with hydrogen:



Reaction of Fe containing groups with hydrogen:



Reaction of aromatics saturation:

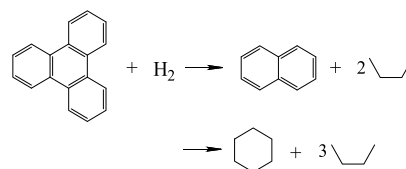


Figure 9. The hydrogenation process for the molecular groups of heavy oil

Because the particle size of the chelate is only 2–8 nm, the particle size in the reaction system (the number of chelate particles corresponding to the unit volume reactants) and the surface volume (the total surface area of the chelate particles corresponding to the unit volume reactants) are very large, and the d electron layer of the metal elements of the chelate metal elements is high and can be high. The activation hydrogen molecules become activated hydrogen atoms, which can promote the hydrogenation of the free radicals of hydrocarbon molecules and inhibit the condensation reaction. Therefore, the macroscopic performance of this process is that the light oil yield is relatively high and there is a little coking problem.

CONCLUSIONS

A self-catalyzed method of heavy oil was proposed, which was deeply expounded from the molecular structure and reaction mechanism, and its purpose of the application was proved by hydrogenation tests. The properties of the raw oil were changed by adding modifier, enabling it self-catalyzed. The method was different from the traditional catalytic hydrogenation process. As the modifier could miscible completely with the heavy oil, the catalytic efficiency could be brought into higher content after the two were integrated, and the conversion rate and the light oil yield in the hydrogenation reaction of heavy oil and oil coal mixture were improved greatly. It could be inferred from the autocatalytic method that light distillates such as wax oil, diesel distillate, and naphtha were modified by the modifiers to make them having the function of autocatalysis. This method did not need to add catalyst in the hydrogenation process, hence there was no need to consider the problems of catalyst deactivation, poisoning, fragmentation, etc. Finally, the space occupied by the catalyst in the reactor was released, the effective space of the reactor was greatly improved, and the wear of equipment was reduced.

The self-catalyzed method of heavy oil proposed in this study can be widely used in the field of oil refining. The problem of deep processing of heavy oil would be solved and the yield of refined oil is greatly improved to increase its economy and reduce air pollution in the process of production and use and would promote the development of the refining and catalytic industry. In addition, the method was of great significance for promoting the clean and efficient utilization of coal, broadening the sources of petrochemical heavy oil, and prolonging the service life of petroleum. However, there are still some problems to be solved before they can be industrialised on a large scale. It is necessary to study the effect of polymetallic compounds of heavy oil modifiers to reduce the production cost of modifier. Moreover, the effect of modifier addition amount on the catalytic hydrogenation of heavy oil should be further studied in order to find the balance between the concentration of modifier and catalytic performance.

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AUTHOR CONTRIBUTIONS:

Suan Li: Conceptualization, Supervision; Zhenguang Sun: Writing – Reviewing and Editing, Supervision; Qi Liu: Methodology, Writing, Validation; Hang Ye: Formal analysis, Investigation; Kunpeng Wang: Visualization, Data curation, Formal analysis.

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