

CATALYTIC HYDROCRACKING OF PETROLEUM VACUUM RESIDUE BY USING A COMBINATION OF MOLYBDENUM-BASED OIL-SOLUBLE AND IRON-BASED WATER-SOLUBLE CATALYSTS

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ABSTRACT

Synergism was investigated of molybdenum-based oil-soluble catalyst and iron-based water-soluble catalyst in catalytic hydrocracking system of Liaohu vacuum residue. A combined use of water-soluble catalysts and active oil-soluble catalyst could enhance conversion and effectively inhibit coke formation, without much expense of relatively expensive oil-soluble catalysts. This can be explained by following reasons: (1) At early stage of hydrocracking, some kinds of polyaromatics can be partially hydrogenated to hydroaromatics, which can act as hydrogen donors and can be a complement to the active hydrogen molecules directly activated by catalysts in the subsequent hydrocracking. (2) The cheap water-soluble catalyst can not only activate molecular hydrogen to inhibit coke formation, but also make the sacrifice of the sites of coke deposition, thus save partially the active Mo-based catalyst from deactivation by coke deposition.

Key words: synergism, oil-soluble and water-soluble catalysts, hydrocracking, vacuum residue

INTRODUCTION

The catalytic hydrocracking processes of heavy oils or bitumen concerning the use of dispersed catalysts (oil-soluble, water-soluble or fine particles of catalysts) have been extensively reported [1]. Nearly all these processes are operated at relatively high temperature, well above 430°C, and aim at high conversion to light products and low coke formation. The catalysts or additives used in these processes have little catalytic activity towards the cracking reactions; the conversion to lighter products is almost entirely a thermal process [2]. But these catalysts are more or less effective in inhibiting coke formation, some of which are even really effective [1-3], such as Mo-based oil-soluble catalysts used in M-coke process [4].

The chemical nature, the catalytic activity and the cost of these catalysts are the key factors for the optimization and development of efficient catalytic hydroconversion processes [2]. Some catalysts are active, but much expensive, such as Molybdenum, Nickel, and Vanadium-based oil-soluble catalysts. On considering their high price, a once-through scheme of hydrocracking process can be considered only in employing low catalyst concentrations (< 200ppm, base on metals); but if the catalyst concentration is too low under given hydrogen partial pressure, the large amount of coke formation may result. It is worth noting that higher H₂ partial pressure and higher concentrations of low active and not expensive catalysts, such as Fe-based oil soluble, water-soluble catalysts and powdered catalysts, can counter-balance the activity of Mo-based oil-soluble catalyst as used in trace concentration.

Generally, for the same metal, its oil-soluble salts can be distributed more well in heavy oil than its water-soluble salts and therefore, are usually more active than its water-soluble salts [1]; but may be more expensive than its water-soluble salts. Some oil-soluble catalysts are relatively expensive, but quite active, such as Molybdenum-based oil-soluble catalysts. Some water-soluble catalysts are relatively very cheap, but not quite active, such as iron-based water-soluble salts. To optimize the use of these catalysts, it is possible to use a mixture of these catalysts. If the concentration of a more expensive component can be reduced, the use of the second component could reduce catalyst cost. However, up to date, few studies have been carried out to investigate the synergism of the use of active oil-soluble catalysts and very cheap water-soluble catalysts (quite different solubility systems). In the presentation, a Molybdenum-based oil-soluble catalyst and an iron-based water-soluble catalyst are in combination used in hydrocracking of Liaohu vacuum residue to investigate the synergism of these two kinds of catalysts.

1. EXPERIMENTAL

1.1 Sample

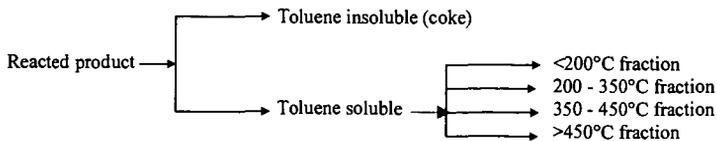
Liaohu vacuum residue (>500°C) was collected from Liaohu Petrochemical Plant in March 1996. Carlo Erba 1160 elemental analyzer was used for C, H, N analysis; atomic absorption method was used to determine Ni, V, Fe and Ca contents. Average molecular weight was measured by using VPO method (benzene as solvent, 45°C) with Knauer molecular weight analyzer. The general properties of Liaohu vacuum residue are listed in Table 1. For comparison, the general properties of Gudao vacuum residue (the feed to VRDS unit at Qilu Oil Company) was also tabulated here.

Table 1 Properties of Liaohe vacuum residue (VR)

Property	Liaohe VR	Gudao VR
Density(20°), g./cm ³	0.9976	0.9998
Viscosity(100°)/mm ² .s ⁻¹	3375	1710
Pour point, °C	42	41
Flash point, °C	312	327
Carbon residue, %	19.0	15.6
Elemental composition		
C, %	87.0	85.4
H, %	11.4	11.4
S, %	0.43	2.52
N, %	1.08	0.80
H/C(Atomic ratio)	1.50	1.60
Total Metal/PPM		
Ni, ppm	122.6	48.0
V, ppm	2.9	2.2
Fe, ppm	37.5	13.8
Ca, ppm	95.6	33.8
Ash, %	0.06	0.03
SARA fractions:		
Saturates, %	17.4	14.5
Aromatics, %	30.3	34.8
Resins, %	50.2	47.2
nC7-Asphaltene, %	2.1	3.5
Structural Parameters		
F _A	0.27	0.18
F _N	0.26	0.33
R _A /R _N	0.93	0.47

1.2 Catalytic hydrocracking of Liaohe vacuum residue

The experiments were carried in a 100ml FDW-01 autoclave reactor with an up-and-down stirrer at 120 times of reciprocation per minute. Initial pressure was 7.0MPa H₂ for catalytic hydrocracking. Catalyst used in the hydrocracking reaction was Molybdenum-based oil soluble and iron-based water-soluble catalyst (ca.50~1000 ppm based on metal concentration in feed). The former was compatible with the vacuum residue and gave rise to the homogeneous system with the vacuum residue, and the later was emulsified into the vacuum residue to form emulsion system. After sulphurization by elemental sulfur at 320°C for 30minute (S/Metal atomic ratio=3/1), these catalyst precursors were in situ reacted to real active catalysts. Then, the temperature was raised to 430°C for hydrocracking reaction. After 1-hour reaction time, the reactor was quenched (cooled) to room temperature, the reactor gas was vented, and toluene slurry was prepared from the reactor contents. Any solids adhering to the reactor walls or internals was carefully scraped off. The slurry was then centrifuged and the toluene insoluble (TI or coke) were separated and washed (extracted) with boiling toluene by using quantitative filter paper. The solids were dried and weighed. The toluene soluble was distilled into several fractions. The distillation scheme is as follows.



2. RESULTS AND DISCUSSION

2.1 The activity of catalysts

In order to make a comparison of catalytic activity between the Mo-based oil-soluble catalyst and the Fe-based water-soluble catalyst used in Liaohe vacuum residue hydroconversion processes, the same concentrations of these two kinds of catalysts were separately used in the hydrocracking tests, the results are listed in table 2. Both of the catalysts could suppress coke formation and cracking reactions in comparison with thermal cracking system without adding catalysts. The Mo-base oil soluble catalyst accounted for lower total conversion yield than the Fe-based water-soluble catalyst did; but the former gave rise to higher conversion per unit coke than the latter did. The conversion per unit coke was 53.1% for the Mo-based oil-soluble catalyst, 11.9% for Fe-based water-soluble catalyst and 8.8% for pure thermal cracking without added catalyst. In consideration of the over-cracking and condensation reactions during Liaohe vacuum residue

hydrocracking, the following formula was proposed for evaluation of the catalytic activity of catalysts: $R=(GL \times \text{Coke})/CP$. Here, R is named coke and over-cracking suppressing index; GL is gas and light fraction yield, strictly the <200°C fraction yield; CP is the conversion per unit coke. Under the given reaction conditions, the R-value is 0.22 for the Mo-based catalyst, 10.7 for the Fe-based catalyst and 25.0 for thermal cracking without catalysts.

Table 2 Hydroconversion of Liaohe vacuum residue by using different catalysts at 430°C, 7.0MPa initial H₂ pressure, 1hr

Cat., ppm	Conv. wt %	conv. per unit coke, wt %	200°C-, wt %	200-350°C, wt %	350-480°C, wt %	Coke, wt %
Mo, 470	49.4	54.9	13.4	11.1	24.0	0.9
Fe, 470	64.4	11.9	23.5	16.5	19.0	5.4
No cat.	69.2	8.8	27.9	12.5	20.9	7.9

Note: cat. ~ Catalyst; conv. ~ conversion; wt % ~ weight percent.

2.2 Catalytic hydrocracking of Liaohe vacuum residue by using the Mo-based oil-soluble and Fe-based water-soluble catalysts

As indicated in table 3, the combined use of Mo-based oil-soluble catalyst and the Fe-based water-soluble catalyst could really give rise to a synergetic effect on coke inhibition. With promotion of 400ppm Fe-based water-soluble catalyst, the relatively expensive Mo-based catalyst could be reduced from 470ppm to only 70 ppm without much loss of total catalytic activity. Under the given reaction conditions, the concentration of the more expensive component can be reduced to under 100ppm, the use of the second component (Fe-based water-soluble catalyst) could reduce total catalyst cost and hence avoid the catalyst recovery [1]. It seems that the synergism of these two kinds of catalysts can not be clearly understood simply by their complementary function; this will be further discussed in section 2.3.

Table 3 Synergetic effect of Mo-based oil-soluble and Fe-based water-soluble catalysts on hydroconversion of Liaohe vacuum residue (430°C, 7.0MPa H₂, 1 hr)

Cat., ppm		Conv. wt %	conv. per unit coke, wt %	200°C-, wt %	200-350°C, wt %	350-480°C, wt %	Coke, wt %	R
Mo	Fe							
470	0.0	49.4	54.9	13.4	11.0	24.0	0.9	0.22
70	400	48.7	48.7	15.5	10.0	22.1	1.0	0.32
25	445	56.4	25.6	18.4	13.0	22.8	2.2	1.58
0.0	470	64.4	11.9	23.5	16.5	19.0	5.4	10.7

Table 4 Synergetic effect of Mo-based oil-soluble and Fe-based water-soluble Catalysts on Hydroconversion of Liaohe vacuum residue

Cat., ppm		Conv. wt %	conv. per unit coke, wt %	200°C-, wt %	200-350°C, wt %	350-480°C, wt %	Coke, wt %	R
Fe	Mo							
0.0	70	50.0	35.7	13.4	8.9	26.3	1.4	0.53
100	70	52.8	33.0	17.7	10.4	23.1	1.6	0.85
200	70	55.9	32.9	18.4	11.4	24.4	1.7	0.95
400	70	48.7	48.7	15.5	10.0	22.2	1.0	0.32
600	70	47.0	52.2	14.4	9.9	21.8	0.9	0.25
800	70	52.0	74.3	15.2	10.5	25.6	0.7	0.14
1000	70	45.7	76.2	13.2	9.9	22.0	0.6	0.10
1000	0.0	56.4	17.8	16.6	12.9	23.7	3.2	2.98

With the Mo-based catalyst being kept in concentration of 70ppm and the Fe-based catalyst being increasingly added from 0ppm to 1000ppm, the coke suppressing ability is at first getting down, and then becoming higher and higher from 400 ppm to 1000ppm of Fe-based catalyst in use. The results were listed in table 4. When Fe-based catalyst added in the hydrocracking system was above 600ppm (total 670ppm Mo and Fe), the performance of the Mo-Fe catalysts in coke inhibition and over-cracking suppression was better than that of pure Mo-based catalyst used in 470ppm; this could be interpreted by their R values.

2.3 The synergism of active oil-soluble catalyst and water-soluble catalyst in the catalytic hydroconversion of Liaohe vacuum residue

At early stage of catalytic hydrocracking of vacuum residue, the oil soluble and water-soluble catalyst precursors are sulphidized, by indigenous sulfur or pre-added sulfur, to dispersed fine molybdenum sulfide and iron sulfide particles, which are real active catalysts. During the stage, the catalytic hydrocracking system was of following characters:

- High activity of the catalysts
- high hydrogen partial pressure
- Low cracking reactions and low free radical concentration

The former two characters could give rise to high concentration of active hydrogen surrounding catalyst fine particles. Therefore, little coke would be formed through polyaromatic radical combination or condensation because active radicals would be timely scavenged or hydrogenated by active hydrogen before their combination. However, condensed phase of asphaltene might be formed because of the adsorption of catalyst fine particles to asphaltene molecules. The latter character along with former two would lead to an excess of active hydrogen beside the active hydrogen used to scavenge polyaromatic free radicals. The excessive active hydrogen would hydrogenate some active polyaromatics to hydroaromatic species, which could act as hydrogen donors in subsequent reactions. This kind of hydrogen donors might be more active in coke suppression than directly activated hydrogen by catalysts because there would exist a higher compatibility and an easier hydrogen transfer between the hydrogen donors and coke precursors.

In fact, there may be large differences between catalysts in the abilities to generate these kinds of hydroaromatics---secondary hydrogen donors. Some catalysts may be not active enough to hydrogenate polyaromatics to hydroaromatics. With Mo-based additives, the reaction system can not only inhibit coke formation through shutting coke precursor radicals by catalytic active hydrogen but also develop a reservoir of active hydrogen---hydroaromatics. However, the less active Fe-based catalyst could not create so active hydrogen. But the less active catalyst could be a promoter of Mo-based catalyst to effectively inhibit coke formation during severe cracking stage. Meanwhile, if used alone, a large amount of less active additives would be needed to reach effective coke inhibition. Besides, some synergism may come from in situ formed combined Mo-Fe bimetal catalysts as the supported catalysts (such as Mo/Ni/Al₂O₃) do. But, in the authors' opinion, even there exists the kind of synergism; it may not be the main synergetic effect in the slurry-phase hydrocracking system.

3. CONCLUSION

The synergetic effect of active Mo-based oil-soluble catalyst and Fe-based water-soluble catalyst is concluded here:

- Active Mo-based catalyst is used for:
 - (1) Inhibiting coke formation of the species with high coke formation tendency especially at the early stage.
 - (2) Creating the secondary hydrogen donors---hydroaromatics that may be quite active in coke suppression.
 - (3) Playing a great role in coke inhibition during the whole hydrocracking process.
- Less active Fe-based catalyst for:
 - (1) Making the sacrifice of the sites of coke deposition, thus partially saving the active Mo-based catalyst from deactivation by coke deposition.
 - (2) Playing significant role in coke suppression during the severe cracking stage when used in relatively large amount.

Therefore, the synergism of Mo-based oil-soluble catalyst and Fe-based water-soluble catalyst in catalytic hydrocracking of Liaohe vacuum residue is not only simple complementary effect, but also comprehensive promotion effect.

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