[Note]

Suppression of Sludge Formation by Two-stage Catalytic Hydrodesulfurization of Arabian Atmospheric Residue

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(Received June 12, 1991)

Two-stage catalytic hydrodesulfurization of Arabian atmospheric residue was studied using commercial Co-Mo and Ni-Mo catalysts in a batch autoclave to achieve a high desulfurization level without producing "dry sludge" (precipitated insoluble droplets in the product oil matrix). Single-stage reactions using a Co-Mo catalyst (KF-742) at 380 and 400°C for 3 h under hydrogen pressure of *ca.* 100 atm achieved desulfurizations of 62 and 75%, respectively, with a very little amount of sludge formed. A higher reaction temperature of 420°C enhanced the rate of desulfurization significantly up to 86%, but much sludge droplets were formed in the product oil. The two-stage hydrotreatment using KF-742 catalyst at 380°C-2 h followed by 420°C-1 h achieved high rate of desulfurization (84%) comparable to that of the single-stage reaction at 420°C-3 h, and produced slightly less dry sludge in the product oil. A combination of using KFR-10 catalyst in the first stage, and KF-742 catalyst in the second stage, under the same two-stage reaction conditions, markedly decreased formation of sludge droplets, although the rate of desulfurization was also reduced slightly to 80%. A first stage reaction at 380°C-2 h with KFR-10 catalyst followed by a second stage reaction at 410°C-2 h with KF-742 catalyst improved the desulfurization level to 85% without increasing dry sludge. The mechanism of sludge formation and its suppression are discussed relative to severities of reaction conditions involved in the hydrotreatment which may also enhance the desulfurization.

1. Introduction

Demand for cleaner distillate from the bottom of the barrel leads to extensive hydrodesulfurization and/or hydrocracking of petroleum residues under more severe conditions¹⁾. The severe conditions cause problems of coke deposition on the catalyst and sludge formation in the product oil²⁾. Coke and sludge are sources of problems: these shorten the life of the catalyst, plug transfer lines and deteriorate the quality of the products³⁾. The formation of these may be intimately related to each other.

Dry sludge is believed to be inevitably produced in both hydrodesulfurization and hydrocracking when the conversion to distillate is high. Reaction temperature must be raised to maximize level of desulfurization at the final stage in long-term operation of hydrodesulfurization, when the catalyst has become highly deactivated⁴⁾. Procedures to overcome the dilemma of sludge formation at high conversion have not yet been fully clarified⁴⁾.

According to previous reports^{5)~7)}, dry sludge

produced in a hydrocracked oil from a vacuum residue is soluble in aromatic solvents such as 1-methylnaphthalene, and miscible with the matrix of hydrocracked product at elevated temperatures. Hence, successive extensive hydrogenation should be effective to convert it to a miscible product at room temperature. This reasoning suggests procedures of hydrocracking that would prevent sludge formation. Accordingly, a two-stage catalytic hydrocracking was proposed to achieve higher than 50% conversion to 540°C-distillate with a minimum formation of dry sludge. The basic idea stands on the following mechanism: deep hydrogenation of the aromatic fraction in the residue by the first lower temperature stage may enhance cracking and solubility of its heaviest portion. The enhanced cracking and solubility of the heavy fraction may suppress retrogressive reactions in the second higher temperature stage, where major hydrocracking takes place, leaving little or no dry sludge in the product.

In the present study, catalytic two-stage hydrodesulfurization of Arabian atmospheric residue was examined, using commercial Co-Mo and Ni-Mo catalysts to achieve a high level of desulfurization without producing dry sludge.

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In other words, the highest allowable non-sludge-producing temperature of the second-stage desulfurization was sought.

2. Experimental

An atmospheric residue of Arabian-light crude (ALAR, 10 g, see Table 1) was hydrotreated by single- and two-stage reactions under 100 atm of hydrogen. Reaction temperature was varied, and either Co-Mo or Ni-Mo catalyst (1 g) was employed. The reactions were carried out in a batch autoclave of 100 ml capacity. The catalysts (see Table 2) were presulfided in 5% H₂S/H₂ flow at 360°C for 6 h, before the reaction.

The standard conditions were 380°C-3 h, 400°C-3 h and 420°C-3 h for the single-stage reaction, and 380°C-2 h (first stage) and 420°C-1 h or 410°C-2 h (second stage) for the two-stage reaction. After replacing the atmosphere in the autoclave with hydrogen, the reactor was pressurized with hydrogen and heated up to the reaction temperature at heating rate of *ca.* 8°C/min. After the first stage reaction, the reactor was cooled to room temperature, and pressurized with fresh hydrogen, followed by the second stage reaction at heating rate same as the first stage reaction.

After recovery of the reaction mixture from the autoclave, the catalyst was filtered and washed with THF. The product oil, which was recovered by evaporating out the THF, was analyzed by a sulfur-microanalysis system (Yoshida Science Co.) to estimate the level of desulfurization. The recovered product oil was also observed under an optical microscope to examine the presence of dry sludge of insoluble precipitates. The amount of sludge was always <0.1 wt%, under the present conditions.

3. Results

3.1 Properties of Original ALAR

The original ALAR contains 4.1 wt% hexane-

insolubles (HI), where major heteroatoms and metals are concentrated. No insoluble precipitate was observed in the hexane-soluble (HS) matrix under an optical microscope (Fig. 1(a)), indicating that the HI fraction was dissolved or homogeneously dispersed in the HS matrix of the original

(a) Original ALAR

(b) Hydrotreated ALAR at 380°C-3 h (KF-742 catalyst)

(c) Hydrotreated ALAR at 420°C-3 h (KF-742 catalyst)

Fig. 1 Microphotographs of ALAR before and after the Single-stage Hydrodesulfurization

Table 1 Elemental Analyses of ALAR and Its Fractions^{a)}

Sample	Contents [wt%]	wt%					
		C	H	N	S	O ^{b)}	Ash
ALAR-OR	—	85.1	11.3	0.23	3.24	0.15	—
HS	95.9	85.1	11.6	0.20	3.01	0.12	—
HI	4.1	83.9	7.0	0.95	6.62	1.12	0.39

a) HS: hexane solubles, HI: hexane insolubles.

b) Difference.

Table 2 Properties of Catalysts

Name	Support	S.A. [m ² /g]	Metal load [wt%]			
KF-742	alumina	268	CoO	4.4	MoO ₃	15
KFR-10	alumina	147	NiO	1.0	MoO ₃	5.0

Table 3 Single-stage Hydrotreatment of ALAR

Reaction conditions ^{a)}	S content [wt%]	HDS ^{b)} [%]	Amount of sludge
380°C-3 h	1.24	62	Trace
400°C-3 h	0.81	75	Trace
420°C-3 h	0.44	86	Some

a) Catalyst: KF-742, H₂ reaction press.: 100 atm.

b) Hydrodesulfurization (sulfur removal).

ALAR.

3. 2 Single-stage Hydrodesulfurization

Table 3 summarizes the results of single-stage hydrodesulfurization using the Co-Mo catalyst (KF-742). The reactions at 380 and 400°C provided desulfurizations of 62 and 75%, respectively, with very little sludge formation (Fig. 1(b)).

A higher reaction temperature of 420°C, for 3 h, increased the rate of desulfurization significantly up to 86%. Much sludge droplets were found in the product oil (Fig. 1(c)), although about half of the asphaltenes (HI) was certainly converted into HS under the conditions.

3. 3 Two-stage Hydrodesulfurization

Results of two-stage hydrodesulfurization are summarized in Table 4. The two-stage hydrode-

sulfurization, using KF-742 catalyst in both stages at 380°C-2 h and 420°C-1 h, produced many sludge droplets in the product oil (Fig. 2(a)). However, the amount was certainly less than that found after the single-stage desulfurization at 420°C-3 h, in spite of the same level of desulfurization (as high as 84%).

A combination of KFR-10 catalyst in the first stage with KF-742 catalyst in the second stage, under the same reaction conditions, significantly decreased the number of sludge droplets (Fig. 2(b₂)), although the desulfurization level was also reduced slightly, to 80%. The second stage reaction at 410°C-2 h (a lower reaction temperature and a longer reaction time), with KF-742, after the same first stage reaction at 380°C-2 h with KFR-10, enhanced the desulfurization up to 85% without

Table 4 Two-stage Hydrotreatment of ALAR

Conditions (catalyst)		S content [wt%]	HDS [%]	Amount of sludge
1st	2nd			
380°C-2 h (KF-742)	420°C-1 h (KF-742)	0.53	84	Some
380°C-2 h (KFR-10)	420°C-1 h (KF-742)	0.64	80	Trace
380°C-2 h (KFR-10)	410°C-2 h (KF-742)	0.49	85	Trace

(a) 1st stage: 380°C-2 h (KF-742) and 2nd stage: 420°C-1 h (KF-742)

(b₁) 1st stage: 380°C-2 h (KFR-10)

(b₂) 1st stage: 380°C-2 h (KFR-10) and 2nd stage: 420°C-1 h (KF-742)

(c) 1st stage: 380°C-2 h (KFR-10) and 2nd stage: 410°C-2 h (KF-742)

Fig. 2 Microphotographs of ALAR after the Two-stage Hydrodesulfurization

any definite increase of sludge droplets (**Fig. 2(c)**). The H/C atomic ratio of the product increased to 1.65 from 1.59 of the original ALAR by the first stage with KFR-10 catalyst, while the ratio increased to 1.63 with KF-742 catalyst.

4. Discussions

The present study revealed that catalytic two-stage hydrodesulfurization of Arabian atmospheric residue using commercial Co-Mo and Ni-Mo catalysts is very effective in achieving a higher desulfurization level of 85% with reduced dry sludge formation, relative to single-stage hydrodesulfurization. With the single-stage reaction it is possible to achieve deep desulfurization at higher temperatures ($>410^{\circ}\text{C}$) using Co-Mo catalyst. Sludge formation, however, is inevitable. Only a small number of sludge droplets are formed in the single-stage reaction at lower temperatures ($<400^{\circ}\text{C}$), but the desulfurization level of 70% is barely reached. In contrast, the two-stage hydrodesulfurization procedure, consisting of extensive hydrogenation at a lower temperature of 380°C in the first stage, and deep desulfurization at a higher temperature of 420°C in the second stage, solves the dilemma of the single-stage treatment, satisfactorily.

Combined use of the most appropriate catalysts at each of the two-stage reaction further improved the hydrodesulfurization without formation of sludge. Employing the hydrogenation activity of

Ni-Mo catalyst for the asphaltene fraction in the first stage and hydrodesulfurization activity of Co-Mo catalyst, with minimum hydrogen consumption in the second stage, may be the most appropriate two-stage reaction. More effective catalysts for improved performance, emphasized in each step, can be designed easily, because their respective mono-function is to be separately enhanced.

It is of value to point out that the reaction condition, especially temperature, which may be the most influential factor on both desulfurization and sludge formation, can be separately optimized, at the respective stages, for the best total performance.

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要 旨

アラビアン常圧残さの接触二段水素化脱硫によるスラッジ生成の抑制

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振とう式オートクレープ（内容積：100 cc）を用いて，反応温度：380～420℃，反応水素圧：100 atm の条件下で，市販の Co-Mo（KF-742）あるいは Ni-Mo（KFR-10）触媒によるアラビアン常圧残さの単段および二段水素化脱硫処理を行い，精製油中にスラッジを生成せずに高い脱硫率を達成できる反応条件を探索した。KF-742 を用いる 380℃ および 400℃-3h の単段反応では，極く少量のスラッジしか生成しなかったものの，脱硫率はそれぞれ 62，75% にとどまった。420℃-3 h の高温単段反応では，86% の高い脱硫率が達成できたが，精製油中に多くのスラッジ粒子が生成した。一方，両段で KF-742 触媒を用いる 380℃-2 h および引き続き 420℃-1 h の二段反応

では，高温単段反応に匹敵する脱硫率（84%）が得られ，かつ精製油中の生成スラッジ粒子は高温単段反応より少量であった。同一反応条件下の二段反応において，KFR-10（第 1 段）および KF-742（第 2 段）触媒を組み合わせると，精製油中のスラッジ粒子数は顕著に減少したものの，脱硫率（80%）も若干減少した。第 1 段：380℃-2 h（KFR-10 触媒）および引き続き 410℃-2 h（KF-742 触媒）の二段水素化脱硫処理を行うと，生成スラッジ粒子を増大させることなく，脱硫率を 85% まで上昇できた。スラッジ生成とその抑制機構について，脱硫率を最大限にする反応条件と関連付けて考察した。

Keywords

Hydrodesulfurization, Atmospheric residue, Sludge formation, Cobalt-molybdenum catalyst, Nickel-molybdenum catalyst