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Spillover Effects on Transfer-Hydrocracking of Heavy Oils

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A Ni-Mo/SiO_2-Al_2O_3 catalyst which contained 1000 ppm of platinum exhibited an excellent activity for hydrocracking of Kuwait atmospheric residue without any activation. Coke on the catalyst was burned off by air at much lower temperature than that on a catalyst without platinum.

An efficient technology which produces high grade distillates from heavy oils has not developed yet. The present authors have been developing a transfer hydrocracking method of heavy oils.1) In the process, a heavy oil is thermally cracked in liquid phase in the presence of a metal added solid acid catalyst under slightly pressurized hydrogen atmosphere. Where, polycyclic moiety in the oil is adsorbed on the carrier surface to be cracked and dehydrogenated. Hydrogen atoms which are liberated during dehydrogenation are effectively transferred to light fractions of product hydrocarbons. Thus the process gives paraffin-rich distillates and asphaltene-free residual oils with small or no hydrogen consumption. In the present work a new catalyst suitable for the process was developed based on the spill-over effect.

Catalysts were prepared by impregnating a commercially available SiO_2-Al_2O_3 (Nikki Kagaku N631, Al_2O_3 28 wt%, 400 m^2/g) with nickel, molybdenum and platinum from their mixed aqueous solutions followed by drying in an air oven and calcining at 450 °C for 3 h. Some of the catalysts were activated by treating in a H_2-H_2S mixed gas ($H_2/H_2S=4/1$) at 400 °C for 1 h.

Cracking reactions of Kuwait atmospheric residue were conducted in an autoclave reactor system, whose details have been described before.2) Standard reaction conditions were : reaction temperature ; 435 °C, reaction time ; 60 min, hydrogen pressure ; 34-75 atm, Feed oil ; 40 g, catalyst ; 8 g. The procedures of reaction and analysis were also described before.[2)]

Reduction characteristics of catalysts determined by TPR method (Fig. 1) show that the reduction of a Mo catalyst begins at around 350 °C and proceeds quickly at above 400 °C. The TPR spectrum of a Ni-Mo catalyst is just a superimposed of the Ni catalyst and the Mo catalyst showing that little synergistic effect is generated by mixing them. However, a Ni-Mo catalyst containing 1000 ppm of Pt gives a TPR spectrum characterized as follows ; its reduction begins at 200 °C or lower and the reduction peak at around 250 °C is much lower than the corresponding peak of the non-platinized catalyst at around 400 °C. It suggests that the reduction of some Mo-species which is reducible at around 400 °C is markedly accelerated. This is just the "spillover" effect which has been first observed for a Pt-WO_3 system.[3)]

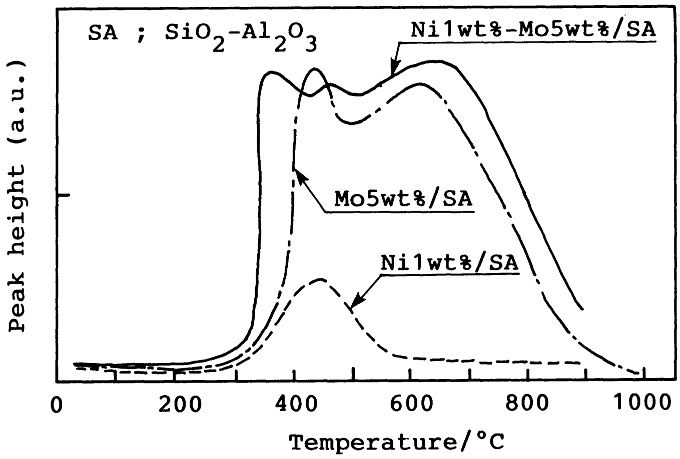

Fig. 1. TPR spectra.
6% H_2-Ar 30 ml/min·g-cat., 5 °C/min

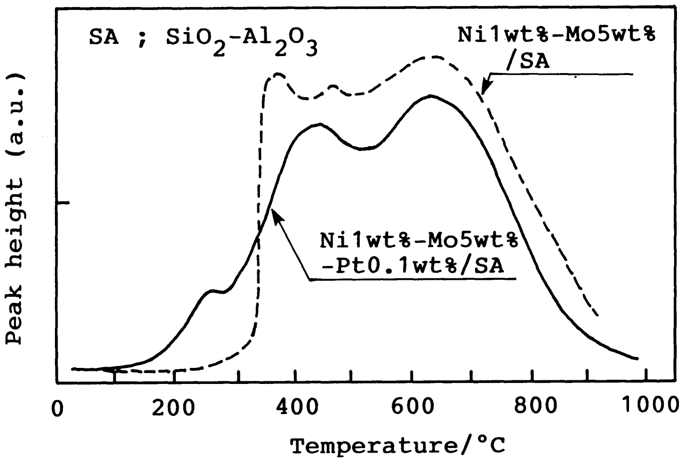

Fig. 2. Effects of Pt addition on TPR spectra.
6% H_2-Ar 30 ml/min·g-cat., 5 °C/min

One can expect from the data that the platinized catalyst is able to be used for hydrocracking without any pretreatment with hydrogen because it should be reduced during cracking reaction under pressurized hydrogen. In Table 1 are shown some of the results of hydrocracking of Kuwait atmospheric residue (KAR). It is apparent that the reaction on a Ni/SiO_2-Al_2O_3 catalyst, activated by hydrogen treatment, consumes hydrogen of about 84 N m^3/kl-oil and gives 3.0 wt%

Table 1. Hydrogen transfer-hydrocracking with metal supported SiO_2-Al_2O_3 catalyst. Reaction conditions : 435 °C, 1 h, H_2 pressure 75 atm, KAR 40 g, catalyst 8 g.

Catalyst	Nonmetal	Ni	Ni	Ni-Mo	Ni-Mo-Pt	Ni-Mo[a)]	Ni-Mo-Pt[a)]	Ni-Mo[a)]
Pretreatment	Air	Air	H_2+H_2S	Air	Air	Air	Air	H_2+H_2S
Conversion/%	67.4	58.3	55.3	58.2	56.3	75.1	71.9	70.7
H_2 consumption /N m^3 kl^{-1}	-2	46	84	103	109	13	24	30
S removal/%	20.2	21.6	36.1	68.4	72.1	44.9	51.9	75.7
Product distribution/wt%								
Gas	4.1	3.3	5.2	4.0	3.4	6.8	6.3	8.4
Naphtha	16.6	14.7	14.0	14.3	12.8	19.6	19.0	19.0
Kerosene	15.5	12.0	10.9	10.6	10.7	10.4	11.5	11.3
Gas oil	24.8	23.5	21.9	26.2	26.7	27.3	28.1	26.5
343 °C+	33.1	41.2	45.0	41.8	43.5	25.2	28.4	28.1
Coke	5.9	5.3	3.0	3.1	2.9	10.7	6.7	6.7
Gas analysis/wt%								
C_1	30.4	34.4	31.9	23.1	21.9	26.2	26.1	26.3
C_2	25.7	27.1	26.9	26.1	25.1	27.4	28.9	25.8
$C_2{}^=$	2.6	0.2	0.1	-	-	-	-	-
C_3	20.1	22.0	23.9	30.6	31.2	28.3	29.6	28.8
$C_3{}^=$	2.8	1.4	0.8	0.1	-	0.2	-	-
C_4	15.6	14.1	15.6	20.0	21.8	17.7	15.3	18.8
$C_4{}^=$	2.8	0.8	0.8	0.1	-	0.2	-	0.2

Nonmetal ; SiO_2-Al_2O_3, Ni ; Ni2.5wt%/SiO_2-Al_2O_3, Ni-Mo ; Ni1wt%-Mo5wt%/SiO_2-Al_2O_3
Ni-Mo-Pt ; Ni1wt%-Mo5wt%-Pt0.1wt%/SiO_2-Al_2O_3
a) H_2 pressure 34 atm.

of coke yield, which corresponds 1/2 of that on a non metal catalyst. While the reaction on the same catalyst which has never experienced a hydrogen pretreatment gives a coke yield comparable to that of the non-metal catalyst system, a hydrogen consumption of 46 N m^3/kl-oil and gaseous products with higher olefin content. This means that the Ni/SiO_2-Al_2O_3 does not exhibit enough hydrogenation activity without hydrogen pretreatment. The Ni-Mo/SiO_2-Al_2O_3 is highly active without hydrogen pretreatment whether it containes platinum or not under the pressure of 75 atm, giving a high hydrogen consumption, a low coke yield, and a low olefin content. However, in case of the reaction under a lower hydrogen pressure (34 atm), the promotional effect of added platinum is clear. The reaction on the catalyst containing platinum gives a hydrogen consumption by about 80% larger, a desulfurization by about 20% higher, a coke yield 30% lower and much lower olefin content in the gaseous products, comparing the reaction on the non platinized catalyst. Since platinum has little activity for desulfurization, the higher level of desulfurization with the platinized catalyst should be attributed to the higher level of molybdenum reduction. Thus, it can be concluded that a Ni-Mo/SiO_2-Al_2O_3 catalyst which contains a small amount of platinum can be used effectively for heavy oil hydrocracking without any hydrogen pretreatment. The higher conversion under lower hydrogen pressure should be attributed to the lower efficiency of the hydro-quenching of free radicals.$^{2)}$

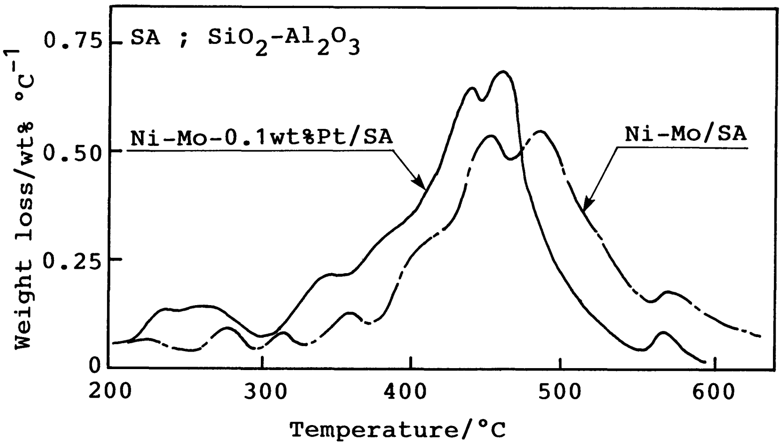

Fig. 3. Effects of Pt addition on DTG spectra.

Since the characteristic feature of the present method is that the reaction is not a simple hydrocracking but a transfer hydrocracking, coke formation is inevitable. Thus the catalyst should be regenerated by burning off the coke. Figure 3 shows DTG spectra of used catalysts in air. Apparently, the DTG curve of platinized catalyst shifts to lower side by about 50 °C. For example the level of coke burning up to 450 °C is 69% for the platinized catalyst and 49% for the non-platinized catalyst. Similar phenomena have been observed on FCC catalysts.$^{4)}$ Although the reason is not clear yet, the most plausible interpretation is that the adsorbed oxygen on platinum spills over to carrier to oxidize coke.$^{5)}$

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