

Effect of Addition of K to Ni/SiO₂ and Ni/Al₂O₃ Catalysts on Hydrothermal Cracking of Bitumen

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Abstract

Hydrothermal cracking of Canadian Athabasca bitumen was performed over Ni/SiO₂ and Ni/Al₂O₃ catalysts under 703 K and 5.0 MPa of hydrogen pressure in a batch reactor. Comparing with thermal cracking under the same reaction conditions, hydrothermal cracking process obviously suppressed the formation of coke from 5.5wt% to 3.5wt% (Ni/SiO₂) and to 3.0wt% (Ni/Al₂O₃), and the formation of gaseous hydrocarbon products. To decrease coke formation further, a small amount of potassium was impregnated in the catalysts. The spectroscopy of NH₃-TPD showed that the amount of acidic sites in both catalysts, Ni/Al₂O₃ and Ni/SiO₂, was dramatically decreased by K₂O modification. The acid-catalyzed polymerization of residuum induced by acidic sites in the catalyst, that might result in the formation of coke, was suppressed by neutralization of the acidic sites. Adding 3% of potassium onto Ni/SiO₂ decreased the yield of coke from 3.5wt% to 2.1wt%.

Keywords

Hydrothermal process, Catalyst modification, Acidity, TPD

1. Introduction

Hydrothermal cracking of heavy oil is a tailor-made combined process of thermal cracking and catalytic hydrogenating that has been developed to produce high quality transportation fuels and middle distillate products from residual oils¹⁾. This process can suppress the formation of gas and coke, and it can as well promote the yield of middle distillate (kerosene + gas oil) compared with thermal and hydrocracking at the same levels of conversion^{2),3)}. Higher reaction temperatures can increase residuum conversion, but the selectivity of gas and coke will be increased simultaneously.

Coke is an unavoidable by-product in any heavy oil upgrading processes. But the mechanism of coke formation during petroleum refining is only now beginning to be understood⁴⁾. It is closely related to the mechanism of thermal decomposition of petroleum constituents and changes in the character of the liquid medium. When catalytic hydroprocess is applied to a residuum, some molecular species within the asphaltene fraction, which contain nitrogen and other heteroatoms, or complex molecules formed during reaction, are absorbed readily by the catalyst. These species may condense and degrade to coke, and eventually may deactivate the active sites of the catalyst. The authors modified hydrothermal cracking catalysts by adding potassium and these catalysts obviously suppressed the formation of coke in the upgrading of bitumen.

2. Experimental

2.1 Catalyst Preparation and Modification

Catalysts, 10%Ni/SiO₂ and 10%Ni/Al₂O₃, were prepared by impregnation *via* incipient wetness method. The precursor of active metal Ni was an aqueous solution of Ni(NO₃)₂·6H₂O. The supports used were SiO₂ (Q15, Fuji Silysia) and γ-Al₂O₃ (ALO-4, JCS reference). After impregnation, the catalysts were degassed in vacuum, dried at 393 K for 12 h in air, and then calcinated at 773 K for 4 h. The catalysts were modified by doping potassium, and they were impregnated consecutively with an aqueous solution of KNO₃ and then treated with the same procedure used in the catalyst preparation. Before using the catalysts (in oxide state), they were reduced in hydrogen with a flow rate of 120 cm³ min⁻¹ at 723 K for 4 h and then sulfurized in a 20%H₂S/H₂ flow under the same conditions.

2.2 Experimental Procedure and Product Analysis

The feedstock was Canadian Athabasca oil sand bitumen, whose properties are listed in Table 1. The feedstock is characterized with high metal impurities (Ni+V+Fe = 567 wt ppm), high aromatic content (61.5 wt%) and low API degree. Reactions of bitumen hydrothermal cracking were carried out in a 75 cm³ autoclave reactor in which the feedstock and catalyst were loaded. After having pressurized with hydrogen to the target pressure at room temperature, the reactor was heated and shaken up and down at a speed of 70 rpm during the whole reaction period to ensure an efficient contact with gas, liquid, and solid. It took about 10 min to raise the temperature from room temperature to the target temperature. The reaction time was identified when the desired reaction temperature was attained. After the reaction, the reactor was cooled down quickly to room temperature. The gaseous product was released to a collecting bag, and the liquid product was separated from the solid.

Reaction conditions were as follows: temperature, 703 K; initial H₂ pressure, 5.0 MPa, reaction time, 60 min.; weight ratio of catalyst/oil, 0.2; oil weight, 10.0 g.

Among the gaseous products, H₂S was detected by a hydrogen sulfide detector tube; H₂ was analyzed by a gas chromatography (Shimadzu GC-3B) with TCD. Light hydrocarbons were measured by a gas chromatography (Shimadzu GC-8A FID) with an active alumina column. The liquid products were separated by a distillation gas chromatography (Shimadzu GC-14A) with silicone OV-1 glass column into 5 components: naphtha (initial boiling point-443 K), kerosene (443-503 K), gas oil (503-616 K), vacuum gas oil (616-798 K), and residue (>798 K). The coke yield (wt%) was determined as percentage of toluene insoluble in the product to feed. The conversion of hydrothermal cracking of bitumen was calculated as follows:

$$\text{Conversion} = \left(1 - \frac{\text{residue in product}}{\text{residue in feed}}\right) \times 100\%$$

2.3 NH₃ Adsorption and NH₃-TPD

The strength and amount of acidic sites in catalysts were detected by NH₃-TPD following the procedure: (1) 0.05 g of sample was introduced into a quartz cell and evacuated; (2) the sample was heated at 703 K (same as the reaction temperature) for 30 min; (3) after cooling to room temperature, NH₃ was introduced into the sample cell to be adsorbed for 45 min; (4) after evacuation for 30 min, the cell was connected to a quadri-pole mass spectroscopy (Balzers QMS 200) to conduct TPD at a rate of 7 K/min.

3. Results and Discussion

The 10%Ni/SiO₂ catalyst was modified by doping potassium, 1%, 3%, 5% (weight percentage of K respect to the weight of support), respectively. Conversion, hydrogen consumption, and coke production in SiO₂, K/SiO₂ (absence of Ni), Ni/SiO₂, and modified Ni/SiO₂ (with varying K content) are shown in Table 2. Herein, the reaction carried out in SiO₂, K/SiO₂ was referred to as thermal cracking. One of the differences between hydrothermal cracking and thermal cracking is the presence of transition-metal-supported catalyst (Ni, Mo, W, etc.) in the hydrothermal cracking. The conversion level of residue was similar in all cases, ranging from 67.3% to 71.9%. This indicated that conversion depended mainly on thermal reaction. Compared with thermal cracking (SiO₂), hydrothermal cracking decreased the formation of coke from 7.0% (absence of K) to 5.5% and to 3.5% by addition of 3% K and increased the selectivity of distillates, but hydrogen consumption increased from 55 to 94 Nm³m⁻³. However, the conversion was nearly the same, from 68.3 % to 71.6%, with hydrothermal cracking catalysts. This was related to the properties of bitumen, which contained a large amount of aromatics, 61.5%. It was assumed that during hydrothermal cracking, the catalyst assisted the reaction of thermally generated phenyl radicals, or polyaromatic radicals with molecular hydrogen that resulted in decomposition of the condensed aromatic units to give gas and distillate. The concentration of the radicals formed was controlled by the activated hydrogen from the coexisting metal catalyst to reduce the possibility of over-cracking and coupling of the radicals. Consequently, gaseous products selectivity and coke selectivity decreased. Hydrogenation active sites readily suppressed conversion of the precursor to coke by the spill-over of activated hydrogen, but it still produced some coke (3.5%).

A process for phase separation in the residuum under thermal conditions⁵⁾ is available. When Canadian bitumen was brought into contact with a catalyst in the batch reactor under hydrothermal cracking conditions, there was a rapid build-up of solids on the catalyst that was independent of whether or not hydrogen was present.⁶⁾ This reaction was most likely an acid-catalyzed polymerization induced by acidic sites on the support⁷⁾ (alumina or silica). Part of the solids might be converted to distillates, while others might be converted to coke and gas. When Ni/SiO₂ was modified by K₂O, which was produced by thermal decomposition of KNO₃, the formation of coke in the thermal cracking of bitumen was obviously decreased from 3.5% (without modification) to 2.1% (modified with 3% K). Similarly, 3% K modified SiO₂ greatly suppressed coke formation from 7.0% to 5.5%. Residue conversion and gas yield decreased but slightly with increasing amount of potassium involved. Hydrogen consumption was reduced by about 10% after modification with 3% K.

The γ -Al₂O₃ supported Ni catalyst was modified by adding potassium, and it was employed in hydrothermal cracking. The product distribution, hydrogen consumption, and conversion are also listed in Table 2. Similar to that of supported silica catalyst, the performance of Ni/Al₂O₃ was promoted by doping 3 wt% potassium. K₂O decreased the formation of coke from 3.0% to 2.5%, the yield of gas (C₁-C₄ hydrocarbon) from 4.0 % to 3.8%, and it decreased conversion but slightly from 66.9% to 65.7%. Hydrogen consumption was reduced from 122 to 114 Nm³m⁻³. However, its addition hardly changed the yield of liquid products (naphtha, kerosene, gas oil, and VGO); it only suppressed the formation of coke.

In order to study the mechanism of coke formation suppressed by K₂O, the strength and amount of acidic sites of Al₂O₃, Ni/Al₂O₃, 3%K-Ni/Al₂O₃, Ni/SiO₂, and 3%K-Ni/SiO₂ were identified by NH₃-TPD. The spectroscopy of TPD-MS of Al₂O₃ supported catalysts

is shown in Fig. 1. It was clear that only 3 wt% addition of potassium, remarkably decreased the amount of acidity. Also supporting Ni onto Al_2O_3 decreased the acidic sites on Al_2O_3 to some extent. The desorption temperature of NH_3 on both strong acidic and weak acidic sites was almost the same in Al_2O_3 , $\text{Ni}/\text{Al}_2\text{O}_3$, and $\text{K-Ni}/\text{Al}_2\text{O}_3$. This indicated that K_2O only neutralized the acidic sites more effectively by decreased the amount of acidic site, but it did not much change the strength distribution of acidity. Now we'll discuss acidic site itself, although we have been discussing the effect of neutralization of acidic site above. Acidic site is preferable to the polymerization or condensation reactions, resulting in the formation of coke during hydrothermal cracking of heavy oil. By introducing basic K_2O in the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, the amount of acidic sites was decreased. This was unfavorable for absorption of polyaromatics and polar complexes in residual oil, readily suppressing the polymerization of condensation reaction induced by acidic sites; and decreasing the rate of formation of coke. The spectroscopy of TPD-MS of SiO_2 supported catalysts is shown in Fig. 2. The over-all strength of the acidic sites of SiO_2 was significantly lower than that of Al_2O_3 . It was also presumed that K_2O resulted in the decrease in acidity suppressing the formation of coke and gas. It has been reported that proper acidity of the support not only can promote the hydrogenation activity of NiMo catalyst or that of CoMo catalyst⁸⁾, but it also can benefit coke formation. A basic support has a tendency to obstruct the adsorption of coke precursors suppressing coke formation³⁾.

Coke formation is a complex process involving both such foregoing chemical reactions, polymerization and condensation, and involving also thermodynamic behavior. Modification by potassium only suppressed the coke formation by chemical reaction; thus it seemed invalid for coke formation from other means. This may be the reason as to why it still produced 2.1% of coke by adding 5% of K in Ni/SiO_2 . More effective methods will be studied to further decrease the formation of coke during hydrothermal cracking of residual oil.

4. Conclusions

By hydrothermal cracking of Athabasca bitumen, the formation of by-products, coke and gas, was greatly suppressed by catalyst Ni/SiO_2 and $\text{Ni}/\text{Al}_2\text{O}_3$ via hydrogen transfer to the precursor of coke and gas. Modification of the above catalysts by doping a small amount of potassium (K_2O), which neutralization of acidic sites in the catalysts, decreased the formation of coke further. It also mitigates the formation of coke during hydrothermal cracking of bitumen.

References

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Table 1 Properties of Athabasca Oil Sand Bitumen

API Gravity	6.0
CCR, wt%	15.0
C, wt%	82.89
H, wt%	10.14
S, wt%	4.90
N, wt%	0.45
V, wtppm	192
Ni, wtppm	75
Fe, wtppm	300
Saturates, wt%	10.9
Aromatics, wt%	61.5
Resins, wt%	18.1
Asphaltenes, wt%	9.5
Residue (798K ⁺), wt%	65.2

Table 2 Potassium Doping Effect on Catalysts Ni/Al₂O₃ and Ni/SiO₂

Catalyst	Ni/Al ₂ O ₃		SiO ₂		Ni/SiO ₂			
Potassium content/wt%	0	3	0	3	0	1	3	5
H ₂ consumption/Nm ³ m ⁻³	122	114	55	61	94	92	85	84
Conversion/%	66.9	65.7	71.9	68.3	71.6	69.8	69.2	67.3
Product distribution, wt%								
H ₂ S	2.3	2.2	1.4	1.4	1.6	1.5	1.5	1.5
C ₁ -C ₄	4.0	3.8	6.3	5.6	5.0	4.7	4.7	4.5
Naphtha	7.0	6.7	9.1	9.0	10.3	9.7	9.9	9.4
Kerosene	7.9	7.9	10.5	10.6	10.3	9.6	10.2	9.5
Gas oil	22.4	22.6	22.6	22.9	23.6	22.9	22.3	22.4
VGO	31.8	32.0	24.8	24.4	27.2	29.4	29.2	29.3
Residue	21.6	22.3	18.3	20.6	18.5	19.7	20.1	21.3
Coke	3.0	2.5	7.0	5.5	3.5	2.5	2.1	2.1
Yield*, %	69.1	69.2	67.0	66.9	71.4	71.6	71.6	70.6

703 K, 5.0 MPa, 60 min, catalyst 2.0 g, bitumen 10.0 g.

*: Naphtha + Kerosene + Gas oil + VGO

Fig. 1 NH₃-TPD spectroscopy of Al₂O₃, Ni/Al₂O₃ and K-Ni/Al₂O₃

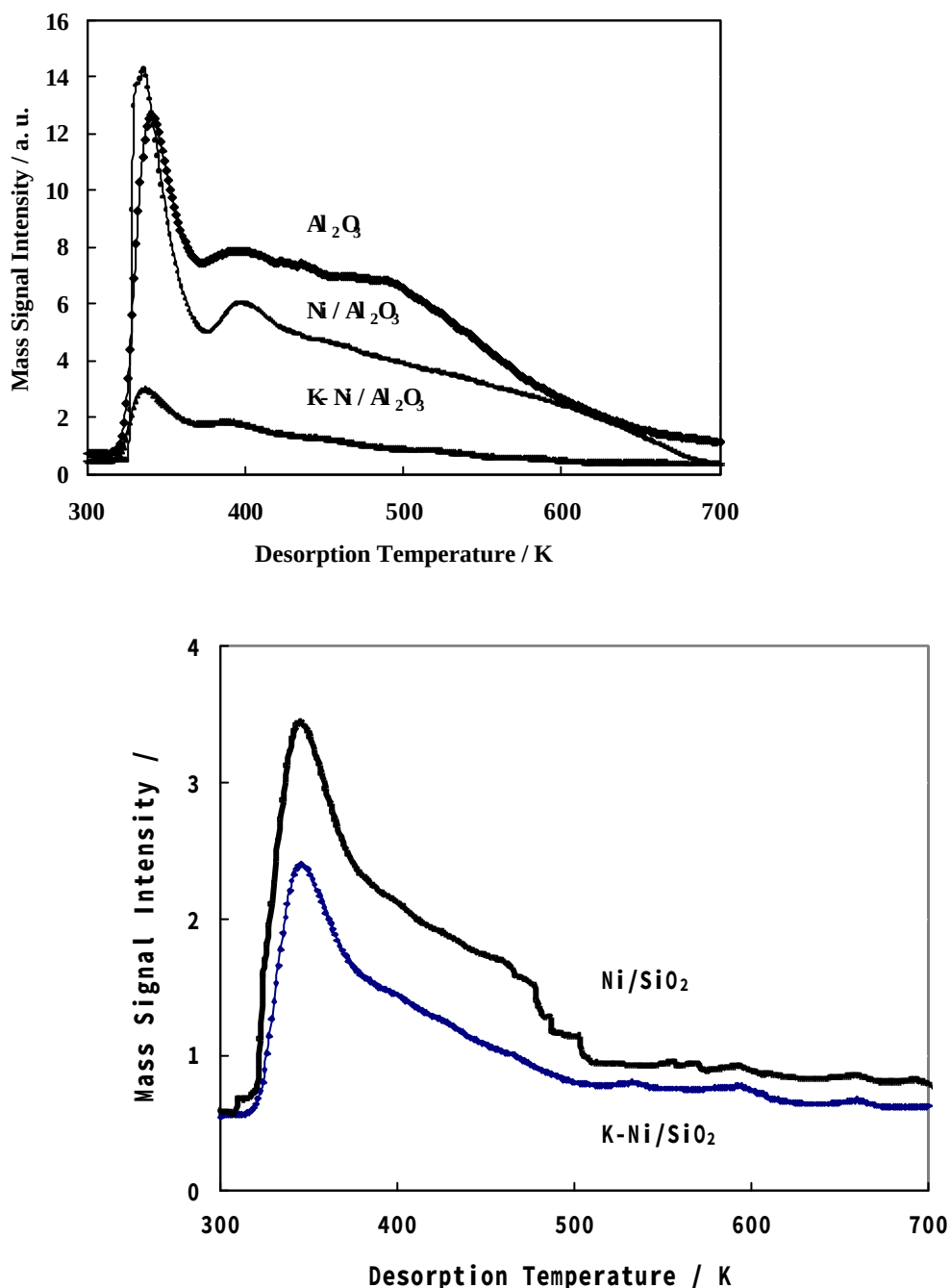


Fig. 2 NH_3 -TPD spectroscopy of Ni / SiO_2 and $\text{K-Ni} / \text{SiO}_2$

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