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Deactivation Control through Accelerated Precoking for the CoMo/γ-Al_2O_3 Catalysts in Thiophene Hydrodesulfurization

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Abstract−Information on the degree of deactivation is very important for predicting catalyst life, from which the catalyst design could be further improved. The CoMo/Al_2O_3 catalysts, used for the hydrodesulfurization of light oil, are known to have a commercial operation time of around two years. Our goal was to establish the accelerated precoking conditions for obtaining a desired degree of deactivation for CoMo/Al_2O_3 catalysts. The effect of coking temperature on the catalytic activity for thiophene hydrodesulfurization was investigated for three coke precursors. Precoking with heavier precursors resulted in higher coke content and higher aromaticity as expected, i.e., in order of anthracene>naphthalene>cyclohexene. It is suggested that the established conditions of precoking for the commercial catalysts could provide a quantitive reference for evaluating the lifetime of any commercial catalysts.

Key words: Accelerated Deactivation, Precoking, Hydrodesulfurization, Coke Deposit, Aromaticity

INTRODUCTION

Elucidation of catalyst deactivation is one of the most important issues for better design of catalysts in petroleum refining. In general, the deactivations are due to the accumulation of carbonaceous and metallic deposition and/or the structural changes of the catalyst components [Yokoyama et al., 1996; Makishima et al., 1996]. Brito et al. [2001] studied deactivation by coke deposition for NiMo/Al_2O_3 catalyst, finding that maximum deposition occurred on the outer edge of the catalyst and that coke deposition considerably reduced catalyst pore size and activity. Callejas et al. [2001] studied long-term (7,400 hr) petroleum residue hydroprocessing for commercial NiMo/Al_2O_3 catalyst, finding that coke deposited rapidly on the catalyst surface during the early hours of the run (100 hr), reaching as high as 12.4 wt%. Coke deposit is the primary cause of CoMo catalyst deactivation not only for the alumina-supported catalysts but also for the zeolite-supported catalysts or nitride catalysts in the hydrotreating process [Li et al., 2000; Choi, 2002; Kim et al., 2002]. However, questions still remain regarding to what extent each deactivation contributes to the total catalyst deactivation. Quantitative understanding of the catalyst deactivation is needed for further improvement of long-life catalysts. Tanaka et al. [1998] used the accelerated deactivation through a higher reaction temperature for several kinds of laboratory prepared CoMo/Al_2O_3 and NiW/Al_2O_3 catalysts, and compared the coke deposit with a commercial catalyst used in a hydrodesulfurization plant for one year. They reported that a high reaction temperature employed in the accelerated aging resulted in a large amount of carbonaceous deposition with high aromaticity, which was found to be the major deactivation cause.

In this work, accelerated precoking with three different coke precursors was introduced at an elevated temperature for a relatively short period of time prior to the thiophene hydrodesulfurization reaction to control the coke deposit of commercial CoMo/Al_2O_3 catalysts. The amount and aromaticity of coke could be controlled by precoking condition, the nature and amount of coke precursors, and the precoking temperature and time. It is expected that the established conditions of precoking for the commercial catalysts could provide a quantitive reference for evaluating the lifetime of any commercial catalysts.

EXPERIMENTAL

1. Accelerated Precoking of Commercial CoMo/Al_2O_3 Catalysts

The catalyst used was a commercial CoMo/Al_2O_3 with 4.0 wt% of Co as CoO and 19.7 wt% of Mo as MoO_3. The spent CoMo/Al_2O_3 catalyst, which had been used for 2 years in a light oil treating plant, was chosen as a reference catalyst. Accelerated precoking treatments were performed in a batch reactor. Five grams of catalyst was loaded in the 300 ml reactor and then H_2S (10 vol%)/H_2 was introduced with 30 ml/min to presulfide the catalyst at 400 °C and 2 hours. The reactor was cooled down to room temperature and fed with 150 ml of coke precursor solution (coke precursor in n-hexadecane). Three different coke precursors, cyclohexene, naphthalene and anthracene, were used. The reactor was gradually heated at a rate of 5 °C/min to a desired temperature (400, 500, 600 and 700 °C) and the pressure was set to 10 atm. The time of accelerated precoking treatments was 1 to 5 hours.

2. Characterization

Surface area and pore size distribution were measured by using N_2 adsorption technique (Micromeritics, ASAP 2010). Total weight of coke deposit on catalysts was determined by combustion method using an elemental analyzer (Elemental Analysensystem, GmbH Vario EL). CP/MAS-^{13}C-NMR spectra were analyzed to determine the aromatic content of coke deposit on catalysts by an FT NMR

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[‡] This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

spectrometer (Bruker AM-300).

3. Thiophene Hydrodesulfurization

Thiophene HDS reaction was carried out over 0.02 g of catalyst at 400 °C in a stainless steel microreactor operated at 20 atm. The liquid thiophene flow rate was 0.035 ml/min and the mole ratio of hydrogen to thiophene was 15. Before the reaction was started, fresh catalyst was presulfided *in situ* at 400 °C for 2 hrs with flowing H_2S (10 vol%)/H_2 at 30 ml/min, while the precoked catalysts were not presulfided. Steady state was achieved after 3 hrs of runtime. Reaction products were analyzed with a gas chromatograph equipped with TCD and the column packed OV-101. The thiophene conversions reported were taken after 5 hours of runtime.

RESULTS AND DISCUSSION

1. The Characteristics of Fresh and Spent Commercial CoMo/Al_2O_3 Catalysts

Fig. 1 shows the thiophene HDS conversion with time on stream over fresh and spent CoMo/Al_2O_3 catalysts in commercial light oil HDS plant for 2 years. These results show that the conversion of fresh catalyst was 81% and that of spent catalyst was 55%. After sulfiding for the spent catalyst, the activity was recovered to 69% conversion. This indicates that some of active sites of the spent catalyst could be regenerated through sulfidation. Table 1 shows the physical properties of fresh and spent commercial CoMo/Al_2O_3 catalysts.

The surface area of spent catalyst was about half of that of fresh catalyst. The coke deposit and aromaticity of spent catalyst were 13% and 36%, respectively.

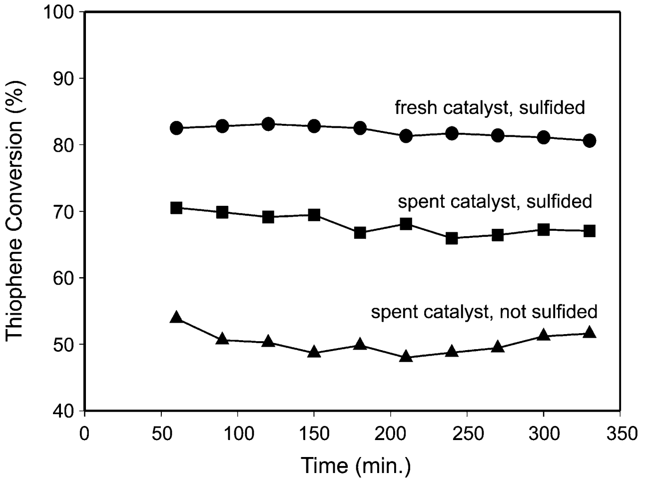

Fig. 1. Thiophene HDS conversion over fresh and spent CoMo/Al_2O_3 catalysts (reaction; 400 °C, 20 atm, H_2/thiophene=15).

Table 1. Physical properties of fresh and spent commercial CoMo/Al_2O_3 catalysts

	Fresh catalyst	Spent catalyst
Surface area (m^2/g)	226	107
Pore volume (ml/g)	0.47	0.30
Coke amount[a] (coke wt/catalyst wt)	~0	13
Aromaticity[b] (aromatic wt/coke wt)	~0	36

[a] measured by elemental analysis.
[b] measured by CP/MAS-^{13}C-NMR.

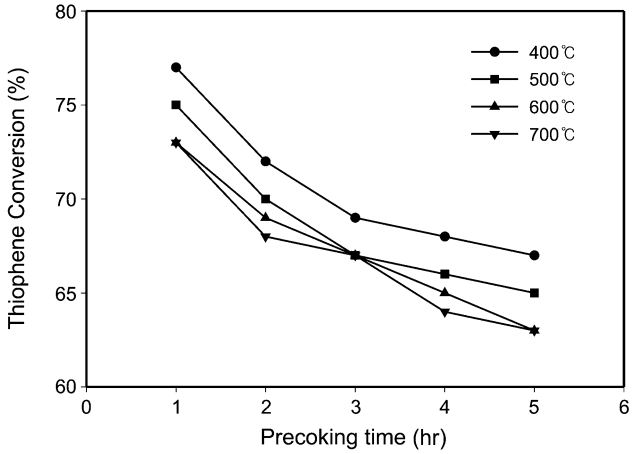

Fig. 2. Activity change with precoking time at different precoking temperature with 10 wt% cyclohexene (reaction; 400 °C, 20 atm, H_2/thiophene=15).

2. Activity Change Due to Accelerated Precoking

Fig. 2 shows the change of thiophene HDS conversion with precoking time at different precoking temperature with cyclohexene as a precoking precursor. As precoking treatment time and temperature increased, the conversions of precoked catalysts decreased. The upper limit of precoking temperature was 700 °C in this study. In the case of the precoking treatment with naphthalene and anthracene, similar effects on the thiophene HDS conversion were observed over precoking treated catalysts, as shown Fig. 3.

The difference in the nature of the coke precursors was investigated by using cyclohexene, naphthalene and anthracene. Fig. 4 shows that anthracene induced the precoking more efficiently. Heavier precursor (anthracene) resulted in more precoking and deactivation.

Fig. 5 shows the thiophene conversion over precoked catalyst with different amount (10 and 15 wt%) of anthracene. The thiophene conversion decreased with higher amount of precursor, as expected.

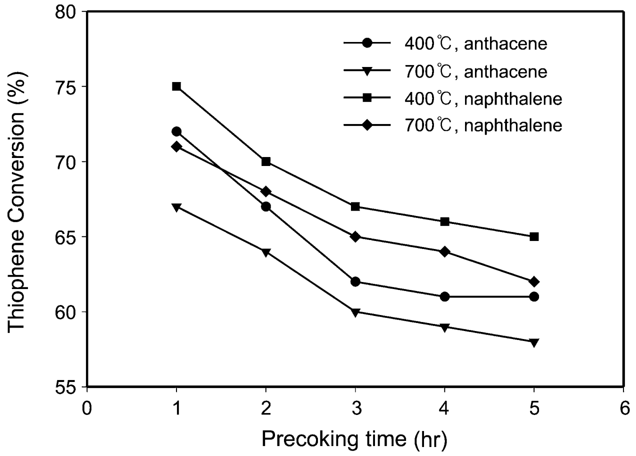

Fig. 3. Activity change with precoking time at different precoking temperature with 10 wt% each of naphthalene and anthracene (reaction; 400 °C, 20 atm, H_2/thiophene=15).

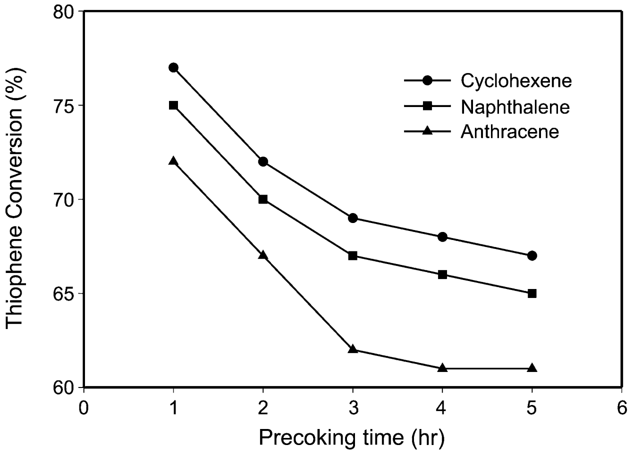

Fig. 4. Activity change with precoking time with different coking precursor (precoking temperature; 400 °C, 10 wt% each, reaction; 400 °C, 20 atm, H_2/thiophene=15).

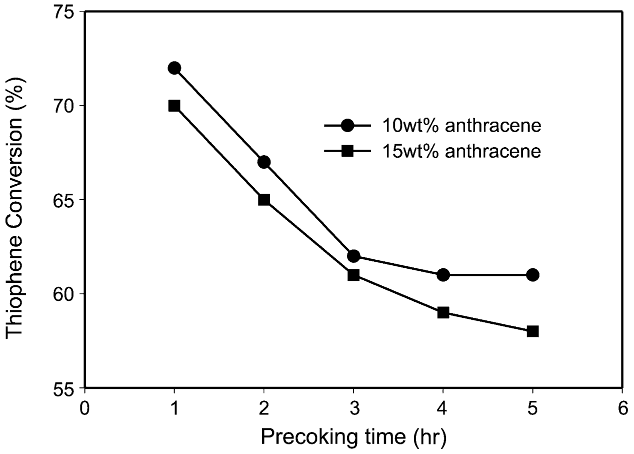

Fig. 5. Activity change with precoking time with different amount of anthracene (precoking temperature; 400 °C, reaction; 400 °C, 20 atm, H_2/thiophene=15).

Table 2 shows the physical properties and the nature of coke deposit on the catalysts used in precoking treatment. The surface area and pore volume of the precoked catalysts decreased with increasing precoking temperature, and the decrease was more significant with heavier coke precursor. Aromaticity of coke deposit on precoked catalysts increased with precoking temperature and also with heavier coke precursors.

3. Selection of the Precoking Treatment Conditions

The precoking conditions had better be established such that the precoked catalyst shows similar activity to the spent catalyst operated in a commercial light oil HDS plant for two years. Four different conditions were chosen as listed in Table 3. The amount of coke deposit was around 13 wt%, similar to that of used commercial catalyst if the precoking time is 5 hours. Precoking condition B to D showed 13 wt% of coke deposit, while condition A showed about 10 wt%. The variables of precoking conditions were the precoking time, the precoking temperature, the nature of coke precursor and the amount of coke precursor. The precoking temperature was fixed at 500 °C. As shown in Fig. 6, the precoking condition D, which shows the deactivation properties similar to those of spent commercial catalysts used for 2 years, can be proposed as a reference method of accelerated deactivation for predicting the life of $CoMo/Al_2O_3$ catalysts in the thiophene HDS. The life of any $CoMo/Al_2O_3$ catalysts might be longer or shorter than 2 years, depending on whether the activity of precoked catalyst is higher or lower than reference activity.

Table 3. Selection of the precoking treatment conditions at 500 °C

Condition	A	B	C	D
Time (hr)	1	5	5	5
Precursor[a]	Cy	Cy	N	A
wt%	10	15	20	20

[a] Cy: cyclohexene, N: naphthalene, A: anthracene

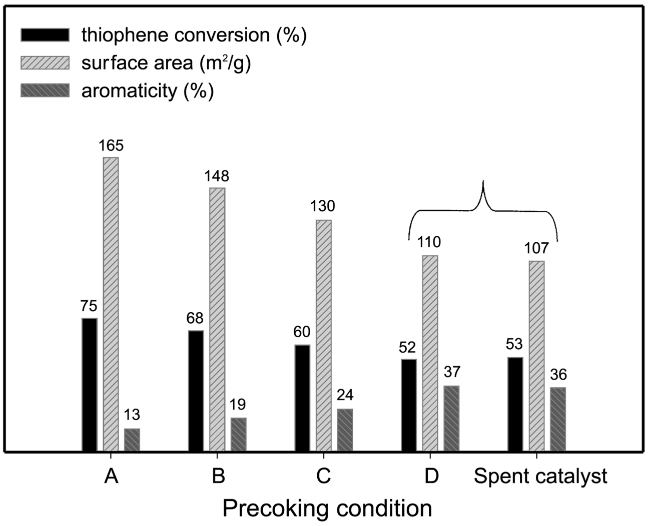

Fig. 6. Thiophene conversion, surface area and aromaticity of precoking treated catalysts.

CONCLUSION

The accelerated precoking of commercial $CoMo/Al_2O_3$ catalysts

Table 2. Physical properties of precoked commercial $CoMo/Al_2O_3$ catalysts at 400 and 700 °C

	PC400C5	PC700C5	PC400N5	PC700N5	PC400A5	PC700A5
Aromaticity (%)	15	20	22	25	24	28
Surface area (m^2/g)	152	143	151	130	150	120
Average pore diameter (nm)	7.6	7.5	7.4	7.3	7.2	7.3
Pore volume (ml/g)	0.40	0.35	0.36	0.32	0.36	0.32

*PC400C5 indicates that the $CoMo/Al_2O_3$ catalyst was precoked at 400 °C for 5 hrs with cyclohexene as coke precursor.

resulted in different amount and aromaticity of coke deposit, which was the major source of the catalyst deactivation in the light oil HDS process. The heavier coke precursor such as anthracene induced more carbon deposit with higher aromaticity, leading to a significant reduction in the thiophene conversion, the surface area and pore volume of the catalysts. The precoking condition D, which shows deactivation properties similar to those of spent commercial catalysts used for 2 years, can be proposed as a reference method of accelerated deactivation for predicting the life of $CoMo/Al_2O_3$ catalysts in the thiophene HDS.

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