Elucidation of Sulfur Behavior on Alumina-Supported Ruthenium Sulfide-Cesium Catalysts Using Radioactive ^{35}S as a Tracer

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In hydrodesulfurization of ^{35}S-labeled dibenzothiophene over alumina-supported ruthenium sulfide-cesium catalysts, the role of cesium was elucidated by tracing the behavior of ^{35}S on the working ruthenium catalysts; the addition of cesium increased the catalytic activity by strengthening Ru-S bonds of ruthenium sulfide. It is suggested that there is an optimum Ru-S bond strength to obtain the high catalytic activity.

In recent years, much attention has been focused on deep desulfurization of light gas oil and the development of new catalyst for deep desulfurization has been one of urgent issues in the world.[1] Among a number of attempts made to develop the new catalyst, nonsupported[2] and supported[3] ruthenium sulfide catalysts have been found to be most active for hydrodesulfurization (HDS) of thiophenes in transition metal sulfides. Recently, the authors reported that in HDS of dibenzothiophene (DBT) the catalysts derived from supported metal carbonyls showed higher catalytic activity than conventional catalysts.[4] The cesium promoted ruthenium catalysts revealed the comparable activity with a conventional Co-Mo/Al_2O_3.[5]

On the other hand, it is essential for the elucidation of the HDS mechanism to know the behavior of sulfur on HDS catalysts. However, it has not been well-known how sulfur in catalysts acts in the practical HDS reactions. The authors reported that the behavior of sulfur on the catalysts could be determined in HDS of ^{35}S-labelled dibenzothiophene (^{35}S-DBT) catalyzed by Al_2O_3-supported molybdenum sulfide.[6,7]

In the present study, we report HDS of ^{35}S-DBT catalyzed by Al_2O_3-supported ruthenium catalysts to elucidate the role of cesium in HDS. It was found that the addition of cesium increased the catalytic activity by strengthening Ru-S bonds of ruthenium sulfide.

The methods for catalyst preparation and analysis and the reaction apparatus were described elsewhere.[4,5] Typical operation procedures were as follows: A catalyst precursor was presulfided at 300 °C for 3 h in H_2S/H_2 (H_2S 3%). (a) a decalin solution of 1.0 wt% ^{32}S-DBT was pumped into the reactor until the conversion of DBT became constant (about 3.5 h). (b) After that, the reactant solution was switched to a decalin solution of 1.0 wt% ^{35}S-DBT. The reaction was performed until the amount of ^{35}S-H_2S released from the exit of reactor became constant (about 7 h). (c) The reactant solution of ^{35}S-DBT was replaced by a decalin solution of 1.0 wt% ^{32}S-DBT again and the reaction was continued for 8 h.

Figure 1 shows the changes in the radioactivities of unreacted ^{35}S-DBT and produced ^{35}S-H_2S with the reaction time at 280 °C using $Ru_3(CO)_{12}$-6CsOH/Al_2O_3 catalyst. The radioactivities of unreacted ^{35}S-DBT in liquid products increased with the reaction time and reached a steady state immediately. On the contrary, the time delay for about 6 h was observed for the radioactivities of ^{35}S-H_2S to reach a steady state. Then, the decalin solution of ^{32}S-DBT was again substituted for ^{35}S-DBT in a similar way, the time delay for decrease in radioactivities of unreacted ^{35}S-DBT from the steady state to normal state was also 30 min while that for the ^{35}S-H_2S was about 6 h. The result indicates that the sulfur in DBT is not directly released as hydrogen sulfide, but accommodated on the catalyst for a certain period. This phenomenum is consistent with those observed for Al_2O_3-supported molybdenum catalysts.[6,7]

Data for the alumina-supported ruthenium sulfide-cesium catalyst were treated as follows: The first order plot of the radioactivity of the decreasing period ^{35}S-H_2S in Fig. 1 indicates the linear relationship revealed as

$$\ln y = \ln z - kt \qquad (1)$$

where y represents the radioactivity of ^{35}S-H_2S (dpm/min); z the radioactivity of ^{35}S-H_2S at steady state (dpm/min); k the rate constant of the release of ^{35}S-H_2S (min^{-1}); t reaction time (min). The value of k represents the relative ease of migration of sulfur on the catalyst.[6,7] When ^{32}S-DBT was substituted for ^{35}S-DBT after radioactivities of ^{35}S-H_2S reached the steady state, all ^{35}S accommodated on the catalyst was released as ^{35}S-H_2S. From the total amount of radioactivities of the released ^{35}S-H_2S (Area A), the amount of labile sulfur on the catalyst (So), which may represent the amount of the active sites, can be caluculated.[6,7] The values of k and So for several catalysts are shown in Table 1. The values of So for the catalysts increased with an increase in the amount of cesium added and reached maximum at Ru:Cs=1:2 which was kept with further addition of cesium (Ru:Cs=1:3). This shows that the active sites on the catalyst were not poisoned

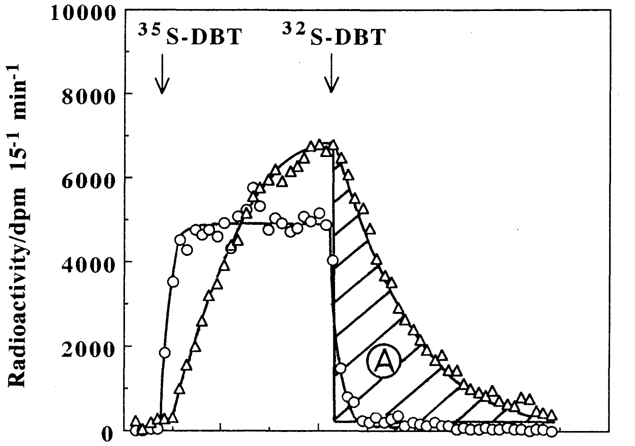

Figure 1. Change in the radioactivities of unreacted DBT and released hydrogen sulfide with reaction time. $Ru_3(CO)_{12}$-6CsOH /Al_2O_3 catalyst; 50 kg/cm^2, 280 °C. ○: Radioactivity of ^{35}S-DBT; △: Radioactivity of ^{35}S-H_2S.

Table 1 . Hydrodesulfurization of ^{35}S-labeled dibenzothiophene over $Ru_3(CO)_{12}$-nCsOH/Al_2O_3 catalysts[a]

Run	Catalyst (Ru:Cs)	Conversion /%	So[b] /mg g-cat^{-1}	So/St[c] /%	k /10^{-2} min^{-1}	HDS Rate[d] /10^{-1} mg g-cat^{-1} min^{-1}	So x k /10^{-1} mg g-cat^{-1} min^{-1}
1	1:0	50.1	9.2($RuS_{0.36}$)	18	2.34	2.03	2.15
2	1:1	87.7	17.2($RuS_{0.68}$)	34	1.92	3.56	3.30
3[e]	1:2	60.0	30.4($RuS_{1.20}$)	60	0.79	2.43	2.40
4[f]	1:2	70.0	34.3($RuS_{1.35}$)	68	0.86	2.84	2.95
5	1:2	94.0	38.5($RuS_{1.52}$)	76	1.01	3.81	3.89
6	1:3	52.5	39.3($RuS_{1.55}$)	78	0.60	2.13	2.36

[a] Catalyst: $Ru_3(CO)_{12}$-nCsOH/Al_2O_3, 0.5 g, Ru 8 wt%, 320 °C, 50 kg/cm^2, WHSV 14 h^{-1}, H_2 18 l/h, DBT 1 wt% in decalin. [b] The value given in a parenthesis represents the ratio of labile sulfur to ruthenium. [c] For the value of St (total sulfur), it was assumed that ruthenium species would be present as RuS_2. [d] Calculated from the conversions. [e] 280 °C. [f] 300 °C.

because So did not decrease with the addition of excess amount of cesium. The maximum value of So at Ru:Cs=1:2 corresponds to $RuS_{1.52}$. If it is assumed that ruthenium species are present as RuS_2, 76% of sulfur on the catalyst is labile. The result shows that the dispersion of ruthenium species is significantly high. The rate constant of the release of $^{35}S\text{-}H_2S$ (k) decreased with increasing cesium, indicating that the mobility of sulfur on the catalysts decreased by the addition of cesium. These results suggest that cesium strengthened Ru-S bonds of ruthenium sulfide. As a result, the C-S bond scission of DBT was promoted and the activity increased. However, Ru-S bonds became too strong with the addition of excess amount of cesium. The formation of H_2S and the regeneration of the coordinatively unsaturated sites were prevented, which results in decreasing the activity. It is also suggested that there is an optimum Ru-S bond strength to obtain the high catalytic activity.[8]

The amount of labile sulfur represents the amount of active sites which give the coordinatively unsaturated sites while the rate constant of the release of $^{35}S\text{-}H_2S$ represents the mobility of such active sites. As shown in Table 1, the HDS rate calculated from the conversion is in good agreement with the product (So x k) of the amount of labile sulfur on the catalyst and the rate constant of the release of $^{35}S\text{-}H_2S$. The result indicates that the amount of labile sulfur and the rate constant of the release of $^{35}S\text{-}H_2S$, which control the HDS rate, can be determined separately by using a ^{35}S tracer method as shown here.

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