

Molybdenum Nitride As a Long Lifetime Catalyst for Hydrodesulfurization

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(Received March 9, 2000; CL-000235)

The molybdenum nitride catalysts are long-lifetime catalysts due to resistance to carbon deposition compared to the sulfided catalysts. The deactivation of the molybdenum nitride catalysts at the initial stage was related to the depositions of sulfur and carbon at the steady state.

Interest has increased in exploring the catalytic properties of molybdenum nitrides for hydrodesulfurization (HDS) of diesel oils. Recently, for the HDS of thiophene¹⁻⁴ and dibenzothiophene,⁵⁻⁷ an NH_3 -treated molybdenum oxide catalyst was shown to be more active than the sulfided catalysts. However, the activities in the HDS's of thiophene and dibenzothiophene sometimes extremely decreased to similar activities of the sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts since a thin layer of sulfided molybdenum was formed on the surface of the molybdenum nitride particles during the reaction.¹⁻³ In this study, we found that the nitrated catalysts are long-lifetime catalysts due to a resistance to carbon deposition measured by XPS in the steady state of the reaction, with longer lifetime than the sulfided catalysts.

A 97.1% $\text{MoO}_3/\text{Al}_2\text{O}_3$ (Nikki Chemicals Co.) was prepared using a mixture of ammonium paramolybdate and γ -alumina.^{7,8} γ -Alumina (2.9%) was used as a binder to maintain durability and to prevent crumbling of the catalyst during the reaction. The 97.1% $\text{MoO}_3/\text{Al}_2\text{O}_3$ precursor (1 g) was treated in a stream of ammonia at 4 Lh^{-1} at a rate of 1 K min^{-1} from 573 K to 773, 973, or 1173 K, and held at this temperature for 3 h. For the activity measurement, the granular NH_3 -treated catalysts (1.0 g, 0.84–1.19 mm) were passivated in a stream of 1% O_2/He after nitridation. The fresh 97.1% $\text{MoO}_3/\text{Al}_2\text{O}_3$ was presulfided in flowing 10% $\text{H}_2\text{S}/\text{H}_2$ (15 Lh^{-1}) at 573, 623 and 673 K for 3 h for comparison. The XPS binding energies of molybdenum, sulfur, and carbon atoms^{5,7-9} in the catalysts were analyzed using a Shimadzu ESCA 3200 spectrometer with monochromatic $\text{MgK}\alpha$ exciting radiation (8 kV, 30 mA). The HDS of dibenzothiophene was carried out using a microreactor at a total pressure of 10.1 MPa and 573 K. The liquid feed, consisting of 0.25wt% dibenzothiophene in xylene, was introduced into the reactor at 20 mLh^{-1} in a H_2 flow of 6 Lh^{-1} . The HDS rate for dibenzothiophene HDS on the catalysts was calculated based on the rate of disappearance of dibenzothiophene.

The catalyst lifetime of the NH_3 -treated catalysts was simulated based on eq (1),^{10,11} which was the deactivation function (Φ) for the HDS of dibenzothiophene and represented the deactivation degree with time on stream. A good fit was observed over the entire range as shown in Figure 1. The results for the simulation of the deactivation are shown in Table 1. From the simulation results, the catalyst lifetime for the 973 K-nitrated was 1.2 and 4.9 times longer than the 773 K- and 1173 K-nitrated catalysts, respectively. The 973 K-nitrated catalyst is

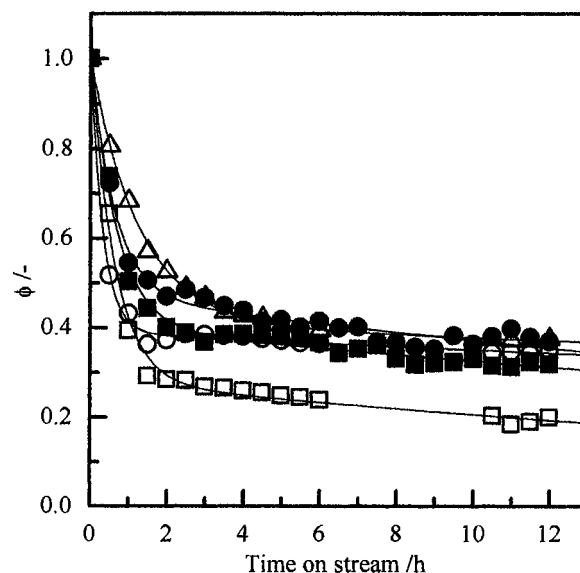


Figure 1. Simulation of the catalyst lifetime of the (O) 773, (Δ) 973, and (\square) 1173 K treated catalysts and (\bullet) 573 and (\blacksquare) 673 K sulfided catalysts as a function of time on stream in the HDS of dibenzothiophene at 573 K and a total pressure of 10.1 MPa.

Table 1. Physical properties of the catalysts and parameters for simulated deactivation functions

Parameters and physical properties	Catalyst				
	Nitrated at			Sulfided at	
	773	973	1173 K	573	673 K
Surface area / m^2g^{-1}	$10^4(5)^b$	7(29)	8(9)	12	17
HDS rate ^c / $\mu\text{molg}^{-1}\text{h}^{-1}$	34.7	50.5	25.9	51.0	37.5
α_1	3.05	0.786	1.60	1.57	1.48
α_2	0.010	0.0087	0.031	0.024	0.021
$\chi^2 \times 10^{3d}$	0.1	0.07	0.47	0.38	0.32
Catalyst lifetime ^e /h	131	163	33	65	66

^aBefore and ^bafter the reaction. ^cAt 12 h after start of the reaction. ^d χ^2 (chi)-square test. ^eTime (catalyst lifetime) was estimated by a value at the conversion of at 10%.

resistant to deactivation. Furthermore, the experimental and simulated data are shown in Figure 1. The catalyst lifetime (163 h) of the 973 K-nitrated catalyst was longer than those of the sulfided catalysts (65 and 66 h). This result indicated that the nitrated catalyst is a good catalyst because of long-time-duration of the HDS activity.

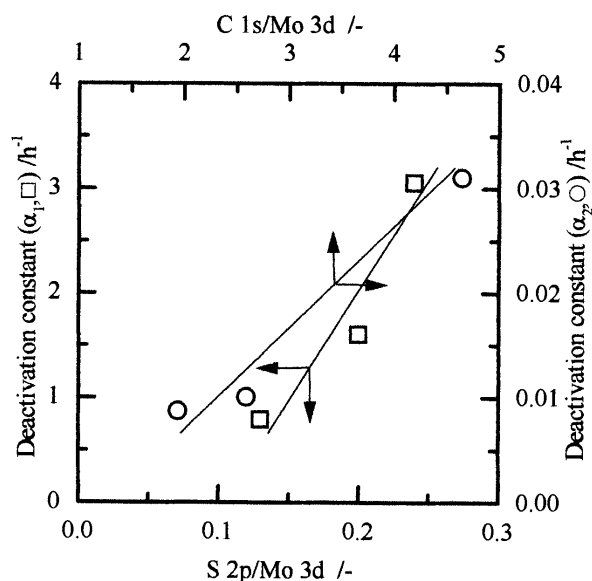


Figure 2. Relationship between the deactivation constants (α_1 and α_2) and the atomic ratios of the (\square) XPS S 2p/Mo 3d and (\circ) C 1s/Mo 3d, respectively, in dibenzothiophene HDS on the nitrated catalysts at 573 K.

The XPS spectra of Mo 3d, S 2p, and C 1s in the nitrated catalysts were measured by XPS to determine the decrease in the activity of the NH_3 -treated catalysts during the HDS. The deactivation parameters (α_1 and α_2) are plotted against the ratios of S/Mo (at 3 h) and C/Mo (at 12 h), respectively, in Figure 2. The parameter α_1 was correlated to the formation of sulfur species at the initial stage of the reaction. The deposition of sulfur removed from dibenzothiophene led to poisoning the active sites (easily deactivated sites) and deactivating the catalysts. The parameter α_2 was correlated to carbon deposition for preventing the active sites (deactivated sites with difficulty) in the pores of the catalysts by plugging the pore mouth. The slops of α_1 against S/Mo and α_2 against C/Mo are 20.8 and 0.00768, respectively. The deactivation of molybdenum nitride catalysts by sulfur accumulation at the initial stage was 2.7×10^3 times greater than that by carbon deposition at the steady state. Furthermore, there is no correlation between the deactivation and the decrease in the O/Mo and N/Mo ratios (the difference in oxygen and nitrogen contents before and after the reaction). In

conclusion, the 973 K-treated catalyst has a long catalytic lifetime for dibenzothiophene HDS. The active sites of the nitrated catalysts were easily deactivated by sulfur deposition at the initial stage of the reaction but were hardly deactivated by carbon deposition at the steady state by a factor of one hundredth compared to the initial deactivation.

This research project was carried out by a Grant-In-Aid for Scientific Research of the Ministry of Education, Science, Sports, and Culture (09555244).

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- 11 The deactivation (Φ) of the nitrated catalysts, representing the decreasing rate of active sites on the nitrated catalysts was in the first order against the number of active sites and was expressed by eq (1).

$$\Phi = r/r_0 = \{r_1^0 \exp(-\alpha_1 t) + r_2^0 \exp(-\alpha_2 t)\} / r_0 \quad (1)$$

where the rate (r) of nitrated catalysts in initial time ($t=0$) is r^0 , the constants are r_1^0 and r_2^0 , the deactivation (first order rate) constant is α_1 , and time on stream is t . The equation was described as the summation of the deactivated species such as easily deactivated active species (r_1^0 , α_1) and hardly deactivated active species (r_2^0 , α_2).