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Activity of alumina-supported molybdenum nitride for carbazole hydrodenitrogenation

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The alumina-supported molybdenum nitride catalyst was extremely active in the hydrodenitrogenation of carbazole at 553–633 K and 10.1 MPa total pressure when compared with the sulfided and reduced catalysts.

Keywords: Carbazole hydrodenitrogenation; molybdenum nitride on alumina

Molybdenum nitride is known to be a superconducting material having a high melting point, and also an active catalyst for a variety of reactions to emulate the catalytic properties of noble metals for NH_3 synthesis [1], CO hydrogenation, C_2H_4 hydrogenolysis and hydrogenation [2], and the methanation of CO [3]. An increasing interest has developed in exploring the catalytic properties of molybdenum nitrides for solving environmental problems. Hydrodenitrogenation (HDN) is a very important process in hydrotreating and is generally conducted on supported molybdenum-based catalysts. More recently, it was reported that γ-Mo_2N powder was active for quinoline HDN [4] and acetonitrile hydrogenation [5]. The catalytic activity of molybdenum catalysts appeared to be determined by the molybdenum nitride surface layers, regardless of the structure or composition of the bulk [1,6]. In this study, alumina is used as a support to obtain high surface area for industrial applications. An alumina-supported molybdenum nitride catalyst with high surface area was prepared and tested to determine the activity and selectivity in the HDN of carbazole.

The alumina-supported molybdena catalyst was prepared by a mixture of hexa-ammonium molybdate and γ-alumina xerogel and calcined in air at 827 K for 3 h. The activity measurements for carbazole HDN were carried out in a stainless-steel flow system, fixed-bed microreactor. The alumina-supported molybdena catalyst (2.0 g) was preheated in air at 723 K for 3 h in the reactor and was nitrided with flowing NH_3 by temperature-programmed reduction of

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Table 1
The composition of the nitrided catalysts

Catalyst		Nitrogen (wt%)					BET surface area [b] (m^2/g)
loading (wt%)	nitridation [a]	evacuated at				stoichiometric value	
		473 K	673 K	773 K	973 K		
11.7	MTN	1.5	0.6	0.6	–	0.6	267.2
	HTN	1.6	1.0	0.8	0.5	0.6	195.4
97.1	MTN	8.5	7.1	6.2	–	6.8	39.7
	HTN	10.2	9.2	8.8	7.0	6.8	39.2

[a] The MTN and HTN catalysts were nitrided with flowing NH_3 at 773 and 973 K, respectively.
[b] The catalysts were evacuated at 10^{-4} Torr at 473 K before measurement of the nitrogen content of the catalyst.

MoO_3/Al_2O_3 with ammonia [1]. After the fresh catalyst was oxidized at 723 K for 3 h and cooled to 573 K, the catalyst was heated with pure NH_3 at 4 ℓ/h from 573 to 773 or 973 K at 1 K/min and held for 3 h (MTN or HTN catalyst). The catalyst pretreatment unit was used to prepare the samples for nitriding at 973 K. The catalyst was then cooled to room temperature and passivated in 1% O_2/He at room temperature. All experiments were performed in the temperature range 533–633 K at 10.1 MPa total pressure, at a flow rate of 6 ℓ/h H_2 flow and 20 ml/h flow of the feed which consisted of 0.25 wt% carbazole in xylene. The reaction products and reactant in the reaction were analyzed by gas chromatography. The HDN activity of the catalyst represents the rate of the formation of bicyclohexyl per unit of surface area.

The elemental analysis data and the N_2 BET surface area of the catalysts are shown in table 1. The surface area of the HTN 11.7% Mo/Al_2O_3 catalyst for the HTN treatment was 70 m^2/g lower than that for the MTN catalyst. For the 97.1% Mo/Al_2O_3 catalyst, the surface area was about 39 m^2/g by both the HTN and MTN conditions. The nitrogen contents were increased with increasing both NH_3 pretreatment temperature and the alumina content in the catalyst. When the catalysts were evacuated at 10^{-4} Torr at 473 K, the nitrogen contents of the catalysts were 2.5 and 1.3 times the stoichiometric value for the 11.7 and 97.1% Mo/Al_2O_3 catalysts by the HTN pretreatment, respectively. However, the nitrogen contents of the MTN catalysts were decreased with increasing degassing temperature and approached the value 0.6 and 6.2 wt% nitrogen when the evacuation temperature was increased to 773 K. A high temperature treatment at more than 773 K can remove ammonia adsorbed on the catalyst. These results indicate that the surface of the prepared 11.7% Mo/Al_2O_3 catalyst retains a significant amount of adsorbed NH_3 left over from the reduction of the MoO_3/Al_2O_3 in an NH_3 flow.

The HDN activity of the 11.7% Mo/Al_2O_3 catalysts with the HTN, MTN, sulfiding and reducing pretreatment for the HDN of carbazole is shown in fig. 1.

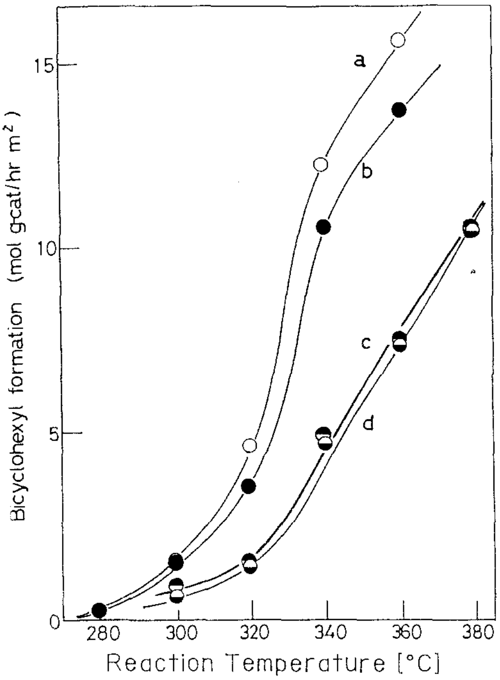

Fig. 1. Hydrodenitrogenation of carbazole on the (a) HTN, (b) MTN, (c) 673 K sulfided, (d) 673 K reduced catalysts.

The MTN catalysts are 3.1- and 2.8-fold more active than the sulfided and reduced catalysts at 573 K, respectively. For the nitrided catalysts, the HTN catalyst is 1.3 times more active than the MTN catalyst at 593 K. The results showed that nitriding of the MoO_3/Al_2O_3 catalyst promoted the HDN activity for carbazole HDN. Sajbowski and Oyama [7] reported that M_2N catalyst showed remarkable activity in HDN, performing better than a Mo_2S/Al_2O_3 catalyst by a factor of 3.5. Thus, nitriding was a preferable method of catalyst preparation for the HDN reaction, when compared with the sulfiding and reducing method.

The product distribution for carbazole HDN on the MTN 11.7% Mo/Al_2O_3 catalyst at 10.1 MPa total pressure is shown in fig. 2. The major product was bicyclohexyl in the reaction products. Hexylcyclohexene was also formed in a small amount. The hydrogenated carbazole compounds, such as hexahydrocarbazole, decahydrocarbazole and perhydrocarbazole, were barely observed in the reaction products. The results showed that nitriding of the catalyst enhanced the formation of hydrocarbons without increasing the amounts of hydrogenated products. Moreover, hexylcyclohexene was formed in a small amount probably due to the C–N hydrogenolysis of decahydrocarbazole. The activation energies for carbazole HDN stay approximately unchanged after MTN, HTN and 400°C reducing ($E_a < 5$ kJ/mol). They are about 150 kJ/mol for the C–N bond

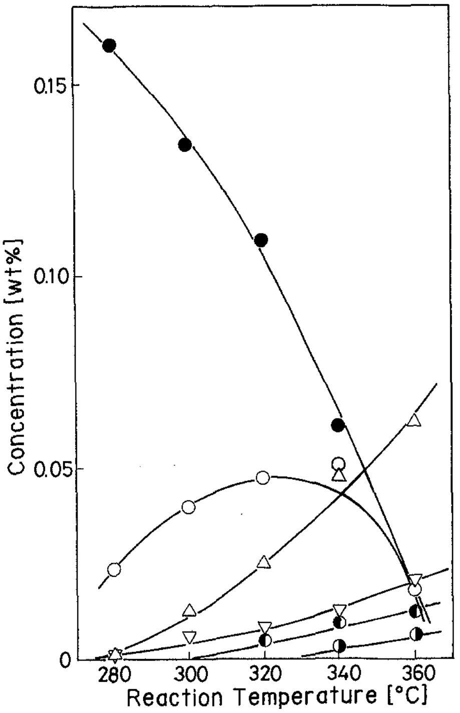

Fig. 2. Product distribution for the hydrodenitrogenation of carbazole on the MTN catalyst at 10.1 MPa total pressure. (●) Carbazole, (○) tetrahydrocarbazole, (△) bicyclohexyl, (◑) cyclohexylbenzene, (◐) ethylbicyclo[4.4.0]decane, (▽) cyclohexylhexene.

breakage. Hexylcyclohexene was produced in small amount from the C–N bond scission of perhydrocarbazole through the successive hydrogenation of carbazole. This result indicated the C–N hydrogenolysis of partially hydrogenated carbazole prior to complete hydrogenation. Since the HDN process removes the nitrogen atom from polynuclear heteroaromatic nitrogen compounds after the heteroaromatic and aromatic rings are completely hydrogenated [8,9], the formation of hexylcyclohexene suggests the possibility of the development of the active catalyst for HDN with less hydrogen consumption.

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