Active Sites of a Reduced Molybdena-Alumina Catalyst. A Transient Study of Hydrodenitrogenation of Carbazole and Acridine

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Synopsis. A response study of the hydrodenitrogenation of acridine and carbazole on a reduced MoO_3/Al_2O_3 catalyst was performed at 300 °C and 10.1 MPa total pressure. Acridine was strongly adsorbed on the acidic sites of the catalyst surface for hydrogenation, while carbazole was weakly adsorbed not only on the same sites as acridine, but also on the terminal oxygen anion sites in the presence of strong bases.

Molybdena–alumina catalysts have been extensively investigated in an effort to understand the nature of their catalytically active sites for hydrogenation and hydrogenolysis. The chemisorption of NO,[1] oxygen,[2] and pyridine[3,4] has been applied to reduced and sulfided molybdena–alumina catalysts at reduced pressure. The chemisorptions were correlated with the hydrogenation activity and coordinatively unsaturated sites (Lewis acid sites) of the pretreated molybdena surface.

However, hydrodenitrogenation (HDN), hydrogenolysis of a carbon–nitrogen bond of polynuclear aromatic nitrogen compounds, proceeds at high pressure and high reaction temperature.[5–7] The nature of the active sites for HDN should be determined under these reaction conditions. Our recent poisoning studies at 10.1 MPa of the total pressure revealed that both hydrogenation and denitrogenation sites exist on the surface of the molybdenum catalysts.[6,7] The active sites of a sulfided $NiMo/Al_2O_3$ catalyst for hydrogenation were correlatable with the gas-phase basicity of the nitrogen compound,[8] which was proportional to their proton affinity; therefore, hydrogenation takes place on the Brönsted acid sites of molybdenum atoms of the catalyst. Furthermore, the active sites of the catalysts for denitrogenation were related with the gas-phase acidity of the sulfur and oxygen compound;[9] therefore, denitrogenation occurs on the terminal oxygen anion sites which exist on the reduced catalyst as well as desulfurization.[7,9]

A polynuclear nitrogen compound contains two types of nitrogen compounds: a basic (acridine) and nonbasic (carbazole) polynuclear aromatic nitrogen compound. The non-basic nitrogen compound becomes the basic nitrogen compound during hydrogenation. This observation suggested that the adsorption sites of a reduced molybdenum catalyst were different for the two typical nitrogen compounds.

In this work, a transient response study of the HDN of these two typical nitrogen compounds has been applied in order to facilitate an understanding of the nature of the active sites of a reduced Mo/Al_2O_3 catalyst for the HDN of carbazole and acridine at 300 °C and 10.1 MPa.

Experimental

The reagents, the catalyst, and the reactor used in this study are shown elsewhere.[6] Two grams of the 12.5% MoO_3/Al_2O_3 catalyst were placed in the reactor during a typical series of experiments. The catalyst was oxidized in air at 450 °C for more than 24 h and then reduced in hydrogen for 4 h at 400 °C before a run. After reduction, the reactor was cooled to the desired temperature by a flowing hydrogen stream. A solution containing a mixture of 0.013 mol L^{-1} of carbazole and 0.013 mol L^{-1} of acridine in xylene was injected at 20 ml h^{-1}. A steady state was usually reached within 3 h. The reaction products, having higher boiling points than xylene, were analyzed by F.I.D. gas chromatography (Dexsil 400, 2.5%). The lower boiling point products, such as NH_3 and any light cracking products, were not determined because the amounts formed during reactions were negligible.

Results and Discussion

In previous studies,[6,7] acridine was easily hydrogenated to produce perhydroacridine and octahydroacridine on the Brönsted acid sites. The major denitrogenated compound was dicyclohexylmethane by the C–N scission of perhydroacridine on the terminal oxygen anion sites. Carbazole was difficult to hydrogenate to tetrahydrocarbazole. Other hydrogenated carbazole compounds were barely formed at any of the other reaction temperatures. The major denitrogenated product was 1,1′-bicyclohexyl together with 2-ethylbicyclo[4.4.0]decane and hexylcyclohexane.

The transient experiment provided two different aspects for the HDN of acridine and carbazole with different basicities. The HDN of acridine on the reduced Mo/Al_2O_3 catalyst at 300 °C and 10.1 MPa in the presence and absence of carbazole is shown in Fig. 1. A transient response occurred during the first 2.5 h; the HDN reaction then reached a steady state. The addition of carbazole increased the amount of octahydroacridine formed and decreased both dicyclohexylmethane and benzylcyclohexane amounts. This result showed that the addition of carbazole hindered the hydrogenation of octahydroacridine to perhydroacridine. This result suggested that carbazole was adsorbed and hydrogenated on the same active site as both acridine and octahydroacridine.

The concentration of perhydroacridine initially jumped for the first 2.5 h upon the addition of carbazole and, then, gradually decreased again to its initial concentration before the addition of carbazole. This implied that the addition of carbazole expelled

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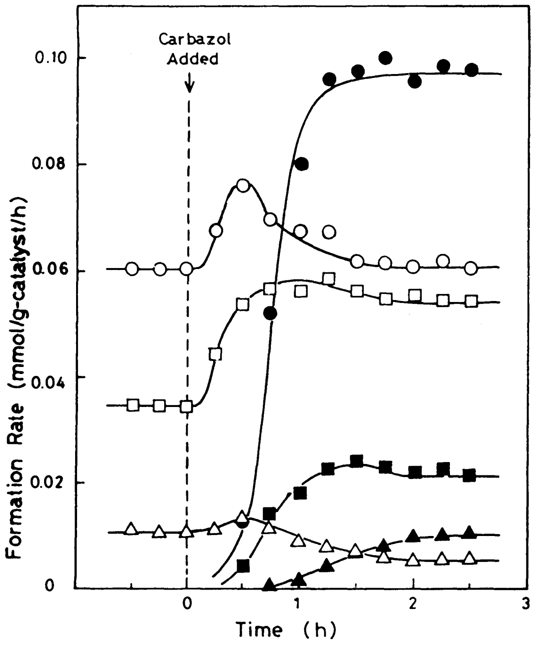

Fig. 1. The addition of carbazole to the HDN of acridine on the reduced Mo/Al_2O_3 catalyst at 300 °C and 10.1 MPa total pressure. Key: □, 1,2,3,4,4a,9,9a,10-octahydroacridine; ○, perhydroacridine; △, dicyclohexylmethane; ●, carbazole; ■, 1,2,3,4-tetrahydrocarbazole; ▲, 1,1′-bicyclohexyl.

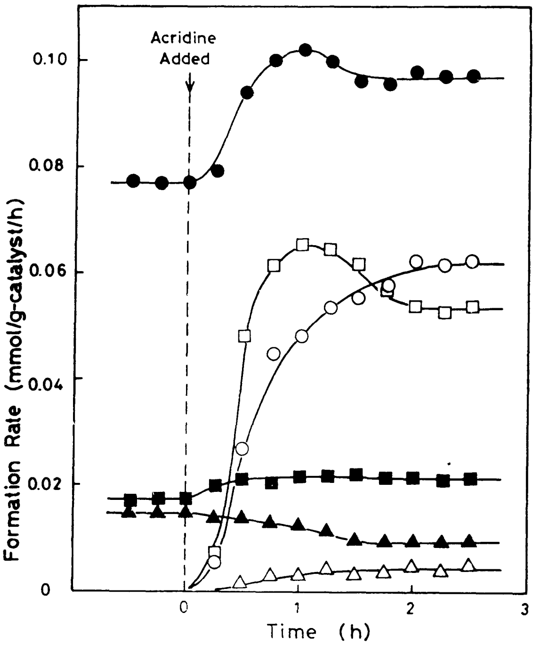

Fig. 2. The addition of acridine to the HDN of carbazole on the reduced Mo/Al_2O_3 catalyst at 300 °C and 10.1 MPa total pressure. The symbols are the same as those in Fig. 1.

the perhydroacridine adsorbed from the active site of the catalyst. The amount of perhydroacridine adsorbed was calculated as being 11.8 µmol g^{-1} on the basis of the area of the increased perhydroacridine. This observation indicated that carbazole was also adsorbed on the same active site where perhydroacridine was adsorbed. Since perhydroacridine was adsorbed on the terminal oxygen anion sites, carbazole was competitively adsorbed on the same anion sites as perhydroacridine as well as on the Brönsted acid sites.

On the other hand, for the addition of acridine to carbazole HDN, there was no similar observation to that when perhydroacridine was desorbed by the addition of carbazole. Figure 2 shows that the addition of acridine to carbazole HDN decreased 1,1′-bicyclohexyl and then 5.7 µmol g^{-1} of both carbazole and tetrahydrocarbazole were released to the solution from the catalyst surface in 2.5 h. The addition of acridine appears to have inhibited the hydrogenations of tetrahydrocarbazole to perhydrocarbazole. In addition, 5.8 mol g^{-1} of both acridine and the hydrogenated compounds were adsorbed on the catalyst's surface. The adsorbed amount of acridine hydrogenated compounds was almost equal to the released amount of the carbazole hydrogenated compounds. Therefore, acridine was adsorbed and hydrogenated on the Brönsted sites of the catalyst, but not adsorbed on the anion sites. Acridine is also competitively hydrogenated with the resulting hydrogenated acridine compounds on the same sites. On the other hand, carbazole is actually a very weak base, but carbazole turns to a basic compound during the reaction; therfore carbazole is weakly adsorbed on the same sites as acridine, and even adsorbed on the terminal oxygen anion sites in the presence of a stong base.

Estimating the amount of denitrogenation sites on which perhydroacridine and carbazole were adsorbed found that the 12.5 wt% MoO_3 catalyst (N_2 BET surface area: 188 m^2 g^{-1}) contains 5.16×10^{18} Mo molecules/m^2. The amount of perhydroacridine (11.8 µmol/g-cat) released from denitrogenation sites corresponds to 3.7×10^{16} molecules/m^2. The number is two orders of magnitude smaller than the total molybdenum available on the catalyst. It could be estimated that 0.72% of the molybdenum sites have become active sites.

Suarez et al.[4] studied the adsorption of pyridine on reduced Mo/Al_2O_3 (7.48 wt% Mo, BET 211 m^2 g^{-1}) at 400 °C. The amount of adsorbed pyridine (Lewis acid site) was 0.18×10^{18} molecules/m^2 when the catalyst was exposed for 6 h. When the value was converted to that on the 12.5 wt% Mo/Al_2O_3, it was 0.3×10^{18} Mo molecules/m^2, which was three times that obtained in this study. They reported that adsorbed pyridine (Brönsted acid site) barely exists on the surface of the reduced catalyst. Furthermore, Segawa and Hall[2] found that the Brönsted acidity could be eliminated by a reduction of the catalyst; Lewis acid sites were present on both the molybdenum and alumina portions of the catalyst's surface. The reduced catalyst held many Lewis acid sites, but rarely Brönsted acid sites under reduced pressure. Thus, there was a great gap between the results of our study at high hydrogen pressure and that of the adsorption experiment under reduced pressure. The acidity and number of active sites on the surface of the Mo/Al_2O_3 catalyst during the reaction would be expected to be different from those measured under vacuum. It is suggested that molybdenum Lewis acid sites turned to Brönsted sites at high hydrogen pressure.

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