

LIQUID PHASE HYDROGENATION OF NAPHTHALENE IN THE PRESENCE OF CO OVER SUPPORTED Ni CATALYST

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Abstract

The liquid phase hydrogenation of naphthalene was tried in the presence of CO over a commercial Ni/SiO₂-Al₂O₃ catalyst. Naphthalene was hydrogenated even in the presence of CO at elevated temperatures, accompanying the hydrogenation of CO. Two activation energy values were obtained for the naphthalene hydrogenation depending on the reaction temperature. FT-IR measurement of the adsorbed CO was also tried. Hydrogenation of the adsorbed CO created sites active for the naphthalene hydrogenation.

Key words: Naphthalene hydrogenation, Ni catalyst, CO deactivation, Adsorbed CO

INTRODUCTION

The organic chemical hydride method is expected as a means for hydrogen storage and transportation using the hydrogenation and dehydrogenation cycle of aromatic hydrocarbons such as naphthalene [1-6]. This method is advantageous because of its high storage density as well as safety in handling. Because the hydrogenation of aromatics is an exothermic reaction, it easily proceeds under mild conditions [5]. It will be very advantageous if low-grade hydrogen, containing CO, is available for the hydrogenation step, because the steel industry produces a huge amount of such hydrogen, containing ~5% CO, as a coke oven gas [1]. To do so, it is important to find a catalyst which shows a high activity of aromatic hydrogenation in the presence of CO. The hydrogenation of aromatic hydrocarbons in the presence of sulfur compounds has been studied in detail in order to upgrade diesel fuels [7-10], but hydrogenation using CO-containing H₂ has not been studied in detail.

In our previous paper, we reported that Pd has the highest activity for the hydrogenation of naphthalene in 2%CO/H₂ mixture among the various studied alumina supported metal catalysts (Co, Ni, Ru, Rh, Pd, Pt) [11]. Pd was outstanding because only naphthalene reacted with hydrogen, without the formation of the CO hydrogenation product, methane.

However, Pd is an expensive noble metal, therefore we focused on Ni, which was also found to be highly active in the presence of CO, accompanying the CO hydrogenation. In this paper, we studied the

behavior of the Ni/SiO₂-Al₂O₃ catalyst during the hydrogenation of naphthalene in 2%CO/H₂ and compared it to Pd/Al₂O₃.

EXPERIMENTAL

50wt%Ni/SiO₂-Al₂O₃(C28-1) was supplied by Süd-Chemie Catalyst Japan, Inc. 2wt%Pd/Al₂O₃ was prepared in the same manner as described in a previous paper [11].

The hydrogenation of naphthalene was carried out using a 100 ml autoclave. Catalysts were pre-reduced in flowing hydrogen at 773K (Ni) or 673 K (Pd) for 1 h. 0.1 g of naphthalene was dissolved in 40 ml of *n*-tridecane and used as the reactant over 50-100 mg of catalyst. After purging the autoclave with hydrogen, the reactor was heated to the reaction temperature (303-473K), and then pure hydrogen or 2%CO/H₂ of 10 kgf/m² was introduced into the reactor, and the reaction started. The reaction was carried out for 1 h with 1000 rpm of stirring. The reaction rate was estimated by the initial rate method. In such a case, only tetralin was found as the product of the naphthalene hydrogenation, and methane was found as the product of the CO hydrogenation over the Ni catalyst.

The adsorption amount of CO was measured by the Ohkura-Riken BP-1 system, using the dynamic pulse method in flowing He. FT-IR of the adsorbed CO was observed through a self-supporting thin disk of catalyst with a 10 mm diameter at room temperature using a Jasco FT/IR-350.

RESULTS AND DISCUSSION

Hydrogenation of naphthalene over Pd/Al₂O₃

The hydrogenation of naphthalene was examined over 2wt%Pd/Al₂O₃ using either pure H₂ or 2%CO/H₂ as the reactant. The reaction temperature range was 303-343K under pure H₂, but it was elevated to 393-433K under 2%CO/H₂ due to catalyst deactivation by CO. Under 2%CO/H₂, no hydrogenation of CO was observed even at 473K and the naphthalene conversion was 98.8% as all the hydrogen reacted with the naphthalene. The activation energy was obtained from the temperature dependence of the reaction rate. Under pure hydrogen, the activation energy was found to be 56 kJ/mol. On the other hand, it was 95 kJ/mol in 2%CO/H₂. The presence of CO significantly increased the apparent activation energy. As reported in a previous paper [11], the desorption of CO from the Pd surface takes place in the temperature range of hydrogenation. Therefore, the area of the free Pd surface increased as the reaction temperature increased. Such an effect modified the apparent activation higher than the real value.

Hydrogenation of naphthalene over Ni/SiO₂-Al₂O₃

The hydrogenation of naphthalene was examined over 50%Ni/SiO₂-Al₂O₃ at 303-318 K under pure H₂, and at 383-428 K under 2%CO/H₂, as shown in Table 1. Under 2%CO/H₂, the hydrogenation of CO to form methane proceeded as well as the naphthalene hydrogenation in the temperature

range higher than 403K. However, the rate of CO hydrogenation was much slower than that of the naphthalene hydrogenation, and most of the hydrogen was consumed for storage as tetralin.

The apparent activation energy of the naphthalene hydrogenation was estimated from the Arrhenius plot. Under pure hydrogen, the activation energy was 45 kJ/mol. Under 2%CO/H₂, the Arrhenius plot of the naphthalene hydrogenation was composed of two lines, as shown in Fig.1. In the lower temperature range (383-403K), the activation energy was 34 kJ/mol, and in the higher temperature range (413-428K), it was 146 kJ/mol. Because the CO hydrogenation took place at temperatures higher than 413 K, the competitive reaction affected the activation energy. As the temperature increased, the CO hydrogenation was accelerated and the coverage of CO on the Ni surface was reduced, and the number of active sites increased. Such an effect seemed to increase the apparent activation energy.

FT-IR spectra of adsorbed CO

In order to clarify the behavior of the adsorbed CO, the FT-IR measurement was examined over Ni and Pd catalysts. After adsorbing 20 Torr of CO at room temperature, the catalyst disk was evacuated at elevated temperature and the FT-IR spectra were observed. The hydrogenation of adsorbed CO was also observed by FT-IR, introducing 100 Torr of H₂ at elevated temperatures.

The FT-IR spectra of CO adsorbed on Ni/SiO₂-Al₂O₃ are shown in Fig.2.

Figure 2(a) shows the IR spectra of CO adsorbed on Ni and evacuated at different temperatures. The peak at 2100-2000 cm^{-1} is attributed to the linear CO. The absorption bands those appeared at 2000-1800 cm^{-1} are attributed to the bridge CO and multibonded CO [12-14]. The CO strongly adsorbed on Ni and most of CO remained on the Ni surface even after evacuation at 473K. The peak area of CO decreased at 573K. Figure 2(b) shows the IR spectra of CO after H_2 treatment at different temperatures. It is clear that the peak area significantly decreased at 473K due to hydrogenation of adsorbed CO. In this way, the presence of H_2 remarkably promoted the disappearance of CO from the Ni surface. Such a behavior is shown in Table 2 as the dependence of the peak area on a temperature.

The IR spectra of the adsorbed CO on the Pd catalyst also suggested both linear and bridge types of adsorptions. As shown in Table 2, however, the peak area decreased even at 373K, indicating a weaker interaction than on Ni surface. The peak area decreased as the temperature was elevated in a similar manner both under evacuation and in an H_2 atmosphere.

These results suggest that the Pd surface is open and used for the naphthalene hydrogenation by the thermal desorption of CO. On the other side, a CO-free Ni surface is created by hydrogenation of the adsorbed CO.

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Figure Captions

Fig.1. Arrhenius plot of naphthalene hydrogenation over Ni/SiO₂-Al₂O₃ catalyst under 2%CO/H₂.

Activation energy ; Ea(1)=146 kJ/mol, Ea(2)=34 kJ/mol.

Fig.2. Infrared spectra of adsorbed CO on Ni/SiO₂-Al₂O₃ catalyst.

(a) after evacuation at different temperatures, (b) after H₂ (100 Torr) treatment at different temperatures.

Temperature, 1:300K, 2:373K, 3:423K, 4:473K, 5:573K, 6:673K.



