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The effect of support structure on CO_2 hydrogenation over a rhodium catalyst supported on niobium oxide

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The hydrogenation of CO_2 was investigated over a rhodium catalyst supported on niobium oxide at atmospheric pressure. Niobium oxide was prepared by the hydrolysis of niobium chloride and its crystallitic structure was controlled by calcination temperature. It was found that the activity was lower but the selectivity of C_{2+} hydrocarbons was higher for the γ and γ' forms than for the β and α forms of the niobium oxide.

Keywords: Hydrogenation; carbon dioxide; rhodium; niobium oxide

1. Introduction

Rhodium is a very interesting metal for CO_2 hydrogenation. It was found that the activity of hydrogenation over rhodium was much higher for CO_2 than for CO [1]. This tendency was not observed using other noble metals [2]. The activity and selectivity of rhodium catalysts are very sensitive to the nature of the support material and metal promoter [3]. The results of Nozaki et al. [4] showed that the activities of Rh/Al_2O_3 and Ni/Al_2O_3 were almost the same and the selectivities of methane were 100% for these catalysts in CO_2 hydrogenation. However, in the case of a Nb_2O_5 support, the conversion using Rh catalyst was lower than that using Ni catalyst, but Rh catalyst gave not only methane but also a significant amount of C_{2+} hydrocarbons even at atmospheric pressure [4].

This support effect may be due to the so-called SMSI (strong metal–support interaction) effect [5]. The SMSI effects on catalytic activity and selectivity were observed for Rh/TiO_2 and Rh/Nb_2O_5 in CO_2 hydrogenation [6].

The support effect can be also explained by the spillover of a H–CO complex on the support [7,8]. Mao and Falconer [7] have reported that the spillover was observed even on a Pt/TiO_2 catalyst in CO hydrogenation. They insisted that the CO methanation occurred on metal sites and on the surface of a support and that this induced the difference of the specific rates on different supports.

In the present study, the effects of the crystallitic structure of niobium oxide on the activity and selectivity in CO_2 hydrogenation was studied using Rh/Nb_2O_5 catalysts. The structure of niobium oxide was controlled by calcination temperature.

2. Experimental

2.1. CATALYST

Niobium oxide was prepared by the hydrolysis of niobium chloride. The precipitate of niobium hydroxide was prepared by dropping an ethanol solution of niobium chloride into an aqueous solution of potassium hydroxide [9]. The solution was stirred for 4 h during the hydrolysis reaction. After aging for 1 h, the precipitate was hot filtered, washed with boiling deionized water and dried at 383 K overnight. After the obtained precipitate was calcined in an electric furnace at prescribed temperature, it was used as a support. The structure of niobium oxide was determined by X-ray diffraction analysis. The surface area of the niobium oxide was measured by the nitrogen adsorption method in which the BET equation was used in the calculations. Pore size distribution was also obtained by measurement of the nitrogen adsorption and desorption isotherms using the volumetric method. The number of rhodium surface atoms was determined by hydrogen chemisorption at 300 K using a static chemisorption system.

The catalyst was prepared by impregnating Nb_2O_5, which was obtained by the processes described above, with an aqueous solution of rhodium nitrate. After drying in an oven overnight at 383 K, the powder was pelleted and sized from 48 to 280 mesh for use. The catalyst containing 0.5 wt% Rh was used in the reaction experiment.

2.2. EXPERIMENTAL EQUIPMENT

The hydrogenation of CO_2 was carried out in a fixed bed tubular reactor under atmospheric pressure. A 6.0 mm i.d. stainless tube enclosed by an aluminum block was used as reactor. The block was heated on its surface by a flexible electrical heater.

The catalyst was oxidized in an air flow at 723 K for 2 h and was reduced in a H_2 flow at 823 K for 3 h in the reactor. After these treatments, the temperature was adjusted to the reaction temperature, 593 K. The mixture of CO_2 and H_2 gas was introduced into the reactor at a flow ratio of 1 : 2, and the reaction was carried out. The product gases were analyzed by gas chromatography.

3. Results and discussion

The structure of the niobium oxide prepared by hydrolysis was affected by calcination temperature. Fig. 1 shows the X-ray diffraction pattern obtained for niobium oxides calcined at various temperatures. The crystallization temperature of niobium oxide was about 855 K [9]. In the present study, when the calcination temperature was 723 K, no peak was observed and the niobium oxide was in an amorphous state. The peaks corresponding to the γ form appeared at 873 K. The structure changed from γ to α form as the calcination temperature increased.

Fig. 2 shows the effect of calcination temperature on the average particle size and the surface area of the niobium oxide. The particle size was calculated based on scanning electron micrographs. The value of the surface area was highest for the amorphous state and it decreased with increasing calcination temperature. This was due to an increase in particle size. The surface area was almost inversely proportional to the size of the primary particles. This is because the surface area was mainly represented by the outer surface area of the particles. As shown in fig. 3, the niobium oxide was found to have a narrow pore size distribution of around 2 nm. The pore volume was also much smaller than that of γ-alumina. Thus, the area in the pores of the niobium oxide was negligible and the outer surface area of the particles was important. It should be noted that by "particle" we do not mean the catalyst particles but the niobium oxide particles produced primarily by the hydrolysis and calcination.

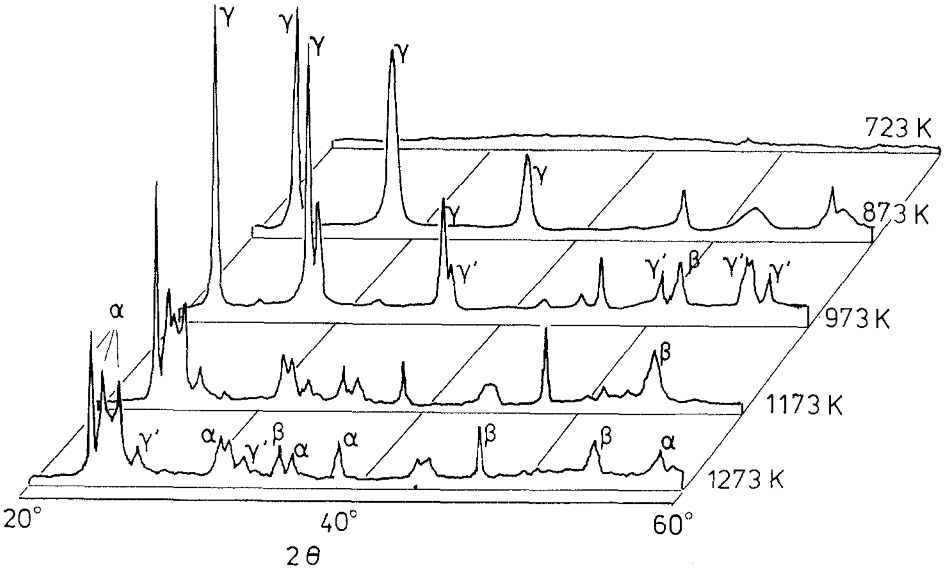

Fig. 1. X-ray diffraction pattern of niobium oxide.

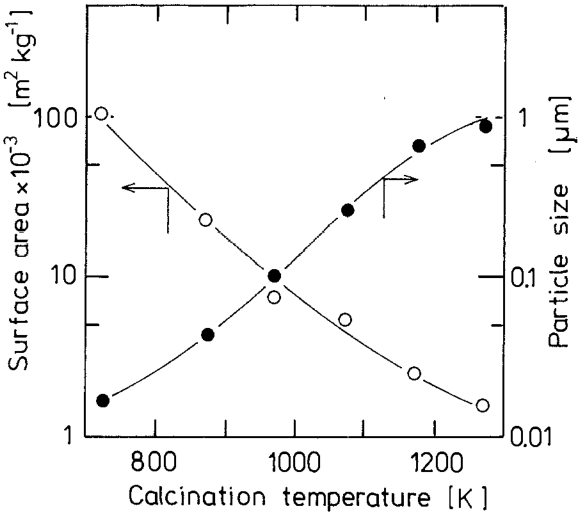

Fig. 2. Effect of calcination temperature on particle size and surface area of niobium oxide.

Since the reduction temperature, 823 K, was higher than the calcination temperature, 723 K, of the niobium oxide of the amorphous state, the amorphous state support was not used for the hydrogenation. Table 1 gives the hydrogen uptake and the dispersion of rhodium metal on the Nb_2O_5 support. The dispersion of rhodium was calculated from the hydrogen uptake and rhodium loading. The dispersion decreased with increasing calcination temperature. This is considered to be due to the decrease in the surface area of niobium oxide.

The turnover frequency was obtained from the results of differential reactor tests when the conversion was below 1%. The results are also given in table 1. It is observed that the turnover frequency increased with increasing calcination

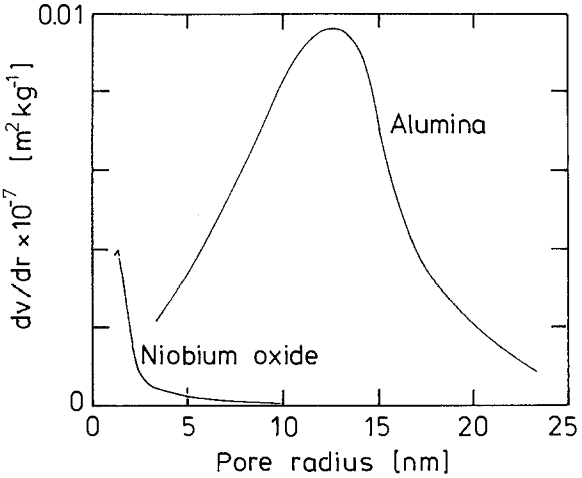

Fig. 3. Pore size distribution of the prepared niobium oxide calcined at 873 K.

Table 1
Some characteristic data for Rh/Nb_2O_5 catalyst

Calcination temperature (K)	Hydrogen uptake (mol kg^{-1})	Dispersion (%)	Turnover frequency (s^{-1})
873	1.58×10^{-2}	74	0.29
973	7.13×10^{-3}	29	0.65
1073	4.36×10^{-3}	18	0.83
1173	4.98×10^{-3}	21	0.80
1273	2.95×10^{-3}	12	0.78

temperature. In this case, the effect of the metal particle size and the crystallitic structure of the support were considered to be the possible reasons. As shown in fig. 4, the rhodium dispersion decreased with the rhodium loading. The activity slightly increased with the loading, but the effect of the loading on the turnover frequency was small. Therefore, it is considered that the catalytic activity was influenced by the structural effect and that the effect of the metal particle size was small. As shown in table 1, the catalytic activity per rhodium surface atom was smaller for the γ form than for the α form oxide.

The selectivity of C_{2+} hydrocarbons initially increased with increased conversion. However, it reached a maximum value at about 20% conversion. We checked the hydrogenolysis of ethane on the rhodium catalyst as used in CO_2 hydrogenation. The results showed that the decomposition of ethane was insignificant. Carbon monoxide was not also produced above 20% conversion. It was reported that CO in the gas phase was an intermediate for the formation of C_{2+} hydrocarbons [4]. Therefore, the decrease in the C_{2+} yield was considered to be caused by the decrease in CO formation.

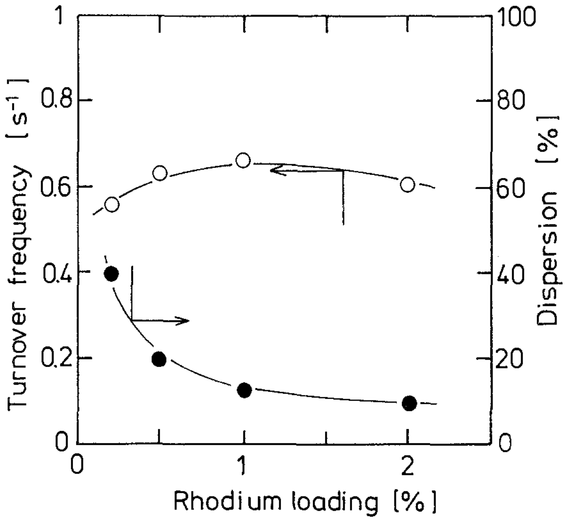

Fig. 4. Effect of rhodium loading on the turnover frequency for the support calcined at 873 K.

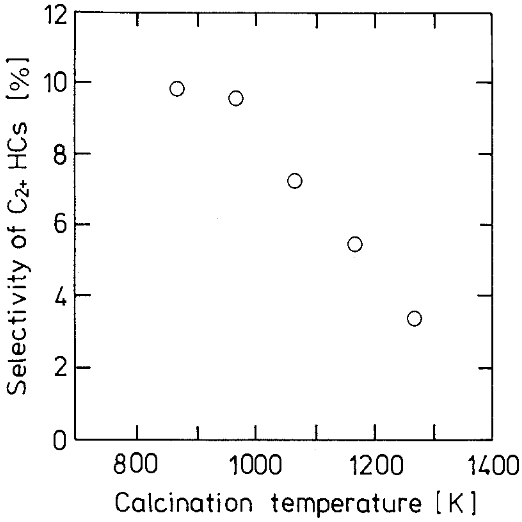

Fig. 5. Change in the selectivity of C_{2+} hydrocarbons when the calcination temperature was varied.

The selectivity was compared at the same conversion level. Fig. 5 shows the selectivity of C_{2+} hydrocarbons when the conversion was about 13%. The selectivity decreased with the increasing calcination temperature and was higher for the γ form support than for the α form.

From these results, it appears that the activity and the selectivity depend on the crystallitic structure of the Nb_2O_5 support. The activity of the overall reaction was lower but the selectivity of C_{2+} hydrocarbons was higher for the γ and γ' forms than for the β and α forms of niobium oxide. However, it is uncertain how the change in the structure of Nb_2O_5 affected the activity and selectivity. One possible explanation is that the γ form Nb_2O_5 reaches the SMSI state more readily than the α form Nb_2O_5. The other explanation is that the reaction rate of a C–HO complex [7,8] on the support surface is influenced by the structure of Nb_2O_5. In CO_2 hydrogenation on Rh/Nb_2O_5, Nozaki et al. [4] did not observe the effect of reduction temperature on the selectivity, but Trovarelli et al. [6] reported the effect of the reduction temperature. We also found that the selectivity of C_{2+} hydrocarbons increased with reduction temperature. Thus, the mechanism cannot be resolved because of the disagreement of the results of some investigators and the lack of experimental data such as TPR data.

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