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EFFECT OF STRONG METAL-SUPPORT INTERACTION (SMSI) ON ETHYLENE HYDROFORMYLATION OVER NIOBIA-SUPPORTED PALLADIUM CATALYSTS

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The high-temperature reduction at 773 K (HTR) of Pd/Nb_2O_5 catalyst caused suppression in the capacity of H_2 and CO chemisorption (SMSI behavior). However, the rate of ethylene hydroformylation increased drastically by HTR. The infrared study of chemisorbed CO showed that the HTR caused the severe suppression in the abundance of bridged carbonyl and the appearance of linearly bonded carbonyl. These results suggest that the site for the linear-type CO adjacent to NbO_x appears to increase the rate of CO insertion.

1. Introduction

The effects of temperature reduction on catalytic activities have been studied extensively since Tauster and co-workers reported the strong metal-support interaction (SMSI) phenomenon [1]. It has been shown that the high-temperature reduction at 773 K (HTR) caused a strong activity suppression for hydrocarbon hydrogenolysis reactions but only a modest suppression for hydrocarbon dehydrogenation reactions [2]. It is thus recognized that SMSI has a great influence on structure sensitive reactions but only a minor effect on structure insensitive reactions.

In contrast to the case of hydrogenolysis reactions, the HTR caused only a small decrease in the activity of NH_3 decomposition on a Rh/Nb_2O_5 catalyst, which is, like hydrogenolysis, a structure sensitive reaction [3]. However, no catalytic reaction which exhibits a dramatic rate enhancement by SMSI has been reported so far.

In a current model of SMSI, a reduced oxide species (TiO_x, NbO_x etc.) formed by HTR migrates onto metal particles and then blocks surface metal atoms, leading to suppression in the capacity for H_2 and CO chemisorption and also affecting preferentially those reactions which require a large ensemble of the

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surface active sites (decoration model) [2,4]. Ichikawa et al. [5] have shown that the activity of ethylene hydroformylation on Rh catalysts is increased by the oxide promoter (e.g., Zn). The presence of the oxide promoter on metal surfaces suppresses CO dissociation and presumably increases the rate of CO insertion [5].

With the similarity between the additives effect on metal and SMSI (decoration model) in mind, we have studied the effects of SMSI on ethylene hydroformylation. In this letter, we will report the rate enhancement on Pd/Nb_2O_5 catalyst after HTR, and discuss the effect in terms of the change in the infrared spectra of adsorbed CO as a function of catalyst reduction temperature.

2. Experimental

The 5.0 wt% Pd/Nb_2O_5 catalyst was prepared by impregnating the Nb_2O_5 support (CBMM International LTDA), which had been precalcined in air at 973 K, to incipient wetness with an aqueous solution of $PdCl_2$. The 5.0 wt% Pd/SiO_2 catalyst was prepared by impregnating the SiO_2 support (JRC-SIO-3), which had been precalcined in air at 773 K, to incipient wetness with an aqueous solution of $PdCl_2$. The impregnated material was dried at 393 K overnight followed by reduction in H_2 for 1 h at 773 K.

The ethylene hydroformylation reaction was carried out in a closed circulating system ($C_2H_4 : CO : H_2 : He = 50 : 50 : 50 : 550$ Torr). Analysis was performed by an on-line gas chromatograph mass spectrometer. The catalysts were treated in O_2 at 673 K for 1 h followed by H_2 reduction for 1 h at 473 K (LTR) or 773 K (HTR) before each activity measurement.

Hydrogen and CO chemisorption measurements were carried out at room temperature by a conventional volumetric adsorption apparatus [6]. The infrared spectra of chemisorbed CO were obtained by a diffuse reflectance FT-IR apparatus, which is capable of in-situ pretreatments of the catalysts.

3. Results and discussion

3.1. VOLUMETRIC ADSORPTION OF H_2 AND CO

Table 1 shows the H_2 and CO chemisorption data and the catalytic activities of the Pd/Nb_2O_5 and Pd/SiO_2 catalysts. Because the reversibly adsorbed CO are mainly associated with supports [4,6], the CO chemisorption values (CO/Pd) were obtained by subtracting the reversibly adsorbed CO, measured by re-adsorption after evacuation in vacuo at room temperature for 10 min [4], from the total adsorption. For the Pd/SiO_2 catalyst, the Pd dispersion estimated from X-ray diffraction (XRD) measurement was about 0.2. This value is in good agreement with the H_2 chemisorption capacity after LTR. For the Pd/Nb_2O_5 catalyst, the

Table 1
Effect of the reduction temperature on the H_2 chemisorption and the rate of ethylene hydroformylation [a]

Catalyst	Reduction temp (K)	Chemisorption		Rate [b] ($\times 10^{-3}$ molecule/(surface Pd sec))		
		H/Pd	CO/Pd	C_2H_6	Oxo product	Total
$5\%Pd/SiO_2$	473	0.22	0.12	4.07	0.22	4.29
	773	0.22	0.12	3.82	0.22	4.04
$5\%Pd/Nb_2O_5$	473	0.056	0.0053	5.78	0.00 [c]	5.78
	773	0.015	0.0021	3.74	4.77	8.51

[a] Reaction temp. = 337 K.

[b] based on the H/Pd value after LTR.

[c] The rate was less than 1×10^{-6} molecule/(surface Pd sec) based on the detection limit of our analyses system.

Pd particle size was about 160 Å by XRD, which is equivalent to the Pd dispersion of 0.06. This value is also in good agreement with the H_2 chemisorption capacity after LTR. There was almost no change in the H_2 and CO chemisorption capacity with increasing the reduction temperature for the Pd/SiO_2 catalyst.

On the other hand, the amount of H_2 or CO chemisorption decreased drastically with increasing the reduction temperature for the Pd/Nb_2O_5 catalyst. It should be noted that the H_2 and CO chemisorption capacity was recovered if the catalysts were treated in O_2 at 673 K followed by low-temperature reduction at 473 K (LTR). The H_2 chemisorption behavior of the Pd/Nb_2O_5 catalyst was consistent with our previous work in the similar Pd/Nb_2O_5 catalyst system [7]. One interesting point here is that the CO chemisorption capacity was much less than the H_2 chemisorption for the Pd/Nb_2O_5 catalyst. The origin of this anomalous suppression of CO chemisorption is not clear in the present stage, but may be related to the similar behavior of the $RhNbO_4/SiO_2$ catalyst system which exhibited an extreme SMSI behavior after HTR [8].

3.2. ETHYLENE HYDROFORMYLATION

The reaction rate of ethylene hydroformylation at 337 K was calculated from the conversion, and expressed in molecules converted per surface Pd atoms per s. The number of surface Pd atoms was based on the H_2 chemisorption after the low-temperature reduction at 473 K (LTR).

As shown in Table 1, ethane was found to be the main product in ethylene hydroformylation over the Pd/SiO_2 catalyst. The oxo product was mainly 2-methyl-2-pentenal which may be formed by a condensation of propionaldehyde. These compounds were confirmed by mass spectrometer. There was no change in the selectivity and the activity with increasing the reduction temperature for the Pd/SiO_2 catalyst. For the Pd/Nb_2O_5 catalyst after LTR, only ethane was formed and no oxo products were detected. After HTR, ethane decreased slightly as compared with LTR. It is considered that SMSI has a minor effect on structure insensitive reactions such as ethylene hydrogenation. On the other hand, the rate (per g cat) of ethylene hydroformylation was increased dramatically by HTR, and 2-methyl-2-pentenal became the main product after HTR. It appears that CO insertion was enhanced in the SMSI state. As a result, the total reaction rate, based on Pd loading, was increased by HTR, as shown in table 1.

3.3. INFRARED SPECTRA OF CHEMISORBED CO

Figure 1 shows the effects of reduction temperature on the infrared spectra of CO adsorbed on the 5 wt% Pd/SiO_2 catalyst. The spectrum of the catalyst exhibits a broad band in the region of 1973 cm^{-1} and a sharp band at 2093 cm^{-1}, which are reasonably assigned to bridged carbonyl and linearly bonded carbonyl, respectively [9]. There was almost no change in the spectrum with increasing the reduction temperature.

In contrast, the infrared spectra of CO adsorbed on the 5 wt% Pd/Nb_2O_5 catalyst show remarkable changes with reduction temperature (fig. 2). After LTR, the spectrum of the catalyst exhibits two bands in the region of 1995 cm^{-1} and 1938 cm^{-1}, which may correspond to two-bonded CO chemisorption on Pd(100) and three-bonded CO on Pd(111), respectively [9]. The intensity of the band at around 1938 cm^{-1} first decreased substantially with increasing the reduction temperature, and finally the band at around 1995 cm^{-1} disappeared after high

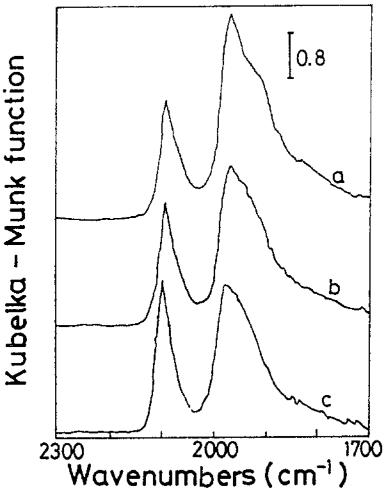

Fig. 1. IR spectra of CO adsorbed on Pd/SiO_2 catalyst after the H_2 reduction. (a) at 473 K, (b) at 573 K, and (d) at 673 K.

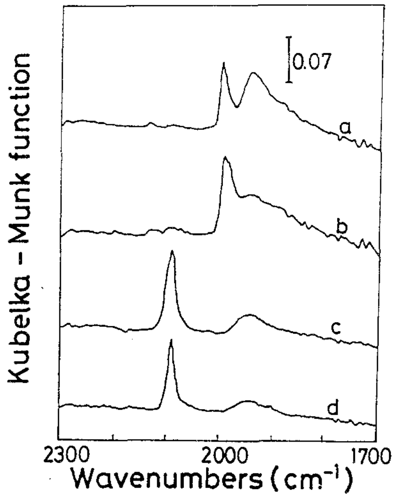

Fig. 2. IR spectra of CO adsorbed on Pd/Nb_2O_5 catalyst after the H_2 reduction (a) at 373 K, (b) at 473 K, (c) at 573 K, and (d) at 673 K.

temperature reduction. At the same time, the linear-type CO band appeared in the region of 2090 cm^{-1}.

These results presented here seem to be consistent with a recently proposed model for SMSI (decoration model) [2,4]. It may be considered that the high-temperature reduction of the Pd/Nb_2O_5 catalyst leads to uniform covering of the Pd surface with reduced niobia NbO_x. The suppression of the bridged CO with increasing reduction temperature may be attributed to a physical blockage of Pd surface site by NbO_x. Blocking of the bridged CO site consisting of adjacent Pd atoms by NbO_x may force the adsorbing CO molecules into "on top" or "linear" positions [5]. Therefore, the rate enhancement of ethylene hydroformylation on the Pd/Nb_2O_5 catalyst after HTR may be explained by a structural change in the surface atoms, i.e., the site isolation of Pd (a geometric effect), although we would not rule out the influence of an electronic interaction [4,8].

In summary, the HTR of Pd/Nb_2O_5 catalyst produces the site for linear-type CO adjacent to NbO_x, which appears to cause the acceleration of CO insertion.

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