Rh/One-atomic Layer GeO_2/SiO_2 as a New Catalyst for Ethyl Acetate Hydrogenation at a Low Pressure

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A new Rh/one-atomic layer GeO_2/SiO_2 catalyst was prepared by supporting $Rh_6(CO)_{16}$ precursor on the one-atomic layer GeO_2/SiO_2 followed by reduction at 423-523 K. The obtained catalyst was active and selective for conversion of ethyl acetate to ethanol by H_2 under mild reaction conditions, whereas Rh/bulk-GeO_2 and Rh/SiO_2 were inactive for this reaction. Rh carbonyl cluster, Rh metal, and RhGe alloy were formed on the one-atomic layer GeO_2/SiO_2 depending on the pre-reduction temperature. A combination of metallic Rh particles and one-atomic layer GeO_2 was most active for the ethanol production.

Catalytic hydrogenation of esters to the corresponding alcohols has been studied for so many years; copper chromite has been applied as a commercial catalyst to the production of diols from diesters or the synthesis of methanol in two-steps processes via methyl formate hydrogenation.[1-4] In commercial processes, however, copper chromite is operated at the pressure as high as 23 MPa, under which condition this catalyst is not so stable and is deactivated. To develop new catalysts for ester hydrogenation, several groups have investigated the catalytic properties of a soluble anionic Ru-hydride complex,[5] RhSn alloy catalysts,[6,7] and a Ru-Sn boride catalyst.[8] The alcohol synthesis processes via ester hydrogenation are thermodynamically superior to conventional direct hydrogenation of CO with H_2.

We have found the excellent catalytic property of Rh/one-atomic layer GeO_2/SiO_2 in the ethyl acetate hydrogenation to ethanol under mild reaction conditions. Activity and selectivity of this new catalyst were entirely different from those of Rh/bulk-GeO_2, Rh/SiO_2, and Rh/three-dimensional GeO_2 particles/SiO_2.

Preparation of one-atomic layer GeO_2 on SiO_2 will be reported elsewhere,[9,10] $Ge(OMe)_4$ (Soekawa Chemicals Co.; 99.999%) was purified by distillation in vacuum before use. SiO_2 (Aerosil 300; 300 m^2g^{-1}) was evacuated at 473 K for 1 h and exposed to given amounts of $Ge(OMe)_4$ vapor at 393 K for 1 h, followed by evacuation at 473 K to remove the unreacted $Ge(OMe)_4$ and the organic products. The obtained sample was calcined at 693 K for 1 h under 20.0 kPa of oxygen in a closed circulating system. Loading of Ge was fixed at 7.4 wt%, which corresponds to 0.2 ML of the SiO_2 surface. The one-atomic layer structure was characterized by means of EXAFS, XRF, XRD, TPD, and FT-IR.[9,10] Rh was supported on the one-atomic layer GeO_2/SiO_2 by an impregnation method using a chloroform solution of $Rh_6(CO)_{16}$ (Aldrich Chem. Co.; purity: 98%), followed by evacuation to enforce the support of $Rh_6(CO)_{16}$ on the GeO_2/SiO_2. The obtained sample was reduced at given temperatures for 2 h under 13.3 kPa of hydrogen. The catalyst thus obtained is denoted as Rh/GeAL/SiO_2. $Rh_6(CO)_{16}$ was also supported on SiO_2 (Aerosil 300), GeO_2 (hexagonal type; Wako Pure Chem. Co.), and GeO_2 particles/SiO_2[10] to prepare Rh/SiO_2, Rh/bulk-GeO_2, and Rh/GeO_2 particle/SiO_2(denoted as Rh/GeP/SiO_2) in a similar manner to the case of the GeO_2 layer/SiO_2. Catalytic hydrogenation reactions of ethyl acetate over 0.1 g of catalyst were conducted under a mixture of 6.6 kPa of hydrogen and 1.3 kPa of ethyl acetate at 473 K in a closed circulating system equipped by a gas chromatograph.

Table 1. The activities and selectivities(S) of the supported Rh catalysts for $CH_3COOC_2H_5$ hydrogenation[a]

Catalyst	Red[b] / K	Initial rate(r)[c] C_2H_5OH	CH_3CHO	CH_4	C_2H_6	S[d] / %
Rh/GeAL/SiO_2	423	3.0	0	1.5	0	80
	523	3.2	0	2.7	0	70
	623	2.8	0.76	4.0	0	50
	723	1.3	1.5	2.8	0	31
Rh/bulk-GeO_2	523	0	0.07	0	0	0
Rh/SiO_2	523	0	0	1.8	5.1	0
Rh/GeP/SiO_2	423	0.65	0	1.3	0	50
	723	0.27	2.4	2.0	0	8

[a]Reaction temperature:473 K; P(H_2):6.6 kPa; P($CH_3COOC_2H_5$): 1.3 kPa; [b]Prereduction temperature; [c]10^{-5} mol min^{-1} g-Rh^{-1}; [d]Selectivity to ethanol=r(C_2H_5OH)/(2 x r($CH_3COOC_2H_5$)).

Table 1 shows the catalytic activities and selectivities of Rh/GeAL/SiO_2, Rh/SiO_2, Rh/bulk-GeO_2, and Rh/GeP/SiO_2 prereduced at different temperatures for the ethyl acetate hydrogenation. It was found that Rh/GeAL/SiO_2 catalyzed the ethyl acetate hydrogenation with the highest selectivity of 80% when the catalyst was reduced at 423 K, whereas Rh/SiO_2 and Rh/bulk-GeO_2 were inactive for this reaction. The major products on Rh/SiO_2 were methane and ethane. The Rh/GeAL/SiO_2 catalysts reduced at 423-523 K were most active for ethanol formation. Acetaldehyde as a by-product was produced on the Rh/GeAL/SiO_2 reduced at 623 K and the formation was enhanced by increasing prereduction temperature. The temperature of the beginning of acetaldehyde formation agreed with that of the RhGe alloy formation as characterized by EXAFS (see below).

The activity and selectivity of Rh/GeP/SiO_2 for the ethyl acetate hydrogenation were much less as compared with those of Rh/GeAL/SiO_2. A drastic effect of the morphological change of GeO_2 from the one-atomic layer to the three-dimensional crystalline particles was observed with the formation of ethanol which was suppressed drastically by the crystallinity of GeO_2. On the other hand, the formation of methane and acetaldehyde is insensitive to the morphology of the GeO_2 on SiO_2.

We measured EXAFS spectra for Rh/GeAL/SiO_2 to characterize active species for the catalytic hydrogenation (KEK PF Proposal No.94G-203). Figure 1 shows Rh K-edge EXAFS spectra for $Rh_6(CO)_{16}$ cluster, the incipient supported $Rh_6(CO)_{16}$ on GeAL/SiO_2, and the Rh/GeAL/SiO_2 reduced with H_2 at 423-

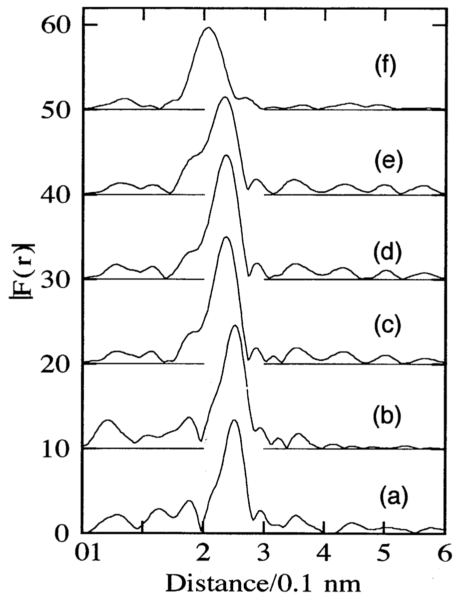

Figure 1. Rh K-edge EXAFS Fourier transforms for $Rh_6(CO)_{16}$(a) and Rh/one-atomic layer GeO_2/SiO_2 (b-f); (b) incipient supported $Rh_6(CO)_{16}$, (c) reduced at 423 K, (d) reduced at 523 K, (e) reduced at 623 K, and (f) reduced at 723 K.

723 K. The framework of the Rh carbonyl cluster is retained on the $GeAL/SiO_2$ surface (Figure 1 and Table 2). The EXAFS data for the samples reduced at the higher temperatures than 423 K reveal destruction of the cluster framework accompanied with aggregation to small Rh particles with coordination numbers of 7.4-7.5 for Rh-Rh bond. The Rh-Rh bond length was determined to be 0.266 nm by a curve fitting technique (Table 2), which is close to the Rh-Rh bond distance of Rh metal (0.269 nm).

The peak intensity in the Fourier transform decreased by reduction of the sample at 623 K as shown in Figure 1(e). The peak in the Fourier transform for $Rh/GeAL/SiO_2$ reduced at 723 K (Figure 1(f)) shifted toward a shorter distance. The curve fitting by Rh-Ge one-wave gave the best result (Table 2). The Ge K-edge EXAFS analysis also confirmed the Ge-Rh bonding at 0.244 nm. The change in the bonding modes of Rh-Rh and Rh-Ge indicates gradual RhGe alloy formation on the $GeAL/SiO_2$ at 623 K, and RhGe alloy formation was completed by reduction at 723 K.

From these results, it may be concluded that the most active phase for the ethanol formation from ethyl acetate is the Rh metallic particles supported on the $GeAL/SiO_2$ which dissociates ethyl acetate to form unidentate acetate and ethoxide (FT-IR).[11] The Rh particles themselves do not catalyze the selective ethanol formation because the Rh/SiO_2 catalysts were inactive for the ethyl acetate hydrogenation (Table 1). The RhGe alloy particles produce acetaldehyde rather than ethanol. This study

Table 2. Curve fitting results of Rh K-edge EXAFS spectra for $Rh/GeAL/SiO_2$

Sample	Scatterer atom	CN[a]	r/nm[b]	ΔE_0/eV[c]	σ/nm[d]	R_f /%[e]
Incipient	Ct	2.1±0.3	0.186±0.003	0.8	0.0054	
supported	Cb	2.0±0.3	0.217±0.003	0.8	0.0054	5.6
$Rh_6(CO)_{16}$	Rh	2.8±0.4	0.280±0.002	0.9	0.0059	
reduced at 423 K	Rh	7.4±1.3	0.266±0.002	-9.0	0.0085	1.8
reduced at 523 K	Rh	7.5±1.3	0.266±0.002	-9.1	0.0085	1.8
reduced at 723 K	Ge	3.5±1.0	0.244±0.003	-5.8	0.0086	2.5

[a]coordination number, [b]bond distance, [c]difference in the origin of photoelectron energy between the reference and the sample (±3 eV), [d]Debye-Waller factor(±0.0020 nm), [e]residual factor.

demonstrates the significance of the use of monolayer sample as a support for metal in the catalytic hydrogenation of ethyl acetate and exemplifies the advantageous applications of inorganic oxide monolayer.

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11 IR peaks appear at 2980 cm^{-1} (ν_{C-H} of ethoxide and acetate), 2934 cm^{-1} (ν_{C-H} of acetate), 2901 cm^{-1} (ν_{C-H} of ethoxide), 1728 cm^{-1} ($\nu_{C=O}$ of unidetate acetate), and 1391 cm^{-1} and 1376 cm^{-1} (δ_{C-H} of ethoxide and acetate).