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NOTE

Effects of Chlorine on Formation of 3-Pentanone during Ethene Hydroformylation over Rh/Active-Carbon Catalyst

In ethene hydroformylation over supported rhodium catalysts under atmospheric pressure, a common product is propanal (1–6). As previously reported, 3-pentanone was found to be another hydroformylation product over the Rh/active-carbon catalyst (7–9). Comparing 3-pentanone formation with propanal formation over the Rh/active-carbon catalyst reveals the difference in the dependence of the rate of formation of propanal and 3-pentanone on (i) reaction temperature, (ii) pretreatment of catalyst with H_2, and (iii) partial pressure of CO. These results imply that the active sites for 3-pentanone formation are different from those for propanal formation. However, further details of the difference between them have not been clarified. In the present work, the catalytic behaviors of the Rh/active-carbon catalysts prepared by using different kinds of active-carbon supports have been compared.

Rh/active-carbon catalysts were prepared by a conventional impregnation method, where rhodium trichloride trihydrate ($RhCl_3 3H_2O$) or rhodium trinitrate ($Rh(NO_3)_3$) was deposited on the support from the aqueous solution of them. Three kinds of commercial active-carbon were used as supports: active-carbon(A) (denoted by AC(A)), obtained from Wako Pure Chemical Ind., Ltd., AC(B), from Kanto Chemicals Inc.; and AC(C), from Kishida Chemical Co., Ltd. Active-carbon supports were used either without treatments or after a treatment with hydrogen chloride (HCl), sodium hydroxide (NaOH), and so on. The treatment was performed as follows; the active-carbon support was immersed in an aqueous solution containing the compound for the treatment (0.5 mol/dm^3) and then separated from the solution by decantation. The solid thus obtained contained about 1.2 cm^3 of the solution per g-(active-carbon). The solid was then dried at 383 K for 12 h in an oven. Pretreatment of the catalyst with hydrogen at 573 K for 3 h was followed by ethene hydroformylation at 393 K with a reactant gas mixture of He–C_2H_4(20%)–CO(20%)–H_2(20%) (total flow rate = 100 cm^3 (STP)/min) in a fixed-bed-type reactor with a continuous flow operated at atmospheric pressure. If necessary, the pretreatment with hydrogen was followed by a treatment with carbon monoxide at 473 K for 1 h prior to the reaction performance. The values for specific surface area and average pore size of active-carbon supports were measured by Carlo Erba Sorptmatic 1900 in cooperation with Amco Co., Ltd. The temperature-programmed desorption (TPD) of CO was carried out by using a conventional flow system operated at atmospheric pressure at a heating rate of 5 K/min in a He flow of 30 cm^3(STP)/min. Details for TPD performance were described elsewhere (10, 11). Measurements of X-ray photoelectron spectra were carried out using a Rigaku XPS-7000 spectrometer employing Al$K\alpha$ X-radiation, where adhesive tape on a sample holder was used to support a Rh/AC sample in a fine powder form. Binding energy values are referenced to the peak at 285.0 eV for C 1*s*.

In ethene hydroformylation over Rh/active-carbon, formation of propanal, 3-pentanone, and ethane was observed (7–9). The rates of formation for propanal and ethane (denoted by r_{PA} and r_E, respectively) decreased with time on stream. The rate of formation for 3-pentanone (denoted by r_{3-P}) increased with time on stream at the early stage of the reaction for about 8 h, and then it decreased slowly. In the present work, catalytic activities for these three products were evaluated by the rates of formation at time on stream of 10 h.

Catalytic activities for ethene hydroformylation of Rh/AC catalysts, which were prepared from $RhCl_3$ by using three kinds of active-carbon supports, are summarized in Table 1. The catalytic behavior on Rh/AC(A) was found to be very similar to that on Rh/AC(B) as shown by runs 1 and 4. These two catalysts were characterized by the high activity for 3-pentanone formation. On the other hand, r_{3-P} on Rh/AC(C) was found to be lower than that on Rh/AC(A) or on Rh/AC(B) as shown by run 5. On the three active-carbon supports, similar values of specific surface area (A, 930; B, 1060; C, 900 m^2/g) and of average pore radius (A, 1.9; B, 2.2; C, 1.8 nm) were obtained, suggesting almost the same pore structure on them. Therefore, the difference in the pore structure among the three supports would not be a main reason for the difference in the catalytic behavior. Usually, acidic compounds or basic compounds are present on active-carbon. Such compounds may affect the catalytic activity for 3-pentanone formation. To make it clear which

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TABLE 1

Catalytic Behavior of Rh/AC Catalysts Prepared from $RhCl_3$ for Ethene Hydroformylation

			Catalytic activity		
Run	Support	pH[a]	r_{PA}	r_{3-P}	r_E
			(10^{-2} mol · min^{-1} · mol-Rh^{-1})		
1	A	4.5	1.04	0.40	2.30
2	A NaOH	9.2	1.29	0.15	1.40
3	A-(NH_3)[b]	—	1.01	0.01	1.10
4	B	4.5	1.03	0.38	1.68
5	C	9.5	1.48	0.12	1.71
6	C-HCL	4.7	1.81	0.43	3.56
7	C-HNO_3	2.6	2.01	0.01	2.24
8	C-HBr	2.2	1.40	<0.01	1.76
9	C-NaCl	5.5	1.52	0.22	2.43

[a] pH values of water (50 cm^3) in which 1.0 g of the support was immersed.

[b] Treatment with NH_3(aq) was carried out after reduction of the catalyst with H_2 and the catalyst was treated again with H_2 at 573 K before the reaction performance.

TABLE 2

Catalytic Activities of Rh/Active-Carbon Catalysts Prepared from $Rh(NO_3)_3$ for Ethene Hydroformylation

		Activity		
Run	Support	r_{PA}	r_{3-P}	r_E
		(10^{-2}mol · min^{-1} · mol-Rh^{-1})		
1	A-NaOH	0.84	<0.01	1.04
2	C	1.02	<0.01	1.40
3	C-(HCl)[a]	1.94	0.02	1.52
4	C-(NaCl)[b]	0.95	0.05	0.74

[a, b] 6×10^{-4} mol of HCl(run 3) or NaCl(run 4) was introduced on the catalyst after reduction of the catalyst with H_2 and the catalyst was treated again with H_2 at 573 K before the reaction performance.

kinds of compounds were present on the support, the pH value of water in which active-carbon had been immersed (1.0 g of active-carbon in 50 cm^3 of distilled water) was measured. Active-carbons (A) and (B) showed the pH values of around 4.5 as shown in Table 1, indicating the presence of acidic compounds. On the other hand, the pH value on AC(C) was obtained as 9.5, indicating the presence of basic compounds.

Effects of treatment of active-carbon support with several compounds (acids, bases, or salts) on the catalytic behavior for ethene hydroformylation are also shown in Table 1. Treatment of AC(A) with an aqueous solution of NaOH increased the pH value to 9.2 (AC(A) thus treated is denoted by AC(A–NaOH)). The r_{3-P} on the catalyst using this support (0.15×10^{-2} mol · min^{-1} · mol-Rh^{-1}) was observed to be lower than that on Rh/AC(A) untreated (0.40×10^{-2} mol · min^{-1} · mol-Rh^{-1}) as shown by run 2. On the other hand, treatment of AC(C) with an aqueous solution of HCl decreased the pH value to 4.7. As shown by run 6, r_{3-P} on Rh/AC(C–HCl) was found to be 0.43×10^{-2} mol · min^{-1} · mol-Rh^{-1}, and this value was much higher than that on Rh/AC(C) untreated (0.12×10^{-2} mol · mon^{-1} · mol-Rh^{-1}). These results indicate an important role of HCl in the formation of active sites for 3-pentanone formation and/or in the reaction to form 3-pentanone.

In order to clarify which component(s) in HCl (H^+ and/or Cl^-) would be essential to form 3-pentanone, effects of the treatment with other compounds were studied. Treatment of AC(C) with diluted nitric acid lowered the pH value to 2.6. Treatment of AC(C) with HBr also lowered the pH value to 2.2. However, values for r_{3-P} on the catalysts prepared by using AC(C–HNO_3) and AC(C–HBr) were very low compared with that on Rh/AC(C) untreated as shown by runs 7 and 8, respectively. On the other hand, treatment of AC(C) with NaCl slightly enhanced r_{3-P} as shown by run 9, implying an important role of Cl^- for 3-pentanone formation. The effect of NaOH in run 2 would be due to a decrease in the effective Cl^- concentration at the rhodium sites. As shown by run 3, Rh/AC(A), which was treated with aqueous solution of NH_3 after the reduction with H_2, showed almost no appreciable activity for 3-pentanone formation. The effects of NH_3 would be due to formation of NH_4Cl, which has relatively high vapor pressure (2.6×10^4 Pa at 566 K), resulting in a decrease in the amount of Cl^- at the rhodium sites through the vaporization of NH_4Cl during the treatment of the catalyst with H_2 at 573 K before the reaction.

In the case of the catalyst preparation from $RhCl_3$, a certain amount of Cl^- was always introduced into the catalyst. Recent studies on Rh/SiO_2 prepared from $RhCl_3$ have shown the presence of Cl^- at the surface of rhodium metal particles even after the reduction with H_2 (12). In order to confirm the important role of Cl^-, the effects of HCl and NaCl on r_{3-P} were studied on the catalysts prepared from $Rh(NO_3)_3$. As shown in Table 2, Rh/AC(A–NaOH) and Rh/AC(C), which were prepared from $Rh(NO_3)_3$, showed no appreciable activity for 3-pentanone formation, where comparable values for r_{PA} and r_E with those on the catalyst prepared from $RhCl_3$ were observed. In cases of runs 3 and 4, the treatment of the catalyst with H_2 at 573 K for 3 h was followed by the modification of the catalyst with a solution of HCl or NaCl (0.5 mol/dm^3). In both cases, formation of a small amount of 3-pentanone was observed. These results indicate a strong relation between the presence of a certain amount of Cl^- on the catalyst and the catalytic activity for 3-pentanone formation. X-ray photoelectron spectra for Cl 2*p* on Rh/AC(A) (4.0 wt% Rh) are shown in Fig. 1, where the intensities are normalized as the peak intensities (heights) for C 1*s* on the samples are to

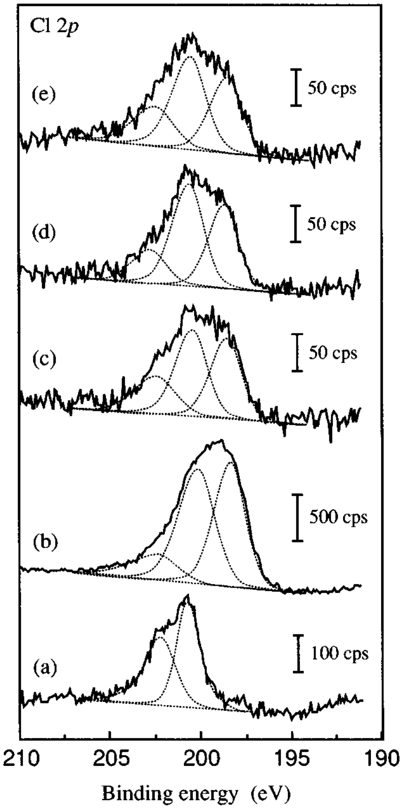

FIG. 1. XP spectra of Cl $2p$ on Rh/AC(A) (4.0 wt%). (a) AC(A); (b) Rh/AC without treatment; (c) Rh/AC with H_2 treatment at 573 K; (d) Rh/AC with CO treatment at 353 K after the H_2 treatment; (e) Rh/AC with CO treatment at 473 K after the H_2 treatment.

TABLE 3

Effects of CO Treatment of Rh/AC(B) Catalysts on the Catalytic Activity for 3-Pentanone Formation during C_2H_4 Hydroformylation

Run	Rhodium loaded (wt%)	Treatment with CO at 473 K for 1 h	C_2H_4 hydroformylation		
			r_{PA}	r_{3-P}	r_E
			(10^{-2} mol · min^{-1}.mol-Rh^{-1})		
1	0.5	no	0.56	0.47	1.28
2		yes	1.11	0.04	1.30
3	1.0	no	0.56	0.52	1.15
4		yes	1.96	0.10	2.26
5	1.5	no	0.43	0.47	1.07
6		yes	2.19	0.25	2.21
7	2.0	no	1.03	0.38	1.68
8		yes	3.08	0.24	2.90
9	4.0	no	1.35	0.18	2.35
10		yes	3.61	0.08	3.12

be 100,000 counts per second (cps). Active-carbon support itself contains a small amount of Cl^- as shown by spectrum (a). The spectrum is decomposed into two peaks at 202.3 eV for Cl $2p_{1/2}$ and 200.7 eV for Cl $2p_{3/2}$. By supporting $RhCl_3$, the amount of Cl^- on the catalyst remarkably increased, where the spectrum might be decomposed into three peaks at 202.4, 200.4, and 198.6 eV, indicating the presence of at least two kinds of Cl species (two sets at 202.4–200.4 eV and 200.4–198.6 eV). Although the amount of Cl^- decreased after the pretreatment with H_2, a small amount of Cl^- was still present on the catalyst as shown by spectrum (c) (intensity ratio, (a) : (b) : (c) = 1 : 8.7 : 0.9).

As previously reported, the active species for 3-pentanone formation were unstable at the temperatures higher than 433 K, while the active sites for propanal formation were stable even at 453 K (7, 8). The activities for propanal and ethane formation were enhanced by the pretreatment of the catalyst with CO at temperatures >433 K (9). However, the activity for 3-pentanone formation was reduced by the treatment with CO at 473 K as shown in Table 3. In the previous work, we have reported that a considerable amount of CO was adsorbed on Rh/AC(A) prepared from $RhCl_3$ (9, 11). TPD spectra of CO on the three Rh/AC catalysts prepared from $RhCl_3$ are compared in Fig. 2, where the desorption peaks are observed at almost the same position. The spectrum on Rh/AC(A) was almost the same as that on Rh/AC(B), and the amounts of CO desorbed were evaluated as 500×10^{-6} mol · g^{-1} for the former and 520×10^{-6} mol · g^{-1} for the latter, respectively. On the other hand, the amount of CO desorbed from Rh/AC(C) was evaluated as 230×10^{-6} mol · g^{-1}, and this value was less than that from Rh/AC(A) or Rh/AC(B).

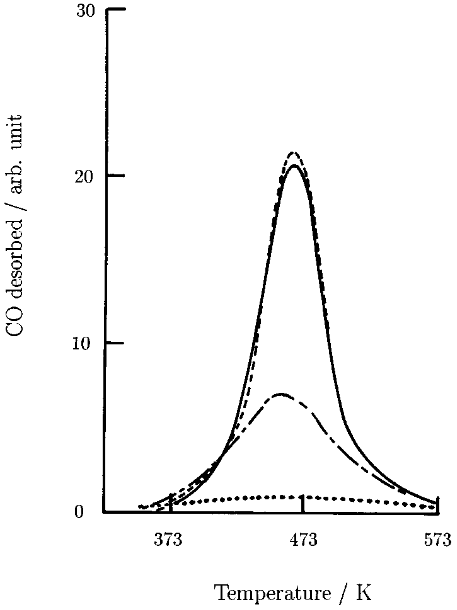

FIG. 2. TPD spectra of CO from Rh/AC catalysts exposed to CO at 353 K (Rh/AC catalysts prepared from $RhCl_3$ (AC(A) (——), AC(B) (– – – –), AC(C) (— - — - — -), respectively) and Rh/AC(C) prepared from $Rh(NO_3)_3$) (· · · · · · · · ·).

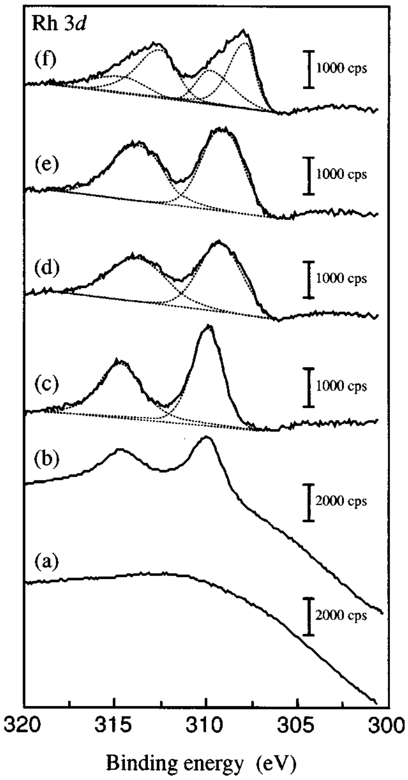

FIG. 3. XP spectra of Rh 3*d* on Rh/AC(A) (4.0 wt%). (a) AC(A); (b) Rh/AC without treatment; (c) a difference spectrum (b)-(a); (d) Rh/AC with H_2 treatment at 573 K; (e) Rh/AC with CO treatment at 353 K after the H_2 treatment; (f) Rh/AC with CO treatment at 473 K after the H_2 treatment. Spectra (d)–(f) were obtained in the same manner as (c).

As also shown in Fig. 2, the TPD spectrum of CO on Rh/AC(A) prepared from $Rh(NO_3)_3$, which was found to be almost inactive for the formation of 3-pentanone, showed a very small desorption peak ($30 \times 10^{-6} \mathrm{mol} \cdot \mathrm{g}^{-1}$). In addition, it was already reported that the amounts of CO desorbed from the catalysts treated with CO decreased with an increase in the temperature for the CO exposure in the region >433 K (9, 11). Thus, the higher value for the amount of CO desorbed was observed on the catalyst which showed the higher activity for the formation of 3-pentanone.

X-ray photoelectron spectra for Rh 3d on Rh/AC(A) (4.0 wt% Rh) are shown in Fig. 3, where the intensities are normalized by using the C 1*s* peak intensity. As shown by spectrum (a), the active-carbon support showed a curved baseline in this region. On the sample without treatment, spectrum (b) was obtained. A difference spectrum, (b)-(a), is obtained as spectrum (c), where Rh 3d peaks (Rh $3d_{3/2}$ and $3d_{5/2}$) were observed at 314.7 and 310.0 eV, respectively. On the sample pretreated with H_2 at 573 K, Rh 3*d* peaks were observed at 313.8 and 309.2 eV as shown by the difference spectrum (d). Although samples for XPS measurements were kept under N_2 atmosphere during crushing of them into a fine powder form and transfer into XP spectrometer, they would be exposed to O_2 at low concentration level in the atmosphere. In the case of Rh/SiO_2, the sample exposed to air after treatment with H_2 showed the peaks at 312.3 and 307.7 eV as already reported by Chuang and Pien (13). Thus, the Rh species derived from $RhCl_3$ on the active-carbon support by the H_2 treatment are found to be very different from those on the silica gel support. As shown by the difference spectrum (e), the sample exposed to CO at 353 K showed the peaks at 313.8 and 309.1 eV in Rh 3*d* region, where the pattern is very similar to that of spectrum (d). As shown by the difference spectrum (f), peaks at 312.7 and 308.0 eV appeared on the sample exposed to CO at 473 K besides the small peaks at 314.6 and 309.8 eV. The binding energy values for the predominant species are close to those on Rh/SiO_2 exposed to air. Thus, the Rh species formed on the sample after exposure to CO at 473 K are found to be different from those at 353 K. As shown by spectrum (c) in Fig. 1 for Cl 2*p*, an appreciable amount of Cl^- is present on the catalyst even after treatment with H_2. As shown by spectrum (d), no appreciable decrease in Cl^- concentration was observed on the sample exposed to CO at 353 K, on which a high activity for 3-pentanone formation was observed. However, the sample treated with CO at 473 K also contained almost the same amount of Cl^- as shown by spectrum (e), on which the activity for 3-pentanone was found to be much lower than that on the sample treated with CO at 353 K. These results imply an important role of Cl^- in forming the active sites for 3-pentanone formation rather than in reaction sequences in 3-pentanone formation from the reactants. On the other hand, the active sites for propanal formation did not require the presence of Cl^-. It was already clarified that the rate of propanal formation was accelerated by the presence of rhodium metal particles (4, 8, 11, 14). Chuang *et al.* have shown Rh^0 and Rh^+ sites on SiO_2 as the active sites for hydroformylation (13, 15, 16).

Consequently, an important role of Cl^- in forming active sites for 3-pentanone formation has been suggested. In addition, a strong relation between the amount of CO adsorbed and the activity for 3-pentanone formation has been suggested. At the present time, however, we have not clarified whether the active sites for 3-pentanone formation require the presence of Cl^- as an essential component to keep the active structure or not.

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