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Comparison of Ethylene with Propylene Hydroformylation over a Rh–Y Zeolite Catalyst under Atmospheric Pressure

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Hydroformylation of ethylene and propylene over the Rh–Y zeolite was carried out in a continuous-flow system under atmospheric pressure. The activity of the catalyst used for the formation of propionaldehyde and butyraldehyde was observed to be constant for a period of over 1 month. Pretreatment of the catalyst with He–H_2 (10%) at 127°C considerably affected the steady-state rate (r_{PA}) and the apparent activation energy (E_{PA}) for the propionaldehyde formation. On the Rh–Y zeolite with a rhodium content of less than 110×10^{-6} mol/g cat (1.13 wt%), the enhancement in r_{PA} was observed with no appreciable change in E_{PA}. On the other hand, on the Rh–Y zeolite (No. 6) with a rhodium content of 280×10^{-6} mol/g cat (2.88 wt%), r_{PA} was somewhat reduced by the pretreatment while E_{PA} was considerably enhanced, i.e., 40 kJ/mol on the untreated catalyst and 56 kJ/mol on the pretreated one. In the propylene hydroformylation, the pretreatment of the Rh–Y (No. 6) remarkably reduced r_{BA} compared with r_{PA}, but it enhanced the *n*-isomer selectivity ($S_{n\text{-BA}}$). The enhancement in $S_{n\text{-BA}}$ is closely related to the enhancement in E_{PA}. On the basis of the results obtained, it is concluded that (1) the active sites formed either at the entrance of the pore or the external surface can effectively catalyze both the hydroformylation of ethylene and propylene and (2) the active sites formed in the pore at a very short distance from the entrance can catalyze the hydroformylation of ethylene but not propylene.

INTRODUCTION

As it has been already pointed out by several investigators, rhodium trivalent cations supported on zeolites can be converted into stable supported rhodium–carbonyl complexes (*1–3*). In some cases, the Rh–Y zeolite is found to be active for the reactions which are originally catalyzed by the homogeneous rhodium complexes, e.g., ethylene dimerization (*4*) and methanol carbonylation (*5–7*). Mantovani *et al.* (*8*) reported that hexene-1 hydroformylation is catalyzed by the Rh–Y zeolite at elevated pressures of carbon monoxide and hydrogen. Recently, Arai and Tominaga (*9*) have reported that hydroformylation of olefins is catalyzed by the Rh–Y zeolite at atmospheric pressure, where the relative ease of hydroformylation is found to be ethylene > propylene > butene-1.

The details of the catalytic behavior of the Rh–Y zeolite for olefin hydroformylation, however, have not been clarified to date. In addition, it is still uncertain whether all of the active sites formed within the zeolite cavity are effectively used for the reaction. It would be necessary to clarify this point for the evaluation of the Rh–Y zeolite as a catalyst for olefin hydroformylation, with particular emphasis on propylene, since *n*-butyraldehyde is much more useful in the chemical industry than isobutyraldehyde (*10*). If the active rhodium species were located within the narrow channel of the zeolite where the formation of the intermediate leading to the iso-isomer would be more retarded than that leading to the *n*-isomer, then higher selectivity to *n*-butyraldehyde may be possible.

In order to obtain information concerning the nature of the Rh–Y zeolite as a hydroformylation catalyst, the catalytic behavior for ethylene hydroformylation was com-

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pared with that for propylene hydroformylation.

EXPERIMENTAL

Chemicals. Rhodium trichloride trihydrate was obtained from Wako Pure Chemical Ind., Ltd. and was used without further purification. Ethylene, propylene, carbon monoxide, and hydrogen which were used as the reactants, and helium which was used as a diluent gas were obtained from commercial sources. Na–Y zeolite used as a fine powder without binder was Linde SK-40.

Catalysts. The Rh–Y zeolites were prepared from Na–Y and a rhodium trichloride trihydrate aqueous solution by stirring the mixture at 80°C for 12 h. After it was dried at 120°C for 12 h, the solid was pressed and crushed, then sieved to 20–42 mesh size. The catalysts for which silica gel or alumina were used as supports were prepared by the usual impregnation method.

Procedure. Hydroformylation of ethylene and propylene was carried out in a fixed-bed type apparatus with a continuous-flow system at atmospheric pressure. The catalyst was placed in a reactor (Pyrex glass tube), and the system was purged with helium for 1 h at room temperature. The reactor, which was immersed in an oil bath, was heated up to 127°C at a rate of about 2°C/min in the reaction gas stream when the reaction was started on the fresh catalyst or in He–H_2 (10%) when the reaction followed pretreatment with hydrogen at 127°C for 5 h. For ethylene hydroformylation, the partial pressure of each reactant was 0.1×10^5 Pa; whereas for propylene hydroformylation, the partial pressure was 0.3×10^5 Pa for propylene and hydrogen and 0.1×10^5 Pa for carbon monoxide. The total flow rate was 70 cm^3 (STP)/min. The effluent gas was analyzed by gas chromatography.

RESULTS

1. Time Course of the Products in the Hydroformylation

For ethylene hydroformylation over the Rh–Y zeolite, typical changes in propionaldehyde and ethane formation with time on stream are shown in Fig. 1. The increase in the propionaldehyde formation and the decrease in the ethane formation each approaching asymptotic values were observed for as long a period as several tens of hours. Propionaldehyde and ethane were found to be the main products after the steady-state activities were attained. In the propylene hydroformylation, the time course of the rates of formation of *n*- and iso-butyraldehyde and propane is similar to that of the rates of formation of propionaldehyde and ethane, respectively, as shown in Fig. 1. Propane and *n*- and iso-butyraldehyde are the main products in the propylene hydroformylation. In both ethylene and propylene hydroformylation, the active sites formed in the zeolite were extremely stable under the reaction conditions and the constant activity lasted more than 1 month.

After the reaction, the Rh–Y zeolite showed a deep red–purple color and exhibited absorption bands at 436, 475, and 504

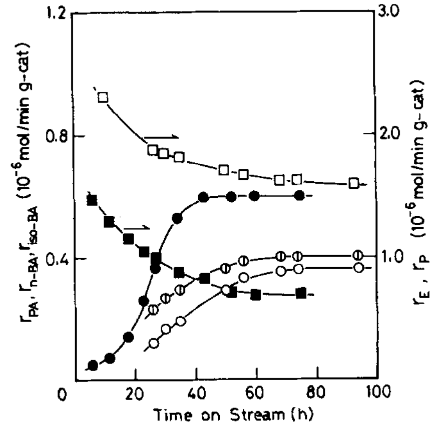

FIG. 1. Changes in the formation of products in the ethylene and propylene hydroformylation. Ethylene hydroformylation: Rh–Y (No. 2) pretreated with He–CO(10%)–H_2(10%) at 400 K for 48 h, He–C_2H_4(10%)–CO(10%)–H_2(10%) at 400 K; ●, propionaldehyde; ■, ethane. Propylene hydroformylation: Rh–Y (No. 6) untreated, He–C_3H_6(30%)–CO(10%)–H_2(30%) at 400 K; ○, *n*-butyraldehyde; ⦶, iso-butyraldehyde; □, propane.

nm in the visible spectrum, while the fresh catalyst did not show those absorption bands. This color never diminished after the removal of reversibly adsorbed propionaldehyde from the catalyst. An essentially identical spectrum was obtained from Na–Y on which propionaldehyde had been adsorbed. The amount of irreversibly adsorbed propionaldehyde on the fresh catalyst (the identical pretreatment as that on the catalyst used in Fig. 1 was performed) was measured by using a pulse technique and was determined to be 3.4 × 10^{-3} mol/g cat. This amount is almost the same as that on the Na–Y zeolite. After the irreversible adsorption was completed, the reaction gas was fed into the system to start the reaction. As Fig. 2 shows, the induction period was remarkably shortened by the preadsorption, while the steady activity was scarcely affected.

2. *Effects of Catalyst Pretreatment with He–H_2 on Ethylene Hydroformylation*

The effects of the pretreatment of the Rh–Y zeolite with He–H_2 (10%) at 127°C on the steady states of propionaldehyde formation (r_{PA}) and ethane formation (r_E) are summarized in Table 1. The r_{PA} and more remarkably r_E were enhanced by the pretreatment of the Rh–Y zeolite containing less than 175 × 10^{-6} mol Rh/g cat. On the other hand, r_{PA} was somewhat reduced by the pretreatment of the Rh–Y (No. 6), which contains 280 × 10^{-6} mol Rh/g cat. Even though the correlation between rhodium content and r_{PA} or r_E was not satisfactory, both of the rates seem to increase with the rhodium content on the untreated catalyst while they seem to quickly reach a plateau on the pretreated catalyst.

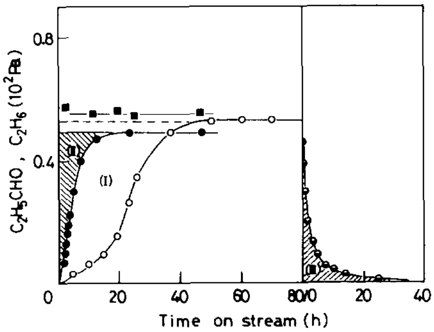

FIG. 2. Effect of preadsorption of propionaldehyde on the catalytic activity. ○,●: Propionaldehyde formation on the fresh and the preadsorbed catalyst, respectively. ■, Ethane formation on the preadsorbed catalyst. ◒, Desorption of propionaldehyde from the catalyst into the He–CO(10%) stream at 400 K (total flow rate = 70 cm^3/min). Reaction conditions were the same as those in Fig. 1, and the catalyst weight was 2.5 g.

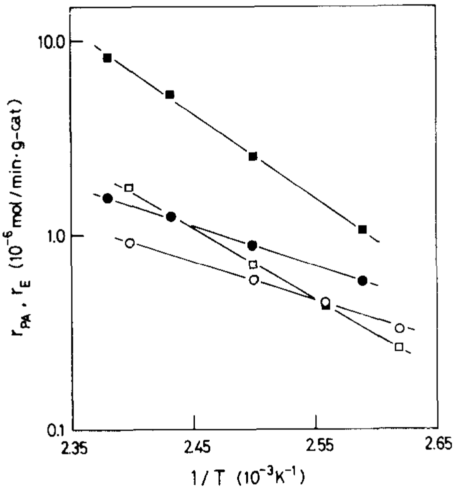

FIG. 3. Effect of reaction temperature on r_{PA} and r_E on the Rh–Y (No. 2). ○,□: r_{PA} and r_E on the untreated catalyst; ●,■: r_{PA} and r_E on the catalyst pretreated with He–H_2, respectively. Reaction conditions: He–C_2H_4 (10%)–CO(10%)–H_2(10%).

The temperature dependence of r_{PA} and r_E on the Rh–Y (No. 2) which contains 77 × 10^{-6} mol Rh/g cat are shown in Fig. 3. The pretreatment with He–H_2 does not affect the apparent activation energy for the hydroformylation (E_{PA}), 39 kJ/mol on the untreated catalyst and 40 kJ/mol on the pretreated catalyst. On the other hand, pretreatment does affect considerably the apparent activation energy for the hydrogenation (E_E), 72 kJ/mol on the former and 87 kJ/mol on the latter. In the case of the Rh–Y (No. 6), the E_{PA} and E_E on the pretreated catalyst, 56 and 89 kJ/mol, respectively, are higher than those on the untreated catalyst, 41 and 76 kJ/mol, respectively, as shown in

TABLE 1

Ethylene Hydroformylation over the Rh–Y Zeolite

Run No.	Cat. No.	Rh content (10^{-6} mol/g cat)	Pretreatment with He–H_2 (0.1×10^5 Pa, 400 K, 5 h)	Hydroformylation		Hydrogenation	
				r_{PA}[a] (10^{-6} mol/min g cat)	E_{PA}[b] (kJ/mol)	r_E[a] (10^{-6} mol/min g cat)	E_E[b] (kJ/mol)
1	1	50	No	0.33	39	0.38	72
2[d]			Yes	0.60	40	1.98	87
3	2	77	No	0.59	39	0.70	72
4			Yes	0.89	40	2.67	87
5	3	110	No	0.47	40	0.71	72
6			Yes	0.89	42	2.35	88
7	4	150	No	0.41	39	0.76	73
8			Yes	0.89	56	1.82	88
9	5	175	No	0.51	40	0.82	70
10			Yes	0.70	56	2.07	90
11	6	280	No	1.02	41	2.43	76
12			Yes	0.84	56	2.69	89
13	$RhCl_3$/	170	No	0.009	[c]	0.059	[c]
14	SiO_2		Yes	1.69	42	3.06	87
15	$RhCl_3$/	170	No	0.012	[c]	0.094	[c]
16	Al_2O_3		Yes	0.40	43	3.88	82

Note. The pretreatment was performed in a flow system with a total flow rate of 70 cm^3 (STP)/min at atmospheric pressure, and reaction conditions were He–C_2H_4 (10%)–CO(10%)–H_2 (10%) at 400 K.

[a] Steady state rates for the formation of propionaldehyde and ethane, respectively.

[b] Apparent activation energies for the formation of propionaldehyde and ethane, respectively.

[c] Not measured.

[d] The pretreatment was performed for 48 h.

Fig. 4. The values for E_{PA} and E_E on the Rh–Y zeolites with a wide range of rhodium content are summarized in Table 1. On the untreated Rh–Y zeolites, E_{PA} is ca. 40 kJ/mol over the whole range of rhodium content. On pretreated catalyst whose rhodium contents exceed 150 × 10^{-6} mol/g cat, higher values for E_{PA}, 56 kJ/mol, are obtained; whereas, on the pretreated catalysts with rhodium contents less than 110 × 10^{-6} mol/g cat, the same value for E_{PA} as that for the untreated catalyst is obtained. Over the whole range of rhodium content, E_E is ca. 72 kJ/mol on the untreated catalyst or ca. 88 kJ/mol on the catalyst pretreated with He–H_2.

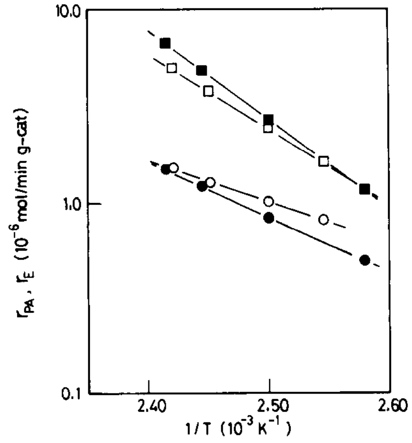

FIG. 4. Effect of reaction temperature on r_{PA} and r_E on the Rh–Y (No. 6). ○,□: r_{PA} and r_E on the untreated catalyst; ●,■: r_{PA} and r_E on the catalyst pretreated with He–H_2, respectively. Reaction conditions: He–C_2H_4(10%)–CO(10%)–H_2(10%).

3. *Effects of the Pretreatment with He–H_2 on the Propylene Hydroformylation*

The effect of the pretreatment of the Rh–

Y zeolite with He–H_2 on the steady-state rates for the formation of *n*- and iso-butyraldehyde ($r_{n\text{-BA}}$, $r_{\text{iso-BA}}$, and r_{BA}, respectively), and propane (r_P) are shown in Table 2. The r_{BA} was enhanced by the pretreatment of the Rh–Y (No. 1) but reduced by the pretreatment of the Rh–Y (No. 6). The reduction in r_{BA} by the pretreatment was also observed on the Rh–Y (No. 7). With the exception of runs 6 and 8, the propylene hydroformylation was performed on fresh catalyst. In the case of the two exceptions, the reaction with ethylene was followed by the reaction with propylene. Almost no appreciable differences were found between the two cases. In the case where the reaction of propylene was followed by the reaction with ethylene, almost the same results as those shown in Table 1 were obtained. Thus, the sequence of the reactions does not affect the steady-state rates.

The effect of the pretreatment on the *n*-isomer selectivity (denoted by $S_{n\text{-BA}}$) is also summarized in Table 2. The untreated Rh–Y zeolite showed $S_{n\text{-BA}}$ around 0.44–0.50. Pretreatment of Rh–Y (No. 6 and 7) greatly enhanced $S_{n\text{-BA}}$, while pretreatment of Rh–Y (No. 1) seemed to reduce $S_{n\text{-BA}}$. An intermediate value for $S_{n\text{-BA}}$ was observed for Rh–Y (No. 4).

The effects of the reaction temperature on $r_{n\text{-BA}}$ and on $r_{\text{iso-BA}}$ are shown in Fig. 5 for the Rh–Y (No. 6) both treated with He–H_2 and untreated. The effects of the pretreatment were only on both of the apparent activation energies, $E_{n\text{-BA}}$ and $E_{\text{iso-BA}}$; 48 and 54 kJ/mol for the untreated catalyst and 48 and 57 kJ/mol for the pretreated one, respectively.

4. *Catalytic Behavior of $RhCl_3/SiO_2$ and $RhCl_3/Al_2O_3$ Catalysts*

On two catalysts, $RhCl_3/SiO_2$ and $RhCl_3/Al_2O_3$, the effects of pretreatment with He–H_2 on the rates and on the apparent activation energies are shown in Table 1. Both of the rates on those two catalysts are enhanced by the pretreatment; the effect is

TABLE 2

Propylene Hydroformylation over the Rh–Y Zeolite

Run	Catalyst	Rh content (10^{-6} mol/g cat)	Pretreatment with He–H_2 (0.1×10^5 Pa, 400 K, 5 h)	10^{-6} mol/min g cat			$S_{n\text{-BA}}$[b]	r_P[a] (10^{-6} mol/min g cat)
				$r_{n\text{-BA}}$[a]	$r_{\text{iso-BA}}$[a]	r_{BA}[a]		
1	1	50	No	0.10	0.11	0.21	0.48	0.38
2[c]			Yes	0.15	0.24	0.39	0.38	1.06
3	4	150	No	0.15	0.15	0.30	0.50	0.55
4			Yes	0.24	0.21	0.45	0.53	1.38
5	6	280	No	0.36	0.40	0.76	0.47	1.60
6[d]			No	0.35	0.41	0.76	0.46	1.60
7			Yes	0.16	0.12	0.28	0.57	1.26
8[d]			Yes	0.14	0.10	0.24	0.58	1.43
9	7	350	No	0.38	0.48	0.86	0.44	1.80
10			Yes	0.08	0.06	0.14	0.57	1.18
11	$RhCl_3/SiO_2$	170	Yes	0.53	0.96	1.49	0.36	1.29

Note. Reaction conditions were He–C_3H_6 (30%)–CO (10%)–H_2 (30%) at 400 K.

[a] Steady-state rates for the formation of *n*-butyraldehyde, iso-butyraldehyde, both butyraldehydes, and propane, respectively.

[b] The *n*-isomer selectivity is defined by $r_{n\text{-BA}}/(r_{n\text{-BA}} + r_{\text{iso-BA}})$.

[c] The pretreatment was performed for 48h.

[d] The ethylene hydroformylation was followed by the propylene hydroformylation.

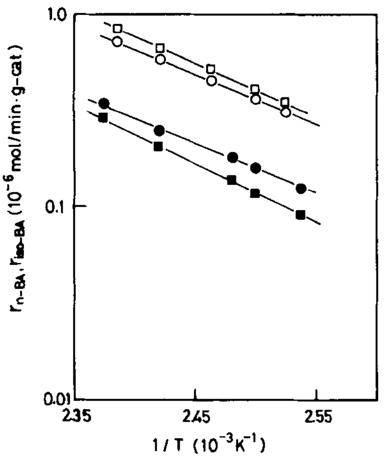

FIG. 5. Effect of reaction temperature on $r_{n\text{-BA}}$ and $r_{iso\text{-BA}}$ on the Rh–Y (No. 6). ○,□: $r_{n\text{-BA}}$ and $r_{iso\text{-BA}}$ on the untreated catalyst, ●,■: $r_{n\text{-BA}}$ and $r_{iso\text{-BA}}$ on the catalyst pretreated with He–H_2, respectively. Reaction conditions: He–C_3H_6(30%)–CO(10%)–H_2(30%).

remarkable particularly with the $RhCl_3/SiO_2$ catalyst. The observed E_{PA} is 42 kJ/mol on the pretreated $RhCl_3/SiO_2$ and 43 kJ/mol on the pretreated $RhCl_3/Al_2O_3$ catalyst.

The $RhCl_3/SiO_2$ catalyst can promote propylene hydroformylation, with the *n*-isomer selectivity being 0.36 (Table 2).

5. *Desorption of Propionaldehyde and Butyraldehyde*

The desorption of propionaldehyde from the catalyst into the He–CO (10%) stream at 127°C was compared with that of butyraldehyde in Fig. 6. It was observed that butyraldehyde desorbs much faster than propionaldehyde.

DISCUSSION

As shown in Fig. 2, the long induction period is shortened by the preadsorption of propionaldehyde. The amount of irreversibly adsorbed propionaldehyde on the fresh catalyst, 3.4 × 10^{-3} mol/g cat, is similar to that on the Na–Y zeolite. This amount corresponds to ca. 0.25 cm^3/g cat of liquid at 20°C, and it is roughly estimated that about three-quarters of the pore volume of the Y-type zeolite (0.34 cm^3/g) is occupied by the accumulated products. The area (II) in Fig. 2 gives the approximate amount of reversibly adsorbed propionaldehyde which is estimated to be 0.15 × 10^{-3} mol/g cat at its corresponding partial pressure. This amount nearly coincides with the amount of desorbed propionaldehyde from the catalyst which is estimated to be 0.12 × 10^{-3} mol/g cat from the area (III) in Fig. 2. These results indicate that the large amount of propionaldehyde required to complete the irreversible adsorption is produced during the induction period. The irreversible adsorption presumably corresponds to the formation of nonvolatile compounds due to aldol condensation which is observed on the silica-supported rhodium complex catalyst by Gerritsen *et al.* (*11*). The area (I) in Fig. 2 corresponds to the total amount of decomposed and adsorbed propionaldehyde on the catalyst if it is assumed that the constant activity is attained at the beginning of the reaction. This amount is estimated to be 0.82 × 10^{-3} mol/g cat and is much less than the amount of irreversibly adsorbed propionaldehyde on the fresh catalyst. These findings indicate that, in spite

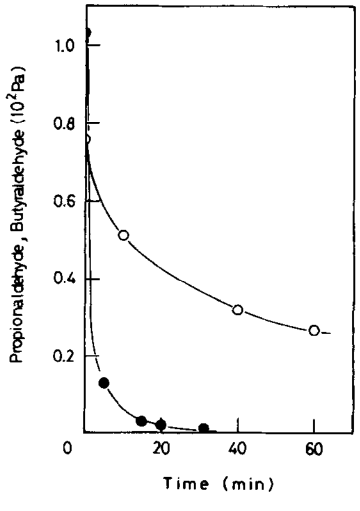

FIG. 6. Desorption of propionaldehyde and butyraldehyde from the catalyst into the He–CO(10%) stream at 400 K. ○, propionaldehyde (Rh–Y (No. 4) pretreated with He–H_2, 2.5 g); ●, butyraldehyde (Rh–Y (No. 7) untreated, 3.5 g).

of the apparent increase, the formation of propionaldehyde decreases with time on stream so as to complete the irreversible adsorption.

The pretreatment of the catalyst with He–H_2 affects both of the rates, r_{PA} and r_{BA}, and the apparent activation energy, E_{PA}, considerably. However, the catalyst with a relatively low rhodium content is very different from the catalyst with a relatively high rhodium content when the effects of the pretreatment are compared. The Rh–Y (No. 1), pretreated and untreated, and the Rh–Y (No. 6) untreated are clearly distinguishable from the Rh–Y (No. 6) pretreated. The former ones are characterized by the lower E_{PA} as well as by the lower $S_{n\text{-BA}}$ and are denoted as Type A. The latter, on the other hand, is characterized by the higher E_{PA} and the higher $S_{n\text{-BA}}$, and is denoted as Type B. The untreated catalysts over the whole range of rhodium content and the pretreated catalysts with a rhodium content less than 110 × 10^{-6} mol/g cat belong to Type A. Only two catalysts, the pretreated Rh–Y (No. 6) and Rh–Y (No. 7), belong to Type B. Such classification is made on the basis of the following results; (1) E_{PA} on the catalysts in the same class is equal, (2) as shown in Fig. 7, the plots of r_{PA} vs r_{BA} on the catalysts of Type A give a straight line through the origin, but those on the catalysts of different type do not fall on or near the same line.

The mean pore size in silica gel is greater than that in zeolites. On the $RhCl_3/SiO_2$ catalyst, E_{PA} is very close to that on Type A, and $S_{n\text{-BA}}$ is smaller than that on Type A. In addition, Fig. 7 shows that the active sites on Type A can catalyze both the hydroformylation of ethylene and propylene. These results suggest that the active sites on Type A are located at the external surface of zeolite or in the entrance of the pore.

The higher E_{PA} on the catalysts of Type B, indicates that an appreciable change in the nature of the active sites is induced by the pretreatment. The higher reduction in r_{BA} relative to r_{PA} by the pretreatment suggests that some portion of the active sites on Type B is effectively used for the hydroformylation of ethylene but not for propylene. Appreciable differences in the nature of the active sites which can catalyze propylene hydroformylation are also found on Type B, since $S_{n\text{-BA}}$ on Type B is much higher than that on Type A. The fact that there is no change in $E_{n\text{-BA}}$ and $E_{\text{iso-BA}}$ as a function of the pretreatment suggests that changes in the nature of the active sites which can catalyze propylene hydroformylation are not as remarkable as those on the active sites which can catalyze only ethylene hydroformylation. It may be that the active sites on Type B are in the pore and at a somewhat further distance from the entrance than that on Type A. The active sites which can catalyze ethylene but not propylene hydroformylation are located in the pore much further from the entrance than the active sites which can catalyze both kinds of hydroformylation. The higher energy barrier to forming the activated complex leading to propionaldehyde may be due to the greater steric influence by the walls of the zeolite pore and by the accumulated products. This would account for the higher E_{PA} on Type B. The higher $S_{n\text{-BA}}$ can also be explained by the steric influence in the zeolite pore.

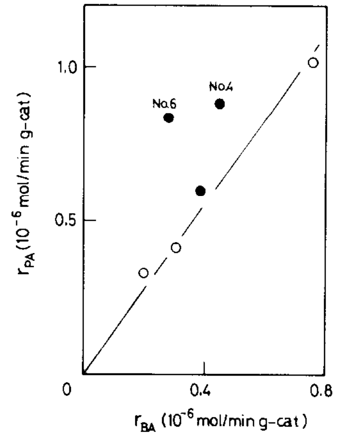

FIG. 7. r_{PA} vs r_{BA} plots. ○, on the untreated catalyst; ●, on the catalyst pretreated with He–H_2.

The intermediate values for r_{PA}/r_{BA} and $S_{n\text{-BA}}$ as a function of the He–H_2 pretreatment of the Rh–Y (No. 4 and 5) suggest the broad distribution in location of the active sites in these catalysts.

Since butyraldehyde is more bulky than propionaldehyde, if the pores of the zeolite were used in the propylene hydroformylation as well as in the ethylene hydroformylation, the desorption of butyraldehyde from the catalyst might be slower than that of propionaldehyde. The fact is that butyraldehyde desorbs much faster than propionaldehyde as shown in Fig. 6, indicating that butyraldehyde is produced on the active sites located at the entrance of the pores or external surface, and that a smaller portion of the pores is used for the reversible adsorption of butyraldehyde compared to propionaldehyde.

Consequently, the active sites which contribute to the steady-state activity are the ones located in the pores at a very short distance from the entrance and the ones at the external surface of the zeolite. This may be the location of the rhodium species in the Rh–Y zeolite prepared by our technique. Rhodium would be present partly in anionic and partly in nonionic form when rhodium trichloride trihydrate is dissolved in water (*12*), since the compound available from commercial sources usually contains excess amount of Cl in "$RhCl_3$." In fact, rhodium is supported on an anion-exchange resin (Amberlite IRA 410). This might exclude the direct cation exchange of rhodium species with Na–Y zeolite. Rhodium, however, is also supported on a cation-exchange resin (Amberlite 120 B), although the rate of rhodium anchored on a H-Type resin is considerably slower than that on a Na-type resin (*13*). It may be assumed that rhodium sticks on the Na-type resin as a rhodium hydroxide (containing one or two Cl^-) due to the increase in OH^- concentration in the solution which is caused by the cation exchange between H^+ in the solution and Na^+ on the solid. The formed hydroxide, however, would not fall from the resin as a separate phase, suggesting that it might strongly interact with the anionic site(s) of the resin. This process may correspond to the replacement of Cl^- in the rhodium species by the anionic sites in the resin. The same process might be occurring on the Na–Y zeolite. Therefore, the majority of rhodium species might be present at the external surface of the zeolite, and the minority of them in the pore but near the entrance. Andersson and Scurrell (*14*) have suggested that the rhodium species loaded on the Rh–X zeolite have strongly interacted with the zeolite lattice and that the concentration of rhodium at the surface has been higher than that expected for the uniform dispersion of rhodium through the catalyst bulk. One of the important roles of hydrogen in forming the active species may be an action of removing OH^- and Cl^- from the rhodium sites. These points will be discussed later.

Although we do not discuss the hydrogenation in detail, it is suggested that the active sites for the hydrogenation are different from those for the hydroformylation. The apparent activation energy, E_E, was enhanced by the pretreatment even on the catalysts with a rhodium content less than 110×10^{-6} mol/g cat, and the enhancement in r_E was much more remarkable than that in r_{PA} in most of the Rh–Y zeolite catalysts. It is not clear whether the active sites for the hydroformylation can catalyze hydrogenation. Nevertheless, it seems that the hydrogenation is mainly catalyzed by metallic rhodium particles which are active for the hydrogenation but not for the hydroformylation, since the catalyst pretreated with He–H_2 at 310°C exhibited almost no activity for the hydroformylation while it did catalyze the hydrogenation (*13*).

CONCLUSION

Rh–Y zeolite can promote both ethylene and propylene hydroformylation under atmospheric pressure in a continuous-flow system. Constant activity lasts more than 1 month even though the activity and the selectivity are not high enough to use for the synthesis of propionaldehyde. The active sites which are responsible for the constant activity are located at the external surface or in the pore at a very short distance from the entrance. On the active sites formed at an inner position from the entrance, propylene hydroformylation is not possible while ethylene hydroformylation is still possible. It is suggested that the active site is too bulky to catalyze the reaction for olefins which are more bulky than propylene in the pore of the zeolite, where it might be partly blocked by the accumulated products from aldehyde.

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