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Comparison of Pentan-3-one Formation with Propionaldehyde Formation during Ethylene Hydroformylation over Rh/Active Carbon Catalyst

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The rhodium supported on active carbon has been found to be active for pentan-3-one formation from C_2H_4, CO, and H_2, as well as propionaldehyde formation. Among three Rh/active carbon catalysts prepared from different kinds of rhodium compounds ($RhCl_3$, $Rh(NO_3)_3$, and $Rh(CH_3COO)_3$), one prepared from $RhCl_3$ showed the highest activity for pentan-3-one formation. Comparing pentan-3-one formation with propionaldehyde formation, the effects of the following factors on the catalytic activity were observed to be different in both reactions; (i) effects of reaction temperature, (ii) effects on H_2 pretreatment of catalysts, and (iii) effects of partial pressure of CO. On pentan-3-one formation, $^{13}C_2H_5CO^{13}C_2H_5$ and $C_2H_5^{13}COC_2H_5$ were found to be the predominant products in the reaction of propionaldehyde–$^{13}C_2H_4$–CO–H_2 and of propionaldehyde–C_2H_4–^{13}CO–H_2, respectively. These results indicate that the route for pentan-3-one formation is the reaction among two molecules of C_2H_4 and each one molecule of CO and H_2, and not the reaction between C_2H_4 and propionaldehyde.

INTRODUCTION

In olefin hydroformylation over heterogeneous rhodium catalysts, aldehyde(s) and alcohol(s) have been observed to be hydroformylation products (*1–8*). Aldol condensation products from aldehyde(s) are also reported to be byproducts (*3, 9*). Ketone formation from olefin, carbon monoxide, and hydrogen has not been a common reaction over the heterogeneous rhodium catalysts, while a few homogeneous catalyst systems have been found to be active for this reaction (*10, 11*). Rode *et al.* reported that 2-methylhexan-3-one and heptan-4-one were produced by Rh/zeolites from propylene (C_3H_6), CO, and H_2 (12). They have proposed the bifunctional behavior of the Rh/Y-zeolite for the ketone formation; i.e., butyraldehyde formation by hydroformylation over the rhodium sites and ketone formation by the reaction between C_3H_6 and butyraldehyde on the zeolite support.

Rhodium supported on active carbon has been found to be active for ethylene hydroformylation as well as other supported Rh catalysts. In the former case, however, a considerable amount of pentan-3-one (diethylketone; DEK) was formed during the reaction, particularly at the reaction temperatures lower than 393 K (*13*). This catalytic behavior is very different from that of other supported rhodium catalysts. In the present work, the catalytic behavior of Rh/active carbon for pentan-3-one formation has been compared with that for propionaldehyde formation. In addition, the reaction route for pentan-3-one formation has been discussed.

EXPERIMENTAL

Rh/active carbon catalysts were prepared by a conventional impregnation method

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from an aqueous solution of rhodium salt and active carbon (obtained from Wako Pure Chemicals Inc., specific surface area = 930 m^2/g). In the present work, the following three kinds of rhodium salts were used: rhodium trichloride trihydrate ($RhCl_33H_2O$ will be simply represented by $RhCl_3$ in this work), rhodium trinitrate ($Rh(NO_3)_3$), and rhodium triacetate ($Rh(CH_3COO)_3$). The standard Rh/active carbon catalyst (denoted by Rh/AC) was prepared from $RhCl_3$. The catalysts prepared from $Rh(NO_3)_3$ and $Rh(CH_3COO)_3$ are denoted by Rh(N)/AC and Rh(A)/AC, respectively. Other supported rhodium catalysts were prepared in the same manner using $RhCl_3$ and the following supports: SiO_2, Al_2O_3, SiO_2–Al_2O_3, ZrO_2, $ZrSiO_4$, or MgO. Rh/Y-zeolite was prepared by a conventional cation exchange procedure from $RhCl_3$ and Na/Y-zeolite (*4*). The rhodium contents on the catalysts prepared were 2.0 wt%-Rh as a metal (194×10^{-6} mol/g-cat).

An apparatus used for ethylene hydroformylation was a fixed-bed-type reactor with a continuous flow at atmospheric pressure. The catalyst (0.50 g) placed in the reactor was pretreated with hydrogen (50 cm^3(STP) min^{-1}), usually at 573 K for 3 h, and cooled below 323 K in the H_2 flow. A reaction mixture of He–C_2H_4–CO–H_2 (total flow rate = 100 cm^3 min^{-1}, and a concentration of each reactant was usually 20%) was fed to start the reaction, and then the catalyst bed was heated to the temperature at which the reaction should be performed. Concentrations of products in the effluent gas stream were determined by gas chromatography. The reaction between propionaldehyde and ethylene was also carried out in the same apparatus.

The reaction of propionaldehyde–$^{13}C_2H_4$(98 atom%)–CO–H_2 or propionaldehyde–C_2H_4–^{13}CO(99 atom%)–H_2 was carried out by using a glass-made apparatus with a recirculating system (390 cm^3) connected to a vacuum line. The catalyst (0.50 g) placed in the reactor was pretreated with H_2 at 573 K for 3 h, and cooled to room temperature. Introduction of propionaldehyde (0.6×10^{-3} mol) and each 1.8×10^{-3} mol of other reactants into the system was followed by the reaction at 393 K. After the reaction for 8 h, organic compounds in the reaction mixture were collected in a liquid nitrogen trap, and the sample was analyzed by a GC-MS spectrometer in order to determine the distribution of ^{13}C in pentan-3-one formed.

Adsorption measurements of hydrogen (H_2) were carried out by a conventional static method using a glass-made vacuum line at room temperature. The amount of H_2 required to attain the monolayer coverage was estimated by extrapolating a linear part of adsorption isotherm to zero of equilibrium pressure. The values for %-exposed of Rh were estimated on the basis that each one surface rhodium atom can adsorb one hydrogen atom.

RESULTS AND DISCUSSION

Main products in the reaction of C_2H_4, CO, and H_2 over the Rh/AC catalyst were found to be propionaldehyde, pentan-3-one, and ethane (rates of formation for these three products are denoted by r_{PA}, r_{DEK}, and r_E, respectively). Changes in the rates with time on stream during the reaction at 373, 393, and 413 K are shown in Fig. 1 ((a) propionaldehyde; (b) pentan-3-one; (c) ethane), and the values of the reaction rates at time on stream of 10 h are summarized in Table 1 (runs 1–4). In the reaction at 373 and 393 K, r_{DEK} increased with time on stream at the early stage of the reaction, and then it decreased very slowly (r_{DEK} at 72 h of time on stream was ca. 70% of that at 10 h). The difference in the shape of the time course between r_{PA} and r_{DEK} is probably due to the accumulation of pentan-3-one on the catalyst because of its high boiling point (373.7 K). In the reaction at 373 K, r_{DEK} was observed to be slightly higher than r_{PA} after time on stream of ca. 7 h. As can be seen from the results shown in Table 1 (runs 1–4), the ratio of r_{DEK}/r_{PA} increased with the decrease in the reaction temperature. How-

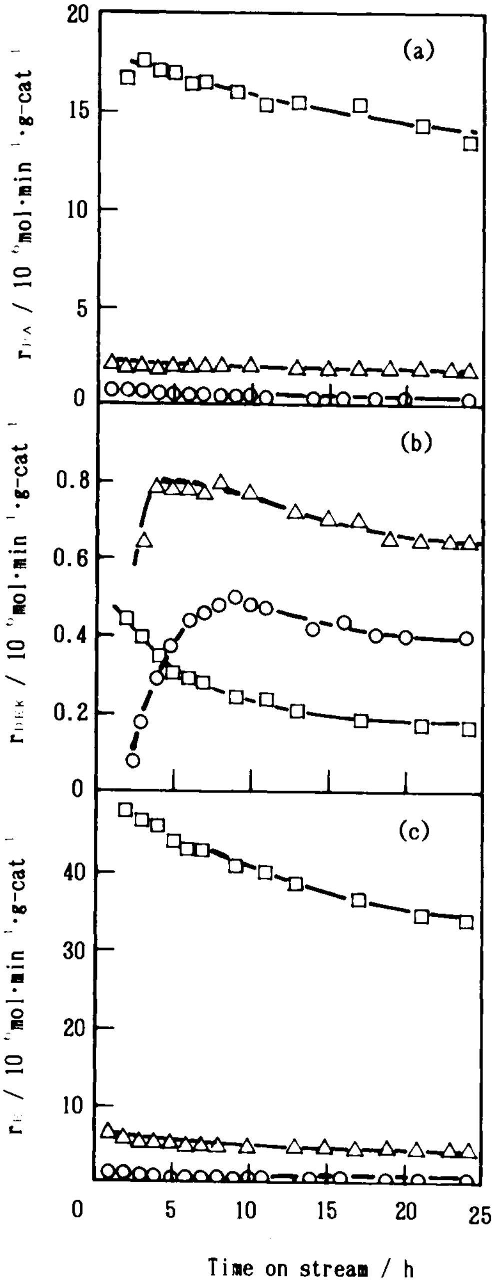

FIG. 1. Changes in r_{PA}, r_{DEK}, and r_E with time on stream during ethylene hydroformylation ((a), propionaldehyde; (b), pentan-3-one; (c), ethane) (○, at 373 K; △, at 393 K; □, at 413 K).

TABLE 1

Reaction of C_2H_4, CO, and H_2 over Various Supported Rh Catalysts

Catalyst	Reaction temperature	Activity[a]		
		r_{PA}	r_{DEK}	r_E
		(10^{-6}mol · min^{-1} · g-cat^{-1})		
Rh/AC	363	0.1	0.2	0.4
	373	0.4	0.5	0.7
	393	2.0	0.8	4.5
	413	16.0	0.3	40.2
Rh/SiO_2	393	1.6	—[b]	2.3
Rh/Al_2O_3	393	1.3	—	5.2
Rh/SiO_2–Al_2O_3	393	1.6	—	6.0
Rh/ZrO_2	393	1.3	—	4.4
Rh/$ZrSiO_4$	393	0.9	—	1.9
Rh/MgO	393	0.1	—	0.4
Rh/Y-zeolite	393	1.7	0.1	2.7

[a] Activities were evaluated by r_{PA}, r_{DEK}, and r_E at time on stream of 10 h (reaction temperature: 393 K).

[b] Formation of pentan-3-one was not observed.

ever, the decrease in r_{DEK} with time on stream at 413 K was much faster than those at 373 and 393 K, and r_{DEK} at 413 K (at 10 h) was observed to be much lower than that at 373 K. In addition, r_{DEK} at 393 K on the catalyst once used for the reaction at higher temperatures than 413 K, was much lower than that on the catalyst not used for the reaction at >413 K. These results suggest the fast and irreversible deactivation of the active sites for pentan-3-one formation during the reaction at temperatures >413 K. Namely, the decrease in r_{DEK} observed at 413 K was due to the decrease in number of the active sites for pentan-3-one formation. On the other hand, the activities, r_{PA} and r_E, sharply increased with the increase in the reaction temperature, as shown in Fig. 1. Both of the apparent activation energies for r_{PA} and r_E were estimated to be more than 100 kJ/mol, and these values were much higher than those on other supported rhodium catalysts reported (*2*, *5*). On this point, however, will be discussed in detail at another time.

Other catalysts prepared were active for propionaldehyde and ethane formation as well as the Rh/AC catalyst. Time courses for both products were found to be similar to those on the Rh/AC catalyst, except the Rh/Y-zeolite on which an induction period for several hours was observed for propionaldehyde formation. The catalytic activities

TABLE 2

Comparison of Catalytic Behavior of Rh/AC Catalysts Prepared from Different Rh Compounds

Catalyst	Rhodium compound	Activity[a]			%-exposed[b]
		r_{PA}	r_{DEK}	r_E	
		(10^{-6} mol · min^{-1} · g-cat^{-1})			
Rh/AC	$RhCl_3 \cdot 3H_2O$	2.0	0.8	4.5	29
Rh(N)/AC	$Rh(NO_3)_3$	2.7	0.2	2.9	33
Rh(A)/AC	$Rh(CH_3COO)_3$	3.6	<0.1	3.3	9

[a] Activities were evaluated by r_{PA}, r_{DEK}, and r_E at time on stream of 10 h (reaction temperature: 393 K).

[b] Values for %-exposed were estimated from the amounts of H_2 adsorbed.

evaluated by the values of r_{PA}, r_{DEK}, and r_E at the time on stream of 10 h are summarized in Table 1. No appreciable formation of pentan-3-one, however, was observed when rhodium was supported on SiO_2, Al_2O_3, SiO_2–Al_2O_3, ZrO_2, and $ZrSiO_4$, where both r_{PA} and r_E were found to be almost comparable to those on the Rh/AC catalyst. Rhodium supported on MgO was much less active for ethylene hydroformylation than other catalysts, and it also did not show any activity for pentan-3-one formation. One exception was Rh/Y-zeolite, where r_{DEK} on it was found to be much lower than that on the Rh/AC catalyst.

The activities on the catalysts prepared from different rhodium compounds are shown in Table 2. Among these three catalysts, the Rh(A)/AC catalyst prepared from $Rh(CH_3COO)_3$ was the most effective for propionaldehyde formation, not only in the activity but also in the selectivity. On the other hand, the Rh/AC catalyst prepared from $RhCl_3$ was found to be much effective for pentan-3-one formation compared with the Rh(N)/AC and Rh(A)/AC catalysts. The value for %-exposed of Rh are also listed in Table 2. The value on the Rh/AC catalyst was close to that on the Rh(N)/AC catalyst, and it was much higher than that on the Rh(A)/AC catalyst. Thus, any strong relation between the activity and the %-exposed was not observed for both reactions.

Effects on the temperature for the pretreatment of the Rh/AC catalyst with H_2 on the activities are shown in Fig. 2. The rates, r_{PA} and r_E, increased with the increase in the temperature for the pretreatment. However, changes in r_{DEK} with the pretreatment temperature were found to be small compared with those on r_{PA}.

Effects of partial pressures of the reactants on the activities are examined as follows. The pretreatment of the fresh catalyst with H_2 at 573 K was followed by the reaction at 393 K in the reaction gas with the desired composition of reactants. The reaction orders with respect to the three reactants (C_2H_4, H_2, and CO) are summarized in Table 3, when a rate is expressed by a power-law form as shown by the following:

$$r = kP^{l}_{C_2H_4}P^{m}_{H_2}P^{n}_{CO}.$$

The rate, r_{DEK}, increased with the increase in the partial pressure of C_2H_4 as well as r_{PA} and r_E. The rates, r_{PA} and r_E, increased with the increase in H_2 partial pressure with almost first-order dependence and they rapidly decreased with the increase in the CO partial pressure. On the other hand, with respect to r_{DEK}, the order on the H_2 partial

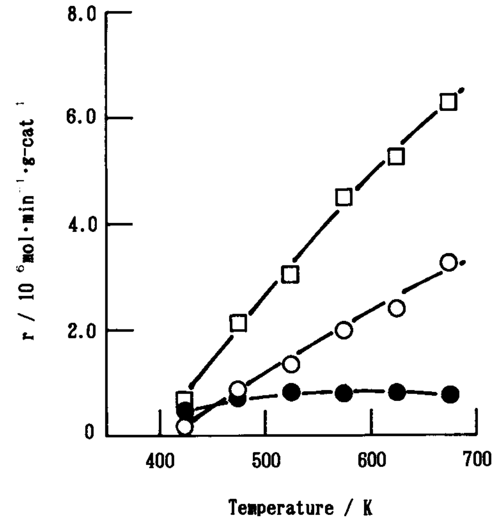

FIG. 2. Effects of temperature for pretreatment of the catalyst with H_2 on r_{PA}, r_{DEK}, and r_E (○, propionaldehyde; ●, pentan-3-one; □, ethane).

TABLE 3

Partial Pressure Dependencies of Reaction Rates on Three Reactants

Rate	C_2H_4 l	H_2 m	CO n
r_{PA}	0.5	0.9	−1.1
r_{DEK}	0.7	0.4	0.5
r_E	0.8	0.9	−1.6

Note. l, m, n are reaction orders in a power-low form rate expression, $r = kP^l_{C_2H_4}P^m_{H_2}P^n_{CO}$.

pressure (ca. 0.4) was found to be lower than that on r_{PA} (0.9). In addition, a positive order for CO (0.5) was obtained with respect to r_{DEK}. Namely, r_{DEK} increased with the increase in the CO partial pressure in contrast to r_{PA}.

Accordingly, the catalytic behavior of Rh/AC for pentan-3-one formation was observed to be different from that for propionaldehyde formation in the following points: (1) effects of reaction temperature, (2) effects of pretreatment temperature with H_2, and (3) effects of partial pressure of CO. These results suggest that the active sites for pentan-3-one formation are different from those for propionaldehyde and ethane formation. At the present time, however, we have not clarified the difference between them.

Rode *et al.* have reported that the selectivity to ketone formation was significantly enhanced when the Rh/Y was prepared by a cation exchange procedure in the presence of NaCl (*12*). Effects of modification of the Rh/AC catalyst with LiCl, NaCl, or KCl on the catalytic activities are shown in Table 4. In contrast to the Rh/Y-zeolite, the selectivity to pentan-3-one decreased when the catalyst was modified with such salts.

The reaction route for propionaldehyde formation is generally proposed as follows:

$$C_2H_4 + * \rightleftharpoons *(C_2H_4) \qquad (1)$$

$$H_2 + 2* \rightleftharpoons 2*(H) \qquad (2)$$

$$CO + * \rightleftharpoons *(CO) \qquad (3)$$

$$*(C_2H_4) + *(H) \rightarrow *(C_2H_5) + * \qquad (4)$$

$$*(C_2H_5) + *(CO) \rightarrow *(C_2H_5CO) + * \qquad (5)$$

$$*(C_2H_5CO) + *(H) \rightarrow *(C_2H_5CHO) + *. \qquad (6)$$

In the above reaction steps, * represents the active site for propionaldehyde formation. Steps (1) and (3) correspond to the adsorption of C_2H_4 and CO, respectively, and (2) corresponds to the dissociative adsorption of H_2 on the active sites.

The following two reaction routes may be possible for pentan-3-one formation. The first one is the reaction between propionaldehyde and C_2H_4 over the support or the catalyst as reported on ketone formation from C_3H_6, CO and H_2 over Rh/Y-zeolite by Rode *et al.* (*12*) (this reaction route will be expressed by route (A) in the following part). The second one is the reaction among two molecules of C_2H_4 and each one molecule of CO and H_2, and this route may be expressed by the reaction sequences similar to those for propionaldehyde, where * in steps (1)–(5) is replaced by *′, which represents the active site for pentan-3-one formation. And step (6) is also replaced by step (6′) as follows:

$$*'(C_2H_5CO) + *'(C_2H_5) \rightarrow *'(C_2H_5COC_2H_5) + *'. \qquad (6')$$

TABLE 4

Effects of Catalyst Modification by LiCl, NaCl, or KCl on Catalytic Activities

Additive	Molar ratio against Rh	r_{PA}	r_{DEK} (10^{-6} mol · min^{-1} · g-cat^{-1})	r_E
None	—	2.0	0.8	4.5
LiCl	1.0	2.1	0.4	2.7
LiCl	3.0	1.5	0.2	1.9
NaCl	1.0	2.1	0.7	4.2
NaCl	3.0	2.2	0.6	3.8
KCl	3.0	2.5	0.3	3.3

Note. Reaction conditions: He–C_2H_4(20%)–CO(20%)–H_2(20%), at 393 K. Activities were evaluated by the values of r_{PA}, r_{DEK}, and r_E, at time on stream of 10 h.

TABLE 5

Reaction of Propionaldehyde (PA) in the Various Reaction Mixtures over Materials Used as a Support and Catalysts

Reaction mixture	Catalyst	Formation of pentan-3-one
I PA + CO + H_2	Rh/AC, Rh/Y-zeolite	NO
II PA + C_2H_4	AC, SiO_2, Na/Y-zeolite Rh/AC, Rh/SiO_2, Rh/Y-zeolite	NO
III PA + C_2H_4 + H_2	AC, Na/Y-zeolite Rh/AC, Rh/Y-zeolite	NO
IV PA + C_2H_4 + CO	AC, SiO_2, Na/Y-zeolite Rh/AC, Rh/SiO_2, Rh/Y-zeolite	NO

Note. Feed rates: propionaldehyde = 3.0×10^{-6} mol · min^{-1} · g^{-1}; each other components = 0.84×10^{-3} mol · min^{-1} · g^{-1}; total flow rate = 100 cm_3 (STP) · min^{-1} (balanced with He).

This reaction route will be denoted by route (B).

In order to clarify the possibility of reaction route (A), the following experiments were carried out. The reaction gas mixtures containing propionaldehyde (denoted by PA) and C_2H_4 shown in Table 5, were passed over the support (active carbon, Na/Y-zeolite, SiO_2) or the catalyst (Rh/AC, Rh/Y-zeolite, Rh/SiO_2) at 393 K. We confirmed that formation of pentan-3-one from the mixture of PA + CO + H_2 did not take place over the Rh/AC catalyst as well as the Rh/Y-zeolite (case I).

In the case of PA + C_2H_4 over the supports themselves (case II), almost all of PA and C_2H_4 introduced into the system was recovered except at the early stage of the reaction where the irreversible adsorption of PA was observed. On every supports investigated, no appreciable formation of pentan-3-one was observed not only during the irreversible adsorption of PA but also after the completion of it. Even in the presence of H_2 or CO, every supports did not show any activity for pentan-3-one formation from PA + C_2H_4 (cases III and IV).

In the case of the Rh catalysts, however, a large part of PA (ca. 70% at time on stream of 5 h in the case of Rh/AC) was decomposed into C_2H_6 when the reaction mixture of II (PA + C_2H_4) was passed over the catalyst. The presence of H_2 in the reaction mixture (case III), accelerated ethylene hydrogenation as well as propionaldehyde decomposition. Although almost all of PA and C_2H_4 was converted into C_2H_6 at the early stage of the reaction, a small amount of PA and C_2H_4 was recovered at the exit of the reactor after several hours of time on stream. In both cases of II and III, no appreciable formation of pentan-3-one was observed. In the presence of CO in the reaction gas mixture, the decomposition of propionaldehyde was considerably suppressed. As shown by case IV, however, the three Rh catalysts also did not show any activities for pentan-3-one formation from PA + C_2H_4. Consequently, neither the supports themselves nor the Rh catalysts were found to be effective for pentan-3-one formation from propionaldehyde and C_2H_4 under the conditions studied.

The results shown in Table 5, however, never exclude the possibility of reaction route (A) perfectly, since all of reaction components, i.e., propionaldehyde, C_2H_4, CO, and H_2, were present in the system when the formation of pentan-3-one was observed. In order to get more concrete

TABLE 6

Composition of Pentan-3-one Formed during Reaction of Mixtures Containing Propionaldehyde (PA) and ^{13}C-Labeled Compound over Rh/AC (Samples 1 and 2) and Rh/Y-Zeolite (samples 3 and 4)

Sample		Relative intensity						
	MN[a]	84	85	86	87	88	89	90
Pentan-3-one				100	4			
Sample 1						4	8	100
Sample 2				2	100	5		
Sample 3							5	100
Sample 4					100	3		

Note. Samples 1 and 3: PA + $^{13}C_2H_4$ + CO + H_2; samples 2 and 4: PA + C_2H_4 + ^{13}CO + H_2.

[a] Mass number.

evidence to exclude the possibility of route (A), the following experiments using ^{13}C-labeled compounds were carried out. The first run was the reaction of propionaldehyde, $^{13}C_2H_4$, CO, and H_2. The second run was the reaction of propionaldehyde, C_2H_4, ^{13}CO, and H_2. Although the composition of $^{13}C_2H_5CHO$ or $C_2H_5^{13}CHO$ increased with the reaction time in the actual catalytic runs, pentan-3-one expected from reaction route (A) should be mainly $C_2H_5CO^{13}C_2H_5$ (mass number (MN) = 88) (not $^{13}C_2H_5CO^{13}C_2H_5$ (MN = 90)) in the first run and $C_2H_5COC_2H_5$ (MN = 86) (not $C_2H_5^{13}COC_2H_5$ (MN = 87)) in the second run, respectively. On the other hand, if pentan-3-one was formed through reaction route (B), the mass number of pentan-3-one formed should be 90 in the first run and 87 in the second run. As shown in Table 6, pentan-3-one formed was almost predominantly $^{13}C_2H_5CO^{13}C_2H_5$ (MN90) in the first run (sample 1) and $C_2H_5^{13}COC_2H_5$ (MN87) in the second run (sample 2), respectively. These results clearly show that almost all of pentan-3-one is directly formed from C_2H_4, CO, and H_2, not from ethylene and propionaldehyde. Namely, the reaction route for pentan-3-one formation over the Rh/AC catalyst is route (B). Accordingly, the reaction route for pentan-3-one formation was found to be similar to that for propionaldehyde formation except the final step, which was the reaction between an acyl group and an ethyl group in the former and the reaction between an acyl group and an adsorbed hydrogen in the latter.

The control experiments on Rh/Y-zeolite with use of ^{13}C-labeled compounds were carried out. As shown in Table 6 (samples 3 and 4), the results obtained on Rh/Y-zeolite and on Rh/AC are essentially the same, suggesting the same reaction route for pentan-3-one formation on both catalysts. Thus, the reaction route for pentan-3-one formation from C_2H_4, CO, and H_2 has been found to be very different from that for ketone formation from C_3H_6, CO, and H_2 over Rh/Y-zeolite. At the present time, however, we have not clarified the relation between these two cases.

In conclusion, we have found that the rhodium supported on active carbon was effective for pentan-3-one formation from C_2H_4, CO and H_2. Particularly, the Rh/AC catalyst prepared from $RhCl_3$ was found to be much more active for pentan-3-one formation than the catalysts prepared from $Rh(NO_3)_3$ or $Rh(CH_3COO)_3$. The effects of reaction temperature, of pretreatment temperature with H_2, and of partial pressure of CO on the formation of pentan-3-one, were found to be very different from those on the formation of propionaldehyde. By using ^{13}C-labeled compounds, it is clarified that pentan-3-one is formed from two molecules of C_2H_4 and each one molecule of carbon monoxide and hydrogen over the active sites on the Rh/AC catalyst, and not from each one molecule of C_2H_4 and propionaldehyde.

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