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Reaction of Propionaldehyde over Rh-Y Zeolite

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During the desorption of propionaldehyde from the Rh-Y zeolite into a He–CO(10%) stream, the concentration of propionaldehyde decreased with desorption time. *n*-Propanol formation was enhanced in the desorption of propionaldehyde into a He–H_2(10%) stream, while no appreciable enhancement was observed in the desorption into a He–H_2(10%)–CO(10%) stream. A faster decrease in the concentration of propionaldehyde was observed during the desorption into a helium stream than the desorption into the He–CO stream. In the desorption into the helium stream, formation of pentene was observed. However, no formation of pentene was observed in the desorption into a He–C_2H_4(10%) stream. In the desorption into a He–C_3H_6(10%) stream, the rate of pentene formation was lower than that in the desorption into the helium stream. These results suggest that the pentene is not formed by ethylene–propylene codimerization. The reduced $RhCl_3/SiO_2$ catalyst which was physically mixed with the Na-Y zeolite showed comparable activity for pentene formation to that of Rh-Y zeolite in the reaction of propionaldehyde. However, neither the $RhCl_3/SiO_2$ catalyst nor the Na-Y zeolite was effective by itself for pentene formation. The reduced $RhCl_3/SiO_2$ and Rh-Y zeolite catalysts also showed activity for pentene formation in the reaction of 2-methyl-2-pentenal which is the product of aldol condensation of propionaldehyde. On the basis of the results, two sequential reactions, aldol condensation of propionaldehyde by the zeolite support followed by decarbonylation of 2-methyl-2-pentenal by rhodium metal particles, are proposed as a reaction path for the formation of pentene over the Rh-Y zeolite.

INTRODUCTION

Zeolite catalysts containing transition metal cations are expected to be bifunctional in some cases; the first function is attributed to the supported transition metal component and the second one is due to the zeolite support. Such dual function is typically observed in hydrocarbon reforming over noble metal-containing zeolites, where isomerization occurs over the acid sites on the zeolite support and hydrogen abstraction and hydrogenation occur over the supported noble metals.

The Rh-Y zeolite is active for the following reactions; ethylene dimerization (*1, 2*), methanol carbonylation (*3–5*), and olefin hydroformylation (*6–9*). These reactions are essentially catalyzed by rhodium species on the catalyst. Previously, we have found that pentene was formed from propionaldehyde adsorbed on the Rh-Y zeolite (*10*). Propionaldehyde undergoes various reactions; for example, aldol condensation is catalyzed by bases or acids, and hydrogenation or decomposition in the presence of hydrogen is catalyzed by transition metal catalysts (e.g., Ni/SiO_2) (*11*). However, there have been few reports with respect to the details of pentene formation from propionaldehyde. The aim of the present study is to clarify the catalysis of the Rh-Y zeolite for propionaldehyde.

EXPERIMENTAL

Catalysts. The Rh-Y zeolite which contains 150×10^{-6} mol-Rh/g-cat (1.55 wt% Rh) was prepared from Na-Y zeolite and an aqueous solution of rhodium trichloride trihydrate. The $RhCl_3/SiO_2$ catalyst (2.0 wt% of Rh) was prepared by a conventional impregnation method. Details of catalysts

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preparation have been described elsewhere (*8*).

Desorption of propionaldehyde. The apparatus used was a fixed-bed reactor with a continuous flow system at atmospheric pressure. Desorption of propionaldehyde from the catalyst was carried out as follows. The catalyst (2.5 g) was placed in the reactor and pretreated with a He–H_2(10%) stream (total flow rate = 70 cm^3(STP)/min) at 400 K for 5 h. Ethylene hydroformylation was carried out at 400 K with a gas mixture of He–C_2H_4(10%)–CO(10%)–H_2(10%) at a total flow rate of 70 cm^3(STP)/min. After steady state for ethylene hydroformylation was attained, the gas stream was switched from the reactant gas to the carrier. Concentrations of products in the effluent gas stream were determined by gas chromatography.

Reaction of propionaldehyde and 2-methyl-2-pentenal. The propionaldehyde was purified by distillation of commercially available propionaldehyde. 2-Methyl-2-pentenal was prepared by aldol condensation of propionaldehyde.

In the case of the reaction of propionaldehyde, the catalyst (1.0 g) which was placed in a glass reactor was pretreated with the He–H_2 stream at 393 K for 5 h in the flow system described above. After the pretreatment with the He–H_2 stream, the catalyst was exposed to the helium stream containing propionaldehyde vapor until irreversible adsorption of propionaldehyde on the catalyst was completed. Then, the reactor was connected to a glass apparatus with a recirculating system (volume: 390 cm^3) connected to a vacuum line, and 3.2×10^{-3} mol of propionaldehyde was introduced into the system to start the reaction (reaction temperature = 400 K).

In the case of the reaction of 2-methyl-2-pentenal, the reactor was connected to the gas recirculating system after the catalysts had been reduced with the He–H_2 stream in the flow system. And then, 2.0×10^{-4} mol of 2-methyl-2-pentenal was introduced into the system to start the reaction at 400 K.

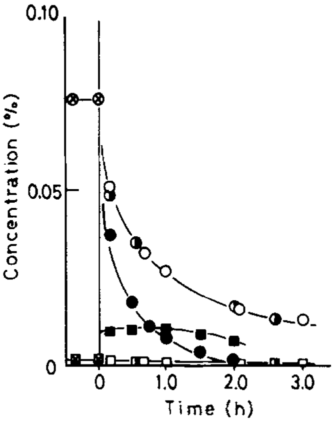

FIG. 1. Desorption of propionaldehyde from the Rh-Y zeolite—I (circles for propionaldehyde and squares for *n*-propanol). ○, □, into the He–CO(10%) stream; ●, ■, into the He–H_2(10%) stream; ◑, ◨, into the He–CO(10%)–H_2(10%) stream. ⊗, ☒, concentration at the steady state for ethylene hydroformylation.

RESULTS AND DISCUSSION

As shown in Fig. 1, the concentration of propionaldehyde decreased with time on stream during desorption into the He–CO(10%) stream. The concentration of *n*-propanol was very low when compared with that of propionaldehyde, and decreased very slowly with time on stream. During desorption into the He–H_2(10%) stream, the *n*-propanol formation was enhanced. The sum of the amounts of propionaldehyde and *n*-propanol desorbed into the He–H_2 stream nearly agreed with the amount of propionaldehyde desorbed into the He–CO stream. However, no acceleration of *n*-propanol formation was observed during desorption into the He–CO(10%)–H_2(10%) stream, suggesting that carbon monoxide adsorbed more strongly on the catalyst than hydrogen.

No products other than propionaldehyde and *n*-propanol were observed in the desorption runs shown in Fig. 1. On the other hand, desorption of propionaldehyde into the helium stream showed formation of several products. In this case, the concentration of desorbed propionaldehyde decreased more rapidly than that in the

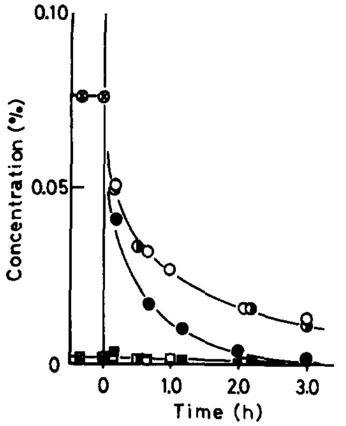

FIG. 2. Desorption of propionaldehyde from the Rh-Y zeolite—II (circles for propionaldehyde and squares for *n*-propanol). ○, □, into the He–CO(10%) stream; ●, ■, into the helium stream; ◑, ◨, into the He–C_2H_4(10%) stream.

desorption products in the He–CO stream as shown in Fig. 2. The main products were found to be 1-, *trans*-2-, and *cis*-2-pentene.

Neither Na-Y zeolite nor H–Na–Y zeolite (27 or 74% exchanged) was effective for pentene formation. The Rh-Y zeolite reduced with hydrogen at 583 K for 5 h, was scarcely active for ethylene hydroformylation but quite active for ethylene hydrogenation (*8*) (dispersion of rhodium metal determined by H_2 chemisorption was about 40%). The Rh-Y zeolite thus reduced was placed in the reactor, and propionaldehyde was adsorbed on it at 400 K by passing propionaldehyde vapor diluted with helium through the reactor (without reactants for ethylene hydroformylation). Pentene was formed during the desorption of propionaldehyde from the reduced Rh-Y zeolite into the helium stream, suggesting that pentene was formed by the reaction of propionaldehyde. The results also indicate that the rhodium metal particles on the catalyst are responsible for the formation of pentene.

Typical results for the product distribution during the desorption into the helium stream are shown in Table 1. The majority of ethylene desorbed had been adsorbed on the catalyst during the reaction. A small amount of propylene was also observed during the desorption; propylene is, probably, formed by dehydration of *n*-propanol, since the Rh-Y zeolite is active for the reaction. The butene found in small quantity would be formed by ethylene dimerization since the Rh-Y zeolite has been known to be active for this reaction (*1, 2*). By analogy with homogeneous rhodium complex catalysts (*12*), the Rh-Y zeolite is also expected to be active for ethylene–propylene codimerization which is one of the possible routes for pentene formation. In order to obtain information on this point, effects of ethylene and propylene on the formation of pentene were examined. In the desorption into the He–C_2H_4(10%), no formation of pentene was observed, and the desorption curve of propionaldehyde agreed with that into the He–CO(10%) stream (Fig. 2). Results on the desorption into the He–C_3H_6(10%) stream are shown in Fig. 3. During the desorption into the He–C_3H_6 stream, pentene was formed but the amount was considerably less than that formed in the desorption into the helium stream. The effect of small amounts of propylene on the pentene formation was examined as follows; after 5 min of desorption into the He–C_3H_6(10%) stream, the carrier gas was changed from the mixture to helium only. Concentration of propylene in the effluent gas stream decreased from 10% to less than 0.1% rapidly within the first 5

TABLE 1

Product Distribution in the Desorption of Propionaldehyde into the Helium Stream at 400 K from the Relatively Fresh Rh-Y Zeolite (2.5 g)

Flow rate (cm^3/min)	Time (min)	Concentration (10^{-2} %)			
		C_2H_4	C_3H_6	C_4H_8	C_5H_{10}
70	24	8.74	0.16	0.08	1.11
	87	5.45	0.16	0.05	0.69
20	22	21.4	0.08	0.12	2.36
	98	12.9	0.07	0.11	1.46

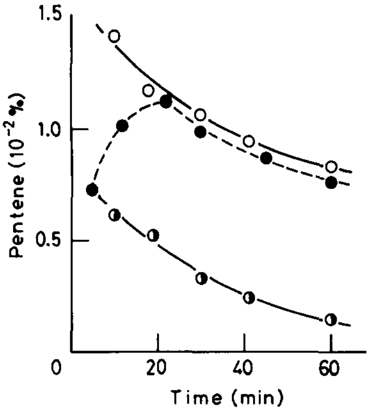

FIG. 3. Desorption of propionaldehyde into the He–C_3H_6 stream. ○, desorption into the helium stream; ◑, desorption into the He–C_3H_6(10%) stream; ●, after desorption into the He–C_3H_6(10%) stream for 5 min, the carrier was switched to the helium stream.

min and then decreased slowly during the desorption (ca., 0.02% at 2 h of the desorption). As shown by full circles in Fig. 3, no appreciable increase in the rate of pentene formation was observed in the presence of a small amount of propylene when compared with the rate in the desorption into the helium stream. These results suggest that the pentene formation proceeds via a mechanism other than ethylene–propylene codimerization. The suppression of the pentene formation in the presence of olefin may be due to the occupancy of active rhodium sites by olefins.

The active rhodium species on the zeolite responsible for ethylene hydroformylation or for ethylene hydrogenation are stable under the reaction conditions, and constant activities last for more than 1 month (*8*). In the repetition of the desorption–reaction cycle on the same catalyst, changes in the propionaldehyde concentration were very reproducible; steady-state rates for propionaldehyde and ethane formation were totally recovered within several hours after switching the gas stream from the carrier to the reactant gas. As shown in Fig. 4, however, the aged catalyst, which was used in ethylene hydroformylation for 10 days, was much less active for pentene formation than the relatively fresh catalyst, which was used for 4 days. This contrast suggests that the formation of pentene requires at least one more active site besides rhodium metal particles.

In order to obtain further information on the pentene formation over the Rh-Y zeolite, a reaction of propionaldehyde was carried out in the gas recirculating system. As shown in Fig. 5, the amount of pentene formed increased with reaction time over the Rh-Y zeolite. The relative compositions of pentene formed were 1-:*trans*-2-:*cis*-2- = 23:16:61, and this was almost constant throughout the reaction run. The fraction of *cis*-2-pentene and of 1-pentene is considerably higher than that at thermal equilibrium (1-:*trans*-2-:*cis*-2- = 4:67:29). The $RhCl_3/SiO_2$ catalyst pretreated in the same manner as the Rh-Y zeolite, however, was scarcely active for the formation of pentene.

It has been shown that the $RhCl_3/SiO_2$ catalyst pretreated with hydrogen at 393 K exhibited comparable catalytic activity for ethylene hydroformylation and hydrogenation as the Rh-Y zeolite (*8*). On the ethylene hydroformylation over the Rh-Y zeolite, accumulation of irreversibly adsorbed propionaldehyde was observed. Such accu-

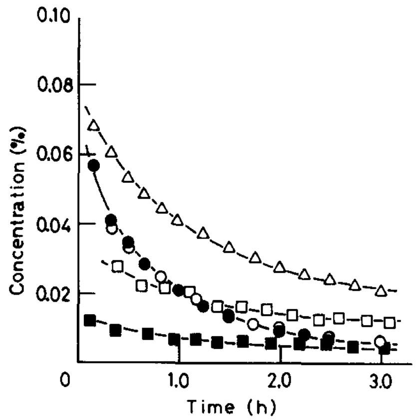

FIG. 4. Desorption of propionaldehyde into the helium stream. △, propionaldehyde into the He–CO(10%) stream; ○, □, propionaldehyde and pentene on the relatively fresh catalyst, respectively; ●, ■, propionaldehyde and pentene on the aged catalyst, respectively.

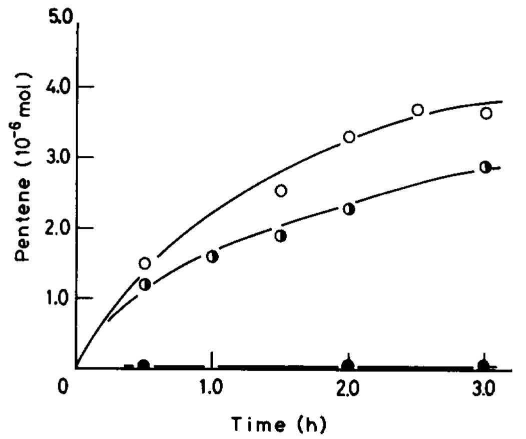

FIG. 5. Reaction of propionaldehyde over the Rh-Y zeolite in the gas recirculation system at 400 K. ○, Rh-Y zeolite (1.0 g); ●, $RhCl_3/SiO_2$ (1.0 g); ◑, Na-Y zeolite (1.0 g) + $RhCl_3/SiO_2$ (1.0 g).

mulation also occurred on the Na-Y zeolite and the H-Na-Y zeolite (27 or 74% exchanged). The accumulation, probably, partly contains higher molecular weight compounds formed by aldol condensation of propionaldehyde, since aldol condensation is catalyzed by not only acids but also bases. In fact, trace amount of 2-methyl-2-pentenal, which is formed from propionaldehyde by aldol condensation, was detected by gas chromatography during the reaction of propionaldehyde over the Rh-Y zeolite. On the other hand, the amount of propionaldehyde accumulated on the $RhCl_3/SiO_2$ catalyst was considerably less than that on the Rh-Y zeolite. Thus, one of the notable differences between the Rh-Y zeolite and the $RhCl_3/SiO_2$ is found in the capacity for the accumulation of irreversibly adsorbed propionaldehyde.

Our speculation on the pentene formation is that pentene is formed by two subsequent reactions, first, aldol condensation, and second, decarbonylation.

$$2\ C_2H_5CHO \xrightarrow{-H_2O} CH_3CH_2CH{=}C(CH_3)CHO \xrightarrow{-CO} C_5H_{10}$$

The first step would proceed over the zeolite support. And then, the second step may be catalyzed by rhodium species on the catalyst since decarbonylation generally proceeds over the catalysts which are active for carbonylation. We have already reported that the rhodium species acting as a catalyst are only on the external surface of zeolite particles and in the pores just at the entrance. This happens after the accumulation of irreversibly adsorbed propionaldehyde is completed, after which the internal part of the pores is completely blocked by the accumulated nonvolatile products (*8*). Therefore, the role of the rhodium species present on the external surface would be important. When the reduced $RhCl_3/SiO_2$ catalyst (percentage dispersion was about 20%) was physically mixed with the Na-Y zeolite, the intermediate formed by aldol condensation on the Na-Y zeolite would then interact with the rhodium metal particles on the $RhCl_3/SiO_2$ catalyst as long as the life of the intermediate is in the same order as the time required for the movement. As shown in Fig. 5, in fact, the catalyst which was a physical mixture of $RhCl_3/SiO_2$ and Na-Y zeolite showed comparable activity to the Rh-Y zeolite. The important role of the Na-Y zeolite as well as the rhodium metal particles on the reduced $RhCl_3/SiO_2$ catalyst strongly supports the reaction scheme proposed. Furthermore, if the reaction scheme is reliable, pentene should be formed from 2-methyl-2-pentenal over the reduced $RhCl_3/SiO_2$ catalyst and/or the reduced Rh-Y zeolite. The results on the reaction of 2-methyl-2-pentenal over both of the catalysts are shown in Fig. 6. Pentene was formed over both catalysts, while the silica support was ineffective for the formation. Accordingly, the formation of pentene thus reflects the bifunctional property of the Rh-Y zeolite, i.e., aldol condensation by the zeolite support and decarbonylation by the rhodium metal particles. Recently, Rode *et al.* (*13*) have found that the Rh-Y zeolite acts bifunctionally in the synthesis of ketones (2-methylhexane-3-one and heptan-4-one) from propylene, carbon monoxide, and hydrogen. They have interpreted

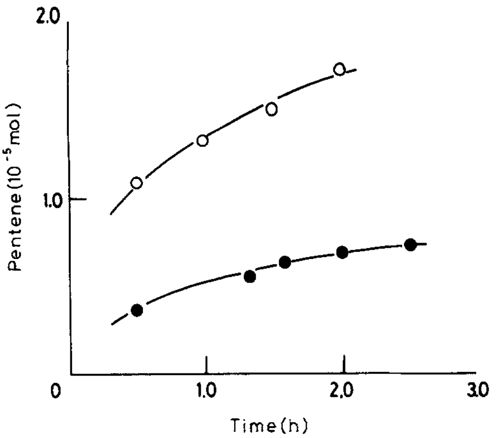

FIG. 6. Reaction of 2-methyl-2-pentenal in the gas recirculation system at 400 K. ○, $RhCl_3/SiO_2$ (1.0 g, reduced at 623 K for 5 h with H_2); ●, Rh-Y (1.0 g, reduced at 400 K for 5 h with H_2, and exposed to propionaldehyde vapor of ca. 0.4×10^5 Pa at 400 K for 1 day, and then evacuated at 400 K for 3 h).

that ketones are formed by the reaction of butyraldehyde (formed by propylene hydroformylation) with propylene over the zeolite support. At the present stage, however, we cannot discuss the relation between the bifunctional behavior of the Rh-Y zeolite found by Rode *et al.* and that found by us, because catalyst preparations, pretreatments, and reaction environments are different.

As can be seen from Fig. 3, however, the amount of propionaldehyde consumed to produce pentene (twice the amount of pentene formed) on the relatively fresh catalyst exceeds the amount of propionaldehyde estimated from the difference between the desorption into the He–CO stream and that into the helium stream at the early stage of the desorption. Probably, this is due to the contribution of 2-methyl-2-pentenal intermediate stored on the catalyst during the ethylene hydroformylation reaction. The decrease in the rate of pentene formation on the aged catalyst may reflect the decrease in the activity for the formation of the intermediate by aldol condensation, since the rhodium species are stable under the reaction conditions. By the reaction mechanism proposed, pentene formed should be 2-pentene. The fractions of *cis*-2-pentene and 1-pentene were much higher than those at thermal equilibrium throughout all experiments where the formation of pentene was observed. It seems to be feasible that the primary product is *cis*-2-pentene which is then isomerized to 1-pentene and *trans*-2-pentene, since the Rh-Y zeolite is known to be active catalyst for olefin isomerization (*1*).

CONCLUSION

During the desorption of propionaldehyde into the helium stream, formation of pentene was observed. The rate of pentene formation on the relatively fresh catalyst is observed to be higher than that on the aged catalyst. From the results concerning the effect of ethylene or propylene on the formation of pentene, it is suggested that the route for pentene formation would not be codimerization of ethylene and propylene. The $RhCl_3/SiO_2$ catalyst mixed with Na-Y zeolite showed comparable activity for pentene formation as the Rh-Y zeolite, while the $RhCl_3/SiO_2$ catalyst itself shows little activity for it. On the basis of the results, the sequence of the reaction, aldol condensation of propionaldehyde followed by decarbonylation, is proposed as plausible route for pentene formation. In fact, pentene was formed over the reduced $RhCl_3/SiO_2$ catalyst from 2-methyl-2-pentenal, which is thought to be an intermediate on the reaction scheme proposed.

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