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Pentan-3-one Formation from Ethylene, Carbon Monoxide and Hydrogen over Rhodium Supported on Active Carbon

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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, whereas other supported Rh catalysts investigated were inactive for this reaction. In the reaction at temperatures < 373 K, the rate of formation of pentan-3-one was higher than that of propionaldehyde. However, the deactivation of the active species for pentan-3-one formation was observed in the reaction at 413 K.

Several heterogeneous rhodium catalysts such as Rh/zeolites[1-4] and Rh/oxides[3,5-7] have been known to be active for olefin hydroformylation under atmospheric pressure, where aldehydes and the corresponding alcohols were found to be the main hydroformylation products. In some homogeneous transition metal complex catalyst systems, the formation of ketone was observed during the reaction of olefin, CO and H_2O, where the water gas shift reaction was suggested to be the key step.[8,9] However, almost no attention has been focussed on the ketone formation during the reaction of olefin, CO and H_2 over heterogeneous rhodium catalysts. In the present study, we have found that pentan-3-one (diethylketone) was formed as one of the major products during ethylene hydroformylation over the rhodium supported on active carbon.

The rhodium supported on active carbon (denoted by Rh/AC) was prepared by a conventional impregnation method from rhodium trichloride trihydrate ($RhCl_33H_2O$) (obtained from N. E. Chemcat Corp.) and active carbon (obtained from Wako Pure Chemicals Inc., specific surface area = 900 m^2g^{-1}). Other supported rhodium catalysts were prepared in the same manner using SiO_2, Al_2O_3, SiO_2-Al_2O_3, ZrO_2, $ZrSiO_4$, or MgO as a support. The Pd/active carbon (denoted by Pd/AC) was also prepared in the same manner from palladium chloride (dissolved in a diluted HCl solution) and the active carbon. The catalysts prepared contained 2.0 wt% of Rh or Pd as metal. Apparatus used 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}) at 573 K for 3 h, and cooled below 323 K in a hydrogen flow. A reaction mixture of He-C_2H_4(20%)-CO(20%)-H_2(20%)

($100cm^3$(STP) min^{-1}) 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.

Main products in ethylene hydroformylation over Rh/AC 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), r_{PA}; (b), r_{DEK}; (c), r_E). The effects of reaction temperature on the catalytic activities are summarized in Table 1 (runs 1-4). The rates, r_{PA} and r_E, increased with the increase in the reaction temperature, while the rates gradually decreased with time on stream. 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. This behavior is probably due to the accumulation of pentan-3-one on the catalyst because of its high boiling point (374.7 K). In the reaction at 373 K, r_{DEK} was found to be slightly higher than r_{PA} after time on stream of ca. 7 h. The ratio of r_{DEK}/r_{PA} increased with the decrease in the reaction temperature, and the ratio at 363 K was found to be ca. 1.8 at time on stream of 8 h (run 1). As shown in Fig.1-(b), however, r_{DEK} at 413 K was 0.45×10^{-6} mol min^{-1}(g-cat)$^{-1}$ at 1 h, and it decreased with time on stream (0.29×10^{-6} mol min^{-1}(g-cat)$^{-1}$ at 8 h). Thus, the activity for pentan-3-one formation at 413 K was observed to be lower than that at 393 K.

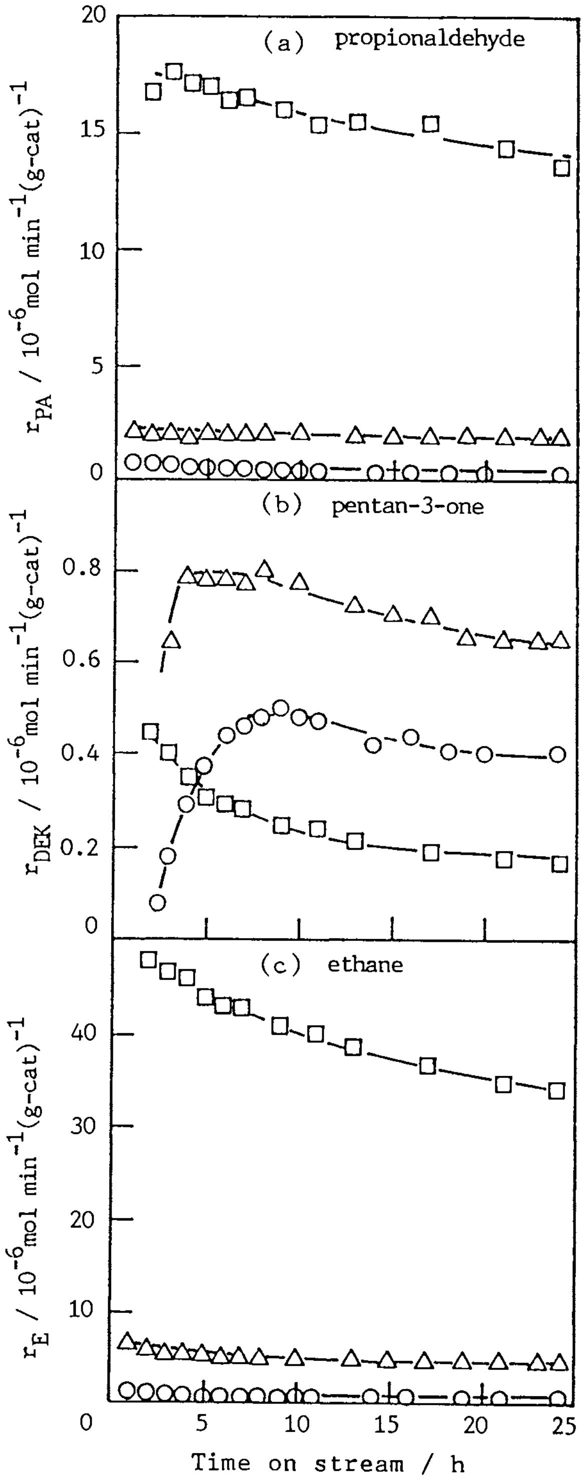

Fig.1. Changes in r_{PA}, r_{DEK}, and r_E with time on stream during reaction of C_2H_4, CO, and H_2 over Rh/AC (○, at 373 K; △, 393 K; □, 413 K).

In addition, r_{DEK} on the catalyst once used for the reaction at 413 K decreased with the decrease in the reaction temperature. These results suggest the deactivation of the active sites for pentan-3-one formation during the reaction at 413 K.

Other Rh catalysts also catalyzed ethylene hydroformylation with r_{PA} and r_E comparable to those on Rh/AC as shown in Table 1, where the activities were evaluated by the rates at time on stream of 8 h. However, no appreciable formation of pentan-3-one was observed when rhodium was supported on SiO_2, Al_2O_3, SiO_2-Al_2O_3, ZrO_2, $ZrSiO_4$ or MgO. Thus, the formation of pentan-3-one during ethylene hydroformylation was pronounced on the Rh/AC catalyst.

Rode et al. reported that 2-methylhexan-3-one and heptan-4-one were produced by rhodium zeolites from propylene, CO and H_2.[10)] They have proposed that ketones were formed from propylene and butyraldehyde on the zeolite support, since a zeolite Y was active for ketone formation when propylene saturated with butyraldehyde was passed over the sample. In order to clarify the role of active carbon for the production of pentan-3-one on Rh/AC, the reaction of propionaldehyde with ethylene over active carbon was carried out (reaction conditions: active carbon = 0.50 g, reaction temperature = 373 K, propionaldehyde = 0.31×10^{-6}mol min^{-1}, C_2H_4 = 20 cm^3(STP) min^{-1}, He = 80 cm^3(STP) min^{-1}). No appreciable formation of pentan-3-one was observed. This result contrasts with the result reported by Rode et al., although the reactants and the support in

Table 1. Reaction of C_2H_4, CO, and H_2 over various supported Rh catalysts

Run	Catalyst	Reaction temperature	Activity[a)]		
			r_{PA}	r_{DEK}	r_E
		/K	/10^{-6}mol min^{-1}(g-cat)$^{-1}$		
1	Rh/AC	363	0.09	0.15[b)]	0.40
2		373	0.41	0.43	0.70
3		393	2.10	0.80	4.86
4		413	16.0	0.29	42.1
5	Rh/SiO_2	393	1.70	----	2.50
6	Rh/Al_2O_3	393	1.34	----	5.24
7	Rh/SiO_2-Al_2O_3	393	1.70	----	6.25
8	Rh/ZrO_2	393	1.40	----	4.43
9	Rh/$ZrSiO_4$	393	0.91	----	1.95
10	Rh/MgO	393	0.10	----	0.45
11	Pd/AC	373	12.8	----	133

a) the rate of formation at time on stream of 8 h (PA, DEK and E represent propionaldehyde, pentan-3-one and ethane, respectively).

b) r_{DEK} was still increasing with time on stream.

their work ((propylene)-(butyraldehyde) and Na-Y zeolite, respectively) were different from those in the present work. Furthermore, in the case that the (ethylene)-(propionaldehyde) mixture was passed over the Rh/AC catalyst instead of the active carbon (other conditions were the same as those noted above), formation of pentan-3-one was not observed. Namely, the results obtained in the present work indicate that neither the active carbon itself nor the Rh/AC was effective for pentan-3-one formation from propionaldehyde and ethylene. The Pd/AC was found to be more active for ethylene hydroformylation than the Rh/AC as shown by run 11 in Table 1, whereas the rate of ethane formation on the former was much higher than that on the latter. No appreciable formation of pentan-3-one was observed on the Pd/AC catalyst. This result also supports the ineffectiveness of the active carbon itself as the active sites for pentan-3-one formation. Accordingly, formation of pentan-3-one took place over the active rhodium sites on the Rh/AC catalyst. However, we have not clarified the structure of active sites and the reaction route for the pentan-3-one formation yet.

In conclusion, we have found that the rhodium supported on active carbon was effective for the formation of pentan-3-one from C_2H_4, CO and H_2 at appropriate reaction conditions, whereas other supported Rh catalysts investigated did not show any activity for pentan-3-one formation.

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