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EFFECTS OF VARIOUS PRETREATMENTS OF THE Rh-Y ZEOLITE ON THE CATALYTIC ACTIVITY FOR ETHYLENE HYDROFORMYLATION UNDER ATMOSPHERIC PRESSURE

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The active species for ethylene hydroformylation formed in the Y zeolite are extremely stable under the reaction conditions and the steady activity lasts more than one month. The catalytic activity is remarkably affected by the pretreatment of the catalyst; the He-H_2 pretreatment at 338 - 453 K enhances the activity while the He-CO or He-CO-C_2H_4 pretreatment at 400 K reduces it.

One of the successful methods to develop heterogenization of a homogeneous metal complex catalyst has been achieved by using a zeolite as a support where supported cations through ion-exchange process are convertible into precursors to form corresponding active species in the zeolite cavity. Mantovani et al.1) carried out hexene-1 hydroformylation at an elevated pressure of carbon monoxide and hydrogen over the Rh-Y zeolite which was pretreated with an equimolar mixture of carbon monoxide and hydrogen at $8x10^6$Pa at 403 K for 48 h. Recently, Arai and Tominaga2) have reported that the Rh-Y zeolite can catalyse olefin hydroformylation in a continuous flow system even at atmospheric pressure. On the fresh Rh-Y zeolite, rhodium is loaded as a trivalent cation, Rh(III).2-4) Every reactant in the hydroformylation may act on Rh(III) as a reducing agent; hydrogen reduces Rh(III) finally into Rh(0), olefin does it into monovalent rhodium species,5,6) and carbon monoxide does it into monovalent rhodium carbonyl species.7) Therefore, it is expected that the pretreatments of the catalyst with various gas mixtures affect the catalytic activity. In the present study, the effects of the various pretreatments of the Rh-Y zeolite on the catalytic activity for ethylene hydroformylation are studied.

Rhodium trichloride trihydrate was obtained from Wako Pure Chemical Ind. Ltd. and was used without further purification. Reactants (C_2H_4, CO and H_2) and helium were obtained from commercial sources. The Rh-Y zeolite catalysts were prepared by a conventional cation exchange procedure using Na-Y(SK-40) and a rhodium trichloride trihydrate aqueous solution at 353 K for 12 h. The rhodium contents of the catalysts were found in Table 1. Ethylene hydroformylation was carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure. The catalyst was placed in the reactor (Pyrex glass tube) and the system was purged with helium for 1 h at room temperature before the reaction started. The reactor, which was immersed in an oil bath, was heated up to 400 K at a rate of about 2 K/min in the reaction gas stream or in a gas stream for the pretreatment of the catalyst. The effluent gas was analysed by gas chromatography.

Propionaldehyde and ethane were found to be the main products in ethylene hydroformylation over the Rh-Y zeolite catalyst. n-Propanol was also found in negligible quantities. Typical changes in propionaldehyde and ethane formation with time on stream are shown in Fig.1. A remarkable increase in the propionaldehyde formation and a decrease in the ethane formation to reach their asymptotic values were observed for more than 50 h. The active species formed in the zeolite were extremely stable under the reaction conditions and the steady activities lasted more than one month.

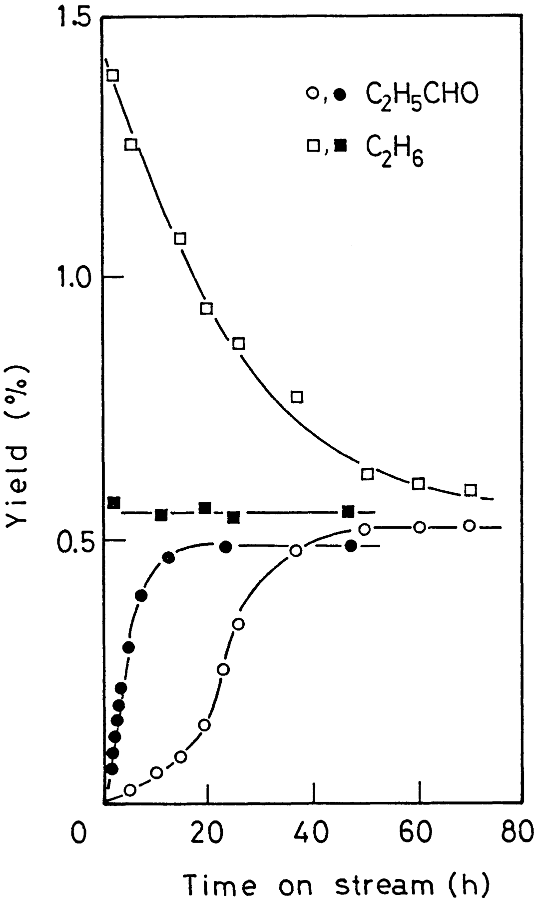

Fig. 1. Ethylene hydroformylation over the Rh-Y zeolite. Reaction conditions: Rh-Y(No.2)=2.5 g, He-C_2H_4(0.10×10^5Pa)-CO(0.10×10^5Pa)-H_2(0.10×10^5Pa) at 400 K.
○,□ : run 6 in Table 1.
●,■ : on the catalyst with the preadsorption of propionaldehyde.

After the performance of the reaction, the Rh-Y zeolite showed a deep red-purple color which was characterized by absorption bands at 436, 475 and 504 nm in its visible spectrum, while the fresh catalyst did not show these absorption bands. This color never diminished after the removal of reversibly adsorbed propionaldehyde from the catalyst, suggesting the formation of nonvolatile compounds on the catalyst. The fresh catalyst irreversibly adsorbed considerable amount of propionaldehyde. The irreversible adsorption prior to the reaction had been completed by introducing propionaldehyde vapor into the helium stream which passed through the catalyst bed, then the reaction gas was fed into the system to start the reaction. As shown in Fig.1, the induction period on the propionaldehyde formation was remarkably shortened by the preadsorption, while the steady activity was scarcely affected. The ethylene hydrogenation was also affected by the preadsorption, i.e., almost no decay in the ethane formation was observed on the catalyst on which propionaldehyde was preadsorbed. Thus, the changes in the yields for a long period on the catalyst without the preadsorption was mainly due to the irreversible adsorption of propionaldehyde on the catalyst.

The effects of various pretreatments on the steady state rates of propionaldehyde formation (r_{PA}) and ethane formation (r_E) were shown in Table 1. The Rh-Y zeolite with no pretreatments can catalyse ethylene hydroformylation (runs 1, 5,and 14). In the comparison of the catalyst pretreated with He-CO-H_2 (runs 2 and 6) with the catalyst untreated, no appreciable differences in r_{PA} and r_E were found. The effects of the pretreatment with He-H_2 on r_{PA} and r_E are noticeable. Namely, r_{PA} was enhanced by the pretreatment with He-H_2 at the temperature ranging from 338 to 453 K to about one and a half fold that of the untreated catalyst, while r_E was much more enhanced than r_{PA} (runs 8-11). On the other hand, the pretreatment with the gas mixture which did not contain H_2, with He-CO-C_2H_4(runs 3 and 7) or He-CO (run 15), remarkably reduced r_{PA}. Accordingly, it is suggested that hydrogen promotes the formation of the active species for the hydroformylation but carbon monoxide rather suppresses it. The pretreatment with He-H_2 at 583 K, however, remarkably reduced r_{PA} to less than 0.02% of that on the untreated catalyst.

As a reason for the lower catalytic activity of the catalyst pretreated with He-CO-C_2H_4 or He-CO, one might speculate that some portion of the rhodium loaded on the catalyst fell from the catalyst as a result of the formation of volatile rhodium carbonyl complexes. The effect of the pretreatments on the

Table 1. Effects of various pretreatments on r_{PA} and r_E over the Rh-Y zeolite.

Run No.	Cat. No.	Rh-content (10^{-6}mol/g-cat)	Pretreatment					r_{PA} (10^{-6}mol/min g-cat)	r_E (10^{-6}mol/min g-cat)
			CO (10^5Pa)	H_2	C_2H_4	Temp (K)	Time (h)		
1	1	50	no pretreatment					0.33	0.38
2			0.10	0.10	0	400	48	0.31	*
3			0.10	0	0.10	400	48	0.08	*
4			0	0.10	0	400	48	0.60	1.98
5	2	77	no pretreatment					0.59	0.70
6			0.10	0.10	0	400	48	0.58	0.71
7			0.10	0	0.10	400	48	0.05	0.05
8			0	0.10	0	338	5	0.89	2.58
9			0	0.10	0	368	5	0.93	2.44
10			0	0.10	0	400	5	0.89	2.67
11			0	0.10	0	453	5	0.92	2.90
12			0	0.10	0	583	5	0.0001	0.26
13**			0	0.10	0	400	5	0.91	2.19
14	3	150	no pretreatment					0.41	0.76
15			0.10	0	0	400	48	0.10	0.15
16			0	0.10	0	400	5	0.89	1.82

All pretreatments were performed in the flow system with a total flow rate of 70 cm^3(STP)/min at atmospheric pressure, and the reaction conditions were He-C_2H_4 ($0.10x10^5$Pa)-CO($0.10x10^5$Pa)-H_2($0.10x10^5$Pa) at 400 K and 70 cm^3/min.

* not measured.

** The pretreatment shown in the Table was followed by the treatment with He-O_2 ($0.10x10^5$Pa) at 400 K for 2 h and then the flash with helium for 15 min to remove oxygen from the system.

extent of the loss in rhodium content can be seen from Table 2. The rhodium content of the catalyst pretreated with He-CO was slightly less than that in the catalyst pretreated with He-H_2. The pretreatment with He-CO-H_2 also slightly reduced the rhodium content. But the difference among them was very small compared with that in the catalytic activity. Therefore, the loss of rhodium during the pretreatment with He-CO should not be the main reason for the lower catalytic activity.

Table 2. Effects of the various pretreatments on the rhodium content of Rh-Y.

Pretreatment	Rhodium content (10^{-6}mol/g-cat)
He-CO (400 K, 48 h)	142
He-CO-H_2 (400 K, 48 h)	145
He-H_2 (400 K, 5 h)	150

All pretreatments were performed in the same way shown in Table 1. Partial pressures of CO and H_2 were 0.10×10^5Pa.

On the Rh-Y zeolite of No.2, the various pretreatments resulted in the different ratio of r_{PA}/r_E as follows; 0.84 on the catalyst untreated and pretreated with He-CO-H_2, unity on the catalyst pretreated with He-CO-C_2H_4, 0.33 on the catalyst pretreated with He-H_2 at the temperature ranging from 338 to 453 K, and less than 0.0004 on the catalyst pretreated with He-H_2 at 583 K. These results indicate the presence of the rhodium species which is active for the hydrogenation but not for the hydroformylation. The decrease in the hydroformylation activity by the pretreatment with He-H_2 at 583 K is remarkable compared with that in the hydrogenation activity, suggesting that metal particles of rhodium formed by the pretreatment are not thought to be the active species for the hydroformylation. The precursors of the active species for the hydroformylation are stable for oxygen even at 400 K since no appreciable effects of the pretreatment with He-O_2 on r_{PA} were observed as shown by run 13 in Table 1.

Consequently, it is found that the active species for the hydroformylation formed in the zeolite are very stable under the reaction conditions and the catalytic activity lasts more than one month without any deactivation. The results which indicate the important role of hydrogen in forming the active species at the relatively low temperature are presented.

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