CHEMISTRY LETTERS, pp. 1067 - 1068, 1984.

# PENTENE FORMATION FROM PROPIONALDEHYDE ADSORBED ON Rh-Y ZEOLITE

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Pentene formation is observed during desorption of propionaldehyde from Rh-Y zeolite into a helium stream, while neither Na-Y zeolite nor H-Na-Y zeolite is effective for pentene formation.

Rh-Y zeolite has been known to be a catalyst for ethylene hydroformylation under atmospheric pressure.[1-3] During desorption of propionaldehyde from Rh-Y zeolite into a helium stream, formation of pentene is observed. Propionaldehyde undergoes various reactions. However, the reaction of propionaldehyde to pentene has never been reported.

Rh-Y zeolite ($150\times10^{-6}$mol-Rh/g-cat) was prepared from Na-Y zeolite and an aqueous solution of rhodium trichloride trihydrate. The apparatus used was a fixed-bed type reactor with a continuous flow system. The catalyst (2.5 g) was pretreated with He-$H_2$(10%) at 400 K for 5 h in the reactor. Desorption of propionaldehyde at 400 K was carried out as follows: After steady state for ethylene hydroformylation was attained, the gas stream was switched from the reactant gas to the carrier. The total flow rate of the gas stream was 70 $cm^3$ (s.t.p.)/min in both cases. The products were analyzed by gas chromatography and mass spectrometry.

As shown in Fig.1, the concentration of propionaldehyde decreases with time on stream during the desorption into a He-CO(10%) stream. In the desorption into a helium stream, the concentration of desorbed propionaldehyde more rapidly decreased when compared with that into the He-CO stream. In this case, several products other than propionaldehyde were formed. The main products were 1-, trans-2- and cis-2-pentene. The steady state rate for propionaldehyde formation was totally recovered within several hours after switching the gas stream from the carrier to the reactant gas. Changes in the propionaldehyde concentration during the desorption were very reproducible on the same catalyst. As shown in Fig.1, however, the catalyst used in ethylene hydroformylation for a longer period (for 10 days) was much less active for pentene formation than the relatively fresh catalyst (for 4 days).

The Rh-Y zeolite reduced with hydrogen at 583 K for 5 h, which was scarcely active for ethylene hydroformylation,[2)] was placed in the reactor, and propionaldehyde was adsorbed on it by passing propionaldehyde vapor diluted with helium (without reactants for ethylene hydroformylation) through the reactor. Pentene was formed during the desorption of propionaldehyde from the reduced Rh-Y zeolite into the helium stream. In this case, a small amount of propionaldehyde simultaneously decomposed to ethylene. Neither Na-Y zeolite nor H-Na-Y zeolite (27% or 74% exchanged) was effective for the pentene formation. These results suggest that the pentene formation takes place on the rhodium metal particles.

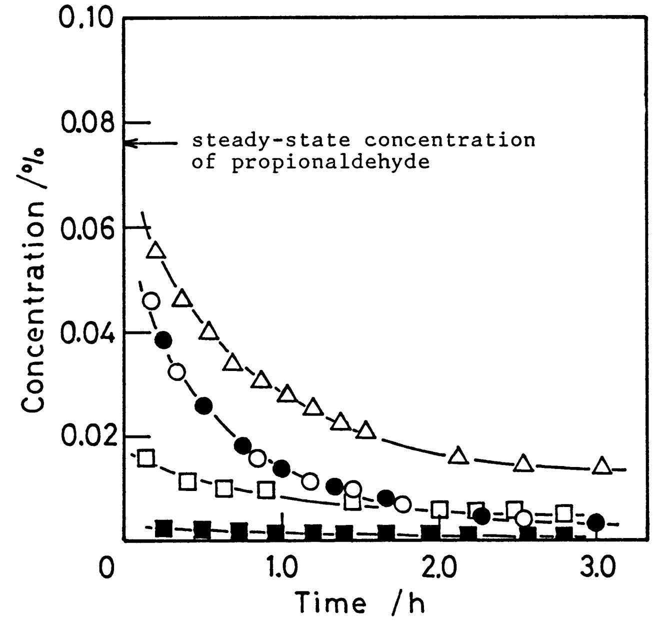

Fig.1.
Desorption of propionaldehyde into the helium stream.
△: Propionaldehyde into the He-CO(10%) stream.
○, □: Propionaldehyde and pentene on the relatively fresh catalyst, respectively.
●, ■: Propionaldehyde and pentene on the altered catalyst, respectively.

Typical results for the product distribution in the desorption into the helium stream are shown in Table 1. Ethylene and propylene were observed during the desorption, while the concentration of propylene was much lower than that of ethylene. One of the possible routes for the formation of pentene is co-dimerization of ethylene and propylene, since the Rh-Y zeolite has been known to be an active catalyst for ethylene dimerization.4) However, no appreciable effects of the addition of a small amount of propylene (0.02%) in the helium stream on the pentene formation were observed. In the desorption into a He-$C_3H_6$(10%) stream, pentene was formed in amount less than one third of that in the desorption into the helium stream. In the desorption into a He-$C_2H_4$(10%) stream, formation of pentene did not take place. These results suggest that the main route for the formation of pentene would not be co-dimerization of ethylene and propylene.

The studies on the reaction mechanism for pentene formation are now in progress.

Table 1.
Product distribution during desorption of propionaldehyde into the helium stream

| Time | Concentration /$10^{-2}$% | | | |
|---|---|---|---|---|
| min | $C_2H_4$ | $C_3H_6$ | $C_4H_8$ | $C_5H_{10}$ |
| 24 | 8.74 | 0.16 | 0.08 | 1.11 |
| 87 | 5.45 | 0.16 | 0.05 | 0.69 |

(Results on the relatively fresh catalyst)

References

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(Received March 21, 1984)