JOURNAL OF CATALYSIS 75, 188–189 (1982)

Hydroformylation and Hydrogenation of Olefins over Rhodium Zeolite Catalyst

Rh(III)-Y zeolite catalyst was found active for hydroformylation of olefins at 150°C at 1 atm in vapor phase. The relative ease of olefin hydroformylation was as follows: ethylene > propylene > 1-butene.

A new category of solid catalyst has recently stemmed from coordination of the activity and selectivity of a homogeneous catalyst with the practical advantages of a heterogeneous one. Such a catalyst is a transition metal compound chemically bound to an organic polymer, or a transition metal ion loaded on zeolite (*1*).

Some rhodium complexes have been noted as highly active for hydroformylation of olefin to aldehyde (*2*). In the present study, rhodium(III)-zeolite catalyst was prepared and its activity for hydroformylation was tested under atmospheric pressure at 150°C in vapor phase.

Linde molecular sieve of type NaY in powder form was used to prepare the catalyst. The zeolite, after being boiled in distilled water to remove excess sodium, was treated with 0.1 *N* NaCl aqueous solution. To the above zeolite–NaY suspension in water, an aqueous solution of $RhCl_3$ was added dropwise for 2 hr. Meanwhile, the pH of the suspension was kept not lower than 6, the temperature being kept at 95°C. Vigorous stirring of the suspension was continued for another 5 hr at 90°C, and then it was allowed to stand overnight. After that, the zeolite was filtered and washed with hot distilled water until no chlorine ion was detected in the filtrate. The catalyst was dried at 150°C for 3 hr to give the Rh-13Y catalyst of which the Rh content was 3.7 wt%, and was pressed at 150 kg/cm^2 and crushed into ~10- to 20-mesh particles.

A catalyst activity test was performed by use of an atmospheric flow reactor, made of a Pyrex glass tube, 50 cm in length and 18 mm in inner diameter, equipped with the usual devices such as reactant gas flow controllers, temperature controller, etc. The reactor was usually loaded with 1.0 g of catalyst. Standard reaction conditions were 150°C catalyst bed temperature, and 10 g-cat · hr/mol in W/F, where W is the catalyst weight (g) and F is the total gas flow rate (mol/hr), consisting of olefin, hydrogen, and carbon monoxide, in a 3 : 3 : 1 mole ratio. The gaseous products exited from the bottom of the reactor were cooled by a water condenser, and aldehyde was collected in a glass flask containing water, which was analyzed by gas chromatography using a 3-m PEG 1500 column at 110°C.

Both the activity and selectivity changed in the initial stage of use of Rh-13Y catalyst as is shown in Fig. 1. Namely, in the first 4 hr, the activity for hydrogenation of olefin decreased while that for hydroformylation of olefin largely increased. The number of moles of aldehyde produced in 7 hr of the above experiment was calculated as 2.5 times larger than those of rhodium on the catalyst employed.

The XPS binding energies of Rh $3d_{5/2}$ for fresh and used catalysts of Rh-NaY were 309.7 and 308.6 eV, respectively. These can be assigned to Rh(III) for a fresh catalyst and Rh(I) for a used one (*3*). This change from Rh(III) to Rh(I) during reaction was found in dimerization of ethylene over the Rh-Y catalysts (*3*). In this connection, ESR study on the fresh and used catalysts was made and neither Rh(0) nor Rh(II) was

0021-9517/82/050188-02$02.00/0

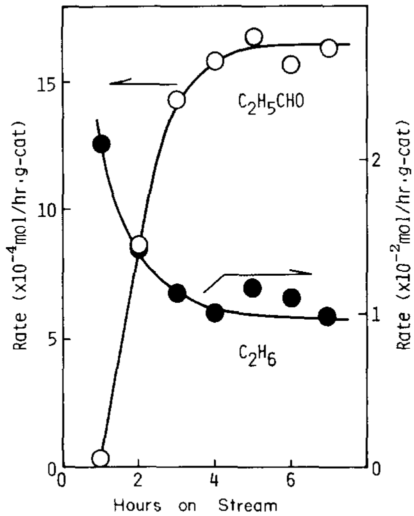
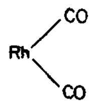


FIG. 1. Reaction rates vs hours on stream: W/F, 10 g-cat · hr/mol; temperature, 150°C; $C_2H_4 : H_2 : CO = 3:3:1$; catalyst, Rh-zeolite (Rh, 3.7 wt%).

found. Some Rh(I) complexes are known to be highly active for hydroformylation of olefins (*2*). Eventually, hydroformylation is seemingly catalyzed through redox reaction of Rh(I) and Rh(III).

Reaction kinetics and mechanism of olefin hydroformylation are very complicated. Kinetic study revealed the fact that the rates of both hydroformylation and hydrogenation of olefins were inversely proportional to the concentration of carbon monoxide varied in some ranges. Stopping of carbon monoxide supply was found to give an increase in aldehyde yield but temporarily. With the absence of carbon monoxide, however, olefin gives no aldehyde but paraffin in nearly 100% yield. Infrared spectroscopic study on the adsorption of carbon monoxide on Rh(III)-13Y has disclosed that the adsorbed species is in a twin form,



which is stable to newly introduced gaseous hydrogen or ethylene giving no reaction product below 180°C (*4*). These findings indicate that to carry out the hydroformylation of olefin more efficiently a very delicate balance of the reactants' concentrations is required.

TABLE 1

Reactivities of Olefin Hydroformylation and Hydrogenation over Rhodium-Zeolite Catalyst

Olefin	Product	Rate[a] (mol/g · cat-hr)	E[b] (kcal/mol)
C_2H_4	C_2H_5CHO	1.4×10^{-3}	6.4
	C_2H_6	7.5×10^{-3}	21.4
C_3H_6	n-C_3H_7CHO	3.7×10^{-5}	8.7
	iso-C_3H_7CHO	3.2×10^{-5}	7.3
	C_3H_8	2.6×10^{-3}	24.2

Note. Catalyst: rhodium (3.7 wt%)-zeolite, W/F = 10 g-cat · hr/mol. Feed ratio: olefin : H_2 : CO = 3 : 3 : 1.

[a] At 150°C.

[b] At ~130–170°C.

Table 1 summarizes the reaction products and their rates of formation from ethylene or propylene. Butene isomers were also subject to the reaction. *cis*- and *trans*-2-butene were scarcely hydroformylated on this catalyst. The relative ease of olefin hydroformylation was in the following order: ethylene > propylene > 1-butene.

REFERENCES

1. Arai, H., *J. Catal.* **51**, 135 (1978).
2. Evans, D., Osborn, J. A., and Wilkinson, G., *J. Chem. Soc. A*, 3133 (1968). Brown, C. K., and Wilkinson, G., *J. Chem. Soc. A*, 2753 (1970).
3. Okamoto, Y., Ishida, N., Imanaka, T., and Teranishi, S., *J. Catal.* **58**, 82 (1979).
4. Arai, H., and Tominaga, H., *J. Catal.* **43**, 131 (1976).

HIROMICHI ARAI

Department of Material Science and Technology
Graduate School of Engineering Sciences
Kyushu University
Fukuoka 812, Japan

HIROO TOMINAGA

Department of Synthetic Chemistry
Faculty of Engineering
The University of Tokyo
Hongo, Tokyo 113, Japan

Received August 27, 1980; revised November 30, 1981