JOURNAL OF CATALYSIS 56, 294–295 (1979)

LETTERS TO THE EDITORS

Catalytic Sites of α-Zirconium Phosphate in Oxidative Dehydrogenation

Recently, Clearfield and Pack (*1*) reported that α-zirconium phosphate exchanged with copper(II) ions was a good catalyst for the oxidation of carbon monoxide and the oxidative dehydrogenation of cyclohexene, and they tentatively concluded from ESR study that the oxidative dehydrogenation proceeds via the oxidation–reduction cycle of copper ions. The purpose of the present letter is to show that α-zirconium phosphate, hereinafter referred to as α-ZrP, is a good catalyst for the oxidative dehydrogenation of ethylbenzene without ion exchange.

α-ZrP used in the present work was a semicrystalline α-ZrP, and its preparation and characterization were reported elsewhere (*2*). The reaction was carried out with a conventional flow reactor at atmospheric pressure. The catalyst (4.5 g) was packed in glass tubing with an inside diameter of 10 mm and heated in a fluidized bath with an electrically heated wire. The reaction temperature was measured with a thermocouple in the glass tubing with an outside diameter of 5 mm installed at the center of the reactor. The partial pressure of ethylbenzene, oxygen, nitrogen, and water vapor in the feed was 1.61×10^4, 2.00×10^4, 4.30×10^4, and 2.23×10^4 N m^{-2}, respectively, and the total feed rate was 295 mmol/h. An analysis of reaction products was carried out gas chromatographically.

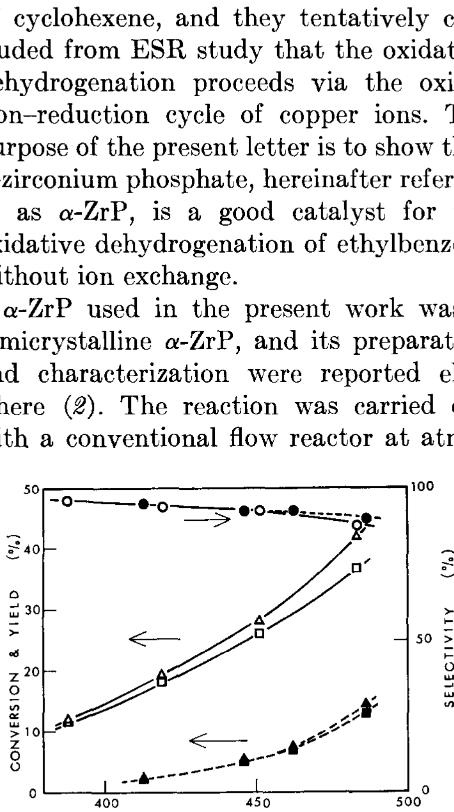

FIG. 1. Activity and selectivity of α-ZrP dried at 110°C (open points) and calcined at 550°C (closed points) in the oxidative dehydrogenation of ethylbenzene. (○, ●), Selectivity of styrene; (△, ▲), conversion; (□, ■), yield of styrene.

When α-ZrP dried at 110°C was used as a catalyst without further pretreatment, good conversion and selectivity were obtained, as shown in Fig. 1. Carbon monoxide and carbon dioxide were the major by-products, and traces of benzene and toluene were detected only at the highest reaction temperature, 480°C. The X-ray diffraction pattern of the catalyst indicated that the phase transformation of the catalyst to the ζ phase (*3*) occurred during the reaction but the condensation of phosphate groups did not. On the other hand, α-ZrP calcined at 550°C gave good selectivity but low conversion, as shown in the figure. Carbon monoxide and carbon dioxide were again the major by-products. The BET surface area of α-ZrP was about 7 m^2/g independently of the calcination at 110–800°C, but the calcination above 490°C destroyed the crystal structure and reduced the acidity

0021-9517/79/020294-02$02.00/0

to less than one-tenth of its original value (*2*). These findings suggest that the catalytic sites for oxidative dehydrogenation of ethylbenzene is associated with the crystal structure of α-ZrP, maybe, with the acid site. α-ZrP has the acid site with the acid strength of $-3 \geq H_0 \geq -5$ (*2*) and has the catalytic activity in some acid-catalyzed reactions such as the dehydration of alcohols and the isomerization of butene (*4*). Lisovskii *et al.* (*5*) also reported that the acidity of alumina catalyst had an effect on the oxidative dehydrogenation of ethylbenzene.

REFERENCES

1. Clearfield, A., and Pack, S. P., *J. Catal.* **51**, 431 (1978).
2. Hattori, T., Ishiguro, A., and Murakami, Y., *J. Inorg. Nucl. Chem.* **40**, 1107 (1978).
3. Clearfield, A., and Pack, S. P., *J. Inorg. Nucl. Chem.* **37**, 1283 (1975).
4. Hattori, T., Ishiguro, A., and Murakami, Y., *Nippon Kagaku Kaishi* **1977**, 761 (1977).
5. Lisovskii, A. E., Alkhazov, T. G., and Safarov, M. G., *Kinet. Katal.* **13**, 159 (1972).

T. HATTORI
H. HANAI
Y. MURAKAMI

Department of Synthetic Chemistry
Faculty of Engineering
Nagoya University
Chikusa, Nagoya 464 Japan

Received June 14, 1978