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CATALYTIC CONVERSION OF PROPYLENE INTO ACETYLENE AND BUTADIENE OVER ION-EXCHANGED ZEOLITES

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It was found that propylene was catalytically converted into acetylene and butadiene accompanied with the foramtion of coke at 150°-250° over ion-exchanged zeolites, although the yield and the catalyst life were insufficient. The activity of the ion is found in the order of Ca > Zn > Mn > H > Ni > Ag > Co > Fe > Cu. The catalytic activity may be related with the Lewis acidity.

Industrial processes of acetylene formation by thermal cracking are usually carried out at temperatures higher than 1500°.$^{1)}$ The high temperature is required because of large endothermic reaction of acetylene formation as shown below.

$$2CH_4 \longrightarrow C_2H_2 + 2H_2 \qquad (1)$$

$$C_2H_6 \longrightarrow C_2H_2 + 2H_2 \qquad (2)$$

The partial oxidation process is adopted for lowering the reaction temperature by compensating the large endothermic heat with that of combustion, however, the reaction temperature higher than 1000° is still required.$^{2)}$

In the present study, the catalytic activities of ion-exchanged zeolites for the propylene conversions were investigated because the high acidity of the zeolite may help the conversion of propylene into acetylene in the thermodynamic as well as catalytic aspects through the concurrent production of cokes.

The ion-exchanged molecular sieve catalysts were prepared by ion-exchange of Y(Linde, SK-40; Na(I)-Y), X(Linde, Na(I)-X), Z(Norton, zeolon; H-Z) with an aqueous solution of ammonia or metal ion in a suitable form not too acidic nor basic. This treatment was followed by a thorough washing with deionized water, drying at 100° and calcination at 450° in atmosphere. Neither acetylene nor butadiene was detectable in the reactant by gas chromatography. The catalytic activity was observed by an ordinary flow reactor with a fixed catalyst bed. The total flow rate was 60 ml/min and the weight of catalyst was around 1 g. The partial pressure of propylene was 0.01 in a nitrogen carrier. Acetylene, propane, propylene, butenes, butadiene, and hexenes were analyzed by means of gas chromatography. A column of 7 m VZ-7 was used at room temperature for all reagents except for hexenes, and 2 m PEG-400 was used at 30° for hexenes. Although hydrogen was found in the products, no ethylene, ethane, nor methane was detected at all.

The catalytic activities of ion-exchanged zeolites are shown in Table, where the activity is indicated by the yield of the products on the inlet propylene base. The catalytic activity is in the order of Ca-Y > Zn-Y > Mn-Y > H-Y > Ni-Y > Ag-Y > Co-Y > Fe-Y > Cu-Y. The carbon balance of the reaction indicated that ca. 40-50 % propylene stayed on the catalyst to be converted into cokes. The catalytic activity was completely lost by 45 hr reaction in the case of Zn-Y. Nevertherless, acetylene and butadiene were produced in significant yields, although the thermodynamics of the following reactions is quite unfavorable at these temperatures,

$$C_3H_6 \longrightarrow \frac{1}{2}C_2H_2 + \frac{1}{2}C_4H_6 + H_2,\ \delta\Delta G^\circ = 22.7\ \text{kcal/mole at 500 K} \qquad (3)$$

$$C_3H_6 \longrightarrow \frac{1}{4}C_2H_2 + \frac{1}{4}C_4H_6 + \frac{1}{2}C_3H_8,\ \delta\Delta G^\circ = 4.22\ \text{kcal/mole} \qquad (4)$$

The concurrent formation of coke with the reaction may alter the thermodynamics favorable as suggested by the following equations

$$C_3H_6 \longrightarrow \frac{1}{4}C_2H_2 + \frac{1}{4}C_4H_6 + 2H_2 + \frac{3}{2}C(\text{graphite}),\ \delta\Delta G^\circ = 0.11\ \text{kcal/mole} \qquad (5)$$

$$C_3H_6 \longrightarrow \frac{1}{8}C_2H_2 + \frac{1}{8}C_4H_6 + \frac{1}{4}C_3H_8 + \frac{3}{2}C(\text{graphite}) + \frac{3}{2}H_2,\ \delta\Delta G^\circ = -9.09\ \text{kcal/mole} \qquad (6)$$

The amount of products did not satisfy the stoichiometry of these reactions so that the real reaction may be intermediate between eqs.(5) and (6) to be compatible with the amounts of propane and hydrogen produced.

Catalytic activity of H-Y depended very much on the calcination temperature. It was almost none by the calcination at 300°C and increased by the treatment of higher temperature to level off at 500°C. In contrast, the calcination temperature had a small influence on the activity of Ca-Y. It showed the same activity by the calcination at 300°C and 550°C. Ward[3)] suggested the presence of Lewis acid sites on H-Y calcined at 550°C. These results may indicate that a kind of Lewis acidity has a relation with the activity for acetylene formation, although the activity order of metal ions is different from that of their electron-negativity.

Catalytic abilities of X and Z were not so good as that of Y. The activity of H-Z was lost very quickly, and that of X was very low.

Table. Catalytic Activities[a)] of Ion-exchanged Zeolites for the Conversion of Propylene

Catalyst Products	Ca-Y	Zn-Y	Mn-Y	H-Y	Ag-Y	Co-Y
acetylene	28.5	22.2	18.9	16.3	13.6	10.4
butadiene	8.5	8.21	6.75	5.85	5.20	4.55
butenes	0.2	0.791	0.568	0.593	0.159	0.568
hexenes	0.2	0.832	0.292	1.05	1.17	0.292
propane	4.2	4.87	3.37	4.21	5.86	3.37
propylene	10.0	12.4	13.4	15.4	1.74	34.5

a) Conversion data(mole product/mole propylene %) at 20 min after the reaction started.
Reaction temperature; 210°, W/F = 1.67×10^{-2} g·min/ml.

Reference

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