Considerable Reduction in Crystallization Time in the Preparation of a New Type of Zeolite Catalyst for Olefin Synthesis from Methanol

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Summary A new type of zeolite catalyst for a highly selective (*ca.* 77%) synthesis of C_2—C_4 olefins from methanol has been prepared; the crystallization time at 187 °C may be made very short (2 h) using tetramethylammonium hydroxide as the modifier.

THE synthesis of lower olefins from C_1 compounds, instead of from petroleum naptha, provides a challenge that is increasing in importance. Of particular interest are the production method and properties of the new zeolite ZSM-34 which catalyses the synthesis of ethylene and propylene from methanol and which has been reported by researchers of the Mobil Oil Company.[1] There are some difficulties in the synthesis of this catalyst, however, such as the fact that a large amount of expensive choline chloride is used as the crystallization modifier, and that very long periods of time (25—196 days) are required for the crystallization; it is also reported that the catalyst life is very short (a few hours), owing to carbon deposit. We present here notable improvements in the crystallization time, type and quantity of crystallization modifier, and resulting catalyst performance (especially catalyst life).

The catalysts were prepared as follows. Silica-sol suspended water was added with vigorous stirring at 0 °C to a mixed aqueous solution of KOH, NaOH, $NaAlO_2$, and organic bases, and this was maintained under heating for crystallization to occur. After washing with water, the crystals were dried at 110 °C; then calcination under passage of air at 540 °C for 3·5 h provided the catalyst. The ratio of Si/Al in the preparation was 9·3 : 1. The atomic ratios of (Na + K) : Al and K : (Na + K) were fixed at 7·28 and 0·167, respectively.

The reaction was carried out in an ordinary flow reactor at atmospheric pressure. 150 mg (*ca.* 0·2 cm^3) of catalyst were packed in powder form into a Pyrex tubular reactor of inner diameter 5 mm, then the reaction gas (methanol 12%, N_2 88%) was passed through during several hours usually at 400 °C with a gas space-velocity of 1 000 h^{-1}. The gas formed was analysed by a flame ionisation detection-type gas chromatograph.

We confirmed that the crystallization time required is certainly more than 25 days to achieve maximum yield from the patented procedure[1] using a choline chloride *vs.* alkali molar ratio (r) of 2 : 3 at 99 °C. When choline itself was used as the modifier[2] the result was similar to that of choline chloride; tetramethylammonium hydroxide, however, caused crystallization even at r = 1 : 15. When the crystallization temperature was raised to 200 °C to shorten the crystallization time, both choline chloride and choline caused crystals to form which contained carbonaceous matter which could not be removed even by calcination in air and which shortened the catalyst life; in the case of choline chloride, both the catalytic activity and olefin selectivity were impaired. In contrast, addition of Me_4NOH to give just r = 1 : 15 provided a more efficient olefin-forming catalyst than that obtained after 25 days at 100 °C.

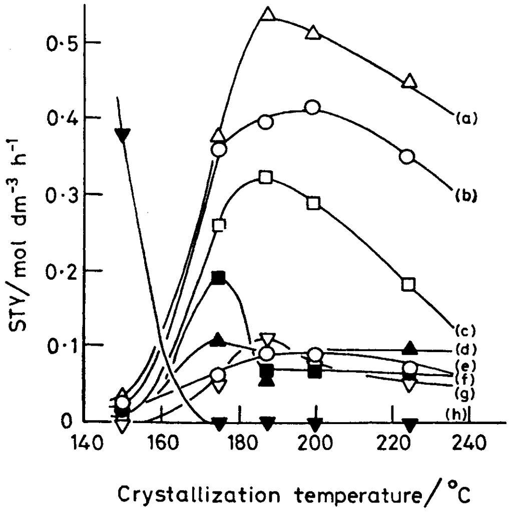

FIGURE. Effect of crystallization temperature on the catalytic activity. STY = space-time yield, of (a) C_3H_6, (b) C_2H_4, (c) C_4H_8, (d) C_3H_8, (e) CH_4, (F), C_4H_{10}, (g) C_5 hydrocarbons, (h) dimethyl ether.

In addition the crystallization time required was only 2 h at *ca.* 190 °C (Figure) and the life was not shortened. When *r* was decreased to 1 : 30, the performance of the resulting catalyst was increased. The selectivity (mol%) in this case was, ethylene 25%, propylene 32·7%, butene 19·2%, methane 4·6%, propane 6·4%, butane 4·7%, and C_5 hydrocarbons 7·5% at complete methanol conversion. Even when the crystallization time was extended to 10 h, there was no great difference. Similar results were obtained using Et_4NOH as modifier but when Pr^i_4NOH or Bu^t_4NOH were used the olefin-forming activity of the resulting catalyst was considerably decreased and stopped at the stage of dimethyl ether formation. For Si/Al atomic ratios in the range 6·5 : 1–11·5 : 1, there was no formation of dimethyl ether and olefin selectivity was high. Also in this range, when the ratio was low, propylene formation predominated and when the ratio was high, ethylene formation predominated. The *X*-ray diffraction patterns of these zeolites differed from those of ZSM-34, ZSM-5, and ZSM-11 zeolites of Mobil Oil.

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[1] Mobil Oil Co., Japanese Patent Tokkokai, **53** Showa (1978), 58499.

[2] T. Inui, E. Araki, T. Sezume, T. Ishihara, and Y. Takegami, *React. Kinet. Catal. Lett.*, in the press.