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Preparation of Synthetic Zeolites containing Some Transition Element

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Abstract

A simple method of preparing the Linde Molecular Sieve Type A and X containing transition elements such as iron, cobalt and nickel was developed to produce material which would be useful as a catalyst. Ethyl orthosilicate was directly hydrolysed by the sodium aluminate solution with excess sodium hydroxide to produce LMS A and X after 24 hours keeping the mixture at 100°C. When the sulphate or chloride of iron or nickel or cobalt was added to the excess alkaline sodium aluminate solution, LMS containing the transition element was formed. For the starting solution, the ratio of silica to alumina, 7, sodium oxide to silica, 5, was the best in case of the X type, and the former ratio, 2 or 3, the latter ratio 3 or 6 was preferable for the A type. All the experiments was proceeded in the starting mixture with the ratio of water to sodium oxide equal to 50. The produced synthetic zeolite containing iron or cobalt or nickel with the ratio of silica to the transition elemet equal to 30 or 20% was as crystalline as the commercial LMS using powder X-ray method.

Introduction

Synthetic zeolites have become more and more important in the recent years as catalysts, catalyst carriers, and molecular sieves. But there is little information on their synthesis except in the patent literature. J. Turkevich and S. Ciborowski[1] reported a simple method of preparing a faujasite material (Linde Na-Y). It was felt desirable to develop according to the preceding literature a simple producible way to make in the laboratory crystalline zeolite X and A containing the transition element with the particular view of catalysts.

Experimental Section

I mole of 99.9 % pure aluminum metal sheet (27.0 g) was dissolved in a sodium hydroxide solution containing 2 moles (80.0 g) of extra pure sodium hydroxide in 250 ml of distilled water. The metal under I mm thick, scissored in flakes was dissolved slowly and the solution was allowed to stand overnight; then it was diluted to the desired volume. In case of the synthetic zeolite containing iron, cobalt or nickel, its sulphate or chloride solution was added.

Calculated amount of extra pure ethyl orthosilicate was dropwise poured into the excess alkaline sodium aluminate solution with vigorous stirring, then the mixture was completely stirred supersonically for over 30 minutes. The mixture in the flask was continued to vibrate mechanically overnight. The flask keeping it from slight contact with the atomosphere through the I m long glass tube, was kept at 100°C using the air bath. It gradually changed into the desired crystalline product. 24 hours are sufficient for crystallization. The produced zeolite was filtered, washed several times with distilled water, and dried at 105°C. Powder X-ray spectra[2] were used to identify the crystalline species present. For X type the (III) line at d = 14.3 A and for A type the (III) line at d = 12.3 A were used for estimating the amount of these crystals formed. The contents of the elements were determined by ordinary wet analysis.

The following observations were made on the synthesis. 24 hours are sufficient for crystalization, while 8 hours are short at 100°C. The crystal can be produced even at 70°C; then several days are needed. When the ratio of SiO_2 / Al_2O_3 is equal to 7 and the ratio of Na_2O/SiO_2 is equal to 5, the most crystalline X type zeolite can be formed; while the good A type crystal is easily obtained, when the former ratio is equal to 2 or 3 and the latter ratio is equal to 3 or 6. Under the conditions far from the ratios, mixed crystals, other aluminosilicate crystals, or gels are formed. All the experiments were done in the starting gel mixture before warming to 100°C with the ratio of H_2O / Na_2O equal to 50. In the produced synthetic zeolite X or A containing Fe, Co, or Ni, over 70% crystallinity comparing with the commercial Linde Molecular Sieve using powder X-ray spectra, was achieved even at the molar ratio of alumina to the metal element equal to 30 or 20%.

This is the simple direct hydrolysis method the authors developed, by which zeolite X or A and its good crystal containing Fe, Co, or Ni are obtained. This method will be extended to other type synthetic zeolites and the crystals containing other transition elements.

References

1) J. Turkevich and S. Ciborowski, J. Phys. Chem., **71**, 3208(1967).

2) A. S. T. M. Powder X-ray Spectral Cards.