EFFECT OF CRYSTALLINITY IN HZSM-5-AMORPHOUS ALUMOSILICA SYSTEMS ON THEIR CATALYTIC PROPERTIES IN THE SYNTHESIS OF DIMETHOXYMETHANE

N. V. Pavlenko,¹ Yu. N. Kochkin,¹ N. V. Vlasenko,¹ K. N. Khomenko,² and V. V. Brej²

Granulated catalysts with 3-5% H-ZSM-5 phase were obtained from a highly dispersed alumosilica and were used for the synthesis of dimethoxymethane (DMM) from methanol and formaldehyde. The activity of these catalysts is greater than the activity of pure zeolite. A linear correlation was found between the yield of DMM and the content of Bronsted acid sites in the catalysts.

The synthesis of dimethoxymethane (DMM), which is a high-octane additive to motor fuel, is carried out, as a rule, by the condensation of methanol with formaldehyde in the presence of homogeneous acid catalysts [1, 2]:

\[2\text{CH}_3\text{OH} + \text{H}_2\text{CO} = \text{CH}_2(\text{OCH}_3)_2 + \text{H}_2\text{O}.\] (I)

This reaction under conditions of homogeneous catalysis is accompanied by a series of typical, well-known disadvantages characteristic of homogeneous catalytic reactions. Thus, the search for new heterogeneous catalysts for the synthesis of DMM is an important current scientific problem. Hydrogen forms of polymeric ion-exchange resins [1] or high-silica zeolites [2] may be used as heterogeneous catalysts for this reaction.

The use of synthetic zeolites in pure form in catalytic petroleum refining is very limited. The preparation of zeolite-containing catalysts usually involves the mechanical mixing of the active component, namely, crystalline zeolite, and an inert carrier with subsequent granulation [3]. Methods have also been proposed for the one-step hydrothermal synthesis of zeolite catalysts, in which silica gel and aluminum oxide granules are used as the carrier [4, 5]. These methods yield strong catalyst granules but, as a rule, diminish their specific activity relative to pure zeolite. Undoubted interest is found in the preparation of granulated catalysts with a controlled amount of zeolite using an alumosilicate matrix with catalytic activity comparable to zeolite. A convenient material for such catalysts is synthetic highly-dispersed alumosilica obtained by the hydrolysis of a mixture of silicon chloride and aluminum chloride in a hydrogen torch flame. Alumoaerosils with Al₂O₃ content less than 10 wt.% are amorphous aluimosilicates in the H-form and display rather high catalytic activity in the dehydration of 2-propanol and cumene cracking [6].

In the present work, data are given on the hydrothermal synthesis of HZSM-5 catalysts derived from alumoaerosil granules and the effect of the crystallinity of such composites on their activity in the synthesis of dimethoxymethane.

1L. V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, 31 Prospekt Nauki, Kiev 03039, Ukraine.
2Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 31 Prospekt Nauki, Kiev 03028, Ukraine.

EXPERIMENTAL

The method for preparing cylindrical catalyst granules with varying ZSM-5 zeolite content involved the following steps: mixing of alunomaisil (SiO₂/Al₂O₃ = 25) with 3% aqueous ammonia, extraction of the resultant pasty mass through a die head with 2-mm holes, drying of the granules at 390 K for 3 h, hydrothermal treatment at 450 K for 4 h, and roasting the granules at 810 K. In order to obtain catalysts containing ZSM-5, the granules were placed into aqueous sodium hydroxide with tetrapropylammonium bromide as the added template and crystallization was carried out in an autoclave at 440 K. In contrast to the reported methods for obtaining zeolites, the alunomaisil granules in this procedure served as the only source of silica and alumina for the synthesis of Pentasil. The samples were converted to the H-form by ion exchange with 2 N NH₄Cl followed by drying and roasting at 810 K.

The ZSM-5 zeolite content in the samples was determined from the X-ray diffraction patterns taken on a DRON-UM1 diffractometer, CuKα radiation, and nickel filter according to Barrer [8]. The microphotographs of the sample were taken using a Jeol scanning electron microscope. The specific surface of the samples was determined relative to the thermal desorption of argon. The acidity of the zeolite samples was studied using the thermoprogrammed desorption of ammonia at room temperature to 900 K with an MI-1201 mass spectrometer as the gas phase analyzer. The acid site concentration was determined thermogravimetrically relative to the adsorption of ammonia in the evacuation temperature range 323-773 K assuming that one ammonia molecule may be adsorbed on one acid site.

The catalytic properties of these samples were studied in a flow reactor with fixed catalyst bed. The catalyst bulk was 1.5 cm³ and the granule size was 0.5-2 mm. The measurements were taken at 423 K and 1 MPa. The methanol/formaldehyde mole ratio was 2.5. The total volumetric rate of the liquid consisting of methanol and formaldehyde was 3 h⁻¹ and the volumetric flow rate of the helium gas carrier was 200 h⁻¹. The products of reaction (I) except for formaldehyde were analyzed on a Hewlett Packard 5880A gas chromatograph on a 60-m quartz capillary column packed with Carbowax 20M and flame ionization detection. The analysis was carried out with temperature programming from 348 to 448 K at 8 K/min. The concentration of unreacted formaldehyde was calculated using the analysis data of the other reaction products assuming a stoichiometric reaction and taking account of the starting molar ratio of the reagents.

RESULTS AND DISCUSSION

A series of granulated catalysts was obtained with different contents of ZSM-5 zeolite (Table 1). The synthesis time for samples with ZSM-5 content from 3 to 59% varied from 6 to 15 h. The granules with greater zeolite content lose their mechanical strength. The X-ray diffraction patterns of these samples corresponded to the pattern of ZSM-5 zeolite.

Our studies showed that the zeolite phase begins to form on the alunomaisil globule surface as isolated, clearly nonfaceted crystals (sample No. 4 with 36% zeolite). Further crystallization leads to the formation of associated crystals varying in length from 1 to 10 μm (sample No. 5 with 59% zeolite). Pure Pentasil is formed as uniform isolated crystals (3.5-4 μm).

The spectra for the thermal desorption of ammonia from the surface of these catalysts are similar to the corresponding spectra of NH₃ for HZSM-5 and alunomaisil given in our previous work [6] displaying peaks at 378 and 590 K. The high-temperature peak broadens and the peak intensity drops with a decrease in the ZSM-5 phase content. Gravimetric analysis for ammonia desorption with stepwise increase in sample temperature to 750 K showed that these zeolite catalysts possess different amounts of acid sites (Table 1). Depending on the sample crystallinity, the change in the concentration of their acid sites is rather complex, apparently as a consequence of the different sizes of the zeolite crystals formed and different Si/Al ratio in the crystals. Thus, enrichment of the crystals in aluminum ions in comparison to the starting gel occurs in the synthesis of ZSM-5. The Si/Al ratio in the larger crystals is lower than in the finer crystals [8]. This may correlate with the greatest content of Brønsted acid sites in sample No. 5 with the largest Pentasil crystals.

All these zeolite-containing samples proved catalytically active in DMM synthesis from methanol and formaldehyde (Table 2). The samples retained their activity during the entire 7 h testing period. We observed 100% formaldehyde conversion and greatest DMM content in the organic reaction products per 1 g catalyst for sample No. 5 with 59% zeolite. On the other hand, sample No. 7 obtained by the mechanical mixing of 59 wt.% zeolite with alunomaisil is less active. We should also note that the DMM yield increases with increasing concentration of acid sites in the catalysts obtained (Fig. 1). This correlation suggests that methanol and formaldehyde molecules adsorbed on the acid sites of the catalyst take part in the formation of DMM (Langmuir–Hinselwood mechanism).