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FACTORS AFFECTING THE STABILITY AND SELECTIVITY OF ZEOLITES IN THE CONVERSION OF METHANOL TO HYDROCARBONS.

COMMUNICATION 1. EFFECT OF HEAT TREATMENT IN STEAM

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High-silica zeolites of the ZSM type are effective catalysts for the synthesis and conversion of hydrocarbons [1, 2]. In the course of the synthesis of hydrocarbons from methanol they undergo a gradual, reversible deactivation on account of coke formation. The prolonged action of high temperature and steam gives rise to nonreversible deactivation of zeolites [3, 4]. A similar effect for Ultrazet zeolite was observed in [5], under various conditions of preliminary heat treatment in steam, during a study of the effect of the treatment on the physicochemical properties of the zeolite.

The present work was directed to a study of the influence of preliminary heat treatment of ZSM zeolites in steam on their resistance to coke formation and their selectivity in the conversion of methanol to hydrocarbons.

EXPERIMENTAL

All the experiments were carried out using ZSM zeolite prepared according to the method of [6] with a molar ratio of $SiO_2/Al_2O_3 = 54$ and Na_2O content = 0.03%. The effective surface of the samples after treatment was calculated from argon absorption at liquid nitrogen temperature. The degree of crystallinity was characterized in terms of the intensity of lines on the diffractogram corresponding to a reflection angle $2\theta = 23.2°$. The diffractograms were obtained on URS-50 and DRON-1 diffractometers. NMR studies were carried out on samples which had been heated at 520°C in air and then stored for 24 h over water in a desiccator at 20°C. The measurements were carried out on a Bruker CXP-300 impulse NMR spectrometer. The ^{27}Al spectra (78.2 MHz) were recorded over a frequency range of 125 kHz with a 0.5-μsec radiofrequency impulse. The spectra were run, with the samples rotated to the "magic angle," at a frequency of 3.0-3.5 kHz.

The zeolite in H-form, in a close-packed, thick layer, was treated with steam at 500-800 °C, with a space velocity of 1 h^{-1} referred to water, for 2.5 h. The selectivity of the prepared catalysts in the conversion of methanol to hydrocarbons was determined on a flowthrough apparatus at a temperature of 380-420°C and a feed rate of liquid MeOH of 2 h^{-1}. Experiments

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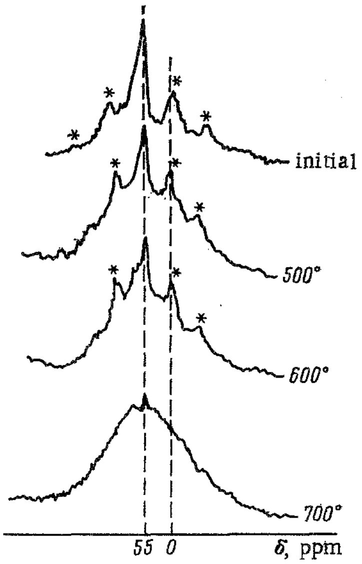


Fig. 1

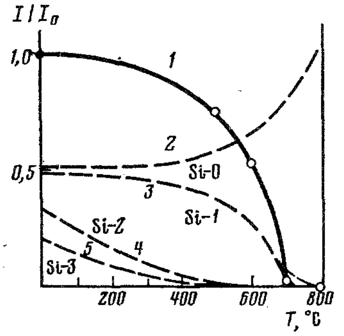


Fig. 2

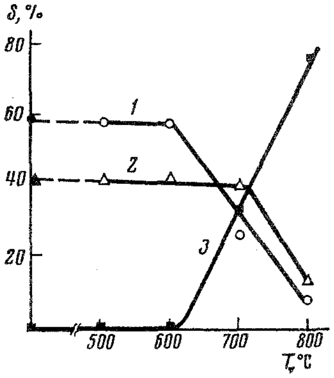


Fig. 3

Fig. 1. ^{27}Al NMR spectra of samples with different STT.

Fig. 2. Variation of intensity of NMR signals from Al atoms in tetrahedral coordination (1) and theoretical curves for relative content of $Si(OAl)_n(SiO_4)_{4-n}$ groups relative to STT: 2) n = 0; 3) n = 1; 4) n = 2; 5) n = 3.

Fig. 3. Variation of yields with STT: 1) ΣC_{5+}; 2) ΣC_1–C_4; 3) DME.

on the dynamics of the formation of coke on the zeolites in the methanol conversion process were carried out in a flowthrough tubular reactor with isothermal internal walls, the temperature of which was controlled by means of a boiling liquid. Along the axis of the tube was inserted a quartz tube along which a thermocouple was moved periodically with a velocity v_T, considerably greater than the rate of travel of the reaction front v_R; since $v_t \gg v_R$, the reaction zone could be considered stationary relative to the movement of the thermocouple so that it was possible to obtain a temperature profile of the working layer of the catalyst. This technique is similar to that described in [7], where it was shown that the reaction zone coincides with the zone of heat emission and moves along the catalyst layer in the course of the reaction with constant velocity. This is connected with the layerwise poisoning of the catalyst by deposited coke. In this way the rate of coke formation on the catalyst layer could be characterized by the rate of travel of the heat-emission zone. The reaction products were analyzed by chromatography using columns packed with γ-alumina and polyphenyl ether on C-22 carrier.

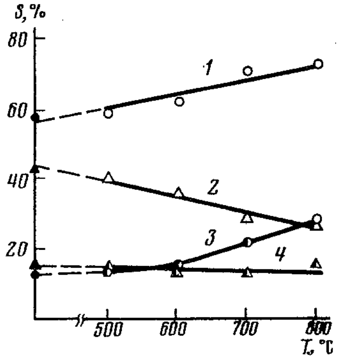


Fig. 4

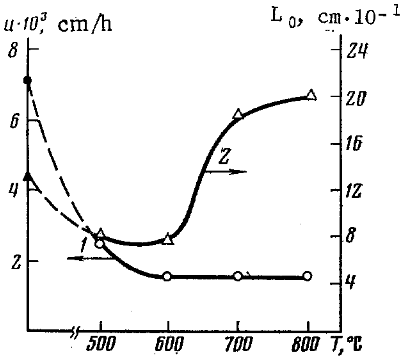


Fig. 5

Fig. 4. Relationship between STT and the content in the ΣC_{5+} fraction of (1) aliphatic, (2) aromatic hydrocarbons, (3) heavy aliphatics ΣC_{7+}, and (4) heavy aromatics ΣC_{9+}.

Fig. 5. Rate of coking of the catalyst layer (1) and width of reaction zone (2) as a function of STT.

TABLE 1. Surface Area and Degree of Crystallinity of Treated Zeolites

STT, °C	Zeolite surface, m²/g	Degree of crystallinity, %
Original sample	420	100
500	405	100
600	430	97
700	380	97
800	380	97

DISCUSSION OF RESULTS

Effect of Steam Treatment Temperature (STT) on the Physicochemical Properties of Zeolite. The ^{27}Al NMR spectra, run with the sample rotated at the magic angle (Fig. 1), indicate that with increase in treatment temperature the intensity of the signal with chemical shift of 55 ppm (which corresponds to an Al form in tetrahedral coordination) is reduced. After treatment of the zeolite at 700°C the signal has practically disappeared. At the same time, the intensity of the broad NMR signal increases; this could be assigned to Al atoms, for example in amorphous Al_2O_3. On rotating the sample at the magic angle, side bands (from rotation, marked *) appear in the ^{27}Al NMR spectrum; the position of one of them coincides almost exactly with the signal for Al atoms in octahedral coordination ($\sigma = -3$ ppm). For this reason it was considered impracticable to determine octahedrally coordinated Al by NMR in subsequent samples. However, as can be seen from Fig. 1, the intensity of these signals falls as the temperature of steam treatment is increased, which is evidence at least that Al atoms leaving the framework do not pass into cation positions.

The relative intensity of the signal from Al atoms in tetrahedral coordination varies with STT (Fig. 2). The intensity of this signal falls to zero at 700-800°C, whereas the overall surface and the degree of crystallinity vary little over this range (see Table 1). Hence, breakdown of the crystalline framework of the zeolite does not occur.

The intensity of certain lines in the diffractograms also changes as the steam-treatment temperature is increased. Thus, for example, the intensity of the line with diffraction angle $\theta = 3.8\text{-}4.5°$ increases somewhat and the intensity of the $\theta = 11.5\text{-}12.5°$ line decreases. Analogous changes are usually observed on dealuminization of the zeolite framework or on increase of the SiO_2/Al_2O_3 ratio in the zeolite.

Effect of STT of Zeolites on the Selectivity of Methanol Conversion. On increasing the zeolite treatment temperature up to 600°C, the yields of the ΣC_{5+} hydrocarbon fraction (Fig. 3, curve 1) and of dimethyl ether (DME) (curve 3) remain unchanged. On further increase of temperature the yield of the ΣC_{5+} fractions falls sharply and the yield of DME sharply rises.

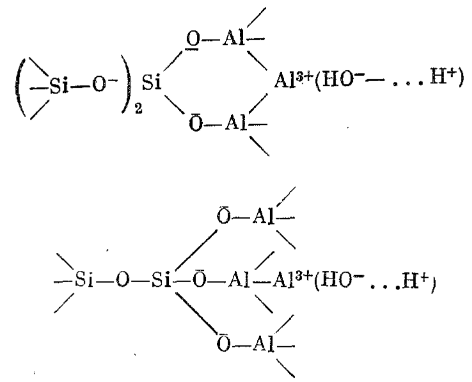
The yield of the gaseous ΣC_1-C_4 hydrocarbons remains constant up to a pretreatment temperature of 700°C and then sharply falls. Here the composition of the liquid ΣC_{5+} fraction changes uniformly with respect to the different classes of hydrocarbon (Fig. 4). The aliphatic hydrocarbon content (saturated and unsaturated) (curve 1) increases and the aromatic hydrocarbon content (curve 2) decreases. With steam treatment temperatures of 600-800°C the aliphatic hydrocarbon content increases on account of the increase in the proportion of heavy fractions of unsaturated ΣC_7 hydrocarbons (curve 3). The amount of aromatic hydrocarbon falls at the expense of the light fractions (benzene, toluene, xylene); the proportion of heavy ΣC_9 aromatics remained the same at all the levels of STT examined.

Although the yield of overall gaseous hydrocarbons remains unchanged up to STT = 700°C, the composition varies. Thus, beginning with STT = 600°C, ΣC_2 and ΣC_4 increase and ΣC_3 decreases. On increasing STT, the ratio of paraffin to olefin in the ΣC_2 fraction falls to zero along an exponential curve while it increases exponentially in the C_4 fraction.

Effect of STT on the Rate of Coking of the Catalyst Layer. The rate v of layerwise coking of the catalyst characterized in terms of the rate of movement of the reaction zone along the length of the reactor (Fig. 5, curve 1) falls with increase of STT up to 600°C and thereafter remains unchanged. At the same time, the width of the reaction zone (defined as the height of the catalyst layer participating in the reaction) decreases insignificantly up to STT = 600°C and rises abruptly on further increasing the temperature (curve 2).

Using the approach of [8, 9], based on an evaluation of the nature of the statistical distribution of Al atoms in the zeolite framework, new ^{29}Si NMR data [10, 11], and the results of a study of the catalytic properties of zeolites in relation to their SiO_2/Al_2O_3 ratios [12], it is possible to put forward the following suggestion: the distribution of Al atoms in the zeolite framework is such as to permit the formation of $Si(OAl)_n(SiO_4)_{4-n}$ groups, where n varies from 1 to 4 with statistical distribution according to n [10].

The selectivity of the catalytic action of groups with differing values of n is different. As n increases, the selectivity of the action of the zeolite in relation to the formation of aromatic hydrocarbons and coke forerunners also increases. In [13-15], on the basis of comparison of NMR data and the selectivity of action of the zeolites, it was suggested that the reactions leading to coke formation are associated with the appearance of Al atoms in cation positions in the zeolite. These may enter into the composition of centers of type (I), having 2 or 3 Al atoms in the second coordination sphere of the Si atoms of the zeolite framework (Si-2 and Si-3), and accelerate the hydrogen redistribution reactions with the formation of extensively dehydrogenated compounds



(I)

Thermal treatment can lead to loss of nonframework Al from the zeolite, converting it to Al_2O_3 as well as to hydrolysis of Si—O—Al bonds and loss of Al from the zeolite framework [16].

On increasing the temperature of the preliminary steam treatment, hydrolysis of Si—O—Al bonds and loss of Al atoms from the framework does in fact take place; this is confirmed by the fall in the intensity of the NMR signal for tetrahedrally coordinated Al (see Fig. 2). On this figure are plotted (by dashed lines) hypothetical, theoretical curves for the distribution of Al (according to the calculations of [8, 9]). It seems that up to STT = 600°C loss of all the Al from the cation positions occurs, together with Si-2 and Si-3 groups, and only the Si-0 and Si-1 groupings remain. On further increasing the STT, further hydrolysis of the Si—O—Al bonds occurs with loss of Al from Si-1 locations. Thus, increase of STT leads to dealuminization of the zeolite framework. At the first level, the aluminum situated in cation positions is lost together with that in locations of high Al concentration in the framework – Si-2 and Si-3. The Al lost from the framework passes, apparently, into the amorphous Al_2O_3 phase, and the increase in the intensity of the broad band in the NMR spectrum (see Fig. 1) is evidence of this. That the framework loses aluminum without loss of structure is supported by the change in intensity of certain lines observed in the diffractograms.

From this viewpoint it is easy to explain the effect of STT on the selectivity of methanol conversion and the rate of coking of the catalyst. The Si-2 and Si-3 group content in the zeolites studies was small in comparison with the quantity of Si-1 groups because the overall Al content of the zeolite was small. Loss of Si-2 and Si-3 at 600°C is not reflected in the degree of conversion of methanol to hydrocarbons but has an effect only on the selectivity of its conversion and the rate of coking of the catalyst layer. The selectivity is increased for aliphatic hydrocarbons and reduced for aromatic (see Fig. 4). The rate of coke formation falls sharply here (see Fig. 5) on account of the reduction in the proportion of hydrogen transfer reactions, the rate of which is higher on type (I) centers and on Si-2 and Si-3 locations than on Si-1.

On further increasing the STT, there is an abrupt fall in the quantity of Si-1 groups, and this leads to a reduction in the degree of conversion of methanol into hydrocarbons (see Fig. 3). The primary hydrocarbon formed from methanol is ethylene and, as products of its dimerization, butylene and heavier aliphatic saturated and unsaturated hydrocarbons. Aromatic hydrocarbons, and ΣC_3 fractions, are secondary products of aromatization and cracking, respectively. When STT is increased from 600 to 800°C, a further reduction in selectivity for the formation of aromatic hydrocarbons takes place (see Fig. 3), accompanied by an increase in ΣC_2 and ΣC_4 and a reduction in ΣC_3 hydrocarbons in the gas phase; this is evidence of a reduction in the secondary cracking and aromatization reactions and an increase in the primary products of the methanol conversion. The proportion of C_4 hydrocarbons formed as a result of cracking is apparently reduced (the paraffin/olefin ratio in the products of cracking $\leqq 1$), and the proportion of C_4 hydrocarbons resulting from the synthesis reaction increases.

The rate of coking of the catalyst layer over the STT range 600-800°C remains unchanged, which is additional evidence of the uniformity of the active centers remaining in the zeolite (Si-1, see Fig. 5). When STT is increased from 600 to 800°C, the composition of the active centers does not change but their number is reduced, and this leads to an increase in the width of the working layer of the catalyst (see Fig. 5).

The authors wish to thank V. M. Mastikhin for running the NMR spectra.

CONCLUSIONS

1. Thermal steam treatment of ZSM zeolites leads to their dealuminization, but the crystal structure is retained.

2. When the steam-treatment temperature is increased to 600°C, as a first step aluminum is lost from the cation positions and probably from the locations where it is concentrated in the framework; this leads to a reduction in secondary reactions and hydrogen transfer reactions and, as a result, to an increase in the resistance of the zeolite to coking.

3. When the steam-treatment temperature is increased to 600°C, the overall number of active centers falls sharply and hence also the degree of conversion of methanol to hydrocarbons. The active centers which remain are uniform.

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FACTORS AFFECTING THE STABILITY AND SELECTIVITY OF ZEOLITES IN THE CONVERSION OF METHANOL TO HYDROCARBONS

COMMUNICATION 2. EFFECT OF DEALUMINIZATION

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It has been shown by ^{27}Al NMR [1, 2] that when zeolites of type Y are deactivated, Al atoms appear in their composition in an octahedral environment of oxygen atoms, i.e., in cation positions. It has been established by ^{29}Si NMR that the Al is distributed nonuniformly along the zeolite framework with the formation of fragments containing more than one Al atom in the secondary coordination sphere of the Si atoms, and it has been suggested that such groups could be the centers of multipoint interactions with the reactant and of acceleration of hydrogen transfer reactions leading to the formation of extensively dehydrogenated products [3, 4].

To check this hypothesis, IR and ^{27}Al and ^{29}Si NMR spectroscopy have been employed in the present work to study the effect of dealuminization on the state of the Al and Si atoms and on the selectivity and stability of the catalytic activity of Y and ZSM zeolites.

EXPERIMENTAL

Zeolites which are rapidly poisoned by coking were selected for study: Y and ZSM with SiO_2/Al_2O_3 ratios of 4.80 and 38, respectively. Deactivated zeolites were prepared by twofold treatment with a solution of $NH_4OH + NH_4Cl$. The technique of [5] was used for dealuminization by $SiCl_4$ vapor. Examination of the zeolites by IR and NMR spectroscopy was carried out by the method described in [6]. ESCA was employed to determine the intensity of the Si 2p and Al 2p lines, and from this the SiO_2/Al_2O_3 (M) ratio on the surface of the zeolite crystal (to a depth of 25-30 Å) was calculated. The selectivity and stability of the catalytic action of the zeolites were evaluated for the synthesis of hydrocarbons from methanol in a flow apparatus at 380-420°C and a space velocity in terms of liquid MeOH of 1-1.5 h^{-1}. The dynamics of coke formation were investigated using a method similar to that of [7].

DISCUSSION OF RESULTS

Thermochemical treatment of Y and ZSM zeolites with $SiCl_4$ vapor leads to their dealuminization, i.e., to an increase in the value of M (Table 1). From the ESCA results, for samples HZ, Z-1, and Z-2 the values of M on the crystal surface are, respectively, 130, 120, and 140. Increase in M following thermochemical treatment of the zeolites with $SiCl_4$ vapor leads to a reduction in the difference between the values of M determined by chemical analysis and ESCA.

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