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Synthesis and Study of Catalytic Properties of Beryllium Silicates Having Zeolite-type Structure

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Beryllium silicates having the ZSM-5-type crystalline structure were synthesized in the presence of tetraethylammonium hydroxide. The chemical shifts in the ^{9}Be NMR spectra show that Be^{2+} cations in these synthesized samples are located in a tetrahedral coordination different from that for Be^{2+} in BeO and $[Be(H_2O)_4]^2$. Methanol conversion on beryllium-silicate zeolites yields primarily olefins, while on aluminum silicates having the same crystalline structure paraffins and aromatic hydrocarbons were obtained. It is proposed that the observed differences in the catalytic action result from the lower strength and concentration of Lewis acid sites in the composition of catalytically active groups in beyllium silicates. © 1985 Academic Press, Inc.

INTRODUCTION

Crystalline silicates having zeolitic structures in which part of silicon atoms of a three-dimensional silicon–oxygen framework is substituted by aluminum atoms are known to catalyze the synthesis and conversion of hydrocarbons (*1*, *2*). Catalytically active sites are associated with the aluminum cations, whose coordination environment determines the character of the catalytic action (*3*).

Based on the known ideas about the nature of acid–base properties of binary oxide systems (*4*), one may expect that by modifying the nature of the cation which substitutes silicon in the zeolite framework it is possible to change the activity and selectivity of the latter over wide ranges.

Beryllium silicates, including those with zeolite-type structure, e.g., analcime (*5*), can be obtained by hydrothermal synthesis. This method has been used by us to synthesize beryllium silicates having the ZSM-5-type structure. ^{9}Be NMR was employed to examine the state of the Be^{2+} ions. The catalytic properties of beryllium silicates toward the reaction of hydrocarbon synthesis from methanol have been characterized.

EXPERIMENTAL

The synthesis of beryllium silicates having the ZSM-5-type structure was carried out by hydrothermal crystallization of beryllium-containing silica sol in the presence of tetraethylammonium hydroxide over the temperature interval 170–180°C for 80–120 h as described earlier (*6*). Crystallization having been completed, the samples were filtered, rinsed with distilled water, dried, calcined in oxygen flow at 500–550°C for 2–3 h, and ion-exchanged using 0.1 *M* ammoniacal buffer solution at room temperature with subsequent thermal treatment at 550°C for 2 h.

Beryllium silicate having a nonzeolite structure was synthesized by the same method, but in the absence of organic base.

Chemical analysis of the samples was carried out by "Spectr" type atomic absorption spectrophotometry.

X-Ray powder diffraction analysis was carried out with a DRF-type diffractometer with Cu$K\alpha$ monochromatic radiation in the range $3° \leq \theta \leq 15°$. The content of zeolites in solid phases was calculated from the intensity of reflections in the range 11–12° θ. ZSM-5-type zeolite synthesized earlier (*6*)

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was chosen as a reference. It shows a 100% degree of crystallinity both in terms of the intensity of reflections on X-ray diffractograms, and of scanning electron micrographs as well as transmission electron micrographs.

Registration of ${}^9Be$ NMR spectra was performed on a Bruker CXP-300 pulse spectrometer at a frequency of 42.17 MHz, magnetic field intensity of 7.0463 T, and a pulse duration of 1 μs. Spectra were recorded at room temperature, using equal quantities of the samples. A 0.05 *M* aqueous solution of sodium beryllate was used as a reference in the shift measurements. The shifts toward weak field were indicated and designated positive. The narrowing of NMR lines was achieved by magic angle spinning of samples at 4 kHz.

The selectivity of methanol conversion was investigated in a flow-circulating installation at 370 and 450°C, contact time being 1.0 ± 0.1 s. The reaction mixture contained 2–44 vol% of methanol vapor in helium. Inlet and outlet reaction mixtures were analyzed using a gas chromatograph with columns filled with γ-Al_2O_3 (with a surface area of about 500 m^2/g) and polyphenyl ether on C-22 support.

The selectivity of the product (S_i) was calculated by the equation $S_i = W_i \cdot n_i \cdot 100/W_0$ (mol%), where W_i is the rate of product accumulation, and W_0 is the rate of methanol consumption (both in mol · sec^{-1} · g_{cat}^{-1}); n_i is the number of carbon atoms in the product molecule. ZSM-5-type zeolites of the aluminum-silicate chemical composition (*6*) and beryllium silicate having a nonzeolite structure with a molar ratio SiO_2/BeO equal to 14 and a surface area of about 11 m^2/g were investigated as samples for comparison.

RESULTS

Nature of the samples. Zeolites of beryllium-silicate chemical composition with molar ratio SiO_2/BeO equal to 30, 60, and 90 were synthesized and investigated in this work. The aluminum content in the samples did not exceed 0.03 wt%. Al_2O_3, i.e., the SiO_2/Al_2O_3 ratio in the beryllium-silicate zeolites was not less than 4000. A qualitative phase analysis has shown that the samples contain not less than 90% of the crystal phase having the ZSM-5-type zeolite structure (*7*).

${}^9Be$ NMR spectra for H-forms of the

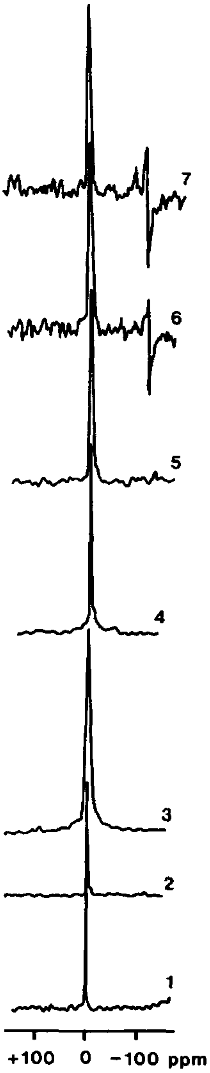


FIG. 1. ${}^9Be$ NMR spectra for beryllium-silicate zeolites and reference samples. (1) 0.05 *M* solution of sodium beryllate (pH ≈ 12); (2) 0.05 *M* solution of beryllium sulfate (pH ≈ 1); (3) beryllium oxide; (4) beryllium silicate having nonzeolite structure; and (5, 6, 7) beryllium-silicate zeolites with molar ratios SiO_2/BeO equal to 30 (5), 60 (6), and 90 (7).

samples studied are shown in the Fig. 1. It follows from the quantitative comparative analysis of the samples and a reference solution that NMR is observed in zeolites from the majority (not less than 75–95%) of the beryllium atoms. The chemical shift in beryllium-silicate zeolites does not depend on beryllium content upon variation of SiO_2/BeO ratio over the range 30–90 and is equal to −5.8 ppm (Table 1). At the same time there is a marked difference between this value and the chemical shifts in crystalline beryllium silicate having nonzeolite structure, in beryllium oxide and in an aquo-complex $[Be(H_2O)_4]^{2+}$ (Table 1).

Selectivity of hydrocarbon synthesis from methanol is presented in Table 2. Products of methanol conversion on beryllium silicates having zeolite structure contain mainly olefin hydrocarbons. At the same time, dimethyl ether is the only product of methanol conversion on crystalline beryllium silicate having nonzeolite structure.

DISCUSSION

The results show that beryllium silicates having zeolite structure and containing aluminum in traces only, are catalysts of the acid–base type which accelerate methanol-to-hydrocarbons conversion. Similar properties of known silicates were established so far only for zeolites of aluminum-silicate chemical composition (*2*, *8*).

Methanol-to-hydrocarbons conversion on zeolites occurs via the following the principal Scheme 1 (*2*). Separate stages of this process proceed at different rates, which allows one to obtain intermediates as the main products by varying reaction conditions (contact time, temperature, degree of reactant dilution, partial deactivation of catalysts by coke).

$$CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} CH_3OCH_3 \xrightarrow{-H_2O} \text{olefins } C_2\text{–}C_5 \rightarrow \text{paraffins} + \text{aromatic hydrocarbons}$$

SCHEME 1.

Under the reaction conditions employed in this work methanol conversion on ZSM-5-type zeolites with SiO_2/Al_2O_3 in the range 72–216. (Table 2) passes through practically the whole reaction pathway (Scheme 1); as a result the reaction products contain only traces of dimethyl ether (4 mol%), some olefins (31–39 mol%), but mainly paraffins and aromatic hydrocarbons (57–75 mol%). Under the same reaction conditions methanol conversion on beryllium silicates with atomic ratio Si/Be close to the Si/Al ratio in corresponding zeolites terminates either at the stage of dimethyl ether forma-

TABLE 1

Values of ^9Be NMR Chemical Shifts (δ) in Beryllium-Silicate Zeolites and in Samples for Comparison[a]

	Sample					
	0.05 *M* Solution of beryllium sulfate (pH ≈ 1)	Beryllium oxide	Beryllium silicate having nonzeolite structure	Beryllium-silicate zeolites of ZSM-5-type structure with different SiO_2/BeO ratios		
				30	60	90
δ (ppm)	−1.73	−2.3	−3.47	−5.8	−5.8	−5.79

[a] Reference: 0.05 *M* aqueous solution of sodium beryllate.

TABLE 2

Selectivity (mol%) of Methanol Conversion on Isostructural Beryllium-Silicate and Aluminum-Silicate Zeolites

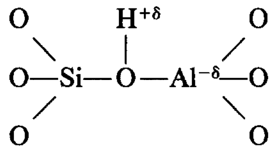
Molar ratio SiO_2/E_nO_m in the samples	$SiO_2/BeO = 30$	$SiO_2/Al_2O_3 = 72$	$SiO_2/BeO = 60$	$SiO_2/Al_2O_3 = 127$	$SiO_2/BeO = 90$	$SiO_2/Al_2O_3 = 216$	$SiO_2/BeO = 14$
Atomic ratio Si/*E*	30	36	60	63.5	90	108	14
Reaction temperature, °C	370, 450	370	370, 450	370	370	370	370
Initial methanol concentration, vol%	16.4, 22.5	12.4	11.3, 14.6	14.0	26.4	16.1	11.5
Total methanol conversion, %	71.3, 70.9	95.9	84.0, 85.3	95.3	74.7	93.1	31.8
Methanol-to-hydrocarbon conversion, %	0.5, 21.6	92.0	49.6, 80.9	91.2	12.6	89.7	0.0
Selectivity							
Dimethyl ether	99.3, 69.6	4.0	39.7, 5.1	4.3	83.1	3.7	100
Aliphatic hydrocarbons	0.7, 25.4	69.0	57.3, 84.2	74.7	16.0	75.5	—
Ethane	— —	—	— —	—	—	—	—
Ethylene	0.4, 5.2	7.2	6.9, 11.3	8.0	2.1	7.1	—
Propane	— 0.2	7.2	1.0, 3.6	7.0	—	3.6	—
Propylene	0.3, 9.2	13.3	25.3, 31.7	14.4	5.6	18.2	—
isoButane	— 0.5	12.9	2.3, 2.6	13.9	—	9.6	—
n-Butane	— 0.6	2.9	1.8, 0.2	3.8	—	2.4	—
Butylenes	— 4.6	10.5	11.0, 17.7	12.8	3.7	14.1	—
isoPentane	— 1.8	2.7	2.8, 3.0	2.5	1.4	3.2	—
n-Pentane	— 0.9	6.6	4.0, 2.6	6.6	0.9	6.9	—
C_{6+}	— 2.4	5.7	2.2, 11.5	5.7	2.3	10.4	—
Aromatic hydrocarbons	— 5.0	27.0	3.0, 10.7	21.0	0.9	20.8	—
Benzene	— —	—	— —	—	—	—	—
Toluene	— 0.4	1.7	0.3, 1.0	1.7	—	1.5	—
(*m* + *p*)-Xylenes	— 2.0	8.0	1.6, 4.6	8.0	0.5	6.8	—
o-Xylene	— —	2,3	— 0.5	2.1	—	1.4	—
(*m* + *p*)-Ethyltoluene	— 0.9	2.5	— 1.6	2.0	—	2.0	—
Pseudocumene	— 0.9	6.7	1.1, 1.5	4.2	0.4	6.2	—
C_{10+}	— 0.8	5.8	— 1.5	3.0	—	2.9	—

Note. Space velocity relative to initial gaseous mixture is 3600 ± 200 h^{-1}.

tion (Si/Be = 30) or olefin formation (Si/Be = 60 and 90). Noticeable quantities of aromatic hydrocarbons and paraffins are formed on beryllium silicates having zeolite-type structure only at much higher reaction temperatures (450°C, Table 2).

The fact that methanol conversion on zeolites of beryllium-silicate and aluminum-silicate chemical compositions follows the same general route allows one to propose that there is a common nature for the active sites in these zeolites. The difference in the rates of the reaction proceeding via the same pathway (Scheme 1) seems to indicate a difference either in the concentration or in the strength of active sites. To elucidate the nature of the specific catalytic action of beryllium-silicate zeolites, let us consider the following data.

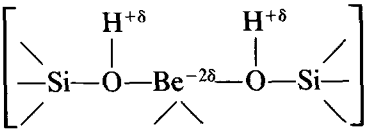
The sites which are catalytically active in acid–base transformations are supposed (*1*) to form in zeolites at the sites of isomorphous substitution $(SiO_4)^{4-} \leftrightarrow (AlO_4)^{5-}$. An excess negative charge of the framework which appears as a result of such substitution is compensated in decationated zeolites by a proton of the polarized bridge hydroxyl group in the following way:



We must now consider whether sites of a similar nature but involving beryllium atoms instead of aluminum form in the beryllium-silicate zeolites synthesized by us. The tetrahedral oxygen surrounding is known to be thermodynamically the most favorable for Be^{2+} in oxide systems (*9*). Therefore, isomorphous substitution $(BeO_4)^{6-} \leftrightarrow (SiO_4)^{4-}$ is possible for many silicate minerals. Indeed, the probability of isomorphous substitution is high when the values of radii (r) and electronegativities (X) of mutually substituting cations are nearly the same, which is the case for the $BeO{-}SiO_2$ system because r and X for Be^{2+} and Si^{4+} are 0.35 and 0.42 Å, and 210 and 260, respectively (*10*).

However, based on the criterion of stability of the crystalline structure of given type (*4*), we may assume that the trigonal oxygen surrounding is also possible for Be^{2+}.

The tetrahedral surrounded by water molecules is typical for aquo-complexes $[Be(H_2O)_4]^{2+}$ (*11*). A narrow symmetric line in the ^9Be NMR spectrum corresponds to this state. In the case of the tetrahedral surrounding of Be^{2+}, this line shifts from −12 to *f*1 ppm with respect to the signal from $[Be(H_2O)_4]^{2+}$ as the electronegativity of the substituent increases. When passing to the trigonal coordination of Be^{2+}, the chemical shift toward weak field increases from −21 to −10 ppm (*11*). The intensity of the signal with a chemical shift of −5.8 ppm observed by us corresponds to 75–95% of beryllium content determined by chemical analysis. A low value of the chemical shift with respect to hydroxyberyllate anions in aqueous solution provides additional evidence for the tetrahedral coordination of Be^{2+} which includes more electronegative substituents than water molecules. Moreover, the fact that the value of this shift differs from those typical for nonzeolite beryllium silicate, beryllium oxide and beryllium aquo-complex, i.e., from the states which, with different probabilities, can be an alternative to beryllium fixation in the zeolite framework, suggests that Be^{2+} in our zeolites is predominantly in the silicon–oxygen framework at positions of isomorphous substitution of Si^{4+}. However, such substitution must give rise to an excess negative charge (Scheme 2).



$$[(SiO)_{4-n}Si(OBe)_n]^{-2n\delta}(H^{+\delta})_{2n}$$
$$(0 < n \leq 4).$$

SCHEME 2.

If this latter is also compensated by protons, the number of such protons (i.e., Brønsted acid sites, BAS) in beryllium silicates must be two times higher than in aluminum-silicate zeolites, provided their atomic ratios Si/E (E = Al or Be) are nearly the same. Moreover, if we take into account that e/r of Be^{2+} (6.5) is higher than that of Al^{3+} (6.0), the degree of protonation of bridge hydroxyl groups in the field of Be^{2+} cations is to be expected to exceed that in the field of Al^{3+} cations. Hence, if the above model is valid, the strength of BAS in beryllium-silicate zeolites must be higher than that of aluminum-silicate sites at similar atomic ratios Si/E.

Consequently, if methanol-to-hydrocarbons conversion involved only BAS formed via Scheme 2, the selectivity with respect to paraffins and aromatic hydrocarbons on beryllium-silicate zeolites would be significantly higher than the corresponding value for aluminum-silicate zeolites, which is not confirmed experimentally (Table 2).

It is proposed in Ref. (*3*) that the reaction of olefin aromatization on aluminum-silicate zeolites involves an ion pair which consists of anions of the framework and Al^{3+} cations emerged from the framework and compensating its excess charge (Scheme 3).

$$[(SiO)_{4-n}Si(OAl)_n]^{-n\delta}\,(H^{+\delta})_{n-m}(Al^{+3\delta})_{m/3}$$
$$(0 \leq m < n \leq 4).$$

SCHEME 3.

If this is really the case, the specificity of the acid–base action of zeolites must depend not only on the concentration and strength of BAS, i.e., of the proton of the bridged hydroxyl group, but also on the concentration and donor–acceptor properties of Lewis acid sites, i.e., Al^{3+} or Be^{2+} cations for beryllium silicates, which formed as a result of the zeolite decationation process.

Since Be^{2+} cations tend to hydrolysis (*9*), one may expect that in beryllium-silicate zeolites Be^{2+} emergence into cation positions producing the sites via Scheme 4 is also possible.

$$[(SiO)_{4-n}Si(OBe)_n]^{-2n\delta}(H^{+\delta})_{2(n-m)}(Be^{+2\delta})_m \quad (0 \leq m < n \leq 4).$$

SCHEME 4.

In such a situation, a signal with a shift of about −1.7 ppm (Table 1) should appear in the ^9Be NMR spectrum. The absence of this signal in the experimental spectrum (see Fig. 1) may indicate that quite a small part of Be^{2+} is localized at the cation positions of beryllium-silicate zeolites. Because the Lewis acid properties of Be^{2+} are far weaker than those of Al^{3+} (*12*), the catalytic activity of beryllium-silicate sites of type 4 (Scheme 4) in olefin aromatization should be lower than that of aluminum-silicate sites of type 3 (Scheme 3).

Thus, both concentration and strength of Lewis sites for beryllium-silicate zeolites must be considerably lower compared to aluminum-silicate zeolites at similar Si/E atomic ratios. Apparently, just for these reasons the catalytic activity of beryllium-silicate zeolites toward the secondary olefin conversion is markedly lower than that of aluminum-silicate zeolites with similar compositions (Table 2).

Using the above assumptions, one can anticipate that an increase in the temperature of methanol conversion on beryllium-silicate zeolites will increase not only the total activity of these catalysts (i.e., the degree of methanol-to-hydrocarbons conversion), but also the rate of secondary reaction of olefin aromatization. In fact, as can be seen from Table 2, a temperature rise up to 450°C leads to a pronounced increase in the selectivity with respect to paraffins and aromatic hydrocarbons.

CONCLUSION

The above data allow us to conclude that the specificity of the acid–base action of beryllium-silicate zeolites, in which Si^{4+} of the framework are isomorphously substituted by Be^{2+}, depends on the concentration and strength of both Brønsted and Lewis acid sites, similarly to isostructural zeolites of the aluminum-silicate chemical composition. The relation between the concentrations and activities of these sites, which affect the rate and selectivity of methanol-to-hydrocarbons conversion, is determined, eventually, both by the degree of substitution $(BeO_4)^{6-} \leftrightarrow (SiO_4)^{4-}$ and by the nature of Be^{2+}, i.e., by its polarization ability and donor–acceptor properties.

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