

Template-Free Sol–Gel Synthesis of Catalytically Active Mesoporous Aluminosilicates

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Abstract—A template-free sol–gel synthesis method has been developed for obtaining mesoporous aluminosilicates with a narrow pore size distribution. The effect of the synthesis conditions on the formation of the porous structure and on the phase composition and surface acidity of the aluminosilicates has been elucidated. The catalytic properties of the synthesized aluminosilicates with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ in the oligomerization of α -methylstyrene and 1-octene have been investigated. The highest oligomerization activity is shown by the aluminosilicate synthesized in two steps. The mesoporous aluminosilicates far exceed zeolite H-Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 18$) in activity and in selectivity toward products with a higher degree of oligomerization.

Keywords: mesoporous aluminosilicates, sol–gel synthesis, porosity, surface acidity, olefin oligomerization

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At present, zeolite-containing catalysts are widely used in heterogeneous catalytic acid–base reactions of organic compounds [1, 2]. However, the microporous structure of zeolites, whose pore size is <1 nm, prevents these catalytic systems from being employed in reactions of large molecules.

It was expected that mesoporous mesostructured (MM) metal silicates would be more efficient in these reactions. Their synthesis and catalytic properties have been the subject of numerous studies, whose results have been systematized in recent publications [3–5]. The structure of these materials results from the interaction between an inorganic component and a surfactant (template) accompanied by the self-assembly of liquid-crystal mesophases. The removal of the template leads to the formation of a porous material with a regular mesopore packing. The surface area of the mesopores can be up to ~ 1000 m²/g, and their volume can be ~ 1 cm³/g. The pore size may vary between 2 and 35 nm.

Of greatest significance for acid–base catalysis are MM aluminosilicates, since they are the most acidic in the Al–Ga–La–Fe silicates series [6, 7].

Mesoporous mesostructured aluminosilicates whose walls are an amorphous phase are usually synthesized. Among these materials, AIMCM-41 and AISBA-15 were studied in greatest detail [3]. Syntheses of mesoporous aluminosilicates with partially crystallized walls were also described. They are obtained by zeolite recrystallization [8] or by the crystallization of an amorphous wall [9]. Mesostructured aluminosilicates with amorphous walls differ markedly in catalytic properties

and porous structure from those with partially crystallized walls.

It was demonstrated [10, 11] that, in some reactions yielding bulky (>1 nm) molecules, MM aluminosilicates are more active and more selective than the known zeolites. However, although more than 20 years has passed since the appearance of the first publication on the synthesis of MM aluminosilicates [12], there have been no reports concerning their use as industrial catalysts. In our opinion, this situation is due to the fact that the synthesis of catalytically active mesoporous materials is a complicated multistep procedure and the templates involved in the synthesis are expensive.

Sol–gel synthesis involving silicon and aluminum alkoxides seems to be a more practicable method of preparing catalytic MM aluminosilicates. This method allows the forming structure of the material to be controlled in every preparation step from the hydrolysis of the silicon and aluminum sources to the heat treatment of the gel. The pore space in these materials results from a loose packing of the primary sol particles.

The sol–gel synthesis of aluminosilicates has been comprehensively described in the literature [13–17]. The greatest attention has been focused on the preparation of high-temperature ceramics, membranes, and fibers. There is very little information about the targeted sol–gel synthesis of catalytically active mesoporous aluminosilicates and about the effect of preparation conditions on their physicochemical properties. Here, we report a template-free sol–gel synthesis of

these materials from readily available sources of silicon and aluminum.

EXPERIMENTAL

Aluminosilicate Synthesis

Porous aluminosilicates were synthesized using tetraethyl orthosilicate (TEOS, 98%, Acros Organics) and a water–ethanol solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Merck). Based on our earlier data [18], we set the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio to be 20. For more complete hydrolysis, the $\text{H}_2\text{O}/\text{TEOS}$ molar ratio was set to be 10 [14]. The solvent was ethanol (98%), with $\text{TEOS} : \text{C}_2\text{H}_5\text{OH} = 10 : 1$ mol/mol. The starting components were combined, and the mixture was homogenized at 20–25°C for 25–30 min. Owing to aluminum nitrate hydrolysis, the resulting solution to be used in the subsequent aluminosilicate synthesis had pH ~3.

Three synthesis variants will be considered: (1) synthesis in an acid medium (pH ~3), (2) synthesis in an alkali medium (pH ~19), and (3) two-step synthesis.

(1) The initial solution, with pH ~3, was kept at 58–60°C in a thermostat for 30 h. The processes that occurred at this stage were the hydrolysis of the starting compounds, the polycondensation of the hydrolysis products, and sol formation followed by gelation. In some experiments, 50 vol % of the ethanol was replaced with dioxane (99%, Acros Organics). The sample prepared using dioxane will be designated ASM-1D.

(2) A solution of ammonia in ethanol was added to the initial solution (pH ~3) until pH ~10. The resulting gel was kept at 23–25°C for 3–4 days.

(3) The initial solution (pH ~3) was thermostated at 58–60°C for 20 h until the gel point. Thereafter, an ethanolic solution of ammonia (99%, Acros Organics) was added so as to reach pH ~10 ($\text{TEOS} : \text{NH}_4\text{OH} = 1 : 2$ mol/mol) and the mixture was left standing at 25°C for 24 h.

All of the gels prepared in this way were subjected to stepwise heat treatment, being kept at 50°C for 12 h, at 150°C for 24 h, and at 650°C for 5 h. The resulting aluminosilicates were ground into powders with a particles size of <100 μm.

The samples prepared via procedures (1), (2), and (3) will be designated ASM-1, ASM-2, and ASM-3, respectively.

Characterization of Porous Aluminosilicates

The chemical composition of the synthesized aluminosilicates was determined by X-ray fluorescence spectroscopy using an EDX 720/900HS spectrometer (Shimadzu, Japan). X-ray diffraction (XRD) patterns were obtained on a D8 Advance diffractometer (Bruker, Germany) using monochromated $\text{CuK}\alpha$ radiation. Scanning was performed in the $2\theta = 5$ –40 deg range with 0.5-deg increments and a counting time of 20 s per data point.

The state of aluminum in calcined samples was estimated by ^{27}Al NMR spectroscopy. The spectra were recorded on an Avance-400 NMR spectrometer (Bruker, Germany) fitted with an SD4 multinuclear probe (single-pulse excitation, sample spinning with a frequency of $\sim 10^4$ Hz at the magic angle in a zirconia rotor). The external standard was an aqueous 1 M AlCl_3 solution.

The porous structure was characterized by low-temperature (77 K) nitrogen adsorption and desorption using an ASAP 2020 surface area and porosity analyzer (Micromeritics, United States). Before being analyzed, the samples were pumped for 6 h at 350°C. The specific surface area was measured by the BET method at a relative partial pressure of $P/P_0 = 0.2$. The pore size distribution was calculated from the desorption curve by the Barrett–Joyner–Halenda (BJH) method. The total pore volume was determined by the BJH method at $P/P_0 = 0.95$. The micropore volume in the presence of mesopores was determined by Lippens and de Boer's *t* method [19].

The acidic properties of aluminosilicates were studied by IR spectroscopy using the low-temperature adsorption of CO probe molecules. IR spectra were recorded on an FTIR-8400 Fourier transform spectrometer (Shimadzu, Japan) in the 700–6000 cm^{-1} range. Pelletized catalyst samples, whose density was 0.009–0.013 g/cm^2 , were placed in a quartz cell with CaF_2 windows and were conditioned in air at 500°C (5 h) and then in a vacuum at 500°C (1.5 h) until a residual pressure of $P < 10^{-3}$ Torr. Adsorption experiments were performed at 77 K while raising the CO pressure from 0.1 to 10 Torr. The Lewis acid site (LAS) concentration was estimated from the integral intensity of the absorption bands of adsorbed CO in the 2180–2240 cm^{-1} range. The strength of Brønsted acid sites (BAS's) was estimated using the proton affinity (PA) scale: $\text{PA} (\text{kJ}/\text{mol}) = 1390 - 0.00226^{-1} \times \log((\Delta\nu_{\text{OH}}^{\text{OH}\dots\text{CO}})/(\Delta\nu_{\text{OH}}^{\text{SiOH}\dots\text{CO}}))$, where $\Delta\nu_{\text{OH}}^{\text{OH}\dots\text{CO}}$ is the bathochromic shift of the absorption band of the OH stretching vibrations caused by the formation of a hydrogen bond with a CO molecule and $\Delta\nu_{\text{OH}}^{\text{SiOH}\dots\text{CO}}$ is the shift of the absorption band of the SiOH groups of aerosil due to the formation of a hydrogen bond with CO. The site concentration was estimated from the integral intensity of the absorption bands of the OH groups perturbed by their hydrogen bonding with adsorbed CO (3290–3500 cm^{-1}). The acid site concentration and strength determination procedures are detailed elsewhere [20].

Investigation of Catalytic Properties

The catalytic properties of MM aluminosilicates were studied in the oligomerization of α -methylstyrene and 1-octene. For comparison, the same reactions were carried out in the presence of zeolite H-Beta

($\text{SiO}_2/\text{Al}_2\text{O}_3 = 18$) synthesized by heat-treating zeolite NH_4 -Beta (Angarsk Catalysts and Organic Synthesis Plant) at 540°C in air for 4 h.

α -Methylstyrene oligomerization was conducted at 20°C in chlorobenzene (99%, Acros organics) for 1–3 h in an isothermal stirred batch reactor. The catalyst concentration was 10 wt % on the α -methylstyrene basis. A more detailed description of the experimental procedure is presented in an earlier publication [21]. Freshly distilled α -methylstyrene (99 wt %) that had been dried over calcined barium oxide was used in the experiments. The initial α -methylstyrene concentration in chlorobenzene was 3.3 mol/L.

1-Octene (98%, Acros Organics) was oligomerized for 5 h in a continuously rotating, temperature-controlled autoclave at 150°C without a solvent. The amount of catalyst was 10 wt %.

Before catalytic tests, the catalyst was calcined at 350°C for 3 h.

The quantitative analysis of the reaction mixture was carried out by gas–liquid chromatography on a GC-2014 chromatograph (Shimadzu, Japan) fitted with a flame-ionization detector (2000×3 mm column, SE-30 stationary phase (5%) on Chromaton N-AW-HMDS (0.20–0.25 mm), temperature-programmed heating from 50 to 280°C at a rate of $8^\circ\text{C}/\text{min}$, detector temperature of 250°C , injection port temperature of 300°C , helium carrier gas).

For determining the oligomer composition, the products were analyzed by high-performance liquid chromatography (HPLC) on an HP 1090 chromatograph (Hewlett-Packard, United States) with a refractive index detector (PLgel 100 Å polystyrene column, toluene inlet rate of 0.8 mL/min, ribbon speed of 1.5 cm^{-1}).

The structure of the α -methylstyrene and octene dimers was determined by us earlier [21].

RESULTS AND DISCUSSION

Effect of Synthesis Conditions on the Phase Composition of the Product

It was established that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the synthesized aluminosilicates was 20.

It follows from XRD data that all samples are X-ray-amorphous. Irrespective of the conditions under which they were prepared, their diffraction patterns show a halo at $2\theta \approx 20$ deg.

According to present-day views [22], the acidity of amorphous aluminosilicates is due to the interaction between hydrolyzed aluminum and silicon complexes yielding Al–O–Si bonds. Accordingly, for generating acid sites on the surface, it is necessary to ensure that this interaction between the hydrolyzed aluminum and silicon complexes takes place.

In the formation of Al–O–Si bonds in aluminosilicates, aluminum typically finds itself in a tetrahedral oxygen environment, while in the formation of

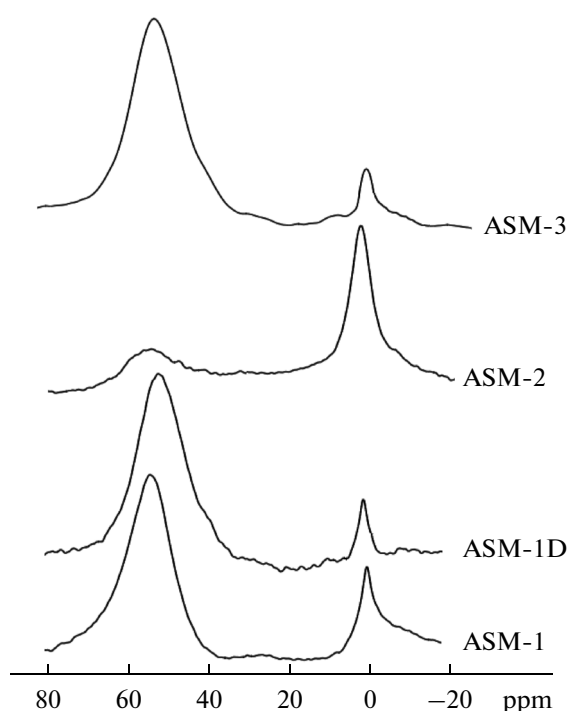


Fig. 1. ^{27}Al NMR spectra of the ASM aluminosilicates prepared via the three sol–gel synthesis variants.

Al–O–Al bonds, aluminum gains an octahedral coordination environment, which is often attributed to the formation of an aluminum oxide phase [14].

Figure 1 shows the ^{27}Al NMR spectra of the aluminosilicates obtained by the three sol–gel synthesis variants. The signal in the 50–80 ppm range is characteristic of aluminum in tetrahedral oxygen environment, and the signal in the range from –30 to 15 ppm is characteristic of aluminum in octahedral oxygen environment [14]. The spectrum of the ASM-2 sample, which was synthesized in the alkali medium, is dominated by the signal at –30 to 15 ppm. Therefore, this sample consists mainly of the aluminum oxide phase and only a small part of the aluminum oxide is incorporated in the silica lattice. These data are explained by TEOS and aluminum nitrate differing in their hydrolyzability in an alkali medium. Because aluminum nitrate hydrolyzes at a high rate and the hydrolysis products undergo rapid polycondensation, the latter have no time to react with the TEOS hydrolysis products.

For the ASM-1 sample, which was synthesized in the acid medium, the dominant NMR signal is in the 50–80 ppm range (Fig. 1). Therefore, the greater part of aluminum is incorporated in the silica structure and only a small part of it is in the form of an individual phase. The formation of the Al–O–Si bonds is explained by the fact that, in the acid medium, aluminum nitrate and TEOS hydrolyze at similar rates, so the resulting aluminum and silicon complexes have

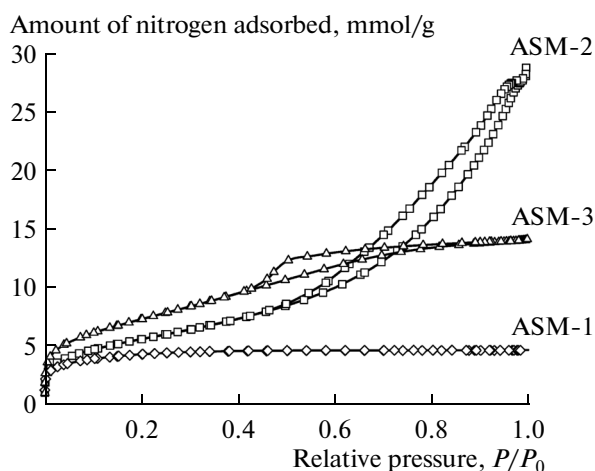


Fig. 2. Nitrogen adsorption–desorption isotherms for the ASM aluminosilicates prepared via the three sol–gel synthesis variants.

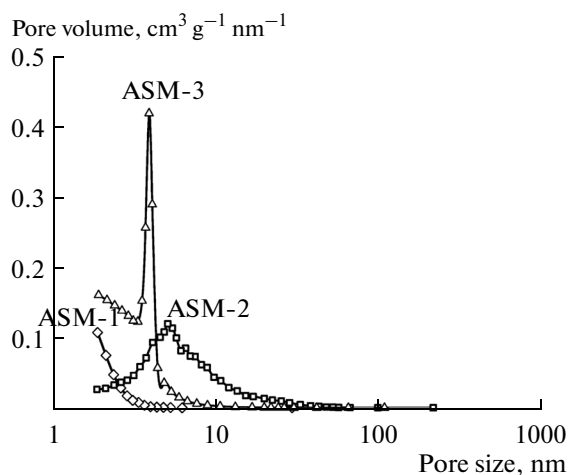


Fig. 3. Pore size distribution for the ASM aluminosilicates prepared via the three sol–gel synthesis variants.

sufficient time to interact, yielding an aluminosilicate phase.

The aluminum nitrate and TEOS hydrolysis rates can be further equalized by replacing part of the ethanol with dioxane, since the latter effectively slows down the hydrolysis of the ester [14]. It is clear from Fig. 1 that replacing 50% of the ethanol with dioxane (sample ASM-1D) reduces the signal between -30 and 15 ppm by a factor of 2.

Thus, tetrahedrally coordinated aluminum will dominate only if the hydrolysis is carried out in an acid medium.

In the spectrum of ASM-3, which was obtained by the two-step synthesis, the major signal is in the 50 – 80 ppm range (Fig. 1). The signal at -30 to 15 ppm in this spectrum is weaker than in the spectra of the other samples. Therefore, in this synthesis variant the product is dominated by the aluminosilicate phase.

pH Effect on the Formation of the Porous Structure

The main factor in the formation of the porous structure of the materials obtained by sol–gel synthesis is the precipitation pH [14]. Figure 2 shows the nitrogen adsorption–desorption isotherms for aluminosilicates prepared at different pH values. For the ASM-2 sample, which was synthesized in the alkali medium, the nitro-

gen adsorption–desorption isotherm is type IV, according to the IUPAC classification, displaying a hysteresis loop (H1) [19], which is characteristic of mesoporous structures. For the ASM-1 sample, which was prepared in the acid medium, the isotherm is type I, having no hysteresis loop. Therefore, aluminosilicates mainly having a micro/mesoporous structure form in the acid medium. The ASM-3 sample, which was prepared by the two-step synthesis, shows a type IV isotherm, with a hysteresis loop (H2) in a narrower relative pressure range.

The characteristics of the porous structure of the samples obtained via the three sol–gel synthesis variants are presented in Table 1 and Fig. 3. The aluminosilicate synthesized in the alkali medium is characterized by a broad pore size distribution extending from 2 to 40 nm (Fig. 3, ASM-2) and has a total pore volume of 1.0 cm^3/g (Table 1). By contrast, the sample synthesized in the acid medium is characterized by a narrow pore size distribution confined between 2 and 3 nm and is dominated by micropores (Fig. 3, ASM-1). The aluminosilicates prepared by the two-step synthesis are characterized by a narrow pore size distribution confined between 2 and 5 nm and has a pore volume of 0.75 cm^3/g (Fig. 3, ASM-3).

The observed effect of the pH of the medium on the formation of the aluminosilicate structure is explained by the fact that pH variations change the ratio between the hydrolysis rate and the rate of condensation of the hydrolysis products [14]. The hydrolysis rate in the acid medium is very high. As a consequence, strong supersaturation takes place even at the early stages of the interaction. This yields finely dispersed, 5 -nm sol particles, which then aggregate into a micro/mesoporous structure via close packing during drying. In the alkali medium, the condensation rate is higher than the hydrolysis rate. In this case, hydrolysis is extended in time, favoring the formation of larger, polydisperse

Table 1. Precipitation pH effect on the characteristics of the porous structure of the product

Sample	pH	S_{BET} , m^2/g	V_{micro} , cm^3/g	V_{meso} , cm^3/g	D_{av} , nm
ASM-1	3	350	0.20	0.15	2
ASM-2	10	605	0.1	0.90	20
ASM-3	3–10	640	0.05	0.70	5

sol particles, which then yield a wider pore structure. Nonmacromolecular complexes additionally deposit in the places of contact between primary particles, and this leads to the formation of tightly linked aggregates that are poorly compressible under drying. In the two-step synthesis, the first step, performed in the acidic medium, yields ~5-nm particles, which then form a gel network. The introduction of urea near the gel point causes uniform deposition of nonmacromolecular complexes in the places of contact between sol particles, leading to the formation of a uniform porous structure that is resistant to compression under atmospheric drying. Mesopores with a narrow size distribution form as a result.

Acidity of the Aluminosilicates

The catalytic properties of mesoporous aluminosilicates depend considerably on their acidity [23].

Both BAS's and LAS's were observed on the surface of all samples. The IR spectrum of CO adsorbed on ASM-3 is shown in Fig. 4.

According to IR spectroscopic data, the surface of all samples has five types of LAS's. The bands at 2223 and 2231 cm^{-1} are characteristic of CO complexes with pentacoordinated Al^{3+} ions, which are typical structure defects in aluminosilicates and zeolites. The bands at 2210–2212, 2200–2202, and 2190 cm^{-1} are due to CO complexes with Al^{3+} ions, probably in aluminum oxide clusters [20]. The LAS types and concentrations are listed in Table 2.

The CO probe molecule, a weak base, can be used to estimate the strength and concentration of BAS's in aluminosilicates [20]. CO adsorption at 77 K shifts the absorption bands of OH groups to lower frequencies ($\Delta\nu_{\text{OH}}^{\text{OH}\cdots\text{CO}}$), the larger the shift, the stronger the acid site. This shift of the absorption bands of the OH groups is caused by the perturbation of the stretching vibrations of these groups as a consequence of the formation of the OH–CO hydrogen bond. On the surface of the sample examined, we identified type I strong BAS's with PA 1180 kJ/mol, which pertain to bridging Si–O(H)–Al groups ($\nu_{\text{CO}} = 3612\text{--}3620 \text{ cm}^{-1}$), and type 2 strong BAS's with PA 1190–1210 kJ/mol ($\nu_{\text{CO}} = 3730$ and

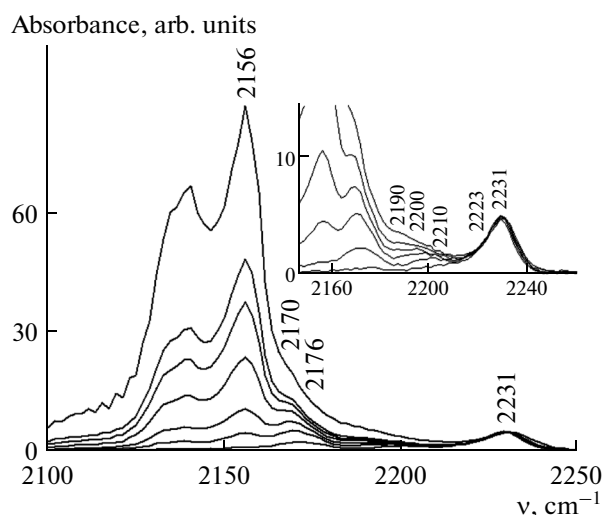


Fig. 4. IR spectra of CO adsorbed on the ASM-3 sample recorded at 77 K while raising the CO pressure from 0.1 to 10 Torr.

3650 cm^{-1}), which pertain to silanol groups located near an LAS (Si–O(H)... Al^{3+}) and to Al–O(H)–Al groups, respectively. In addition, the surface of the samples has weakly acidic silanol groups with PA 1310 and 1390 kJ/mol and basic Al–OH groups. The concentrations of strong BAS's are listed in Table 3.

Thus, both the BAS concentration and the LAS concentration depend on the precipitation pH and gelation conditions. As was expected, the aluminosilicate ASM-1, although its specific surface area is smaller than that of ASM-2, has a higher concentration of acid sites, because it contains more aluminum incorporated in the silica matrix. The largest number of acid sites was found on the surface of the aluminosilicate ASM-3, which was obtained via the two-step synthesis.

Catalytic Properties of the Aluminosilicates in α -Methylstyrene Oligomerization

We demonstrated in an earlier study [21] that α -methylstyrene oligomerization over zeolite-con-

Table 2. LAS types and their concentrations in the aluminosilicates determined by IR spectroscopy of adsorbed CO

Sample	LAS type	Strong, absorption band at 2231 cm^{-1}	Medium-strength, absorption bands at 2223 and 2210–2212 cm^{-1}	Weak, absorption bands at 2202–2200 and 2190 cm^{-1}	Σ LAS
		LAS concentration, $\mu\text{mol/g}$			
ASM-1		31	31	50	112
ASM-2		28	23	36	87
ASM-3		39	64	100	203

Table 3. BAS types and their concentrations in the aluminosilicates determined by IR spectroscopy of adsorbed CO

Sample	BAS type*	Strong, type I, 1180 kJ/mol	Strong, type II, 1190–1210 kJ/mol	Σ strong BAS
		BAS concentration, μmol/g		
ASM-1		7	40	47
ASM-2		4	32	36
ASM-3		10	46	56

* The strength of BAS's was estimated in terms of proton affinity PA.

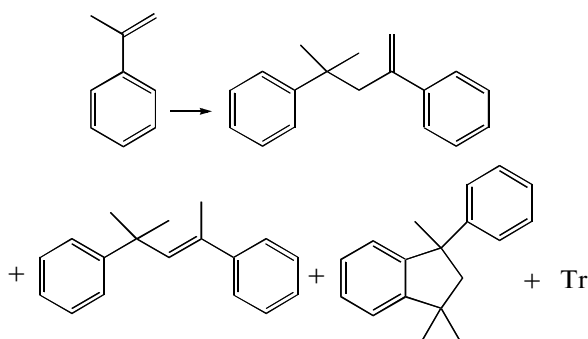
Table 4. α-Methylstyrene oligomerization over the aluminosilicates and zeolite H-Beta

Sample	α-Methylstyrene conversion, %	Selectivity, %			
		I	II	III	Tr
ASM-1	25	86	12	—*	2
ASM-2	20	70	10	—	20
ASM-3	98	30	8	12	60
H-Beta	78	40	50	8	2

Reaction conditions: 10 wt % catalyst, chlorobenzene solvent, 20°C, 3 h.

* The product does not form under the given conditions.

taining catalysts yields linear (**I**, **II**) and cyclic (**III**) dimers and a trimer (**Tr**).



Among the amorphous aluminosilicates, the most active one is the mesoporous aluminosilicate ASM-3, which was obtained by the two-step synthesis (Table 4). The α-methylstyrene conversion over ASM-3 (98%) is significantly higher than in the presence of zeolite H-Beta (78%), which is more acidic [1]. Obviously, the mesoporous structure of ASM-3 ensures accessibility of catalytic sites and improves the transport of reactant molecules and reaction products. These are important factors in the activity of the catalyst in α-methylstyrene oligomerization. Another very significant factor is that the catalyst has a sufficient quantity of strong acid sites. This is indicated by the data obtained for ASM-2, which also has a mesoporous structure but fewer strong acid sites. With this catalyst, the α-methylstyrene conversion is much lower (20%) than in the case of ASM-3.

The ASM-1 sample, which has a microporous structure and a fairly low concentration of strong

BAS's, also showed a low α-methylstyrene oligomerization activity.

Note that the high α-methylstyrene conversion was attained at a low temperature (20°C). This is not typical of oligomerization reactions occurring under the action of heterogeneous catalysts.

The composition of α-methylstyrene oligomers also depends on the porous structure of the catalyst (Table 4). In the oligomerization carried out over the microporous aluminosilicates (zeolite H-Beta and the ASM-1 sample), the main products are dimers (98%), while the same reaction carried out over the mesoporous samples (aluminosilicates ASM-2 and ASM-3) yields a considerable amount of trimers (20 and 60%, respectively). This finding can be explained by the absence of steric hindrance to the formation of bulky trimer molecules in the mesopores of the ASM-2 and ASM-3 samples.

The products of dimerization over the aluminosilicates ASM-1 and ASM-2 are solely linear isomers (**I**, **II**). The oligomerization over ASM-3 yields not only the linear dimers but also the cyclodimerization product (**III**). This fact can be explained by the presence of a larger number of strong acid sites.

Catalytic Properties of the Aluminosilicates in 1-Octene Oligomerization

Under the action of the aluminosilicate catalysts, 1-octene turns into *cis* and *trans* isomers of 2-, 3-, and 4-octene, into isooctenes, including methylheptenes

Table 5. 1-Octene oligomerization over the aluminosilicates and zeolite H-Beta

Sample	Conversion, wt %	Selectivity, %			
		<i>i</i> -C ₈ H ₁₆	C ₁₆ H ₃₂	C ₂₄ H ₄₈	C ₃₂ H ₆₄
ASM-1	40	50	45	5	—*
ASM-2	45	25	45	25	5
ASM-3	100	20	35	30	15
H-Beta	80	40	52	8	—

Reaction conditions: 10 wt % catalyst, 150°C, 5 h.

* The product does not form under the given conditions.

and dimethylhexenes, and into oligomers (di-, tri-, and tetramers) (Table 5).

The largest 1-octene conversion values were observed for ASM-3 and zeolite H-Beta. The activity of the zeolite catalyst is due to the high concentration of acid sites, and the activity of ASM-3, which is less acidic, is due to the presence of a developed mesopore system, which ensures a better access of olefin molecules to the active sites of the aluminosilicate and facilitates oligomer transport from the catalyst pores.

A comparison of the selectivities of the catalysts demonstrates that the products of the reaction over zeolite H-Beta contain about 60% oligomers and 40% of octene isomers. The reaction mixture obtained with ASM-1, another microporous aluminosilicate, contains still more isomers (50%). The mesoporous catalysts—ASM-3 and ASM-2—are much more selective toward the formation of octene oligomers: their oligomer selectivity is 80 and 75%, respectively.

The oligomers forming in the presence of the microporous catalysts (zeolite H-Beta and ASM-1) contain about 90% 1-octene dimers. The mesoporous aluminosilicates make it possible to obtain 1-octene oligomers with a broader molecular weight distribution. Trimers and tetramers form along with the dimers, and their total proportion in the case of the ASM-3 aluminosilicate is even larger than the proportion of the dimers (Table 5).

These data are significant for practice, since the oligomerization of higher α -olefins over most heterogeneous catalysts (e.g., acidic clays and zeolites) mainly yields dimers. These oligomers have found only limited application: they can serve only as a base for low-viscosity oils, such as spindle oil, drilling fluid, and vaccine and cosmetic oils, and for hydraulic liquids in aviation [24]. 1-Octene trimers and tetramers, which can be synthesized using mesoporous aluminosilicates, are in higher demand in the manufacturing of synthetic lubricants.

CONCLUSIONS

In the sol–gel synthesis using TEOS and aluminum nitrate, precipitation pH has a significant effect on the state of aluminum in the resulting aluminosili-

cates. At pH ~10, the source of aluminum precipitates as an oxide phase and only a small part of it incorporates into the silica matrix. At pH ~3, the greater part of the aluminum incorporates into the silica matrix and the proportion of aluminum oxide is small. The interaction between the aluminum and silicon components can be enhanced by partially replacing ethanol with dioxane, which slows down TEOS hydrolysis. Carrying out the sol–gel synthesis in two steps maximizes the incorporation of aluminum into the silica matrix.

A mesoporous structure with a broad pore size distribution forms only in an alkali medium. The synthesis in an acid medium mainly yields a micro/mesoporous structure. The two-step sol–gel synthesis developed in this study provides means to obtain a mesoporous structure with a narrow pore size distribution.

Precipitation pH has a marked effect on the surface acidity of the resulting materials. The aluminosilicates synthesized in the acid medium are richer in both BAS's and LAS's than the samples synthesized in the alkali medium. The highest acidity is observed for the aluminosilicates prepared by the two-step synthesis.

The activity of the catalysts in α -methylstyrene and 1-octene oligomerization depends on their porous structure and on the acid site concentration. The highest activity is shown by the mesoporous aluminosilicate obtained by the two-step synthesis. The reaction catalyzed by the mesoporous aluminosilicates yields oligomers with a higher degree of oligomerization than the reaction catalyzed by the micro/mesoporous aluminosilicates.

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