ISOMORPHOUS SUBSTITUTION OF Si FOR Al, Ga, Fe, In AND B IN MOLECULAR SIEVES OF MFI STRUCTURE. A QUANTUM CHEMICAL, AMMONIA DESORPTION AND CATALYTIC ACTIVITY STUDY OF FRAMEWORK Si-OH-M ACID SITE STRENGTH

Rudolf ZAHRADNÍK, Pavel HOBZA, Blanka WICHTERLOVÁ and Jiří ČEJKA

The J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, The Czech Republic

Received May 4, 1993
Accepted June 30, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

A theoretical and experimental study of metallosilicates with MFI structure revealed the order Al > Ga > Fe > In > B in the acid Si-OH-M framework site strength. *Ab initio* calculations of the energy and geometry characteristics in a simple structural unit modelling the isomorphous substitution were carried out for Al, Ga, In and B as heteroatoms in silicates. Experimental data on toluene alkylation with ethylene and temperature-programmed desorption of ammonia allowed to distinguish the acid site strength of Al-, Fe- and In-silicates, thus, completing the acidity sequence of metallosilicates synthesized so far. Moreover, the study confirmed rather short-range effects resulting from isomorphous substitution of a heteroatom into the molecular sieve framework.

Alumosilicate molecular sieves of the MFI structural type have been recognized for twenty years as extremely interesting materials that are applied in a large scale as catalysts in a number of selective transformations of hydrocarbons and their derivatives[1-3]. These applications result from the presence of very strong acid sites (framework bridging Si-OH-Al groups) located in the structural channels with a size comparable to the kinetic diameter of the alkylbenzenes. This fact directs the reaction path towards shape selective and even *para*-shape selective products in the synthesis and transformations of hydrocarbons, such as methanol to olefins and/or aromatics up to C_{10}, alkylaromatic and dialkylaromatic synthesis and their further transformations. Among other metallosilicates, the Fe- and B-silicates of MFI structure, exhibiting bridging OH groups with lower acidity, seem to be promising catalysts for synthesis of alkylaromatics[4,5].

The isomorphous substitution of trivalent heteroatoms in silicates with MFI structure by Al, Ga, Fe, B and other atoms[6] provides a unique opportunity to tailor both the acidity of the framework bridging OH groups, reflected in the acid-base catalytic activity, and the unit cell volume, which can control the pore opening of the structural

channels. On the basis of the X-ray data, it was shown that borosilicates exhibited a decrease, while ferri- and gallo-silicates showed an increase in the unit cell volume compared to the parent silicates[6,7]. The IR frequency of the bridging OH groups[8] (Al 3 612 , Ga 3 620, Fe 3 630, B 3 725 cm^{-1}), temperature maxima in ammonia desorption and acid-base catalytic activity[6,8 - 12], clearly indicate the decrease in the acid site strength of the metallosilicates from Al- to B-silicates.

Quantum chemical calculations, both *ab initio* and semiempirical, have been found to be a useful tool for the characterization of molecular sieve acid sites as well as the geometry and stability of their structures[13 - 16]. Although a wide range of structural types was investigated, studies have been focused mainly on those molecular sieves where the most important and widely used heteroatom, aluminium, was a framework-forming component. Recently, *ab initio* Si-OH-M (M = Al, Ga, B) model quantum chemical calculations published by Derouane et al.[17] and Dwyer[18] led to a sequence of acid Si-OH-M site strength Al > Ga > B in accordance with that following from the IR frequencies of these OH groups[8].

The Sanderson average electronegativity values[7,19] did not correlate well with the acidity of the bridging OH groups neighboring with a particular heteroatom. The electronegativity equalization principle together with the changes of the frequency of the framework vibrations in isomorphously substituted silicates has been employed to correct this discrepancy for gallium[20]. Vetrivel et al.[21] studied the properties of ferrisilicates with MFI structure using an empirical EHMO procedure and a small "dimeric" model. They found lower acidity of Fe compared to Al analogues and a decreased pore diameter of the elliptical sinusoidal structural channels.

Very recently indium silicates with MFI structure have been successfully synthesized[22,23]. The strength of the Si-OH-In acid sites, formed by incorporation of indium into the silicate framework, has not yet been established. Because of the ability to prepare structurally stable metallosilicates with MFI structure that are relatively "clean" in composition, it is tempting to compare their characteristics obtained from experimental and theoretical studies.

This study deals with the *ab initio* calculations of the characteristics of metallosilicates, using a very simple (geometry-optimized) model, such as the energy characteristics and bond lengths and angles depending on the isomorphous substitution of Si by trivalent Al, Ga, In, B. Despite great deal of effort, we were not able to overcome the convergency difficulty connected with the model containing an iron atom. On the other hand, the experimental data of temperature-programmed desorption of ammonia and the catalytic activity of metallosilicates in toluene alkylation with ethylene allow to distinguish Fe- and In-silicates in a metallosilicate sequence with respect to the acid site strength of the framework Si-OH-M sites.

EXPERIMENTAL

Metallosilicates of MFI structure (usually denoted ZSM-5) with trivalent Al, Fe and In substituted tetravalent Si have been used. The chemical composition, differing in the number of heteroatoms in the framework and in the extra-framework positions, the latter located in silicate channels as undefined isolated cations and/or oxidic clusters, is given in Table I. The number of heteroatoms incorporated into the framework sites was obtained from the high-temperature peak of ammonia desorption and from the NH_4^+ ion-exchange capacity of the metallosilicates. The crystal size was not uniform, exhibiting an average size of 1 – 3, 1 – 3 and 3 – 6 μm for Al-, Fe- and In- silicates, respectively. It is clear from Table I that the relative number of extraframework heteroatoms increases in the sequence Al < Fe < In, corresponding to the ionic radius sequence 0.50 < 0.64 < 0.81 Å, respectively, which differ from that for Si (0.41 Å) much more for In than for Al.

Temperature-programmed desorption of ammonia was performed on metallosilicates pretreated in an oxygen stream at 770 K (Al-silicates) and 720 K (Fe- and In-silicates) for one hour followed by ammonia adsorption at 373 K. Desorption of ammonia was carried out in a helium stream (100 ml/min) using a temperature-increase rate of 20 K/min. The spectra consist of two peaks, where the high-temperature peak corresponded to ammonia desorbed from strongly acidic Si-OH-M groups (for details see ref.[24]).

Toluene alkylation with ethylene was performed in a down-flow glass microreactor at a toluene concentration of 18.5 vol.% in helium and at a toluene to ethylene molar ratio of 3.8, with WHSV 10.0 h^{-1} and at a temperature of 620 K. The reaction time-on-stream up to 200 min was followed. The toluene conversion and product composition were determined using "on-line" high resolution capillary chromatographic analysis with flame ionization and mass-spectrometric detectors[25,26].

TABLE I
Characterization of metallosilicates[a]

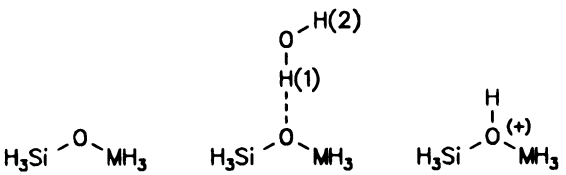
Metallosilicate	Bulk chemical analysis		Framework positions	
	SiO_2/Me_2O_3	M^b	$M^{b,c}$	%Me
H-(Al)ZSM-5A	45	4.08	4.02	99
H-(Al)ZSM-5B	53	3.49	3.04	87
H-(Al)ZSM-5C	90	2.09	1.90	91
H-(Al)ZSM-5D	146	1.30	1.22	94
H-(Al)ZSM-5E	1 200	0.18	0.17	94
H-(Fe)ZSM-5A	55	3.37	2.48	74
H-(Fe)ZSM-5B	70	2.67	2.20	82
H-(Fe)ZSM-5C	134	1.42	1.39	98
H-(In)ZSM-5A	67	2.78	1.10	40
H-(In)ZSM-5B	80	2.34	0.81	34
H-(In)ZSM-5C	104	1.81	0.69	39

[a] Taken from ref.[33]; [b] M is the number of heteroatoms per unit cell; [c] given by temperature programmed desorption of ammonia and NH_4^+ ion-exchange capacity

RESULTS AND DISCUSSION

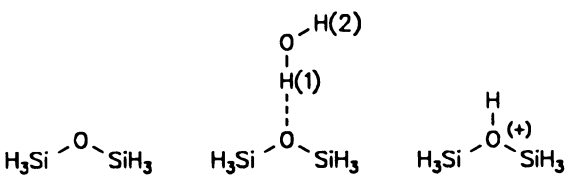
Computation

Methods and models. Quantum chemical calculations were carried out with the GAMESS *ab initio* program[27], using the 3-21G split valence basis set[28]. All the electrons were included in all the systems. Our studies were carried out using reliable relative calculated characteristics. On the basis of previous extensive experience we decided not to use beyond Hartree–Fock methods and to neglect the basis set superposition error. Both of these must be considered in calculation of more quantitative numerical characteristics. Simple prototypes of metallosilicate structural units *I* and *III* (protonized) modelled the structure of H forms of silicates with isomorphous substitution of a heteroatom M (Al, Ga, In, B) in the silicate structure. In addition, the complexes with water molecule *II* were studied. The molecular geometry of all the structural units was completely optimized. The energies are given in Table II. The optimized bond lengths and bond angles, and Löwdin population characteristics are summarized in Tables III and IV, respectively.



I *II* *III*

In formulae *I* – *III* : *a*, M = B; *b*, M = Al; *c*, M = Ga; *d*, M = In



IV *V* *VI*

The derived energy characteristics in Table II are defined by Eqs (*1*) – (*4*).

$$\Delta E(\mathrm{B}\ldots\mathrm{H_2O}) = E(\mathrm{B}\ldots\mathrm{H_2O}) - E(\mathrm{B}) - E(\mathrm{H_2O}), \qquad (1)$$

where B...H_2O is a complex of a parent system B under study (base B) and water:

$$\mathrm{B} + \mathrm{H_2O} \longrightarrow \mathrm{B}\ldots\mathrm{H_2O}. \qquad (2)$$

Furthermore,

$$\Delta E(PA) = E(\mathrm{B}\ldots\mathrm{H^+}) - E(\mathrm{B}) - E(\mathrm{H^+}), \qquad (3)$$

TABLE II
Total SCF 3-21G energies of the studied systems and energy changes ΔE(B...H_2O) and $\Delta E(PA)$

System	Structure	E a.u.	ΔE(B...H_2O) kcal/mol	$\Delta E(PA)$ kcal/mol
Si-OH-B	*IIIa*	–390.456679		–343.7
Si-O-B	*Ia*	–389.908969		
Si-O(H_2O)-B	*IIa*	–465.524819	–18.76	
Si-OH-Al	*IIIb*	–606.523734		–323.9
Si-O-Al	*Ib*	–606.007514		
Si-O(H_2O)-Al	*IIb*	–681.613991	–12.87	
Si-OH-Ga	*IIIc*	–2 279.781331		–327.6
Si-O-Ga	*Ic*	–2 279.259234		
Si-O(H_2O)-Ga	*IIc*	–2 354.867362	–13.91	
Si-OH-In	*IIId*	–6 080.997890		–331.4
Si-O-In	*Id*	–6 080.469756		
Si-O(H_2O)-In	*IId*	–6 156.078715	–14.43	
Si-OH-Si	*VI*	–653.112209		–201.6
Si-O-Si	*IV*	–652.790979		
Si-O(H_2O)-Si	*V*	–728.382591	–3.55	

TABLE III
Calculated 3-21G bond lengths and angles

System	Structure	Bond lengths, Å							Bond angles, deg
		H–Si	Si–O	O–M	M–H	O–H	O–H(1)	O–H(2)	X–O–M[a]
Si-O-B	*Ia*	1.508	1.632	1.537	1.240	–	–	–	133
Si-O-Al	*Ib*	1.505	1.618	1.757	1.663	–	–	–	180
Si-O-Ga	*Ic*	1.506	1.614	1.793	1.657	–	–	–	177
Si-O-In	*Id*	1.507	1.617	2.018	1.834	–	–	–	175
Si-O-Si	*IV*	1.486	1.647	1.647	1.486	–	–	–	176
Si-O(H_2O)-B	*IIa*	1.500	1.652	1.558	1.233	1.673	0.991	0.968	124
Si-O(H_2O)-Al	*IIb*	1.498	1.642	1.788	1.654	1.758	0.980	0.967	144
Si-O(H_2O)-Ga	*IIc*	1.499	1.641	1.821	1.647	1.744	0.982	0.966	142
Si-O(H_2O)-In	*IId*	1.500	1.643	2.057	1.824	1.720	0.985	0.967	141
Si-O(H_2O)-Si	*V*	1.482	1.669	1.670	1.482	1.927	0.968	0.966	150
Si-OH-B	*IIIa*	1.477	1.721	1.685	1.206	0.963	–	–	122
Si-OH-Al	*IIIb*	1.475	1.732	1.930	1.620	0.967	–	–	129
Si-OH-Ga	*IIIc*	1.475	1.726	1.957	1.607	0.965	–	–	128
Si-OH-In	*IIId*	1.474	1.720	2.233	1.789	0.966	–	–	130
Si-OH-Si	*VI*	1.467	1.804	1.804	1.467	0.974	–	–	130

[a] Only the X–O–M bond angles are presented here. The remaining values can be obtained from the authors on request.

TABLE IV
Löwdin charges and Mulliken overlap populations

System	Structure	Si	O	M	H	O	H	H–Si	Si–O	O–M	M–H	O–H	O–H(1)	O–H(2)
Si-O-B	*Ia*	0.793	−0.580	−0.186	–	–	–	0.693	0.708	0.526	0.744	–	–	–
Si-O-Al	*Ib*	0.823	−0.735	0.328	–	–	–	0.578	0.686	0.370	0.644	–	–	–
Si-O-Ga	*Ic*	0.817	−0.732	0.239	–	–	–	0.568	0.694	0.400	0.674	–	–	–
Si-O-In	*Id*	0.792	−0.762	0.346	–	–	–	0.552	0.732	0.316	0.642	–	–	–
Si-O-Si	*IV*	0.845	−0.749	0.845	–	–	–	0.654	0.514	0.514	0.654	–	–	–
Si-O(H_2O)-B	*IIa*	0.788	−0.582	0.198	0.267	−0.552	0.202	0.616	0.612	0.476	0.759	0.106	0.478	0.518
Si-O(H_2O)-Al	*IIb*	0.806	−0.737	0.302	0.265	−0.530	0.215	0.609	0.606	0.338	0.662	0.092	0.482	0.526
Si-O(H_2O)-Ga	*IIc*	0.803	−0.730	0.205	0.266	−0.535	0.215	0.601	0.610	0.368	0.690	0.096	0.478	0.526
Si-O(H_2O)-In	*IId*	0.782	−0.756	0.314	0.261	−0.540	0.213	0.589	0.640	0.284	0.660	0.108	0.472	0.524
Si-O(H_2O)-Si	*V*	0.820	−0.744	0.820	0.243	0.499	0.227	0.668	0.476	0.576	0.335	0.058	0.502	0.530
Si-OH-B	*IIIa*	0.828	−0.435	0.164	0.325	–	–	0.692	0.396	0.252	0.816	0.538	–	–
Si-OH-Al	*IIIb*	0.830	−0.537	0.329	0.331	–	–	0.698	0.380	0.200	0.702	0.520	–	–
Si-OH-Ga	*IIIc*	0.830	−0.535	0.241	0.327	–	–	0.696	0.382	0.216	0.722	0.518	–	–
Si-OH-In	*IIId*	0.818	−0.561	0.350	0.314	–	–	0.700	0.416	0.162	0.690	0.518	–	–
Si-OH-Si	*VI*	0.824	−0.538	0.824	0.352	–	–	0.742	0.284	0.284	0.742	0.522	–	–

where B...H$^+$ is a protonized base; $\Delta E(PA)$ is closely related to the proton affinity. If the base is represented by an anion then, of course, the protonation product is a neutral system:

$$B + H^+ \longrightarrow B \ldots H^+ . \qquad (4)$$

ΔE(X) in Eqs (*1*) and (*3*) corresponds to the total 3-21G energies of a system X.

The plausibility of cluster models. Numerous calculations[13 - 16,29,30] on small clusters frequently yielded physically meaningful information. Recently, a significant step forward was made more convincingly demonstrating the validity of a local description. Kramer et al.[29] showed, on the basis of a combination of quantum chemical and force field calculations that very small cluster models can represent a physically sound description. It seemed to us that especially the changes in the properties of the bridging framework OH groups are affected most by the neighboring heteroatom.

Trends in the Al, Ga, In and B series from model calculations. It is instructive to consider the dependences between $\Delta E(B...H_2O)$ and $\Delta E(PA)$ defined by Eqs (*1*) and (*3*) and the position of the element in the periodic system (Fig. 1*a*). The expected ΔE decreases on passing from a B- to a Al-containing system are not accompanied by a decrease when progressing to Ga and In derivatives. This is a consequence of the "*d*-block contraction" resulting from the fact that the ten *d* electrons do not completely shield the ten positive charges on the nucleus. The dependences for the calculated $\Delta E(PA)$ and $\Delta E(B...H_2O)$ values show a clear minimum for the Al-containing system. This type of dependence is well known for the majority of physical characteristics of B-, Al-, Ga-, In-, and Tl-containing systems[31] (e.g., the standard enthalpies of forma-

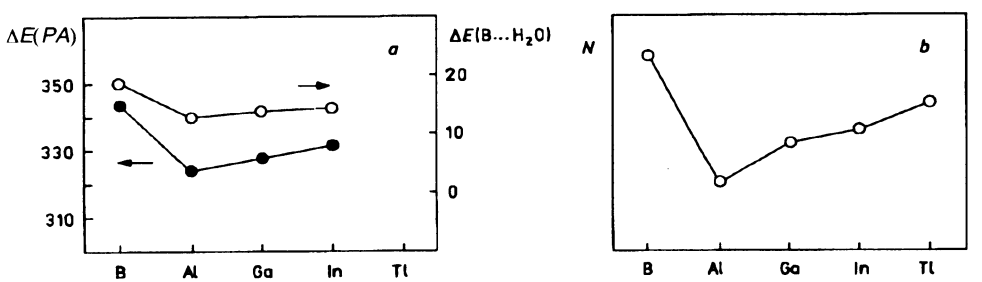


FIG. 1
Dependence of physical characteristics on the isomorphic substitution by atoms of the IIIa group; *a* calculated 3-21G values of $\Delta E(PA)$ and $\Delta E(B...H_2O)$ and *b* a typical, purely qualitative plot for the observed dependence in an arbitrary scale for any quantity *N* noted in the text

tion of trihalides, ionization energies of atoms, standard electrode potentials and electronegativities[31]). This is depicted *purely qualitatively* in Fig. 1*b*.

The calculated acid site strength. The order of calculated proton affinities (Table I) is as follows: B (344) > In (331) > Ga (328) > Al (324). This is not in line with the order of changes in the Sanderson average electronegativities of the metallosilicate framework resulting from the substitution of Si by a heteroatom. The sequence of Mulliken electronegativities of the free atoms is B (2.0) > Fe (1.8) > In (1.7) > Ga (1.6) > Al (1.5). However, we were not able to estimate the Si-OH-Fe acid site strength from the calculated proton affinities because of convergency difficulties. However, the agreement between the calculated sequence of proton affinities (not including Fe) and Mulliken electronegativities should not be overestimated (cf. experimental results below). The empirical correlations are still valuable from a practical point of view but the energy or Gibbs energy changes should be preferred for correlating acid-base behavior. As only relative experimental values are available, it would not be expedient to pass from ΔE to ΔG because their order will obviously be the same in our case. Let us add that, when plotting $\Delta E(PA)$ vs $\Delta E(B...H_2O)$, the points for the two neutral systems are clearly separated from points for the charged systems, which is not unusual when correlating quantum chemical data. It should also be noted that the calculated values of the proton affinities correspond to typical values, i.e. about 150 – 200 kcal/mol for molecules and 300 – 350 kcal/mol for anions. On the other hand, the calculated hydrogen bond energies are clearly overestimated; the relative values are, however, sound.

It is known[32] that the 3-21G H-bond energies of small complexes may be overestimated (in comparison with the 6-31G* values) by as much as 100%. Correcting the interaction energies for the basis set superposition error yields reasonable values of the stabilization energies comparable to the 6-31G* values.

It should be pointed out that the calculated O–M bond lengths follow the ionic radius values of the trivalent heteroatoms M. Similarly, the O–H bond lengths are correlated with the proton donor ability of bridging OH groups. The O–H bond lengths of interacting water molecules are less affected; nevertheless, they follow the opposite trends, i.e. they are shorter when interacting with more basic Si–O–M groups.

The order of acid Si-OH-M site strength according to the quantum chemical calculations, Al > Ga > In > B, places the acid site strength of In-silicates between Ga- and B-silicates, i.e. in the same position as Fe-silicates according to the experimental data[8 – 10]. As the model calculations for Fe-silicates failed to converge, the differences in acid site strength of the In-silicates and Fe-silicates had to be compared only experimentally, i.e. in terms of the temperature-programmed desorption of ammonia and acid-base alkylation of toluene with ethylene.

Experimental Determination of Acid Site Strength

The temperature-programmed desorption of ammonia from Al-, Fe- and In-silicates exhibits two peaks. The higher of them was ascribed to the desorption of ammonia from the strongly acidic Si-OH-M sites[24]. It is clearly seen that the desorption of ammonia from Si-OH-Fe sites proceeds at lower temperatures (655 – 680 K) compared to Si-OH-Al groups (710 – 745 K). In the case of In-silicates, the two peaks are not well resolved, nevertheless, two maxima, one at 400 – 420 K and the other at 605 – 615 K, have been found (Fig. 2). As the ammonia desorption from the Si-OH-In sites (605 – 615 K) occurs at a lower temperature than from Si-OH-Fe and Si-OH-Al sites, it indicates the lowest acid strength of the Si-OH-In sites. It should be considered that the temperature maximum is affected not only by the acid site strength, but also by the concentration of ammonia in the gas phase during the desorption of ammonia. This is controlled, in addition to the heating rate and carrier gas flow rate, by the number of acid sites (for the constant sample weight), i.e. by the amount of ammonia desorbed from the sample. Even though that the values of the temperature maxima can be affected by the number of Si-OH-M sites, the obtained large differences in the temperature maxima for metallosilicates, containing various heteroatoms, clearly indicate that the proton acidity of Si-OH-M site, in terms of ammonia desorption, follows the order Al > Fe > In.

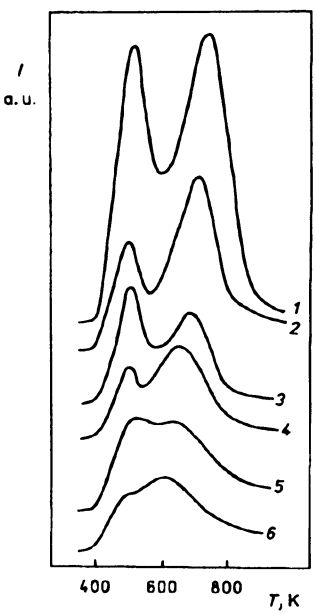


FIG. 2
Temperature-programmed desorption curves of ammonia: *1* H-(Al)ZSM-5A, *2* H-(Al)ZSM-5C, *3* H-(Fe)ZSM-5A, *4* H-(Fe)ZSM-5B, *5* H-(In)ZSM-5A, *6* H-(In)ZSM-5B

The toluene conversion in toluene alkylation with ethylene and product composition for Al-, Fe- and In-metallosilicates after time-on-stream of 15 min are given in Table V. The main products are ethyltoluenes. The higher the number and acid site strength of the Si-OH-M groups, the higher is the rate of competitive reactions decreasing the selectivity to ethyltoluenes. For Fe- and In-silicates and for Al-analogues with a higher Si/Al ratio (H-(Al)ZSM-5C-E), the selectivity to ethyltoluenes is higher than 95%. A decrease in the ethyltoluene selectivity for H-(Al)ZSM-5A,B is caused mainly by the formation of C_8 aromatics, via side reactions such as toluene disproportionation and dealkylation. Simultaneously, alkyl and ethylene oligomerization followed by subsequent aromatization and/or oligomer alkylation of benzene or toluene were responsible for formation of C_{10+} aromatics and of high molecular-weight products causing deactivation of the metallosilicates. A detailed investigation of the behaviour of Al-, Fe- and In-silicates in various transformations of aromatic hydrocarbons will be given elsewhere[33].

Three lines of the dependence of toluene conversion in toluene alkylation with ethylene on the number of a particular heteroatom in the silicate framework have been found for individual Al-, Fe- and In-silicates (Fig. 3). The highest activity is connected with Si-OH-Al sites in the silicates while In analogues exhibit the lowest activity per Si-OH-In group. Thus, according to the activity of metallosilicates in toluene alkylation with ethylene, the following order of the acid site strength of these metallosilicates is established: Al > Fe > In. It should be mentioned here that the experimentally obtained sequence of metallosilicate acidity agrees with the conclusions obtained from the quantum chemical calculations. However, the Mulliken electronegativities do not follow this order (see above).

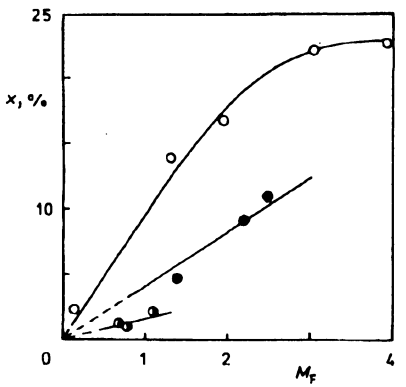


FIG. 3
The dependence of toluene conversion x in toluene alkylation with ethylene on the number of framework heteroatoms M_F after 15 min of time-on-stream, WHSV 10.0 h^{-1}, temperature 620 K, toluene/ethylene molar ratio 3.8; ○ H-(Al)ZSM-5A-E, ● H-(Fe)ZSM-5A-C, ◑ H-(In)ZSM-5A-C

TABLE V

Conversion and product distribution in toluene alkylation with ethylene over metallosilicates after time-on-stream of 15 min, WHSV 10.0 h^{-1}, temperature 620 K, toluene/ethylene molar ratio 3.8

	H-(Al)ZSM-5 forms					H-(Fe)ZSM-5 forms			H-(In)ZSM-5 forms		
	A	B	C	D	E	A	B	C	A	B	C
Conversion, %	22.9	22.1	17.0	14.3	1.8	10.7	9.0	4.8	1.8	0.9	1.2
Product distribution, vol.%											
Benzene	6.7	0.6	–	0.3	0.1	0.3	0.3	0.3	–	–	–
Ethylbenzene	4.6	0.9	0.5	0.5	0.4	0.5	0.5	–	–	–	–
p-Xylene	3.1	0.3	0.5	0.5	0.6	0.2	0.2	–	–	–	–
m-Xylene	3.6	0.5	0.2	0.1	–	–	–	–	–	–	–
o-Xylene	1.2	0.2	–	–	–	–	–	–	–	–	–
p-Ethyltoluene	22.7	31.1	53.7	71.0	81.2	41.5	49.3	67.5	74.3	61.5	84.8
m-Ethyltoluene	51.2	59.2	42.5	26.7	14.0	52.5	45.7	31.5	23.8	36.2	14.8
o-Ethyltoluene	1.7	2.6	0.9	0.1	0.4	1.2	0.8	–	–	–	–
C_{10+}	5.2	4.6	1.7	0.8	3.3	3.8	2.9	0.7	0.9	2.3	0.4
Selectivity in aromatics, vol.%											
C_8 aromatics	12.5	1.9	0.7	1.1	1.0	0.7	0.7	–	–	–	–
C_9 aromatics	75.6	92.9	97.1	97.7	95.6	95.2	95.8	99.0	99.1	97.7	99.6
Selectivity in ethyltoluenes, %											
p-Ethyltoluene	30.0	33.5	55.3	72.6	85.0	43.6	51.5	68.2	75.7	62.9	85.1

For evaluation of metallosilicate *para*-selectivity, the values of toluene conversion should be considered as they strongly affect the actual *para*-selectivity values. Figure 4 depicts the dependence of the *para*-selectivity on the toluene conversion for Al-, Fe- and In-silicates. It is clearly seen that Fe- and also In-silicates exhibit a lower *para*-selectivity compared to Al-analogues. This result does not agree with the conclusions of Raj and coworkers[34,35] on the higher *para*-selectivity of metallosilicates with a lower acid site strength of Si-OH-M groups. However, the *para*-selectivity of metallosilicates is affected by several competitive processes which are controlled not only by the silicate acidity: (i) alkylation and isomerization reactions in the channels, (ii) desorption and transport rate of the individual isomers from the molecular sieve channels, (iii) positional isomerization of ethyltoluenes on the surface acid sites. It is clear that the transport rate is strongly dependent on the crystal size ($D \sim 1/r^2$) which is not homogeneous and identical for synthesized metallosilicates. Moreover, as the ionic radii of the individual heteroatoms differ from that of silicon, it is difficult to incorporate larger metal ions into the silicate framework and some of them, therefore, remain in the molecular sieve channels (Table I). In addition, concentration of heteroatoms, both the framework and extra-framework, close to the crystal surface can strongly affect the molecular sieve *para*-selectivity[36].

CONCLUSIONS

1) The Hartree–Fock SCF (3-21G basis set) energy changes $\Delta E(PA)$ and $\Delta E(B...H_2O)$ (Eqs (*1*) and (*3*)) increase and the bridging OH bond lengths decrease in the order Al, Ga, In, B. This is also the order of decreasing theoretical proton donor ability.

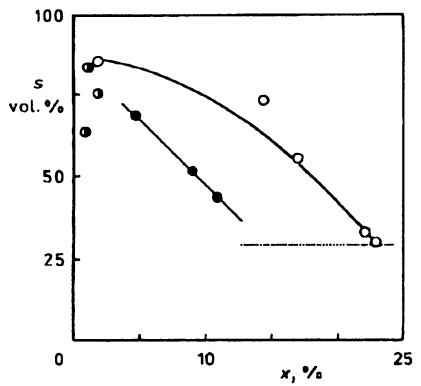


FIG. 4
The dependence of *p*-ethyltoluene selectivity *s* on toluene conversion *x* in toluene alkylation with ethylene after 15 min of time-on-stream, WHSV 10.0 h^{-1}, temperature 620 K, toluene/ethylene molar ratio 3.8; ○ H-(Al)ZSM-5A-E, ● H-(Fe)-ZSM-5A-C, ◑ H-(In)ZSM-5A-C

2) The *ab initio* quantum chemical energy characteristics of the simple cluster, modelling the isomorphous substitution of trivalent heteroatoms in silicates, are correlated with the experimentally observed acidities of isomorphously substituted metallosilicates. This indicates that the isomorphous substitution of heteroatom M is connected with a rather short-range, localized effect. This is probably the reason why an analogous acidity sequence exists for other structural types of molecular sieves.

3) The experimentally determined metallosilicate activity obtained from conversion of toluene in its alkylation with ethylene and the temperature of ammonia desorption clearly indicate that In-silicates exhibit Si-OH-In sites of a lower acidity compared to Fe-and Al-analogues.

4) The following order has been established for the proton acidity of metallosilicates: Al > Ga > Fe > In > B.

The authors are indebted to Drs G. Vorbeck and R. Fricke (Berlin) for providing this study with Fe- and In-silicates. The work of B. W. and J. Č. was supported by a grant from the Academy of Sciences of the Czech Republic (No. 44003).

REFERENCES

1. Chen N. Y., Garwood W. E.: Catal. Rev.-Sci. Eng. *28*, 185 (1986).
2. Kaeding W. W., Barile G. C., Wu M. M.: Catal. Rev.-Sci. Eng. *26*, 597 (1984).
3. Parton R. F., Jacobs J. M., Huybrechts D. R., Jacobs P. A.: Stud. Surf. Sci. Catal. *46*, 163 (1989).
4. Ratnasamy P. in: *Advances in Catalyst Design* (M. Graziani and C. N. R. Rao, Eds), p. 67. World Scientific, London 1991.
5. Holderich W., Eichorn H., Lehnert R., Marosi L., Mross W., Reinke R., Ruppel W., Schlimper H.: *Proceedings of the 6th International Conference on Zeolites, Reno 1983*, p. 545. Butterworths, London 1984.
6. Szostak R.: *Molecular Sieves. Principles of Synthesis and Indentification.* Van Nostrand Reinhold, New York 1989.
7. Tielen M., Geelen M., Jacobs P.A.: Acta Phys. Chem. Szegendiensis *1985*, 1.
8. Chu C. T. W., Chang C. D.: J. Phys. Chem. *89*, 1569 (1985).
9. Ratnasamy P., Kumar R.: Catal. Today *9*, 328 (1991).
10. Simmons D. K., Szostak R., Agrawal P. K., Thomas T. L.: J. Catal. *106*, 287 (1987).
11. Beyer H. K., Borbély G.: Stud. Surf. Sci. Catal. *28*, 867 (1986).
12. Chu C. T. W., Kuehl G. H., Lago R. M., Chang C. D.: J. Catal. *93*, 451 (1985).
13. Sauer J.: Chem. Rev. *89*, 199 (1989).
14. Beran S. in: *Theoretical Aspects in Heterogeneous Catalysis* (J. C. Moffat, Ed.). Van Norstrand Reinhold, New York 1990.
15. Fripiat J. G., Andre F. B., Andre J. M., Derouane E. G.: Zeolites *3*, 306 (1983).
16. Derouane E. G., Fripiat J. G.: Zeolites *5*, 165 (1985).
17. Derouance E. G., Fripiat J. G.: J. Phys. Chem. *91*, 145 (1987).
18. O'Malley P. J., Dwyer J.: Chem. Phys. Lett. *143*, 97 (1988).
19. Jacobs P. A.: Catal. Rev.-Sci. Eng. *24*, 415 (1982).

20. Dompas D. H., Mortier W. J., Kenter O. C. H., Janssen M. J. G., Verduijn J. P.: J. Catal. *129*, 19 (1991).
21. Vetrivel R., Pal S., Krishnan S.: J. Mol. Catal. *66*, 385 (1991).
22. Vorbeck G., Čejka J., Janchen J., Parlitz B., Schreier E., Storek W., Fricke R.: *Proceedings of the 9th International Conference on Zeolites, Montreal 1992*, Extended Abstracts RP129.
23. Vorbeck G. et al.: Unpublished results.
24. Kapustin G. I., Brueva T. R., Klyachko A. L., Beran S., Wichterlová B.: Appl. Catal. *42*, 239 (1988).
25. Čejka J., Wichterlová B., Bednářová S.: Appl. Catal. *79*, 215 (1991).
26. Wichterlová B., Vorbeck G., Fricke R., Richter-Mendau J., Čejka J.: Collect. Czech. Chem. Commun. *57*, 799 (1992).
27. Schmidt M. W., Baldridge K. K., Boatz J. A., Jensen J. H., Koseki S., Gordon M. S., Nguyen K. A., Windus T. L., Elbert S. T.: *GAMESS: General Atomic and Molecular Electronic Structure System*. QPCE Bulletin *10*, 52 (1990).
28. Binkley J. S., Pople J. A., Hehre W. J.: J. Am. Chem. Soc. *102*, 939 (1980).
29. Kramer G. J., de Man A. J. M., van Santen R. A.: J. Am. Chem. Soc. *113*, 6435 (1991).
30. Vetrivel R., Catlow C. R. A., Colbourn E. A.: Proc. R. Soc. London, A *417*, 81 (1988).
31. Greenwood N. N., Earnshaw A.: *Chemistry of Elements*. Pergamon Press, Oxford 1984.
32. Hobza P., Zahradník R.: Chem. Phys. Lett. *82*, 473 (1981).
33. Čejka J., Vondrová A., Wichterlová B., Vorbeck G., Fricke R.: Zeolites, in press.
34. Raj A., Reddy K. R., Reddy J. S., Kumar R.: *Proceedings of the 10th International Congres on Catalysis, Budapest 1992* (L. Guczi et al., Eds), p. 1715. Akademiai Kiado, Budapest 1993.
35. Raj A., Reddy J. S., Kumar R.: J. Catal. *138*, 518 (1992).
36. Čejka J., Wichterlová B., Krtil J., Křivánek M., Fricke R.: Stud. Surf. Sci. Catal. *69*, 347 (1991).

Translated by the author (R. Z.).