

# Acidic properties of ZSM-5 zeolite modified with Ba<sup>2+</sup>, Al<sup>3+</sup> and La<sup>3+</sup> ion-exchange

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## Abstract

The acidity of a ZSM-5 zeolite was modified with Ba<sup>2+</sup>, Al<sup>3+</sup> and La<sup>3+</sup> ion-exchange. The ion-exchange process was repeated three times and after each ion-exchange cycle the samples were calcined. The acidity of the modified zeolites was characterized by IR and MAS NMR spectroscopy. The number of strong Brönsted acid sites decreases rapidly with increasing degree of barium ion-exchange since the effect of Plank–Hirschler mechanism is quite negligible due to the relatively low electrostatic potential of Ba<sup>2+</sup> cations. However, the splitting of water molecules resulting in the formation of new Brönsted acid sites and acidic M(OH)<sub>2</sub><sup>+</sup> groups is more probable in La<sup>3+</sup> and Al<sup>3+</sup> ion-exchanged zeolites. The formation of new Brönsted acid sites was observed in the IR spectra of highly Ba<sup>2+</sup> exchanged zeolite after the chemisorption of pyridine. This may be due to the formation of pyridinium ions via the reaction of base pyridine with unsplit water molecules coordinated to Ba<sup>2+</sup> ions. The catalytic activity of the modified zeolites was measured in an *n*-hexane cracking reaction. Zeolites with a high degree of Al<sup>3+</sup> and La<sup>3+</sup> ion-exchange were found to be slightly more active than unmodified zeolite, in accordance with the formation of new acid sites. The aluminium and lanthanum ion-exchange enhanced slightly the formation of C<sub>5</sub> and olefinic products and decreased the formation of C<sub>3</sub> and aromatic products.

*Keywords:* ZSM-5; Acidity; Lanthanum; Aluminium; Barium; Ion-exchange

## 1. Introduction

ZSM-5 zeolite is a member of crystalline microporous aluminosilicates with low aluminium content. Due to the specific framework structure and the low aluminium content ZSM-5 zeolites have special properties and they are used as shape-selective catalysts in many important industrial processes like catalytic cracking, alkylation and isomerization reactions.

Ion-exchange has been used to modify catalytic activity and molecular sieving properties of zeolites. The ion-exchange has been observed to occur in the case of almost every cationic form of the elements [1]. Not all zeolites are good ion-exchange materials, for example zeolites with high density and low porosity.

Most commonly the zeolite ion-exchange is understood as a process in which the cations (usually Na<sup>+</sup>) neutralizing the negative charge resulting from the structural aluminium tetrahedra are replaced by other mono-, di- or trivalent cations. Moreover, a framework aluminium atom

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can be replaced by another trivalent cation, for example B, Fe or Ga [2]. Because of this isomorphous substitution reaction new acid sites similar to Brönsted acid sites are formed. The acidity of these groups is found to increase according to  $\text{SiOH} < \text{B(OH)Si} \ll \text{Fe(OH)Si} < \text{Ga(OH)Si} < \text{Al(OH)Si}$ .

In the present work we have studied the effect of  $\text{La}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Ba}^{2+}$  ion-exchange on the acidic and catalytic properties of ZSM-5 zeolite.

## 2. Experimental

The ZSM-5 zeolite with a Si:Al ratio of 45.6 and a crystallinity of 83% was prepared according to the literature methods [3]. The NaZSM-5 zeolite was ion-exchanged twice with 3 M  $\text{NH}_4\text{NO}_3$  solution at 353 K for 2 h. After drying at 393 K for 3 h the zeolite was calcined to hydrogen form under air at 813 K for 2 h.

The La, Al and BaZSM-5 zeolites were prepared by stirring 20 g of HZSM-5 zeolite at 353 K for 2 h with 600 ml of 1 M  $\text{La}(\text{NO}_3)_3$ ,  $\text{Al}(\text{NO}_3)_3$  and  $\text{Ba}(\text{CH}_3\text{COO})_2$  solution, respectively. After drying at 393 K part of the zeolite was separated for a chemical analysis and the rest was calcined at 813 K for 2 h. The calcined sample was further ion-exchanged as above. The process was repeated until three samples with different degree of  $\text{La}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Ba}^{2+}$  exchange were obtained. For chemical analysis  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  ion-exchanged samples were transferred into liquid phase by HF/ $\text{HNO}_3$  treatment. Ion-exchanged aluminium was dissolved by using a HCl/ $\text{HNO}_3$  method. The metal contents of the samples were analyzed by flame atom absorption spectrometer (Varian Spectra AA-400).

The acidic properties of the ion-exchanged zeolites were studied by a Nicolet Magna 750 FTIR-spectrometer using a diffuse reflectance method. The sample chamber was equipped with nitrogen and vacuum line connections. Zeolite samples with a 50 wt% diamond powder matrix

were activated under vacuum and a nitrogen flow at 673 K for 2 h. A nitrogen flow saturated with pyridine was introduced into the IR chamber during 15 min at 388 K and at a pressure of 0.2 Torr. Physisorbed pyridine was removed by heating the sample at 423 K for 2 h.

NMR measurements were carried out with Bruker AM-250 and Bruker AMX-400 FT NMR spectrometers equipped with magic angle spinning probes. During  $^{29}\text{Si}$  (49.695 MHz) and  $^{27}\text{Al}$  (65.177 MHz) MAS NMR measurements the spinning rate of the sample was 4.8 kHz. During  $^1\text{H}$  (400.131 MHz) MAS NMR measurements the spinning rate was for Al and La exchanged samples 4.7 and 9.0 kHz, respectively. Before  $^{27}\text{Al}$  MAS NMR measurements the samples were contacted with the vapor of 3 M  $\text{NH}_4\text{NO}_3$  solution for three days in vacuum conditions. Before  $^1\text{H}$  MAS NMR measurements the samples were dried in vacuum at 673 K for 8 h.

The effect of ion-exchange on the activity and selectivity of the zeolite catalyst was studied in an *n*-hexane cracking reaction at 643 K. The *n*-hexane flow was introduced through the catalyst for 6 h and the cracking products were analyzed from the product flow with online gas chromatography (Hewlett Packard 5890 Series II Gas Chromatography) after 2, 4 and 6 h from the beginning of the reaction. The WHSV value for *n*-hexane was  $16.0 \text{ (g } n\text{-hexane) h}^{-1} \text{ (g of zeolite)}^{-1}$ .

## 3. Results and discussion

### 3.1. Chemical analysis

The metal content and the degree of ion-exchange after each ion-exchange cycle is shown in Table 1 and in Fig. 1. According to the shapes of the curves presented in Fig. 1 it may be supposed that  $\text{Ba}^{2+}$  ion-exchange takes place differently from  $\text{La}^{3+}$  and  $\text{Al}^{3+}$  ion-exchanges. The amount of exchanged  $\text{Ba}^{2+}$  cations decreases after each cycle. Also the degree of ion-exchange approaches 100% with increasing

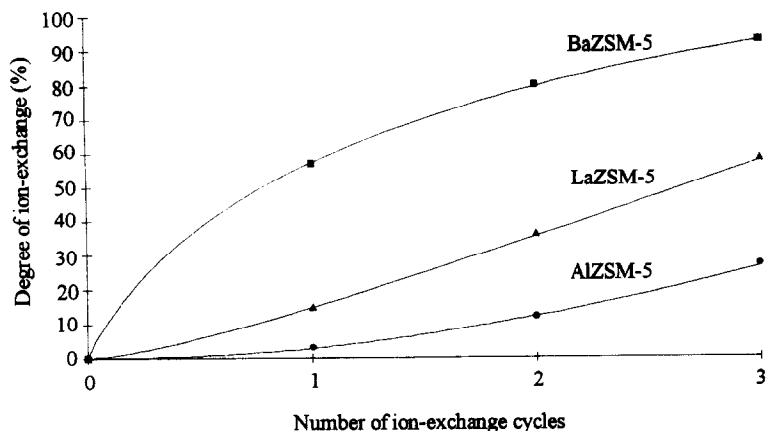


Fig. 1. The degree of Ba, La and Al ion-exchange after each ion-exchange cycle.

number of exchange cycles. The ion-exchange capacity of  $\text{Al}^{3+}$  and  $\text{La}^{3+}$  modified zeolites is relatively low at the beginning of the process but increases slowly after each exchange cycle.

The HF/ $\text{HNO}_3$  dissolution method used in dissolving La and Ba exchanged ZSM-5 was not useful for aluminium exchanged samples. The HF/ $\text{HNO}_3$  treatment dissolves the whole zeolite framework and in the liquid phase the liberated silicon and aluminium ions form a complex which causes interferences in flame atom absorption spectrometric analysis of aluminium [4,5]. During a HCl/ $\text{HNO}_3$  treatment the zeolite framework is not affected and only ion-exchanged aluminium and extra-framework aluminium should be transferred into the liquid phase. Therefore, the aluminium content of 0.12 wt% determined for untreated zeolite (HZSM-5) is equal to the extra-framework aluminium content of the zeolite.

Table 1  
The degree of ion-exchange (%) of a ZSM-5 zeolite after 1, 2 and 3 ion-exchange cycles

Number of cycles	$\text{Al}^{3+}$		$\text{La}^{3+}$		$\text{Ba}^{2+}$	
	a	b	a	b	a	b
1	0.010	3.0	0.30	15	1.5	57
2	0.040	12	0.60	36	2.0	80
3	0.090	27	1.0	58	2.3	92

a: Metal content (wt%) of the ZSM-5 zeolite.

b: The degree of ion-exchange (%) of the ZSM-5 zeolite.

### 3.2. FTIR measurements

The intensity of the Brönsted acid site signal at  $3614\text{ cm}^{-1}$  decreases as the degree of ion-exchange of the zeolite increases (Fig. 2) but in the case of BaZSM-5 after the third ion-exchange almost all Brönsted acid sites have dis-

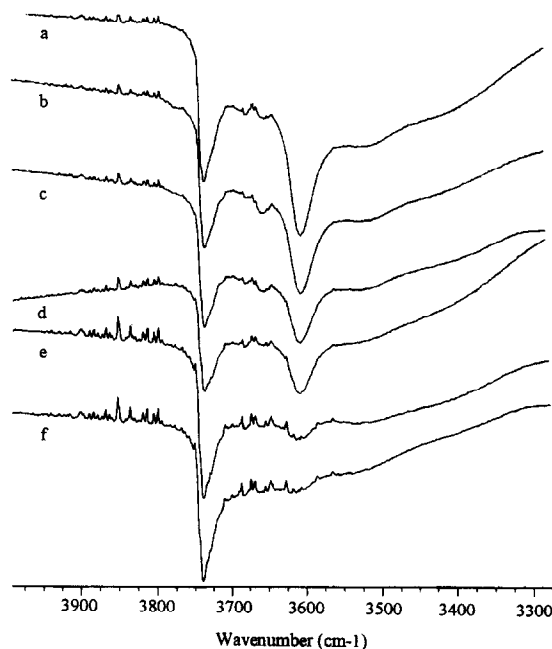


Fig. 2. FTIR-spectra of unmodified and ion-exchanged ZSM-5 zeolites on the OH-region: (a) unmodified ZSM-5, (b) AlZSM-5 after third ion-exchange, (c) LaZSM-5 after third ion-exchange, (d) BaZSM-5 after first ion-exchange, (e) BaZSM-5 after second ion-exchange, (f) BaZSM-5 after third ion-exchange.

appeared. The occurrence of Plank–Hirschler mechanism [6] is observed in the ion-exchange of zeolites with di- and trivalent cations. Ion-exchange with divalent and trivalent metal cations results in the formation of metal hydrate cations  $M(H_2O)_n^{2+}$  and  $M(H_2O)_n^{3+}$ , respectively. Due to the electrostatic field of the metal cations the splitting of water molecules takes place according to  $M(H_2O)_n^{2+} \rightleftharpoons MOH^+ + H^+$  and  $M(H_2O)_n^{3+} \rightleftharpoons M(OH)_2^+ + 2H^+$ . The splitting of coordinated water molecules takes place most easily in the case of small cations with high electrostatic field and polarizing power. Due to a relatively low electrostatic potential ( $1.48 \text{ \AA}^{-1}$ ) of quite large  $Ba^{2+}$  cations ( $1.35 \text{ \AA}$ ) the number of formed new Brönsted sites is low [9]. In the case of  $La^{3+}$  ( $1.17 \text{ \AA}$ ) and  $Al^{3+}$  ( $0.67 \text{ \AA}$ ) cations with electrostatic potentials of 2.56 and  $4.44 \text{ \AA}^{-1}$ , respectively, the occurrence of Plank–Hirschler mechanism should be more probable. The intensity of the signal at  $3614 \text{ cm}^{-1}$  is slightly higher in the spectrum of triply La exchanged zeolite compared with the spectra of the singly Ba exchanged sample, although the degree of ion-exchange in these samples is practically the same. This indicates the formation of new Brönsted acid sites during the  $La^{3+}$  modification. However, the presence of LaOH groups observed at  $3630 \text{ cm}^{-1}$  in the IR spectra of LaY zeolites [7] was not detected in the measured IR spectra of LaZSM-5.

The introduction of pyridine causes the disappearance of the Brönsted acid site signal at  $3614 \text{ cm}^{-1}$  due to the formation of pyridinium ions  $PyH^+$  (Fig. 3). The intensity of a signal at  $3265 \text{ cm}^{-1}$  increases after pyridine chemisorption and decreases with increasing degree of ion-exchange. This signal could be due to the N–H stretching mode of a pyridinium ion. The signal at  $3175 \text{ cm}^{-1}$  may be assigned to the same group, too, since the behavior of these two signals is quite similar.

The IR spectra of pyridine chemisorbed at Brönsted and Lewis acid sites are presented in Fig. 4. Pyridinium ion signals (pyridine on Brönsted acid sites) appear at wave numbers of

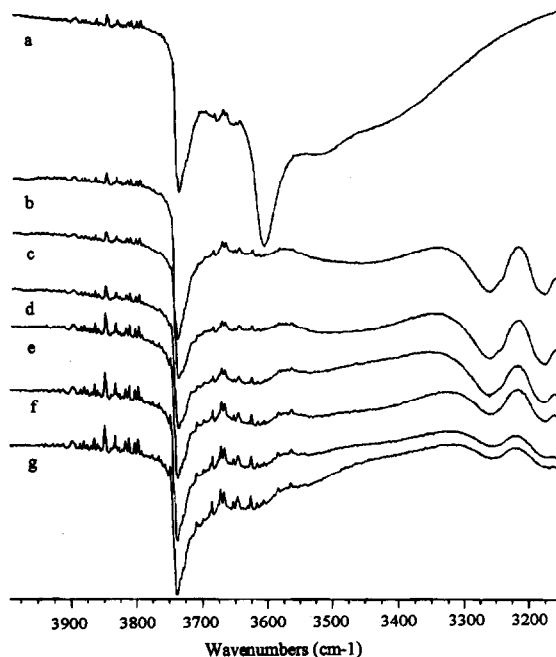


Fig. 3. FTIR-spectra of ZSM-5 zeolites after pyridine chemisorption: (a) unmodified ZSM-5 before pyridine adsorption, (b) unmodified ZSM-5, (c) AlZSM-5 after third ion-exchange, (d) LaZSM-5 after third ion-exchange, (e) BaZSM-5 after first ion-exchange, (f) BaZSM-5 after second ion-exchange, (g) BaZSM-5 after third ion-exchange.

$1638$  and  $1547 \text{ cm}^{-1}$  and pyridine on Lewis acid sites at  $1625$ ,  $1455$  and  $1450 \text{ cm}^{-1}$ . The signal at  $1491 \text{ cm}^{-1}$  is assigned to pyridine on both Brönsted and Lewis acid sites. The signal at  $1638 \text{ cm}^{-1}$  was assigned to a pyridinium ion on the basis of the previous photo acoustic spectroscopy measurements of silica alumina materials [8]. The intensities of pyridinium ion signals decrease as the degree of ion-exchange of the zeolite increases due to the loss of Brönsted acid sites. The intensity of the pyridinium ion signal is stronger in the spectrum of LaZSM-5 (Fig. 4c) compared with the spectrum of BaZSM-5 (Fig. 4d). Although having the same degree of ion-exchange the lanthanum modified zeolite shows more acidity due to formation of new acidic centers via the Plank–Hirschler mechanism. If water and pyridine are present at the same time the splitting of water and the formation of a pyridinium ion may take

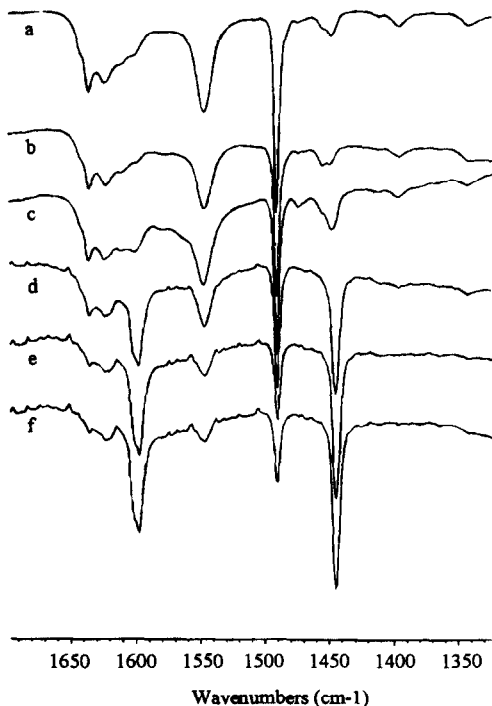


Fig. 4. Pyridine in Brønsted and Lewis acid sites: (a) unmodified ZSM-5, (b) AlZSM-5 after third ion-exchange, (c) LaZSM-5 after third ion-exchange, (d) BaZSM-5 after first ion-exchange, (e) BaZSM-5 after second ion-exchange, (f) BaZSM-5 after third ion-exchange.

place according to  $M^{2+} + H_2O + \text{pyridine} \rightleftharpoons MOH^+ + PyH^+$  even in the case of a cation with a low electrostatic field such as  $Ba^{2+}$ . This is because base pyridine shifts the reaction equi-

librium to the right. The detection of IR bands due to pyridinium ions even though the OH region of IR spectra shows no Brønsted acidity at all may be explained by unsplitted water molecules which remain in the coordination sphere of  $Ba^{2+}$  cations even after proper dehydration.

The signal at  $1455\text{ cm}^{-1}$  is caused by pyridine coordinated with an aluminium atom and the intensity of this signal naturally is the strongest in the case of aluminium ion-exchanged zeolite (Fig. 4c). In the case of lanthanum and barium ion-exchanged zeolites the corresponding signals appear at  $1447\text{ cm}^{-1}$  and  $1444\text{ cm}^{-1}$ , respectively. Furthermore for barium exchanged zeolites a new signal appears at ca.  $1600\text{ cm}^{-1}$  (Fig. 4e–f). The intensity of this signal increases as a function of barium ion-exchange. The corresponding signal was not observed in the spectra of the aluminium and lanthanum exchanged zeolites.

There is a linear correlation between the wave number of the pyridine–metal complex and the electronegativity of the ion-exchanged metal cation. The wave number of the pyridine–metal complexes is presented as a function of the electronegativity of some mono-, di- and trivalent metal cations in Fig. 5. The data is obtained from our present work and from the previous studies [9]. In the literature a similar correlation

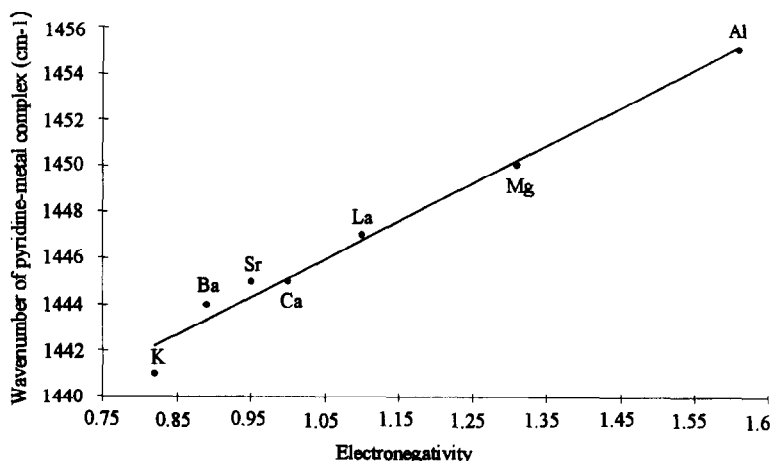


Fig. 5. Correlation between the wave number of the pyridine–metal complex and the electronegativity of the metal cation.

has been found between the frequency of the signal due to coordinatively bound pyridine and the cation radius, electrostatic field and electrostatic potential of ion-exchanged alkali and alkaline earth metal cations in zeolite Y [10].

### 3.3. MAS NMR measurements

The effects of La, Al and Ba ion-exchange on the ZSM-5 zeolite structure was studied by  $^{29}\text{Si}$ ,  $^{27}\text{Al}$  and  $^1\text{H}$  MAS NMR-spectroscopy. In  $^{29}\text{Si}$  NMR spectra three signals at the chemical shifts of  $-106$ ,  $-112$  and  $-115$  ppm were observed. The signal at  $-106$  ppm was caused by a  $\text{SiO}_4$  tetrahedron surrounded by three other  $\text{SiO}_4$  tetrahedra and one  $\text{AlO}_4$  tetrahedron. The signals at  $-112$  and  $-115$  ppm were assigned to a  $\text{SiO}_4$  tetrahedron connected to four other silicon

tetrahedra [11]. In  $^{27}\text{Al}$  NMR spectra only one signal at 55 ppm due to a framework aluminium atom was observed. The signal of extra framework aluminium atoms at 0 ppm was not detected. In the proton NMR spectra two signals at 3.8 and 1.4 ppm were observed due to Brönsted acid sites and terminal silanol groups, respectively. In  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR-spectra no changes were observed compared with the spectra of unmodified zeolite. In  $^1\text{H}$ -NMR spectra the intensity of the bridging hydroxyl group at 3.8 ppm decreased with increasing degree of ion-exchange, especially in the case of barium ion-exchanged zeolites (Fig. 6). The intensity of the Brönsted acid signal of triply Al and La exchanged zeolites did not decrease significantly compared with Ba exchanged samples. This is due to the occurrence of the

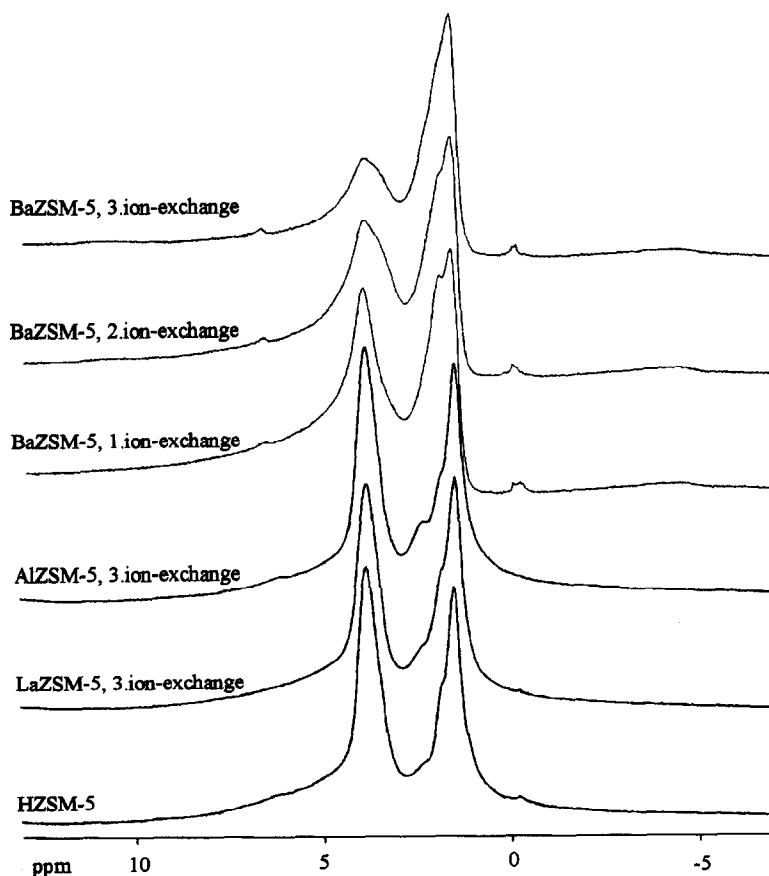


Fig. 6.  $^1\text{H}$  MAS NMR spectra of unmodified and Al, La and Ba ion-exchanged ZSM-5 zeolites.

Plank–Hirschler mechanism described above. In the spectrum of AlZSM-5 a new weak signal at ca. 2.5 ppm, probably due to a terminal AlOH group, was observed (Fig. 6). The signal of the terminal LaOH group was not seen and probably the chemical shift of this signal is in the same region as that of the terminal silanol group.

#### 3.4. Activity and selectivity measurements

The catalytic activity of zeolite catalyst in hydrocarbon cracking reactions is related to the number of acid sites, especially strong Brönsted acid sites, in the zeolite framework. Therefore the ion-exchange process is supposed to decrease the cracking activity, although some new Brönsted sites are formed via the Plank–Hirschler mechanism. Cracking products were analyzed with on-line gas chromatography after 2, 4 and 6 h from the beginning of the reaction. A small decrease in *n*-hexane conversion was observed during the reaction due to formation of coke. No remarkable differences in coke formation rates were observed between the different samples. Coke formation occurs mainly on the external surface of the ZSM-5 zeolite and therefore the passivation of the external surface would slow down the aging of the catalyst [12]. The conversion levels of *n*-hexane after 2 h for the La, Al and Ba ion-exchanged zeolites are shown in Fig. 7. In barium ion-exchanged zeolites the

cracking activity decreases gradually to zero. The decrease in activity is due to the loss of strong Brönsted acid sites. In aluminium and lanthanum ion-exchanged zeolites the activity first decreases but as the degree of ion-exchange increases the cracking activity increases, too. The enhanced activity is due to the active centers formed by ion-exchanged lanthanum and aluminium ions and to the formation of new Brönsted acid sites via the Plank–Hirschler mechanism.

In the literature there is varying information about the catalytic activity of lanthanum ion-exchanged ZSM-5 zeolite. Lanthanum ion-exchange has been reported to increase the number of weak acid sites and to decrease the number of strong acid sites in ZSM-5 and therefore to decrease the *n*-hexane cracking activity [13]. Due to the large size of aqueous lanthanum species ( $\text{La}(\text{H}_2\text{O})_6^{3+}$ ,  $d \sim 6.6 \text{ \AA}$ ) the La ion-exchange is supposed to occur on the outer surface of the zeolite at relatively low temperatures. According to other authors, the number of both strong and weak acid sites in ZSM-5 zeolite was increased by lanthanum ion-exchange. The cracking activity remained nearly the same with the unmodified zeolite [14]. ZSM-5 zeolites with a high degree of lanthanum ion-exchange have been prepared by hydrothermal liquid-solid exchange. The catalytic activity of ZSM-5 with a high lanthanum content was found to be higher

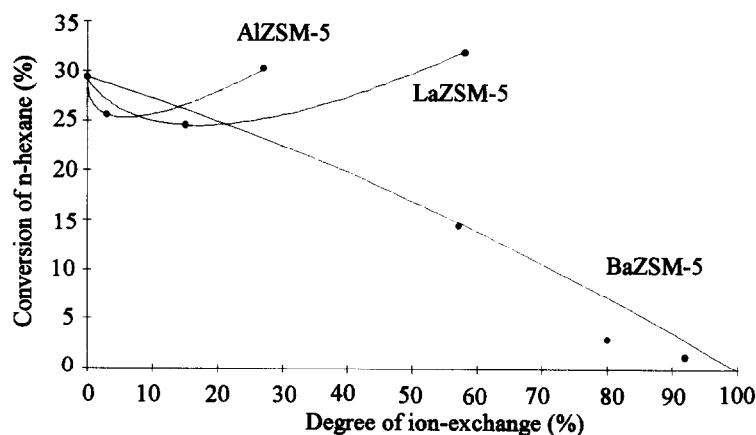


Fig. 7. Activity of La, Al and Ba ion-exchanged ZSM-5 zeolites in the *n*-hexane cracking reaction.

Table 2

The effect of La<sup>3+</sup> and Al<sup>3+</sup> ion-exchange on the selectivity of ZSM-5 zeolite in the *n*-hexane cracking reaction <sup>a</sup>

Catalyst <sup>b</sup>	Conversion (%)	Amounts in reaction products (wt%)						
		C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	linear	branched	aromatic	olefinic
1	29.4	32.2	41.8	8.6	64.8	21.5	5.5	6.2
2	25.6	32.1	42.3	8.7	65.4	20.6	5.8	6.9
3	30.4	30.0	42.3	10.1	64.7	21.9	4.9	7.8
4	24.6	32.0	42.3	9.0	65.3	20.7	5.5	6.7
5	32.0	29.6	42.1	10.3	64.6	21.8	4.9	8.1

<sup>a</sup> Reaction conditions: *T* = 370°C, *p* = 1 atm, WHSV = 16.0 (g *n*-hexane) h<sup>-1</sup> (g zeolite)<sup>-1</sup>.<sup>b</sup> Catalyst numbers: 1 HZSM-5, 2 AlZSM-5 (1 ion-exchange), 3 AlZSM-5 (3 ion-exchanges), 4 LaZSM-5 (1 ion-exchange), 5 LaZSM-5 (3 ion-exchanges).

than HZSM-5 zeolite [15]. Trivalent metal cations have a strong electric field and they generate new Brönsted and Lewis acid sites in the zeolite. It has been reported that lanthanum exchanged zeolites were active only after contact with water [16,17]. That shows that Lewis acidity has no significant catalytic importance in catalytic cracking reactions.

The effect of La, Al and Ba ion-exchange on the selectivity of ZSM-5 zeolite was investigated by analyzing the amounts of cracking products in the feed after 2 h from the beginning of the reaction. The selectivity study was done by means of the number of carbon atoms of the products, the amounts of linear and branched product molecules and the amounts of olefinic and aromatic product molecules. The comparison was done for the catalysts with nearly the same conversion level. A high degree of Al and La ion-exchange was found to enhance the formation of C<sub>5</sub> and olefinic products and to decrease the formation of C<sub>3</sub> and aromatic products (Table 2).

#### 4. Conclusions

In the present work we have studied the effect of Ba<sup>2+</sup>, Al<sup>3+</sup> and La<sup>3+</sup> ion-exchange on the acidity and catalytic activity of ZSM-5 zeolite. The ion-exchange process was repeated for three times in order to obtain highly exchanged

zeolites. The number of strong Brönsted acid sites decreased rapidly with increasing degree of Ba ion-exchange due to quite negligible effect of the Plank–Hirschler mechanism. However, in La and Al exchanged zeolites the splitting of coordinated water molecules to form new Brönsted acid sites and acidic metal hydroxyl groups was concluded.

No changes in <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra of La<sup>3+</sup> and Al<sup>3+</sup> exchanged zeolites were observed compared with the unmodified ZSM-5. In <sup>1</sup>H MAS NMR spectra the intensity of the Brönsted acid site signal decreased as the degree of ion-exchange increased, especially in the case of BaZSM-5. On the basis of IR studies no remarkable changes in Brönsted acidity was observed in triply Al- and La-exchanged samples.

The *n*-hexane cracking studies showed that the conversion levels of BaZSM-5 decreased gradually to zero but for LaZSM-5 and AlZSM-5 the activity started to rise as the degree of ion-exchange increased. A high degree of Al and La ion-exchange enhanced slightly the formation of C<sub>5</sub> and olefinic products and decreased the formation of C<sub>3</sub> and aromatic products.

We are currently exploring the nature of the active sites formed in the La- and Al- exchange. Our preliminary results [18] from <sup>129</sup>Xe NMR studies show that the La and Al ions do not locate in the zeolite channels.



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