

Novel method for the preparation of Cs-containing FAU(Y) catalysts for aniline methylation

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Abstract Cs-containing FAU(Y)-type zeolite catalysts were prepared by conventional and novel ion exchange procedures followed by incipient wetness impregnation with CsOH. The novel ion exchange procedure involved hydrothermal treatment of NaY zeolite in aqueous solution of CsCl at 140–200 °C for 6–24 h. The samples were characterized by low-temperature nitrogen adsorption, X-ray fluorescence analysis, X-ray powder diffraction, scanning electron microscopy, ²³Na, ²⁷Al and ¹³³Cs magic angle spinning nuclear magnetic resonance, CO₂ and NH₃-Temperature programmed desorption. The results show that hydrothermal treatment at 200 °C allows to obtain higher degrees of ion-exchange (up to 83%) with respect to conventional method giving maximum 66%–69%. Catalytic properties of Cs-containing FAU(Y) were studied in aniline methylation. The yield of *N*-methylaniline is shown to correlate with catalyst's basicity. The best catalyst performance was achieved over the catalyst with the highest ion-exchange degree impregnated with CsOH. The selectivity to *N*-methylaniline over this catalyst reached 96.4%.

Keywords FAU(Y) zeolite, ion exchange with cesium, aniline alkylation, *N*-methylaniline

1 Introduction

Cs-containing FAU(Y) zeolites are known to be efficient catalysts for the reactions catalyzed by basic sites, such as alcohols dehydrogenation [1–4], alkenes isomerisation [5,6], side-chain alkylation of toluene [5,7–10], acetonitrile [10] and aniline [11,12], methyloctanoate deoxygenation [13], MIBK oxidation [14] and others. The major methods

of preparation of these catalysts include ion exchange of NaY zeolite with cesium cations and incorporation of Cs-containing basic compounds, such as cesium oxide or hydroxide, in zeolite porous system. The catalytic properties of basic forms of zeolites are governed by the presence of alkaline metal cations being the weak Lewis acids and the framework oxygen atoms playing the role of Lewis bases. The content of cations, their type and location in zeolite framework determine the adsorption and catalytic properties of basic zeolites. Therefore, the preparation of FAU-type zeolites with high degrees of ion-exchange is of great importance.

The analysis of the literature data points that only 68% of sodium cations can be exchanged in FAU(Y) via conventional ion-exchange procedure in aqueous solution [15]. This limit exists because large cesium cations (ionic diameter = 3.38 Å) can not enter the sodalite cages and hexagonal prisms of zeolite FAU structure through the small 6-ring entrances (diameter ~2.2 Å). To overcome this problem other more specific approaches are required. Thus, it was reported [16,17] that higher exchange levels of 83%–90% can be achieved by 4-fold successive ion exchanges in cesium chloride or nitrate solutions at 85 °C followed by drying at 100 °C and dehydration in vacuum at 450 °C. Removal of water by evacuation allows for diffusion of cesium cations into the sodalite cages and migration of sodium into supercages, where they can be further exchanged with cesium. This procedure however is time consuming and requires ~24 d for sample preparation. Karge et al. reported another procedure leading to totally exchanged CsY [4]. This was achieved in two steps including: (1) 20-fold ion exchange of NaY with NH₄⁺ cations followed by (2) stepwise heating of the mixture of NH₄Y with CsCl under vacuum up to 452 °C, maintaining at each temperature for 22–24 h. The duration of the whole procedure was up to 1 month. Thus, all the approaches described in the literature for deep ion exchange of NaY with cesium are rather time-consuming, require special

vacuum equipment and therefore can be used only at the laboratory scale for the preparation of small batches of samples.

In this contribution we focused our efforts at the development of more simple and fast method for deep ion-exchange of NaY with cesium cations. The procedure elaborated is based on the hydrothermal treatment of NaY in aqueous solution of CsCl at elevated temperatures and allows reaching the exchange level of up to 83%. The effect of several parameters of synthesis, such as the number of ion exchange cycles, temperature and time of treatment on cesium content and location in faujasite structure, physicochemical and catalytic properties has been investigated. Catalytic properties were tested in aniline alkylation, which is a good model reaction for basic sites responsible for *N*-alkylation and acidic sites leading to *C*-alkylation.

2 Materials and methods

2.1 Sample preparation

CsNaY samples were prepared by conventional ion-exchange procedure of NaY zeolite (Si/Al = 2.4) in 0.1 mol/L CsCl solution at 80 °C and hydrothermal ion exchange of NaY with 4 mol/L CsCl solution in an autoclave at elevated temperature. The temperature of hydrothermal treatment was varied from 140 to 200 °C and the duration was 6–24 h. Initial NaY and the sample with the highest cesium content were impregnated with 50% CsOH solution to achieve 7.2 wt-% Cs₂O. The samples are designated as CsNaY/N/T/H, where N is the number of conventional ion exchange cycles at 80 °C, T is the temperature of hydrothermal treatment and H is the duration of hydrothermal treatment in hours. If the sample was impregnated with CsOH solution “/CsOH” is added to the sample designation.

2.2 Characterization

Elemental analysis of the samples prepared was performed by X-ray fluorescent spectrometry on Thermo Scientific ARL Perform'X equipped with 3.5 kW Rh-tube. X-ray powder diffraction data were collected on BRUKER D2 Phaser diffractometer with CuK α tube ($\lambda = 1.54 \text{ \AA}$) in 2θ range of 5° to 70°. Diffraction patterns were quantified in Bruker Diffrac.Suite Eva software. ICDD PDF2 database was used for phase identification. Low-temperature nitrogen adsorption isotherms were collected by automatic sorbometer ASAP2000 (Micromeritics, USA). Micropore volume was analysed by t-plot method. Overall pore volume including adsorption in micropores, mesopores and on external surface was calculated from nitrogen adsorbed at the relative pressure of $p/p_0 = 0.95$. The

morphology of the samples was investigated by scanning electron microscopy on Hitachi Tabletop Microscope TM3030Plus with 15 kV accelerating voltage.

The location of cesium cations in FAU(Y) structure was investigated by solid state ²³Na and ¹³³Cs magic angle spinning nuclear magnetic resonance (MAS NMR) on Varian Unity Inova Plus AS500. Prior to experiments the samples dehydrated at 500 °C for 48 h. MAS Spinning rate was 15 kHz. Operating frequencies for ²³Na, ²⁷Al and ¹³³Cs were 132.2, 130.3 and 65.6 MHz respectively. Standard single-pulse sequences were used. The external references were 1 mol/L aqueous solutions of NaCl, AlCl₃ and CsCl.

The basic properties of the samples were studied by thermoprogrammed CO₂ desorption (TPD CO₂) with universal sorption gas analyzer USGA-101. Samples were calcined at 450 °C in a flow He and then cooled down to 60 °C. Saturation with carbon dioxide was carried out at 60 °C during 30 min in a flow of CO₂. Then the gas flow was switched to helium and physisorbed carbon dioxide was desorbed for 30 min at 60 °C. After that the sample was cooled down to room temperature. In a typical TPD CO₂ experiment the temperature was raised with the rate of 8 °C/min up to 600 °C in a helium flow (30 mL/min) and the amount of evolved carbon dioxide was measured by thermal conductivity detector. The acidic properties of the samples were studied by thermoprogrammed NH₃ desorption (TPD NH₃) with universal sorption gas analyzer USGA-101. Samples were calcined at 500 °C for 1 h in a helium flow, saturated with ammonia at 60 °C for 15 min, physically adsorbed ammonia was removed in a helium flow at 100 °C. Thermoprogrammed desorption of NH₃ was carried out in a helium flow (30 mL/min), the temperature was increased with the rate of 8 °C/min, the evolved ammonia was registered by a thermal conductivity detector.

2.3 Catalyst evaluation

Catalytic properties were tested in aniline alkylation by methanol. The reaction was carried out in fixed-bed reactor under atmospheric pressure and 400 °C. The molar composition of the feed was aniline:methanol:N₂ = 1:5:3, the weight hourly space velocity being 1.8 h⁻¹. The reaction products were analyzed by gas-liquid chromatography on capillary column with “SE-30” phase and by chromatomass-spectrometry with HP-5890 on 50m quartz capillary column “ULTRA-1”. Sanderson's electronegativity was calculated as proposed by Mortier [22] according to the following equation:

$$S = (S_p^p S_Q^q S_R^r)^{1/(p+q+r)},$$

where S_p , S_Q , S_R are the electronegativities of P, Q and R atoms in a compound with chemical formula: P_pQ_qR_r.

3 Results and discussion

Physicochemical characteristics. The samples prepared are summarized in Table 1. The conventional ion-exchange procedure carried out at 80 °C leads to stepwise increase the ion exchange level up to 69%, being 21% after the first cycle, and 69% after the fifth cycle that corresponds to 8.6 wt-% and 25.2 wt-% Cs₂O respectively. It should be mentioned that the properties of CsNaY/5 does not differ significantly from CsNaY/4 which means that no additional cesium introduction into the cationic positions is taking place during the 5th ion exchange at 80 °C.

Hydrothermal ion exchange in autoclave conditions allows for deeper exchange of sodium cations with cesium, the ion-exchange level being higher at longer duration and higher temperature of treatment. The increase of the temperature from 140 to 200 °C and the duration of treatment from 6 to 24 h allow for the increase of ion exchange degree from 73%–75% (samples CsNaY/5/140/24, CsNaY/5/200/6) to 83% (sample CsNaY/5/200/24). It is interesting to note that the direct 1-fold hydrothermal ion exchange of parent NaY leads to ion exchange level of 73% (sample CsNaY/0/200/24), which is much higher than in the case of conventional ion exchange procedure giving only 21% after the first cycle (sample CsNaY/1). It should be noted that the replacement of sodium cations by cesium in zeolite structure is accompanied by the significant decrease pore volume. For the sample with the highest ion-exchange degree of 83% (CsNaY/5/200/24) the pore volume is 48% lower than in parent NaY. This observation can be accounted for by bigger size of cesium cations.

X-ray powder diffraction patterns of CsNaY samples are given in Fig. 1. The results show that no change in phase composition of the samples takes place neither after conventional, nor after hydrothermal ion-exchange. However the intensity of the reflexes decreases with ion exchange: the higher the cesium content, the less intensive

the x-ray reflexes are. These results are in line with the literature data [8,18]. Wei et al. suggested that lowering of the reflex's intensities is the result of the zeolite partial destruction [18], whereas Borgna et al. pointed out that it can be due to different extinction coefficient of CsY with respect to NaY [8].

To verify whether zeolite destruction does occur during ion-exchange, we analyzed our samples with SEM and ²⁷Al MAS NMR. SEM images indicate that neither ion exchange, nor impregnation, lead to the appearance of amorphous phase; the size of parent zeolite crystals is preserved after all the treatments (Fig. 2). ²⁷Al MAS NMR spectra of CsNaY with different exchange levels and impregnated with CsOH solution samples (Fig. 3) showed the only NMR line at ca. 61 ppm corresponding to tetracoordinated aluminum atoms in the faujasite structure. No signal at ca. 0 ppm, which can be attributed to octahedral aluminum in extraframework positions is observed. Therefore, we consider that no zeolite destruction is taking place during the ion exchange or impregnation procedures. We also would like to mention that alongside with the change in x-ray extinction coefficient, the reason of x-ray reflexes intensity decrease could be also due to the change in the density of samples caused by Cs cations introduction.

Sodium and cesium cations location in the structure of CsNaY catalysts was investigated by ²³Na and ¹³³Cs MAS NMR of the samples dehydrated at 500 °C. According to crystallographic data, there are 5 cation positions in FAU (Y) structure: SI stands for in hexagonal prism, SII and SIII in supercage and SI' and SII' in sodalite cage. ²³Na MAS NMR spectra (Fig. 4) of parent NaY show 3 NMR resonances: Intensive signal at ca. –13 ppm and two overlapping wide NMR lines at ca. –30 and –50 ppm. The former signal can be attributed to sodium cations in SI positions. Whereas the latter two maxima are most probably caused by sodium cations in SI + SII positions

Table 1 Catalyst characteristics

Sample	Si/Al	Na/Al	Cs ₂ O content /wt-%	Ion exchange level /%	Pore volume /(cm ³ ·g ⁻¹)
NaY	2.4	0.97	0	0	0.289
NaY/CsOH	2.4	0.97	7.2	0	0.233
CsNaY/1	2.4	0.74	8.6	21	0.259
CsNaY/2	2.4	0.81	17.4	32	0.235
CsNaY/3	2.4	0.39	22.8	60	0.220
CsNaY/4	2.4	0.33	24.8	66	0.207
CsNaY/5	2.4	0.30	25.2	69	0.203
CsNaY/5/140/24	2.4	0.20	24.9	73	0.209
CsNaY/5/200/6	2.4	0.24	25.2	75	0.199
CsNaY/0/200/24	2.5	0.22	27.4	73	0.164
CsNaY/5/200/24	2.4	0.16	36.1	83	0.150
CsNaY/5/200/24/CsOH	2.4	0.16	43.3	83	0.110

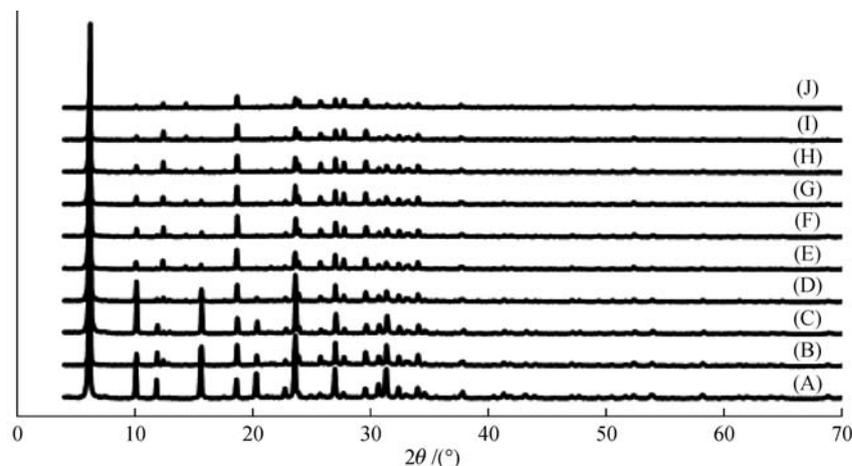


Fig. 1 X-ray diffraction data for (A) NaY, (B) NaY/CsOH, (C) CsNaY/1, (D) CsNaY/2, (E) CsNaY/3, (F) CsNaY/4, (G) CsNaY/5, (H) CsNaY/5/140/24, (I) CsNaY/5/200/24 and (J) CsNaY/5/200/24/CsOH samples

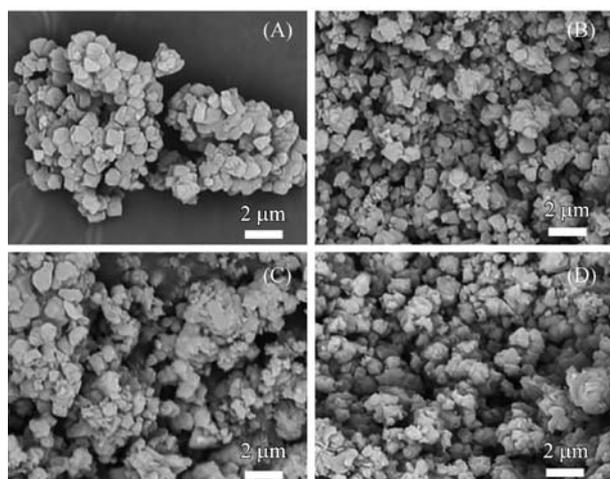


Fig. 2 SEM microphotographs of (A) NaY, (B) CsNaY/5, (C) CsNaY/5/200/24 and (D) CsNaY/5/200/24/CsOH samples

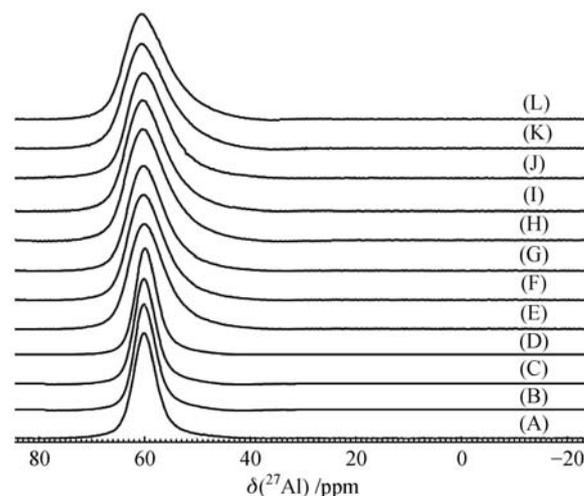


Fig. 3 ^{27}Al MAS NMR spectra for (A) NaY, (B) NaY/CsOH, (C) CsNaY/1, (D) CsNaY/2, (E) CsNaY/3, (F) CsNaY/4, (G) CsNaY/5, (H) CsNaY/5/200/6, (I) CsNaY/5/140/24, (J) CsNaY/0/200/24, (K) CsNaY/5/200/24 and (L) CsNaY/5/200/24/CsOH samples

[17,19]. The ion exchange of sodium with cesium causes gradual decrease of the signals at ca. -30 and -50 ppm, suggesting that sodium cations in SI' and SII positions are exchanged. The peak at -13 ppm is preserved in the spectra even at high ion exchange levels indicating that sodium cations remain only in hexagonal prisms.

^{133}Cs MAS NMR spectra of dehydrated faujasites are shown in Fig. 5. Signals attribution is performed as proposed by Hunger et al. [20]. In the spectrum of CsNaY/1 with the lowest degree of ion exchange the only signal at ca. -142 ppm is observed due to the ion exchange with cesium in SI' positions of sodalite cage. Further ion exchange (sample CsNaY/2) leads to the appearance of the intensive signal at ca. -123 ppm with a shoulder at ca. -95 ppm, which can be attributed to cesium cations occupying SII' and SIII positions in sodalite cage and supercage. At the same time no noticeable signal at ca. -80 ppm is detected indicating that cesium does not enter

in SII positions in CsNaY/2 sample. Therefore the decrease of sodium content in SII positions of this sample (Fig. 4) is rather due to sodium migration to other positions than due to sodium exchange with cesium. The increase of the exchange level up to 60% (sample CsNaY/3) leads to the appearance of the intensive signal at ca. -98 ppm with a shoulder at -80 ppm, indicating that at this exchange level cesium cations occupy all available positions except SI in hexagonal prisms; the most part of cesium cations being located in supercage in SII and SIII positions. Further increase of the ion exchange degree up to 69%–83% (samples CsNaY/5–CsNaY/5/200/24) leads to gradual increase of the intensity of the signal at ca. -80 ppm, corresponding to cesium cations in SII positions (Fig. 5).

To summarize our ^{23}Na and ^{133}Cs MAS NMR results

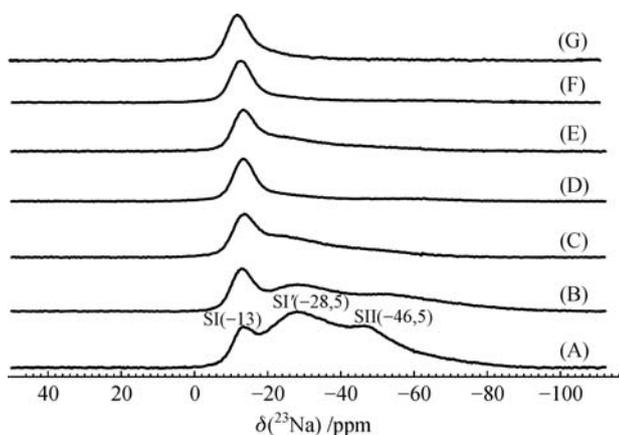


Fig. 4 ^{23}Na MAS NMR spectra for (A) NaY, (B) CsNaY/1, (C) CsNaY/2, (D) CsNaY/3, (E) CsNaY/4, (F) CsNaY/5 and (G) CsNaY/5/200/24 samples

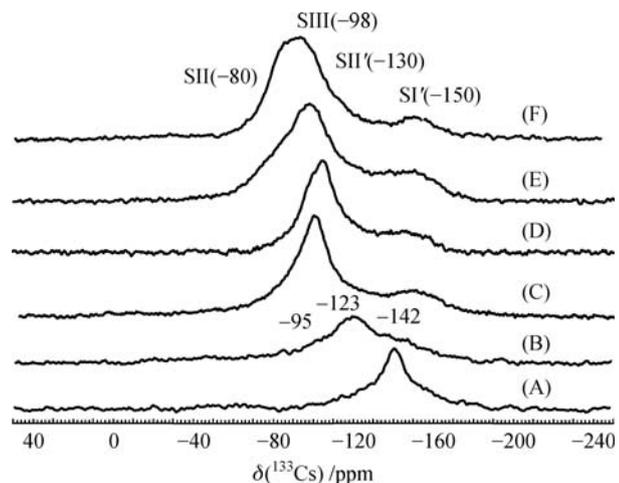


Fig. 5 ^{133}Cs MAS NMR spectra for (A) CsNaY/1, (B) CsNaY/2, (C) CsNaY/3, (D) CsNaY/4, (E) CsNaY/5 and (F) CsNaY/5/200/24 samples

demonstrate that cesium cations firstly substitute sodium in SI' positions of sodalite cages, then in SII' and SIII positions and finally in SII positions of the supercage. These results suggest that ion-exchange in sodalite cages is energetically more favorable with respect to supercages. In the latter, cesium cations first occupy SIII positions and then SII. Additional ion exchange in supercages (exchange levels higher than 70%) is most probably due to increased mobility and hydrate shell distortion of cesium cations at harsh conditions of ion exchange in autoclave at high temperatures. Our results on cesium and sodium distribution among different positions during ion-exchange are in good agreement with the literature data [16,17,20,21]. Thus, Koller et al. [17] pointed that the samples with exchange levels of 20% and 40% are drastically different from those for the samples with higher exchange levels.

Although the authors didn't interpret the spectra collected, outward appearance of their spectra is very similar to those found in this work. Jelinek et al. [21] found that cesium first exchanges sodium cations occupying SIII positions and then SII positions in the samples with exchange levels of 50%–65%, what also matches our results.

Acidic properties of the samples were studied by TPD NH_3 (Fig. 6). TPD NH_3 profile of NaY sample has a maximum at 200 °C representing ammonia desorption from weak acidic sites. Ion exchange with cesium results in drastic decrease of acidic sites content. The sample CsNaY/5/200/24/CsOH has almost no acidic sites. Basic properties of the samples were studied by TPD CO_2 (Fig. 7). The results point that parent NaY sample do not contain basic sites. Ion-exchange of sodium with cesium results in the appearance of weak basic sites desorbing carbon dioxide at 120 °C. Further impregnation with CsOH leads to the appearance of medium and strong sites, showing desorption peaks at ca. 240 and 300–500 °C. The total amount of basic sites in CsNaY/5/200/24/CsOH is found to be 20 times higher than in the case of CsNaY/5. This observation can be explained by the presence of small cesium oxide particles being strong basic sites in the porous system of impregnated samples [6].

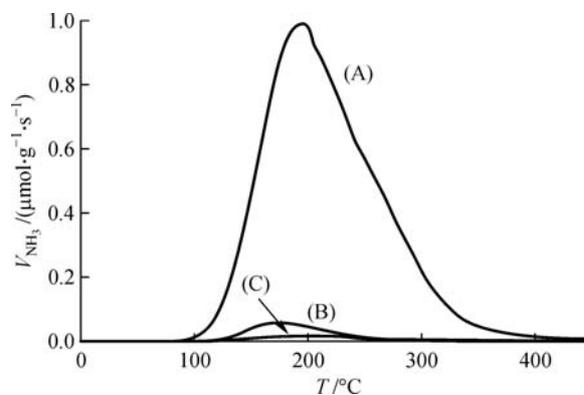


Fig. 6 TPD NH_3 profiles of (A) NaY, (B) CsNaY/5 and (C) CsNaY/5/200/24/CsOH samples

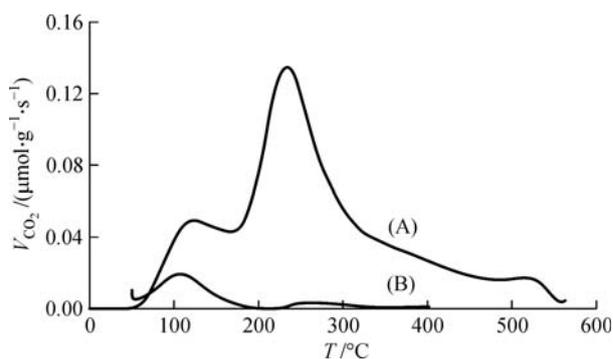


Fig. 7 TPD CO_2 profiles of (A) CsNaY/5/200/24/CsOH and (B) CsNaY/5 samples

Catalytic properties. Catalytic properties were evaluated in aniline alkylation with methanol. Samples NaY, NaY/CsOH, CsNaY/5, CsNaY/5/200/24 and CsNaY/5/200/24/CsOH were selected for the catalytic tests. The reaction products observed over these catalysts include *N*-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA), methyl-, dimethyl- and trimethylaniline (MA, DMA, TMA) and small amounts of methyl-*N*-methylaniline and methyl-*N,N*-dimethylaniline. According to the literature data the products of *N*-alkylation (NMA and NNDMA) are formed over basic sites, whereas the products of *C*-alkylation (MA, DMA and TMA) are generated over acidic sites. The comparison of the selectivity of various catalysts to different products at the same conversion level is given in Table 2.

The main reaction product observed over the NaY catalyst is para-methylaniline (*p*-MA) due to weak Lewis acidic sites generated by sodium cations in the faujasite structure. Ion exchange of sodium cations with cesium leads to gradual increase of the contribution of *N*-alkylation pathway (Table 2): the selectivity to NMA and NNDMA increases from 8.4 wt-% (NaY) to 21.7 wt-% after the exchange of 69% Na⁺ cations with Cs⁺ (CsNaY/5) and reaches 41.9 wt-% after the exchange of 83% of cations (CsNaY/5/200/24). However, even after deep ion-exchange the products of ring-alkylation are still present in the effluent, which is probably due to low basicity of the sites created by ion exchange.

Impregnation with CsOH largely increases contribution of *N*-alkylation. This observation is due to the formation of superfine cesium oxide particles being strong Lewis basic sites inside zeolite pores. The highest *N*-alkylation selectivity of ca. 97% is reached over CsNaY/5/200/24/CsOH with the exchange level of 83% impregnated with CsOH. The comparison of the data obtained over NaY/CsOH, CsNaY/5/200/24 and CsNaY/5/200/24/CsOH suggest that both Cs⁺-cations and Cs₂O superfine particles are necessary for selective alkylation. It should be mentioned that the impregnation with CsOH also favors the formation

of mono-alkylated products on the expense of dialkylated: the content of NMA in the products of *N*-alkylation increases from 81% to 99.8% (Table 2). Apparently, the introduction of large cesium cations and the presence of superfine cesium oxide particles in zeolitic pores creates steric hindrances for bulky NNDMA formation. The decrease of pore volume with cesium content increase is also confirmed by the low-temperature adsorption data (Table 1). Thus to obtain highly NMA-selective catalysts ion exchange and impregnation are necessary. To correlate the catalytic activity with basic properties of the catalysts the Sanderson's electronegativity was calculated as described in the experimental part. The yield of *N*-alkylated products is plotted *versus* the Sanderson's electronegativity in Fig. 8. The results point to the linear correlation of *N*-alkylation with catalysts basicity represented by Sanderson's electronegativity.

4 Conclusions

The novel approach for deep ion-exchange of NaY with cesium cations has been elaborated. The procedure is based on the hydrothermal treatment of NaY in aqueous solution of CsCl at 140–200 °C for 6–24 h. The method is fast and simple giving the exchange levels of 73% in one cycle, which is much higher than in the case of conventional ion exchange procedure providing only for 21%. It is demonstrated that the level of ion-exchange can be varied by the number of treatments, the duration and the temperature of treatments. The highest degree of ion-exchange achieved is 83%.

The basicity of Cs-containing catalysts is shown to increase with Cs content. Ion-exchange with cesium results in the appearance of weak basic sites, whereas impregnation with CsOH generates medium and strong sites. The evaluation of Cs-containing FAU(Y) catalysts in aniline methylation points to the correlation of their basicity with the yield of *N*-methylaniline. The best catalyst perfor-

Table 2 Aniline alkylation with methanol over Cs-containing catalysts^{a)}

Catalyst	NaY	NaY/CsOH	CsNaY/5	CsNaY/5/200/24	CsNaY/5/200/24/CsOH
Aniline conversion/%	38.6	31.9	34.3	28.7	34.9
Selectivity/wt-%					
NMA	8.1	34.4	19.6	34.3	96.4
NNDMA	0.3	2.5	2.1	7.6	0.2
<i>p</i> -MA	64.2	47.6	52.7	35.2	2.2
<i>o</i> -MA	0.9	0.0	0.0	0.9	0.0
2,4-DMA	14.2	3.7	12.3	13.6	1.0
<i>p</i> -MNMA	2.0	10.2	1.2	0.2	0.0
<i>p</i> -MNNDMA	6.5	0.9	7.6	5.5	0.0
TMA	3.8	0.7	4.5	2.7	0.2

a) Reaction conditions: 0.1 MPa, 400 °C, aniline:methanol:N₂ = 1:5:3 (mol), 1.8 g·g⁻¹·h⁻¹

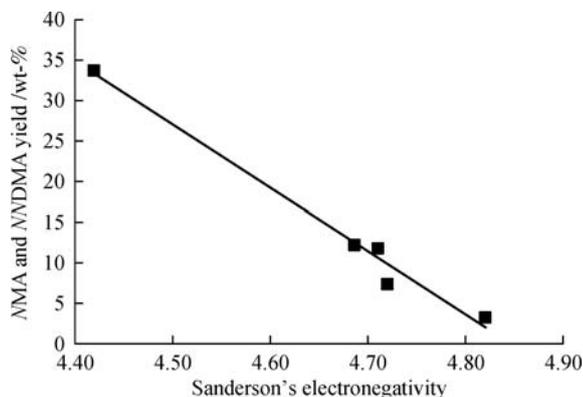


Fig. 8 *N*-methylaniline and *N,N*-dimethylaniline yield as function of Sanderson's electronegativity

mance is achieved over the catalyst with the highest ion-exchange degree impregnated with CsOH. The selectivity to *N*-methylaniline over this catalyst reaches 96.4%.

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