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"CATALYSIS: FUNDAMENTALS AND APPLICATIONS"

On the Equivalence of Acidic Centers in H-Beta Zeolites Tested by Fries Rearrangement of Phenyl Acetate[1]

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Abstract—The heterogeneously catalyzed liquid phase Fries rearrangement reaction of phenyl acetate was carried out on Beta zeolites reexchanged with different amounts of metal cations. The aim of this work was to determine the influence of the amount of Brønsted acid sites as the catalytic active centers on the conversion. Sodium and potassium ions as well as divalent calcium and zinc ions were used in the reexchange procedure. The conversion shows a linear dependency on the degree of ion reexchange following the theoretically expected values. So the results prove that the bridged hydroxyl groups are indeed the dominating active centers and that their strength seems to be independent of the degree of reexchange; consequently, their acidic strength should be identical. A special emphasis was placed on the reexchange with divalent metal ions. It was shown that one divalent ion is not able to replace two protons as is supposed to be necessary for the charge balance—so a 1 : 1 stoichiometry is needed to assume to explain the catalytic results.

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1. INTRODUCTION

The Fries rearrangement of phenyl acetate is an established reaction for the formation of hydroxyacetophenones [1], which are important intermediates in pharmaceutical and fine chemical industry processes [2–4]. Usually, in the heterogeneous catalyzed reaction, H-Beta zeolites are used as catalysts. Typical products of the conversion of phenyl acetate (PA) are phenol, *ortho*-hydroxyacetophenone (*o*-HAP), *para*-hydroxyacetophenone (*p*-HAP), and *para*-acetoxyacetophenone (*p*-AAP) [5–7]. Scheme 1 shows the proposed reaction pathway [6, 8, 9]. *o*-HAP can be formed via an *intra*molecular pathway, whereas in a parallel reaction, the acid catalyzed ester cleavage of phenyl acetate yields phenol and a surface bonded acylium ion is generated. The reaction of this species with phenol and PA results in the formation of *p*-HAP and *p*-AAP, respectively.

Even though this reaction is well understood, there are controversial discussions about the nature of the catalytic active centers. Although the bridging Si–OH–Al groups are supposed to have dominating influence on the conversion of phenyl acetate, their role in the reaction is not yet experimentally proven. Vogt et al. [10] investigated the conversion of phenyl acetate in the Fries reaction over HZSM-5 zeolites with different Si/Al-ratios. They found a strong dependence of the conversion and selectivity on the Si/Al ratio. With decreasing aluminum content in the framework, the conversion was drastically reduced. On the other hand, Harvey et al. [11] described only a slight change in the activity of H-Beta zeolites with different Si/Al ratios. Freese et al. [7] claimed the presence of Brønsted acidic centers as a prerequisite for the catalytic activity, while their investigations on the acylation of anisole over dealuminated Beta zeolites confirmed the results of Harvey et al. [11].

Gaare et al. [12] compared different sodium reexchanged Y- and Beta zeolites and their H-forms in the acylation reaction of anisole. While the sodium exchanged form was expected not to contain any active Brønsted centers, the yields of *p*-methoxyacetophenon over both zeolite forms were almost identical. The authors explained this by nonexchangeable active sites. Ion exchange of zeolite Beta with rare earth metal salts leads to an improvement of the activity in the Fries rearrangement of phenyl acetate. The modified catalysts have shown higher conversion and selectivity of the products and faster deactivation in comparison with the H-form. This effect was explained in terms of the formation of new Brønsted acidic sites on the external surface of the zeolite during calcination [12, 13].

The aim of this work was to study the influence of the bridging Si–OH–Al Brønsted centers on the Fries rearrangement reaction. If these sites are indeed involved in the reaction, then there should be a linear correlation between their number and the observed catalytic activity. In this paper we present the results of the influence of the degree of cation reexchange on the conversion. A special emphasis was placed on valency of

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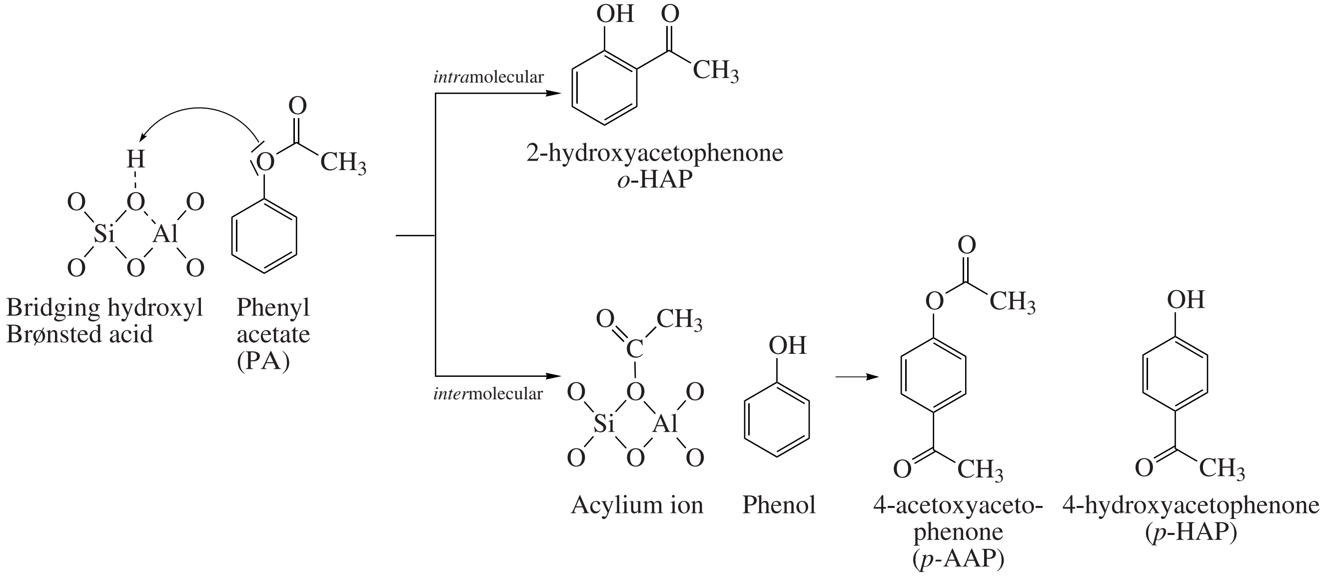
[1] This article was submitted by the authors in English.



Scheme 1. Products of the zeolitic catalyzed Fries rearrangement of phenyl acetate.

the extraframework cation. So, sodium, potassium, calcium, and zinc ions were used during the reexchange procedure of H-Beta zeolites.

2. EXPERIMENTAL

2.1. Cation Reexchange

The Fries rearrangement was studied using Beta zeolites with Si/Al ratios of 25 and 80.3 provided by Sued-Chemie AG, Munich. The zeolites were calcined and supplied in the H-form. The Si/Al$_{\mathrm{framework}}$ ratios of the zeolites were determined by ^{27}Al-MAS-NMR measurements. Catalysts reexchanged with sodium and potassium were prepared by liquid phase ion exchange, suspending the zeolite in an aqueous solution of stoichiometric amounts of alkali hydroxide and stirring for two hours at 353 K under nitrogen. Finally, the zeolite was filtrated, washed with water, and dried for 15 h at 773 K. Solid state ion exchange was performed by impregnation of the zeolite with stoichiometric amounts of either aqueous calcium nitrate or zinc chloride solution and subsequent calcination under nitrogen at 753 K for three hours.

2.2. Fries Rearrangement

The liquid phase Fries rearrangement was carried out in a soxhlet-based reaction set-up [14] with 2.0 g of fresh activated catalyst and 0.35 mol phenyl acetate. In the rearrangement reaction, the catalyst was used in fraction size of 200 to 315 µm. In nitrogen flow the catalyst was activated in a tubular oven for two hours at 623 K and transferred into the flask. The Fries rearrangement was performed in nitrogen atmosphere at ambient pressure without any solvent. The reaction time was six hours. Samples of about 150 µL were taken periodically and analyzed by gas chromatography to follow the reaction progress. Sample analysis was carried out on a PerkinElmer Autosystem gas chromatograph equipped with flame ionization detector and a 30 m HP-5 capillary column (0.25 µm 5%-phenylmethylpolysiloxane, 0.32 mm diameter). Conversion and selectivity are given in % and mol %, respectively, and were calculated on the basis of peak areas of the chromatogram considering the response factor of the individual compound.

2.3. Characterization

Temperature programmed desorption (TPD). Temperature programmed desorption of ammonia was used to determine the amount and strength of the acidic centers in the Beta zeolites. The measurements were carried out on a temperature programmed desorption unit by Raczek Analysentechnik equipped with a thermal conductivity detector. In a nitrogen flow, 0.5 g of the sample was heated up to 923 K with 20 K/min to remove the adsorbed water and then cooled down to 343 K. Ammonia was adsorbed at this temperature for 30 min using an ammonia–helium mixture (5% ammonia in helium). The physisorbed ammonia was removed by heating the sample to 423 K with 10 K/min and keeping the temperature constant for 15 h. The desorption of the remaining chemisorbed ammonia was recorded while increasing the temperature by 20 K/min up to 923 K to get the resulting TPD spectrum of the sample.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). DRIFT spectra were recorded with a Bruker Equinox 55 FTIR spectrometer equipped

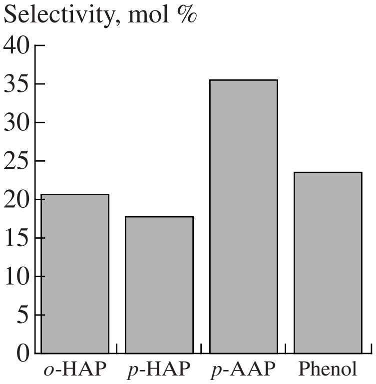


Fig. 1. Typical product distribution of the heterogeneously catalyzed Fries rearrangement of phenyl acetate on H-Beta zeolite (0% reexchanged; Si/Al = 25) after a reaction time of 6 h at 469 K at a maximum conversion of 33%.

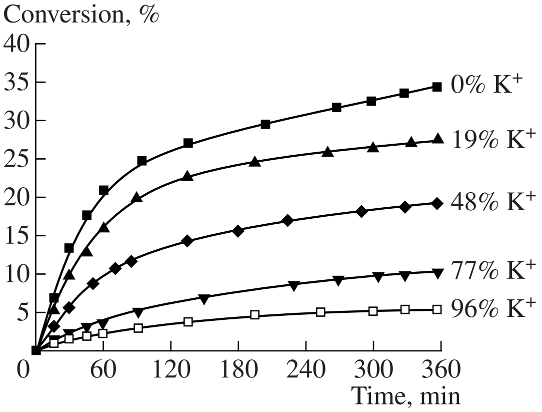


Fig. 2. Comparison of the activity-time-behavior in the Fries rearrangement of phenyl acetate at 469 K on zeolite H-Beta with different degree of reexchange with potassium ions.

with a Praying Mantis diffuse reflectance arrangement and a Harrick low pressure dome reaction chamber purged with nitrogen. All spectra were measured in the range between 550 and 7500 cm^{-1} with a resolution of 4 cm^{-1} using an MCT detector.

Spectra were measured by heating the sample up to 773 K in N$_2$-Flow with a rate of 10 K/min. During heat up a spectrum was taken every minute. After holding 773 K for 30 min, 1000 single spectra were taken and averaged to the sample. An averaged spectrum of 2000 scans of KBr measured at 773 K was used as the background spectrum. For transformation of the measured spectra, the program Opus version 3.1 was used.

X-ray fluorescence spectroscopy (XRF). X-ray fluorescence spectroscopy was used for elemental analyses of the calcium and zinc reexchanged Beta zeolites. For sample preparation 0.3 to 0.5 g of zeolite were mixed with 0.1 g ammonium nitrate and 3.0 g Spectromelt® A12 (33% Lithium meta borate, 67% di-lithium tetra borate; VWR GmbH) and then fused for 20 min at 1323 K in a Minifuse® (PANALYTICAL GmbH). Analysis was carried out in an X-ray fluorescence spectrometer PW 2404 (PANALYTICAL GmbH) with SEM-IQ-Software. The loss of mass during the glass making procedure was considered in the calculation assuming an oxide stoichiometry.

3. RESULTS AND DISCUSSION

In the Fries rearrangement reaction on H-Beta zeolites beside phenol *p*-acetoxyacetophenone, *o*- and *p*-hydroxyacetophenones are formed as the main products (Fig. 1). Furthermore, only traces of acetic acid were detected. According to Heitling et al. [15], *o*-hydroxyacetophenone is formed mainly via an intramolecular path, while *para*-substituted compounds are the result of an intermolecular pathway. Therefore, the *o*-/*p*-ratio of the products gives a hint about the preferred reaction pathway. For H-Beta zeolite the highest selectivities were found for *p*-acetoxyacetophenone with 35 mol % and phenol with 23 mol %. The reaction rate decreases rapidly during the reaction time of 60 min (Fig. 2). After 90 min the reaction rate is drastically retarded which can be explained in terms of product inhibition of the catalyst, as reported before [9].

3.1. *Catalysts Reexchanged with Alkali Metal Cations*

Figure 2 shows the conversion in dependence on the reaction time for H-Beta zeolites reexchanged with different amounts of potassium cations. The reaction is kinetically controlled; i.e, the decrease of the reaction rate is caused by catalyst deactivation. The activity is high in the initial period, and the conversion rate declines after 60 to 90 min. The degree of conversion decreases with increasing cation content. The reaction

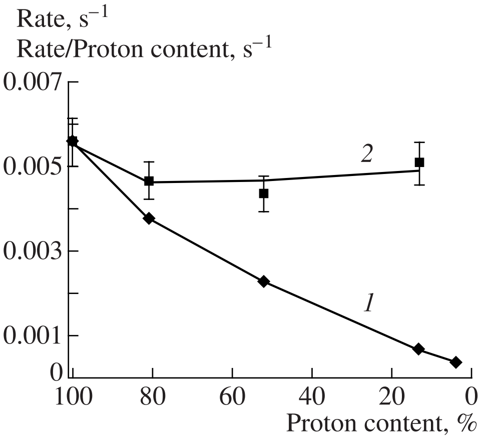


Fig. 3. Calculation of the reaction rate (*1*) and the specific rate (*2*) for the Fries rearrangement of phenyl acetate at 469 K on zeolite H-Beta with different degrees of reexchange with potassium ions.

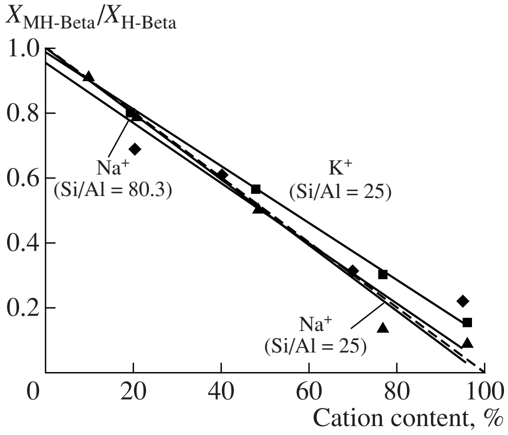


Fig. 4. Conversion of phenyl acetate on MH-Beta zeolites reexchanged with cations (M = Na^+, K^+), normalized to the conversion of the corresponding H-Beta, dependent on the degree of reexchange (t = 6 h; T = 469 K) in comparison to the theoretical value (dashed line).

rate was calculated for the initial 60 min assuming a first order reaction for the conversion of phenyl acetate. Figure 3 shows the rates for the reaction on zeolites reexchanged with potassium ions. It is clearly shown that the reaction rate decreases with decrease of the proton content. An approximate reaction rate constant of $k = 5 \times 10^{-5}$ min^{-1} (±10%), related to the number of remaining hydroxyl groups (specific rate), was calculated. These results suggest that all Brønsted sites should have an equal contribution to the overall catalytic activity.

After a reaction time of 6 h, the conversion on H-Beta (25) and H-Beta (80.3) was 34.2 and 29.3%, respectively. To compare the influence of the nature of the reexchanged cations, the conversion, normalized to the corresponding H-form, i.e., the ratio of conversion on MH-Beta (X_{MH}-Beta) to conversion on H-Beta (X_{H}-Beta) with the same Si/Al ratio, was plotted versus the cation content (Fig. 4). Both for MH-Beta (25) and for (80.3) the results show a linear dependency on the reexchange degree independent of the nature of the alkaline ion. Therefore, for a given Si/Al ratio the contribution of each Brønsted acidic site to the overall conversion is identical, which allows us to speculate that the acidic strength was also not affected by the change of the number of remaining hydroxyl groups. Otherwise, a deviation from the linearity should be observed.

The reexchange degree of cations, which is inverse to the number of remaining bridged Si–OH–Al groups, was calculated on the basis of the amount of tetrahedrally coordinated framework aluminum determined by ^{27}Al MAS NMR. It was assumed that each tetrahedrally coordinated framework aluminum creates a bridged Si–OH–Al group. For the sodium and potassium ion exchanged zeolites with Si/Al = 25, the decline of conversion follows the theoretically expected values corresponding to the number of remaining protonic centers in the zeolite (dashed line). The linearity of this dependency proves the hypothesis on equal specific activity of the Brønsted acidic sites in the Fries rearrangement. The deviation in case of the Beta zeolites with Si/Al = 80.3 could be explained by the low aluminum content, which made it difficult to determine the exact exchange degree.

Figure 5 shows the profile of the temperature programmed desorption of ammonia of different beta zeolites reexchanged with sodium ions. One main peak can be found at about 650 K. Hedge et al. [16] assigned this peak to desorption of ammonia molecules chemisorbed on Brønsted acid sites. With increasing cation content, the intensity of the peak decreases with reduction of adsorption centers. The shift to lower temperatures could be explained in terms of reduced readsorption and/or improved intracrystalline diffusivity of ammonia. At a reexchange degree higher than 48%, a new

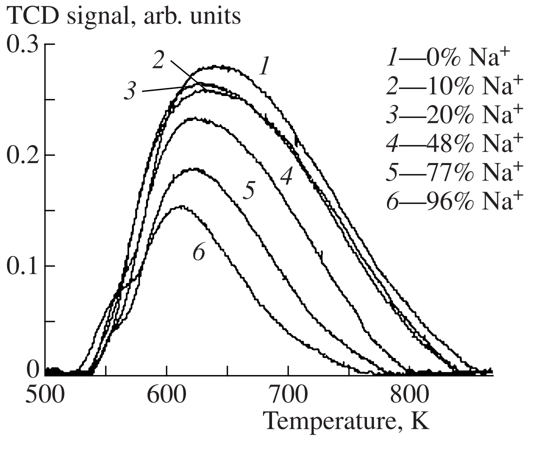


Fig. 5. Temperature programmed desorption of ammonia from H-Beta zeolites (Si/Al = 25) with different degrees of reexchange with sodium ions.

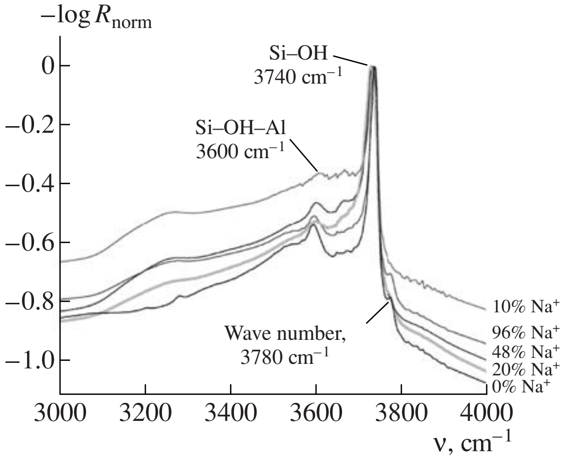


Fig. 6. DRIFT spectra of Beta zeolites reexchanged with sodium ions recorded at 773 K.

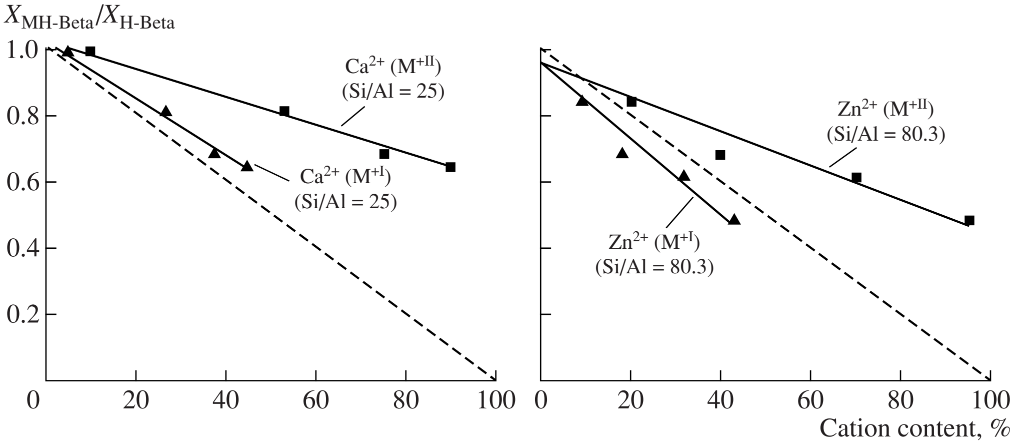


Fig. 7. Conversion of phenyl acetate on MH-Beta zeolites reexchanged with cations (M = Ca^{2+}, Zn^{2+}), normalized to the conversion of the corresponding H-Beta, dependent on the degree of reexchange (t = 6 h; T = 469 K). The dashed line shows the theoretical value. The cations are considered either as a divalent or a monovalent ion.

peak around 550 K can be clearly distinguished. This peak could be assigned to desorption from a newly formed weak Lewis acidic site, e.g., cations balancing the framework charge.

The DRIFT spectra verify the decrease of acidic centers due to the reexchange modification (Fig. 6). The peak at 3600 cm^{-1} can be assigned to the bridging Si–OH–Al groups. Its intensity declines with increasing cation content. Furthermore, for the H-Beta and the low reexchanged catalysts, a small peak at 3780 cm^{-1} can be observed. This can be assigned to hydroxyl groups on extraframework aluminum oxide. In the spectra of the higher reexchanged Beta, this peak disappeared. Consequently, ion exchange properties should be also attributed to this species, which can to a certain degree influence on the number of cations introduced on crystallographical ion exchangeable positions in the zeolite. Therefore, in the case of the highly reexchanged samples, the stoichiometric amount of supplied cations was insufficient to suppress the catalytic activity of all centers (Fig. 4), which is also supported by the ammonia desorption (Fig. 5).

3.2. Catalysts Reexchanged with Divalent Metal Cations

In the case of H-Beta zeolites reexchanged with calcium or zinc ions, the obtained conversions are higher than expected (Fig. 7). For modification by ion exchange, it was assumed that one divalent calcium ion should replace two protons. Assuming a statistical distribution of aluminum in the zeolite, even the zeolite with Si/Al = 25 contains only one active bridging Si–Al–OH group in every second twelve-ring. So, it seems to be impossible from the steric point of view that a divalent ion can replace two protons. When a 1 : 1 stoichiometry is assumed instead, the results fit to the theoretically expected values. This assumption is also confirmed by the value of the *o*-/*p*-ratio of the reaction products (Fig. 8). In the reaction of the sodium and potassium ion reexchanged Beta zeolites, this ratio is nearly constant at a value of 0.4 until the exchange degree exceeds 40%. Catalysts with more than 40% of cation reexchange produce more o-hydroxyacetophenone, which indicates a change in the preferred reaction pathway from an inter- to an intramolecular reaction (Fig. 1). In the case of a modification with calcium ions, no change in this *o*-/*p*-ratio was found. This behavior is typical for the Na^+ and K^+ re-exchanged zeolites with an ion exchange degree lower than 50%; i.e., only 50% of the aluminum centers are compensated by Ca ions. Since the supplied amount of Ca ions was calculated for a 100% exchange (charge compensation), this effect can be explained in two different terms:

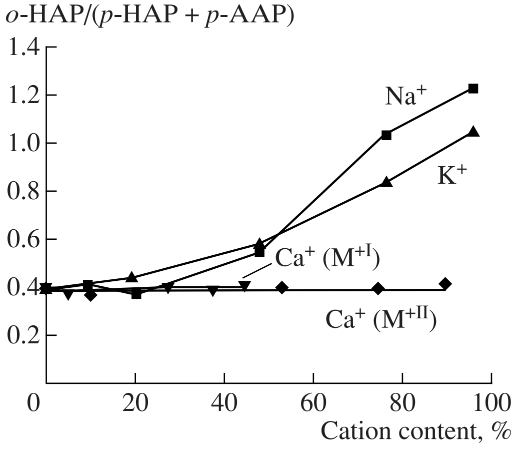


Fig. 8. The *o*-/*p*-ratio of the products as a function of the degree of cations in MH-Beta zeolite (Si/Al = 25) reexchanged with Na^+, K^+, and Ca^{2+} after a reaction time of t = 6 h.

$$\underset{\substack{\text{metal}\\ \text{cation}}}{2[\mathrm{M(H_2O)}]^{z+}} + \underset{\substack{\text{zeolitic}\\ \text{framework}}}{4\mathrm{OZ}^-} \rightleftharpoons \underset{\substack{\text{hydroxo}\\ \text{cation}}}{2[\mathrm{M(OH)}]^{(z-1)+}} + \underset{\substack{\text{bridging}\\ \text{hydroxyl}\\ \text{Brønsted}\\ \text{acid}}}{2\mathrm{H{-}OZ}} + 2\mathrm{OZ}^- \rightleftharpoons [\mathrm{M{-}O{-}M}]^{2(z-1)+} + \mathrm{H_2O} + 2\mathrm{H{-}OZ} + 2\mathrm{OZ}^-$$

Scheme 2. Compensation of the excess charge in the zeolite reexchanged with divalent cations by condensation of hydroxo cations accompanied with the formation of multinuclear metal-oxygen species.

(i) One divalent cation compensates only one framework charge. Therefore, a question about the compensation of the excess charge arises. The discussion in terms of condensation of hydroxo cations, as observed for Y zeolites, accompanied with the formation of bridged cation-oxygen-species seems to be a suitable explanation (Scheme 2). Kazansky [17] investigated the localization of divalent metal ions in high silica zeolites by DRIFT measurements. In zeolites with a high aluminum content, these ions are localized at the next two nearest negatively charged aluminum tetrahedra. In contrast, in high silica zeolites the divalent cations are located at single charged framework sites. The arising excess charge is compensated indirectly by electrostatic interaction with the surrounding divalent cations.

(ii) The divalent cation compensates two framework charges. Then, half of the amount of supplied divalent cations was removed during the washing procedure. To exclude this possibility, the sample was washed three times with deionized water and the cation content was determined by XRF measurements. The results are given in the table. They show that the 1/2 $M^{2+}/Al_{tetrahedral}$ ratio is indeed higher than 0.5 for the higher reexchanged zeolites. That means that all the supplied metal ions are introduced in the catalysts and remain in the zeolite after the modification treatment, which should result in a lower catalytic activity.

4. CONCLUSIONS

The results show that bridged hydroxyl groups are entirely responsible for the conversion of phenyl acetate. The conversion depends linearly on the degree of proton reexchange, thus on the number of the remaining Brønsted acidic centers. This relationship does not depend on the Si/Al ratio of H-Beta zeolite. Therefore, there is no necessity to involve nonframework alumina, which is usually related to the Lewis acidity, into the discussion on the catalytic activity. NH_3-TPD and DRIFT measurements confirm the reduction of Brønsted acidic sites after the modification process, while the composition of the catalysts was verified by XRF analyses.

Furthermore, it was shown that Brønsted sites have an equal specific activity. In the case of divalent ion reexchange, it was shown that a 1 : 1 stoichiometry has to be assumed, in which the compensation of the excess charge could be discussed in terms of condensation of hydroxo cations and the formation of cation-oxygen species.

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Si/Al ratios determined by ^{27}Al MAS NMR and XRF and cation contents of zeolite Beta reexchanged with Ca^{2+} and Zn^{2+} determined by XRF

Sample	Si/Al_{NMR}	Si/Al_{XRF}	$M^{2+}/Al_{tetrahedral}$	Cation content, %
CaH-Beta 10% Ca^{2+}	25	22.4	0.12	12
CaH-Beta 53% Ca^{2+}	25	22.8	0.50	50
CaH-Beta 75% Ca^{2+}	25	22.2	0.70	70
CaH-Beta 90% Ca^{2+}	25	22.3	0.74	74
ZnH-Beta 20% Zn^{2+}	80.3	72.9	0.38	38
ZnH-Beta 40% Zn^{2+}	80.3	70.6	0.66	66
ZnH-Beta 70% Zn^{2+}	80.3	75.8	1.01	101
ZnH-Beta 95% Zn^{2+}	80.3	69.5	1.08	108

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