Activity of H-Beta Zeolites Re-Exchanged with Alkaline and Earth-Alkaline Cations in the Fries Rearrangement of Phenyl Acetate

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Received on May 21, 2007 Accepted on Dec. 16, 2007

Abstract
The heterogeneously catalysed liquid phase Fries rearrangement reaction of phenyl acetate was carried out on Beta zeolites re-exchanged 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 centres on the conversion and to study differences in their acidic strength. Sodium and potassium ions as well as bivalent calcium and zinc ions were used in the re-exchange procedure. The conversion shows a linear dependency on the degree of ion re-exchange following the theoretically expected values. So the results prove that the bridged hydroxyl groups are indeed the dominating active centres and that their strength seems to be independent on the degree of re-exchange. A special emphasis was placed on the re-exchange with bivalent metal ions. It was shown that one bivalent ion is not able to replace two protons as supposed to be necessary for the charge balance - so a 1:1 stoichiometry is needed to assume to explain the catalytic results.

Keywords: Zeolite; Beta; Cation re-exchange; Phenyl acetate; Fries rearrangement.

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, 3, 4]. Usually, in the heterogeneous catalysed 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, 6, 7]. Scheme 1 shows the proposed reaction pathway [6, 8, 9]. o-HAP can be formed via an intramolecular pathway whereas in a parallel reaction, the acid catalysed 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.

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Scheme 1: Products of the zeolitic catalysed Fries rearrangement of phenyl acetate.

Even though this reaction is well understood, there are controversial discussions about the nature of the catalytic active centres. 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. investigated the conversion of phenyl acetate in the Fries reaction over H-ZSM-5 zeolites with different Si/Al-ratios. They found a strong dependence of the conversion and selectivity on the Si/Al ratio. With decreasing aluminium content in the framework the conversion was drastically reduced. On the other hand, Harvey et al. described only a slight change in the activity of H-Beta zeolites with different Si/Al ratios. Roessner and co-workers claimed the presence of Brönsted acidic centres 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.

Gaare et al. compared different sodium re-exchanged 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 Brönsted acidic centres the yields of acetyl chloride over both zeolite forms were almost identical. The authors explained this by a catalytic active species which is resistant to the modification procedure. Ion exchange of zeolite Beta with rare earth metal oxides 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 Brönsted acidic sites on the external surface of the zeolite during impregnation.

The aim of this work was to study the influence of the bridging Si-OH-Al Brönsted acidic centres 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 re-exchange on the conversion. A special emphasis was placed on valency of the extra-framework cation. So, sodium, potassium, calcium and zinc...
ions were used during the re-exchange procedure of H-Beta zeolites.

**Experimental**

*Cation re-exchange*

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 ratios of the zeolites were determined by $^{27}\text{Al-MAS-NMR}$ measurements. Catalysts re-exchanged with sodium and potassium were prepared by liquid phase ion exchange, suspending the zeolite in aqueous solution of stoichiometric amounts of alkali hydroxide and stirring for two hours at 353 K under nitrogen. Finally, the zeolite was filtered washed with water and dried for 15 hours at 773 K. Solid state ion exchange was performed either by impregnating the zeolite with stoichiometric amounts of aqueous calcium nitrate or zinc chloride solution and subsequent calcination under nitrogen at 753 K for three hours.

*Fries rearrangement*

The liquid phase Fries rearrangement was carried out in a soxhlet-based reaction set-up $^{14}$ with 2 g of fresh activated catalyst and 0.35 mole phenyl acetate. In the rearrangement reaction the catalyst was used in fraction size of 200 to 315 µm. The catalyst was activated under nitrogen atmosphere in a tubular oven for two hours at 623 K and transferred into the flask. The Fries rearrangement was performed under nitrogen atmosphere at ambient pressure without any solvent. The reaction time was six hours. Samples of about 150 µL were taken periodically and analysed by gas chromatography to follow the reaction progress. Sample analysis was carried out on a Perkin Elmer Autosystem gas chromatograph equipped with flame ionisation detector and a 30 m HP-5 capillary column (0.25 µm 5%-phenyl-methylpolysiloxane, 0.32 mm diameter).

*Characterisation*

*Temperature programmed desorption (TPD)*

Temperature programmed desorption of ammonia was used to determine the amount and strength of the acidic centres in the Beta zeolites. The measurements were carried out on a temperature programmed desorption unit by Raczek Analysentechnik (http://www.latonline.de/) equipped with a thermal conductivity detector. 0.5 g of sample was heated up in a nitrogen flow 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 kept 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 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 a MCT (mercury-cadmium-telluride) detector.

Spectra were measured by heating the sample up to 773 K in N\(_2\)-flow with a heating rate of 10 K/min. During heat up a spectrum was taken every minute. After holding 773 K for 30 minutes 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 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 re-exchanged 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\textsuperscript{®} A12 (33% Lithium meta borate, 67% di-lithium tetra borate; VWR GmbH) and then fused for 20 minutes at 1323 K in a Minifuse\textsuperscript{®} (PANALYTICAL GmbH). Analysis was carried out in an X-ray fluorescence spectrometer PW 2404 (PANALYTICAL GmbH) with SEM-IQ\textsuperscript{©}-Software. The loss of mass during the glass making procedure was considered in the calculation assuming an oxide stoichiometry.

**Results and Discussion**

In the Fries rearrangement reaction on H-Beta zeolites beside phenol \(p\)-acetoxyacetophenone, \(o\)- and \(p\)-hydroxyacetophenones are formed as main products (figure 1). Furthermore, only traces of acetic acid were detected. According to Ismail, \cite{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 give 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 minutes (figure 2). After 90 minutes the reaction rate is drastically retarded what can be explained in terms of product inhibition of the catalyst \cite{9}. Therefore, the conversion after six hours was used to compare the activity of different H-Beta zeolites.
Figure 1: Conversion and product spectrum of the heterogeneously catalysed Fries rearrangement of phenyl acetate over H-Beta zeolites after a reaction time of 6 h at 469 K.

Catalysts re-exchanged with alkali metal cations

Figure 2 shows the conversion in dependence on the reaction time for H-Beta zeolites re-exchanged with different amounts of potassium cations. All graphs have the typical form for the Fries rearrangement reaction with a high activity in the initial period and a decline of conversion after 60 to 90 minutes. The maximum conversion decreases with increasing cation content.

Figure 2: Comparison of the conversion of phenyl acetate in the Fries rearrangement at 469 K on zeolite H-Beta with different degree of re-exchange.
The comparison of the conversion after 6 h with the degree of cation re-exchange is given in figure 3. The re-exchange 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 aluminium determined by $^{27}$Al MAS NMR. It was assumed that each tetrahedrally coordinated framework aluminium 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 centres in the zeolite (dashed line). The linearity of this dependency proofs the hypothesis on equal specific activity of the Brönsted 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 aluminium content which made it difficult to determine the exact exchange degree.

![Graph](image)

**Figure 3:** Conversion of the Fries rearrangement of phenyl acetate over Beta zeolites dependent on degree of protons re-exchanged with Na$^+$ (♦ Si/Al = 80.3, ▲ Si/Al = 25) and K$^+$ (■ Si/Al = 25) depended on the degree of re-exchange in comparison to the theoretically expected values (dashed line); (t = 6 h; T = 469 K).

Figure 4 shows the profile of the temperature programmed desorption of ammonia of different beta zeolites re-exchanged with sodium ions. One main peak can be found at about 650 K. Hedge et al.\textsuperscript{[16]} assigned this peak to desorption of ammonia molecules chemisorbed on Brönsted acidic 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 reducing re-adsorption and/or improved intracrystalline diffusivity of ammonia. At a re-exchange degree higher than 48 % a shoulder around 550 K can be clearly distinguished. This peak may be assigned to desorption from a newly formed weak Lewis acidic site, e.g. cations on bridged Si-Al-O$^-$-groups.
Figure 4: Thermo programmed desorption of ammonia from Beta zeolites with different degree of re-exchange with sodium (TCD – thermo conductivity detector).

The DRIFT spectra verify the decrease of acidic centres due to the re-exchange modification (figure 5). 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 re-exchanged catalysts a small peak at 3780 cm\(^{-1}\) can be found. This can be assigned to hydroxyl groups on extra-framework of aluminium oxide. This peak disappeared in the spectra of the higher re-exchanged Beta. 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 case of the highly re-exchanged samples the stoichiometric amount of supplied cations was insufficient to suppress the catalytic activity of all centres (figure 3) which is also supported by the ammonia desorption (figure 4).
Catalysts re-exchanged with bivalent metal cations

In case of H-Beta zeolites re-exchanged with calcium or zinc ions the obtained conversions are higher than expected (figure 6). For modification it was assumed that one bivalent calcium ion should replace two protons. Assuming a statistical distribution of aluminium 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 bivalent 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 (figure 7). In the reaction of the sodium and potassium ion re-exchanged Beta zeolites this ratio is nearly constant at a value of 0.4 until the exchange degree exceed 40%. Catalysts with more than 40% of cation re-exchange produce more \( o- \)-hydroxyacetophenone, which indicates a change in the preferred reaction pathway from an inter- to an intra molecular reaction (figure 1). In case of a modification with calcium ions no change in this \( o-/p- \)-ratio was found. This behaviour is typically for the \( Na^+ \) and \( K^+ \) re-exchanged zeolites with an ion exchange degree lower than 50%, i.e. only 50% of the aluminium centres 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:

(i) One bivalent 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 \cite{17} investigated the localisation of bivalent metal ions in high silica zeolites by DRIFT measurements. In zeolites with high aluminium content these ions are localised at two next nearest negatively charged aluminium tetrahedra. In contrast in high silica zeolites the bivalent cations are located at single charged framework sites. The arising excess charge is compensated indirectly by electrostatic interaction with the surrounding bivalent cations.

\[
2 \text{[M(H}_2\text{O)}]}^{2+} + 4 \text{OZ}^- \rightarrow 2 \text{[M(OH)}]^3+ + 2 \text{H-OZ} + 2 \text{OZ}^- \rightarrow [M-O-M]^{2n-1}^+ + \text{H}_2\text{O} + 2 \text{H-OZ} + 2 \text{OZ}^-.
\]

**Scheme 2**: Compensation of the excess charge in the re-exchange against bivalent cations by condensation of hydroxo cations accompanied with the formation of metal-oxygen species.

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

**Table 1**: Si/Al ratios and cation contents of different Beta zeolites re-exchanged with Ca\(^{2+}\) and Zn\(^{2+}\), three times washed with de-ionized water, determined by XRF.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al theoretical</th>
<th>Si/Al experimental</th>
<th>% M(^{2+})/Al(_{tetrahedral}^*)</th>
<th>Cation content* / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaH-Beta 10% Ca(^{2+})</td>
<td>25</td>
<td>22.4</td>
<td>0.12</td>
<td>12</td>
</tr>
<tr>
<td>CaH-Beta 53% Ca(^{2+})</td>
<td>25</td>
<td>22.8</td>
<td>0.50</td>
<td>50</td>
</tr>
<tr>
<td>CaH-Beta 75% Ca(^{2+})</td>
<td>25</td>
<td>22.2</td>
<td>0.70</td>
<td>70</td>
</tr>
<tr>
<td>CaH-Beta 90% Ca(^{2+})</td>
<td>25</td>
<td>22.3</td>
<td>0.74</td>
<td>74</td>
</tr>
<tr>
<td>ZnH-Beta 20% Zn(^{2+})</td>
<td>80.3</td>
<td>72.9</td>
<td>0.38</td>
<td>38</td>
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<tr>
<td>ZnH-Beta 40% Zn(^{2+})</td>
<td>80.3</td>
<td>70.6</td>
<td>0.66</td>
<td>66</td>
</tr>
<tr>
<td>ZnH-Beta 70% Zn(^{2+})</td>
<td>80.3</td>
<td>75.8</td>
<td>1.01</td>
<td>101</td>
</tr>
<tr>
<td>ZnH-Beta 95% Zn(^{2+})</td>
<td>80.3</td>
<td>69.5</td>
<td>1.08</td>
<td>108</td>
</tr>
</tbody>
</table>

* Values higher than 1.0 and 100%, respectively, indicate on a non-stoichiometric excess.
Figure 6: Conversion of the Fries rearrangement of phenyl acetate over Beta zeolites dependent on degree of protons re-exchanged with Ca$^{2+}$ and Zn$^{2+}$ ions either as a bivalent or a monovalent ion. The dashed line shows the theoretically expected behaviour.

Figure 7: The o-/p-ratio of the products dependent on degree of protons re-exchanged in Beta zeolite (Si/Al = 25) by cations Na$^+$, K$^+$ and Ca$^{2+}$. Calculation based on the composition of the unit cell.

Conclusion

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 re-exchange, thus on the number of the remaining Brönsted acidic centres. NH$_3$-TPD and DRIFT measurements confirm the reduction of acidic sites after the modification process, while the composition of the catalysts were verified by XRF analyses.

Furthermore, it was shown that Brönsted acidic sites have an equal specific activity. In case of bivalent ion re-exchange 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 a formation of cation-oxygen species.

Acknowledgement

R. Ismail greatly acknowledge the German Academic Exchange Service (DAAD) for the travel grant. The authors thank Dr. H. Toufar (Tricat GmbH) for providing the XRF analyses and to Dr. Y. Meteleva for measuring the DRIFT spectra.
References