

Is the zeolite-catalyzed amination of styrenes possible?

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Abstract

The direct amination of olefins is an elegant and environmentally benign procedure to form amines as could be nicely demonstrated in the BASF *tert*-butylamine process. Therefore, it was of great interest to synthesize the valuable intermediate 1-phenyl-ethylamine according to that method. The conversion of styrene to the desired amine is feasible, but strongly limited by the thermodynamic equilibrium. Furthermore, the strong tendency of styrene to polymerize hinders a smooth reaction to 1-phenyl-ethylamine. The reaction was carried out in the presence of weakly acidic zeolites such as H-B-MFI and H-B-BEA under various reaction conditions. Due to the results, the direct amination of styrene seems to be not possible with high yields whereas the nucleophilic substitution of the 1-phenylethanol with ammonia yields the desired amine. Such investigations have been also transferred to other styrene derivatives. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Amines are important products of the chemical industry. They are used as precursors for a wide range of commercially useful products. There are several approaches for the production of these valuable intermediates, e.g., nucleophilic substitution, the reductive amination, the hydrogenation of nitriles or the direct amination of olefins [1–12]. The industrial importance demands catalytic routes by reducing the reaction temperature and the reaction pressure to realize the amination reaction. The amination of alkenes

provide a more direct route to the desired products. Therefore, the application of several catalysts was examined, e.g., the transition metal and the enzyme-catalyzed reaction [3,13–15].

A very effective group of catalysts is the well-defined three-dimensional and crystalline zeolites, which are applied in several organic reactions in the field of bulk chemicals to the preparation of fine chemicals [4,5,10–12,16–18]. The direct amination of alkenes using zeolites, as in the case of the BASF *tert*-butylamine process, provides several advantages in comparison to the conventional route, e.g., the Ritter reaction: the possibility of an easy separation from the product mixture, the avoidance of corrosion by highly concentrated H₂SO₄, of high salt formation and the use of toxic compounds such as HCN and the elimination of high energy

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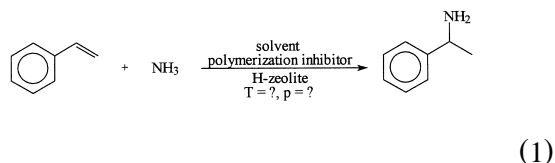
costs caused by the three-step procedure [12]. Therefore, the BASF process is a very elegant and environmentally benign technology.

The amination of ethene requires temperatures of 320–380°C and a pressure of 55 bar. For this amination, H-erionite and H-clinoptilolite were used effectively with a conversion of 10% and a selectivity of 95% [4,5,16,19,20]. The amination of propene is done at a somewhat lower temperature of 300°C and at a similar pressure [4,5,16,21]. A H-Y-zeolite showed a conversion of 2% and a selectivity to the monoamine of 93%. In comparison, a H-ZSM-5 is used at a temperature of 350°C and a pressure 295 bar with the result of 10% conversion and a selectivity of 97% [22]. Isobutene reacts with ammonia at a temperature of 220°C over a H-Y-zeolite with a conversion of 1% and at a temperature of 280°C with a conversion of 9% and a selectivity to *tert*-butylamine of 99% [4,5,16,23]. Also, H-mordenite ($T = 260^\circ\text{C}$, conversion = 6%) and H-ZSM-5 ($T = 200^\circ\text{C}$, conversion = 13%, selectivity = 99%) were used [24].

More recently, zeolites were tested, in which the alumina was substituted with boron [24–26]. It is also favourable to dope the zeolites by metal cations, e.g., a Cr-doped H-B-ZSM-5 catalyzed the amination of *i*-butene at a temperature of 300°C with a pressure of 300 bar, resulting in a conversion of up to 15% and a selectivity of 98% [25]. Furthermore, a H-B-BEA zeolite gave good 24% yields for the amination of *i*-butene at a temperature of 260°C and a pressure of 280 bar [26]. BASF has commercialized its *tert*-butylamine process [27].

Based on the data above, the following order of reactivity of the olefins to the zeolite-induced amination was: isobutene > propene > ethene [4,5,10–12,16]. In all mentioned reactions, the products were functionalized in the Markovnikov position, due to the reaction mechanism involving adsorption of the alkene on the zeolite surface and the formation of a carbocation intermediate, which could be attacked by ammonia or an ammonium ion.

There are several chemical methods for the direct functionalization of styrene to produce the phenylethylamines, e.g., the hydroboration–amination [28,29] or the treatment with alkali amides [30]. In both methods, the alkene is aminated in satisfactory yields, but toxic and hazardous materials were used, which makes those processes unattractive for an industrial application. In quite a number of the described patents, the amination of styrene is mentioned or claimed, respectively, but neither the reaction conditions nor experimental results were presented. Our aim was to prove whether the addition of ammonia to styrene is possible or not by the use of zeolite catalysts following the reaction path according to Eq. 1.



2. Experimental

2.1. Preparation of zeolite materials

The B-BEA zeolite (sample A) was prepared according to the method of de Ruiter et al. [31]. A mixture of 183.64 g H₂O, 3.48 g B(OH)₃, 1.43 g NaOH, 26.58 g silica FK-700 of Degussa and 27.20 g of 40 wt.% TEAOH was stirred for 24 h. Then 31.90 g of TEABr was added and stirred for 5 h. The mixture was heated at 150°C at autogenous pressure for 240 h. The resulting crystals were washed and dried.

For the preparation of the silicalite (sample B), 140 g of a 40% solution of TPAOH was diluted in 420 g of water and added to 250 g TEOS by stirring the mixture. Then 535 g ethanol was added and the mixture was treated in an autoclave at 105°C for 5 days. The resulting solid was calcined at 550°C for 5 h.

The other zeolites have been kindly provided by companies, as shown in Table 1.

Table 1
Zeolites used

Sample	Type	Ion form	Trade name	Source	Si/T ^a	BET [m ² /g]
A	BEA	H	–	–	13	440
B	MFI	H	–	–	∞	–
C	MFI	H	–	BASF	17	359
D	BEA	H	Valfor CP-811	PQ	8	–
E	MOR	H (Na) ^b	CP 561-13S	PQ	8	–
F	FAU	H	Valfor CBV Super	PQ	3	493
G	FER	H	HSZ-720 NH4	TOSOH	7	–
H	MFI	H (Na) ^b	B-ZSM-5	Degussa	81	–
I	MFI	H (Na) ^b	B-ZSM-5	Degussa	123	–

^aMolar Si/Al or Si/B ratio.

^bDelivered in the sodium ion form and before application, ion-exchanged for three times with a 0.1 M NH₄OH solution and then calcined at 550°C.

Some of the used zeolites were produced in the sodium ion form and then ion exchanged by following procedure: 100 ml of a 0.1 M aqueous ammonium nitrate solution and 10 g of the solid sample were stirred at room temperature for 24 h. Then the solid is filtered, washed with distilled water and then calcined.

The zeolites were calcined before use by the following procedure I: the sample was dried for 12 h at 120°C, heated up within 6 h to 500°C or 550°C, calcined at this temperature for 12 h, and then cooled down to room temperature. All steps were done under air and most of the boron in the B-MFI and B-BEA removed out of the lattice.

Calcination by procedure II guaranteed that the boron was kept in the zeolite framework: the sample was calcined under an ammonia atmosphere at 450°C and then ion-exchanged for three times with 100 g of 1.0 M NaBr solution. The resulting Na-B-zeolite was calcined under an oxygen atmosphere at 550°C, ion-exchanged for three times with 100 g of 1.0 M NH₄OH solution and then calcined at 450°C under air.

2.2. Experiments in the autoclave: general procedure

The experiments were carried out in an autoclave with a reaction volume of 75 ml. The

starting materials were separately given in the reactor: first the zeolite (1.00 g), then the solvent (7.50 g) and the polymerization inhibitor (0.07 g) and afterwards styrene (7.50 g). The solvent and styrene were kept under argon and the reaction was carried out under oxygen-free conditions. After that, a certain amount of ammonia was weighed in and in some experiments, high-pressure nitrogen was added into the reactor. The reaction was stopped after a certain time by a rapid cool down by using a stream of compressed air. The autoclave was opened at room temperature and the reaction mixture was filtered from the zeolite. The solid products and the fluid phase were analyzed by gas chromatography after adding 4-methylanisol as an internal standard.

3. Results and discussion

At the beginning of the investigations, three main difficulties had to be faced. If the reaction is initiated by the use of an acidic zeolite as inferred in the patents, the thermodynamics of styrene amination should be determined and the adsorption of ammonia at the zeolite surface has to be discussed. Furthermore, the high polymerization tendency of styrene could lead to a decrease in selectivity.

3.1. Thermodynamic calculation

To estimate if the direct amination of styrene is possible or what yield could be expected, the thermodynamics were calculated. Literature provided the parameters for the starting materials [32–35], but no data on the products. Thus, we calculated the whole process using the Benson method. This method assumed that all compounds are in the ideal gas phase, which does not correspond with the real reaction conditions, e.g., ammonia in the supercritical phase. Due to that, the calculation possesses a certain inaccuracy which cannot be quantified.

The result of the calculation is that the free enthalpy of reaction (1) is positive for a temperature higher than 25°C; thus, the production of 1-phenylethylamine is unfavorable. Fig. 1 gives an example of the calculation and shows the calculated conversion of styrene at different pressures and different ammonia/styrene ratios at a temperature of 175°C. An increase of the reaction pressure and an increase of the molar excess of ammonia to styrene resulted in an increase of the conversion, but only to 0.07% for the calculated temperature. If this temperature is reduced to 25°C, the conversion is increased to 2%.

The calculation shows that the conversion of styrene to phenylethylamine is feasible, but strongly limited by the thermodynamic equilibrium. The calculation follows the principle of Le Chatelier, and the amination is favored by low temperatures, high pressures and a high ammonia/styrene ratio. However, a high reac-

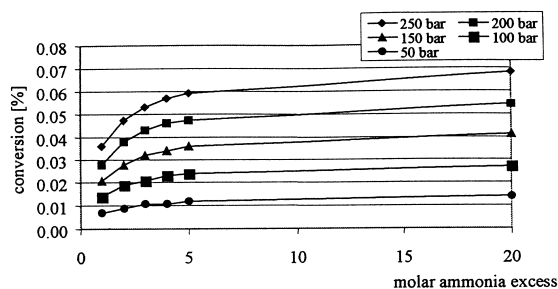


Fig. 1. Thermodynamic calculations for the amination of styrene.

tion temperature is required to activate the olefinic double bond of the styrene molecule, due to the kinetically hindered reaction [12].

3.2. Ammonia adsorption at the zeolite acid sites

The first step in the reaction mechanism is the adsorption and the formation of a carbocation of styrene at the acid sites of the zeolite. If ammonia is added to this intermediate, 1-phenylethylamine is produced. Ammonia is a moderate base and can also adsorb on the acid sites of the zeolite. As a result, the active sites are blocked and the initial step — the formation of carbocation and the amination of styrene — cannot proceed. Therefore, it is necessary that ammonia is desorbed from the acid sites which is favoured at high temperatures and low pressures. Unfortunately, these reaction parameters are in contradiction to the described thermodynamics of the amination reaction [12].

Based on these statements, the demand on the zeolite is to possess many weak acid sites, which desorb ammonia at low temperatures. Therefore, one of the targets of this work was to get a suitable zeolite, which is capable to activate the styrene molecule, but does not form a strongly bounded NH_4^+ ion. It is known that the substitution of alumina through boron in the zeolite framework leads to a decrease in the acidic strength. A connection between the equilibrium of the hydrogen and the ammonium ion form at the zeolite acid sites is given by the help of the temperature-programmed desorption (TPD) of ammonia. As shown in Fig. 2, the TPD spectra of zeolites with different structures were measured. The boron containing MFI type zeolite (sample C) showed a desorption maxima of approximately 200°C. All of the alumina-containing zeolites, such as H-BEA (sample D), H-MOR (sample E), H-Y (sample F) and H-FER (sample G), have higher desorption maximums between 220°C and 280°C. The conclusion of these measurements is that the B-MFI (sample C)-type zeolite has acid sites with lower acidic

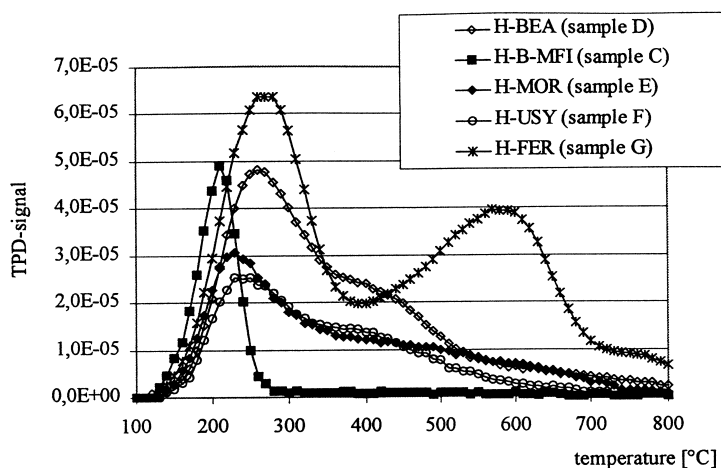


Fig. 2. TPD of several zeolites.

strength compared to the Al-containing samples; thus, the B-MFI zeolite is a good candidate to be tested in the amination of styrene.

3.3. The polymerization of styrene

The third and main difficulty of this project was the handling of styrene and the high polymerization tendency of this alkene which was first observed in 1839 [36]. This reaction limits the selectivity of the process and deactivates the zeolite catalyst.

There are several publications concerning the dimerization, oligomerization and polymerization of styrene [37–45]. An important parameter for avoiding the polymerization is the ceiling temperature at which no polymer is formed. This is 310°C in the case of styrene [45,46]. The polymerization of styrene causes a decrease of the volume and the enthalpy. Due to this, the polymerization is favoured at high pressure and low temperature. These are exactly the same demands for a successful amination reaction. A possibility for avoiding or reducing the polymerization is the addition of a polymerization inhibitor [47–53]. A very effective inhibitor is the combination of nitrophenols, e.g., a mixture of 2,4-dinitrophenol and 2,6-dinitrophenol [54,55].

How can the polymerization of styrene be reduced at a reaction temperature, which is necessary to perform the amination of styrene? To answer this question, several experiments were done. For this, a 100-ml reaction flask fitted with a reflux condenser was used. The reaction mixture [7.50 g styrene, 7.50 g solvent, 0.07 g inhibitor and 1.00 g of the boron MFI type zeolite (sample C)] was stirred by the use of a magnetic stirrer in an inert atmosphere. The influence of several polymerization inhibitors and solvents was determined by measuring the conversion of styrene under several conditions. Furthermore, the reaction temperature was varied, but all runs were done at atmospheric pressure.

Without the addition of a solvent or an inhibitor, it took 90 min to polymerize styrene at a temperature of 150°C and only 55 min after the addition of the B-MFI-type zeolite. Several polymerization inhibitors were tested. Even though 2,6-dinitrophenol showed the best inhibitor properties, the polymerization could not be avoided at temperatures higher than 150°C. Therefore, different solvents were tested for the styrene polymerization [56]. The results indicated that CHCl_3 and toluene were the best solvents for avoiding polymerization. As shown in Table 2, the combination of the inhibitor,

Table 2
Influence of the solvent to the polymerization of styrene

Solvent	Conversion [%]
Chloroform	< 1.0
Toluene	< 1.0
1,1,1-Trichlorethane	1.6
Benzene	3.3
<i>p</i> -Chlortoluene	3.8
<i>m</i> -Xylene	4.2
Chlorbenzene	5.4
Ethylbenzene	6.2
<i>tert</i> -Butylbenzene	21.3
Mesitylene	22.1
Decahydronaphthalene	24.0
1,2,3,4-Tetrahydronaphthalene	28.1
Propylbenzene	30.7
Butylbenzene	31.9
Diphenylmethane	> 99.0
Dichlormethane	> 99.0

2,6-dinitrophenol, and the solvent resulted in a low conversion of styrene of 1% at 150°C for a reaction time of 15 h. Furthermore 1,1,1-trichlorethane diminished the conversion of styrene to 1.6% and benzene to 3.3%. The solvent, *p*-chlorotoluene, reduced the conversion to 3.8%, *m*-xylene to 4.2%, chlorbenzene to 5.4% and ethylbenzene to 6.2%. All those solvents showed good qualities for the amination reaction. The other materials were not able to reduce the polymerization to a conversion of styrene below 10% and are unsuitable for a practical use.

In Fig. 3, the effect of the combination of 2,6-dinitrophenol and toluene in the polymerization of styrene is shown. As mentioned before, without any inhibitor or a solvent, styrene polymerized within 1 h. If toluene is added to the reaction mixture, the conversion is reduced to 40% at a reaction temperature of 150°C. At 175°C, we obtained again a full conversion. With the addition of small amounts of 2,6-dinitrophenol, the conversion is reduced to 15%.

3.4. The amination of styrene

In the first experiments, the reaction was carried out by addition of the polymerization inhibitor, 2,6-dinitrophenol, but without toluene

as a solvent. With this combination, only reaction temperatures up to 150°C were possible to avoid the complete polymerization, but no 1-phenylethylamine was obtained. At higher temperatures, styrene polymerized. Thus, toluene was added to the reaction mixture. With the combination of 7.50 g styrene, 7.50 g toluene and 0.07 g 2,6-dinitrophenol, no solid polymer product was produced at any temperature and pressure.

The influence of the reaction temperature was varied between 220°C and 260°C and the reaction pressure was investigated between 20 and 255 bar with a reaction time of 15 h. An optimum temperature was 250°C and 150 bar with a selectivity to 1-phenylethylamine of 0.4% and a conversion of 98.7%. High conversion of styrene and low selectivity to 1-phenylethylamine are the result of the polymerization reaction of styrene. Some other by-products were detected, e.g., cumene, ethylbenzene, α -methylstyrene and acetophenone. We suggest that these by-products are caused by a proceeding oligomerization and a subsequent cracking reaction. If the reaction time and the reaction temperature are reduced, these by-products do not appear.

To achieve a lower conversion of styrene to the polymer and to obtain a higher selectivity to 1-phenylethylamine, we examined the influence of the toluene and ammonia addition as solvents. If the molar toluene/styrene ratio is increased from 1:1 to 33:1, the conversion is reduced to 84%, but no amine is detected. A

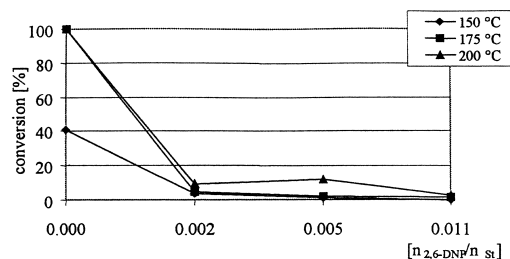


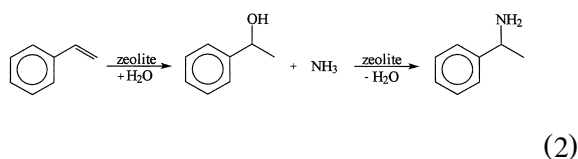
Fig. 3. Inhibition of the styrene polymerization with 2,6-dinitrophenol in toluene as solvent at different temperatures.

molar toluene to styrene ratio up to 1.4 is necessary to avoid the complete polymerization of styrene, but a higher ratio prevents the amination reaction. Ammonia is in the supercritical phase under the used reaction conditions and behaves as a supercritical solvent, which is able to wash the oligomer or polymer from the zeolite and to solve styrene to reduce the polymerization. The thermodynamic calculation of styrene amination indicates that a high content of ammonia favours the production of 1-phenylethylamine. Nevertheless, a higher ammonia addition resulted in no obvious change in the conversion nor the selectivity due to an blocking of the acid sites by the ammonia.

Other possibilities to decrease the polymeric products and to increase the selectivity to 1-phenylethylamine can be the catalyst loading and the reaction time. The variation of the catalyst loading between 19.3 and 2.5 produced no higher selectivities. In a control experiment, no 1-phenylethylamine was formed without the addition of the boron zeolite. Investigations of the reaction time resulted in a maximum selectivity of 0.5% at a reaction time of 3 h but the conversion was still high at 97%.

3.5. Hydration and amination of styrene

From the above studies, the direct acid-catalyzed amination of styrene is possible, but only in very low yields due to the high polymerization tendency of styrene. Another possibility to reduce the polymerization is the addition of water. Water can serve as a solvent and behave as a nucleophile with addition to the olefinic double bond to produce 1-phenylethanol. The alcohol could react further under the chosen reaction conditions in a nucleophilic substitution with ammonia to 1-phenylethylamine according to Eq. 2.



We began to study the influence of the water addition without the addition of ammonia at 200°C at atmospheric pressure to produce 1-phenylethanol. The results are shown in Fig. 4. The same amounts of the starting materials as in the previous amination experiments were used with different amounts of water added to the reaction system.

The addition of 1.24 g water gave a conversion of 10.5% which decreased to 6.0% when 7.04 g water was added. A maximum selectivity of 76.1% to 1-phenylethanol is obtained with 5.06 g of water. These results indicate that the hydration of styrene is working well under the chosen reaction conditions. The B-MFI-type zeolite (sample C) is identified as a very effective zeolite for such addition reactions. This is supported by further experiments, e.g., in the variation of the molar water/toluene ratio. These results also showed that water is a good solvent for the polymerization of styrene. The selectivity to 1-phenylethanol increased with a higher content of water in the reaction system.

The substitution of the alcoholic group in 1-phenylethanol through ammonia to 1-phenylethylamine was examined in an autoclave at a reaction temperature of 250°C and a pressure of 150 bar for 3 h. The selectivity to 1-phenylethylamine was 13.3% and a conversion of styrene was 91.1%. Also in this experiment, the main by-products were polymers.

Both steps — the addition of water to styrene and the substitution of the alcoholic group with ammonia to 1-phenylethylamine — could be

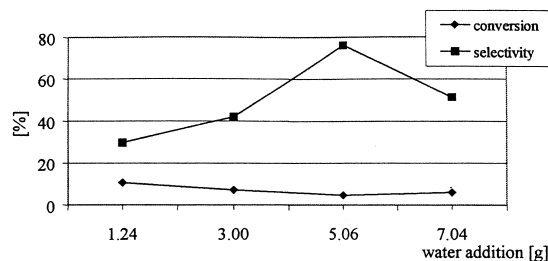


Fig. 4. The hydration of styrene.

performed in acceptable yields. Therefore, a combination of both steps seemed to be worthy for further investigations. Unfortunately, the combination in a “one-pot” process did not work. At 220°C and 150 bar with 0.5–3.0 g water, neither the selectivity to the alcohol nor selectivity to the amine was achieved. In all experiments, the conversion of styrene was still high at 90% due the polymerization reaction. In comparison to these experiments, a control experiment under water-free and inert reaction conditions showed a slightly higher selectivity to the amine but not to alcohol.

These experiments showed that in spite of all our efforts, no high selectivity to 1-phenylethylamine was achieved by direct synthesis route. The reason for this was the polymerization reaction of styrene dominating every experiment.

3.6. The B-MFI and the B-BEA zeolites

The boron zeolites were chosen for this reaction because it is known that the substitution of alumina through boron leads to weaker acid sites [57]. To check this, TPD measurements were compared with the results of the amination of styrene. H-BEA zeolite (sample D), H-MOR (sample E), H-Y zeolite (sample F) and H-FER (sample G) were investigated as shown in Fig. 2. Due to the incorporation of alumina in the zeolite lattice, the first desorption maximum of ammonia was observed between 220°C and 280°C. These zeolites and several H-ZSM-5 materials were tested in the amination reaction at a temperature of 250°C and a pressure of 150 bar. Non of these materials managed more than 0.1% selectivity to 1-phenylethylamine in comparison to the H-B-MFI-type zeolite with 0.4%. The TPD spectrum of H-B-MFI (sample C) and H-B-BEA (sample A) zeolite is shown in Fig. 5.

The desorption maximum of the B-MFI-type zeolite is at 195°C. In comparison to this, the B-BEA zeolite has two desorption maxima: the first at 130°C and the second at 195°C. It is known that the boron MFI possesses Si–OH acid groups and B–OH acid groups, which are

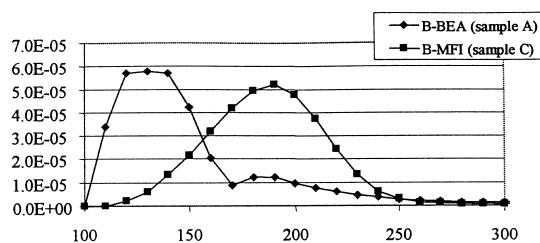


Fig. 5. TPD spectra of boron-containing zeolites.

comparable in acidic strength [12,58–60]. The TPD spectrum of SiO₂ also demonstrated a desorption at 195°C. We suggested that the first desorption temperature in case of B-BEA belongs to B–OH groups and the second to Si–OH groups.

Both boron-containing zeolites were first calcined at air. The optimal calcination temperature was determined to be 500°C based upon experimental and analytical results. Due to the calcination, most of the boron are outside the zeolite framework as an extra framework species [12,61–64].

To decide as to what influence the incorporation of boron or the B–OH groups had on the amination of styrene, several experiments were carried out with other boron materials shown in Table 3. The experiments were performed at 220°C and 150 bar for 3 h with toluene as solvent in the presence of 2,6-dinitrophenol as polymerization inhibitor. The reduced reaction parameters in these runs were chosen because the conversion and the polymerization were decreased to approximately 90%.

Some non-zeolitic samples were tested and compared with the boron-containing zeolites. Interestingly, in these experiments, boron oxide produced traces of 1-phenylethylamine in comparison to boron hydroxide, which showed no activity to the styrene amination. Nearly similar results were obtained using a silicalite (sample B) which initiated no amination under the used reaction conditions. In a further experiment, the material was impregnated with boron hydroxide and then calcined, resulting in a mixture of boron oxide in the silicalite pores. Again, this

Table 3
Influence of different boron-containing samples

Sample	Treatment	Si/B ratio	Conversion [%]	Selectivity [%]
B(OH) ₃	–	–	92.3	0.0
B ₂ O ₃	–	–	92.9	< 0.1
Silicalite (sample B)	calcined at air	–	89.3	0.0
Silicalite (sample B)	impregnated with B(OH) ₃ , calcined at air	9	93.1	< 0.1
B-MFI (sample C)	calcined at air	17	90.0	0.1
B-BEA (sample A)	containing template, not calcined	13	97.5	0.0
B-BEA (sample A)	calcined at NH ₃	15	93.2	0.3
B-BEA (sample A)	calcined at air	12	85.3	0.4

material produced traces of 1-phenylethylamine. On the base of these results, we suggest that the B–OH groups are necessary for the amination reaction. The combination of extra framework boron in a zeolite framework is important for the styrene amination. This fact is supported by the experimental results and IR measurements [64]. These measurements demonstrated that the boron-containing extra framework species interact in the B-MFI zeolite with the zeolite framework. We suggest that this interaction creates a special kind of active sites with a combination of acid and adsorption site center. Various results were found supporting our suggestion about such active sites. MFI-type zeolites were tested, in which the boron atoms are assumed to be incorporated in the zeolite framework (samples H and I). These materials produced no 1-phenylethylamine in comparison to the B-MFI zeolite with a high content of extra framework boron. Furthermore, we studied the effect of acid treatment of the B-MFI and B-BEA zeolite [31,65]. If the precalcined B-MFI zeolite is treated with a 0.1 M HCl solution, most of the framework and extra framework boron oxides are washed out of the zeolite pores, indicated by an increase of the Si/B ratio from 17 to 79, and the selectivity to 1-phenylethylamine is slightly increased. If a templated B-MFI-type zeolite is treated in same manner, the Si/B ratio is only slightly increased to 20 due to the protection of the template. This material produced a selectivity of < 0.1% to 1-phenylethylamine. The ex-

periments with the B-BEA zeolite (sample A) showed that an uncalcined, templated boron zeolite produced no aminated product. This material was then calcined by two methods: procedure I, in which the boron is removed out of the lattice and procedure II, which guaranteed that boron remains in the zeolite lattice. Again, the zeolite with a higher amount of extra framework boron led to a higher selectivity of 1-phenylethylamine. We believe that the reasons why the B-BEA zeolite produced a better result to the styrene amination than the B-MFI zeolite are the larger pore diameter, the higher BET surface with 440 m²/g in comparison to the B-MFI with 359 m²/g and as shown in the TPD spectrum (Fig. 5), and a lower acid strength of the acid sites.

3.7. Transfer to styrene derivatives

It is known from literature that the amination of alkenes with ammonia is easier when the olefinic double bond is adjacent to alkyl groups, e.g., *i*-butene is easier to aminate than propene and ethene. Also, different residues at the aromatic ring should have a positive effect on the formation of the amines.

Therefore, we tested some structural derivatives of styrene using the boron BEA-zeolite. In Table 4, the results with 4-methylstyrene, 4-*tert*-butylstyrene, α -methylstyrene and *trans*-stilbene as starting materials are shown. The reaction temperature was varied between 200°C

Table 4
Amination of styrene derivatives

T [°C]	4-Methylstyrene		4- <i>tert</i> -Butylstyrene		α -Methylstyrene		<i>trans</i> -Stilbene	
	Conversion [%]	Amine [%]	Conversion [%]	Amine [%]	Conversion [%]	Amine [%]	Conversion [%]	Amine [%]
200	77.4	2.1	82.7	0.9	11.2	62.9	19.7	0.0
220	90.9	4.7	90.5	1.3	14.2	41.3	20.3	0.0
240	97.0	0.6	96.1	1.8	15.9	25.6	25.6	0.0

and 240°C and the reaction pressure was 150 bar for 3 h reaction time according to the parameters used in the styrene amination. In the case of *trans*-stilbene as starting material, a reaction time of 10 h was chosen due to a higher amount of solvent in the reaction mixture.

The conversion of 4-methylstyrene and 4-*tert*-butylstyrene is similar to the conversion of styrene. Also for these starting materials, the tendency for the polymerization reaction is high, but the selectivity to the amines is obviously higher. At a temperature of 240°C, 4-*tert*-butylstyrene is aminated with a selectivity of 1.8%. For 4-methylstyrene as a starting material, a lower reaction temperature of 220°C is probable and the selectivity to the amine is 4.7%. We suggest that the alkyl group in *para*-position to the olefinic group at the aromatic ring has a stabilizing effect for the initially formed carbenium ion in comparison to the unsubstituted styrene molecule.

The amination of *trans*-stilbene failed under the chosen reaction conditions. At a reaction temperature of 240°C, only a conversion of 26.6% was obtained. The main product was *cis*-stilbene with a selectivity of 10.4%. Furthermore, the boron MFI-type zeolite was evaluated at temperatures between 200°C and 300°C, but also in these experiments, no 1,2-phenylethylamine was produced.

Interesting yields were obtained for the amination of α -methylstyrene as starting material. The methyl group at the double bond stabilizes the initially formed carbenium ion and higher

selectivities to the 1-methyl-1-phenylethylamine in comparison to 1-phenylethylamine were obtained. The best result was produced at a temperature of 200°C with a conversion of 11.2% and a selectivity of 62.9%. Another reason for such good results is the much lower ceiling temperature of α -methylstyrene with 61°C in comparison to the ceiling temperature of styrene with 310°C [45].

4. Conclusion

We sought to answer the question on whether the direct acid-catalyzed amination of styrene is possible or not. After detailed studies, we obtained only very low selectivities to 1-phenylethylamine using boron-containing zeolites such as H-B-MFI and H-B-BEA or other materials which possess a high number of weak acid sites. The addition of a polymerization inhibitor and working in toluene as solvent was effective for the control experiments, but did not prevent the polymerization under amination reaction conditions. In contrast to amination, the hydration of styrene is possible in reasonable yields. Also, the nucleophilic substitution of the alcohol to produce 1-phenylethylamine is possible, but the one-step reaction failed. In all cases, we observed that the polymerization of styrene is the dominating reaction. However, one can aminate structural derivatives of styrene. The best results were obtained for the amination of α -methylstyrene.

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