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The use of zeolites in the synthesis of fine and intermediate chemicals

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Abstract

This paper deals with two industrially very important reactions. The vapor-phase Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam and the isomerization of α-pinene to campholenic aldehyde. The first reaction represents the synthesis of a significant intermediate in the nylon-6 production route, the latter the formation of fine chemicals for use in the fragrance industry. Both catalytic reactions are carried out heterogeneously over zeolites and demonstrate the advantages of these materials employed as catalysts in industrial processes.

Keywords: Zeolite; Vapour-phase Beckmann rearrangement; Selective isomerization

1. Introduction

The sensibility for environmental protection has increased in the public, political and economical world over the past 15 years, as quality of life is strongly connected to a clean environment. The chemical industry has a key position in the world wide economy. The political demand for zero emissions has to be taken into account further for new developments of products and processes. The priority of different means for environmental protection like avoiding, exploiting and waste management lies on the first step in this order. The aim is "production or reactor integrated environmental protection". This implies the use of better catalysts, the determination of thermodynamic and kinetic properties of the chemical reaction as well as the choice of the most suitable type of reactor and the optimal reaction conditions. The so called cleaning up or end of pipe strategy has been extensively investigated and a lot of progress has been made in this field. However, it should be better to avoid such solving of problems from the beginning.

The industrial production is mainly based on catalytic processes. More than 90% of all chemical products manufactured involve at least one catalytic step, mostly even several catalytic procedures. In the production of bulk chemicals mainly heterogeneous catalysts are employed. However, in the field of fine chemicals and intermediates most processes are still homogeneously catalyzed. Thereby Lewis- or Brønsted acidic as well as Lewis- or Brønsted basic catalysts are used. The use of heterogeneous catalysts should allow the production of desired products with less environmental pollution due to a lower energy consumption and the avoidance of by-products by highly selective reactions [1].

In the tendency towards transforming homogeneously catalyzed processes to heterogeneous catalysis, zeolitic catalysts are gaining in importance. The experience in the use of such catalysts in the petrochemical industry can be increasingly applied to the

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selective organic synthesis of chemical intermediates and fine chemicals. Zeolites with their numerous adjustable catalytic properties offer a broad range of possibilities for this purpose [1–10,23].

In this paper two examples of industrial interest are described; one for an intermediate and one for a fine chemical, i.e.:

- Vapor-phase Beckmann rearrangement.
- Selective isomerization of α-pinene oxide.

These examples should demonstrate the potential of zeolite catalysts in the synthesis of fine and intermediate chemicals.

2. Vapor-phase Beckmann rearrangement

As a starting material for the nylon-6 synthesis, ϵ-caprolactam is of high industrial importance (see Fig. 1).

The classical route starts from the hydrogenation of benzene to cyclohexane which is subsequently oxidized to form a cyclohexanone/cyclohexanol mixture. This mixture is oxidized to cyclohexanone in the next step. After the reaction of the ketone with hydroxylamine in the presence of sulfuric acid cyclohexanone oxime is formed and rearranged to ϵ-caprolactam. This Beckmann rearrangement is also carried out in sulfuric acid. Although very high yields are obtained, the large amount of ammonium sulfate due to the neutralization of the oleum used in the oximation as well as in the rearrangement is considered to be an environmentally unacceptable drawback.

Recently a new route for the production of ϵ-caprolactam and adipic acid was introduced. This route is also based on benzene as starting material but on the use of heterogeneous zeolite catalysts. Thereby, the highly selective partial hydrogenation of benzene to form cyclohexene and the succeeding highly selective hydration in the presence of a special H-ZSM-5

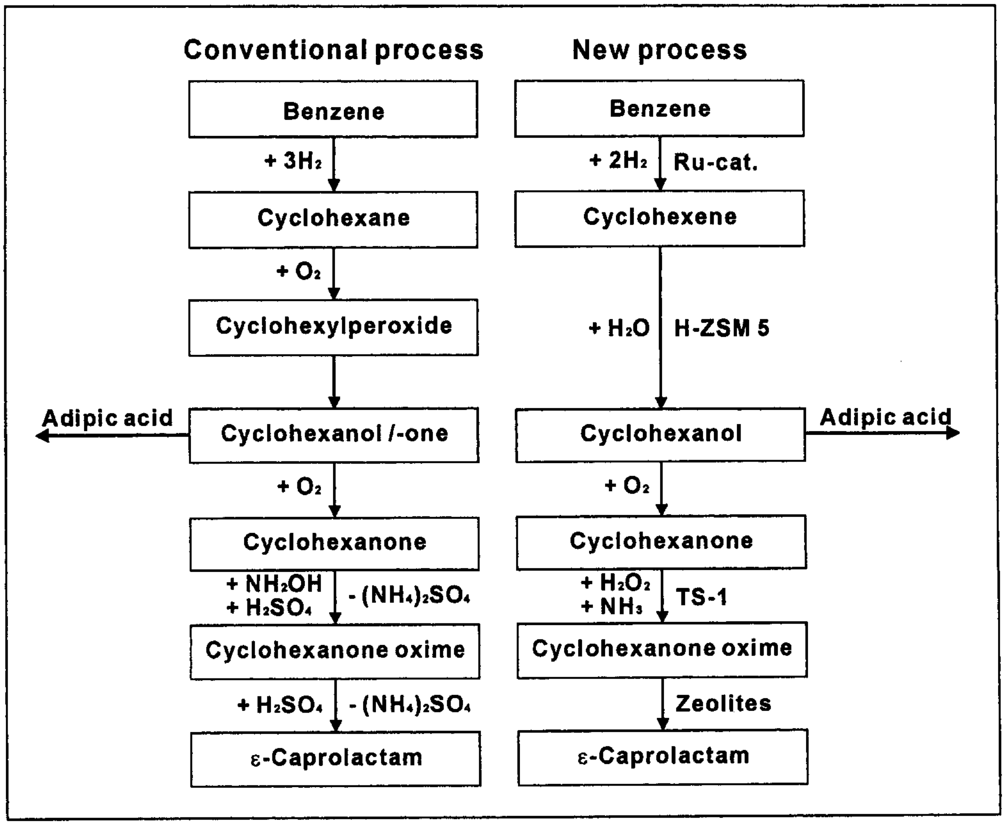

Fig. 1. Routes of synthesis of ϵ-caprolactam and adipic acid.

(Asahi-Process, 60 000 t/a since 1990) are the first steps towards a new adipic acid and caprolactam process. In the case of caprolactam, after the oxidation of the cyclohexanol to cyclohexanone, the oximation to cyclohexanone oxime is carried out in the presence of ammonia and hydrogenperoxide as oxidant over a Ti-containing MFI-zeolite TS-1 (Enichem-Process, 12 000 t/a demonstration plant). There are several studies to rearrange the cyclohexanone oxime to ϵ-caprolactam over zeolitic catalysts. This new route provides advantages compared to the conventional method:

- 1 mol of hydrogen is saved in the first step.
- One reaction step less.
- Avoidance of the dangerous oxidation with oxygen.
- Avoidance of the toxic hydroxyl amine.
- Avoidance of hazardous and corrosive sulfuric acid in the oximation as well as in the Beckmann rearrangement.
- Avoidance of ammoniumsulfate (up to 4.0 t per t ϵ-caprolactam).

This shows the new production procedure to be an energetically and economically favorable as well as an environmentally friendly alternative route. However, the heterogeneously catalyzed rearrangement step is not commercialized so far, because of problems such as catalyst lifetime. These drawbacks still have to be solved as it would not make any sense to manufacture the oxime by the use of a heterogeneous catalyst and still carry out the Beckmann rearrangement in a homogeneously catalyzed procedure.

After the discovery of the heterogeneously catalyzed reaction, research was focused on the gas-phase rearrangement of cyclohexanone oxime using solid acids [11]. The yields achieved at the presence of boron or phosphor impregnated amorphous silicates and aluminosilicates were about 95%. Catalyst lifetime, e.g., because of loss of the volatile boronoxide, was too low to transfer this process into industrial scale [12–16]. In the use of zeolites as catalysts, the MFI-structure appeared more suitable for the Beckmann rearrangement than, e.g., mordenite or HY [17–23]. Compared to amorphous materials, catalyst lifetime of MFI-zeolites was in fact higher, but still not sufficient for technical application.

Based on these former studies we started our investigations using a boron pentasil zeolite as catalyst whose synthesis is described in [24].

2.1. *Results and discussion*

The influence of temperature on the reaction was investigated in an integral continuous fixed bed reactor in the range of 220–400°C. In agreement with literature, the optimal temperature was found at 350°C and ambient pressure (Fig. 2). Highest selectivity obtained over the weakly acidic B-MFI-zeolite was about 65% at 99% conversion using toluene as a solvent. Temperatures above 380°C led to major selectivity reduction due to the decomposition of ϵ-caprolactam and other side reactions. Lower temperatures enhanced depositions on the catalyst surface and therefore also caused a drop in selectivity. Higher temperatures over 250°C should be advisable due to the boiling point of cyclohexanone oxime.

It was observed that catalyst lifetime increased along with temperature. It is assumed that coke precursors or deactivating compounds desorb more easily at elevated temperatures. At 350°C there was no drop in oxime conversion after 8 h time on stream (TOS). At a temperature of 300°C conversion dropped from 99% to 92% and at 250°C the decline was even more severe (Fig. 2).

The most common by-products to be found are 5-cyanopent-1-ene, 5-cyanopent-2-ene and 5-cyanopentane in addition to cyclohexanone, cyclohexenone and traces of aniline in that order [15,16]. The amount of not identified high boiling products did not exceed 1% and can be neglected.

The low catalyst lifetime is assumed to be caused by deactivating compounds as well as coke precursors blocking the acid sites of the catalyst. Thus, the reaction was carried out at a pressure of 0.1 bar in order to facilitate the desorption of deposits on the catalyst surface. The results achieved at different temperatures are shown in Fig. 3.

Obviously, there was no improvement of desorption behavior at reduced pressure. On the contrary, conversion dropped significantly (Fig. 3). Surprisingly, the selectivity to caprolactam increased significantly with reduced pressure (Fig. 3). According to our knowledge these investigations have been carried out the first time.

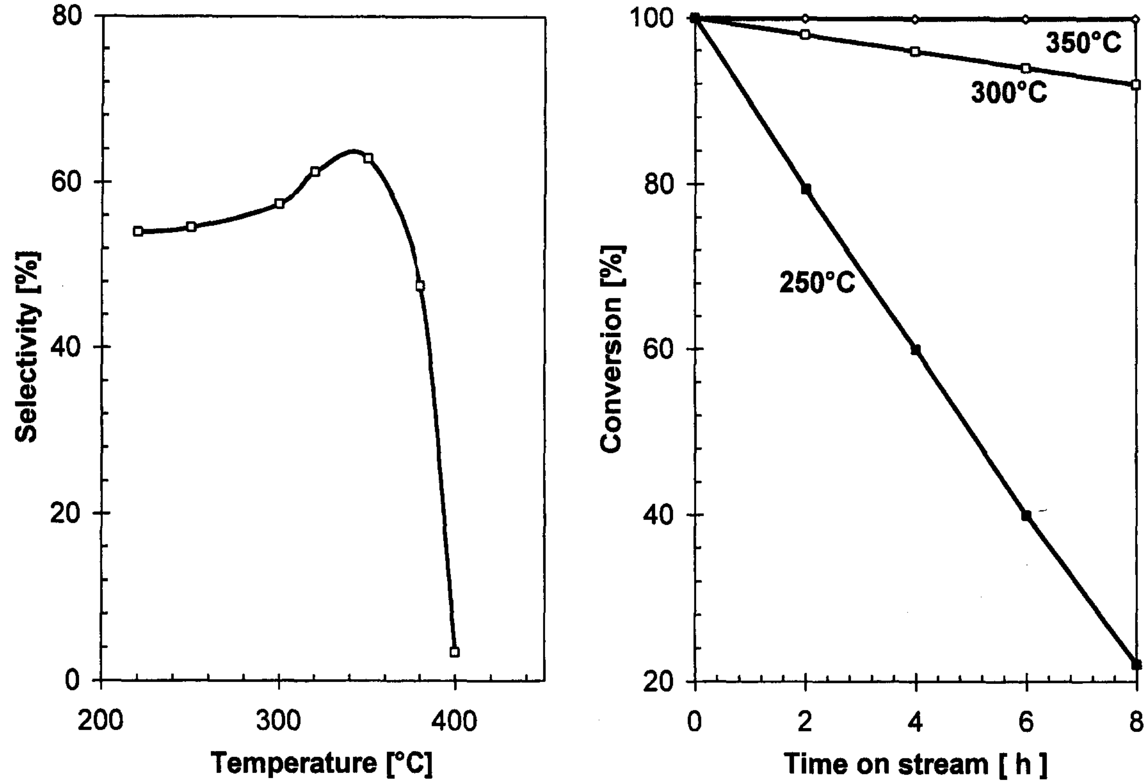

Fig. 2. Influence of temperature: p=1 bar; WHSV=0.25 h^{-1}; 5 l/h N_2-carrier; toluene/oxime =9:1 (mass ratio); B-MFI zeolite.

A further improving step was the adjustment of lower temperatures such as 300°C or even 250°C. The selectivities observed at 250°C and 1 bar as well as 0.1 bar correspond to the values found at 300°C. This represents almost the minimum temperature due to the boiling point of caprolactam. The maximum selectivity obtained was approximately 92% (Fig. 3).

Polar solvents such as methanol or ethanol showed higher yields and lower deactivation rates than non-polar solvents, such as toluene or benzene [25,29].

The addition of water to the reaction with a maximum amount of 0.1–2.5 mol H_2O per mol oxime has been reported [12,26]. In contrary to the disclosed results, it was shown that conversion and selectivity (Table 1) were raised with a larger amount of water up to 6 mol per mol oxime using the B-MFI-zeolite catalyst. Thereby, we found an increase of the conversion from 97% to 99% as well as a slight improvement of the selectivity from 92% to 93%. The effect of the water addition on the catalyst service time is also significant. Without any additional water the conversion of the oxime drops from 97% to 94% within 8 h TOS. By adding 6 mol water per mol oxime the decrease is only 0.7% within 8 h TOS.

The catalyst service time without regeneration is not expected to exceed a few days. Crystalline zeolites, however, can be regenerated without activity loss at 430°C with oxygen [27]. In our investigation the B-MFI-zeolite was regenerated in the presence of air at 500°C for 16 h after 6 h TOS without any problems. The results obtained on the first day are very similar to the results after the 40th day (Table 2). We even realized an increase in conversion and an improvement of selectivity. Conversion was raised from 95% to 96% and the drop of conversion after 6 h TOS was decreased from 5% to 2%. The values for selectivity improved from 93% to 95% after 6 h TOS. Due to the apparent deactivation of catalysts, regeneration seems to be necessary for application in an industrial process. This should be realized with a simultaneous reaction and regeneration procedure.

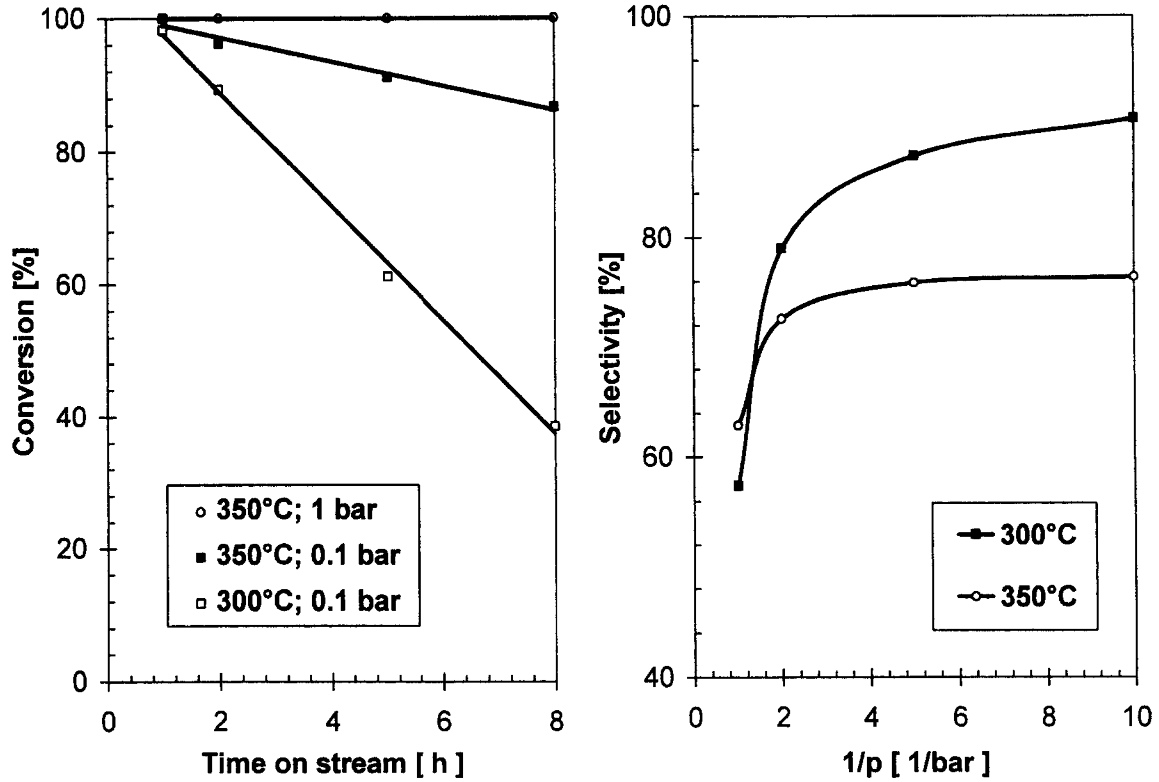

Fig. 3. Influence of pressure: WHSV=0.25 h^{-1}; 5 l/h N_2-carrier; toluene/oxime=9:1 (mass ratio); B-MFI zeolite.

Table 1
Influence of water on conversion and selectivity

	Addition of water (mol water/mol oxime)			
	0	0.62	3.1	6.2
Conversion (%) (1 h TOS)	97.3	97.8	97.8	99.2
Selectivity (%) (1 h TOS)	92	92	92	93
Drop of conversion (%) (8 h TOS)	3	1.5	<1	<1

T=300°C; p=0.1 bar; WHSV=0.25 h^{-1}; 5 l/h N_2-carrier; (ethanol+water)/oxime=9:1 (mass ratio); B-MFI-zeolite.

Table 2
Reaction/regeneration

Day	TOS (h)	Conversion (h)	Selectivity (h)
1	1	95	91
	6	90	93
40	1	96	93
	6	94	95

Reaction: T=300°C; p=0.1 bar; WHSV=0.25 h^{-1}; 5 l/h N_2-carrier; ethanol/oxime=9:1 (mass ratio); B-MFI-zeolite.
Regeneration: T=500°C; p=1 bar; airstream; 16 h.

There was no proof so far where the reaction takes place, whether on the inner or outer surface of the zeolite. Therefore, the Beckmann rearrangement was investigated over B-MFI-zeolites with different crystal sizes. Their catalytic performance can be seen from Table 3.

The catalytic results over these B-MFI-zeolites were strongly influenced by the size of the crystals. The worst conversion rates of 43% (1 h TOS) with intermediate selectivities around 65% were obtained with the largest crystals. The use of smaller, spherical, crystals ($\ll$1 μm) yielded an improvement of conversion up to 100% at selectivities of 90%. Furthermore, the drop of conversion after 6 h TOS was diminished.

These experiments show that with increasing the external surface area, i.e., decreasing crystal size, conversion is raised significantly. This is a strong hint that the external surface area plays an important

Table 3
Influence of crystal size

Crystal size B-MFI (μm)	Shape	TOS (h)	Conversion (%)	Selectivity (%)
$\ll 1$	Spherical	1	99.8	87.8
		6	99.8	89.3
10–20	Spherical	1	53.9	62.8
		6	23.3	72.2
10×100	Cylindrical	1	43.1	64.7
		6	21.3	64.9

T=350°C; p=1 bar; WHSV=0.25 h^{-1}; 5 l/h N_2-carrier; ethanol/oxime=9:1 (mass ratio).

role for the reaction. Therefore, we assume the Beckmann rearrangement not to take place inside the micropores of the MFI-structure but rather on the outer surface. Our supposition is backed up by molecular modeling (Biosym software) demonstrating that ϵ-caprolactam is not capable of entering the MFI-pore system [30].

Nevertheless, the loss of selectivity to values lower than 100% shows that there must be a considerable amount of oxime molecules entering the pore system and being converted to different by-products [29].

2.2. *Characterization of the catalysts*

The fresh and the spent catalysts have been extensively investigated by spectroscopic methods such as XPS, SIMS, MAS NMR, XRD, FT-IR and physical measurements such as thermogravimetric analysis and adsorption experiments [30]. Here only a few remarks should be made with respect to acidic strength of the acid sites which is favorable for the Beckmann rearrangement. According to literature the assumption starts from strong acid sites and ends up in sites with very low acidity and even almost neutral silanol groups. Furthermore, the question arises, why a zeolite is needed if the reaction is assumed to take place on the outer surface as mentioned before. We believe [23] that only weak or even extremely weak Brønsted acid sites are needed for the Beckmann rearrangement.

To exactly determine these active sites for the reaction we investigated three siliceous catalysts at the previously found optimized reaction conditions. The catalytic results obtained over amorphous silica (Aerosil 200, Degussa AG) were compared to silicalite as well as to the same silicalite treated with ammonia according to a patent by Sumitomo company [28]. Table 4 shows that the amorphous silica yielded only moderate selectivities of 55–65% at low conversion rates of 30–20%. Conversion over the silicalite was slightly higher but selectivity was rather poor. The best results were obtained with the modified silicalite. Conversion was raised to values around 75% and selectivity was even higher than 90%.

A closer sight on the properties of these three materials was achieved by their examination with FT-IR analysis. Fig. 4 depicts the catalysts' infrared spectra between 4000 and 3000 cm^{-1} which allows the detection of silanol groups on their surface.

Table 4
Comparison of siliceous catalysts

	Amorphous silica		Silicalite		Silicalite (ammonia treated)	
TOS (h)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
1	32.8	54.0	46.9	29.8	76.0	93.1
3	23.2	62.9	40.1	26.8	74.6	92.3
6	18.4	64.1	33.3	24.4	67.1	91.8

T=300°C; p=0.1 bar; WHSV=0.25 h^{-1}; 5 l/h N_2-carrier; ethanol/oxime=9:1 (mass ratio).

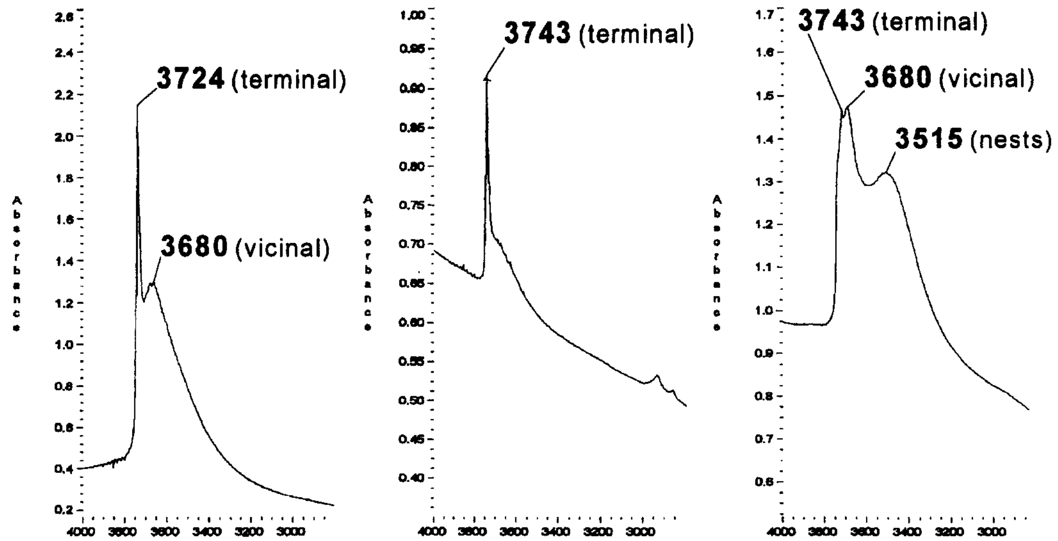

Fig. 4. FT-IR analysis of siliceous catalysts.

The spectra of the silica shows a band at 3740 cm^{-1} for terminal silanol groups and at 3690 cm^{-1} a broader band representing the vicinal silanol groups. The untreated silicalite shows just one band for terminal silanol groups. From the low selectivity obtained with this material it can be concluded that not terminal but rather vicinal, hydrogen bonded, silanols are important for the Beckmann rearrangement. On the contrary, by treating the silicalite with ammonia a third broad band arises at 3500 cm^{-1}. This band is related to internal and external silanol nests on zeolites with MFI structure. These silanol nests should be the most favorable species for the reaction as their appearance is connected to a significant increase of conversion and selectivity. Their advantageous arrangement on the surface of MFI-structure furthermore induces the use of zeolites instead of amorphous materials.

Also in the case of B-MFI-zeolite, such silanol nests have been identified [30].

2.3. Conclusions

The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam has been studied using a B-MFI-zeolite. Optimized process parameters were found, i.e., at reduced overall pressure of 0.1 bar in addition to a temperature of 300°C the highest selectivity of about 95% was achieved at approximately 100% conversion. Thereby, the deactivation rate increased. But through adding water and alcohols to the reactant solution this drawback was compensated for.

The insufficient catalyst service time necessitates the regeneration of the B-MFI-zeolite. It was shown that regenerating with air at an elevated temperature of about 500°C leads to complete reactivation of the catalyst. Regeneration in a fixed bed, though, is not very ingenious. A suitable process of simultaneous reaction and regeneration, both inside a fluidized bed, should provide technical and economical feasibility for industrial use.

We found [29] that in the case of using a fluidized bed of laboratory scale selectivity and starting conversion showed good correspondence with the results obtained in the fixed bed reactor. These results encourage further investigations for a continuous reaction–regeneration process to produce ε-caprolactam in the vapor phase, similar to the commercially operated FCC technology.

Comparison of B-MFI-zeolites of different shapes showed the best catalytic results with the smallest crystal sizes. This effect could prove the reaction taking place on the external surface rather than inside the pores of a MFI-structure. Furthermore, treatment with ammonia generated a great amount of silanol nests on the surface of a silicalite which was accompanied by an enormous improvement of the catalytic results. From these experiments we draw the conclusion that the silanol nests with their very weak acidity and their geometrical arrangement on the external surface of MFI-zeolite are the most favorable sites for the Beckmann rearrangement. Furthermore, those sites have to be well dispersed on the surface as well as in isolated, equidistant positions. Such features can only be obtained in the case of zeolites and not in the case of silicas having also weak silanol groups.

3. Selective isomerization of α-pinene oxide

α-Pinene oxide (1) is a very reactive, sensible substrate which rearranges easily under the influence of acid catalysts [31]. Thereby many products can be formed as shown in Fig. 5. For example the compounds such as isomeric campholenic aldehyde, *trans*-carveol, *trans*-sobrerol, isopinocamphone or *p*-cymene are observed. These are only the main side products. For example, if we run the isomerization at temperatures higher than 100°C, then more than 200 compounds are found [32].

The industrially most desired compound is campholenic aldehyde (2), an important intermediate for the synthesis of sandalwood-like fragrance chemicals like santalol [33]. The reaction mechanism itself is not well understood and still discussed in literature [34].

The zinc halogenides $ZnBr_2$ and $ZnCl_2$ are known as effective homogeneous catalysts with selectivities of about 85% to campholenic aldehyde [35]. The drawbacks are numerous, though; for example destruction of the catalyst after reaction, corrosivity, toxicity and waste water pollution with the heavy metal zinc, which is harmful to sludge treatment facilities.

Hence, a lot of efforts have been made to find a true heterogeneous catalyst to overcome these disadvantages [36]. Previously, alternatively obtained selectivities and yields never exceeded 55% and have not been competitive with the homogeneous zinc halogenide system.

Now, we like to report about a new catalytic process, combining good selectivities with environmental compatibility and reusability.

3.1. Results and discussion

In a catalyst screening a lot of heterogeneous systems such as transition metal oxides, phosphates and zeolites have been checked in fixed bed reaction continuously under gas phase conditions as well as in slurry reactors batchwise at various temperatures, residence time, solvents etc. [37,38]. To make a long story short only the best catalysts and best results are reported here.

Surprisingly, we found that the three-dimensional large pore system (7.4 Å) with supercages of 12 Å and large amount of mesopores make US-Y zeolites very suitable for this kind of reaction. They allow a good migration of the starting material into the channel system. Under the given conditions at a temperature of 0°C, we obtained selectivities of about 75% at a conversion of 30% for commercially available highly dealuminated H-US-Y zeolite (A) which was kindly provided by PQ-Corporation (Fig. 6).

As also shown in Fig. 6 a pretreatment of the catalyst with diluted acid (0.01 M HCl at 25°C for 24 h) and subsequent washing and calcination at 550°C yields a major enhancement in activity without loss of selectivity for the desired aldehyde. The conversion achieved was about 100%.

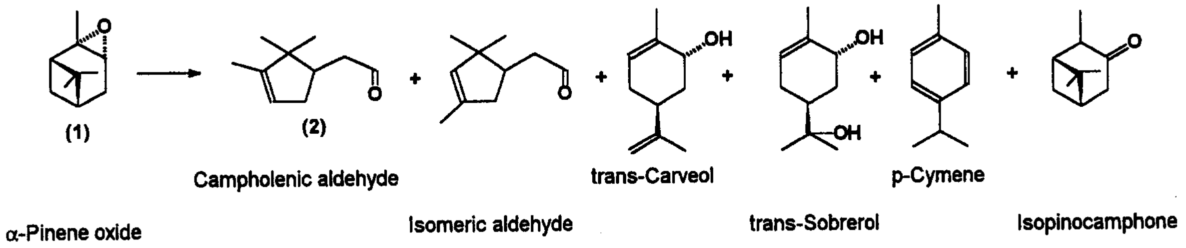

Fig. 5. Products obtained by α-pinene oxide rearrangement.

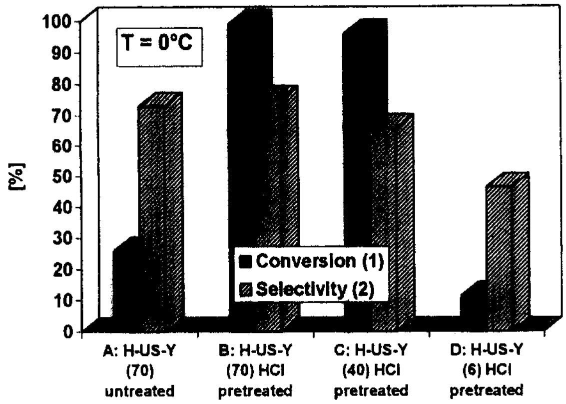

Fig. 6. Influence of acid treatment and SiO_2/Al_2O_3 ratio on the α-pinene oxide isomerization: batch reactor; T=0°C; t=24 h; catalyst loading=7.5 g epoxide/g H-US-Y, solvent 30.0 g toluene.

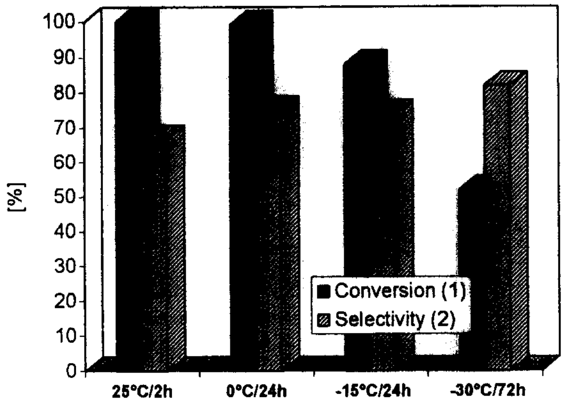

Fig. 7. Influence of temperature (catalyst B): batch reactor; catalyst loading=7.5 g epoxide/g H-US-Y; solvent 30.0 g toluene.

The performance of different H-US-Y zeolites strongly depends on the bulk SiO_2/Al_2O_3 ratio (Fig. 6). The activity as well as the selectivity to campholenic aldehyde increases with decreasing aluminum content. This tendency shows that the Brønsted acid sites do not seem to be responsible for the desired reaction since the number of these sites is equal to the number of aluminum atoms in the framework. From our experiments we cannot exclude that some Brønsted active sites are required, but the performance of these catalysts, especially the good selectivities observed appear to be caused by Lewis acid sites (see later on in this article). They can arise from the dealumination process by steaming and are in general described as extra-framework-alumina (EFAl) species [39]. The first intention of washing with HCl was to remove the EFAl species in order to make the inner part of the zeolite framework more accessible and to diminish the influence of diffusion constraints.

With respect to the temperature influence, Fig. 7 shows increasing selectivity for campholenic aldehyde with lower reaction temperature. At 25°C within 2 h we obtain complete conversion with a selectivity of about 70% to campholenic aldehyde. By running the isomerization at lower temperatures down to −30°C selectivities can be improved to about 80%. Surprisingly, our catalyst B shows, even at such unusually low reaction temperatures, an unexpected high activity. The conversion at −30°C reaches values up to 55% after 72 h (Fig. 7).

The enhancement in selectivity with lower temperature can be explained with an improved kinetic reaction control and/or by the avoidance of side reactions of campholenic aldehyde.

Fig. 8 gives a more detailed picture concerning the time dependence and side products of the reaction at −15°C using catalyst B. The selectivity to campholenic aldehyde is constantly about 78%, within the GC error range. Apparently, conversion increases very fast within the first 5 h reaction time. The decreased incline of conversion after approximately 5 h should probably be caused by blocking of the active sites due to polar, strongly adsorbing reaction products. This effect leads to slower reaction rates. Another explanation to be taken into consideration could be diffusion constraints of the reactant inside the zeolite micropores. In this case reaction would mainly take place on the internal surface.

The most important by-products observed are with 6–7% selectivity the isomeric campholenic aldehyde followed by 2–3% *trans*-carveol (Fig. 8).

In addition, we found that the selectivity and conversion are optimal if the pretreatment of the highly dealuminated Y zeolite is pursued at pH 2 [37,38].

The presented catalytic results of the US-Y zeolites having different silica/alumina ratio showed outstanding performance of our catalyst B at low reaction temperatures. We think that the conversion at such low temperatures is only possible because of highly dispersed, Lewis-acidic EFAl species. Therefore, a

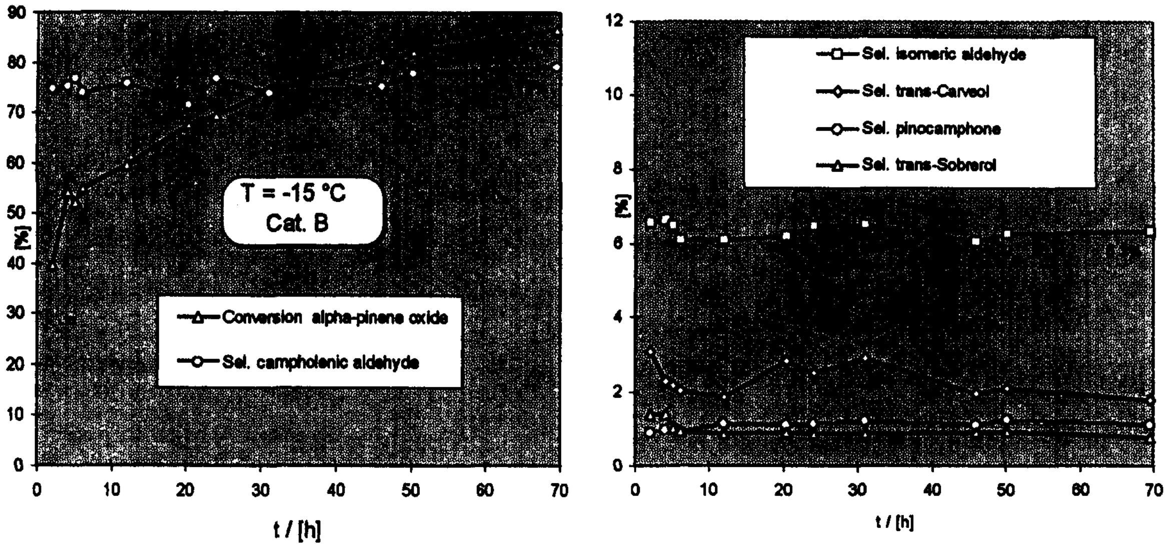

Fig. 8. Influence of low temperature: batch reactor; catalyst loading=7.5 g epoxide/g H-US-Y; solvent 30.0 g toluene.

detailed characterization of this material was conducted to further elucidate its active sites.

3.2. Characterization of the catalysts

The acid treated catalyst B was examined in comparison to the original, untreated catalyst A with different analytical methods (Table 5).

Atomic Adsorption Spectroscopy (AAS) of aluminum and Fourier Transform Infrared Spectroscopy (FT-IR) of both samples indicate that there must exist a large amount of EFAl species in the zeolite (Table 5). By measuring the outer T–O–T stretching frequency, we can calculate with help from the equations disclosed in [40] that only about one Al atom is incorporated into the zeolite framework of catalyst B (Table 5). On the other hand, our experimental results derived from Al-AAS show that hypothetically a higher number, i.e., in total four Al atoms, could be present in the unit cell on the assumption that all Al is incorporated in the framework. This difference tells us that most of the aluminum must exist in form of EFAl.

A hysteresis in the nitrogen adsorption isotherm shows that, besides the high value of surface area due to the micropores, both zeolites have a large mesopore volume. This allows sufficient diffusion transport of organic molecules even at low temperatures.

To distinguish Brønsted from Lewis acid sites, FT-IR measurements of zeolite samples loaded with pyridine at 150°C were performed (Fig. 9) [41].

Intense bands at 1445 cm^{-1} and 1490 cm^{-1} and only weak bands at 1545 cm^{-1} were observed. Since the band at 1445 cm^{-1} and 1545 cm^{-1} can unambiguously be assigned to Lewis and Brønsted acid sites,

Table 5
Comparison of analytical data obtained from Al-AAS, FT-IR and N_2-adsorption

Catalyst	Al-AAS (wt%) (unit cell composition[a])	FT-IR T-O-T stretching frequency (unit cell composition[b])	N_2 adsorption BET surface area
A	0.87	836 cm^{-1}	784 m^2/g+mesopores
B	0.94 ($H_4Al_4Si_{188}O_{384}$)	837 cm^{-1} ($H_1Al_1Si_{191}O_{384}$)	805 m^2/g+mesopores

[a] Assuming all Al incorporated in the framework.
[b] Calculated from the outer symmetric stretching frequency [40].

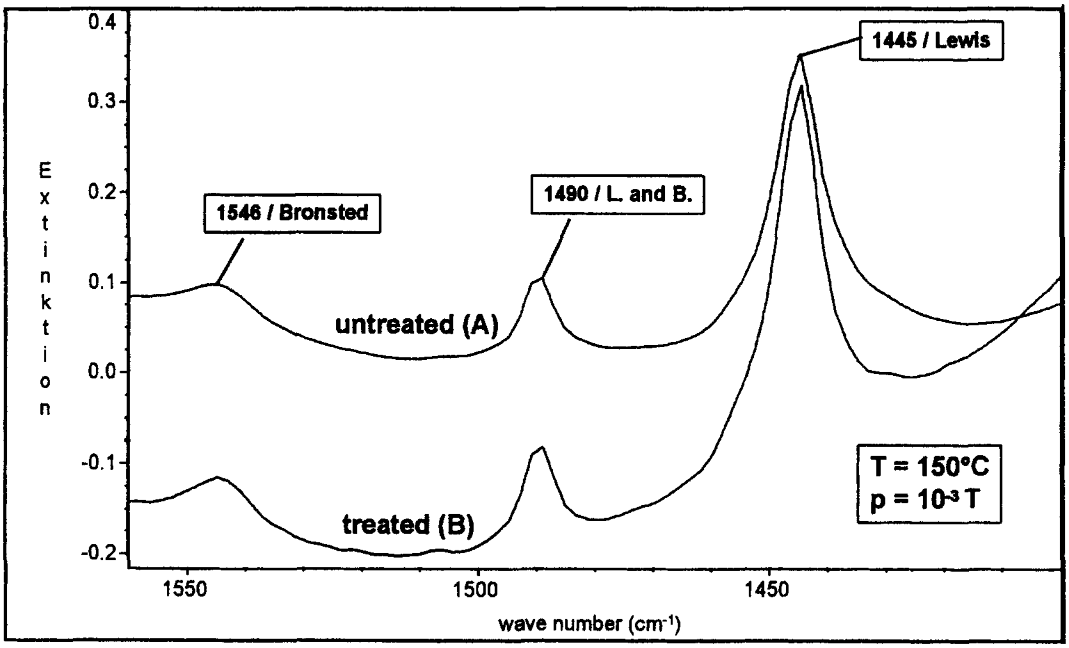

Fig. 9. Adsorption of pyridine on H-US-Y(70) catalysts in FT-IR cell.

respectively, these findings are in agreement with the results from Al-AAS and FT-IR.

More inside information was expected by means of Magic Angle Spinning (MAS) NMR spectroscopy. The ^{29}Si MAS NMR spectrum (Fig. 10) of the untreated sample shows a main signal at -107.7 ppm ($Si(OSi)_4$ in the framework) and a minor one at about -101 ppm ($Si(OSi)_3OAl$ in the framework). The additional spectral intensities can be assigned to amorphous silica and amorphous aluminosilicate produced in the hydrothermal dealumination process.

Fig. 10 shows that after acid treatment with 0.01 molar HCl most of the amorphous silica containing material is removed. This can easily be understood since the maximum solubility of silica [42] is reached at pH 2. However, the improved performance of the treated catalyst cannot be entirely explained by the removal of less active material, i.e., the increase of the number of Lewis acid sites per mass unit. We believe that these silica species block most of the catalytically active centers, i.e., the highly dispersed Lewis acidic alumina sites in the micro- and mesopores of the parent US-Y zeolite.

The correctness of our explanation for the catalytic performance is confirmed by ^{27}Al MAS NMR spectroscopy (Fig. 11) [43]. The ^{27}Al MAS NMR spectra consist of a peak at 61.9 ppm (tetrahedral framework Al) accompanied by two broad peaks centered at about 33 ppm (penta- and tetrahedrally coordinated EFAl) and 0 ppm (octahedrally coordinated EFAl). The sharp signal at -0.3 ppm is caused by highly mobile $Al(H_2O)_6^{3+}$ ions. The NMR lines of the framework aluminum as well as of the EFAl species are not changed by the acid treatment at pH 2. Consequently, neither significant amounts of the framework aluminum nor of the EFAl, which is responsible for the Lewis acidity, are removed by our treatment.

3.3. Conclusions

Our investigations demonstrate the high catalytic value of a strongly dealuminated H-US-Y zeolite for the isomerization of α-pinene oxide to campholenic aldehyde. By applying low temperatures, e.g., 0°C, high selectivities of 75% campholenic aldehyde can be achieved within 24 h reaction time. This is surprising because diffusion limitations would be expected to prevent reactions in zeolites at such low temperatures. This unique catalyst shows highly dispersed, Lewis

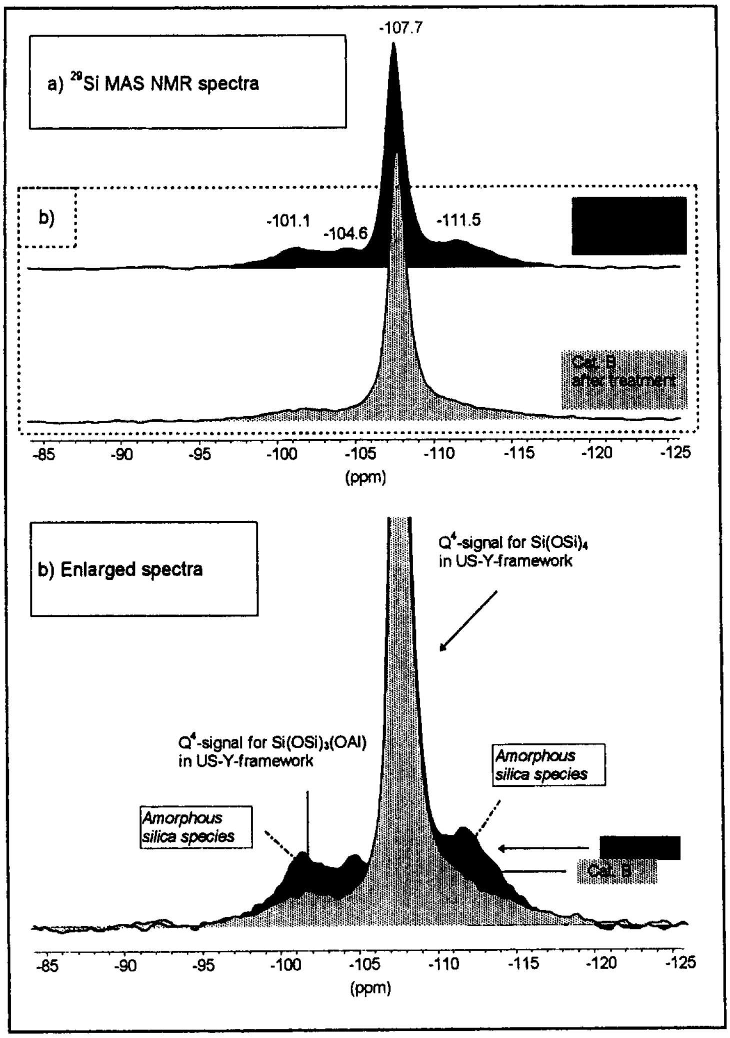

Fig. 10. ^{29}Si MAS NMR spectra of H-US-Y catalysts A and B.

acidic species immobilized in the zeolite framework whose activity and access are not hindered by amorphous silica materials. To remove amorphous silica species, the catalyst has to be pretreated with an excess of 0.01 molar HCl. Analytic investigation with help of ^{27}Al MAS NMR experiments show a relative high content of EFAl, which seems to be highly dispersed in the zeolite. Although the nature of the EFAl species is not exactly known, we believe that they are responsible for the Lewis acidity and in further consequence responsible for the high selectivity to campholenic aldehyde.

4. General remarks

The chosen examples should demonstrate the potential of zeolites as catalysts in the organic synthesis of fine and intermediate chemicals. The main application is still in the field of acid catalyzed reactions, although recently the advent of basic zeolites has opened up the possibility of base catalyzed reaction paths [1,2,10,44,45].

The desire to raise product yield and to lower process costs were always the driving force for catalyst development; this is also true for zeolite cata-

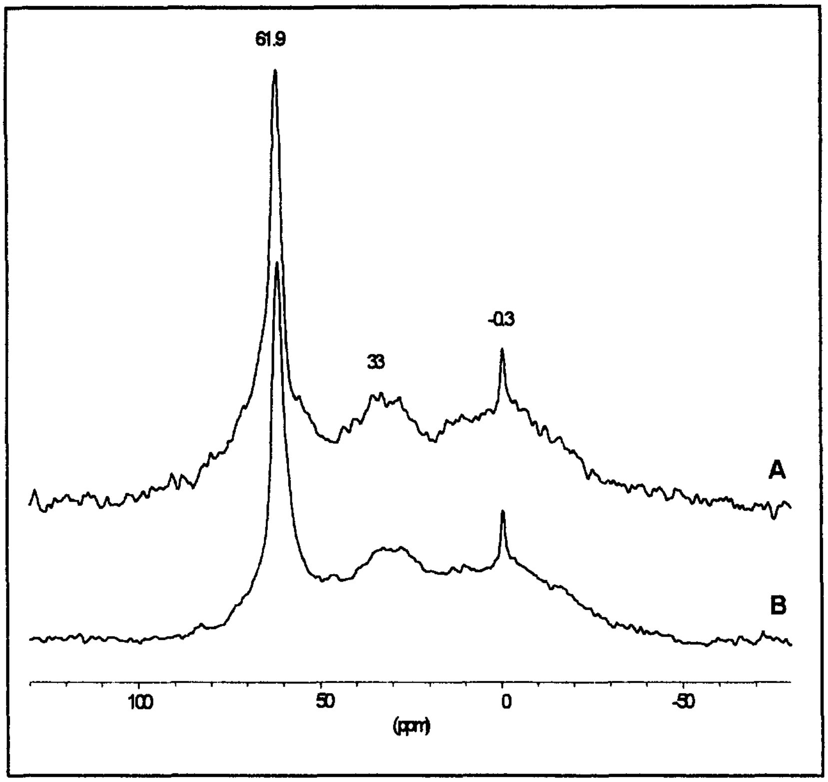

Fig. 11. 130 MHz ^{27}Al MAS NMR spectra of catalysts A and B.

lysts. In recent times the need to protect our environment has induced the chemical industry to develop new, highly selective catalysts which yield purer products and avoid side reactions leading to the formation of undesired and very often toxic by-products and in particular avoid the inevitable formation of salts. We need a clean chemistry!

The conclusion is that new production concepts and new processes using new catalysts have to be found and developed. New, better products, especially in the field of pharmaceuticals and agrochemicals as well as new, interesting monomers for the development of better polymers must be introduced into the market. Thereby, zeolite catalysis can be extremely helpful.

There is still much to be done. However, more and more researchers from the areas of organic chemistry should get involved in the catalysis business and some of them should also evaluate the potential of zeolites in organic synthesis.

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