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Synthesis of intermediate and fine chemicals on heterogeneous catalysts with respect to environmental protection

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Abstract

Heterogenous catalysis holds many potentials for replacing the the outdated 'end-of-pipe' strategy by the application of 'reactor or production integrated environmental protection'. Three industrially important reactions employing zeolites as heterogenous catalysts demostrate to which extent high product yields are achieved accompanied by a minimized amount of contaminations. This attainment includes the search for optimal reaction conditions, as well as the application of an appropriate reactor design. These vital aspects for the realization of industrial processes have to be regarded as a unit instead of investigating catalyst and process desing separately, which could lead to a substantial reduction of development costs.

Keywords: Beckmann rearrangement; Epoxide rearrangement; Olefin amination; Zeolite; Enviromental protection

1. Introduction

The sensibility for environmental protection has increased in the public, political and economical world during the last 10 years, because quality of life is strongly connected to a clean environment. The strongest impulse for developing new, more efficient and selective catalyst systems and for the realization of new process technology is strongly related to environmental compatibility. The target must be no waste production, in particular no salt formation, 100% selectivity and zero emission. That induces: "Reactor or Production Integrated Environmental Protection". This implies the use of better catalysts, the determination of thermodynamic and kinetic properties of chemical reactions as well as the choice of the most suitable type of reactor along with the optimal reaction conditions. Catalyst development, reactor design and/or process development have to be regarded as a unit.

Industrial production is mainly based on catalytic processes. In bulk chemicals production mainly heterogeneous catalysts are employed. Especially in the field of fine chemicals but also of intermediates most processes are still homogeneously catalyzed by the use of Lewis/Brønsted acidic and Lewis/Brønsted basic catalysts. The well known drawbacks of such homogeneous catalysts have to be overcome by applying heterogeneous catalysis. Zeolitic catalysts with their numerous adjustable catalytic properties are gaining in importance in this trend [1–10,12]. In this respect, three examples of industrial interest will be described to demonstrate the potential of zeolitic catalysts and to elucidate to what extent catalyst

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development and process engineering are dependent upon each other. The examples are:

- Beckmann rearrangement in the gas phase at high temperature in a fixed bed as well as in a fluidized bed reactor.
- Epoxide rearrangement in the liquid phase at very low temperature in a slurry reactor.
- Direct amination in the supercritical phase at high temperature and high pressure in a fixed bed reactor.

2. Vapor-phase Beckmann rearrangement

2.1. Introduction

As a starting material for the nylon-6 synthesis, ϵ-caprolactam is of high industrial importance. Recently, a new route for the production of ϵ-caprolactam and adipic acid was introduced. The first steps of this route are 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 (Asahi-Process, 60 000 t/a since 1990). In the case of ϵ-caprolactam, after the oxidation of the cyclohexanol to cyclohexanone, the oximation to cyclohexanone oxime is carried out in the presence of ammonia and hydrogen peroxide 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. Compared to the conventional method this is an energetically and economically favorable as well as environmentally friendly alternative route, e.g., there is no inevitable salt formation of ammonium sulfate. However, the heterogeneously catalyzed Beckmann rearrangement step is not commercialized so far due to some 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 the heterogeneous catalyst, e.g., TS-1, and still perform the Beckmann rearrangement in a homogeneously catalyzed procedure. A great problem is the fast deactivation of the heterogeneous catalysts. Our investigations have been focused on the use of B-MFI [13] zeolite for the Beckmann rearrangement.

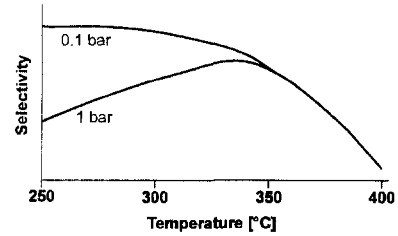


Fig. 1. Influence of temperature and pressure on ϵ-caprolactam selectivity in the presence of B-MFI catalyst in toluene as a solvent.

2.2. Results and discussion

Investigations in the fixed bed showed us [16] that temperatures above 380°C led to major selectivity reduction due to the decomposition of caprolactam and other side reactions. Lower temperatures enhanced depositions on the catalyst surface and therefore also caused a drop in selectivity. Catalyst lifetime increased along with temperature. It is assumed that coke precursors or deactivating compounds desorb more easily at elevated temperatures. Thus, the reaction was carried out at a pressure below 1 bar to facilitate the desorption of deposits on the catalyst surface. A general picture of such dependencies is illustrated in Fig. 1.

Even though the selectivity to ϵ-caprolactam increased significantly with reduced pressure, the service time of the catalyst could not be improved [16]. Polar solvents such as methanol or ethanol showed higher yields and lower deactivation rates than nonpolar solvents, such as toluene or benzene [14,16]. 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 [11,15]. In contrary to the disclosed results, it was shown that conversion and selectivity were raised with a larger amount of water up to 6 mole per mole oxime using the B-MFI zeolite catalyst [16]. The effect of water addition on the catalyst service time is also significant [16].

Nevertheless, the catalyst service time without regeneration is not expected to exceed a few days. 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 (Table 1). The results obtained on the first day are very similar to the results after the 40th day. Conversion, selectivity and drop in conversion within 6 h TOS remained almost the same.

Table 1
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.

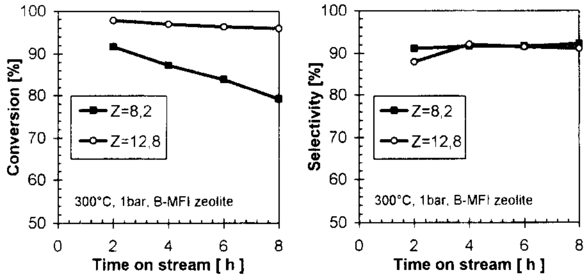


Fig. 2. Beckmann rearrangement in the fluidized bed (Z-number represents gas velocity).

The catalyst service time is still not sufficient and regeneration inside a fixed bed does not represent the most favorable solution. We therefore changed the reactor system to a fluidized bed.

Employing this fluidized bed of laboratory scale we found that selectivity and starting conversion (Fig. 2) are in good agreement with the results obtained in the fixed bed reactor [16]. 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.

2.3. *Characterization*

The rearrangement was investigated over catalysts with different crystal sizes. With increasing external surface area, i.e., decreasing diameter the conversion increases significantly. This is an important hint that the external surface area is of relevance for the rearrangement. Decrease of selectivity, however, shows that there must be a considerable amount of molecules entering the pore system and being converted to different by-products [17]. These findings are in agreement with investigations done by Yashima and coworkers [18,19].

The fresh and the spent catalysts have been extensively investigated by spectroscopic methods such as XPS, SIMS, MAS-NMR, XRD, FTIR and physical measurements such as thermogravimetric analysis and adsorption experiments [17].

Here only a few remarks should be made with respect to their acidic strength. We believe [12] that only extremely weak Brønsted acid sites are needed for the Beckmann rearrangement. To find out whether almost neutral silanol groups are responsible for a good yield and catalyst lifetime, the catalytic performance of amorphous silica was compared to an untreated silicalite as well as to an ammonia treated silicalite. The amorphous silicate gives an intermediate selectivity of 50–60%. The conversion is quite low, about 30%, due to the low density of terminal and vicinal silanol groups (FTIR spectra: 3740 and 3690 cm^{-1}, respectively). The untreated silicalite shows a higher conversion but a lower selectivity of only 26% (FTIR spectra: strong terminal silanol groups at 3740 cm^{-1}). Silicalite treated with ammonia gave a fairly high conversion of about 75% and selectivity of about 93%. In this case investigations with FTIR showed a broad band at 3500 cm^{-1}, which is related to internal and external silanol nests on zeolites with MFI structure. These silanol nests should be the most suitable species for the rearrangement as their appearance is connected to a remarkable increase of conversion and selectivity. Also in the case of B-MFI zeolite such silanol nests have been identified. The MFI-zeolite structure is crucial for the catalytic performance because in contrast to amorphous silica gels the silanol nests are well dispersed on the surface in equidistant positions.

3. Selective isomerization of α-pinene oxide

3.1. *Introduction*

α-Pinene oxide (1) is a reactive substrate which rearranges easily under the influence of acid catalysts [20]. Thereby many products can be formed as shown in Fig. 3. For example, compounds such as isomeric campholenic aldehyde, *trans*-carveol, *trans*-sobrerol, isopinocamphone or *p*-cymene are observed.

The industrially most desired compound is campholenic aldehyde (2), an important intermediate for

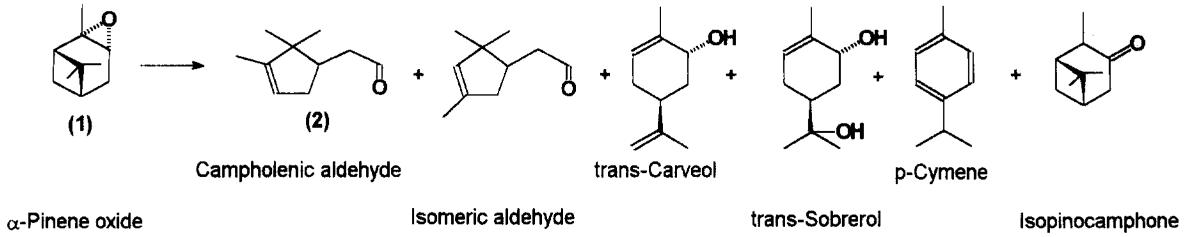


Fig. 3. Products obtained by α-pinene oxide rearrangement.

the synthesis of sandalwood-like fragrance chemicals like santalol [21]. The reaction mechanism itself is not well understood and still discussed in literature [22].

The zinc halogenides $ZnBr_2$ and $ZnCl_2$ are known as effective homogeneous catalysts with selectivities of about 85% to campholenic aldehyde [23,24]. Nevertheless, several drawbacks prevail, like destruction of the catalyst after reaction, corrosivity, toxicity and waste water pollution with the heavy metal zinc, which is harmful to sludge treatment facilities.

Below, we report on a new catalytic process, combining good selectivities with environmental compatibility and reusability.

3.2. *Results and discussion*

In a catalyst screening numerous heterogeneous systems such as transition metal oxides, phosphates and zeolites have been checked in continuous fixed bed reactions under gas phase conditions as well as in slurry reactors at various temperatures, residence times, solvents etc. [25].

Surprisingly we found that the three-dimensional large pore system (7.4 Å) with supercages of 12 Å and a high amount of mesopores make US-Y zeolites very suitable for this reaction. They allow a good migration of above reaction compounds into the channel system. Under the given conditions at a temperature of 0°C in a batchwise operated slurry reactor, we obtained selectivities between 75% and 80% at a conversion of 30% with commercially available highly dealuminated H-US-Y zeolites ($SiO_2/Al_2O_3=70$), which were kindly provided by the PQ-Corporation. 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 gives a strong enhancement in activity without loss in selectivity for the desired aldehyde. The conversion achieved was about 100%.

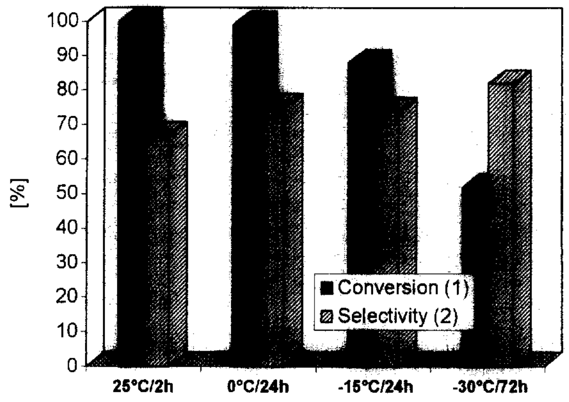


Fig. 4. Influence of temperature with catalyst B. Batch reactor, catalyst loading=7.5 g epoxide/g H-US-Y, solvent 30.0 g toluene.

With respect to the temperature influence, Fig. 4 shows increasing selectivity for campholenic aldehyde with lower temperature, which can be explained by an improved kinetic reaction control and/or by the avoidance of side reactions of campholenic aldehyde. The catalyst is still active even at −15°C and −30°C. Selectivity to campholenic aldehyde reaches nearly 80% (Fig. 4). The fact that a zeolitic catalyst is still very efficient at temperatures down to −30°C is surprising. Finally, the mesoporous H-US-Y (70) which was treated with HCl at pH=2 showed a catalytic performance at temperatures of 0–15°C similar to the homogeneous $ZnBr_2$ system. Yields between 80% and 85% were obtained.

For industrial purpose, the homogeneous catalyst in the batch reactor only has to be replaced by the heterogeneous zeolitic material without any further changes of apparatus.

3.3. *Characterization of the catalysts*

To elucidate the reason for the better performance of the acid treated catalyst (B) having a SiO_2/Al_2O_3

Table 2
Comparison of analytical data obtained from aluminum AAS, FTIR and nitrogen adsorption for H-US-Y(70) before (A) and after acid treatment (B)

Catalyst	Al AAS wt% (unit cell composition[a])	FTIR stretching frequency (unit cell composition[b])	Nitrogen 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 [26].

ratio of 70, we examined it in comparison with the untreated H-US-Y catalyst (A) with different analytical methods (Table 2).

Atomic adsorption spectroscopy (AAS) of aluminum and Fourier transform infrared spectroscopy (FTIR) of both samples indicate that there must exist a large amount of EFAl species in the zeolite. Assuming that all aluminum atoms are incorporated into the framework, a number of four Al atoms could be present in the unit cell according to our AAS results. The position of the FTIR outer T–O–T stretching frequency [26] gives direct information on the aluminum content in the framework. Our experimental results, however, indicate that only about one Al atom per unit cell is incorporated in the framework.

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

To distinguish Brønsted from Lewis acid sites, FTIR measurements of zeolite samples loaded at 150°C with pyridine were performed [27]. Intense bands at 1445 and 1490 cm^{-1} and only weak bands at 1545 cm^{-1} were observed, i.e., the samples contained significantly more Lewis than Brønsted acid sites. These findings are in agreement with the results from Al AAS.

The ^{29}Si MAS-NMR measurements of the untreated as well as of the treated sample show that only amorphous silica, which is created in addition to extraframework aluminum in the hydrothermal dealumination process, is removed by acid treatment with HCl (pH=2) [25]. This can easily be understood since the maximum solubility of silica [29] 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. The correctness of our explanation for the catalytic performance is confirmed by ^{27}Al magic-angle spinning (MAS) NMR spectroscopy [25,28]. We believe the silica species to block most of the catalytically active centers, i.e., highly dispersed Lewis acidic alumina sites immobilized in the micro- and mesopores of the parent US-Y zeolite.

4. Direct amination of olefins

Extensive work has been done by Air Products and BASF [30–36]. Among the heterogeneous catalysts studied, acidic zeolites were found superior to other materials. Acidity is crucial. On neutral sodium zeolites no amination reaction occurs. Thermodynamics state the amination to be favored by low temperature, high pressure and high ammonia to olefin ratio. However, in the presence of zeolites these facts result in a dilemma as the chemical equilibrium between the H^+- and the NH_4^+-form of the zeolites has to be considered:

- The higher the temperature the more the acidic form is favored.
- The higher the NH_3-concentration the more the NH_4^+-form is favored. Nevertheless, an excess of NH_3 over the olefin is needed in order to avoid the oligomerization of the olefins.
- The higher the pressure the more the NH_4^+-form is favored.
- The higher the acidic strength of the zeolite the stronger the NH_4^+-form.

That means the reaction parameters, which favor the amination of the olefins, are in contradiction to the formation of the necessary H^+-form of the zeolite.

Therefore, the right balance between temperature, pressure, ammonia to olefin ratio and acidic strength of the zeolite has to be found.

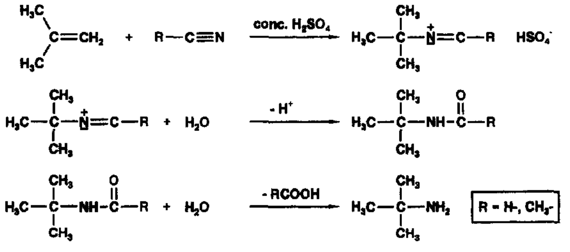
Furthermore, the reaction takes place in the inner part of the zeolite and shape selectivity as well as shape selective restrictions are involved. Even though ethylene is effectively aminated by all zeolitic catalysts and especially by small pore zeolites such as H-erionite or H-clinoptilolite, propene shows only low conversion and isobutene does not react at all over these small pore zeolites. Concerning the reaction mechanism, it is found that acidic sites are necessary and the amination occurs via protonated intermediates as evidenced by the relative ease: isobutene>propene>ethene.

As an example, isobutene reacts with ammonia according to Eq. (1) over pentasil zeolites in a fixed bed at 300°C and 300 bar, i.e., at supercritical conditions, to give excellent results. The selectivity amounts to around 99% at 12–15% conversion.

$$(H_3C)_2C{=}CH_2 + NH_3 \longrightarrow H_3C{-}C(CH_3)_2{-}NH_2 \qquad (1)$$

A recyclization of NH_3 and isobutene is necessary. The oligomerization of isobutene is negligible because ammonia is present in excess (molar ratio ammonia/olefin=1.3–2.0). Furthermore, the dialkylation does not occur due to the transition state shape selectivity. While X and Y zeolites suffer from the disadvantage of rapid deactivation, Re-Y zeolite and the pentasil zeolites yield commercially acceptable service time.

This one step procedure for the production of *t*-butylamine evidently provides advantages over the traditional Ritter reaction according to Eq. (2).



$$(H_3C)_2C{=}CH_2 + R{-}C{\equiv}N \xrightarrow{\text{conc. } H_2SO_4} H_3C{-}C(CH_3)_2{-}\overset{+}{N}{=}C{-}R \quad HSO_4^-$$
$$H_3C{-}C(CH_3)_2{-}\overset{+}{N}{=}C{-}R + H_2O \xrightarrow{-H^+} H_3C{-}C(CH_3)_2{-}NH{-}C({=}O){-}R$$
$$H_3C{-}C(CH_3)_2{-}NH{-}C({=}O){-}R + H_2O \xrightarrow{-RCOOH} H_3C{-}C(CH_3)_2{-}NH_2 \quad \boxed{R = H, CH_3}$$

(2)

The starting olefin for the Ritter route is the same as for the direct amination. However, in the conventional three step reaction course the highly toxic HCN is used in the presence of hazardous highly concentrated sulfuric acid. The resulting toxic formamide has to be hydrolyzed in the presence of HCOOH or CH_3COOH. The reaction sequence is inefficient in both raw material usage and by-product formation; around 4.5 kg of raw material has been used to form 1 kg TBA and approximately 3 kg Na_2SO_4 contamination per kg TBA are inevitably formed as by-product. Therefore, the direct one step amination is really an environmentally benign and economical process even though high pressure and high temperature as well as the recyclization of starting materials are costly factors.

5. General conclusions

The three examples were cited to demonstrate the potential of zeolites as catalysts in the organic synthesis of fine and intermediate chemicals. Their 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 [1,2,10,37,38].

The desire to raise product yield and to lower process costs were always the driving force for catalyst development; this is also true for zeolitic catalysts. 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 the formation of salts. We need a clean, a *green 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, we have to keep in mind the simultaneous development of the catalyst and the process, which together should be considered as a unit.

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