Screening of Co-ZSM-5 and co-beta coatings in a high throughput microreactor for the ethane/ethylene ammoxidation reaction

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2006

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Screening of Co-ZSM-5 and Co-Beta Coatings in a High Throughput Microreactor for the Ethane/Ethylene Ammoxidation Reaction

C.J.B.U Schiepers
May 2006

Graduation Report

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Summary

Recently, the concept of combinatorial approaches to accelerate the development of new and existing catalysts has raised a great deal of interest. Catalyst screening devices and techniques are being developed aiming for the ability to rapidly test various catalysts, and eventually reduce the time-to-market.

In this research, a high throughput microreactor was used to screen various sets of zeolitic Beta (BEA) and ZSM-5 coatings and determine the catalytic activity (TOF), the conversion and the selectivity. As a model reaction, the ammoxidation reaction of ethylene to acetonitrile was applied. Because of the exothermic nature of this reaction, a highly conductive Mo substrate ($\lambda=140 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) was chosen as a support for the zeolitic coating.

Co-BEA and Co-ZSM-5 have proven to be very active catalysts in the ammoxidation reaction of ethylene or ethane. Co-zeolitic coatings were synthesized according to an in-situ synthesis procedure [1,2] and subjected to a post treatment procedure for the activation with cobalt. A number of Co-BEA coatings with Si/Al ratios of 15, 17 and 23 and Co-ZSM-5 with a Si/Al value of 20 were synthesized and featured Co/Al ratios varying from 0.65 to 0.85.

It was observed that the activity in the ethylene ammoxidation decreased with increasing Al content in the zeolite structure, resulting in TOF values of 0.21 s$^{-1}$ and 0.44 s$^{-1}$ on Co-BEA-23 and Co-BEA-15 coatings, respectively. Comparing to data from literature, a catalytic coating activity was observed which was 30 times as high as the one on Co-ZSM-5 pelletized catalysts (0.44 vs. 0.013 s$^{-1}$, respectively). Furthermore, it was demonstrated that the activity of Co-zeolitic coatings was substantially lower in the ammoxidation reaction of ethane to acetonitrile ($1.25\cdot10^{-3} \text{ s}^{-1}$), which was due to the rate limiting oxidative dehydrogenation step from ethane to ethylene.

The temperature and the contact time were varied to optimize the reaction conditions. The conversion of ethylene as well as the selectivity to acetonitrile showed an increase with temperature, up to a value of both 23%. The formation of methanol and hydrogen cyanide was not expected, however, a high selectivity with a maximum of 47% was observed for both of the components. Optima in the TOF value of the catalyst as function of the GHSV were observed at standard process conditions.
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Figure 1: The comparison between the classic (left) and the combinatorial approach (right) in the development of catalysts [3].
1 Introduction

1.1 Scope of the research field

In today’s chemical industries, solid-based catalysis is widely applied in the manufacturing of numerous quantities of chemicals and fuels. The contribution of efficient catalysts to more economical chemical processing is considerable. Manufacturers benefit, for instance, because processes can be carried out at lower temperatures and pressure, resulting in reduced operating costs. Furthermore, a higher selectivity is correlated with smaller quantities of undesired by-products, resulting in increased product yields and a less capital intensive purification process. The development of solid catalysts is often challenging and time-consuming. To maintain a high level of profitability and cope with increased competition, the time-to-market has to be reduced. As a consequence, the development of new and rapid catalyst optimization techniques has attracted a great deal of interest. Recently, high throughput experimental processes have proven to be a very useful tool in this field. A high throughput approach concerns the design, synthesis and simultaneous testing (screening) of wide arrays of catalysts (Fig. 1).

A growing field of chemical interest is the gas to liquid conversion to transform cheap and abundant hydrocarbons from natural gas to liquid fractions, which can be easily stored and transported. Some reactions can be intensified, when carried out in microstructured reactors. The highly exothermic ammoxidation reaction of ethane or ethylene to acetonitrile exemplifies such a process. Comparing to conventional catalysts, an increase of two orders of magnitude in reaction rate was observed on transition metal ion-exchanged zeolite catalysts [4]. These catalysts can be prepared as thin coatings for application in microstructured reactors [1]. This study is focused on the screening of ZSM-5 and zeolite Beta coatings in a high throughput microreactor (HTMR) at realistic process conditions. In this approach the catalytic coating composition as well as the process conditions are optimized for a microreactor application.

1.2 Thesis outline

Chapter 2 contains a literature review on Co-Beta catalyst properties and on the characteristics of the ethane and ethylene ammoxidation reaction.

In Chapter 3, the equipment, experimental procedures and catalyst preparation are described. Furthermore, the experimental data are verified for intrinsic kinetics. In the last section the calculations used for data processing are listed.

Chapter 4 provides the characterization results of the zeolitic catalytic coatings. Furthermore, the results of the screening experiments are discussed as well as the optimization of the reaction conditions.

The main conclusions and recommendations of this study are provided in Chapter 5.
Figure 2: SiO$_4$ tetrahedral building blocks of a zeolite.

Figure 3: 3D representation of the large pore zeolite BEA framework.

Table 1: Properties of some common zeolites.

<table>
<thead>
<tr>
<th>Name</th>
<th>Code</th>
<th>Channels</th>
<th>Window / channel diameter (nm)</th>
<th>Pore volume (cm$^3$·g$^{-1}$)</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>LTA</td>
<td>3D, cages connected by windows, cubic</td>
<td>0.45</td>
<td>0.30</td>
<td>1</td>
</tr>
<tr>
<td>Zeolite X</td>
<td>FAU</td>
<td>3D, cages connected by windows, tetragonal</td>
<td>0.75</td>
<td>0.35</td>
<td>1-1.5</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>FAU</td>
<td>3D, cages connected by windows, tetragonal</td>
<td>0.75</td>
<td>0.35</td>
<td>≥ 2.5</td>
</tr>
<tr>
<td>Mordenite</td>
<td>MOR</td>
<td>1D, one straight channel</td>
<td>0.70; 0.65</td>
<td>0.20</td>
<td>≥ 5</td>
</tr>
<tr>
<td>Zeolite L</td>
<td>LTL</td>
<td>1D, one straight channel, one sinusoidal, mutually perpendicular channels</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>MFI</td>
<td>2D, Cages connected by windows, cubic</td>
<td>0.55</td>
<td>0.15</td>
<td>≥ 10</td>
</tr>
<tr>
<td>Zeolite Beta</td>
<td>BEA</td>
<td>3D, Cages connected by windows, cubic</td>
<td>0.76; 0.64</td>
<td>0.25</td>
<td>≥ 5</td>
</tr>
</tbody>
</table>
2 Literature Review

2.1 Zeolites

Zeolites form a unique class of oxides, consisting of well-defined, microporous, and crystalline aluminosilicates. They can be either found in nature or synthesized artificially and are used in various applications, such as household detergents, desiccants and catalysts. The zeolite framework is very open and contains channels and cages, presenting a high specific surface area, where adsorbed molecules and cations may reside and react. Their specific acidic property makes zeolites very attractive for catalytic application. Consequently, a wealth of zeolite catalyzed reactions of hydrocarbons has been discovered and industrially implemented since the mid-1960s.

The tetrahedral coordinated \([\text{SiO}_2]\) and \([\text{AlO}_2]\^-\) units (Fig. 2) can be arranged by sharing O-corner atoms in many different ways to build a crystalline lattice (Fig. 3). The specific order, in which networks of tetrahedral units are connected, define the crystal structure of the zeolite. During the hydrothermal synthesis of zeolites, template molecules, such as tetraethylammonium hydroxide for zeolite BEA, act as structure directing agents. Zeolites can also exhibit large differences in pore structure and dimensions, which strongly affects the internal surface area and the accessibility of the internal microporous volume. The properties of some of the most common zeolites are listed in Table 1 [5].

The aluminum containing zeolite framework bears a net negative charge, which is to be balanced by cations. The cations located in the channels and cavities of the structure often possess a high degree of mobility, giving rise to easy ion exchanges. The atomic composition of zeolites is given by:

\[
\text{M}^{x+}_{x/n} \cdot \left[ (\text{AlO}_2)_x \cdot (\text{SiO}_2)_y \right] \cdot w\text{H}_2\text{O}
\]

where \(y/x\) represents the Si/Al ratio, \(n\) the cation valence and \(w\) the corresponding number of water molecules in the voids of the zeolite.

2.2 Zeolitic coatings

2.2.1 General

Zeolitic thin coatings are of interest for use as catalysts [6,7,8,9], adsorbents [10,11], and membranes [12]. Advantages of zeolitic coatings comparing to the zeolite pellets or extrudates are an improved accessibility of the crystallites as well as the catalyst sites, an effective heat removal from the reaction zone via a metal substrate, and the absence of meso- and macropores in a single layer of crystals. The high specific surface area of the zeolitic coating and the fact that reaction specific transition metals can be introduced into the structure, results in an optimal utilization of the catalytic material [13]. Zeolitic coatings are, for example, applied as structured packings in catalytic reactors, mostly with respect to environmental processes where a low pressure-drop is required. An even more intensified contacting of the reactants with zeolitic coatings can be obtained in microstructured reactors, which showed promising results in a number of applications [8]. The hydrothermal synthesis of zeolite crystals on substrates is a sophisticated technique used to in-situ grow and immobilize the zeolite crystals on a substrate [1,7,14].
**Figure 4:** 2D projection of the BEA framework structure along the [010] plane (top) and the channel cross-sections along the [010] and [100] planes (bottom).

**Figure 5:** Schematic representation of the interconnecting channels in the BEA framework.

**Al single sites**

**Al pairs**

**Figure 6:** The positioning of the Al single sites and Al pairs in the ZSM-5 framework.

**Figure 7:** Location of α, β, and γ-type Co cations in the framework of polymorph C (left) and polymorph A and B (right) of BEA zeolite.
2.2.2 Zeolite BEA and ZSM-5

This study focuses on zeolite Beta (BEA) and ZSM-5 coatings, which were in situ grown on a metal substrate [1,2,14]. Both zeolite structures are characterized by a very open framework, containing interconnecting channels. Characteristics of ZSM-5 are extensively discussed in [15]. Zeolite Beta (BEA) has a Si/Al molar ratio above 5, which consists of five- and six-membered rings forming an intersecting three-dimensional structure of 12-membered ring channels (Fig. 3). BEA is composed of channels along two different axis, viz. the [001] axis with dimensions of 7.6 x 6.6 Å and the [100] axis with dimensions of 5.6 x 5.6 Å (Fig. 4). The two channel systems are interconnected as schematically shown in Fig. 5. The third zigzag channel is obtained via the intersecting points of the two straight channels.

Zeolite Beta has proven to be a versatile catalyst and is applied in, for example, the reduction of NO \(_x\) and Friedel Crafts reactions [16]. Furthermore, cobalt activated zeolite BEA proved to be very active in the ammoxidation reaction of ethane and ethylene to acetonitrile [17].

2.2.3 Distribution of aluminum in Co-BEA

There are two highly important properties of silicon-rich zeolites (Si/Al > 10) relevant to catalysis; the high acid strength of the protonic sites and the exceptional redox activity of the exchanged transition metal ions. In addition to the zeolite topology, both the concentration and the distribution of aluminum in the framework control these properties. Aluminum atoms can be located in the framework of silicon-rich zeolites as "single" Al atoms \([(\text{Si-O})_{n>2}\text{-Al-O-(Si-O)}_{n>2}\text{]}\), which are balanced by monovalent cations and as Al "pairs" \[\text{Al-O-(Si-O)}_{1,2}\text{-Al}\] located in one ring-forming cationic site for bare divalent cations (Fig. 6). The geometry and charge of zeolite rings accommodating the Al pairs or the single Al atoms affects the coordination of the cations in the zeolites, their redox properties and also the acidity of the protonic sites [18].

Bortnovsky et al. [19] showed that the framework sites bearing close AlO\(_2^−\) groups in the BEA framework represent a rather unstable environment with weakened framework Al-O bonds. Metal cations, such as Co\(^{2+}\), greatly prefer occupation of such cationic sites with two “neighboring” framework AlO\(_2^−\) groups. The Co-occupation of the Al-pairs results in a high stabilization of the BEA zeolite framework. Therefore, it protects the aluminum bonding in the framework against substantial internal rearrangements, which could lead to the formation of octahedrally coordinated Al Lewis sites.

2.2.4 Catalytic sites in Co-BEA

Divalent Co ions can be located in the BEA framework by cation exchange and are balanced by two framework AlO\(_2^−\) groups or one framework AlO\(_2^−\) and a hydroxyl group. At the maximum degree of Co ion exchange the distribution of Co\(^{2+}\) reflects the distribution of Al pairs at different cationic sites [18].

Dĕdeček et al. [20] reported that zeolite Beta represents a mixture of three polymorphs, A, B and C. Three different Co\(^{2+}\) coordinated sites can be distinguished within these BEA polymorphs, which are indicated with α, β and γ in Fig. 5 and 7. The α-type Co\(^{2+}\) ions are four coordinated ions and can be attributed to the cationic site formed by an elongated six-membered ring composed of twofold five-membered rings in the polymorph C type.
Figure 8: Local arrangement of α, β, and γ-sites in BEA zeolite.

Figure 9: Relative concentration of single Al atoms (s) and Al pairs in the α, β and γ sites in ZSM-5; (left) Si/Al=12.5 and Co/Al=0.42; (right) Si/Al=22.5 and Co/Al=0.12 [18].

Table 2: Performance of Co exchanged catalysts in the ammoxidation of ethane and ethylene.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al (molar)</th>
<th>Co/Al (molar)</th>
<th>T (°C)</th>
<th>Hydrocarbon conv. (%)</th>
<th>Select. to C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;N (%)</th>
<th>TOF (10&lt;sup&gt;-3&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane ammoxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-Nb-Mo oxide&lt;sup&gt;1&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>350-500</td>
<td>18.0</td>
<td>10.0</td>
<td>-</td>
</tr>
<tr>
<td>Nb-Sb oxides&lt;sup&gt;2&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>480-540</td>
<td>30.0</td>
<td>50.0</td>
<td>-</td>
</tr>
<tr>
<td>Co-Y&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2.5</td>
<td>0.58</td>
<td>450</td>
<td>8.4</td>
<td>60.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Co-Nu-87&lt;sup&gt;4&lt;/sup&gt;</td>
<td>16.9</td>
<td>0.49</td>
<td>450</td>
<td>26.7</td>
<td>46.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Co-ZSM-11</td>
<td>30.2</td>
<td>0.93</td>
<td>450</td>
<td>38.2</td>
<td>48.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Co-ZSM-5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>11.0</td>
<td>0.49</td>
<td>450</td>
<td>35.3</td>
<td>50.8</td>
<td>8.5</td>
</tr>
<tr>
<td>Co-BEA&lt;sup&gt;4&lt;/sup&gt;</td>
<td>12.9</td>
<td>0.42</td>
<td>450</td>
<td>35.3</td>
<td>50.8</td>
<td>8.5</td>
</tr>
<tr>
<td>Ethylene ammoxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-ZSM-5&lt;sup&gt;2&lt;/sup&gt;</td>
<td>11.0</td>
<td>0.49</td>
<td>450</td>
<td>57.7</td>
<td>77.0</td>
<td>12.8</td>
</tr>
<tr>
<td>Co-ZSM-11&lt;sup&gt;5&lt;/sup&gt;</td>
<td>30.0</td>
<td>1.10</td>
<td>475</td>
<td>41.1</td>
<td>80.2</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>1</sup> Feed: 5% C<sub>2</sub>H<sub>6</sub> / C<sub>2</sub>H<sub>4</sub>, 10% NH<sub>3</sub> and 6.5% O<sub>2</sub> (He-balanced); F=100 mL/min; 0.3 g catalyst
<sup>2</sup> Aliev et al. (1980) [29]
<sup>3</sup> Cavani and Centi (1991) [30]
<sup>4</sup> Li and Armor (1997) [4]
<sup>5</sup> Li and Armor (1998) [28]
The β-type Co\(^{2+}\) ions are six coordinated ions to an elongated six-membered ring present in the framework of Beta polymorphs A and B. The γ-type Co\(^{2+}\) ions are six coordinated ions with approximately octahedral symmetry or bipyramidal ligand field symmetry located inside the Beta cage of polymorphs A and B. Access to this site from the Beta channel system is limited by the size of these six-membered rings. A magnified representation of the coordinated sites is given in Fig. 8.

The relative concentration of single Al sites as well as α, β and γ cationic sites in ZSM-5 can be distinguished and is shown as a function of the Si/Al ratio of ZSM-5 in Fig. 9. It can be seen that the concentration and distribution of Al pairs among the individual cationic sites is strongly affected by the concentration of aluminum in the framework. At high Si/Al ratios mainly single sites are being formed, whereas, at lower Si/Al ratios, the aluminum atoms are not far apart, which results in the predominant formation of α and β sites [18].

Lee et al. [21] reported that excessive cobalt loadings on zeolitic samples lead to the formation of cobalt oxides in an oxygen rich environment at elevated temperatures. Cobalt oxides have an adverse effect on the ammoxidation to acetonitrile, since they are more active in the total oxidation of hydrocarbons and ammonia [22].

### 2.3 Ammoxidation of ethane and ethylene over Co-BEA

Due to the low cost and abundance of light organic chemicals, the conversion of paraffins and olefins directly to higher value organic chemicals has recently become more important in chemical industries. An important example of such a process is the ethane or ethylene ammoxidation reaction to acetonitrile over metal exchanged zeolites:

\[
\begin{align*}
C_2H_6 + NH_3 + 3/2 O_2 & \rightarrow CH_3CN + 3 H_2O & \text{(2.2a)} \\
C_2H_4 + NH_3 + O_2 & \rightarrow CH_3CN + 2 H_2O & \text{(2.2a)}
\end{align*}
\]

Li and Armor [4] reported that metal exchanged zeolite catalysts are much more efficient in the ammoxidation reactions than metal oxide catalysts, which were investigated before. An overview of the performance of various catalysts in the ammoxidation reaction is given in Table 2.

#### 2.3.1 Effect of the zeolite topology and the metal cation

The effect of the zeolite topology on the catalytic activity and selectivity was tested on a variety of cobalt exchanged zeolites by Li and Armor [4]. Cobalt BEA and ZSM-5 were identified as the most effective zeolites for the ammoxidation reaction. They share some common features in the zeolite topology, i.e. a multidimensional channel structures with channel apertures of either 10- or 12-membered rings. They show comparable C\(_2\)H\(_6\) conversions and selectivities to C\(_2\)H\(_3\)N at similar reaction conditions, as can be seen in Table 2. On the other hand, the activity per cobalt site (TOF) is 1.5 times higher on zeolite BEA compared to ZSM-5.

Bulánek et al. [23] reported that the contribution of the zeolite matrix is attributed to the diameter and the architecture of the channels, where the Co\(^{2+}\) ions are located. As mentioned in section 2.2.4, the β-type cobalt cations feature the highest activity in the
Table 3: Performance of metal exchanged ZSM-5 in the ammoxidation of ethane.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Si/Al (molar)</th>
<th>Co/Al (molar)</th>
<th>B (wt. %)</th>
<th>T (°C)</th>
<th>Conversion of C_2H_6 (%)</th>
<th>Selectivity to C_2H_5N (%)</th>
<th>TOF (10^{-3} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co¹</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>450</td>
<td>38.2</td>
<td>48.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Cu¹</td>
<td>13.5</td>
<td>0.65</td>
<td>-</td>
<td>450</td>
<td>15.0</td>
<td>0.8</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni¹</td>
<td>11.0</td>
<td>0.50</td>
<td>-</td>
<td>450</td>
<td>11.9</td>
<td>19.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe¹</td>
<td>14.4</td>
<td>0.17</td>
<td>-</td>
<td>450</td>
<td>9.2</td>
<td>16.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Mn¹</td>
<td>12.7</td>
<td>0.31</td>
<td>-</td>
<td>450</td>
<td>26.9</td>
<td>11.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Pd¹</td>
<td>11.1</td>
<td>0.37</td>
<td>-</td>
<td>450</td>
<td>20.3</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Ag¹</td>
<td>14.1</td>
<td>0.71</td>
<td>-</td>
<td>450</td>
<td>13.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Rh¹</td>
<td>11.5</td>
<td>0.23</td>
<td>-</td>
<td>450</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt¹</td>
<td>14.2</td>
<td>0.12</td>
<td>-</td>
<td>450</td>
<td>21.0</td>
<td>2.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Co²</td>
<td>12.0</td>
<td>0.62</td>
<td>-</td>
<td>475</td>
<td>30.6</td>
<td>31.8</td>
<td>3.1</td>
</tr>
<tr>
<td>B/Co²</td>
<td>12.0</td>
<td>0.62</td>
<td>0.5</td>
<td>475</td>
<td>36.6</td>
<td>49.3</td>
<td>5.9</td>
</tr>
</tbody>
</table>

¹ Feed: 5% C_2H_6, 10% NH_3 and 6.5% O_2 (He balanced); F=100 mL/min; 0.2 g catalyst [4]
² Feed: 10% C_2H_6, 10% NH_3 and 6.5% O_2 (He balanced); F=100 mL/min; 0.3 g catalyst [28]

Table 4: Temperature dependence on the performance of Co exchanged zeolites in ammoxidation of ethane and ethylene.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al (molar)</th>
<th>Co/Al (molar)</th>
<th>B (wt. %)</th>
<th>T (°C)</th>
<th>HC conv. (%)</th>
<th>Select. to C_2H_5N (%)</th>
<th>Select. to C_2H_4 (%)</th>
<th>TOF (10^{-3} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane ammoxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-ZSM-5¹</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>425</td>
<td>36.0</td>
<td>52.0</td>
<td>22.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Co-ZSM-5²</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>450</td>
<td>38.2</td>
<td>48.7</td>
<td>28.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Co-ZSM-5³</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>475</td>
<td>38.4</td>
<td>42.0</td>
<td>30.2</td>
<td>10.1</td>
</tr>
<tr>
<td>Co-BEA¹</td>
<td>12.0</td>
<td>0.65</td>
<td>-</td>
<td>425</td>
<td>26.2</td>
<td>65.5</td>
<td>14.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Co-BEA²</td>
<td>12.0</td>
<td>0.65</td>
<td>-</td>
<td>450</td>
<td>31.7</td>
<td>57.8</td>
<td>22.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Co-BEA³</td>
<td>12.0</td>
<td>0.65</td>
<td>1.0</td>
<td>425</td>
<td>34.3</td>
<td>49.9</td>
<td>29.9</td>
<td>5.3</td>
</tr>
<tr>
<td>B/Co-BEA¹</td>
<td>12.0</td>
<td>0.65</td>
<td>1.0</td>
<td>425</td>
<td>20.3</td>
<td>71.4</td>
<td>40.3</td>
<td>4.5</td>
</tr>
<tr>
<td>B/Co-BEA²</td>
<td>12.0</td>
<td>0.65</td>
<td>1.0</td>
<td>450</td>
<td>27.9</td>
<td>64.9</td>
<td>18.0</td>
<td>5.6</td>
</tr>
<tr>
<td>B/Co-BEA³</td>
<td>12.0</td>
<td>0.65</td>
<td>1.0</td>
<td>475</td>
<td>33.7</td>
<td>57.6</td>
<td>25.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Ethylene ammoxidation

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al (molar)</th>
<th>Co/Al (molar)</th>
<th>B (wt. %)</th>
<th>T (°C)</th>
<th>HC conv. (%)</th>
<th>Select. to C_2H_5N (%)</th>
<th>Select. to C_2H_4 (%)</th>
<th>TOF (10^{-3} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-ZSM-5¹</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>400</td>
<td>48.4</td>
<td>81.4</td>
<td>-</td>
<td>11.3</td>
</tr>
<tr>
<td>Co-ZSM-5²</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>425</td>
<td>53.4</td>
<td>79.8</td>
<td>-</td>
<td>12.3</td>
</tr>
<tr>
<td>Co-ZSM-5³</td>
<td>11.0</td>
<td>0.49</td>
<td>-</td>
<td>450</td>
<td>57.7</td>
<td>77.0</td>
<td>-</td>
<td>12.8</td>
</tr>
</tbody>
</table>

¹ Feed: 5% C_2H_6, 10% NH_3 and 6.5% O_2 (He balanced); F=100 mL/min; 0.2 g catalyst [4]
² Feed: 10% C_2H_6, 10% NH_3 and 6.5% O_2 (He balanced); F=100 mL/min; 0.3 g catalyst [28]

Table 5: Contact time dependence on the performance of Co exchanged zeolites in ammoxidation of ethane.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al (molar)</th>
<th>Co/Al (molar)</th>
<th>Catalyst wt. (g)</th>
<th>GHSV (h⁻¹)</th>
<th>Conversion of C_2H_6 (%)</th>
<th>Select. to C_2H_5N (%)</th>
<th>TOF (10^{-3} s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-ZSM-5</td>
<td>11.0</td>
<td>0.49</td>
<td>0.03</td>
<td>444</td>
<td>7.7</td>
<td>45.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Co-ZSM-5</td>
<td>11.0</td>
<td>0.49</td>
<td>0.06</td>
<td>222</td>
<td>7.8</td>
<td>58.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Co-ZSM-5</td>
<td>11.0</td>
<td>0.49</td>
<td>0.12</td>
<td>111</td>
<td>10.0</td>
<td>60.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Co-ZSM-5</td>
<td>11.0</td>
<td>0.49</td>
<td>0.24</td>
<td>56</td>
<td>28.3</td>
<td>49.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

¹ Feed: 5% C_2H_6, 10% NH_3 and 6.5% O_2 (He balanced); F=100 mL/min; T=475°C [28]
ethane and ethylene ammoxidation reaction. In the framework of e.g. mordenite (MOR) and ferrierite (FER), the β-sites are located in the narrow channels. On the other hand, in Co-ZSM-5 they are found at the well accessible intersection of the sinusoidal and the straight channels and in Co-BEA they are located at open positions in the channels of zeolite Beta. Apparently, the effect of the shape of the pores is very important (Table 2).

The type of metal cation strongly affects the catalytic performance [4,24]. Table 3 shows various transition metals in ZSM-5 and the corresponding catalyst performance. Copper appears to be very selective in the oxidation of ethane to ethylene and carbon dioxide, whereas rhodium enhances the total oxidation of ethane. Co-BEA and Co-ZSM-5 showed the best results in selective formation of acetonitrile. As a result, significantly higher TOF values were observed.

The activity of the cobalt cations is decisively affected by the net negative charge of the zeolite framework [25]. An increase in the negative charge by introducing more aluminum into the zeolite framework potentially results in a higher number of cobalt cations that can be accommodated. This results in a higher activity as well as an enhanced stability of the zeolite framework [19]. The dependence of the Al content on the TOF values and the acetonitrile yield of various zeolites is shown in Fig. 10 and Table 2. The TOF considerably increases with a decreasing Al content, with a Si/Al value of 2.5 up to 13.

Boron-modified Co-ZSM-5 exhibited even higher selectivities and conversions [26]. No explanation was given for the enhanced activity. However, it is likely that electron positive boron species withdraw electrons from the negative zeolite framework, which affects the bonding of the cobalt cation at the aluminum sites. Consequently, the cobalt interaction with reaction intermediates may stimulate the conversion into acetonitrile.

2.3.2 Effect of temperature

Table 4 shows the temperature dependence on the catalytic performance of Co-ZSM-5 and Co-BEA [4,24,26]. The conversion of \( \text{C}_2\text{H}_6 \) increases with temperature below 425°C and reaches a constant value above 425°C on Co-ZSM-5 catalyst. This can be attributed to the depletion of \( \text{O}_2 \). This trend was not observed on Co-BEA, but it is expected that the conversion levels off at temperatures above 475°C. The selectivity to \( \text{C}_2\text{H}_3\text{N} \) decreases with an increasing temperature. At elevated temperatures, the oxidation reaction of the reactants becomes more dominant. A higher conversion, selectivity to \( \text{C}_2\text{H}_3\text{N} \) and TOF value were observed in the ammoxidation reaction of ethylene.

Li and Armor [24] also reported that the catalyst is very stable at the reaction conditions and that the influence of water on this reaction is negligible. No significant changes in the catalytic performance were observed on Co-ZSM-5 catalyst after a time-on-stream period of 120 hours.

2.3.3 Effect of contact time

Li and Armor [26] investigated the effect of the contact time by varying the catalyst weight. The contact time (GHSV) dependence on Co-ZSM-5 in the ethane ammoxidation is shown in Table 5. A higher catalyst weight brings about a higher contact time and this is defined by a lower gas hourly space velocity. Higher conversions are attained at lower GHSV. The selectivity to \( \text{C}_2\text{H}_3\text{N} \) shows an optimum at 111 h\(^{-1}\). The activity of the catalyst per cobalt site (TOF) was also reported higher at increased GHSVs.
Figure 10: Acetonitrile yield and TOF of the ammoxidation reaction of ethane as a function of the Si/Al framework ratio for Y-USY (● and ○, resp.) and zeolites of various topologies (□ and ■, resp.). Feed: 10% C2H4, 5-10% NH3 and 6.5% O2 (He balanced), F= 100 ml/min, 0.2 g catalyst, 450°C [25].

Figure 11: Suggested acetonitrile formation pathway [24].
2.3.4 Reaction mechanism

A large amount of C\textsubscript{2}H\textsubscript{4} was formed during the ammoxidation reaction of ethane (see also Table 4). The effect of the type of hydrocarbon was demonstrated by Li and Armor [26]. Tables 2 and 4 show a higher selectivity to acetonitrile in the ammoxidation reaction of ethylene compared to the one of ethane, e.g. 48.7% vs. 77.0%, respectively. The first step in the ethane ammoxidation pathway seems to be the oxidative dehydrogenation of C\textsubscript{2}H\textsubscript{6} to C\textsubscript{2}H\textsubscript{4} [24], which is in agreement with a higher TOF value in the ethylene ammoxidation reaction.

The elementary steps for the C\textsubscript{2}H\textsubscript{4} ammoxidation are depicted in Fig. 11 [24]. The first step is the adsorption of NH\textsubscript{3} on a hydroxylated Co\textsuperscript{2+} site. This is in line with the bonding strength of reactant species to the Co\textsuperscript{2+} ion [18]:

ethylene << ammonia < acetonitrile < ethylamine

This sequence indicates the importance of the presence of ammonia for the selective transformation of ethylene on the Co\textsuperscript{2+} ions. At the reaction temperature, NH\textsubscript{3} should cover most of the sites, because of the weak adsorption of C\textsubscript{2}H\textsubscript{4} on the Co\textsuperscript{2+} sites. The effect of ammonia is more pronounced with CoH-zeolites in contrast to CoNa-zeolites, which can be ascribed to the formation of basic sites [23].

The second step involves the addition of gaseous C\textsubscript{2}H\textsubscript{4} to the adsorbed NH\textsubscript{3}, leading to the formation of an ethylamine molecule. The gas phase addition of NH\textsubscript{3} and C\textsubscript{2}H\textsubscript{4} to form ethylamine is not thermodynamically favorable at the reaction temperatures. However, the strongly adsorbed NH\textsubscript{3} can lower the Gibbs free energy for the formation of an adsorbed amine molecule. This was validated by means of temperature programmed desorption experiments [24].

The next step is the oxidation of the adsorbed ethylamine. Since the hydrogen atoms associated with the nitrogen atoms feature the largest leaving ability, the dehydration between OH and the adsorbed C\textsubscript{2}H\textsubscript{5}NH\textsubscript{2} results in an amine anion adsorbed on Co\textsuperscript{2+}. The Co\textsuperscript{2+} is thus balanced by a negative charge generated from the zeolite lattice and by a negative charge of the amine anion.

Subsequent dehydrogenation proceeds with O\textsubscript{2} insertion and dehydration. Therefore, C\textsubscript{2}H\textsubscript{5}NH\textsubscript{2} reacting with O\textsubscript{2} over Co-ZSM-5 results in the formation of C\textsubscript{2}H\textsubscript{3}N. However, in absence of O\textsubscript{2}, desorption of C\textsubscript{2}H\textsubscript{5}NH\textsubscript{2} was observed in stead of desorption of C\textsubscript{2}H\textsubscript{3}N. Accordingly, O\textsubscript{2} was required for the formation of C\textsubscript{2}H\textsubscript{3}N.

The dehydrogenation step is followed by the reversible desorption of C\textsubscript{2}H\textsubscript{3}N. As indicated before, ethylamine exhibits a strong bond with the highest stability among possible ligands for the Co\textsuperscript{2+} ions in the ammoxidation reaction, while acetonitrile is less strongly bound. This also implies that, once formed, acetonitrile preferably desorbs from the Co\textsuperscript{2+} ions as a final product.
Figure 12: Schematic representation of the experimental set-up [3].

Figure 13: Layout of the HTMR. (a) Side view of the HTMR, showing three sections of the HTMR, viz, the flow distribution unit, the reactor compartments and the sampling section; (b) Cross-sectional view of HTMR (right), including an enlarged view of a single wall of a compartment, showing the microstructures for mounting of the catalytic plates [3,27].
3 Equipment and Procedures

3.1 Experimental set-up

The flow sheet of the experimental set-up for catalytic screening experiments is depicted in Fig. 12. The set-up can be divided into four modules: the gas preparation module, the reactor module, the sampling module and the analysis module. An overview of the different modules is provided in the subsequent sections.

3.1.1 Gas mixture preparation section

In the inlet gas preparation section, all the reactant gas flows were separately set with Brooks mass flow controllers. The inlet gases were homogenized in micro static gas mixers, after which the gas mixture was preheated to 110°C by electrical tracing. The gas flow towards the reactor could be adjusted by a fine scale needle valve. A four way valve in front of the reactor allowed switching between the pretreatment and the process mode. In the pretreatment mode, helium was fed into the reactor over the catalytic coatings, while the reactant gas mixture was bypassed to the vent. In the process mode, the reactant gas mixture was introduced to the reactor, while helium was bypassed to the vent.

3.1.2 High throughput microreactor (HTMR) section

Fig. 13 shows a side view and a cross sectional view of the high throughput microreactor (HTMR). The HTMR consists of three sections, viz. the flow distribution unit, the reactor compartments and the sampling/outlet section. The gas flow was introduced into the flow distribution header, which divided the flow equally over the reactor compartments. The reactor section consists of a Mo cylinder with a diameter of 32 mm and a length of 40 mm, which is composed of eight identical compartments [1]. Microstructured slits in the side walls of each compartment enabled a maximum loading of eight plates (Fig. 13(b)), with dimensions of 40.0 x 9.9 x 0.1 mm$^3$. A 200 nm protective non-porous Al$_2$O$_3$ layer was deposited on the reactor walls by atomic layer deposition (ALD). Thermocouples were positioned at various locations in the HTMR to monitor the reactor temperature via Lab-Jack software. A band heater was used to control the microreactor temperature in the 20 to 550°C range. The HTMR unit was insulated by quartz wool.

3.1.3 Sampling section

The sampling section of the HTMR consists of a set of 24 capillaries system. Three 20 mm capillaries (OD = 1.2 mm, ID = 1.0 mm) were positioned 6 mm inside each of the eight compartments. The flow scheme of the gases in the sampling section is given by Ekatpure [3]. Via a multi positional valve system a capillary was selected and the corresponding outlet gas flow was directed to the analysis section. All 23 non-selected capillaries as well as the common outlets of the reactor were connected to the vent. The sampling of the product gas flow (ca. 1 mL/min) from the outlet of a reactor compartment through the selected capillary was carried out by a micropump (ThinXS). The capillaries and the multipositional valves were conditioned at 110°C in a convection oven. The outlet gas flows were measured using an Agilent Optiflow 570 soap flow meter. The composition of the selected product gas flow was determined by a micro-GC. Sequential analysis of the samples was automated via Lab-Jack software.


### Table 6: Operating conditions micro-GC.

<table>
<thead>
<tr>
<th></th>
<th>Channel A</th>
<th>Channel B</th>
<th>Channel C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column type</td>
<td>Molsieve 5A</td>
<td>poraPLOT-U</td>
<td>poraPLOT-U</td>
</tr>
<tr>
<td>Pre-column type</td>
<td>poraPLOT-Q</td>
<td>poraPLOT-Q</td>
<td>poraPLOT-U</td>
</tr>
<tr>
<td>Detector type</td>
<td>TCD</td>
<td>TCD</td>
<td>TCD</td>
</tr>
<tr>
<td>Injection temperature (°C)</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Column temperature (°C)</td>
<td>175</td>
<td>65</td>
<td>175</td>
</tr>
<tr>
<td>Column pressure (kPa)</td>
<td>350</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>Backflush time (s)</td>
<td>4</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 7: Properties of molecules for the quantification of methanol.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular structure</th>
<th>Molar mass (g/mol)</th>
<th>Heat capacity¹ (J·mol⁻¹·K⁻¹)</th>
<th>Relative thermal response²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylamine</td>
<td>H₂N—C—CH₃</td>
<td>45.08</td>
<td>52³</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol</td>
<td>HO—CH₂—CH₃</td>
<td>46.07</td>
<td>51⁴</td>
<td>72</td>
</tr>
<tr>
<td>Methanol</td>
<td>HO—CH₃</td>
<td>32.04</td>
<td>40⁴</td>
<td>55</td>
</tr>
</tbody>
</table>

¹ at 200°C  
² with respect to benzene (=100 mol⁻¹) [31]  
³ Cheric KDP Hydrocarbons Properties [39]  
⁴ NIST Chemistry WebBook [40]
3.1.4 Analysis section

The analysis of the effluent gases was conducted using an online Varian micro-Gas Chromatograph (CP-4900). The analysis sample was injected into three separate channels simultaneously. The three injectors of the channels were operated at 110°C, and helium was used as a carrier gas. Channel A consists of an upstream poraPLOT-Q column (0.25 mm ID, 11 m) operated at 175°C and 350 kPa, followed by a backflush unit, a downstream molsieve 5A column (0.25 mm ID, 10 m) and a TCD detector. Heavy components were backflushed after 4 s. Reaction components N₂, O₂, CH₄, NO and CO gases were separated and analyzed in channel A. Channel B consists of an upstream poraPLOT-U column (0.25 mm ID, 10 m) operated at 65°C and 200 kPa, followed by a backflush unit, a downstream molsieve 5A column (0.25 mm ID, 1 m) and a TCD detector. Heavy components were backflushed after 8 s. Channel B was used for the detection of C₂H₆, C₂H₄, CO₂, NH₃ and H₂O. Reaction components N₂, O₂, CH₄, NO and CO gases were separated and analyzed in channel A. Channel C consists of a second poraPLOT-U column operated at 175°C and 150 kPa with TCD detector and without a backflush option. Channel C is used for the detection of C₂H₃N and other relatively heavy products. A single sample injection and subsequent analysis was performed in 80 s. An overview of the operating conditions is given in Table 6.

3.1.5 Quantification of methanol and hydrogen cyanide

Methanol was identified on the C-channel of the micro-GC as a reaction product. However, no calibration data were available for methanol. The methanol concentration was estimated from the calibration curve of ethylamine by correlating the thermal conductivity response with the physical properties of the compounds. Messner et al. [31] showed that the molar response of a thermal detector to hydrocarbon vapors is unique for each compound. Additionally, the relative response proved to be independent of the detector operating temperature, the component concentration, the carrier gas flow rate and the type of thermal detector.

In general, two main physical properties account for a TCD’s thermal response, viz. thermal conductivity and heat capacity. The relative thermal response data as published by Messner is depicted in Appendix I. Although values for ethylamine were not reported, an estimation was made by considering the relative response values for methanol with respect to ethanol. Large differences in thermal conductivity between ethanol and ethylamine were not expected because the thermal conductivity mainly depends on the molecular weight, structure and electron configuration, which is approximately the same for ethylamine and ethanol. As a consequence, only the heat capacity was taken into account. Table 7 provides the heat capacity values of methanol, ethanol and ethylamine as well as the relative response time with respect to benzene [31]. Due to the fact the Cp ratios of ethanol/methanol and ethylamine/methanol show corresponding values of 1.28 and 1.30, respectively, the TCD peak area of C₂H₅NH₂/CH₃OH was taken as 1.31 ± 0.13.

Since methanol can only be formed by the dissociation of acetonitrile (see section 4.3.1), an equimolar quantity of hydrogen cyanide was formed. This was taken into account in the carbon and nitrogen mass balance. The mass balance for the total amount of carbon and nitrogen into the reactor minus the total amount of carbon and nitrogen in the product gases was within an error interval of 10%.
Figure 14: Pretreatment of Mo substrate prior to in-situ zeolite synthesis [15].

Table 8: Chemicals used for the preparation of the zeolite precursor mixtures.

<table>
<thead>
<tr>
<th>Full name</th>
<th>Name</th>
<th>Used for</th>
<th>Concentration</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrapropylammoniumhydroxide</td>
<td>TPAOH</td>
<td>ZSM-5</td>
<td>40%</td>
<td>Merck</td>
</tr>
<tr>
<td>Tetraethyammoniumhydroxide</td>
<td>TEAOH</td>
<td>BEA</td>
<td>35 wt.%</td>
<td>Fluka</td>
</tr>
<tr>
<td>Tetraethyldisilicate</td>
<td>TEOS</td>
<td>ZSM-5</td>
<td>-</td>
<td>Merck</td>
</tr>
<tr>
<td>Ludox HS-40 colloidal silica</td>
<td>Ludox</td>
<td>BEA</td>
<td>40 wt.%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>NaAlO₂</td>
<td>ZSM-5 / BEA</td>
<td>-</td>
<td>Riedel de Haën</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>BEA</td>
<td>-</td>
<td>Merck</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>BEA</td>
<td>-</td>
<td>Merck</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>BEA</td>
<td>-</td>
<td>Merck</td>
</tr>
</tbody>
</table>

Table 9: Synthesis parameters and catalyst properties.

<table>
<thead>
<tr>
<th>Series</th>
<th>Synthesis parameters</th>
<th>Screen exp.</th>
<th>T °C</th>
<th>Time h</th>
<th>Stirring</th>
<th>Cov. g/m²</th>
<th>No. of coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zeolite Si/Al Recipe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Syn. HTS</td>
</tr>
<tr>
<td>A</td>
<td>ZSM-5 20 40 SiO₂:1 Al₂O₃:2 (TPA)₂:0.134 Na₂O : 1600 H₂O</td>
<td></td>
<td>160</td>
<td>24</td>
<td>5</td>
<td>1.01</td>
<td>24 3</td>
</tr>
<tr>
<td>B</td>
<td>BEA 15 46 SiO₂:1.53 Al₂O₃:11.4 (TEA)₂:0.17 K₂O:0.93 HCl:710 H₂O</td>
<td></td>
<td>140</td>
<td>48</td>
<td>1</td>
<td>1.32</td>
<td>32 4</td>
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<tr>
<td>C</td>
<td>BEA 17 46 SiO₂:1.35 Al₂O₃:11.4 (TEA)₂:0.17 K₂O:0.93 HCl:710 H₂O</td>
<td></td>
<td>140</td>
<td>48</td>
<td>1</td>
<td>1.11</td>
<td>32 4</td>
</tr>
<tr>
<td>D</td>
<td>BEA 23 46 SiO₂:1 Al₂O₃:11.4 (TEA)₂:0.156 Na₂O :0.93 K₂O:1.8 HCl:710 H₂O</td>
<td></td>
<td>150</td>
<td>48</td>
<td>1</td>
<td>0.64</td>
<td>32 4</td>
</tr>
<tr>
<td>E</td>
<td>BEA 23 46 SiO₂:1 Al₂O₃:11.4 (TEA)₂:0.156 Na₂O :0.93 K₂O:1.8 HCl:710 H₂O</td>
<td></td>
<td>150</td>
<td>48</td>
<td>5</td>
<td>0.72</td>
<td>10 -</td>
</tr>
</tbody>
</table>

* Series A-D were used in the screening experiments; Series E was used for an optimization study.
* Details of the synthesis experiments are given in [1,2].
3.2 Experimental procedures

3.2.1 High throughput screening

The HTMR is designed for the screening of catalytic coatings. In this study the reactor was applied in the ethane and ethylene ammoxidation reaction over cobalt activated BEA and ZSM-5 coatings. Various sets of coatings were screened in the HTMR. The coatings were pretreated in a helium flow of 200 mL/min for 1 h at 530°C. Subsequently, the HTMR was switched to process mode.

The high throughput screening experiments were carried out by introducing a reactant gas mixture consisting of 2 vol.% of ethane or ethylene, 2 vol.% of ammonia and 2 vol.% of oxygen (balanced by helium) to the reactor. The inlet flow was set to 250 mL/min (STP) and equally distributed over the eight reactor compartments. The reactor was operated at a temperature of 450°C. The separate gas flows from all compartments were analyzed at steady state conditions.

3.2.2 Optimization of reaction conditions

In order to optimize the process conditions two different parameters were varied. The reactor compartments were loaded with a selected series of coatings from the screening experiments. The inlet flow rate was varied in the range of 100 to 500 mL/min (STP) at 450°C. Furthermore, the temperature was varied in the range of 350 to 500°C at a flow rate of 250 mL/min. Blank HTMR experiments were carried out on inert titanium plates to correct for reaction contributions of the reactor material.

3.3 Catalyst preparation

3.3.1 Synthesis of ZSM-5 and BEA coatings

Prior to the in-situ synthesis of zeolitic coatings the molybdenum substrate was pretreated according to the procedure depicted in Fig. 14. The substrates were boiled in xylene for 1 h to remove organic contaminations, dried at 140°C for 1 h, and treated by an etching mixture containing 14 vol.% H₂O₂ and 14 vol.% NH₄OH in distilled water to increase the surface roughness. This is followed by an atomic layer deposition (ALD) of a 170 nm Al₂O₃ film to prevent high temperature oxidation of the metal surface. A 50 nm TiO₂ layer was subsequently deposited on top of the alumina layer by ALD to reach better adhesion of the coatings to the substrate surface. Just before the zeolite synthesis, the titania layer was made super hydrophilic (> 15 OH groups/nm²) by an UV treatment for 3 h at room temperature in a metal box (UV lamp: Hanovia 679A-36). The Titania-Alumina-Molybdenum substrate will be referred to as TAMo substrate hereafter [1.2].

In situ synthesis procedure

The precursor mixtures (3 L) for the synthesis of zeolite Beta and ZSM-5 coatings were prepared according to the recipes listed in Table 9 [1,2]. The chemicals used are listed in Table 8. A large number of substrates were fixed in a holder and placed in the precursor mixture (3 L) directly after the UV treatment. The various series (A – E) of
As synthesized
BEA  ZSM-5
Na,K,TEAOH)-BEA  (Na,TPAOH)-ZSM-5
(Na,K)-BEA  (Na)-ZSM-5
(NH₄)-BEA  (NH₄)-ZSM-5
(H)-BEA  (H)-ZSM-5
(Co₂C₂H₂O₄)-BEA  (Co₂C₂H₂O₄)-ZSM-5
(Co)-BEA  (Co)-ZSM-5
(Co,NH₃BH₃)-BEA  (Co,NH₃BH₃)-ZSM-5
(Co,B)-BEA  (Co,B)-ZSM-5

Figure 15: Post treatment procedure of zeolitic coatings.

Figure 16: Temperature profiles of the one- and two-step calcination procedure.
coatings were synthesized in a large scale autoclave [1,2] according to the parameters listed in Table 9. After the crystallization process, the synthesis mixture was quenched to room temperature, and the zeolitic coatings were subjected to an ultrasonic treatment (50-60 Hz) for 45 min, to remove poorly bonded zeolite particles. Afterwards, the samples were dried overnight at 110 °C and weighted. Series A – D were used in the catalyst screening study, while series E was used for the optimization of the post treatment procedure.

3.3.2 Post treatment of ZSM-5 and BEA coatings

The post treatment procedure is summarized in Fig. 15. The (Na,TPAOH)-ZSM-5 and (Na,K,TEAOH)-BEA coatings (Table 9) were positioned in quartz holders and calcined in a calcination oven (Heraus Instruments) equipped with a Eurotherm 2404 temperature controller. The organic template was removed from the zeolite by applying a two-step calcination procedure (step 1) [32]. The samples were heated to 300°C with a heat ramp rate of 1°C/min in an air flow (100 mL/min) followed by a dwell interval of 2 h. Subsequently, the temperature was increased to 500°C at 1°C/min in a 100 mL/min helium flow with a dwell interval of 2 h. Fig. 16 illustrates the temperature profile of the calcination procedure.

The quartz holders containing the (Na,H)-ZSM-5 and (Na,K,H)-BEA coatings were placed in a 0.5 L vessel with 200 mL of 1 M NH₄NO₃ solution at 78°C for 2 h under continuous stirring and a reflux cooler (step 2). Subsequently, the coatings were washed twice with demineralized water for 45 minutes at 78°C. The NH₄NO₃ treatment was repeated three times. Finally, the coatings were dried overnight at 110°C [2]. H-ZSM-5 and H-BEA coatings were obtained by removing the ammonium and nitrate according to a one-step calcination procedure (step 3) [2]. The oven was heated to 500°C at 1°C/min in helium (100 mL/min) followed by a dwell interval of 2 h. The temperature profile of the calcination procedure is shown in Fig. 16.

The four series of coatings (A, B, C and D in Table 9) were divided into 8 sets (32 sets in total), which were separately treated afterwards. Table 10 shows the various conditions applied in the cobalt ion exchange procedure. The set-up used for the cobalt ion exchange is depicted in Fig. 17. The H-ZSM-5 and H-BEA sets were placed in a 300 mL beaker containing 200 mL of Co(CH₃COO)₂ solution at 78°C for 2 h under continuous stirring and a reflux cooler (step 4). By positioning four beakers in a 0.5 L vessel with preheated water and reflux cooler, four sets could be treated simultaneously. Afterwards, the coatings were washed twice with 200 mL of demineralized water, dried overnight at 110°C and calcined according to the two-step procedure. The total catalyst weight of the Co-ZSM-5 and Co-BEA zeolitic coatings is listed in Table 10.

Separate boron impregnations were applied on the coatings of set V, VI, VII (Table 10). The coatings were placed in a 1 L beaker containing 500 mL of NH₃·BH₃ solution, which was stirred at room temperature for 2 h (step 6). Subsequently, the liquid was drained off at 5 mL/min using a ConstaMetric 3200 Solvent Delivery System pump. The sets were dried overnight at 110°C. In order to remove the excess of borane species, the coatings were treated in the one-step calcination procedure.

The coatings obtained are denoted as follows: [Co(B)ₓ/Hᵧ]-[zeolite]-[Si/Al]-[Co/Al]. For instance, BEA coatings of set V with a Si/Al ratio of 17 and a corresponding Co/Al ratio of 0.75 are denoted as CoBₓV-BEA-17-0.75.
Table 10: Properties of the various zeolitic coatings used for catalyst screening.

<table>
<thead>
<tr>
<th>Set</th>
<th>Ion exchange solutions</th>
<th>Catalyst weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co$_2$C$_2$H$_6$O$_2$ (M)</td>
<td>NH$_3$BH$_3$ (M)</td>
</tr>
<tr>
<td>I</td>
<td>7.5·10$^{-5}$</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>1.0·10$^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>III</td>
<td>1.5·10$^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>IV</td>
<td>2.0·10$^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>1.0·10$^{-4}$</td>
<td>1.0·10$^{-5}$</td>
</tr>
<tr>
<td>VI</td>
<td>1.0·10$^{-4}$</td>
<td>1.0·10$^{-4}$</td>
</tr>
<tr>
<td>VII</td>
<td>1.0·10$^{-4}$</td>
<td>1.0·10$^{-3}$</td>
</tr>
<tr>
<td>VIII</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Theoretically determined from the molecular composition (Eq. 3.13)
2 Corrected for H$_2$O absorption: 15% of catalyst weight
3 Corrected for H$_2$O absorption: 10% of catalyst weight

Figure 17: Representations of the experimental set-up for cobalt ion exchange.
3.3.3 Catalyst characterization

X-ray diffraction (XRD)
Representative samples of the synthesized coatings were analyzed by X-ray diffraction for the identification of the zeolite framework as well as oxides formed. XRD data were collected on a Rigaku geigerflex diffractometer using Cu Kα radiation (1.5405 Å). XRD patterns of zeolitic coatings were recorded in the range of 5 to 50° 2θ using step scanning at 0.02° 2θ and a counting time of 4 seconds per step.

Brunauer Emmett Teller (BET) analysis
The specific surface area, pore size distribution and pore volume were measured using Micromeritics ASAP 2020 equipment. Zeolitic coatings were degassed at 300°C for 30 h below a residual pressure of 0.1 Pa. The surface area of the catalyst was measured with the BET method at -196°C within the 0.008 to 0.20 relative pressure range and with nitrogen as adsorbent. The Horvath-Kawazoe model was applied in order to calculate the pore size distribution. The maximum microporous volume was obtained based on the t-plot Harkins and Jura model.

Infrared (IR) spectrometry
The presence of organic species in the zeolite framework was determined by a Nexus FT-IR spectrometer featuring a Smart Golden Gate single-reflection diamond ATR and zinc selenide focusing optics. The zeolitic coatings were examined within a spectral range of 650 to 4000 cm\(^{-1}\) with a penetration depth of 2 micrometers.

X-ray photoelectron spectroscopy (XPS)
XPS elemental analyses were carried out with a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα X-ray source and hemispherical analyzer with a five-channeltron detector. Data were collected at a penetration depth of 2 – 10 nm using an aluminum anode (Al Kα=1486.6 eV) operating at 250 W and a constant pass energy of 20 eV with a background pressure of 2·10\(^{-9}\) mbar.

Inductively coupled plasma (ICP)
Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the determination of possible molybdenum content in the exchange solution after the ion exchange with cobalt acetate. The measurements were performed with a SPECTRO CiROSCCD spectrometer. A quantity of 25 mL exchange solution was collected and 2.5 mL of 1 M HCl solution was added. The spectrometer was calibrated in the range from 0 to 5·10\(^{-3}\) wt.% Mo.

3.4 Data analysis

3.4.1 Validation of intrinsic kinetics
Reactions can be carried out in three regimes:
1. External mass transfer regime: the reaction is limited by the transport of reactants from the bulk to the catalyst.
2. Internal mass transfer regime: the reaction rate is limited by the transport of reactants in the pore structure of the catalyst particle.
3. Chemical reaction kinetics regime: the reaction rate is limited by the chemical process itself.
In order to evaluate whether the screening experiments were carried out in the intrinsic kinetic regime, one should ensure that the process is operated without transport limitations. Various criteria were evaluated for the ammoxidation reaction on zeolitic coatings, which are discussed in the following sections.

External mass transfer

The external mass transfer depends on the geometrical configuration of the zeolite particle and the convection around it. For the diffusion of a single reactant from the bulk to the zeolite surface Fick’s law applies:

\[ N_A = D_{AB} \frac{\partial C_A}{\partial z} \]  \hspace{1cm} (3.1)

where:
- \( N_A \) = molar diffusion flux of species A (mol·m\(^{-2}\)·s\(^{-1}\))
- \( D_{AB} \) = diffusivity of A in B (m\(^3\)·m\(^{-1}\)·s\(^{-1}\))
- \( C_A \) = concentration of species A (mol·m\(^{-3}\))
- \( z \) = diffusion distance (m)

From this law the expression for the flux from the bulk to the surface can be derived:

\[ N_A = k_s (C_{A,b} - C_{A,s}) \]  \hspace{1cm} (3.2)

where:
- \( k_s \) = mass transfer coefficient (m\(^3\)·m\(^{-2}\)·s\(^{-1}\))
- \( C_{A,b} \) = bulk concentration of species A (mol·m\(^{-3}\))
- \( C_{A,s} \) = surface concentration of species A (mol·m\(^{-3}\))

For first order reactions, the reaction rate is given by:

\[ -r_{obs}^R = \frac{\varepsilon k_{r,obs}^R C_{A,s}}{\rho_b} \]  \hspace{1cm} (3.3)

where:
- \(-r_{obs}^R\) = reaction rate observed per unit of mass (mol·kg\(^{-1}\)·s\(^{-1}\))
- \( k_{r,obs}^R \) = reaction rate coefficient (s\(^{-1}\))
- \( \varepsilon \) = porosity of catalyst (m\(^3\)·m\(^{-3}\))
- \( \rho_b \) = bulk density of catalyst (kg·m\(^{-3}\))
- \( \rho_c \) = apparent density of catalyst (kg·m\(^{-3}\))

At steady state conditions, the net flux through the particle equals zero. \( N_A \) can now be substituted. The mole balance on A yields:

\[ \frac{\varepsilon k_{r,obs}^R C_{A,s}}{(1-\varepsilon)\rho_p} = k_s (C_{A,b} - C_{A,s}) \]  \hspace{1cm} (3.4)
### Table 11: Parameters for the Chapman Enskog diffusivity theory.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molar mass (g·mol$^{-1}$)</th>
<th>σ (Å)$^1$</th>
<th>ε/κ (K)$^1$</th>
<th>Ω$_{D,AB}$ (-)$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>4.003</td>
<td>2.576</td>
<td>10.2</td>
<td>0.696</td>
</tr>
<tr>
<td>Ethylene</td>
<td>30.07</td>
<td>4.388</td>
<td>232</td>
<td>0.692</td>
</tr>
<tr>
<td>He</td>
<td>28.05</td>
<td>4.228</td>
<td>216</td>
<td>-</td>
</tr>
</tbody>
</table>

$^1$ at 450°C

### Table 12: Parameters for the calculation of the Mears’ and Weisz-Prater criterion.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_c$ (kg·m$^{-3}$)$^1$</td>
<td>800</td>
</tr>
<tr>
<td>ε (-)$^2$</td>
<td>0.5</td>
</tr>
<tr>
<td>d (m)</td>
<td>1·10$^{-6}$</td>
</tr>
<tr>
<td>n (-)$^3$</td>
<td>0.5</td>
</tr>
<tr>
<td>$C_{A,b}$ (C$_2$H$_6$) (mol·m$^{-3}$)</td>
<td>0.90</td>
</tr>
<tr>
<td>$C_{A,b}$ (C$_2$H$_4$) (mol·m$^{-3}$)</td>
<td>0.90</td>
</tr>
<tr>
<td>$C_{A,s}$ (C$_2$H$_6$) (mol·m$^{-3}$)</td>
<td>0.89</td>
</tr>
<tr>
<td>$C_{A,s}$ (C$_2$H$_4$) (mol·m$^{-3}$)</td>
<td>0.84</td>
</tr>
<tr>
<td>$r_{obs}^s$ (C$_2$H$_6$) (mol·kg$^{-1}$·s$^{-1}$)$^4$</td>
<td>1.39·10$^{-2}$</td>
</tr>
<tr>
<td>$r_{obs}^s$ (C$_2$H$_4$) (mol·kg$^{-1}$·s$^{-1}$)$^4$</td>
<td>2.45·10$^{-1}$</td>
</tr>
</tbody>
</table>

$^1$ Rebrov et al., 2001 [38]
$^2$ Kärger, J. and Ruthven, D.M., 1992 [37]
$^3$ Li and Armor, 1998 [24]
$^4$ maximum obtained reaction rate of the ethane/ethylene ammoxidation reaction
where: \( a_p = \) specific surface area (\( m_c^2 \cdot m_c^{-3} \))  
\((1-\varepsilon) = \) catalyst volume per unit of reactor volume (\( m_c^3 \cdot m_r^{-3} \))

For a coating with only one accessible side, the specific surface area is defined by \( 1/d \), where \( d \) is the thickness of the catalytic layer. It must be noted that an increase in surface roughness of the support will cause the \( a_p \) value to increase as well, resulting in an enhanced activity.

The mass transfer coefficient \( k_s \) is normally correlated in terms of the Sherwood number. For the HTMR, which exhibits laminar flow (\( Re<2300 \) for helium) between two parallel flat plates, the Sherwood number has the following form [34]:

\[
Sh = \frac{k_s (2h)}{D_{AB}} = 8.23
\]  

where: \( h = \) distance between two plates (\( m_r \))

The diffusivity coefficient for the \( \text{C}_2\text{H}_4/\text{He} \) and \( \text{C}_2\text{H}_6/\text{He} \) system can be deduced from the Chapman-Enskog theory for ideal gases [34]. This theory describes the diffusivity in terms of temperature, pressure and the ‘collision integral’ (\( \Omega_{D,AB} \)).

\[
D_{AB} = 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}}
\]  

where: \( T = \) reaction temperature (K)  
\( M_a = \) molecular weight of species A (\( \text{g} \cdot \text{mol}^{-1} \))  
\( M_b = \) molecular weight of species B (\( \text{g} \cdot \text{mol}^{-1} \))  
\( p = \) pressure (atm)

The dimensionless quantity \( \Omega_{D,AB} \) is a function of the dimensionless temperature \( \kappa T/\varepsilon_{AB} \). This correlation is provided in Appendix II. The binary Lennard-Jones parameters \( \sigma_{AB} \) and \( \varepsilon_{AB}/\kappa \) and can be estimated from the following combining rules:

\[
\sigma_{AB} = \frac{1}{2} \left( \sigma_A + \sigma_B \right); \quad \frac{\varepsilon_{AB}}{\kappa} = \sqrt{\frac{\varepsilon_A}{\kappa} \frac{\varepsilon_B}{\kappa}}
\]  

Using the single component properties in Table 11 and the reaction conditions in Table 12, the diffusivity for the binary \( \text{C}_2\text{H}_4/\text{He} \) and \( \text{C}_2\text{H}_6/\text{He} \) mixtures can be computed. Accordingly, at a reaction temperature of 450°C, \( D_{AB} \) equals \( 1.81 \cdot 10^{-4} \) \( \text{m}^2 \cdot \text{s}^{-1} \) for \( \text{C}_2\text{H}_4/\text{He} \) and \( 1.92 \cdot 10^{-4} \) for \( \text{C}_2\text{H}_6/\text{He} \). The corresponding mass transfer coefficients (\( k_s \)) are 4.18 and 4.44 \( \text{m} \cdot \text{s}^{-1} \), respectively.

To determine whether external mass transfer plays a role, the Mears’ criterion is calculated [36].

\[
C_{\text{Mears}} = \frac{-r_{\text{obs}}^{\text{obs}} \rho_c dn}{(1-\varepsilon) k_s C_{A,b}} < 0.05
\]  

(3.8)
Figure 18: Temperature dependence of effective diffusivity of paraffins [28].
where: \( -r_{\text{obs}} \) = reaction rate observed per unit of mass (mol·kg\(^{-1}\)·s\(^{-1}\))
\( n \) = reaction order (-)
\( d \) = catalyst layer thickness (m)

A reaction order of 0.5 is used, since this was experimentally derived by [24]. Using the additional data provided in Table 12, \( C_{\text{Mears}} \) is obtained for \( C_2H_4/\text{He} \) and \( C_2H_6/\text{He} \) and equals \( 5.0 \times 10^{-5} \) and \( 2.8 \times 10^{-6} \) mol·kg\(^{-1}\)·s\(^{-1}\), respectively.

**Internal mass transfer**

As collisions and interactions with the pore walls slow down the molecular transport, diffusion in meso- or micropored structures is slower than in the bulk. Three mechanisms can describe the molecular transport through pores [35]:

1. Maxwellian diffusion through macropores, which occurs if the mean free path (\( l_m \)) of the molecules is smaller than the pore diameter (\( d_p \)).
2. Knudsen diffusion, which takes place if the mean free path of the molecules is larger than the pore diameter and if the ratio of the molecular diameter (\( d_m \)) and the pore diameter \( d_m/d_p < 0.6 \).
3. Configurational diffusion, which takes place in the case that \( d_m/d_p > 0.6 \). This holds for diffusion of most types of hydrocarbons in 8-, 10- and 12-membered ring zeolites, such as Co-ZSM-5 [7].

As can be derived from Fig. 18 [28], the effective diffusivity of \( C_2 \) hydrocarbons in H-Beta is approximately \( 2 \times 10^{-11} \) m\(^2\)·s\(^{-1}\) at 425°C. The data can be linearly interpolated and a value of \( 4 \times 10^{-10} \) is obtained at 450°C. The \( D_{\text{eff}} \) of Co-Beta is expected to be similar to the one of H-Beta.

In order to determine whether the reaction rate is limited by internal mass transfer, the Weisz-Prater Criterion is calculated [36]:

\[
C_{\text{WP}} = \frac{-r_{\text{obs}} \rho_c d^2}{D_{\text{eff}} C_{\text{As}}} < 0.1
\]  

(3.9)

where: \( -r_{\text{obs}} \) = reaction rate observed per unit of mass (mol·kg\(^{-1}\)·s\(^{-1}\))
\( d \) = catalyst layer thickness (m)
\( D_{\text{eff}} \) = effective diffusivity (m\(^3\)·kg\(^{-1}\)·s\(^{-1}\))
\( C_{\text{As}} \) = surface concentration (mol·m\(^{-3}\))

By applying the properties given in Table 12, one obtains a \( C_{\text{WP}} \) value of \( 5.8 \times 10^{-2} \) for \( C_2H_4/\text{He} \) and \( 3.1 \times 10^{-3} \) for \( C_2H_6/\text{He} \). Internal mass transfer limitations can be neglected, since for both systems the Weisz modulus is smaller than 0.1. It can be concluded that the reaction rates are not diffusion limited and represent the intrinsic kinetics.

Data regarding the ethane ammoxidation reaction on pelletized catalyst can be found in [15] and shows that the reaction on pellets is limited by internal mass transfer at a reaction rate of \( 3.66 \times 10^{-5} \) mol·kg\(_{\text{cat}}^{-1}\)·s\(^{-1}\) and a pellet diameter of 250 μm.
Table 13: Elemental composition of the zeolite BEA and ZSM-5 coatings.

<table>
<thead>
<tr>
<th>Series</th>
<th>Zeolite</th>
<th>Si/Al (-)</th>
<th>Al pairs (%)</th>
<th>Al single sites (%)</th>
<th>Co/Al (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ZSM-5</td>
<td>20</td>
<td>45</td>
<td>55</td>
<td>0.78</td>
</tr>
<tr>
<td>B</td>
<td>BEA</td>
<td>15</td>
<td>70</td>
<td>30</td>
<td>0.65</td>
</tr>
<tr>
<td>C</td>
<td>BEA</td>
<td>17</td>
<td>60</td>
<td>40</td>
<td>0.70</td>
</tr>
<tr>
<td>D</td>
<td>BEA</td>
<td>23</td>
<td>30</td>
<td>70</td>
<td>0.85</td>
</tr>
</tbody>
</table>
3.5 Calculations

3.5.1 Catalyst preparation

Cobalt loading in zeolite:

The cobalt loading was estimated on the basis of the distribution of aluminum in the ZSM-5 framework, which was discussed in section 2.2.4 [18]. It is assumed that there are no significant differences in Al distribution between ZSM-5 and Beta and that the effect of Si/Al on the relative concentration of single Al atoms and Al pairs is the same for zeolite BEA and ZSM-5. For a maximum cobalt ion exchange at all available Al pairs and single sites in the various zeolitic coatings, the total amount of cobalt in the ion exchange solution has to exceed the total number of available Al sites. The maximum Co loading is obtained by assuming only Al single sites are formed. Accordingly, the following criterion can be used:

\[
\frac{C_{ca} V_{ca} M_c}{W_c} > \frac{V_O}{2 (1 + R_{Si/Al})} \]  

(3.10)

where:
- \( C_{ca} \) = concentration of \( \text{Co(CH}_3\text{COO}_2 \) solution \( \text{(mol·m}^{-3} \) )
- \( V_{ca} \) = volume of \( \text{Co(CH}_3\text{COO}_2 \) solution \( \text{(m}^3 \) )
- \( M_c \) = molar mass of catalyst \( \text{(kg·mol}^{-1} \) )
- \( W_c \) = catalyst weight after calcination \( \text{(kg)} \)
- \( n_O \) = stoichiometric coefficient of O in zeolite \( \text{(-)} \)
- \( R_{Si/Al} \) = Si/Al ratio \( \text{(-)} \)

A minimum value of 3.1 is obtained for \( \text{Co}_{-}\text{BEA-15-0.65} \) \( (C_{ca}=7.5 \cdot 10^{-2} \text{ mol·m}^{-3} \); \( V_{ca}=2 \cdot 10^{-4} \text{ m}^3 \); \( M_c=4 \text{ kg·mol}^{-1} \); \( W_c=4 \cdot 10^{-6} \text{ kg} \); \( n_O=128 \); \( R_{Si/Al}=15 \)), which satisfies the criterion. The ratio between the number of Al pairs and Al single sites (Fig. 9) was used to obtain the Co/Al ratio for the different types of coatings [18]. A linear fit (Eq. 3.11) was applied to interpolate the data from Fig. 9. An overview of the data used in this study is given in Table 13.

\[
R_{Co/Al} = 0.025 \cdot R_{Si/Al} + 0.2775 \]  

(3.11)

where:
- \( R_{Co/Al} \) = molar Co/Al ratio \( \text{(-)} \)
- \( R_{Si/Al} \) = molar Si/Al ratio \( \text{(-)} \)

Weight fraction cobalt in zeolite:

\[
x_{Co} = \frac{R_{Co/Al} \cdot M_{Co}}{R_{Si/Al} \cdot M_{SiO_2} + M_{AlO_2} + R_{Co/Al} \cdot M_{Co} + (1 - 2R_{Co/Al}) \cdot M_H} \]  

(3.12)
where: $x_{Co} = \text{weight fraction of Co}$ (kg$_{Co}$·kg$_{c}$⁻¹)

$R_{Co/Al} = \text{molar Co/Al ratio}$ (-)

$M_{Co} = \text{molar mass of Co} (=58.93\cdot10^{-3})$ (kg·mol⁻¹)

$R_{Si/Al} = \text{molar Si/Al ratio}$ (-)

$M_{SiO_2} = \text{molar mass of SiO}_2 (=60.09\cdot10^{-3})$ (kg·mol⁻¹)

$M_{AlO_3} = \text{molar mass of AlO}_2 (=58.98\cdot10^{-3})$ (kg·mol⁻¹)

$M_{H} = \text{molar mass of H} (=1.01\cdot10^{-3})$ (kg·mol⁻¹)

Catalyst weight after post treatment:

$$W_{c,pt} = \left(1 - x_{H_2O}\right) \cdot \frac{W_{c,calc}}{M_{c,calc}} \cdot \left\{1 - \left(R_{Co/Al} \cdot v_{Al} \cdot M_{Co} + v_{Al} \left(1 - 2R_{Co/Al}\right) \cdot M_{H} \right)\right\} \quad (3.13)$$

where: $W_{c,pt} = \text{catalyst weight after post treatment} (=W)$ (kg$_{c,pt}$)

$W_{c,synth} = \text{catalyst weight as synthesized}$ (kg$_{c,synth}$)

$M_{c,synth} = \text{molar mass of zeolite as synthesized} (=f(R_{Si/Al}))$ (kg·mol⁻¹)

$M_{c,calc} = \text{molar mass of zeolite after calcination} (=f(R_{Si/Al}))$ (kg·mol⁻¹)

$R_{Co/Al} = \text{molar Co/Al ratio}$ (-)

$M_{H} = \text{molar mass of H} (=1.01\cdot10^{-3})$ (kg·mol⁻¹)

$R_{Si/Al} = \text{molar Si/Al ratio}$ (-)

$v_{Al} = \text{stoichiometric coefficient of Al in zeolite}$ (-)

$x_{H_2O} = \text{estimated weight fraction of H}_2\text{O in zeolite}$ (-)

= 0.1 (for Co-ZSM-5); 0.15 (for Co-Beta)

3.5.2 Ammonoxidation reaction

Conversion:

$$X_{C_2H_4} = \frac{\left(x_{p, out}^C - x_{p, in}^C\right) \cdot v_{p}^C}{x_{C,H_4, in} \cdot v_{C,H_4}} \cdot 100\% \quad (3.14)$$

where: $x_{p, out}^C = \text{mole fraction of product p in outlet stream}$ (-)

$x_{p, in}^C = \text{mole fraction of product p in inlet stream}$ (-)

$v_{p}^C = \text{stoichiometric coefficient of C in product p}$ (-)

$x_{C,H_4, in} = \text{mole fraction of C}_2\text{H}_4 \text{ in inlet stream}$ (-)

$v_{C,H_4}^C = \text{stoichiometric coefficient of C in C}_2\text{H}_4 (=2)$ (-)
Selectivity:

\[
S_C = \left( \frac{x_{y}^{\text{out}} - x_{y}^{\text{in}}}{\sum (x_{p}^{\text{out}} - x_{p}^{\text{in}})} \right) \cdot v_{y}^{C} \cdot 100\%; \quad S_N = \left( \frac{x_{y}^{\text{out}} - x_{y}^{\text{in}}}{\sum (x_{p}^{\text{out}} - x_{p}^{\text{in}})} \right) \cdot v_{y}^{N} \cdot 100\%
\] (3.15)

where:
- \( S_C \) = selectivity of product y on carbon-base (%)
- \( S_N \) = selectivity of product y on nitrogen-base (%)
- \( x_{y}^{\text{out}} \) = mole fraction of product y in outlet stream (-)
- \( x_{y}^{\text{in}} \) = mole fraction of product y in inlet stream (-)
- \( v_{y}^{C} \) = stoichiometric coefficient of C in product y (-)
- \( v_{y}^{N} \) = stoichiometric coefficient of N in product y (-)
- \( x_{p}^{\text{out}} \) = mole fraction of product p in outlet stream (-)
- \( x_{p}^{\text{in}} \) = mole fraction of product p in inlet stream (-)
- \( v_{p}^{C} \) = stoichiometric coefficient of C in product p (-)
- \( v_{p}^{N} \) = stoichiometric coefficient of N in product p (-)

Reaction rate:

\[
r_{C_{2}H_{4}}^{\text{obs}} = \frac{F_v \cdot \sum (x_{p}^{\text{out}} - x_{p}^{\text{in}}) \cdot v_{p}^{C}}{V_m \cdot W} \quad r_{C_{2}H_{6}}^{\text{obs}} = \frac{F_v \cdot \sum (x_{p}^{\text{out}} - x_{p}^{\text{in}}) \cdot v_{p}^{C}}{V_m \cdot W}
\] (3.16)

where:
- \( r_{C_{2}H_{4}}^{\text{obs}} \) = disappearance rate of \( C_2H_4 \) (for \( C_2H_6 \)) (mol·s\(^{-1}\)·kg\(^{-1}\))
- \( x_{p}^{\text{out}} \) = mole fraction of product p in outlet stream (-)
- \( x_{p}^{\text{in}} \) = mole fraction of product p in inlet stream (-)
- \( v_{p}^{C} \) = stoichiometric coefficient of C in product p (-)
- \( v_{C_{2}H_{4}}^{C} \) = stoichiometric coefficient of C in \( C_2H_4 \) (=2) (-)
- \( v_{C_{2}H_{6}}^{C} \) = stoichiometric coefficient of C in \( C_2H_6 \) (=2) (-)
- \( F_v \) = volumetric flow at STP conditions (m\(^3\)·s\(^{-1}\))
- \( V_m \) = molar volume at STP conditions (=22.4·10\(^{-3}\)) (m\(^3\)·mole\(^{-1}\))
- \( W \) = catalyst weight (kg)

Formation rate of acetonitrile:

\[
r_{C_{2}H_{3}N}^{\text{obs}} = \frac{F_v \cdot (x_{C_{2}H_{3}N}^{\text{out}} - x_{C_{2}H_{3}N}^{\text{in}})}{V_m \cdot W}
\] (3.17)
where:

\[ r_{C_2H_3N}^{obs} = \text{formation rate of } C_2H_3N \]  
\[ x_{C_2H_3N}^{out} = \text{mole fraction of } C_2H_3N \text{ in outlet stream} \]  
\[ x_{C_2H_3N}^{in} = \text{mole fraction of } C_2H_3N \text{ in inlet stream} \]  
\[ F_v = \text{volumetric flow at STP conditions} \]  
\[ V_m = \text{molar volume at STP conditions} \quad (=22.4 \cdot 10^{-3}) \]  
\[ W = \text{catalyst weight} \]  

Turnover frequency:

\[ TOF = \frac{F_v \left( x_{C_2H_3N}^{out} - x_{C_2H_3N}^{in} \right)}{V_m \cdot N_{Co}} \]  

where: \( TOF \) = turnover frequency \( (s^{-1}) \)  
\( x_{C_2H_3N}^{out} \) = mole fraction of \( C_2H_3N \) in outlet stream \( (-) \)  
\( x_{C_2H_3N}^{in} \) = mole fraction of \( C_2H_3N \) in inlet stream \( (-) \)  
\( F_v \) = volumetric flow at STP conditions \( (m^3 \cdot s^{-1}) \)  
\( V_m \) = molar volume at STP conditions \( (=22.4 \cdot 10^{-3}) \) \( (m^3 \cdot mol^{-1}) \)  
\( N_{Co} \) = amount of \( Co^{2+} \) in the zeolite structure \( (mol) \)  

Gas hourly space velocity:

\[ GHSV = \frac{F_v \cdot \rho_b}{W} \]  

where: \( GHSV \) = Gas hourly space velocity \( (h^{-1}) \)  
\( F_v \) = volumetric flow at STP conditions \( (m^3 \cdot h^{-1}) \)  
\( \rho_b \) = bulk density of catalyst bed \( (kg_c \cdot m_c^{-3}) \)  
\( W \) = catalyst weight \( (kg_c) \)
Figure 19: XRD patterns of the ZSM-5 and zeolite Beta coatings: (a) ZSM-5 coating with a Si/Al ratio of 20, (b) BEA coating with a Si/Al ratio of 23, (c) BEA coating with a Si/Al ratio 17, and (d) BEA coating with a Si/Al ratio of 23. Synthesis conditions are summarized in Table x. The reference patterns of the TAMo substrate, BEA [1] and ZSM-5 [2] zeolite structures are given for comparison (f, g, h, respectively).

Figure 20: SEM images (a) ZSM-5 coating with a Si/Al ratio of 20, (b) BEA coating with a Si/Al ratio of 15, (c) BEA coating with a Si/Al ratio 17, and (d) BEA coating with a Si/Al ratio of 23. Synthesis conditions are summarized in Table 9.
4 Results and Discussion

4.1 Catalyst characterization

The XRD patterns of the four series of as synthesized zeolitic coatings (Table 9) were recorded to evaluate the crystalline phase of the coatings (Fig. 19). The patterns of the BEA [41] and ZSM-5 [42] type zeolite structures and the TAMo substrate are given for comparison. BEA coatings obtained at 140°C from the gel with Si/Al ratios of 15 and 17 and at 150°C from the gel with Si/Al ratio of 23 showed very intensive Bragg reflections at 7.0, 7.7, 21.9, and 22.1° 2θ values, corresponding to (100), (101), (205), and (302) planes of the zeolite Beta structure. The XRD patterns of the ZSM-5 coating obtained at 160°C from a solution with a Si/Al ratio of 20 was consistent with the ZSM-5 structure. Strong peaks were observed at 2θ of 7.49, 8.80, 8.90, 23.10 and 23.98°, corresponding to diffraction of (011), (020), (200), (051), and (033) planes, respectively. XRD analysis of the coatings after the post treatment procedure showed also the presence of some oxide phases of the TAMo substrate. Apparently, the protective Al₂O₃ and TiO₂ ALD films were dissolved to some extent during the synthesis procedure in the highly alkaline precursor mixture.

Fig. 19(a-d) shows the SEM images of the ZSM-5 and zeolite BEA coatings. All coatings showed a closed layer of crystals on the TAMo substrate. The average layer thickness of the coatings depends on the coverage (Table 14) and was approximately 1.5 – 2.5 μm. Fig. 19(a) shows the typical cubic shaped crystals of ZSM-5 zeolite, while in Fig. 19(b-d) the spherical shaped crystals of zeolite BEA can be observed.

Table 14 shows the properties of the zeolitic coatings after calcination at 500°C. The IR stretch vibrations of -CH₃- (2934 cm⁻¹) and –CH₂- (2865 cm⁻¹) are typical for the presence of organic template molecules inside the pores of the as synthesized zeolitic framework (E1 and E2). Both IR bands disappeared after the calcination procedure. This indicated that the template was completely removed from the zeolite framework. The values for both the BET surface area and the microporous volume are also given in Table 14. The results were in correspondence with literature [2].

The cobalt ion exchange procedure was investigated on BEA-23 coatings of series E (Table 14). A Co/Al ratio of approximately 0.5 was the target during the optimization study. The elemental composition of the coatings was analyzed by XPS. From series E1 and E2 it was concluded that the cobalt loading (Co/Al ratio) remained the same, when the exchange time was reduced from 16 to 3 h. However, a repeated ion exchange (series E3) showed a clear increase of the Co/Al ratio. This was also observed by [16]. The optimized procedure was applied on the coatings of series A – D. It should be noted that the in-situ crystallization conditions of these BEA coatings considerably differed from those for the coatings of series E. The XPS results showed a rather high value for the Si/Al values (series A – D) compared to the Si/Al value of the precursor mixture. The high XPS values for the Si/Al ratio of the BEA coatings can be explained by the crystallization mechanism of zeolite BEA. The efficiency of the incorporation of framework elements is higher for aluminum than for silicon [14,43,44]. At the applied synthesis conditions, the precursor mixture was already exhausted in aluminum after 30 – 35 h, while the synthesis procedure was stopped after 48 h. Therefore, the Si/Al ratio
Table 14: Properties of the zeolitic coatings after template removal and ion exchange procedures

<table>
<thead>
<tr>
<th>Series of coatings used in screening experiments</th>
<th>Zeolite</th>
<th>Template removal</th>
<th>BET (m²/g)</th>
<th>μpore vol. (cm³/g)</th>
<th>Cobalt ion exchange t (h)</th>
<th>nr¹</th>
<th>XPS</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ZSM-5-20</td>
<td>-</td>
<td>-</td>
<td>450</td>
<td>0.091</td>
<td>3</td>
<td>1</td>
<td>32</td>
<td>0.12</td>
</tr>
<tr>
<td>B BEA-15</td>
<td>-</td>
<td>-</td>
<td>630</td>
<td>0.266</td>
<td>3</td>
<td>1</td>
<td>21</td>
<td>0.34</td>
</tr>
<tr>
<td>C BEA-17</td>
<td>-</td>
<td>-</td>
<td>630</td>
<td>0.237</td>
<td>3</td>
<td>1</td>
<td>27</td>
<td>0.17</td>
</tr>
<tr>
<td>D BEA-23</td>
<td>-</td>
<td>-</td>
<td>540</td>
<td>0.194</td>
<td>3</td>
<td>1</td>
<td>27</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Series of coatings used for optimization of the post treatment procedures

| E1 BEA-23                                     | Yes    | No               | -          | -                 | 16                       | 1   | 20  | 0.47        |
| E2 BEA-23                                     | Yes    | No               | -          | -                 | 3                        | 1   | 21  | 0.48        |
| E3 BEA-23                                     | Yes    | No               | -          | -                 | 3                        | 2   | 20  | 0.69        |

¹ Number of ion exchange steps with a Co(CH₃COO)₂ solution of 1x10⁻⁴M

Figure 21: High throughput screening experiments: comparison of the formation rate of acetonitrile in the ethylene ammoxidation reaction for the series BEA-15-0.65, BEA-17-0.75, BEA-23-0.85 and ZSM5-20-0.78. Each series consist of 8 sets, viz. CoI-IV, CoBv-VII and HvIII. The properties of the catalyst are given in Table 10. Reaction conditions: feed: 2% C₂H₆, 2% O₂, 2% NH₃ (He balanced); flow rate per compartment: 33 mL/min (STP); temperature: 450°C.
of the BEA crystals drastically increased during the crystallization process, viz. from the centre of the crystal to the outer surface.

Since XPS is a surface characterization technique with a penetration depth of 2-10 nm, the analysis only provided information about the elemental composition of the crystal surface, which was indeed higher than expected (Table 14). Because of the low aluminum content at the outer shell of the BEA crystals, also a low cobalt loading was measured. The ZSM-5 synthesis was carried out at a high reaction temperature of 160°C, which resulted in an extremely fast crystallization process, which was stopped after 24 h [6]. Therefore, also the elemental surface composition of the ZSM-5 coating seemed to be not representative for the average elemental composition. For this reason the XPS data of series A – D were not used for further calculation in this study. It was assumed that the average Si/Al value of the crystals was the same as the Si/Al value of precursor mixture, while the Co/Al ratio was estimated based on theoretical considerations (Section 3.5.1).

4.2 High throughput screening of catalytic coatings

The four series of BEA and ZSM-5 coatings, each consisting of 8 sets (Table 10: set I-VIII) were screened in the HTMR at 450°C in the ethylene ammoxidation reaction. Fig. 21 shows the activity of all the 32 sets of catalytic coatings in terms of the formation rate of acetonitrile per zeolite mass. Fig. 21 is divided into three sections, viz. Co-zeolitic coatings (sets I–IV), CoB-zeolitic coatings (sets V–VII), and H-zeolitic coatings (set VIII).

Generally, the following order in activity was observed: ZSM5-20-0.78 < BEA-23-0.85 < BEA-17-0.75 < BEA-15-0.65 (for coating denotation, see Section 3.3.4). The formation rate of acetonitrile was influenced by two main factors: the zeolite topology and the aluminum distribution in the framework. The differences in the zeolite topology are attributed to the pore structure. BEA exhibits a 3D pore system which is more open and is characterized by larger pores compared to ZSM-5. This enables compounds to diffuse easier through the channels. Therefore, the most active cobalt sites in the BEA framework, the β-type sites, are more accessible, which facilitates the accommodation of reactants [23]. Secondly, the aluminum distribution was strongly affected by the Al content in the framework. At lower Si/Al values, the negatively charged AlO$_2^-$ are more likely to form Al pairs, on which a divalent Co$^{2+}$ cation can be accommodated [25]. The formation rate of acetonitrile clearly increased with a larger number of active cobalt sites, which resulted in the highest activity on BEA-15-0.65 coatings.

Four coatings (Co$_0$ set) were selected to examine the activity per cobalt site (TOF) (Fig. 22). Co$_0$-BEA-15-0.65 exhibits the highest activity in the ethylene ammoxidation reaction (0.44 s$^{-1}$). A decrease in activity was observed with decreasing Si/Al ratios. This is in contrast with Fig. 10 [18], which shows an increase of the activity with a decreasing Al content in the framework. However, only zeolites with Si/Al values below 13 were applied in that specific study, while in this study the higher Si/Al range was investigated. Apparently, an optimum in activity can be expected at Si/Al ratios between 12 and 15. This is further supported by the fact that at a Si/Al ratio of 22.5, 65% of the aluminum in the zeolite structure can be considered single sites, which have an adverse effect on the selective formation of acetonitrile [23]. By reducing the Si/Al value down to 12.5, single sites only represent less than 20% of the aluminum in the structure (Fig. 9). The remaining 80% contributes to the number of active Al pairs on which active Co$^{2+}$ centers can be formed. Taking into account the positive effect of the BEA topology
Figure 22: Turnover frequency to C<sub>2</sub>H<sub>3</sub>N for the Co<sub>i</sub> sets of coatings in the ethylene ammoxidation reaction. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 23: Turnover frequency to C<sub>2</sub>H<sub>3</sub>N for the Co<sub>i</sub> sets of coatings in the ethylene and ethane ammoxidation. The properties of the catalyst are listed in Table 10. Reaction conditions ethane ammoxidation: feed, 2% C<sub>2</sub>H<sub>6</sub>, 2% O<sub>2</sub>, 2% NH<sub>3</sub> (He balanced); flow rate per compartment, 33 mL/min; temperature, 450°C. The reaction conditions for the ethylene ammoxidation are given in Fig. 21.

Figure 24: Conversion of C<sub>2</sub>H<sub>4</sub> as a function of the temperature in the ethylene ammoxidation reaction over Co<sub>i</sub> and CoB<sub>v</sub> sets of coatings. The GHSV values are given at the curve ends in 10<sup>3</sup> h<sup>-1</sup>. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 25: Conversion of NH<sub>3</sub> as a function of the temperature in the ethylene ammoxidation reaction over Co<sub>i</sub> and CoB<sub>v</sub> sets of coatings. The GHSV values are given at the curve ends in 10<sup>3</sup> h<sup>-1</sup>. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.
Results and Discussion

described above, our findings are in agreement with this theory; TOF(Co\text{ZSM5-20-0.78}) < TOF(Co\text{BEA-23-0.85}) < TOF(Co\text{BEA-17-0.75}) < TOF(Co\text{BEA-15-0.65}).

The coatings from sets I to IV were treated with various Co(CH_3COO)_2 solutions (Table 10) to investigate the effect on the cobalt loading. No clear trends in activity could be observed in none of the four series A - D. Because of the small discrepancies between the various sets, it was assumed that the cobalt content in the solution was high enough to reach a Co^{2+} cation equilibrium between the liquid and the zeolite voids, in which the major part of the Al sites, especially the Al pairs, were occupied. In Section 3.5.1, it was illustrated that the maximum degree of cobalt in the various series of coatings could be obtained, because of an excess of Co compared to the Al concentration. Therefore, the assumption of cobalt saturation of the Al sites in the zeolite seemed to be reasonable and this indicated that the theoretical Co/Al ratio was allowed to be applied. The observations, however, were not in correspondence with [2,20,45], who reported an increase in the cobalt loading while increasing the precursor concentration. This might be due to the ion exchanges in this study were performed within a smaller range of Co(CH_3COO)_2 solutions and at lower concentrations, resulting in hardly visible discrepancies in reaction rate between the CoI and CoIV sets.

CoB-zeolitic coatings (set V – VII of Table 10) clearly showed a reduced activity compared to the parent CoII sets. From these results no strong conclusions could be drawn on the effect of the boron concentration on the boron loading. For each of the zeolitic coating series rather distinct values in reaction rate were observed. This might indicate that the boron loading was not affected by the boron concentration. However, the boron impregnation used was not in correspondence with the conditions applied by [26]. Therefore, the reduced catalytic activity could also be attributed to an improper method of impregnation. From a chemical point of view, an excess of boron may cause the pores and cobalt sites in the framework to be blocked. In both cases, the molecular transport in the zeolite matrix and the accessibility of the active sites is reduced. Since no data on the actual boron loading was obtained, further investigation is required.

The coating of H-form zeolite BEA (set VIII) exhibited moderate activity of 1.25 mol·g_{cat}^{-1}·s^{-1} (H_{VIII}-BEA-15), which was in the same order of magnitude as in the CoB sets (Fig. 21).

Comparing with literature, the activity of the zeolitic coatings is substantially higher than the one of pelletized catalysts in the ammoxidation to ethylene. For instance, the most active coating, CoI-BEA-15-0.65, exhibited an activity which was three orders of a magnitude higher than the one on Co-ZSM5-11-0.49 pellets (0.44 vs. 0.013 s^{-1}, respectively; Table 2). Moreover, the activity of the coatings can be even considered higher than the values measured due to the fact the Co/Al value accounts for both the active Co^{2+} sites (bound on Al pairs) and the inactive CoOH (bound on Al single sites), although only the ones active accounted for the selective formation of acetonitrile. Since there is always an amount of single sites present [18], the true Co/Al ratio was expected to be slightly lower, resulting in a higher TOF value.

Coatings of set CoI were also tested in the ammoxidation of ethane. The results are depicted in Fig. 23 and showed a similar trend as was observed for ethylene. However, the activity towards acetonitrile is much lower than in the ethylene ammoxidation, viz. 1.25·10^{-3} vs. 4.4·10^{-1} s^{-1} on CoI-BEA-15, respectively. Ethane can only react to
Figure 26: Selectivity to C₂H₃N as a function of the temperature in the ethylene ammoxidation reaction over CoI and CoBᵥ sets of coatings. The GHSV values are given at the curve ends in 10³ h⁻¹. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 27: Selectivity to CH₃OH and HCN as a function of the temperature in the ethylene ammoxidation reaction over CoI and CoBᵥ sets of coatings. The GHSV values are given at the curve ends in 10³ h⁻¹. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 28: Selectivity to CO₂ as a function of the temperature in the ethylene ammoxidation reaction over CoI and CoBᵥ sets of coatings. The GHSV values are given at the curve ends in 10³ h⁻¹. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 29: Selectivity to N₂ as a function of the temperature in the ethylene ammoxidation reaction over CoI and CoBᵥ sets of coatings. The GHSV values are given at the curve ends in 10³ h⁻¹. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.
acetonitrile via the intermediate compound ethylene. The subsequent ammonoxidation reaction pathway of ethylene to acetonitrile occurs rapidly [24], therefore, the oxidative dehydrogenation of ethane to ethylene could be considered as the rate determining step. Apparently, the cobalt cation is not very active in the oxidative dehydrogenation of ethane to ethylene, such as Cu$^{2+}$ zeolites are [17]. The TOF value of the Co$_{I}$-ZSM5-20-0.78 coating was considerably lower than the reported values (Table 2) on Co-ZSM5-11-0.49 pelletized catalyst, viz. $1.25 \cdot 10^{-3}$ vs. $5.3 \cdot 10^{-3}$ s$^{-1}$, respectively. Although the increased activity could be mainly ascribed to an optimal Si/Al ratio, we speculate that the relatively slow oxidative dehydrogenation reaction of ethane limits the advantages the zeolitic coatings in a structured microreactor over a pelletized catalyst (Section 2.2.1). In addition, the reaction rate on coatings could have been limited due to possible negative interactions with the oxides formed on the coating surface or the different in-situ zeolite synthesis procedure.

4.3 Optimization of reaction conditions

4.3.1 Effect of temperature

The Co$_{I}$ and CoB$_{V}$ sets were selected to show the catalytic performance of the zeolitic coatings as function of the temperature (Fig. 24 to 30). The conversion of ethylene as well as ammonia, the selectivity to the main products and the activity in terms of TOF were investigated.

The conversion of ethylene (Fig. 24) increased with temperature and reached an optimum at approximately 475°C. Considerable differences were observed between the coatings tested. Maximum conversions of 23% and 21% were obtained on Co$_{I}$-BEA-15-0.65 and CoB$_{V}$-BEA-15-0.65, respectively, while the lowest conversion (Co$_{I}$-ZSM-5-20-0.78) did not exceed 5%. The same trend was observed in the ammonia conversion (Fig. 25), which showed values up to 65% at 500°C. Whereas Co$_{I}$-ZSM5-20-0.78 exhibited a very low conversion of C$_{2}$H$_{4}$, a very high NH$_{3}$ conversion was obtained. Apparently, the oxidation of ammonia to nitrogen and water is predominant on Co-ZSM5 coatings. Although lower, the conversion of NH$_{3}$ is still considerable on Co-BEA coatings.

The presence of methanol and hydrogen cyanide as reaction products was highly unexpected (Fig. 27). Related studies reported CO$_{2}$, N$_{2}$, and H$_{2}$O as main byproducts, whereas only traces of e.g. HCN, propionitrile and CO were found. Recently, Lu, et al. [46] observed formation of CH$_{3}$OH and HCN from acetonitrile in liquid media (cryptate) incorporating divalent Cu$^{2+}$ ions. Therefore, we speculate that CH$_{3}$OH and HCN were also formed from the undesired dissociation of acetonitrile. A suggested reaction pathway is depicted in Fig. 34. Acetonitrile is formed in line with Fig. 11 [24]. Subsequently, C$_{2}$H$_{3}$N is believed to interact with two adjacent Co sites, binding to one Co atom through its electron pair, and the second Co atom through the filled π-orbital of the sp-hybridized acetonitrile carbon. This results in an electron flow from the π-bond to the Co atom. In the presence of water, acetonitrile dissociates readily into methanol and hydrogen cyanide. Since the quantities of hydrogen cyanide and methanol formed are equimolar, the same selectivities were obtained. This opposes the statement that influence of water is negligible on the reaction characteristics [24].

The selectivity graphs (Fig. 26-29) show that an increase in the selectivity to C$_{2}$H$_{3}$N was obtained as the reaction temperature increased. The selectivity to methanol and
Figure 30: Turnover frequency to $\text{C}_2\text{H}_3\text{N}$ as a function of the temperature in the ethylene ammoxidation reaction over CoI and CoBv sets of coatings. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 31: Conversion of $\text{C}_2\text{H}_4$ and $\text{NH}_3$ as a function of the GHSV in the ethylene ammoxidation reaction over CoI-BEA-15-0.65 coating. The values representing the colored graphs are the GHSV. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 32: Selectivity to $\text{C}_2\text{H}_3\text{N}$, CH$_3$OH, HCN and CO$_2$ as a function of the GHSV in the ethylene ammoxidation reaction over CoI-BEA-15-0.65 coating. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.

Figure 33: Turnover frequency to $\text{C}_2\text{H}_3\text{N}$ as a function of the GHSV in the ethylene ammoxidation reaction over CoI and CoBv sets of coatings. The properties of the catalyst are given in Table 10. The reaction conditions are given in Fig. 21.
Results and Discussion

Hydrogen cyanide gradually decreased with an increasing temperature, while the selectivity to CO$_2$ remained rather constant up to 475°C and then suddenly increased. The NH$_3$ selectivity to N$_2$ showed a decrease with temperature. It is remarkable that, in the case of the Co$_7$-BEA-15-0.65 coating, the selectivity to C$_2$H$_3$N showed a more substantial growth than was observed on the other coatings. Additionally, the CH$_3$OH and HCN graph showed a proportional decrease with the temperature. This could be ascribed to the higher Al content in Co$_7$-BEA-15-0.65. It was reported that the higher the Al content in the framework, the more the negative charge is distributed [18]. As a result, the electron flow towards the cobalt ions decreases, causing the cobalt cation to be less strongly bound. We speculate that a decrease of the electron density on the cobalt ion facilitates the leaving ability of the sp-hybridized acetonitrile. Consequently, the reaction to methanol becomes less predominant. Considering the difference between CoB$_V$ and Co$_7$ only small differences were observed. Again the CoB coatings did not feature an enhanced activity in the ammoxidation reaction [24].

The TOF graph (Fig. 30) shows that the activity increased with temperature. The highest activity was attained on Co$_7$-BEA-15-0.65 (0.82 s$^{-1}$) at 500°C. TOF values up to 0.013 s$^{-1}$ (at 450°C) were found in literature (Table 4). The trends in conversion, selectivity and catalyst activity were similar to those in [28].

4.3.2 Effect of contact time

The catalytic performance of Co$_7$ and CoB$_V$ coatings was investigated as a function of the gas hourly space velocity (GHSV). Since the GHSV is based on the catalyst weight, the contact time was specific for each coating tested.

The dependence of the GHSV on the C$_2$H$_4$ and NH$_3$ conversion on Co$_7$-BEA is illustrated in Fig. 31. It can be clearly seen that an increase in the GHSV (or the correlated flow rate) resulted in a decrease of the conversion. This was also observed by [28] on Co-ZSM-5 pellets (Table 5). The selectivity to the relevant products on Co$_7$-BEA-15-0.65 is depicted in Fig. 32. No clear trends could be discriminated, i.e. the selectivities were not substantially affected by the GHSV. The same applied to the selectivity data reported earlier [28].

Fig. 33 shows the TOF values of the Co$_7$ set and CoB$_V$-BEA-15-0.65 coating. In this study an optimum was observed at a GHSV of approximately 500·10$^3$ h$^{-1}$ on Co$_7$-BEA-15-0.65, Co$_7$-BEA-17-0.75, Co$_7$-ZSM5-20-0.78 and CoB$_V$-BEA-15-0.65. Co$_7$-BEA-23-0.85 showed an optimum at approximately 900·10$^3$ h$^{-1}$. This difference is due to the fact the flow rate was kept constant at 33 mL/min, whereas the catalyst weight of the latter coating was approximately half the catalyst weight of the other ones. In literature [28], an optimum on pelletized Co-ZSM-5 was not observed, however, results were obtained from 50·10$^3$ – 450·10$^3$ h$^{-1}$ (0.03 g catalyst). Within this range the TOF value exhibited an increase up to 7.4·10$^{-3}$ s$^{-1}$ at GHSV = 444·10$^3$ h$^{-1}$. Unfortunately a good comparison cannot be made, since literature only reported values regarding the ethane ammoxidation reaction, whereas we used ethylene as a reactant.

To determine whether diffusion limitations play a role in zeolitic coatings, the reaction rates of the reagents needed to be determined at low conversions. Since the ammonia conversion was rather high, results on limitations were not experimentally obtained. However, a theoretical derivation already showed that no mass transfer limitations were expected with respect to zeolitic coatings (Section 3.4.1).
Figure 34: Suggested reaction pathway of the ethylene ammoxidation to acetonitrile on one Al pair Co site and the subsequent dissociation into methanol and hydrogen cyanide on two Al pair Co sites. The pathway to acetonitrile was taken from [24]
5 Conclusions and Recommendations

5.1 Conclusions

In this study, Co-BEA catalytic coatings with Si/Al ratios of 15, 17 and 23 and Co-ZSM-5 coatings with a Si/Al ratio of 20 were prepared and screened in a high throughput microreactor in the ammoxidation reaction of ethylene to acetonitrile. The catalytic coating composition as well as the process conditions were optimized for a microreactor application.

Reducing the Si/Al ratio from 23 to 15 resulted in a significant increase in the activity of the zeolitic coating in terms of the formation rate of acetonitrile as well as the TOF value. Where Co-BEA-23 showed the highest activity at 0.21 s\(^{-1}\), Co-BEA-15 reached a value of 0.44 s\(^{-1}\). A larger number of active cobalt sites was generated at a higher aluminum content in the zeolite matrix. The enhanced distribution of the negative charge in the framework caused the activity per Co site to increase. The introduction of a more electropositive second cation, boron, exhibited a negative effect on the catalytic performance.

Due to a larger pore system and more accessible cobalt sites, the BEA coatings demonstrated a higher activity than the ZSM-5 ones. The BEA coating with Si/Al ratio of 15 and a Co/Al ratio of 0.65 unambiguously proved to be superior in terms of activity and selectivity in the formation of acetonitrile. TOF values of 0.44 s\(^{-1}\) and selectivities up to 23% were attained. Therefore, this coating is highly recommended for the application in a microreactor.

The zeolitic coatings were particularly efficient in the ethylene ammoxidation reaction and exhibited a TOF value, which was one order of a magnitude higher than the one measured on pelletized catalysts (0.44 vs. 0.013 s\(^{-1}\), respectively). The screening experiments were operated in the intrinsic kinetic regime, whereas the reactions on catalytic pellets were limited by internal mass transfer.

The reaction rate on zeolitic coatings was significantly reduced when using ethane as a reactant and it was shown that their superiority over pelletized zeolites diminished. Co-BEA with a Si/Al ratio of 15 exhibited a TOF value of 1.25\(\cdot\)10\(^{-3}\) in the ethane ammoxidation reaction, while 4.4\(\cdot\)10\(^{-1}\) s\(^{-1}\) was obtained in the case of ethylene. Hence, the oxidative dehydrogenation of ethane to ethylene can be considered as the rate determining step.

The highest ethylene conversion (23%) was observed at 475°C on the Co-BEA-15 coating. The selectivity to acetonitrile increased with temperature to a value of 23% at 500°C, whereas the NH\(_3\) selectivity to nitrogen decreased to 25%. Remarkably, methanol and hydrogen cyanide were found as products in the dissociation of acetonitrile. The corresponding selectivities though, decreased with temperature (from 47% at 350°C down to 35% at 500°C). Optima in the TOF value of the catalyst as function of the GHSV were observed at standard process conditions.
Figure 35: New reactor design for the ammoxidation reaction of ethane to acetonitrile over Co-BEA and Co-ZSM-5 catalytic coatings. The oxidative dehydrogenation of ethane to ethylene takes place in reactor compartment I, whereas part II represents the compartment for the ammoxidation reaction of ethylene to acetonitrile [15].
5.2 Recommendations

A decrease in the Si/Al ratio showed an enhanced activity of the zeolitic coatings. In order to even further improve the activity, BEA coatings with a Si/Al ratio down to 12 need to be considered, since this value is expected to result in an optimal number of active cobalt sites. Furthermore, the impregnation of boron has to be investigated more thoroughly.

The elemental characterization of the zeolitic coating needs to be improved. Since scratching of the thin zeolite was not feasible, ICP forms a good alternative to the XPS surface characterization. The quantification of the species in the ion exchange solution can be used to determine the amounts of cations diffused into the zeolite framework.

The GC analysis of the outlet streams has to be enhanced as well. Components featuring a dipole, such as ammonia, water, ethylamine, hydrogen cyanide and methanol are difficult to distinguish. A poraPLOT amine column can be used for the separation of the components.

In order to enhance the formation of acetonitrile from ethane, a new reactor concept is suggested, which is depicted in Fig. 35 [15]. This concept can be realized by designing a microreactor with two separate inlets and by loading the first reactor compartment with a catalyst which selectively converts ethane into ethylene, e.g. Cu$^{2+}$ based zeolites.

Although possible diffusion limitations were determined based on theoretical considerations, an experimental approach could not be applied due to high conversions of ammonia. By substantially increasing the GHSV, conversions of both ethylene and ammonia could be reduced, which enables an experimental determination of the mass transfer limitations based on the reaction rates of the reagents. Furthermore, the effect of the inlet concentrations of ammonia, ethylene and oxygen needs to be investigated, in order to elucidate the reaction pathway into detail.
6 References


7 Nomenclature

Symbols

\( a_p \) = specific surface area \((\text{m}^{-2} \cdot \text{m}^{-3})\)

\( C_p \) = heat capacity \((\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})\)

\( C_{Ab} \) = concentration of species A in the bulk \((\text{mol} \cdot \text{m}^{-3})\)

\( C_{As} \) = concentration of species A at the surface \((\text{mol} \cdot \text{m}^{-3})\)

\( C_{ca} \) = concentration of Co(CH\(_3\)COO\(_2\)) solution \((\text{mol} \cdot \text{m}^{-3})\)

\( d \) = catalyst layer thickness \((\text{m})\)

\( D_{AB} \) = diffusivity of A in B \((\text{m}^3 \cdot \text{m}^{-1} \cdot \text{s}^{-1})\)

\( D_{eff} \) = effective diffusivity \((\text{m}^3 \cdot \text{m}^{-1} \cdot \text{s}^{-1})\)

\( F_v \) = volumetric flow at STP conditions \((\text{m}^3 \cdot \text{h}^{-1})\)

\( GHSV \) = gas hourly space velocity \((\text{h}^{-1})\)

\( h \) = distance between two catalytic plates \((\text{m})\)

\( k_s \) = mass transfer coefficient \((\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1})\)

\( k_{r}^{\text{obs}} \) = reaction rate coefficient \((\text{s}^{-1})\)

\( M_a \) = molar mass of species A \((\text{g} \cdot \text{mol}^{-1})\)

\( M_b \) = molar mass of species B \((\text{g} \cdot \text{mol}^{-1})\)

\( M_{Co} \) = molar mass of Co \((=58.93 \cdot 10^{-3})\) \((\text{kg} \cdot \text{mol}^{-1})\)

\( M_{SiO_2} \) = molar mass of SiO\(_2\) \((=60.09 \cdot 10^{-3})\) \((\text{kg} \cdot \text{mol}^{-1})\)

\( M_{AlO_2} \) = molar mass of AlO\(_2\) \((=58.98 \cdot 10^{-3})\) \((\text{kg} \cdot \text{mol}^{-1})\)

\( M_H \) = molar mass of H \((=1.01 \cdot 10^{-3})\) \((\text{kg} \cdot \text{mol}^{-1})\)

\( M_c \) = molar mass of zeolite \((\text{kg} \cdot \text{mol}^{-1})\)

\( M_{\text{synth}}^{\text{cat}} \) = molar mass zeolite as synthesized \((=f(R_{Si/Al}))\) \((\text{kg} \cdot \text{mol}^{-1})\)

\( M_{\text{calc}}^{\text{cat}} \) = molar mass zeolite after calcination \((=f(R_{Si/Al}))\) \((\text{kg} \cdot \text{mol}^{-1})\)

\( n \) = reaction order \((-)\)

\( N_C \) = molar diffusion flux of species A \((\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1})\)

\( N_{Co} \) = amount of Co\(^{2+}\) present in the zeolite structure \((\text{mol})\)

\( p \) = pressure \((\text{atm})\)

\( r_{Co/Al}^{\text{obs}} \) = reaction rate observed per unit of mass \((\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1})\)

\( r_{C_2H_3N}^{\text{obs}} \) = formation rate of C\(_2\)H\(_3\)N \((\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1})\)

\( r_{C_2H_4}^{\text{obs}} \) = disappearance rate of C\(_2\)H\(_4\) \((r_{C_2H_6}^{\text{obs}} \text{ for C}_2\text{H}_6)\) \((\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1})\)

\( R_{Co/Al} \) = molar Co/Al ratio \((-)\)

\( R_{Si/Al} \) = molar Si/Al ratio \((-)\)

\( S_C \) = selectivity of product y on carbon-base \((\%)\)

\( S_N \) = selectivity of product y on carbon-base \((\%)\)

\( t \) = time \((\text{s})\)
Nomenclature

\( T \) = temperature \((^\circ \text{C})\)  
\( \text{TOF} \) = turnover frequency \((\text{s}^{-1})\)  
\( x_{\text{H,O}} \) = estimated weight fraction of H\(_2\)O in zeolite \((-)\)  
\( x_{\text{Co}} \) = weight fraction cobalt \(( \text{kg}_{\text{Co}} \cdot \text{kg}_{\text{c}}^{-1} )\)  
\( x_{\text{out}}^{\text{C}_2\text{H}_3\text{N}} \) = mole fraction of C\(_2\)H\(_3\)N in outlet stream \((-)\)  
\( x_{\text{in}}^{\text{C}_2\text{H}_4} \) = mole fraction of C\(_2\)H\(_4\) in inlet stream \((-)\)  
\( x_{\text{in}}^{\text{C}_2\text{H}_3\text{N}} \) = mole fraction of C\(_2\)H\(_3\)N in inlet stream \((-)\)  
\( x_{\text{p}} \) = mole fraction of product p in inlet stream \((-)\)  
\( x_{\text{y}} \) = mole fraction of product y in inlet stream \((-)\)  
\( x_{\text{out}}^{\text{p}} \) = mole fraction of product p in outlet stream \((-)\)  
\( x_{\text{out}}^{\text{y}} \) = mole fraction of product y in outlet stream \((-)\)  
\( V_{\text{ca}} \) = volume of Co(CH\(_3\)COO\(_2\)) solution \((\text{m}^3)\)  
\( V_{\text{m}} \) = molar volume at STP conditions (=22.4\(\cdot10^{-3}\)) \((\text{m}^3\cdot\text{mol}^{-1})\)  
\( W \) = catalyst weight \((\text{kg}_{\text{c}})\)  
\( W_{\text{cat}} \) = catalyst weight after calcination \((\text{kg}_{\text{c}})\)  
\( W_{\text{pt}}^{\text{cat}} \) = catalyst weight after post treatment (=W) \((\text{kg}_{\text{c}})\)  
\( W_{\text{synth}}^{\text{cat}} \) = catalyst weight as synthesized \((\text{kg}_{\text{c}})\)  
\( z \) = diffusion distance \((\text{m}_{\text{c}})\)

Greek symbols

\( \varepsilon \) = porosity of catalyst \((m_{g}^3\cdot m_{r}^{-3})\)  
\( 1 - \varepsilon \) = catalyst volume per unit of reactor volume \((m_{c}^3\cdot m_{r}^{-3})\)  
\( \varepsilon / \kappa \) = Lennard-Jones parameter \((\text{K})\)  
\( \nu_{\text{al}} \) = stoichiometric coefficient of Al in zeolite \((-)\)  
\( \nu_{\text{O}} \) = stoichiometric coefficient of O in zeolite \((\text{mol}^{-1})\)  
\( \nu_{\text{C}}^{\text{C}_2\text{H}_4} \) = stoichiometric coefficient of C in C\(_2\)H\(_4\) (=2) \((-)\)  
\( \nu_{\text{C}}^{\text{C}_2\text{H}_6} \) = stoichiometric coefficient of C in C\(_2\)H\(_6\) (=2) \((-)\)  
\( \nu_{\text{C}}^{\text{p}} \) = stoichiometric coefficient of C in product p \((-)\)  
\( \nu_{\text{p}}^{\text{N}} \) = stoichiometric coefficient of N in product p \((-)\)  
\( \nu_{\text{C}}^{\text{y}} \) = stoichiometric coefficient of C in product y \((-)\)  
\( \nu_{\text{y}}^{\text{N}} \) = stoichiometric coefficient of N in product y \((-)\)  
\( \rho_b \) = bulk density of catalyst \((\text{kg}_{\text{c}}\cdot \text{m}_{\text{c}}^{-3})\)  
\( \rho_c \) = apparent density of catalyst \((\text{kg}_{\text{c}}\cdot \text{m}_{\text{c}}^{-3})\)
Nomenclature

\[ \sigma = \text{Lennard-Jones parameter} \quad (\text{Å}) \]
\[ \Omega_{AB} = \text{“collision integral” of species A and B} \quad (-) \]

Dimensionless numbers

\[ Sh = \text{the Sherwood number} \quad (-) \]
Appendix I

Table 15: Relative thermal response data [31].

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<td></td>
<td>Carbon monoxide</td>
<td>42</td>
</tr>
</tbody>
</table>

* All values measured relative to benzene (benzene = 100%).
* Values reported by Rosic and Gero (7).
Appendix II

The collision integral for the prediction of transport properties of gases at low density as given by [34]:

$$\Omega_{D,AB} = \frac{1.06036}{T^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$

where:

$$T^* = \frac{\kappa T}{\varepsilon_{AB}}$$

$$\frac{\varepsilon_{AB}}{\kappa} = \sqrt{\frac{\varepsilon_A \varepsilon_B}{\kappa \kappa}}$$

$$\frac{\varepsilon}{\kappa} = \text{Lennard-Jones parameter}$$