# OXIDATIVE DEHYDROGENATION ACTIVITY OF HIGH-SILICA Co-ZEOLITES. INFLUENCE OF PRESENCE OF AMMONIA

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*The aim of this study is to bring a view on possibility to use high-silica zeolites modified with ion-exchanged $Co^{2+}$ ions in oxidative dehydrogenation and ammoxidation of propane. The MFI zeolites chosen are known to possess catalytic activity in ammoxidation of ethane. A set of samples with different content of ion-exchanged cobalt, different Si/Al ratios and type of co-cations was prepared. The courses of reaction of propane with oxygen or oxygen and ammonia were measured in dependence on temperature. Co-MFI zeolites exhibited catalytic activity in oxidative dehydrogenation of propane to propene and ammoxidation of propane led to formation of acetonitrile. The formation of acetonitrile is explained by destruction of acrylonitrile formed.*

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# Introduction

Light alkanes are available and cheap raw materials used, because of their low chemical reactivity, mainly in energetics. Considering the continuously rising consumption and the price of olefines as initial raw materials for a variety of chemical products, it is very desirable to find processes that can replace these expensive materials by relatively cheaper alkanes. There are two types of processes converting paraffines to more valuable chemicals. The two-stage process consists of oxidative dehydrogenation in the first step and the proper production of requested products in the second. Oxidative dehydrogenation of light paraffines is already commercially available. The highest activity and selectivity is shown by oxide catalysts either on vanadium base (V-Sb, V-P, V-Mo) or on molybdenum base (Mo-Ni, Mo-Co) [1,2]. However, considering relatively great charges on dehydrogenative unit, the one-step production seems to be much more preferable from economic view.

A breakthrough with this problem was the direct ammoxidation of propane to acrylonitrile catalysed by mixed oxides on V-Sb-Al or V-Mo bases [3–6]. But the reaction involves a temperature of 770 – 820 K, it means about 100 – 150 K higher than in the case of propylene as the starting raw material. The highest yield of acrylonitrile obtained on these catalysts was 55% with 86.7% conversion of propane over $V_{0.3}Te_{0.23}MoO_x$ catalyst [7]. The reaction mechanism proposed for ammoxidation of propane to acrylonitrile over these materials involves formation of propylene as intermediate in the first step.

In analogy to the case of propane there were efforts to carry out direct ammoxidation of ethane to acetonitrile. Unfortunately, these systems were not active in ammoxidation of ethane. Aliev et al. [8] studied conversion of ethane to acetonitrile on Cr-Nb-Mo-O catalyst at 350 – 500 °C and achieved only 10% selectivity to acetonitrile with 18% conversion. The authors suggested a reaction mechanism that does not consider ethene as a reaction intermediate. Recently, Amor et al. reported high catalytic activity of Co-zeolites of types BEA and MFI in ammoxidation of ethane to acetonitrile [9,10]. Rate of formation of acetonitrile was 1 – 2 order higher than on the best oxide catalysts (Nb-Sb-O on $Al_2O_3$ [11] and Cr-Nb-Mo-O [8]). The mechanism of ammoxidation of ethane suggested by Armor includes, as the first step, activation of ethane with formation of ethene, which is added to strongly adsorbed ammonia with formation of ethylamine., which subsequently undergoes dehydrogenation to acetonitrile [12].

From this point of view promising catalysts for ammoxidation of alkanes are the indicated catalysts, which show catalytic activity in oxidative dehydrogenation of the existing alkane with formation of the corresponding olefine. Zeolite materials seem to represent one of promising ways to obtaining highly active and selective catalysts. Atomary dispersed ions of metals, built-in ion sites of molecular sieves matrix, and nano oxidic species in this matrix together with

acidic Lewis and Bronsted centres in this matrix offer entirely new, and in oxide catalysts unavailable, complex catalytic properties. Works of Armor *et al.* showed activity of Co-ions in high-silica zeolites in oxidative dehydrogenation of ethane because ethene was one of the main products of ammoxidation of ethane and, hence, the formation of ethene is one of the basic steps of the presumed reaction mechanism. Considering these facts in this paper, we have studied oxidative dehydrogenation of propane on high silica zeolites type MFI with ion-exchanged ions of cobalt in dependence on composition of zeolitic catalyst. Also we have studied the influence of addition of ammonia to the reaction mixture on run of ammoxidation reaction and examined the possibility of production of acrylonitrile by direct ammoxidation of propane over Co-zeolites.

## Experimental

### Catalysts

Parent zeolites were kindly provided by the institute of Oil and Hydrocarbon Gases, Slovnaft, Slovakia. $NH_4$-MFI (Si/Al 14.0) was prepared from Na-MFI (Si/Al 14.0) by ion exchange with $NH_4NO_3$ solution ( 10 g of Na-MFI was ion exchanged with 150 ml 1M $NH_4NO_3$ solution at 353 K over night ). Co ions were introduced into zeolites by standard ion exchange of the ammonium form of MFI zeolite and sodium form of MFI zeolite with cobalt nitrate or acetate solutions. Conditions of preparation of zeolites and their chemical composition (obtained by Wavelength-disperse X-Ray Fluorescence spectrioscopy (WD XRF)) are given in Table I.

### Catalytic Tests

The reactions runs were made using a plug-flow reactor in a steady state at atmospheric pressure. Typically, a total flow rate of 100 ml min$^{-1}$ and a catalyst weight of 0.2 g mixed with 1.5 cm$^3$ of inert silicon carbide, to prevent local overheating, were used for each run. The feed composition was 5 vol.% propane, 6.5 vol.% $O_2$ and rest of helium for oxidative dehydrogenation of hydrocarbons, and 5 vol.% propane, 6.5 vol.% $O_2$, 10 vol.% $NH_3$ and rest of helium for ammoxidation of hydrocarbons. The reaction was measured in the temperature range of 350 – 510 °C. The catalysts were normally pre-treated with flowing gas mixture (6.5 vol.% $O_2$ in He) at 45 °C for 1 h before each reaction run.

The experiments on reaction of acetonitrile and acrylonitrile with oxygen and ammonia were carried out at 450 °C over 0.2 g sample of $CoNH_4$-MFI/12.5

Table I Chemical composition and ion-exchanged parameters of zeolites. The samples are labelled as, e.g. Co–NH$_4$–MFI/12.5/1.55 (cobalt-cocation-zeolite topology-Si/Al molar ratio-Co/Al molar ratio)

| Sample | Chemical composition | | | | Ion exchange parameter | | | |
|---|---|---|---|---|---|---|---|---|
| | Si/Al | Co/Al | $w_{Co}$ | solution | mol l$^{-1}$ | ml sol. g$^{-1}$ zeolite | time, rep. h$^{-1}$ | T, K |
| CoNH$_4$-MFI/12.5/1.55 | 12.5 | 0.23 | 1.55 | Co(Acet)$_2$ | 0.05 | 16 | 2 × 7 | 343 |
| CoNH$_4$-MFI/12.5/2.87 | 12.5 | 0.42 | 2.87 | Co(Acet)$_2$ | 0.05 | 16 | 2 × 12 | 343 |
| CoNH$_4$-MFI/12.5/3.83 | 12.5 | 0.50 | 3.83 | Co(Acet)$_2$ | 0.10 | 16 | 3 × 12 | 343 |
| CoNH$_4$-MFI/14.0/2.10 | 14.0 | 0.33 | 2.10 | Co(Acet)$_2$ | 0.05 | 42 | 2 × 4 | 333 |
| CoNH$_4$-MFI/14.0/1.59 | 14.0 | 0.27 | 1.59 | Co(Acet)$_2$ | 0.05 | 42 | 2 × 4 | 333 |

/2.87. Nitriles were injected into reaction mixture by means of a saturator at 25 °C. The reaction mixture was composed of 6.5 vol.% O$_2$, 0.4 vol.% acrylonitrile or acetonitrile, while the concentration of ammonia was ranging from 0 to 14 vol.%. Helium was used as inert carrier gas. The total flow rate was 100 ml min$^{-1}$.

The effect of presence of N$_2$O on reaction run was investigated at 450 ° over 0.2 g sample of CoNH$_4$–MFI/12.5/2.87 by addition of 0.5 vol.% and 1 vol.% N$_2$O to standard reaction mixture in the oxidative dehydrogenation and ammoxidation of propane.

The composition of products was analysed by a gas chromatograph CHROM 5 equipped with TCD connected "on-line" to catalytic apparatus. The hydrocarbons, nitriles, CO$_2$ and N$_2$O were separated by a packed column (4/5 Porapak N and 1/5 Carboxen 80/100). Permanent gases (N$_2$, O$_2$, CO and CH$_4$) were separated and analysed by a molecular sieve 5A column. Hydrocarbon conversions, selectivities and yields of products and turn-over-frequency (TOF) value per Co atom were determined.

**Results**

Figure 1 shows a typical example of the catalytic performance of Co-MFI as a function of temperature. The conversion of propane increased with temperature within the whole range monitored. The selectivity of carbon monooxide waried in the range between 25 and 35%, and it seemed to slightly increase in dependence on the reaction temperature. The selectivity of carbon dioxide slightly increased with temperature. The selectivity of propene decreased with the reaction temperature and varied from 50 to 10%. TOF factors of Co-MFI with Si/Al ratio 12.5 showed a decreasing tendency in the activities in dependence on increasing content of cobalt in zeolite (see Table II). The highest activity was obtained on the sample with 1.55 wt.% of ion-exchanged cobalt. The cobalt content has no visible
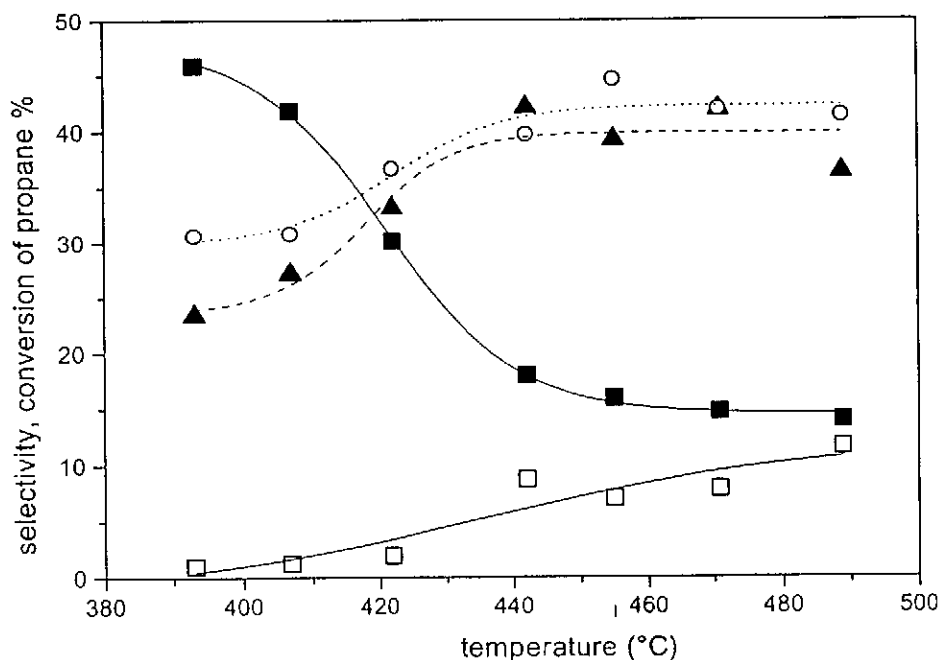
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Fig. 1 Oxidative dehydrogenation of $C_3H_8$ as a function of temperature. The reaction run with 0.2 g Co-NH$_4$-MFI/12.5/1.55, $F$ = 100, ml min$^{-1}$, 5 vol.% $C_3H_8$, 6.5 vol.% $O_2$, $\square$ – conversion of propane; $\circ$ – selectivity for $CO_2$; $\blacksquare$ – selectivity for propene; $\blacktriangle$ – selectivity for CO

Table II Oxidative dehydrogenation of propane over Co-MFI zeolites. 0.2 g zeolite. Feed composition: $F$ = 100 ml min$^{-1}$, 5 vol.% $C_3H_8$, 6.5 vol.% $O_2$, $T$ = 450 °C

| Sample | Conversion, % $C_3H_8$ | Selectivity, % | | | | | TOF, h$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | CO | CO$_2$ | C$_3$H$_6$ | C$_2$H$_4$ | CH$_4$ | |
| CoNH$_4$-MFI/12.5/1.55 | 7.5 | 40.6 | 42.6 | 16.7 | 0.0 | 0.0 | 17.9 |
| CoNH$_4$-MFI/12.5/3.83 | 9.8 | 28.1 | 48.9 | 15.5 | 7.3 | 0.4 | 9.8 |
| CoNH$_4$-MFI/12.5/2.87 | 8.5 | 34.7 | 48.5 | 13.6 | 2.6 | 0.0 | 11.1 |
| CoNH$_4$-MFI/14.0/2.10 | 10.0 | 31.5 | 48.7 | 13.8 | 4.2 | 2.3 | 18.8 |
| CoNH$_4$-MFI/14.0/1.59 | 18.4 | 15.8 | 60.5 | 12.8 | 7.9 | 2.9 | 45.6 |

influence on selectivity except for carbon monooxide. The difference of CO selectivity between the lowest and highest concentration of cobalt reached about 12% at 450 °C. The same course of influence of ion-exchanged cobalt expressed by TOF factors was observed on samples with Si/Al = 14. The colour of sample
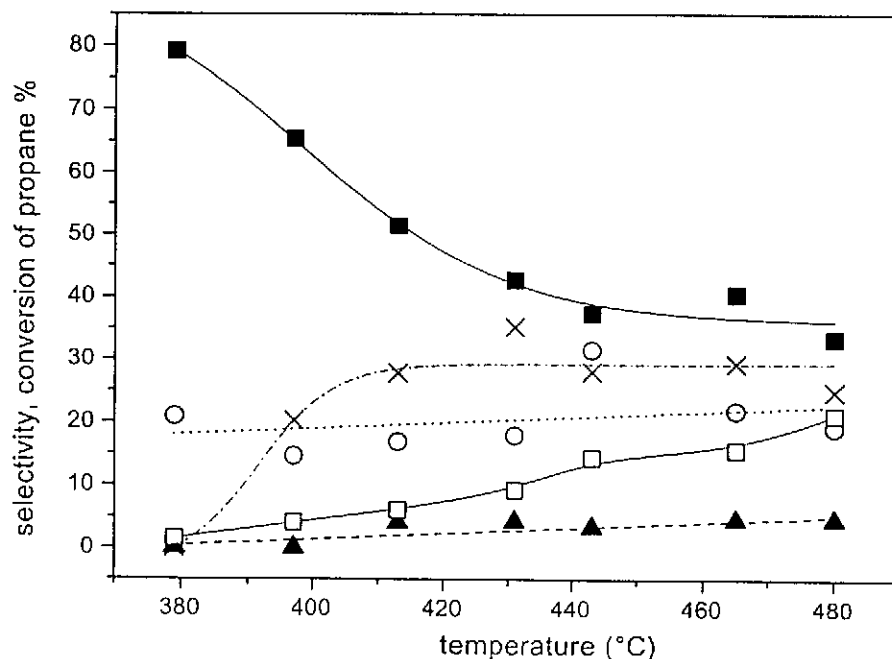
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Fig. 2 Ammoxidation of $C_3H_8$ as a function of temperature. The reaction run with 0.2 g Co-$NH_4$-MFI/12.5/1.55, $F = 100$, ml min$^{-1}$, 5 vol.% $C_3H_8$, 6.5 vol.% $O_2$, 10 vol.% $NH_3$, □ – conversion of propane; ○ – selectivity for $CO_2$; ■ – selectivity for propene; ▲ – selectivity for CO; × – selectivity for acetonitrile

Table III Ammoxidation of propane over Co-MFI zeolites. 0.2 g zeolite. Feed composition: $F = 100$ ml min$^{-1}$, 5 vol.% $C_3H_8$, 6.5 vol.% $O_2$, 10 vol.% $NH_3$, $T = 450$ °C

| Sample | Conversion, % $C_3H_8$ | Selectivity, % | | | | | | TOF, h$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | CO | $CO_2$ | $C_3H_6$ | $C_2H_4$ | $CH_4$ | $C_2H_3N$ | |
| CoNH$_4$-MFI/12.5/1.55 | 14.0 | 4.0 | 22.3 | 38.6 | 1.5 | 0.0 | 27.9 | 33.3 |
| CoNH$_4$-MFI/12.5/3.83 | 12.8 | 0.1 | 22.6 | 46.5 | 3.0 | 0.1 | 23.8 | 12.8 |
| CoNH$_4$-MFI/12.5/2.87 | 18.3 | 3.2 | 29.1 | 36.0 | 4.8 | 0.9 | 25.8 | 23.9 |
| CoNH$_4$-MFI/14.0/2.10 | 17.0 | 0.0 | 31.0 | 39.7 | 6.7 | 2.8 | 19.8 | 31.5 |
| CoNH$_4$-MFI/14.0/1.59 | 16.8 | 0.0 | 32.3 | 40.4 | 6.8 | 2.9 | 17.6 | 41.5 |

changed from white to black because of coking. Other visible changes of samples were not observed. The reaction mixture of raw materials for ammoxidation was obtained by addition of 10 vol.% of ammonia to the reaction mixture of oxidative

dehydrogenation. Figure 2 shows the course of ammoxidation of propane depending on temperature. Conversions of all raw materials increased with temperature. Conversion of propane was 25% at the highest consumption of oxygen. Reactions over Co-MFI samples were limited by shortage of oxygen, because conversion of oxygen was almost 100% at 480 °C. The selectivity for carbon monooxide was max. 10%. The selectivity for carbon dioxide slightly increased or was constant with reaction temperature, varying in the range between 20 and 30%. The selectivity for propene decreased with reaction temperature from 80 to 40%. The products of ammonia reaction were nitrogen (it forms the majority of N-products), nitrous oxide and there was unexpectedly detected acetonitrile. The selectivity for acetonitrile behaved independently on reaction temperature and it varied in the range between 30 and 40% for individual samples. Acrylonitrile was not detected in any amount. TOF factors of zeolites with Si/Al ratio 12.5 showed the same course of activity in dependence on cobalt content (see Table III). The highest activity was found on the sample $Co-NH_4-MFI/12.5/1.55$. No distinct influence on selectivities of products was observed.

Comparison of selectivities and conversions of oxidative dehydrogenation and ammoxidation of propane is shown in Fig. 3. An increase of conversion of propane after addition of ammonia to reaction mixture was observed. The formation of carbon monooxide showed a rapid decrease in comparison to oxidative dehydrogenation. A decrease was also observed on the selectivity for carbon dioxide. An opposite behaviour was found with selectivities for propene and ethene. Acetonitrile is an additional new product formed with high selectivity ($\sim 20\%$).

The results measured showed different behaviour of H and Na forms of MFI zeolites. Their activities expressed by TOF factor are shown in comparison with these two types of zeolites in oxidative dehydrogenation and ammoxidation in Fig. 4. The activity of H-zeolites was lower in the reactions measured. It was found that addition of ammonia to the reaction mixture led to an increase in activity in the case of H-zeolite, but the activity obtained on Na-zeolite in ammoxidation of propane was slightly lower.

The increase in the conversion of propane observed after addition of ammonia could be caused by the presence of $N_2O$ formed by oxidation of ammonia. $N_2O$ has been used as extremely selective reagent in the last decade. Therefore, we added 0.5 and 1 vol.% of $N_2O$ to the reaction mixture of oxidative dehydrogenation and 1 vol.% nitrous oxide to the reaction mixture of ammoxidation (see Tables IV and V). The results showed a decreasing conversion of propane and no distinct changes in selectivitie.

The stability of nitriles was studied on sample $Co-NH_4-MFI/12.5/1.55$ at temperatures between 420 and 480 °C. The concentration of acetonitrile in the reaction mixture was 0.35 vol.%. The selectivity for carbon monooxide was 30% and was independent of temperature. The selectivity for carbon dioxide achieved
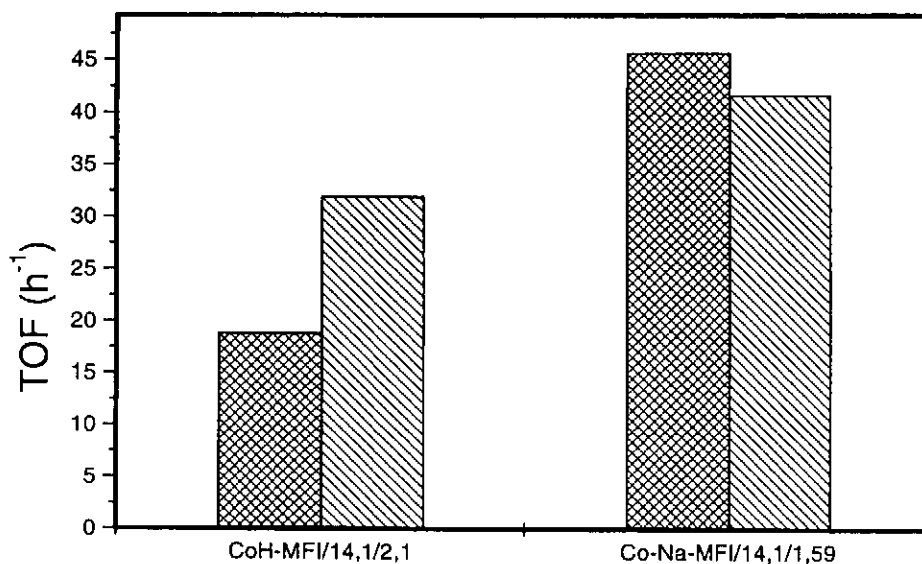
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Fig. 3 Comparison of conversions of propane and selectivities between oxidative dehydrogenation and ammoxidation on $Co-NH_4-MFI/12.5/1.55$, $T$ = 450°C; ▨▨▨ – oxidation, ▧▧▧ – ammoxidation
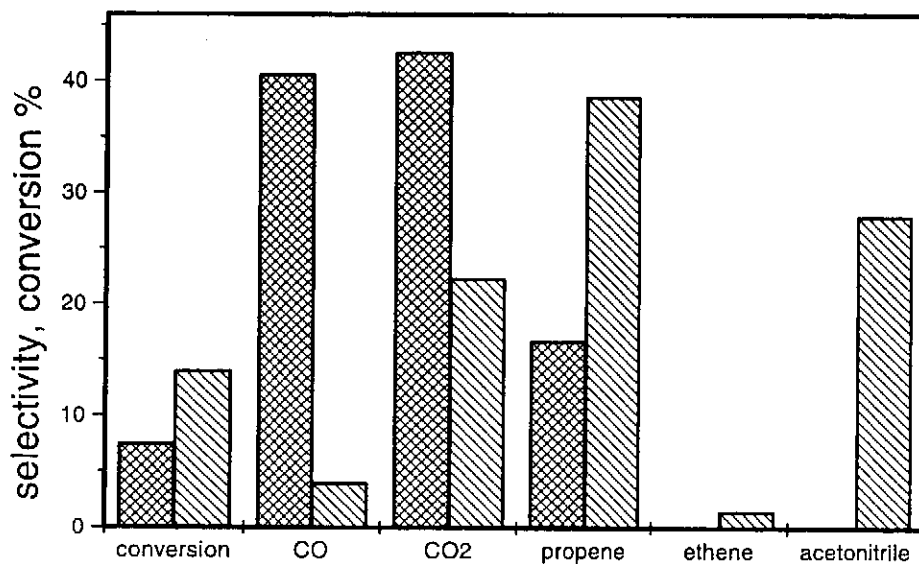


Fig. 4 Comparison of TOF factors ($h^{-1}$) of oxidation and ammoxidation between $Co-NH_4-MFI/14.1/2.1$ and Co-Na-MFI/14.1/1.59: ▨▨▨ – oxidation, ▧▧▧ – ammoxidation

Table IV  Oxidative dehydrogenation of propane with addition of $N_2O$ over $Co-NH_4-MFI$ /12.5/2.87. 0.2 g zeolite. Feed composition: $F$ = 100 ml min$^{-1}$, 5 vol.% $C_3H_8$, 6.5 vol.% $O_2$, and variable concentration of $N_2O$, $T$ = 450 °C

| Vol.% $N_2O$ | Conversion, % $C_3H_8$ | Selectivity, % | | | | |
|---|---|---|---|---|---|---|
| | | CO | $CO_2$ | $C_2H_4$ | $CH_4$ | $C_3H_6$ |
| 0.0 | 11.3 | 33.6 | 36.2 | 9.4 | 2.5 | 18.0 |
| 0.5 | 10.4 | 31.8 | 44.7 | 0.0 | 0.0 | 23.5 |
| 1.0 | 9.0 | 28.6 | 47.8 | 0.0 | 0.0 | 23.6 |

Table V  Ammoxidation of propane with addition of $N_2O$ over $Co-NH\_MFI/12.5/2.87$. 0.2 g zeolite. Feed composition: $F$ = 100 ml min$^{-1}$, 5 vol.% $C_3H_8$, 6.5 vol.% $O_2$, 10 vol.% $NH_3$ and variable volume of $N_2O$, $T$ = 450 °C

| Vol.% $N_2O$ | Conversion, % $C_3H_8$ | Selectivity, % | | | | |
|---|---|---|---|---|---|---|
| | | CO | $CO_2$ | $C_2H_4$ | $C_2H_3N$ | $C_3H_6$ |
| 0.0 | 17.1 | 1.9 | 24.0 | 5.4 | 27.1 | 40.0 |
| 1.0 | 16.0 | 1.8 | 24.4 | 3.1 | 25.9 | 44.7 |

70%. Another product of oxidation of acetonitrile was nitrogen. An addition of ammonia to the reaction mixture (0.35 vol.% acetonitrile, 6.5 vol.% oxygen and variable vol.% ammonia) at 445 °C led to an increase in the conversion of acetonitrile from 8 to 60%. The highest conversion was achieved with 2 vol.% ammonia in the reaction mixture. Further increase in concentration of ammonia did not influence the course of reaction. The selectivity for carbon dioxide increased after addition of ammonia to 97% and the selectivity for CO decreased to 2%, the most distinct changes being observed in the range from 0 to 2 vol.% ammonia in the reaction mixture. The course of reaction is shown in Fig. 5.

The stability of acrylonitrile was measured at similar conditions (0.4 vol.% acrylonitrile, 6.5 vol.% oxygen) as those used for the stability of acetonitrile. The main products of this reaction were carbon dioxide, nitrogen and a small amount of carbon monooxide. An addition of ammonia to the reaction mixture led to a rapid increase in the conversion of acrylonitrile from 7 to 100%. This value of conversion was achieved at 2 vol.% ammonia in the reaction mixture. With zero concentration of ammonia in the reaction mixture, the only reaction product was carbon dioxide. After addition of 0.5 vol.% ammonia, the conversion of acrylonitrile increased to 70% and a new product was obtained — acetonitrile — with the selectivity of 80%. Another increase in concentration of ammonia to 2.5 vol.% led to a decrease in selectivity for acetonitrile and to an increase in selectivity for carbon dioxide. After next addition of ammonia into the reaction mixture, the conversion of acrylonitrile was constant and its value was 100% and
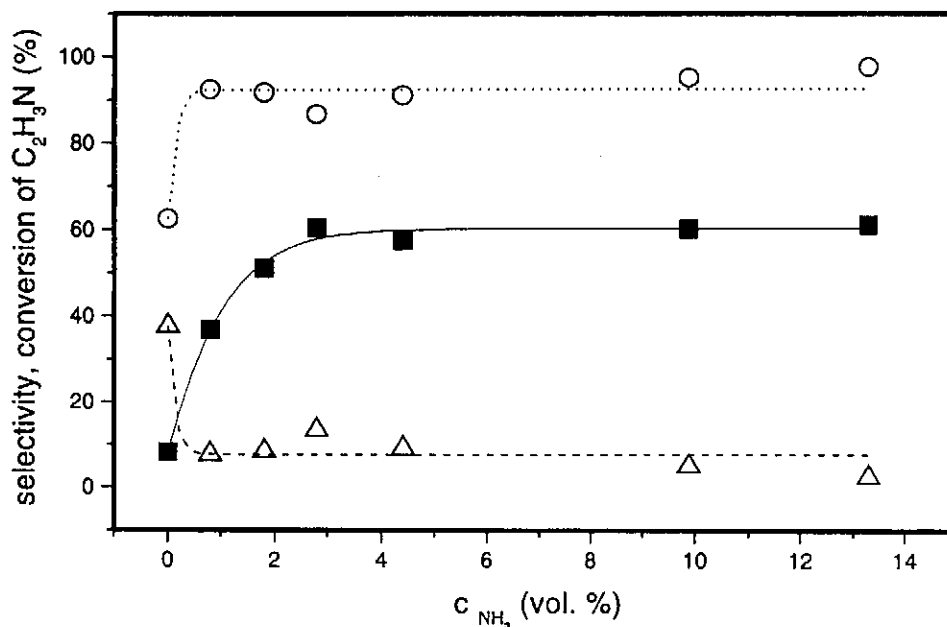
Fig.5  Reaction of acetonitrile over Co $-NH_4-MFI/12.5/2.87$ as a function of $NH_3$. The feed consists of 0.35 vol.% acetonitrile, 6.5 vol.% $O_2$ and variable levels of $NH_3$: ■ $-$ conversion of acetonitrile; ○ $-$ selectivity for $CO_2$; △ $-$ selectivity for CO

the selectivities for acetonitrile (26%) and carbon dioxide (73%) were independent of ammonia concentration. The course of reaction depended on concentration of ammonia in the reaction mixture is shown in Fig. 6.

## Discussion

The study of oxidative dehydrogenation of propane showed the activity of high silica zeolites with ion-exchanged $Co^{2+}$ ions in this reaction with production of propene. Besides propene there were detected oxides of carbon as products of total combustion and small amounts of methane and ethene as a result of cracking. The selectivity for olefine decreased with increasing temperature, and/or with the conversion of paraffine with concomitant of total oxidation to carbon oxides. The activity of Co-ions located in molecular sieves in oxidative dehydrogenation reactions has already been observed earlier. Okamoto et al. [13] were interested in oxidative dehydrogenation of propane over Co-APO-5 and VAPO-5. Co-APO-5 was less active. Its selectivity for propene was 19% at 400 °C, but traces of benzene formed from propylene were found. Its activity slightly increased after treating
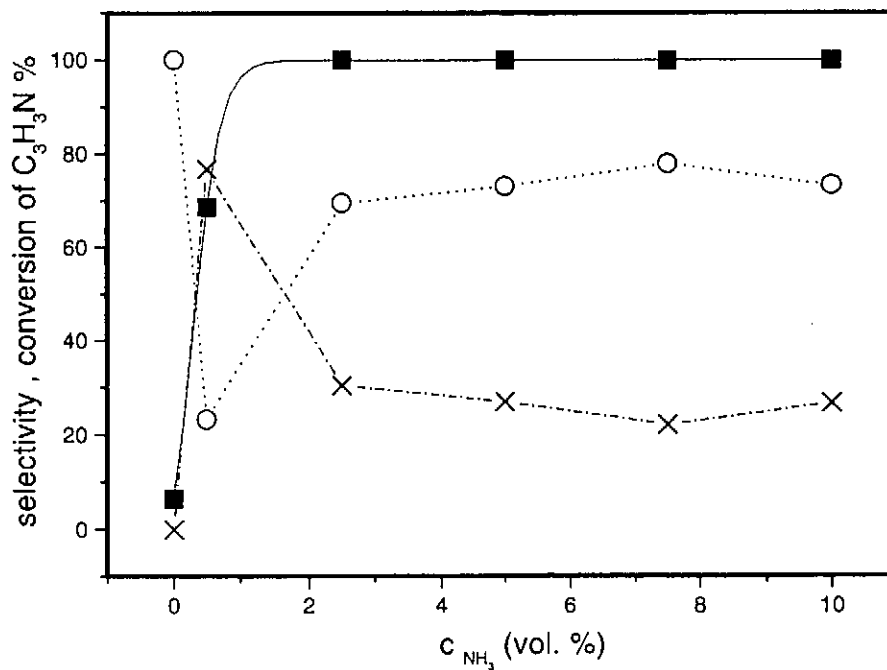
Fig.6 Reaction of acrylonitrile over $Co-NH_4-MFI/12.5/2.87$ as a function of $NH_3$. The feed consists of 0.4 vol.% acrylonitrile, 6.5 vol.% $O_2$ and variable levels of $NH_3$: ■ – conversion of acrylonitrile; ○ – selectivity for $CO_2$; × – selectivity for acetonitrile

Co-APO-5 by vanadyl. The selectivity for propene decreased with the reaction temperature. Cavani *et al.* [14] studied oxidative dehydrogenation of *n*-butane, butene and benzene and the role of oxygen in the reaction mechanism over MFI zeolites ion-changed by Cu, Fe and Co. The dependence of selectivity found by them [14] corresponds to results of our study: at low temperatures (to 380 °C) no burning is observed and saturated and unsaturated hydrocarbons are formed. Above 380 ° the temperature is too high, and burning takes place with formation of carbon oxides. Influence of Co content in zeolite was not examined in detail, one of the assumptions of decreasing activity with cobalt content being the decreasing number of acid sites. Cobalt is not reduced at the conditions used by us (it is stable till 900 °C under reduction atmosphere 5% $H_2$). It is evident that the reaction mechanism is different from that in the case of reducible ion-exchanged cations in zeolite. Derouane *et al.* Proved that Bronsted acid sites in synergy with metal sites can catalyse the ammoxidation of propane [15].

For study of ammoxidation the same mixture of raw materials was used as in the oxidative dehydrogenation with addition of 10 vol.% ammonia with maintaining the same flow (100 ml min$^{-1}$). It was mentioned that there was no

detected acrylonitrile, which was an expected reaction product. Again there was detected acetonitrile with high selectivity, which varied in the range from 20 to 40%. A rising selectivity for propene was observed (from 30 to 50%) as compared to the coarse of oxidative dehydrogenation of propane, and a marked decrease in reaction selectivity for carbon monooxide. Armor [16–18] found that the product of ammoxidation of higher paraffines (propane, butane and pentane) is acetonitrile with great selectivity and almost no acrylonitrile, butanenitrile or pentanenitrile were formed. Armor explains the production of acetonitrile by addition of ammonia across double bond of oleffine formed to β‑position by Markovnikov rule leading to break of C-C bond and formation of acetonitrile. Sokolovskii [19] found that in ammoxidation of propane over oxide catalysts (especially V-Sb-O, Ga-Sb-O) acrylonitrile is formed, but acetonitrile is also always formed. Acrylonitrile is formed from propylene, which is an intermediate of ammoxidation of propane, but propane is also cracked to ethene, and ethene is the startng material for formation of acetonitrile. Selectivity for acetonitrile was 5% max. Another type of formation of acetonitrile from higher hydrocarbons (paraffines) uses the Cr-Mo-O catalyst, which has more destructive properties. The products of ammoxidation of propane over this catalyst include acetonitrile and a great amount of HCN, because the cracking is a major reaction there.

During studies of the stability of both of the main products of ammoxidation reactions in oxidative atmosphere and after addition of ammonia, it was found that both the nitriles are relatively stable in oxidative conditions (the maximum conversion is about 7% at 45 °C). Sokolovskii confirms this too, saying in his work that nitriles are more stable than oxoderivatives of hydrocarbons given. The situation in the presence of small amount of ammonia is quite different. Acetonitrile is more stable than acrylonitrile, and in the case of acetonitrile only combustion to carbon dioxide was observed. It was found that acrylonitrile in the presence of ammonia on zeolite matrix is decomposed with formation of acetonitrile. On the basis of these determinations, an experiment was performed where ammoxidation of propane was carried out in the reaction mixture containing 5 vol.% propane, 6.5 vol.% oxygen and only 0.5 vol.% ammonia. Besides acetonitrile also acrylonitrile was detected in reaction products with the selectivity about 6%. It seems evident that acrylonitrile can be formed by ammoxidation of propane over Co-zeolites, but it consequently undergoes decomposition to acetonitrile by the influence of ammonia.

From these experiments with acetonitrile and acrylonitrile it is clear that ammonia is able to increase the oxidative activity of Co-zeolites as in the case of ammoxidation of propane but we assume that the decrease in conversion of hydrocarbon due to the fact that oxidation of ammonia competes with oxidation of hydrocarbon. $N_2O$ Was used as selective oxidative reagent in the last decade [20–23]. The primary assumption about the increase in activity of catalyst in the reaction of propane with $N_2O$ formed on zeolite surface by oxidation of ammonia

was not confirmed because addition of $N_2O$ to the reaction mixture did not increase the activity of zeolite. It is possible to find similarity in behaviour of zeolites in ammoxidation of propane and oxide catalysts for ammoxidation of propane (Ga-Sb-O). The described reaction mechanism of ammoxidation of propane over these oxide systems includes the activation of hydrocarbon *via* carbenium ion formed by adsorption of hydrocarbon on a basic site. The activation of hydrocarbon on acidic catalyst proceeds on basic sites formed by adsorption of ammonia on acid sites, where $NH_2^{\delta-}$ or $NH^{\delta-}$ is formed which operates as basic sites. Rinsing concentration of ammonia on these systems caused an increase in conversion of hydrocarbons. The behaviour of Co-zeolites corresponds to this scheme. We observed a slight decrease in conversion of propane on Na types of zeolites for this reason, while an addition of ammonia is accompanied by an increase in conversion od acidic types of zeolites.

## Conclusion

The aim of this work was to study the activity and catalytic properties of zeolites with ion-exchanged $Co^{2+}$ ions in ammoxidation and oxidation of propane. The conclusions resulting from experiments are:

1. Co-zeolites are active in oxidative dehydrogenation of propane, the main products being propene and $CO_2$.
2. Ammoxidation of propane leads to formation of acetonitrile and propene as main products.
3. Acetonitrile is formed from the decomposition of acrylonitrile in reaction with ammonia.
4. The presence of ammonia leads to an increase in conversion of hydrocarbon and in selectivity for oleffine and of decrease in formation of CO.
5. The hydrocarbon is activated on basic sites *via* carbenium ion.

## Acknowledgements

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