



High temperature pretreatment of Fe-silicalite for the ammoxidation of propane

Kateřina Raabová*, Roman Bulánek, Eva Baďurová

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, Pardubice 53210, Czech Republic

ARTICLE INFO

Article history:

Received 15 May 2012

Received in revised form 22 June 2012

Accepted 29 June 2012

Available online 5 September 2012

Keywords:

Nitridation

Fe-silicalite

Ammoxidation

Propane

Amide/imide species

ABSTRACT

Fe-silicalite with low concentration of iron was used in the study of the activation by high temperature nitridation (in the temperature range from 540 °C to 700 °C). Nitrided materials were characterized by means of FTIR and UV-Vis spectroscopy. It was found out, that by this high temperature pretreatment, Fe-silicalite undergoes structural changes – iron is extracted to extraframework positions and atom of nitrogen is incorporated into the zeolite structure (either as amide or as imide group), which was confirmed by FTIR spectroscopy. Catalytic performance of nitrided materials together with Fe-silicalite activated by hydrothermal pretreatment was studied and compared in the direct ammoxidation of propane. It was found out, that the nitrided materials reaches better results compared to sample activated in the steam. Selectivity as high as 34% at 32% conversion of propane was reached over the sample activated at 600 °C by nitridation. Nitrided material showed stable catalytic performance in the TOS study for 10 h.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Recently, the nitridation of zeolites at elevated temperature, in which nitrogen atom is introduced into the framework to substitute oxygen atom, in order to synthesize solid basic catalysts, has received much attention. Nitridation increased the Lewis basicity of the framework due to the lower electronegativity of nitrogen than oxygen. This substitution is usually achieved by thermal treatment (hereafter referred to as nitridation) of the parent material under an ammonia flow for a prolonged time. Several nitrogen-incorporated zeolites [1–7], mesoporous materials [8–11] and (silico)-aluminophosphates [12–14] have been reported. Several authors discussed the role of the temperature and time of the nitridation, and they found out, that the amount of nitrogen incorporated into the materials highly depends on these factors [7,10]. Different kinds of characterization techniques (XPS, FTIR) [3–5,7] confirmed that the activated materials contained nitrogen in different coordinations (like amide, imide groups). Nitrided materials were studied for various reactions, mainly for the processes which are catalyzed by basic catalytic systems. The typical example of such based probe reaction is Knoevenagel condensation of benzaldehyde described many times in the literature [1–4,6].

First reported nitrided material studied for direct ammoxidation of propane was VAION (vanadium-aluminum oxynitride) [15], which reached very promising results in this reaction. Recently,

we published the results from the study of activity of Fe-silicalite activated in the diluted mixture of propane and ammonia at 540 °C [16]. We found out, that this pretreatment led to active and stable material, which compared to other materials studied for the direct ammoxidation of propane, achieved very interesting results (mainly acrylonitrile productivity of catalyst was very high). Advantages of this method of activation were low temperature of the activation, using of gas mixture consisting of part of reaction mixture, therefore demanding no additional compounds, and the stability of the resulting material upon the exposure to air. We speculated that nitridation took place during this pretreatment and we called this pretreatment gas reduction nitridation (GRN). We assumed the creation of basic centers (amide/imide groups) in the catalysts, however we were not successful in experimental proving of such functional groups presence in the catalysts due to very low concentration and therefore very hard detection.

Therefore, in order to confirm that oxygen is substituted by nitrogen atom in the presence of ammonia in the gas phase at about 540 °C, we study nitridation in pure ammonia flow and subsequently characterize resulting catalysts by FTIR and UV-Vis spectroscopy. Scope of this contribution is not only to characterize nitrided samples but also to correlate spectroscopic results with catalytic activity. The activity of the nitrided samples will be compared with the samples pretreated by hydrothermal pretreatment (usually described in the literature as the conventional method for the activation of Fe-zeolites [17–20]) in order to determine if the activity is caused only by the extraction of iron to extraframework positions, or if upon the nitridation some active centers are created.

* Corresponding author. Tel.: +420 466 037 052; fax: +420 466 037 068.
E-mail address: Katerina.Raabova@upce.cz (K. Raabová).

2. Experimental

2.1. Preparation of the catalyst, its activation and catalytic tests

Fe-silicalite catalyst with the concentration of Fe 4800 ppm (Si/Fe = 170) introduced during zeolite synthesis was investigated. Fe-silicalite was prepared by hydrothermal synthesis described earlier [16]. Nitridation of the sample was done as follows: 80 mg of the catalyst was calcined in the flow of oxygen in He, (5 vol.% of O₂ in 100 cm³/min). At the temperature of 540 °C the flow of oxygen was stopped and the sample was heated only in the flow of He to the nitridation temperature (540 °C, 600 °C or 700 °C). Subsequently, the samples were nitrided in the flow of ammonia (20 cm³/min) for 5 h at the chosen temperature (samples denoted as follows: N540, N600 and N700). After the activation the temperature was lowered to 540 °C while the sample was treated under the flow of an inert. Subsequently, the sample was treated for 30 min in gas mixture consisting of 5 vol.% of O₂ in He with flow rate 100 cm³/min. After that reaction mixture comprising 2.5 vol.% of propane, 5 vol.% of oxygen and 5 vol.% of ammonia in helium with total flow rate of 100 cm³/min was prepared. The reaction was measured at the temperature of 540 °C. Analysis of the products was made in TOS (time-on-stream) of 50 min. Product gases were analyzed online by GC equipped with TCD and FID detectors. Conversion, selectivity and yields were calculated on the basis of the mass balance. In the case of the hydrothermal pretreatment the parent Fe-silicalite was treated for 5 h in the 30 vol.% H₂O in helium at 600 °C (denoted as HT).

2.2. Characterization

The DR-UV-Vis spectra were measured with UV-Vis spectrometer GBC CINTRA 303 equipped with a diffuse reflectance attachment with an integrating sphere coated with spectralon. Pure fumed silica was used as a reference material and samples were diluted with this silica (ratio 1:5) before measurements. Absorption intensity was expressed using Schuster-Kubelka-Munk equation.

FTIR spectra were recorded on Nicolet 6700 FTIR spectrometer equipped with an MCT/A cryodetector, accumulating 64 scans at a spectral resolution of 2 cm⁻¹. Self supporting pellets (ca. 10 mg/cm²) were prepared from the sample powders and treated directly in a purpose-made IR cell allowing measurements at ambient and liquid nitrogen temperatures. The cell was connected to a vacuum pump allowing a residual pressure ~10⁻⁴ Torr.

3. Results and discussion

3.1. Catalytic activity

Table 1 brings the results from the study of catalytic performance of nitrided materials together with the sample which was activated by hydrothermal pretreatment. The products of ammoxidation of propane were acrylonitrile (ACN), acetonitrile (AcCN),

Table 1

Comparison of the catalytic performance of Fe-silicalite activated by nitridation at different temperatures (540–700 °C) and by hydrothermal pretreatment at 600 °C in the direct ammoxidation of propane. Reaction condition: T = 540 °C, m_{cat} = 80 mg, F = 100 cm³/min, C₃H₈/NH₃/O₂ = 2.5/5/5 vol.%.

	Conversion (%)		Selectivity (%)				Yield (%)
	C ₃ H ₈	O ₂	C ₃ H ₆	AcCN	ACN	CO _x	ACN
HT	7	30	61	6	16	13	1
N540	12	37	40	9	35	14	4
N600	32	100	7	5	34	53	11
N700	25	100	12	4	13	70	3

propylene, carbon oxides and traces of cracking products with the selectivity not exceeding 4%.

As can be seen from the table the catalytic activity differs a lot depending on the method of the pretreatment and the temperature of the nitridation. While the conversion of propane of the sample N540 reaches 12% after 5 h of the activation, higher temperature of the activation (600 °C) leads to much higher conversion (32%). Nitridation at 700 °C does not result in additional increasing of conversion, being about 25%. Regarding the selectivity to ACN, it is very similar for the samples pretreated by nitridation at 540 °C and 600 °C, being about 34–35%. On the other hand, nitridation at 700 °C leads to worse result, showing the selectivity to ACN of only 13%. Catalytic test showed that nitridation at high temperature (700 °C) leads mainly to the formation of CO_x (selectivity being 70%). Regarding the ACN yield, the best result was reached on the sample activated for 5 h by nitridation at 600 °C, 11%. Yields about 3 and 4% were reached over the samples activated by nitridation at 700 and 540 °C, respectively. On the other hand, the activation of Fe-silicalite by HT leads to very poor results; the conversion of propane after 5 h of the activation was only about 7% with 16% of selectivity to ACN, which corresponded to very low yield of ACN, about 1%. These results correlated quite well with the studies of Bulanek et al. [21] and Perez-Ramirez et al. [17], when they described the low activity of hydrothermally activated Fe-silicalite in the direct ammoxidation of propane in the presence of molecular oxygen. They found out, that in order to get better the catalytic activity of hydrothermally activated samples, it was necessary to use nitrous oxide as the co-oxidant. This however is not so convenient from the economical point of view.

These results clearly show that nitridation leads to the material with better catalytic performance than hydrothermal treatment, because it is able to catalyze the reaction only in the presence of oxygen as the oxidizing agent. In order to study the stability of the nitrided material, we chose the sample which reached the best results, N600, and we carried out long term test of ammoxidation of propane. The results are reported in Fig. 1. As can be clearly seen from the figure, the catalytic activity of the nitrided material shows stable behavior. Conversion of propane slightly decreases with the TOS, from 32 to 27%, so does the selectivity to ACN, anyway the changes are very small. The stability of Fe-silicalite, activated by different methods, was already discussed in other papers. Pretreatment by GRN led to very stable catalytic system, which maintained its activity for as long as 1700 min in the reaction [16]. But also the activation by hydrothermal pretreatment led to the stable catalyst as was reported by Bulanek et al. [21] and Perez-Ramirez et al. [17]. On the other hand, study of the catalyst stability of the calcined sample led to the conclusion that

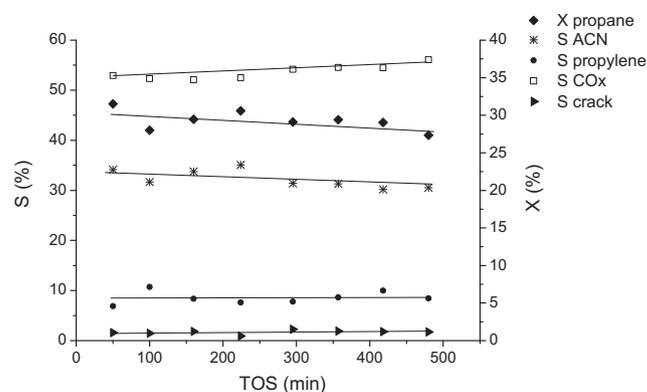


Fig. 1. Stability of the catalytic performance of N600 catalyst during the time on stream. Reaction conditions: T = 540 °C, m_{cat} = 80 mg, F = 100 cm³/min, C₃H₈/NH₃/O₂ = 2.5/5/5 vol.%.

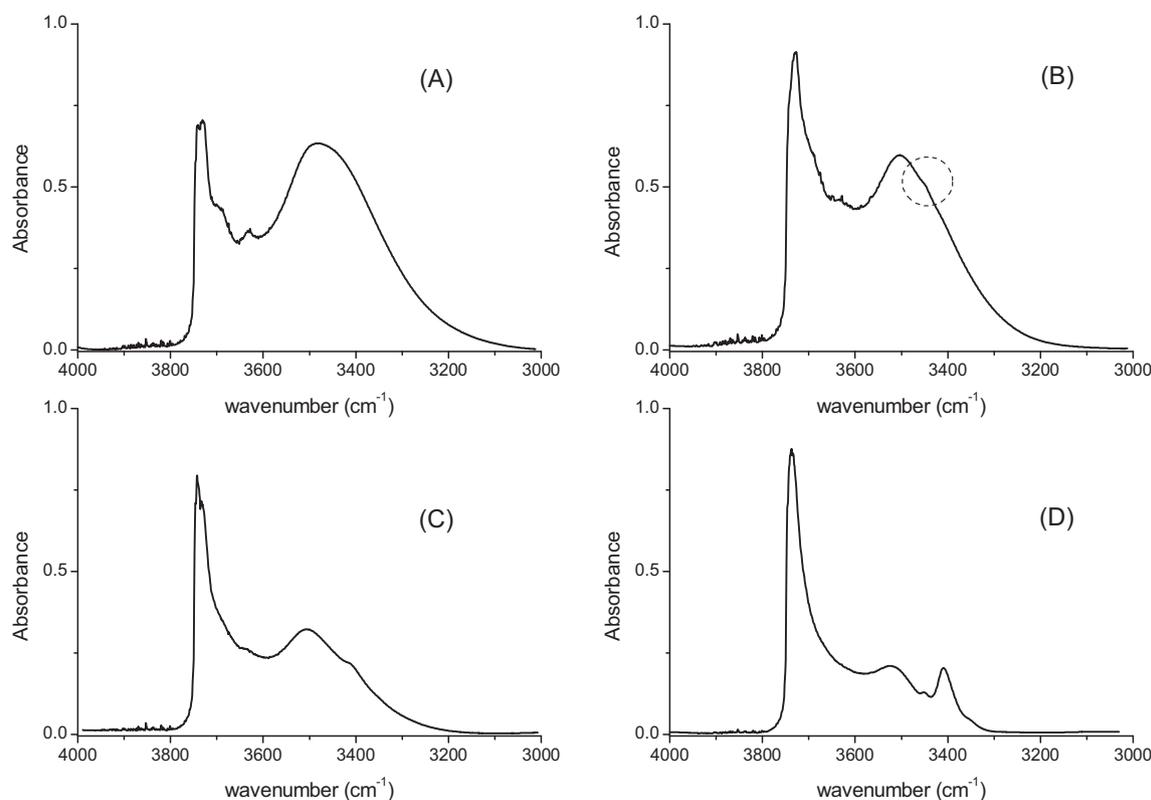


Fig. 2. FTIR spectra of the nitrated materials, calcined overnight in the vacuum at 450 °C. Fresh calcined sample (A), Fe-silicalite activated by nitridation at 540 °C (B), at 600 °C (C), at 700 °C (D) for 5 h.

during the reaction iron was extracted to extraframework positions, thus leading to pronounced changes in the catalyst activity [21]. This emphasizes the importance of the suitable activation, which is able to ensure the extraction of iron to extraframework positions and subsequent coordination of extracted ions in stable positions.

3.2. Characterization

3.2.1. FTIR spectroscopy

All the nitrated samples were characterized by FTIR spectroscopy in order to prove the incorporation of nitrogen into the zeolite structure. Before each measurement, the samples were calcined at 450 °C overnight under vacuum.

Spectra of the fresh sample (Fig. 2A) are characterized by the absorption bands at 3630 cm^{-1} , 3686 cm^{-1} and two not well separated absorption bands at 3726 cm^{-1} and 3742 cm^{-1} . According to the literature, the absorption band at 3630 cm^{-1} should be caused by Brönsted OH group resulting from the iron incorporated into the zeolite lattice. The band at 3686 cm^{-1} would be caused by the hydroxyl groups coordinated to extraframework iron atoms [22]. The absorption band at higher wavenumbers, 3726 cm^{-1} and 3742 cm^{-1} should correspond to silanol groups, either in isolated positions or terminal SiOH groups in the hydrogen bonded silanol chains. The whole spectrum of OH stretching region is dominated by the intense and broad absorption band centered at 3500 cm^{-1} caused by the hydrogen-bonded silanol groups, so called hydroxyl nests.

Individual pretreatments bring substantial changes in the intensity of the absorption bands in OH stretching region depending on the temperature of the nitridation, as is shown in Fig. 2. Sample which was nitridated at 540 °C (Fig. 2B) exhibits absorption bands as the fresh one (however the absorption band at 3726 cm^{-1}

being more dominant than the one at 3742 cm^{-1}), absorption band at 3686 cm^{-1} is more broadened, band of the bridging hydroxyl from Si–OH $\cdot\cdot$ Fe becomes less intense and there is a new absorption band, although hardly distinguishable, centered at 3447 cm^{-1} . Higher temperature of the nitridation (Fig. 2C) leads to pronounced suppression of intensity of the absorption band at 3630 cm^{-1} and 3686 cm^{-1} , the absorption bands of the silanol groups are quite well resolved and there is a new clearly visible absorption band at 3408 cm^{-1} . Finally, sample nitridated at 700 °C for 5 h gives quite different spectrum (Fig. 2D). In this case, the band at 3630 cm^{-1} becomes almost invisible and there are three new absorption bands centered at 3450 cm^{-1} , 3409 cm^{-1} and 3351 cm^{-1} .

According to the literature, the absorption band at 3447 cm^{-1} detected in the sample N540 could be assigned to $\nu_s(\text{NH}_2)$ from Si–NH₂ group [23]. Absorption band detected at 3408 cm^{-1} for the sample N600 would be caused by the $\nu_s(\text{NH})$ from Si–NH–Si group. Such a vibration band was already observed by Fink, Wu and Srasra, when they studied nitridation of H-ZSM-5 [4,23] and of zeolite Y [24]. Finally, the bands detected for the sample N700 at 3450, 3409 and 3351 cm^{-1} should correspond to the $\nu_s(\text{NH}_2)$ from Si–NH₂ group, as already observed for the sample N540, $\nu_s(\text{NH})$ from Si–NH–Si group and the vibration $\nu_{\text{as}}(\text{NH}_2)$ originating from Si–NH₂ $\cdot\cdot$ Fe, respectively. The assumption is made merely based on the similarity of the absorption band $\nu_{\text{as}}(\text{NH}_2)$ from Si–NH₂ $\cdot\cdot$ Al detected at the wavenumber range of 3330–3335 cm^{-1} . This absorption band was observed for the sample ZSM-5 upon the nitridation at the temperature higher than 400 °C [23].

This spectroscopic study confirmed that the parent material contained iron predominantly in the framework positions, as was expected for the used synthesis method. We found out that upon the different temperature of the activation there were non-negligible differences in the intensity of the hydroxyl groups

(either from silanol group or from acidic Brønsted hydroxyl). The intensity of the Brønsted hydroxyl groups is decreasing in order $N540 > N600 > N700$. Thus that means that the pretreatment at high temperature causes dehydroxylation with subsequent formation of Si–O–Fe bridges or another possible explanation of this phenomena would be that iron ions are extracted to extraframework positions (which would correspond to the results from UV–Vis spectroscopy, see below). Worth of notice is that the extent of the dehydroxylation/extraction highly depends on the temperature of nitridation. The temperature of 700 °C leads to almost complete disappearance of signal belonging to Brønsted acid sites. Another important feature is the decreased intensity of the bands corresponding to hydroxyl nests together with increased intensity of isolated and terminal silanols.

This trend can be explained as follows: by the high temperature pretreatment the water is condensed from hydroxyl nests by consecutive release of water and creation of strained Si–O–Si bridges [18]. This corresponds well with the decreased intensity of the absorption band at about 3500 cm^{-1} . The extent of the decrease of its intensity correlates well with the temperature of the nitridation, increasing in order: $N700 > N600 > N540$. Upon the subsequent nitridation the formed strained Si–O–Si bridges can be directly attacked by ammonia, giving rise to –Si–NH₂ group and to silanol group –Si–OH, thus explaining the increased intensity of the silanol group upon the nitridation. Another alternative way is the attack of silanol group by ammonia, creating –Si–NH₂ and water.

In the literature it has been proposed that the possible reaction upon the contact of ammonia and the materials highly depends on the temperature of the nitridation. Srasra et al. has proposed that temperature of the nitridation below 600 °C results mainly in the formation of amide –Si–NH₂ groups [24]. Higher temperature leads to the creation of bridging NH groups either by condensation of two amide groups or of an amide with another hydroxyl groups. In our case we detected both amide and imide groups, depending on the used temperature of the nitridation. Very low temperature (540 °C) resulted in hardly visible signal belonging to amide groups –NH₂. Higher temperature led to creation of Si–NH–Si group and nitridation at 700 °C resulted in both in amide and in imide groups. Moreover in this case, another amide species were created by the amination of bridged Si–OH ··· Fe group which corresponded well with almost vanished absorption band of the bridging hydroxyl from iron in the framework position.

3.2.2. UV–Vis spectroscopy

The samples were characterized by UV–Vis spectroscopy in order to get information about the iron coordination and its changes upon the activation.

Spectrum of the fresh sample (Fig. 3A) shows two well resolved bands, centered at 46,000 and 40,000 cm^{-1} . Upon the activation by nitridation at different temperatures (Fig. 3C–E), coordination of iron in the sample is changed which is documented by the changes in the shape of UV–Vis absorption bands. The activation by nitridation leads to the decrease of the intensity of the absorption bands at 46,000 and 40,000 cm^{-1} , most pronounced in the case of the nitridation at 700 °C. Samples activated at the temperature of 540 °C and 600 °C show two additional absorption bands at around 34,000 and 31,000 cm^{-1} . In the case of the silicalite nitrided at 700 °C these bands cannot be observed due to the very intensive broad band which is observed below 35,000 cm^{-1} . This corresponded well with the color of the sample nitrided at 700 °C which was intensively gray. Worth of notice is that the samples activated at lower temperatures did not change their colors, remaining white after the activation. Sample which was activated by HT (Fig. 3B) at 600 °C shows quite similar spectrum to the samples N600 and N540, however in this case, the bands at 34,000 and 31,000 cm^{-1} are not so well resolved.

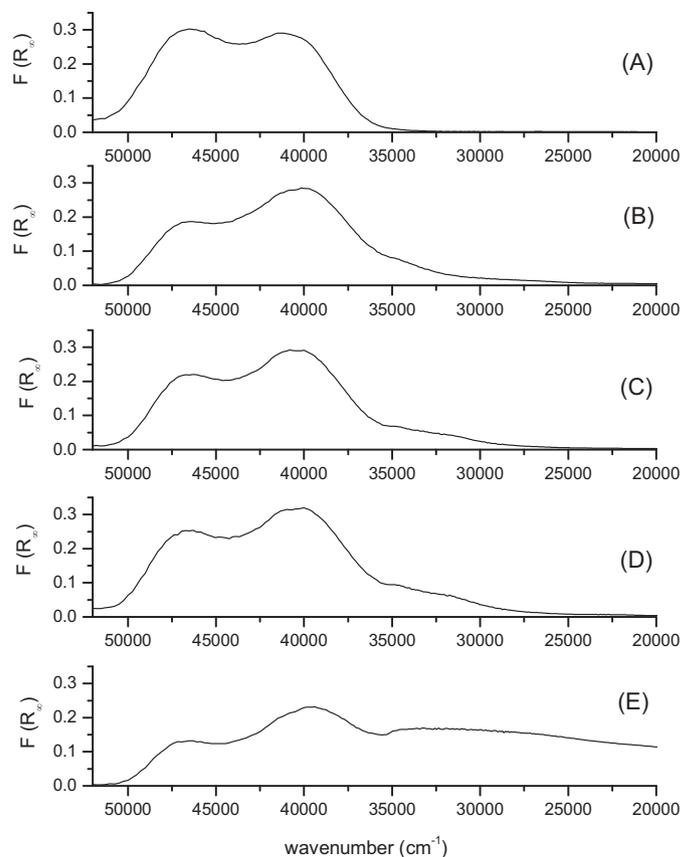


Fig. 3. UV–Vis spectra of hydrated Fe-silicalite. Fresh calcined sample (A), Fe-silicalite activated by hydrothermal pretreatment at 600 °C (B), Fe-silicalite activated by nitridation at 540 °C (C), at 600 °C (D) and at 700 °C (E) for 5 h.

From the literature it is well known, that iron containing samples are characterized by two distinct areas in UV–Vis spectroscopy: first ones are the absorption bands caused by ligand to metal charge transfer Fe–O (observed in the range 50,000–30,000 cm^{-1}) and the second ones are d–d transitions (below 30,000 cm^{-1}). Because the latter are spin and symmetry forbidden, the interpretation of the spectra in the literature is focused mainly on the charge transfer bands.

Our spectra show, that the fresh sample contains tetrahedrally incorporated iron, which is in accordance with the literature, where usually charge transfer bands for transition t_1-t_2 and t_1-e transitions involving Fe³⁺ in FeO₄ tetrahedral group in zeolite lattice were described [25]. Absorption bands which were observed around 35,000–32,000 cm^{-1} could be ascribed to the square pyramidal and distorted octahedra of isolated ions, as was observed in the case of iron on alumina surface [25–27]. The sample nitrided at 700 °C showed intensively gray color after the activation, which caused very broad absorption band below 35,000 cm^{-1} . Due to this strong absorption band, we could not comment on the presence/absence of larger iron cluster, expected to be found in this absorption region. Absorption band detected for the sample activated by HT should be most probably caused by the same iron coordination as in the case of the sample N600 and N540.

In the literature the activation of Fe-silicalite with various concentration of iron by different methods has been several times discussed. It was described that calcination at about 500–550 °C leads to the extraction of iron to extraframework positions and to the formation of oligomeric iron clusters and octahedrally coordinated iron ions [25,28,29]. Thus already the process of the template removal leads in small extent to extraction of iron from framework

to extraframework positions. In our case, we did not observe such clustering, most probably due to the low concentration of iron in our samples. Higher temperature of the calcination at 700 °C in air led to extensive extraction of iron ions from the zeolite lattice and clustering of iron in zeolite channels and to formation of larger Fe₂O₃ particles [25]. Even higher temperature of the calcination (900 °C) led to the similar result as was reported by Waclaw et al. [28]. On the other hand, treatment of the sample in the water vapor led to extensive clustering already at the temperature of 600 °C, as was detected by Perez-Ramirez et al. [29], where they found out that about 15% of iron was present as a clustered oxide phase. Worth of note is that they used higher concentration, 0.68 wt.% Fe. In our case, hydrothermal pretreatment did not lead to creation of larger oxide cluster, but the nitridation at higher temperature did. This activation at such a high temperature resulted in the change of the color of the sample causing absorption band below 35,000 cm⁻¹ which did not permit us to infer upon the presence of oxide cluster of iron.

Our spectroscopic results can be summed up as follows. Low temperature of the nitridation leads to creation of Si–NH₂ group, however in very low concentration. Upon this activation a small amount of iron is extracted to extraframework positions, creating highly coordinated iron ions. Higher temperature, 600 °C, leads to creation of bridged Si–NH–Si group, the coordination of iron being very similar to the one observed at 540 °C. Nitridation at 700 °C leads to creation of isolated NH₂ groups, bridged Si–NH–Si groups and moreover to the exchange of Brønsted OH group by NH₂ group. Most probably this activation also leads to formation of iron nitride and iron oxide particles; however we were not able to prove this hypothesis.

Correlating our spectroscopic results with the results from catalytic study, we can hypothesize that the increased activity is caused by the presence of bridged Si–NH–Si group in the zeolite structure. Regarding the role of the iron ion, we cannot say unequivocally what kind of coordination of iron led to the increased activity (if any) because of the very similar UV–Vis spectra of the samples pretreated by nitridation at 540 °C, 600 °C and by hydrothermal pretreatment. The poor catalytic results reached over the sample activated at 700 °C could be explained by the formation of larger oxide clusters of iron ions – not visible in UV–Vis spectrum because of the broad overlapping band detected at the wavelengths below 35,000 cm⁻¹. Although from FTIR spectroscopy we found out that this sample contained different kinds of amide, imide species, the presence of oxide clusters of iron negatively influenced both the selectivity to ACN and conversion of propane.

Earlier described activation of Fe-silicalite – by gas reduction nitridation was advantageous because of the low temperature of the activation, being 540 °C. Such a low temperature did not cause any extensive clustering of iron ions, as was confirmed by UV–Vis spectroscopy [30]. The result obtained on the sample activated by GRN and by nitridation at 600 °C is reported in Fig. 4. Interestingly, both samples reached the same yield of ACN, however they had different distribution of products and conversion of propane. In the case of GRN the conversion of propane was a little bit lower (25.4%) compared to the sample N600. Another important feature is the high selectivity to CO_x of sample N600 compared to GRN. This correlates with the result from the sample N700 where we detected very high selectivity to CO_x at the expense of selectivity to ACN. From this point of view it would be interesting to further study the nitridation at various temperatures and to find the optimum temperature for the nitridation of Fe-silicalite where we would detect high selectivity to ACN at high conversion of propane.

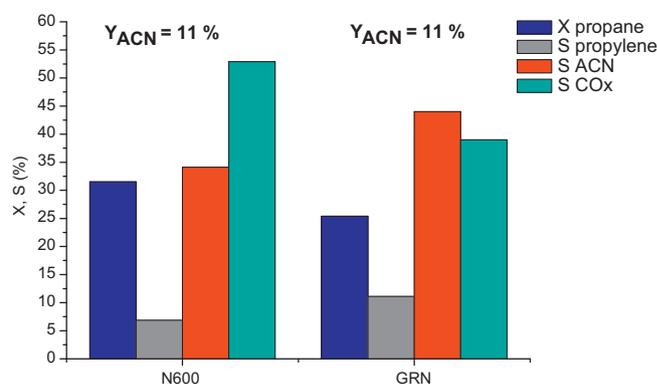


Fig. 4. Comparison of the catalytic performance of Fe-silicalite activated by GRN for 5 h and by nitridation at 600 °C in the direct ammoxidation of propane. Reaction conditions: $T = 540\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 80\text{ mg}$, $F = 100\text{ cm}^3/\text{min}$, $\text{C}_3\text{H}_8/\text{NH}_3/\text{O}_2 = 2.5/5/5\text{ vol.}\%$.

4. Conclusion

Our study was focused on the catalytic performance of Fe-silicalite in the direct ammoxidation of propane, its activation by nitridation and subsequent characterization. Our study led to some very interesting conclusions:

- i) it is possible to insert nitrogen in the zeolite structure at the temperature not excessively high – already 600 °C led to the well distinguishable absorption band in FTIR spectrum at 3408 cm⁻¹ resulting from the presence of Si–NH–Si,
- ii) the structure of nitrated material (the coordination of nitrogen in the zeolite structure) highly depends on the temperature of the nitridation,
- iii) nitridation at 600 °C leads to the material with very good catalytic properties, which does not tend to loose its activity during the TOS and by contact with oxygen,
- iv) from correlation of the spectroscopic results with the results from catalytic study, we suppose that the presence of amide/imide species in the structure of silicalite is advantageous for the catalytic activity of the sample,
- v) regarding the tendency of the material to formation of iron clusters, which negatively influences the catalyst performance, ammonia is better extracting agent with respect to water vapor.

Acknowledgements

A financial support of the Grant Agency of the Czech Republic under the project Nos. P106/12/P083 (KR) and P106/12/G015 (RB) and the UniCRE project (CZ.1.05/2.1.00/03.0071) (EB) are highly acknowledged.

References

- [1] C. Zhang, Z. Xu, K. Wan, Q. Liu, *Applied Catalysis A* 258 (2004) 55–61.
- [2] T. Hasegawa, C.K. Krishnan, M. Ogura, *Microporous and Mesoporous Materials* 132 (2010) 290–295.
- [3] K. Narasimharao, M. Hartmann, H.H. Thiel, S. Ernst, *Microporous and Mesoporous Materials* 90 (2006) 377–383.
- [4] G. Wu, X. Wang, Y. Yang, L. Li, G. Wang, N. Guan, *Microporous and Mesoporous Materials* 127 (2010) 25–31.
- [5] H. Li, Q. Lei, X. Zhang, J. Suo, *ChemCatChem* 3 (2011) 143–145.
- [6] S. Ernst, M. Hartmann, S. Sauerbeck, T. Bongers, *Applied Catalysis A* 200 (2000) 117–123.
- [7] M. Srasra, G. Poncelet, P. Grange, S. Delsarte, *Studies in Surface Science and Catalysis* 158B (2005) 1811–1818.
- [8] F. Hayashi, K. Ishizu, M. Iwamoto, *European Journal of Inorganic Chemistry* 2010 (2010) 2235–2243.
- [9] G. Wu, S. Jiang, L. Li, F. Zhang, Y. Yang, N. Guan, M. Mihaylov, H. Knözinger, *Microporous and Mesoporous Materials* 135 (2010) 2–8.
- [10] N. Chino, T. Okubo, *Microporous and Mesoporous Materials* 87 (2005) 15–22.

- [11] Y. Xia, R. Mokaya, *Angewandte Chemie International Edition* 42 (2003) 2639–2644.
- [12] P. Grange, P. Bastians, R. Conanec, R. Marchand, Y. Laurent, *Applied Catalysis A* 114 (1994) L191–L196.
- [13] A. Massinon, J.A. Odriozola, Ph. Bastians, R. Conanec, R. Marchand, Y. Laurent, P. Grange, *Applied Catalysis A* 137 (1996) 9–23.
- [14] J. Xiong, Y. Ding, H. Zhu, L. Yan, X. Liu, L. Lin, *Journal of Physical Chemistry B* 107 (2003) 1366–1369.
- [15] M. Florea, R. Prada-Silvy, P. Grange, *Catalysis Letters* 87 (2003) 63–66.
- [16] R. Bulanek, K. Raabová, E. Badurova, *Catalysis Today* 179 (2012) 73–77.
- [17] J. Perez-Ramirez, N. Blangenois, P. Cruiz, *Catalysis Letters* 104 (2005) 163–167.
- [18] E.J.M. Hensen, Q. Zhu, R.A.J. Janssen, P.C.M.M. Magusin, P.J. Kooyman, R.A. van Santen, *Journal of Catalysis* 233 (2005) 123–135.
- [19] E.V. Starokon, K.A. Dubkov, L.V. Pirutko, G.I. Panov, *Topics in Catalysis* 23 (2003) 137–143.
- [20] J. Perez-Ramirez, M.S. Kumar, A. Brückner, *Journal of Catalysis* 223 (2004) 13–27.
- [21] R. Bulanek, K. Raabová, G. Kosova-Kucerova, L. Capek, *Catalysis Today* 141 (2009) 254–259.
- [22] A. Zecchina, F. Geobaldo, C. Lamberti, S. Bordiga, G. Turnes Palomino, C. Otero Arean, *Catalysis Letters* 42 (1996) 25–33.
- [23] P. Fink, J. Datka, *Journal of the Chemical Society-Faraday Transactions 1* 85 (1989) 3079–3086.
- [24] M. Srasra, S. Delsarte, E.M. Gaigneaux, *Journal of Physical Chemistry C* 114 (2010) 4527–4535.
- [25] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzolo, G. Vlaic, *Journal of Catalysis* 158 (1996) 486–501.
- [26] G. Centi, S. Perathoner, F. Pino, R. Arrigo, G. Giordano, A. Katovic, V. Pedula, *Catalysis Today* 110 (2005) 211–220.
- [27] G. Lehmann, *Zeitschrift für Physikalische Chemie Neue Folge* 72 (1970) 279–297.
- [28] A. Waclaw, K. Nowinska, W. Schwieger, A. Zielinska, *Catalysis Today* 90 (2004) 21–25.
- [29] J. Perez-Ramirez, J.C. Groen, A. Brückner, M.S. Kumar, U. Bentrup, M.N. Debbagh, L.A. Villaescusa, *Journal of Catalysis* 232 (2005) 318–334.
- [30] K. Raabová, R. Bulanek, E. Badurova, in preparation.