



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

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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.

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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.

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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

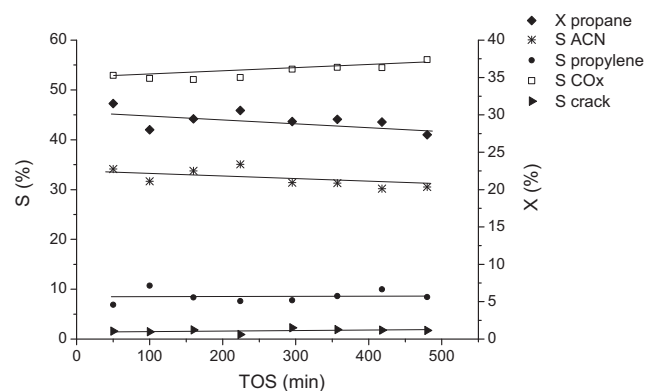


Fig. 1. Stability of the catalytic performance of N600 catalyst during the time on stream. Reaction conditions: T = 540 °C, m_{cat} = 80 mg, F = 100 cm³/min, C₃H₈/NH₃/O₂ = 2.5/5/5 vol.%.

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