

Investigation of HNCO adsorption and hydrolysis on Fe-ZSM5

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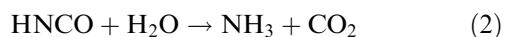
The adsorption of HNCO on Fe-ZSM5 was investigated in detail by DRIFT spectroscopy and compared to the adsorption on H-ZSM5, Al₂O₃, SiO₂, Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂. At 150 °C, HNCO adsorbs dissociatively on Fe-ZSM5 producing principally isocyanate species (–NCO) adsorbed on Al and Fe sites. In the presence of water the hydrolysis of the –NCO groups to NH₃ was observed. Comparison of the DRIFT results with measurements of the catalytic activity of coated cordierite monoliths suggests that –NCO groups are likely intermediate species in the hydrolysis of HNCO over Fe-ZSM5.

KEY WORDS: HNCO adsorption; HNCO hydrolysis; Fe-ZSM5; urea SCR; DeNO_x; DRIFT.

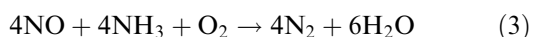
1. Introduction

The necessity to reduce fuel consumption favors Diesel powered vehicles in the near future, which on the one hand are very fuel efficient but on the other hand require internal measures and/or exhaust gas after-treatment systems to minimize their inherent nitrogen oxide (NO_x) and particulate (PM) emissions. The selective catalytic reduction (SCR) process is widely used for the NO_x abatement in stationary power plants, and is also employed for this purpose in Diesel vehicles. Whereas NH₃ is used in stationary SCR systems as the most efficient reducing agent for NO_x, in Diesel vehicles the use of the non-toxic and easy-to-handle urea (H₂N–CO–NH₂) is preferred as NH₃ precursor due to safety reasons [1,2]. The production of NH₃ from urea occurs by a thermo-hydrolysis reaction, i.e. the thermal decomposition of urea to isocyanic acid (HNCO) (1), and the hydrolysis of HNCO to NH₃ and CO₂ (2). Subsequently, NH₃ is reacting with NO and O₂ in the SCR reaction (3).

1.1. Thermo-hydrolysis of urea



1.2. SCR reaction



While the thermal decomposition of urea (1) is a fast reaction, the hydrolysis of isocyanic acid (2) as well as the SCR reaction (3) require a catalyst to proceed efficiently. The catalyst usually employed for the SCR process is V₂O₅ supported on TiO₂ promoted by WO₃, which accelerates both reaction (2) and (3). However, concerns about the potential toxicity of vanadium oxide is opposed to its use and in the near future non-toxic materials will have to be employed [3]. Recently, Fe-ZSM5 received much attention as such a non-poisonous material, which proved to be highly active for the SCR reaction (see for example [4–9]).

Despite the increasing knowledge about the SCR reaction on Fe-ZSM5, only very little information is available about the preceding HCNO hydrolysis occurring on Fe-supported catalysts [10,11]. Solymosi et al. investigated the HNCO adsorption, but specifically on Cu-ZSM5 and hydrolysis was no issue in this study [12].

We present here results on the catalytic hydrolysis of HNCO on Fe-ZSM5 as promising urea-SCR catalyst for Diesel vehicle applications and contribute to the mechanistic understanding of the reaction under consideration of the distributed information in the literature [12–18]. The study has been carried out by means of DRIFT spectroscopy in order to observe the surface species formed upon adsorption of HNCO. To facilitate the interpretation of the spectroscopic data, we first compared the results obtained for Fe-ZSM5 with those obtained for the base material H-ZSM5 as well as its components SiO₂ and Al₂O₃. Finally, a comparison with the Fe-containing samples Fe₂O₃, Fe₂O₃/SiO₂, and Fe₂O₃/Al₂O₃ was performed. The hydrolysis activity of Fe-ZSM5 was also investigated both in the presence and in the absence of NO and NO₂, since these compounds are present in the diesel exhaust gas. The supplemental investigation of the HNCO adsorption on SiO₂ showed

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features that agree well with published theoretical results [19].

2. Experimental

The following base materials were used: H-ZSM5 with a Si/Al ratio of 28, SiO₂ (Grace), Al₂O₃ (Wacker) and Fe₂O₃ (Sigma Aldrich). Over-exchanged Fe-ZSM5 was prepared from H-ZSM5 by solid-state ion exchange with FeCl₂ according to [20]. After preparation, the samples were calcined at 550 °C for 5 h. The amount of iron loaded on the samples was measured by ICP-AES using a Varian Vista AX spectrometer: iron content = 11.4 wt. %.

A Micromeritics ASAP 2000 analyzer was used to measure the N₂ adsorption isotherms of the samples. Micropore volume of H-ZSM5 = 0.11 cm³/g. Micropore volume of Fe-ZSM5 = 0.08 cm³/g.

Iron oxide supported on SiO₂ and Al₂O₃ was prepared by impregnation of 0.5 g of each oxide with a 0.1 M Fe(NO₃)₃·9H₂O solution and subsequent decomposition of the labile nitrate overnight in air at 100 °C. The iron species formed on the surface of the samples were investigated at 20 and –150 °C by EPR spectroscopy using an ELEXYS Bruker instrument (at X-band microwave frequency). The experiments were carried out on the fresh samples without performing any further treatment.

The activity of the catalysts was tested in form of coated cordierite monoliths (volume 7.5 cm³, active mass ~0.8 g) in a glass tubular reactor. The monoliths were coated by immersions in a slurry containing of 0.5 g of catalyst in 2 cm³ of a 0.5 M Al(NO₃)₃·9H₂O solution. The samples were then dried at room temperature for 2 h and, finally, calcined at 500 °C for 5 h. Before the start of the experiments, the samples were treated at 450 °C for 1 h in a flow of N₂/O₂. Isocyanic acid was generated by depolymerization of cyanuric acid as described in [21]. HNCO produced by this method contained NH₃ as impurity (2–4% of the HNCO concentration). The gaseous reaction products were detected and quantified by FTIR spectroscopy according to the experimental set-up and methods described in [21]. A GHSV of 52,000 h^{–1} was used for the tests and the inlet flow was composed of ~1000 ppm HNCO, 2.5% H₂O, and 10% O₂ with N₂ balance. The effect of NO was investigated by adding 700 ppm NO to the inlet flow, while the effect of NO₂ was studied by combined addition of 350 ppm NO and 350 ppm NO₂.

The adsorption of HNCO on the catalyst surfaces was investigated by means of DRIFT spectroscopy. The experiments were carried out with a Nexus FTIR instrument from ThermoNicolet equipped with a Smart Collector DRIFT cell. All spectra were measured by averaging 200 scans at a resolution of 4 cm^{–1}. Before adsorption, the samples were pre-treated at 450 °C in an

N₂ flow for 1 h. The spectral background were collected, and then subtracted from the raw spectra in order to analyze only the adsorbed surface species. For DRIFT investigations the isocyanic acid was purified on a bed of phosphorus pentoxide, yielding 70 ppm HNCO and <0.5 ppm NH₃. The concentrations of HNCO and NH₃ were measured with an ion analyzer as described in [22]. Adsorption of isocyanic acid was performed for 30 min at 150 °C, followed by a flow of pure N₂ for 30 min and a final temperature ramp. The stability of the adsorbed species to water was tested by, first, adsorbing HNCO for 15 min, after which a H₂O/N₂ mixture (4 l_N/h, saturated at RT) was dosed for 10 min at 150 °C.

3. Results

3.1. Characterization of iron exchanged catalysts

The iron adsorbed on the samples is present in form of different species. EPR experiments were carried out to characterize the Fe³⁺ species only, since Fe²⁺ is diamagnetic and thereby EPR-silent. EPR investigation of Fe-ZSM5 revealed signals at *g* ~ 8.5, *g* ~ 5.6, *g* ~ 4.3, *g* ~ 2.3 (broad), and *g* ~ 2 (figure 1A). These signals were attributed to isolated Fe³⁺ sites in strong rhombic or axial distortion, which are incorporated in tetrahedral or octahedral geometry (*g* ~ 4.3 and *g* > 6). The signal at *g* ~ 5.6 corresponds to isolated Fe³⁺ species in higher Fe–O coordination number, whereas the signal at *g* ~ 2 corresponds to isolated Fe³⁺ ions in positions of high symmetry or bulk Fe_xO_y. The broad line at *g* ~ 2.3 refers to Fe₂O₃ particles in the few nanometer range. The detailed peak assignment is reported in [23].

The iron species formed on Fe₂O₃/SiO₂, Fe₂O₃/Al₂O₃, and Fe₂O₃ were also investigated by EPR experiments and the results are shown in figure 2. For pure iron oxide a signal at *g* ~ 2.3 was detected. This signal vanished at very low temperatures (figure 2A),

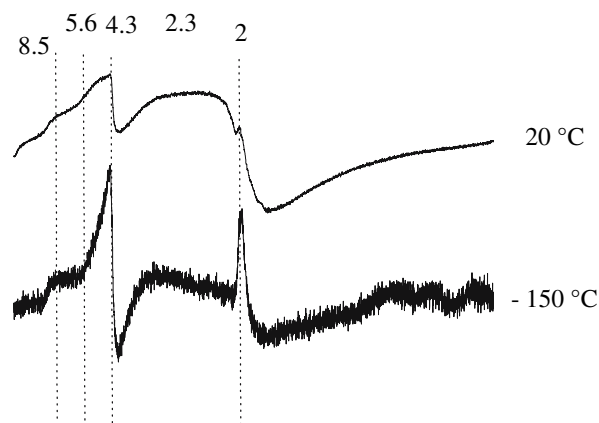


Figure 1. EPR spectra of Fe-ZSM5₁ at 20 °C and –133 °C, respectively.

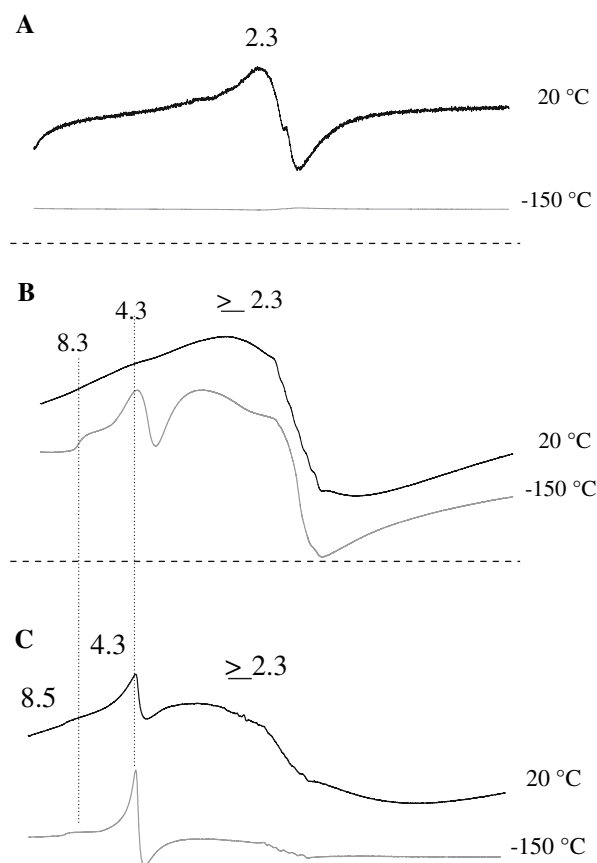


Figure 2. EPR spectra of (A) Fe_2O_3 , (B) Fe-SiO_2 and (C) $\text{Fe-Al}_2\text{O}_3$ at 20 °C and -133 °C, respectively.

and is typical for Fe^{3+} in the bulk Fe_2O_3 . In the EPR spectrum of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ three main signals are visible at $g \sim 8.3$, $g \sim 4.3$, and $g \geq 2.3$ (broad). The intensity of the transitions at $g \sim 8.3$ and $g \sim 4.3$ increased at lower temperatures, which is typical for paramagnetic species. These signals suggest the presence of isolated Fe^{3+} ions with distorted tetrahedral or octahedral coordination [24–26]. The broad signal at $g \geq 2.3$ decreased in intensity and was shifted to lower magnetic fields at -150 °C, thus it does not follow Curie's law. This signal can be attributed to small iron oxide clusters. The analog EPR spectrum obtained for $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ indicates that the same Fe^{3+} species were formed on this material. However, the concentration of the Fe^{3+} species was obviously different due to the different signal intensities.

In the presence of water and oxygen iron tends to form ill-defined mixed oxide and hydroxide species of the form $\text{Fe}_x\text{O}_y(\text{OH})_z$. Thus, the notation Fe-ZSM5 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ does not express the actual structural variety of the iron in these samples as revealed by EPR.

3.2. Adsorption of HNCO on SiO_2

During the adsorption of isocyanic acid on SiO_2 three infrared adsorption bands evolved (figure 3). At the beginning of the adsorption (spectrum not shown), only

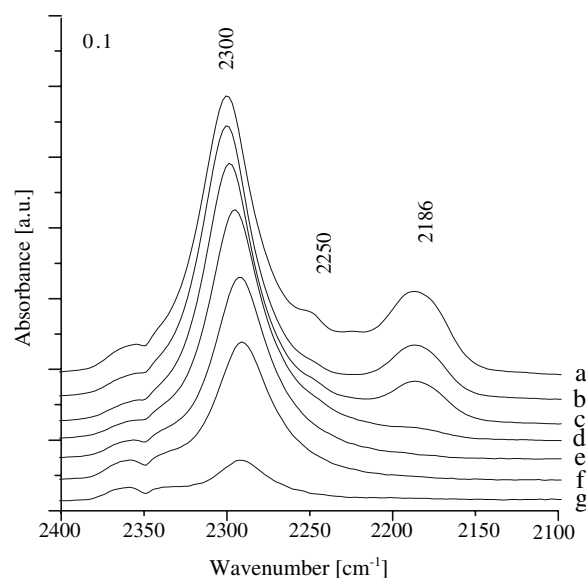


Figure 3. DRIFT spectra of SiO_2 after (a) HNCO adsorption at 150 °C for 30 min followed by (b) purging at 150 °C in N_2 for 30 min, increasing the temperature to (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 450 °C and (g) purging at 450 °C for 60 min.

bands at 2250 and 2186 cm^{-1} appeared, but after a few minutes a band at 2300 cm^{-1} increased in intensity and rapidly become the most intense. This band was not influenced by purging with nitrogen at 150 °C and higher temperatures only slightly affected its intensity. It was necessary to purge the sample at 450 °C for an extended period of time (60 min) to significantly affect this peak. The bands at 2250 and 2186 cm^{-1} were less stable and vanished completely already after purging with nitrogen at 150 °C and 300 °C, respectively. In previous works on the HNCO adsorption on SiO_2 the formation of a band at 2300–2313 cm^{-1} was reported [12,14,16,18]. This band was not observed when adsorption was carried out at $T < 25$ °C, but became more intense at higher adsorption temperatures and could only be removed by long purging at high temperature. Considering these literature results, the peak at 2300 cm^{-1} can be attributed to the Si-NCO groups for its position and temperature stability. The band at 2250 cm^{-1} might be ascribed to the asymmetric ν_a vibration of molecularly adsorbed HNCO due to its position and its poor stability. The ν_2 vibration of HNCO is 2274 cm^{-1} in the gas phase and 2246 cm^{-1} in the solid phase [27]. Bánsági et al. also found evidence for molecularly adsorbed HNCO on SiO_2 at room temperature [18]. While in the above mentioned studies only one or two bands are described arising after adsorption of HNCO on SiO_2 , our spectrum in figure 3 shows a new additional band at 2186 cm^{-1} , that might be attributed to a Si-O-NCO surface species. This is in good agreement with Ferullo et al. who calculated these IR bands for adsorbed NCO on silica [19]. Such a band was not detected in previous studies of HNCO

adsorption on SiO_2 and, differently from the present study, the Si–NCO band at 2300 cm^{-1} was also observed at RT. In order to prove our results the investigation was repeated with silica from other companies, resulting in the same bands. In previous studies the silica was pretreated at $450\text{ }^\circ\text{C}$ in vacuum whereas only temperature treatment at $450\text{ }^\circ\text{C}$ was applied by us. Based on this difference it might be speculated that a higher concentration of OH groups was present on the silica used in our work, preventing the HNCO dissociation at RT and facilitating the formation of the Si–O–NCO group.

3.3. HNCO adsorption on Fe-ZSM5

Dosing of HNCO for 30 min over Fe-ZSM5 at $150\text{ }^\circ\text{C}$ (figure 4A) resulted in the formation of bands at 2278 and 2212 cm^{-1} and small bands at 2139 and 2126 cm^{-1} . At the beginning of the treatment (spectra not shown here), the peaks at 2278 and 2212 cm^{-1} grew much faster in intensity upon HNCO dosing than the peaks at 2139 and 2126 cm^{-1} . After degassing with nitrogen for 30 min at $150\text{ }^\circ\text{C}$ (figure 4A, spectrum a) the band at 2278 cm^{-1} attenuated significantly and disappeared completely while purging at $300\text{ }^\circ\text{C}$. By comparing the position and stability of the IR bands with those obtained for H-ZSM5 both from our experiments (not shown) and from literature data [12], the peak at

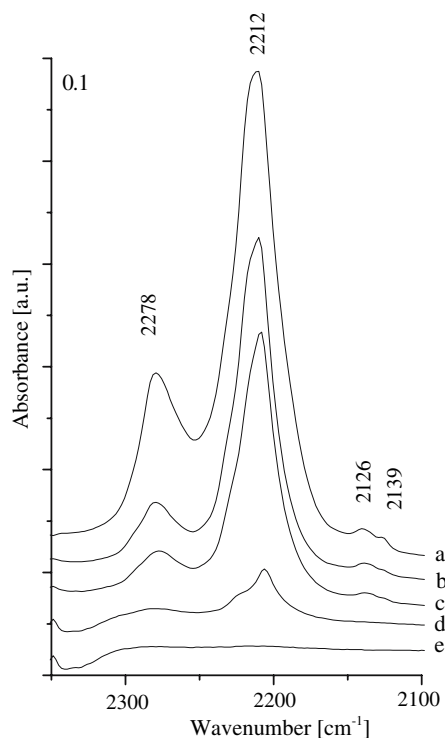


Figure 4. DRIFT spectra of Fe-ZSM5 after (a) HNCO adsorption at $150\text{ }^\circ\text{C}$ for 30 min followed by (b) purging at $150\text{ }^\circ\text{C}$ in N_2 for 30 min and increasing the temperature to (c) $200\text{ }^\circ\text{C}$, (d) $300\text{ }^\circ\text{C}$ and (e) $400\text{ }^\circ\text{C}$.

$\sim 2278\text{ cm}^{-1}$ can be attributed to the formation of Al–NCO groups. However, regarding the slight asymmetry of this band, the presence of –NCO species adsorbed on different Al sites (tetrahedrally and octahedrally coordinated) as suggested by Bion et al. [13] cannot be ruled out. The small signals at ~ 2126 and 2139 cm^{-1} can be attributed to the formation of cyanate ions ($[\text{NCO}]^-$) [16,28] or cyanide groups (CN^-) [29]. Adsorption experiments with HCN are in progress to better identify this signal. For the interpretation of the signal at $\sim 2212\text{ cm}^{-1}$ comparing adsorption experiments on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ were carried out, as reported in the next paragraph.

Figure 3 depicts only the spectral range from 2100 to 2400 cm^{-1} for a better assignment of the peaks related to HNCO adsorption. However, it has to be mentioned that additional bands at 3370 , 3274 , 1654 and 1465 cm^{-1} indicate the adsorption of NH_3 and that the strong negative peaks in the OH region indicate the consumption of surface OH groups by interaction with NH_3 [30].

The adsorption experiments were repeated at $300\text{ }^\circ\text{C}$ and the same bands were formed as those observed at $150\text{ }^\circ\text{C}$. However, the peak intensities were drastically lowered (in particular the peaks at ~ 2278 , 2139 and 2126 cm^{-1}) and they were completely removed after short purging with nitrogen.

3.4. Adsorption of HNCO on Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3/\text{SiO}_2$

The adsorption of HNCO on Fe_2O_3 resulted in the formation of an asymmetric band at 2206 cm^{-1} that grew and shifted to 2212 cm^{-1} in the course of the experiment (figure 5A). The band decreased after 30 min of degassing with N_2 at $150\text{ }^\circ\text{C}$ and disappeared when the temperature was increased to $300\text{ }^\circ\text{C}$. Various studies showed that HNCO adsorbs mainly dissociatively on transition metal oxides thus forming isocyanate species bound to Lewis acid sites [14,29,31,32]. These isocyanate groups show vibrational bands in the range $2200\text{--}2300\text{ cm}^{-1}$. Therefore, it is plausible to attribute the band at 2212 cm^{-1} to Fe–NCO groups.

Adsorption of HNCO on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ (Fe content = 9.7 wt% as detected by ICP-AES) produced bands at 2256 and 2200 cm^{-1} (figure 5B). The former band showed lower intensity and less thermal stability than the second one and vanished completely already at $300\text{ }^\circ\text{C}$. The band at 2200 cm^{-1} was still present at $400\text{ }^\circ\text{C}$, but it was very weak and was completely removed after a few minutes of purging at this temperature. By comparing these results with those obtained for pure Al_2O_3 (not shown) and Fe_2O_3 (figure 5A), these two bands can be assigned to Al–NCO and Fe–NCO species, respectively.

When HNCO was dosed over $\text{Fe}_2\text{O}_3/\text{SiO}_2$ (Fe content = 9.3 wt% as detected by ICP-AES) a band at 2202 cm^{-1} was formed that became very intense and

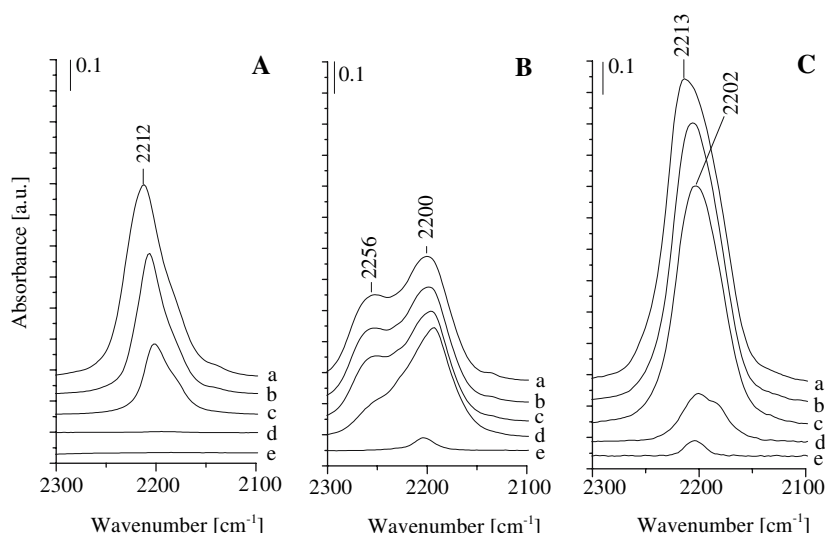


Figure 5. DRIFT spectra of (A) Fe_2O_3 , (B) $\text{Fe}/\text{Al}_2\text{O}_3$ and (C) Fe/SiO_2 after (a) HNCO adsorption at 150 °C for 30 min followed by (b) purging at 150 °C in N_2 for 30 min and increasing the temperature to (c) 200 °C, (d) 300 °C and (e) 400 °C.

shifted to 2213 cm^{-1} at the end of the adsorption (figure 5C). Purging with nitrogen at 150 °C for 30 min decreased the intensity of the band and shifted it to 2202 cm^{-1} . The intensity of this band further decreased at higher temperatures and disappeared at 400 °C. In agreement with the previous observations, this band is ascribed to the $-\text{NCO}$ species adsorbed on iron sites. Remarkably, no $\text{Si}-\text{NCO}$ species were observed usually present at $\sim 2300\text{ cm}^{-1}$ in the DRIFT spectra.

3.5. Stability of adsorbed HNCO species in the presence of water

The stability of the HNCO species adsorbed on Fe-ZSM5 upon water was also investigated. In general, the presence of water in the inlet flow reduced the intensity of the IR bands associated with adsorbed HNCO species (in particular the band at $\sim 2200\text{--}2212\text{ cm}^{-1}$) and increased the intensity of the bands attributed to adsorbed NH_3 ($3370, 3274, 1465\text{ cm}^{-1}$) (figure 6). The intense negative peaks visible in figure 7 in the OH region are attributable to the adsorption of NH_3 on Brønsted acid sites. No additional bands were formed during water addition in the range typical for adsorbed HNCO species.

3.6. Catalytic activity

The catalytic activities of Fe-ZSM5, the pure H-ZSM5 base material, and Fe_2O_3 were tested for HNCO hydrolysis (figure 7). For all samples, 100% selectivity to ammonia was always observed. Fe-ZSM5 showed a much higher activity than H-ZSM5 and Fe_2O_3 , which is clearly discernible below 300 °C. Interesting enough hydrothermal ageing at 650 °C for 5 h even improves the hydrolysis activity of Fe-ZSM5 as reported in our previous investigation [11].

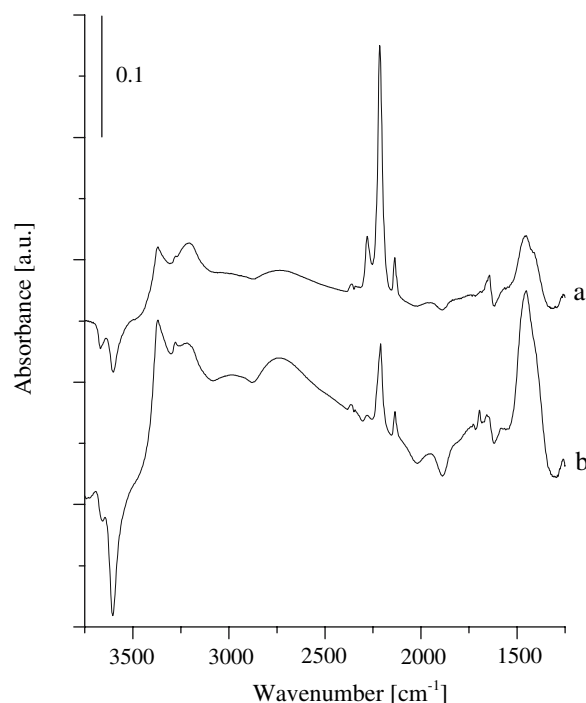


Figure 6. DRIFT spectra of Fe-ZSM5 after (a) HNCO adsorption at 150 °C for 15 min followed by (b) dosing HNCO and water for 10 min.

The influence of NO and NO_2 on the hydrolysis activity of Fe-ZSM5 was investigated (figure 8), since these two components are present in the exhaust gas of Diesel engines. At high temperatures the HNCO hydrolysis was not affected, but for $T < 200\text{ °C}$ the combined addition of NO and NO_2 resulted in a slow decrease of the HNCO conversion from $\sim 95\%$ to $\sim 75\%$ at 175 °C and from $\sim 65\%$ to $\sim 40\%$ at 150 °C. Steady-state conditions were reached only after several minutes

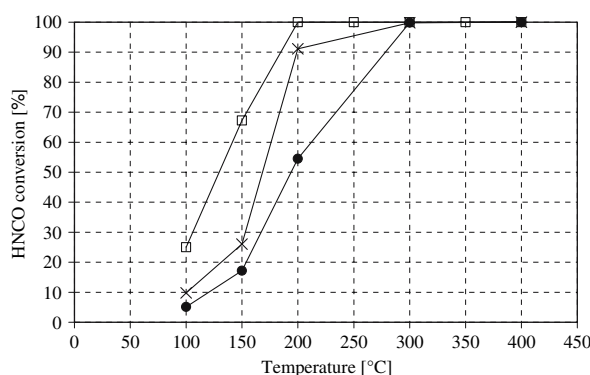


Figure 7. Hydrolysis of HNCO to NH₃ over (□) Fe-ZSM5, (x) H-ZSM5, and (●) Fe₂O₃. S_{NH3} = 100%.

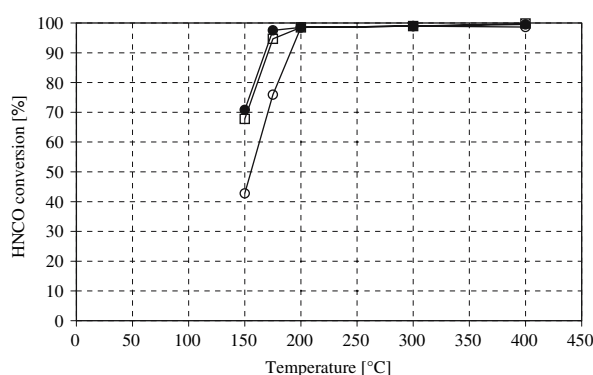


Figure 8. Hydrolysis of HNCO over Fe-ZSM5 (□) without NO and NO₂, (●) in the presence of 700 ppm NO and (○) in the presence of 350 ppm NO + 350 ppm NO₂. S_{NH3} = 100%.

of NO₂ addition. In contrast, the addition of NO alone even induced a small increase of the HNCO conversion.

4. Discussion

The solid-state ion exchange method, chosen in this study, yielded a high iron loading in the final Fe-ZSM5 sample, which is advantageous for its catalytic activity, but resulted also in the formation of various iron species as evidenced by the EPR measurements. The high amount of iron in the zeolite channels caused a considerably reduction of the micropore volume, partly by small iron oxide particles in the range of 20–50 nm, which might have blocked the pores of the catalyst as shown by TEM investigations [23]. It turned out that the formation of different iron species cannot be avoided even when more selective preparation methods with up to 100 times less iron loadings were used (not reported here). Only the formation of iron oxide nanoparticles could be avoided for very low iron loadings. Since the EPR and DRIFT spectra of different samples did not differ in number but only in the intensity of peaks we decided to report and discuss only the spectra of the

practically relevant high-exchanged Fe-ZSM5 sample in the present study.

The adsorption of isocyanic acid on Fe-ZSM5 gave rise to the formation of DRIFT bands in the region 2000–2400 cm⁻¹, which were assigned to species on iron oxide, alumina and silica on the catalyst surface. The peak at ~2278 cm⁻¹ evidenced the formation of Al–NCO species and, by comparing the spectrum with those obtained for Fe₂O₃/SiO₂ and Fe₂O₃/Al₂O₃, it becomes clear that the band at 2212 cm⁻¹ arises from the Fe–NCO groups. This conclusion can be drawn in spite of the different nature of these materials, since EPR spectroscopy confirms the formation of similar iron species in Fe-ZSM5, Fe₂O₃/SiO₂, and Fe₂O₃/Al₂O₃. Due to various iron species detected in Fe-ZSM5 by EPR spectroscopy, different Fe–NCO groups are also expected on the surface, and, in fact, the asymmetry of the Fe–NCO peaks reported in figures 4 and 5 suggests the presence of several overlapped infrared bands. It should be pointed out that –NCO groups adsorbed on the same transition metal with different oxidation state, e.g. Fe²⁺ and Fe³⁺, give rise to different IR signals [30], whereas Fe²⁺ is EPR silent. Beside the lack of surface sensitivity, this is the main reason why EPR alone is not sufficient to analyze iron containing samples, but should be supplemented by other methods.

It is important to note that the Fe–NCO IR signal was always the most intense in the HNCO adsorption region, irrespective of the iron loading (results not shown). No Si–NCO band was observed, even when adsorption was performed at 300 °C and higher. Even after 30 min of flushing with HNCO, the Fe–NCO peaks were still increasing in intensity, thus indicating that the surface was not yet saturated. Interesting enough, Solymosi et al. investigated the HNCO adsorption on Pt/SiO₂ by infrared spectroscopy and found a migration of –NCO species from the metal centers to silica at room temperature [14]. The same effect was observed for Cu-ZSM5, where –NCO species moved from copper to the silicon in the ZSM5 framework, however at elevated temperatures [12]. Therefore, the temperature at which migration starts indicates the difference in stability of the adsorbed –NCO species on the metal sites compared to the silica sites. Considering these results, the absence of the Si–NCO species on Fe-ZSM5 even at 300 °C suggests that the Fe sites are the most favored for the formation of isocyanate species. The same effect was observed for Fe₂O₃/SiO₂.

The adsorption of HNCO on Fe-ZSM5 at 150 °C resulted also in the formation of bands typical for adsorbed NH₃. Adsorbed NH₃ species might arise from traces of NH₃ present in the inlet flow or, from the reaction of adsorbed HNCO with surface –OH groups. The adsorption of HNCO on Fe-ZSM5 in the presence of water showed that both Al–NCO and Fe–NCO easily react with water to give NH₃. Moreover, no formation of new adsorbed species was observed.

Performance tests with coated monolith samples showed that the activity Fe-ZSM5 is much higher than that of Fe₂O₃, proving that the amount of iron itself is not the only parameter that determines the hydrolysis activity and that the zeolite support is essential for good hydrolysis properties.

The presence of NO in the inlet flow hardly affected the hydrolysis activity of Fe-ZSM5. However, when NO₂ was also added, a deactivation effect was observed. This is attributable to the blockage of the active sites by the formation of ammonium nitrate (NH₄NO₃). In fact, this side-product forms by reaction of NO₂ and NH₃ at low temperature [33,34]. The catalytic activity is then restored at higher temperature due to the decomposition of NH₄NO₃, which is melting above 170 °C and exist in equilibrium with NH₃ and HNO₃.

5. Conclusions

The work reported here shows that the hydrolysis mechanism of HCNO over Fe-ZSM5 agrees with that reported by Solymosi et al. for Cu-ZSM5. DRIFT investigations revealed that at 150 °C HNCO adsorbs dissociatively on Fe-ZSM5 forming Fe–NCO, Al–NCO, little amounts of NCO[−], and probably also CN[−] species. The isocyanate species formed on the catalysts readily reacted with water to yield NH₃. No formation of additional HNCO adsorbed species was observed in the presence of water. The comparison of the stability of the –NCO species in the presence of water with the catalytic activity for the HNCO hydrolysis over Fe-ZSM5 and Fe₂O₃ indicated that the –NCO groups are intermediate species in the hydrolysis mechanism of HNCO over iron-zeolites. The presence of NO₂ decreased the catalytic activity, most probably due to the formation of ammonium nitrate species on the catalyst surface.

In the DRIFT spectra of the HNCO adsorption over SiO₂ a not yet reported signal at 2186 cm^{−1} was observed, which was predicted by Ferullo et al. [19] for a Si–O–NCO surface species.

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