Effect of water on the reduction of NO_x with propane on Fe-ZSM-5. An FTIR mechanistic study

K. Hadjiivanov [a,b,*], H. Knözinger [a], B. Tsyntsarski [b] and L. Dimitrov [c]

[a] *Institut für Physikalische Chemie, LMU München, Bütenandtstrasse 5–13 (Haus E), 81377 München, Germany*
[b] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[c] *Institute of Catalysis, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Received 28 April 1999; accepted 5 August 1999

Adsorption of NO on Fe-ZSM-5 leads to formation of Fe^{n+}–NO ($n = 2$ or 3) species (1880 cm^{-1}), $Fe^{2+}(NO)_2$ complexes (1920 and 1835 cm^{-1}) and NO^+ (2133 cm^{-1}). Water strongly suppresses the formation of NO^+ and $Fe^{n+}(NO)_2$ and more slightly the formation of Fe^{n+}–NO. Introduction of oxygen to NO converts the nitrosyls into surface nitrates (1620 and 1575 cm^{-1}) and this process is almost unaffected by water. The nitrates are thermally stable up to ca. 300 °C, but readily interact with propane at 200 °C, thus forming surface C–H–N–O deposit (bands in the 1700–1300 cm^{-1} region). Here again, water does not hinder the process. The C–H–N–O deposit is relatively inert (it does not interact with NO or $NO + O_2$ at ambient temperature) but, at temperatures higher than 250 °C, it is decomposed to NCO^- species (bands at 2215 (Fe–NCO) and 2256 cm^{-1} (Al–NCO)). In the presence of water, however, the Fe–NCO species only are formed. At ambient temperature the NCO^- species are inert towards NO and O_2, but easily react with a $NO + O_2$ mixture. The mechanism of the selective catalytic reduction of nitrogen oxides on Fe-ZSM-5 and the effect of water on the process are discussed.

Keywords: Fe-ZSM-5, carbon monoxide, FTIR spectroscopy, nitrates, nitrogen monoxide, selective catalytic reduction, adsorption, zeolites

1. Introduction

A large number of investigations aimed at establishing the mechanism of the selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons have been performed or are now in progress [1]. The classic catalyst for this reaction, Cu-ZSM-5, is not efficient in the presence of water [2]. At present, many hopes are concentrated on Fe-ZSM-5 since it keeps a high activity in the presence of large amounts of water [3–6]. Nevertheless, there are only few investigations on the SCR mechanism on Fe-ZSM-5. It has been reported [6] that $NO + O_2$ co-adsorption leads to formation of NO_y ($y \geqslant 2$) species that react with hydrocarbons giving a nitrogen-containing deposit. The latter reacts with NO_2 to form nitrogen. No data explaining the stability of Fe-ZSM-5 towards water vapour have been reported.

The aim of this work is to establish the effect of water on the SCR of NO_x with propane over Fe-ZSM-5. For this purpose we compared the adsorption of NO and the co-adsorption of NO + O_2 on Fe-ZSM-5 in presence and absence of water (in a D_2O form). The effect of D_2O on the interaction of the stable surface species with propane was also investigated.

2. Experimental

Fe-ZSM-5 was prepared by solid-state ion exchange of H-ZSM-5 (Si/Al molar ratio = 30) with $FeCl_3$. Stoichiometric amounts of H-ZSM-5 and $FeCl_3$ were ground in an agate mortar and then heated for 12 h at 400 °C in a nitrogen flow. The Fe concentration, according to the atomic absorption analysis, was 4.8 wt%.

FTIR spectroscopy studies were carried out with a Bruker IFS-66 apparatus at a spectral resolution of 1 cm^{-1} accumulating 128 scans. Self-supporting pellets were prepared from the sample powders and heated *in situ* in the IR cell. Prior to the adsorption measurements, the pellets were activated by 1 h calcination at 400 °C and 1 h evacuation (10^{-7} Pa) at the same temperature. All IR spectra were recorded at ambient temperature.

3. Results

3.1. Sample characterization

Because of the high light scattering, the signal-to-noise ratio in the ν(OH) region was low. In order the obtain better quality spectra, the effect of water was studied using D_2O and the experiments were performed with deuteroxylated samples. Activated Fe-ZSM-5 was heated for 1 h at 400 °C in 500 Pa of D_2O (90% isotopic purity) and then evacuated at the same temperature. Further on, this sample

---

[*] To whom correspondence should be addressed.

will be denoted as Fe–D-ZSM-5. Two bands, at 2762 and 2660 cm^{-1}, were recorded in the ν(OD) region. The former band is assigned to isolated Si–O–D groups, whereas the latter is due to bridging acidic OD groups. Thus, the results evidence that not all of the acidic hydroxyls have been exchanged with Fe^{3+} (FeO^+) ions.

Adsorption of CO (1000 Pa) on the activated sample is negligible; only a very weak Fe^{2+}–CO band at 2195 cm^{-1} [7,8] was detected. These results indicate that iron on the activated sample is mainly in the Fe^{3+} state, which is consistent with the rusty colour of the sample.

3.2. Adsorption of NO on an activated sample

Introduction of NO (100 Pa) to the activated Fe–D-ZSM-5 sample results in the appearance of an intense band at 1882 cm^{-1}, with a lower-frequency shoulder (figure 1, spectrum (a)). In addition, a weak band at 2133 cm^{-1} was also detected, whereas the intensity of the band characterizing the bridging OD groups at 2660 cm^{-1} (not shown) decreased. With time the 1876 and 2133 cm^{-1} bands grow (figure 1, spectrum (b)). Simultaneously, the intensity of the OD band at 2660 cm^{-1} further decreases. Similar changes have been observed with an equilibrium pressure increase up to 1000 Pa (figure 1, spectrum (c)). In this case, however, a new band at 1814 cm^{-1} clearly appears and a weak band at 1920 cm^{-1} is also visible. In addition, a set of low-intensity bands in the 1650–1500 cm^{-1} region is developed with time (figure 1, spectrum (d)). Evacuation leads to disappearance of the bands at 1814 and 1920 cm^{-1} and a slight decrease in intensity of the bands at 2133 and 1882 cm^{-1} (the latter being shifted to 1880 cm^{-1}).

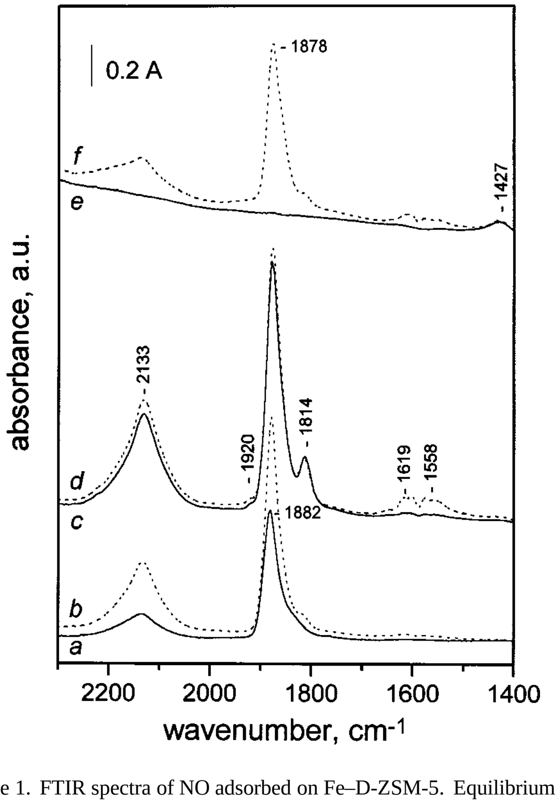

Figure 1. FTIR spectra of NO adsorbed on Fe–D-ZSM-5. Equilibrium NO pressure of 100 Pa, spectrum taken immediately (a) and after 5 min (b); increase of the equilibrium NO pressure to 1000 Pa, spectrum taken immediately (c) and after 5 min (d). FTIR spectra of D_2O adsorbed on Fe–D-ZSM-5 (100 Pa, followed by 5 min evacuation) (e) and after adsorption of NO (1000 Pa equilibrium pressure) (f).

The 2133 cm^{-1} band has been recently attributed to NO^+ species occupying cation positions in zeolites [9]. Since NO^+ is not produced after NO adsorption on H-ZSM-5, its appearance infers either NO oxidation by the catalyst, or NO disproportionation catalysed by Fe–D-ZSM-5. The set of bands at 1920 and 1814 cm^{-1} characterize $Fe^{2+}(NO)_2$ [10–13]. Bands around 1880 cm^{-1} have often been observed after NO adsorption on different Fe-exchanged zeolites [6,10,11,14] and oxide-supported Fe^{n+} ions [12,13,15]. There is general agreement in the assignment of the band to mononitrosyls of the Fe^{n+}–NO type. Some authors claim the oxidation state of iron to be 2+ [10,11,14,15], whereas others assume that it is 3+ [12,13]. Taking into account that the NO^+ band at 2133 cm^{-1} is developed in parallel with the Fe^{n+}–NO band at 1880 cm^{-1} (figure 1, spectra (a–d)), we suggest that oxidation of NO by Fe^{3+} ions leads to the simultaneous formation of NO^+ and Fe^{2+}–NO species (1880 cm^{-1}). Since no relationship between the intensities of the bands due to Fe^{n+}–NO and $Fe^{2+}(NO)_2$ has been detected, and in agreement with literature data [10–13], we infer that the mono- and dinitrosyl species are formed with the participation of different kinds of iron cations.

3.3. Adsorption of NO in the presence of pre-adsorbed D_2O

D_2O (100 Pa) was introduced to the sample and after 5 min evacuated at ambient temperature. The resulting spectrum contained a weak band at 1427 cm^{-1} (figure 1, spectrum (e)) assigned to H–O–D deformation modes. It evidences the presence of residual molecular water after the evacuation. In addition, a broad and tailed band with a maximum at ca. 2700 cm^{-1} (not shown) was registered and was attributed to D-bonded deuteroxyl groups interacting with D_2O molecules. Introduction of NO (1000 Pa) to the sample thus treated (figure 1, spectrum (f)) resulted in the appearance of bands at 2133 (NO^+), 1878 (Fe^{n+}–NO) and 1814 cm^{-1} ($Fe^{2+}(NO)_2$) and a decrease in intensity of the OD band at 2660 cm^{-1}. Comparison of the spectra with those recorded after NO adsorption in the absence of water shows that the Fe^{n+}–NO band has a reduced intensity (by about 30%), whereas the $Fe^{2+}(NO)_2$ bands are much weaker on the D_2O pre-covered sample. The intensity of the NO^+ band has also decreased in the presence of D_2O, which was to be expected due to blocking of the respective sites by water.

3.4. Co-adsorption of NO and O_2

Introduction of O_2 (1000 Pa) to the Fe-ZSM-5 sample in the presence of a NO (1000 Pa) leads to the following changes in the IR spectrum (figure 2, spectrum (b)): (i) the 1880 cm^{-1} NO band is converted into another, less intense and broader one, at 1882 cm^{-1}; (ii) the 1814 cm^{-1} band completely disappears; (iii) strong bands at 1618, 1576 and 1295 cm^{-1} develop; (iv) a shoulder of the NO$^+$ band is observed at 2195 cm^{-1}; and (v) a band at 1744 cm^{-1} with a weak shoulder at 1710 cm^{-1} is produced. After evacuation only the bands at 2133 (with a strongly reduced intensity), 1618 and 1576 cm^{-1} are visible.

According to literature data [6,16–21] the bands near 1620 and 1575 cm^{-1} characterize surface nitro or nitrato groups. We assign the band at 1620 cm^{-1} to bridging nitrates, and that at 1575 cm^{-1}, to bidentate nitrates [18–21]. The 1744 cm^{-1} band with the 1710 cm^{-1} shoulder is unambiguously assigned to N_2O_4 [19]. The band at 1882 cm^{-1}, although coinciding in position with the Fe^{n+}–NO bands, is attributed to adsorbed N_2O_3 [20]. Indeed, this band disappears after evacuation, contrary to the Fe^{n+}–NO band. The other N_2O_3 bands are detected at 1295 cm^{-1} and around 1555 cm^{-1}, the latter being masked by the strong nitrate bands. It is to be noted that both N_2O_3 and N_2O_4 have been observed as weakly adsorbed species on different zeolites [6,16,19,20,22] and their appearance is not specific for Fe–D-ZSM-5. The 2195 cm^{-1} band has been reported and assigned in different ways by several authors [16,22]. It has been found that this band appears in the presence of adsorbed N_2O_4 only, at the expense of the NO$^+$ band [22]. For that reason we tentatively assign it to the N–O modes of NO$^+$ in [NO$^+$][N_2O_4] adducts.

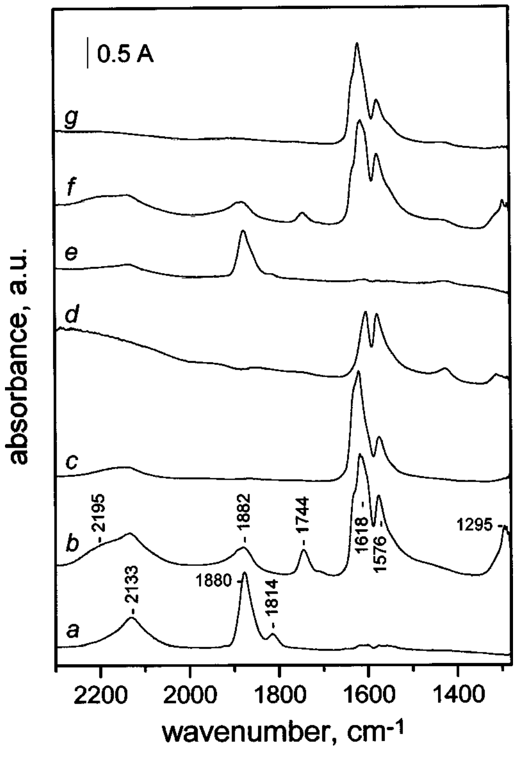

Figure 2. FTIR spectra of NO (1000 Pa equilibrium pressure) adsorbed on Fe–D-ZSM-5 (a), after introduction of 1000 Pa O_2 (b), after evacuation (c) and in the presence of 100 Pa D_2O (d); FTIR spectra of NO (1000 Pa equilibrium pressure) adsorbed on D_2O-covered Fe–D-ZSM-5 (e), after introduction of 1000 Pa O_2 (f) and after evacuation (g).

The results obtained after co-adsorption of NO and O_2 on a D_2O pre-covered sample (figure 2, spectra (e–g)) are very similar to those obtained in the absence of water. The only difference is that the NO$^+$ band completely disappears after evacuation of the D_2O pre-covered sample.

3.5. Stability and reactivity of the surface nitrates

The nitrates for the experiments given in what follows were produced by co-adsorption of NO and O_2, followed by evacuation.

All nitrates (bands at 1620 and 1575 cm^{-1}) are stable towards evacuation at ambient temperature. Their concentration decreases after evacuation at 250 °C, but they are still observed after 300 °C evacuation. The stability of the 1620 cm^{-1} species is a little higher than that of the 1575 cm^{-1} species. The NO$^+$ species are fully destroyed after 100 °C evacuation.

Introduction of NO (1000 Pa) to a sample pre-covered with nitrates results in (i) an increase in intensity of the 2133 cm^{-1} NO$^+$ band; (ii) appearance of N_2O_3 bands at 1295, 1555 and 1884 cm^{-1}; and (iii) a decrease in intensity of the 1620 cm^{-1} band. The results imply some oxidation of NO to NO$^+$ and N_2O_3. The decrease in intensity of the band at 1620 cm^{-1} suggests that the respective species is the oxidizing agent. This confirms the assignment of the 1620 cm^{-1} band to nitrate species since NO_2^- cannot oxidize NO. The 1575 cm^{-1} band characterizes less reactive nitrates, but the probability for it to be due to nitro compounds cannot be ruled out.

Introduction of D_2O (100 Pa) to the nitrate-pre-covered sample (figure 2, spectrum (d)) results in the appearance of features (already described) typical of adsorbed water (D_2O). In addition, the NO$^+$ band at 2133 cm^{-1} disappears and the 1620 cm^{-1} band is strongly reduced in intensity and shifted to 1604 cm^{-1}, whereas the 1575 cm^{-1} band increases in intensity.

Evacuation at ambient temperature leads to removal of part of the adsorbed D_2O, the spectrum of the nitrate species being almost restored. After evacuation at 100 °C the sample is practically dehydrated (according to the intensity of the 1420 cm^{-1} band) and the main differences with respect to the initial spectrum are (i) the absence of the NO$^+$ band and (ii) the somewhat lower intensity of the 1575 cm^{-1} band. The above results indicate that D_2O adsorbed in the vicinity of nitrate species decreases their extinction coefficient. It seems that, like on titania and chromia [21,23], conversion of bridging (1620 cm^{-1}) into bidentate (1575 cm^{-1}) nitrates takes place when D_2O is co-adsorbed in the vicinity. An important conclusion that may be drawn is that, after D_2O adsorption/desorption, the concentration of the nitrates has only slightly decreased.

Introduction of propane (2500 Pa) to a nitrate-pre-covered Fe–D-ZSM-5 sample at ambient temperature (figure 3, spectrum (b)) only leads to (i) the appearance of

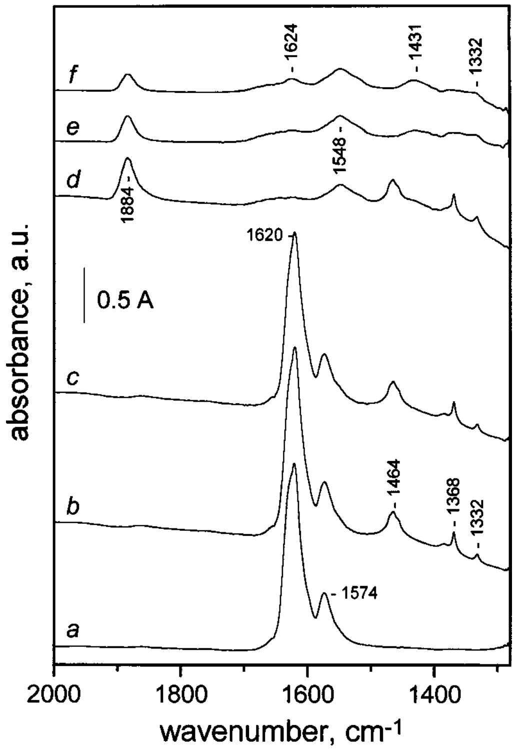

Figure 3. FTIR spectrum of the nitrate species formed on Fe–D-ZSM-5 after co-adsorption of NO and O_2 (1000 Pa of each gas, followed by evacuation at 170 °C) (a), after subsequent introduction of 2500 Pa C_3H_8 (b) and heating in propane for 10 min at 150 (c) and 200 °C (d), and evacuation (e). Spectrum (f) is recorded after analogous treatment of a D_2O-pre-covered sample.

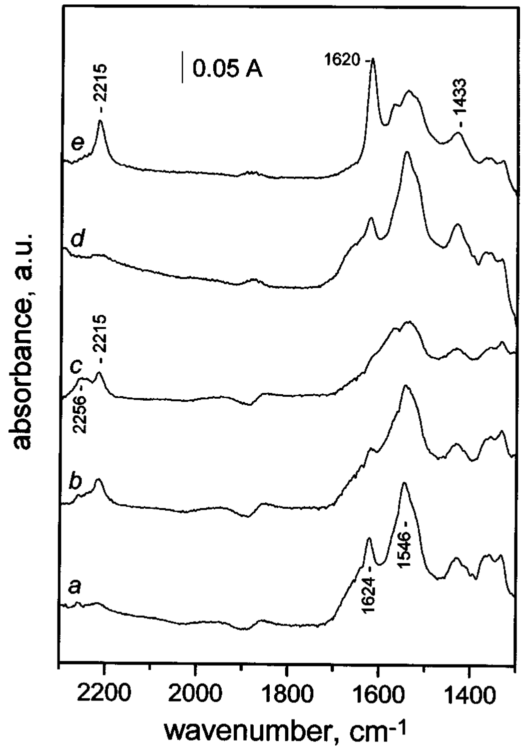

Figure 4. FTIR spectra of the C–H–N–O deposit on Fe–D-ZSM-5 (for details see text) after evacuation at 200 (a), 250 (b) and 300 °C (c). FTIR spectrum of the C–H–N–O deposit on D_2O-covered Fe–D-ZSM-5 after evacuation at 200 (d) and 300 °C (e).

bands arising from adsorbed propane (1464, 1368 and 1332 cm^{-1}) and (ii) a broad absorbance at 2590 cm^{-1} (not shown) with a simultaneous decrease in intensity of the 2660 cm^{-1} band suggesting that (part of) the adsorbed propane has interacted with the acidic OD groups. No substantial changes in the spectra have been noticed after heating the sample in propane for 10 min at 150 °C (figure 3, spectrum (c)). Interaction at 200 °C, however, results in drastic changes (figure 3, spectrum (d)). Firstly, the nitrate bands (1620 and 1575 cm^{-1}) disappear. Secondly, a set of low-intensity bands at 1624, 1548, 1431 and 1332 cm^{-1} and a broad absorbance in the 3100–2850 cm^{-1} region emerge. In addition, a band at 1884 cm^{-1} also appears. After evacuation (figure 3, spectrum (e)), only the bands due to adsorbed propane vanish and the band at 1884 cm^{-1} is slightly reduced in intensity.

The interaction of propane with the nitrates produced on a D_2O-pre-covered sample (figure 3, spectrum (f)) results in the same surface species as those described above for the activated (dehydrated) sample.

The set of bands at 1624, 1548, 1431 and 1332 cm^{-1} can be attributed to organic nitrogen-containing compounds [6,24] which will further on be called C–H–N–O deposit. The band at 1884 cm^{-1} characterizes Fe^{n+}–NO species (it could not be assigned to N_2O_3 for two reasons: it is stable towards evacuation and there is no band at 1295 cm^{-1}). Thus, it appears that one of the products of interaction between the nitrates and propane is NO. These results are very similar to those reported by Chen et al. [13], who have also observed formation of an N-containing deposit and NO after interaction of propane with the surface nitro/nitrato species on Fe-ZSM-5.

3.6. Stability and reactivity of the surface C–H–N–O deposit

For the further experiments, samples with a surface C–H–N–O deposit were prepared by interaction of nitrate-pre-covered Fe–D-ZSM-5 with propane at 200 °C, followed by evacuation at ambient temperature.

A sample containing the C–H–N–O deposit was heated in vacuum at different temperatures. Evacuation at 200 °C slightly affects the spectrum (figure 4, spectrum (a)). After evacuation at 270 °C, however (figure 4, spectrum (b)), two bands at 2256 and 2215 cm^{-1} appear. Simultaneously, the bands characteristic of the C–H–N–O deposit decline. This process continues during evacuation at 300 °C. In this case, however, it is the band at 2256 cm^{-1} that mainly gains in intensity (figure 4, spectrum (c)).

It is well known that interaction between CO and NO can easily produce isocyanates. These isocyanates, formed on Fe-containing systems, absorb around 2200 cm^{-1} [25,26]. Thus, the band at 2215 cm^{-1}, appearing after decomposition of the C–H–N–O deposit, may be assigned to isocyanate (NCO^-) species. The 2256 cm^{-1} band is probably also caused by isocyanates that have spilled over to the support [27]. However, alternative assignment to cyanides is not excluded [28].

When analogous experiments were performed with a D_2O-covered sample at 300 °C (figure 4, spectrum (e)), only the band at 2215 cm^{-1}, with an increased intensity, was produced. This confirms the above assignment of the bands, since it is feasible that the blocking of the support sites by D_2O should hinder the spillover of NCO^-.

Another difference between the decomposition of the C–H–N–O deposit in presence and absence of D_2O is that, in the former case, a strong band at 1620 cm^{-1} is developed. Assignment of this band to surface nitrates is unlikely since they are almost fully decomposed at this temperature (300 °C). It seems that this band is produced at the expense of a broad band at ca. 1650 cm^{-1} and we tentatively assign it to surface organic nitrites [29].

Nitrogen monoxide (100 Pa) was introduced to Fe–D-ZSM-5 containing the C–H–N–O deposit. The only changes in the IR spectra are a significant increase in intensity of the NO band at 1880 cm^{-1} and the appearance of a NO^+ band at 2133 cm^{-1}. Addition of oxygen resulted in a negligible decrease of the NO band and the appearance of a weak nitrate band at 1622 cm^{-1}.

When the sample was heated in this $NO + O_2$ mixture at 200 °C and then evacuated, the intensity of the 1624 cm^{-1} band slightly decreased and some absorbance in the 1500–1300 cm^{-1} region was also lost. The NO band at 1880 cm^{-1} completely disappeared. These results show that even at 200 °C the surface C–H–N–O deposit cannot be removed by interaction with an $NO + O_2$ mixture.

3.7. Reactivity of the surface NCO^- species

The NCO^- species (bands at 2215 and 2256 cm^{-1}) were produced after partial decomposition of the surface C–H–N–O deposit at 300 °C. Then the sample was exposed to 100 Pa of NO. Strong NO (1880 cm^{-1}) and NO^+ (2133 cm^{-1}) bands appeared in the spectrum. Subsequent addition of O_2 (1000 Pa) to the NO resulted in an almost quantitative disappearance of the 2215 cm^{-1} NCO^- band even at room temperature. The behaviour of this band on the D_2O-containing sample was similar. It, however, does not disappear when reacting with oxygen only even at 300 °C.

4. Discussion

4.1. NO_x adsorption species on Fe-ZSM-5

NO adsorption on Fe-ZSM-5 results in the appearance of three kinds of species: Fe^{n+}–NO, $Fe^{2+}(NO)_2$ and NO^+. The Fe^{n+}–NO complexes are relatively stable and water resistant. Comparing this fact with their stretching frequency, which is very close to the gas NO frequency, it is inferred that the Fe–N bond is stabilized by some π back-donation. It has been reported that, when bonded simultaneously with a σ and a π bond, CO can replace water from some c.u.s. cations, e.g., Ag^+ and Pt^{2+} [20,30]. A similar situation seems to be realized here. This explains why D_2O does not significantly affect the formation of Fe^{n+}–NO species. In contrast, the formation of $Fe^{2+}(NO)_2$ and NO^+ is strongly inhibited by water.

The co-adsorption of NO and O_2 on Fe-ZSM-5 results in the formation of N_2O_3, N_2O_4 and nitrates. The only stable species, however, are the nitrates. An important conclusion from our results is that the concentration of all these species is very weakly affected by water. This can be explained by the formation of a stronger bond between NO_3^- and Fe^{n+} than between Fe^{n+} and coordinated water.

In order to play a role in the SCR on Fe-ZSM-5, the surface species have to be (i) thermally stable, (ii) water resistant and (iii) oxygen resistant. The nitrates are the only species answering these requirements. Thus, they may be considered as important intermediates in the SCR. Note, however, that the Fe^{n+}–NO compounds, being thermally stable and water resistant, could be precursors of the formation of nitrates.

4.2. Formation and reactivity of the C–H–N–O deposit and NCO^- species

When the surface nitrates react with propane, a C–H–N–O deposit is produced. The fact that NCO^- species are formed from this deposit proves the deposit composition. It is difficult at this stage to give an exact assignment of all IR bands. Note, however, that organic nitro compounds are characterized by bands at ca. 1550 and 1350 cm^{-1} [17,29], whereas organic nitrites manifest a band around 1650 cm^{-1} [29] which is close enough to the bands observed in our spectra.

Chen et al. [4] have already reported the formation of the nitrogen-containing deposit and have proposed that it reacts with gaseous NO_2 to give nitrogen. Our results show, however, that the deposit is relatively inert and is not removed in an $NO + O_2$ atmosphere even at 200 °C. In contrast, the NCO^- species produced during the thermal decomposition of the deposit are much more reactive: although inert towards NO and oxygen, they disappear in an $NO + O_2$ atmosphere (i.e., in the presence of NO_2) even at ambient temperature.

An important conclusion of this study is that the formation of the C–H–N–O deposit is not affected by water. The only significant effect of the water is the suppression of the NCO^- spillover to the support. It has been found that water suppresses the formation of surface nitrates on Cu-ZSM-5 [19]. Thus, the different behaviours of the nitrate species on Cu-ZSM-5 and Fe-ZSM-5 appear to be crucial for their catalytic performance in the presence of water.

4.3. SCR reaction pathway

The proposed SCR mechanisms can, in general, be divided into two groups. According to one of them, NO_x

reacts with adsorbed hydrocarbons, whereas according to the other, NO_x^- ($x = 2$ or 3) surface species interact with gaseous hydrocarbons. It has been shown that the SCR by hydrocarbons is zero order in NO_x and has a reaction order close to one in hydrocarbons [31]. This favours the view that, under catalytic conditions, the hydrocarbons react with a surface modified by NO_x. Our results also support this mechanism, since the adsorption of propane on Fe-ZSM-5 was found to be weak, whereas stable surface species are formed in an $NO + O_2$ atmosphere.

Thus, it appears that the first step of the SCR of NO_x with propane on Fe-ZSM-5 is the formation of surface nitrates. The second step is, most likely, the interaction of these species with propane and production of a surface C–H–N–O deposit. This deposit is (probably partly) decomposed into NCO^- species. The results suggest that this reaction is the rate-limiting step of the SCR on Fe-ZSM-5 and that it is not affected by the presence of water. The NCO^- species interact easily with $NO + O_2$ gas mixtures producing N_2. Indeed, it has been reported [4] that the formation of dinitrogen is achieved by coupling between one nitrogen atom from the C–H–N–O deposit and one from gaseous NO_x.

5. Conclusions

The only stable (up to ca. 300 °C) surface species formed after $NO + O_2$ co-adsorption on Fe-ZSM-5 are the surface nitrates. They are highly resistant to water but easily interact with propane at 200 °C, thus producing a surface C–H–N–O deposit. Water does not hinder this process.

The C–H–N–O deposit is relatively inert (it does not interact with NO and $NO + O_2$ at ambient temperature and is only slightly affected by $NO + O_2$ at 200 °C) but is thermally decomposed to NCO^- species at temperatures higher than 250 °C. At ambient temperature the NCO^- species are inert towards NO and O_2, but easily react with $NO + O_2$ mixtures to form nitrogen.

Acknowledgement

This work was supported by the Bulgarian National Research Foundation (Project X-534) and by the Deutsche Forschunggemeinschaft (SFB 338). KH acknowledges a fellowship from the Alexander von Humboldt Foundation.

References

[1] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal. B 18 (1998) 1, and references therein.
[2] R.A. Grinsted, H.W. Jen, C.N. Montrenil, M.J. Rokosz and M. Shelef, Zeolites 13 (1993) 602.
[3] X. Feng and W.K. Hall, Catal. Lett. 41 (1996) 45.
[4] H.Y. Chen and W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[5] M. Kogel, R. Monnig, W. Schwieger, A. Tissler and T. Turek, J. Catal. 182 (1999) 470.
[6] H.Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, J. Catal. 180 (1998) 171.
[7] T. Bregadze, V. Seleznev, A. Kadushin and O. Krylov, Izv. Akad. Nauk SSSR, Ser. Khim. 12 (1973) 2701.
[8] B. Wichterlova, L. Kubelkova, J. Navakova and P. Jiru, Stud. Surf. Sci. Catal. 12 (1982) 143.
[9] K. Hadjiivanov, J. Saussey, J.-L. Freysz and J.C. Lavalley, Catal. Lett. 52 (1998) 103.
[10] L. Aparicio, W.K. Hall, Sh. Fang, M. Ulla and W. Millman, J. Catal. 108 (1987) 233.
[11] K. Segawa, Y. Chen, J. Kubsh, J. Dumesic and W.K. Hall, J. Catal. 76 (1982) 112.
[12] F. Boccuzzi, E. Guglielminotti, F. Pinna and M. Signoretto, J. Chem. Soc. Faraday Trans. 91 (1995) 3237.
[13] S. Yuen, J. Kubsh, J. Dumesic, N. Topsøe, H. Topsøe and Y. Chen, J. Phys. Chem. 86 (1982) 3022.
[14] A. Davydov and M.L. Shepot'ko, Coord. Chem. Rev. 17 (1991) 1505.
[15] H. Miyata, Y. Nakagawa, S. Miyagawa and Y. Kubokawa, J. Chem. Soc. Faraday Trans. I 84 (1988) 2129.
[16] L.Y. Lobree, A.W. Aylor, J.A. Reimer and A.T. Bell, J. Catal. 181 (1999) 189.
[17] B. Djonev, B. Tsyntsarski, D. Klissurski and K. Hadjiivanov, J. Chem. Soc. Faraday Trans. 93 (1997) 4055.
[18] D. Pozdnyakov and V. Filimonov, Kinet. Katal. 14 (1973) 760.
[19] K. Hadjiivanov, D. Klissurski, G. Ramis and G. Busca, Appl. Catal. B 7 (1996) 607.
[20] K. Hadjiivanov, Micropor. Mesopor. Mater. 24 (1998) 41.
[21] K. Hadjiivanov, V. Bushev, M. Kantcheva and D. Klissurski, Langmuir 10 (1994) 464.
[22] J. Szanyi and M.T. Paffett, J. Catal. 164 (1996) 232.
[23] K. Hadjiivanov, D. Klissurski and V. Bushev, J. Chem. Soc. Faraday Trans. 91 (1995) 149.
[24] N.W. Hayes, R.W. Joyner and E.S. Shpiro, Appl. Catal. B 8 (1996) 343.
[25] G. Hussain, M.M. Rahman and N. Sheppard, Spectrochim. Acta 47A (1991) 1525.
[26] E. Guglielminotti and F. Boccuzi, Appl. Catal. B 8 (1996) 371.
[27] F. Solymosi and T. Bansagi, J. Catal. 156 (1997) 75.
[28] F. Poignant, J. Saussey, J.C. Lavalley and G. Mabilon, Catal. Today 29 (1996) 93.
[29] T. Tanaka, T. Okuhara and M. Misono, Appl. Catal. B 4 (1994) L1.
[30] K. Hadjiivanov, J. Chem. Soc. Faraday Trans. 94 (1998) 1901.
[31] I. Kogo and E. Kikuchi, Stud. Surf. Sci. Catal. 84C (1994) 1547.