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The activation of NO molecule by Co^{2+} in CoZSM-5 in the presence of ammonia and pyridine molecules – IR studies

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ABSTRACT

The effect of interaction of electron donor ammonia and pyridine molecules with Co^{2+} sites on the properties of these Co^{2+} ions, as well as the effect of adsorbed NO on the properties of NH_3 interacting with Co^{2+} has been followed in the present study.

It has been shown that the molecules NO interacting with Co^{2+} which bonds pyridine or ammonia molecules were strongly activated (NO stretching band was shifted to lower frequency by 60–110 cm^{-1}). This activation could be realized by the transfer of electrons from basic molecules *via* Co^{2+} to antibonding π^* orbitals of NO. The significant NO activation took place when NO interacted with Co^{2+} cations, which coordinated maximum possible number of NH_3 molecules ($NH_3/Co = 6$). For this case the formation of $[Co(NH_3)_6NO]^{2+}$ complexes in which the transfer of full electrons from Co^{2+} to antibonding π^* orbitals of NO occurred. Such strong activation of NO molecules by ammonia and pyridine molecules makes available the formation of N_2O. The fact that NO accepts electron forming NO^- and finally N_2O indicates that NO acts as oxidant in the presence of $[Co(py)]^{2+}$ or $[Co(NH_3)_6]^{2+}$. On the other hand, earlier IR study showed that without preadsorbed basic molecules NO acted as reducer: Co^{3+} was reduced to Co^{2+} whereas NO oxidized to NO^+.

1. Introduction

Cobalt containing zeolites have drowned the attention of research laboratories nearly 20 years ago as potential catalysts for the reduction of NO_x with hydrocarbons (HC-SCR) [1–3]. This process was very attractive because of the possibility of replacing of ammonia with methane as reducing agent. Co-zeolites have been also found to be active in several reactions of organic molecules such as alkanes, e.g. ammoxidation [4], Fisher–Tropsch synthesis [5], regioselective oxidation of alkanes [6]. Therefore, the recognizing the properties of Co^{2+} and Co(III) species in zeolites is crucial for catalysis. Many techniques are employed into investigation of the status of cobalt active species: IR [7–9], UV–VIS [10,11], EPR [12,13] spectroscopies, TPR [14,15], and DFT calculations [13,16]. Very convenient technique for following the nature of Co active moieties and studying the mechanisms of the mentioned above processes is IR spectroscopy. It gives direct information about the nature of the surface species.

It has been reported that the presence of the cobalt oxide forms of high dispersion (as Co_3O_4) is required for the selective reduction of NO_x [17]. The high-siliceous zeolites of the pentasil group CoZSM-5, CoFER, and CoMOR have been found as effective catalysts in the process of reducing NO_x by hydrocarbons, however, zeolites CoY of high cobalt content has revealed the rather low activity. Therefore, the structural factors of zeolites seem to be important in this respect. It has been also shown that weakening of the NO bond by π back-donation of electron from the cation *d* orbitals to the antibonding SOMO in the NO molecule, what results in their dissociation, is vital stage in the selective catalytic reduction of nitrogen oxides. The partial neutralization of the cations with zeolitic oxygen atoms is crucial for the charge transfer mechanism. Extend of the cation neutralization is ruled by the composition of zeolite and structural factors of zeolites [18]. Dependence of π back-donation on the interaction of Co^{2+} cations with oxygens of zeolite framework requires some knowledge on the Co^{2+} cations positions in MFI type zeolite and the relative population of α, β, and γ type cations. As reported in the literature [18,19], the β-type Co^{2+} ions dominate at all Co loadings and they are suggested to be located at the deformed 6-member ring at the intersection of sinusoidal and straight channels.

As mentioned above, the properties of Co^{2+} may be modified by the interaction with framework oxygens. However, they can be also influenced by the engagement into the interaction with reactant molecules [20]. We studied the effect the electron donor ammonia and pyridine molecules on the properties of Co^{2+} in zeolite CoZSM-5. The properties of Co^{2+} were characterized using NO as probe molecules. NO molecule because of relatively low energy of SOMO orbital is good electron acceptor and its stretching frequency is very

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sensitive to the electronic status of adsorption sites. NO is also interesting as reactant molecules in denox processes. The information concerning the effect electron donor molecules such as ammonia and pyridine on the activation of N–O bond may be also helpful in understanding the mechanism of denox process.

2. Experimental

Parent zeolite NH_4ZSM-5 was supplied by ZEOLYST, CBV 2314. Zeolite CoZSM-5 of Si/Al = 11.5 and Co/Al = 0.15 was obtained by ionic exchange of NH_4ZSM-5 in 0.5 M $Co(NO_3)_2$ solution at 350 K. After exchange procedure, samples were filtered and washed with distilled water until the washing was free from nitrate ions and dried at 385 K for 24 h.

Pyridine (POCh Gliwice, analytical grade), ammonia (PRAXAIR 99.96%) and nitrogen oxide (Linde Gas Polska 99.5%) were used as adsorbates.

Usually, the activation procedure applied to the aluminium rich MFI zeolite (as investigated in this study) results in a partial dealumination leading to the formation of Lewis centers attributed to extraframework aluminium. The scrutiny of the spectra of the parent zeolite NH_4ZSM-5/11.5 in the region of OH groups vibration does not exhibit any bands of Al–OH species (spectra not shows). Additionally, the sorption of pyridine in HZSM-5/11.5 exhibits the presence of negligible amount $Py–Al_{Lewis}$ sites. The quantitative studies demonstrate the presence of 0.2 Lewis centers *per* unit cell which corresponds 2.5% of total Al content in HZSM-5/11.5.

Our quantitative IR studies of CO adsorption exhibited that in CoZSM-5/11.5/0.15 all Co ions exist as exchangeable cations, balancing the negative charge of AlO_4^- tetrahedra pairs. Only 1% of total amount Co cations takes the form of oxide-like species being balanced by single AlO_4^- tetrahedron.

Prior to IR studies the zeolite were pressed into thin wafers and activated in IR cell at 770 K at vacuum for 1 h. The IR spectra were recorded at room temperature with a Bruker Tensor 27 spectrometer (equipped with an MCT detector) with the spectral resolution 2 cm^{-1}.

3. Results and discussion

3.1. Sorption of NO in zeolite CoZSM-5 with preadsorbed pyridine

The spectra of presented in Fig. 1 were recorded upon the sorption of NO in zeolite with preadsorbed pyridine. Spectrum *a* was recorded upon the sorption of pyridine at 440 K in CoZSM-5, followed by the evacuation at the same temperature. The amount of pyridine sorbed was sufficient to neutralize all protonic sites and to saturate all Co^{2+} ions. The spectrum of pyridine adsorbed shows the bands of pyridinium ions and pyridine bonded to Co^{2+} (most characteristic ones at 1545 and 1450 cm^{-1}, respectively). Spectrum *b* was recorded upon the sorption of NO at room temperature in CoZSM-5 with preadsorbed pyridine. Spectrum *c* (difference spectrum $c = b - a$) shows a weak NO band at 1800 cm^{-1} of $[Co(py)(NO)]^{2+}$ mononitrosyls. The frequency of this band is lower by 60 cm^{-1} than for mononitrosyls formed in CoZSM-5 without pyridine (1860 cm^{-1}).

As reported in the literature [9,21], the mononitrosyls are formed in zeolite CoZSM-5 without pyridine only if NO is sorbed at temperatures above ca. 600 K. At lower temperatures the second NO molecule interacts with $Co^{2+}NO$ forming dinitrosyls. It may be supposed that, when Co^{2+} bonds pyridine molecule, there is not enough space to bond two NO molecules.

The lowering NO stretching frequency for NO bonded to $[Co(py)]^{2+}$ adducts indicates the important N=O bond activation which can be explained by π back donation of electrons from $[Co(py)]^{2+}$ complex to antibonding π* orbitals of NO. The electrons from strongly basic pyridine molecule are transmitted to NO *via* Co^{2+} cations.

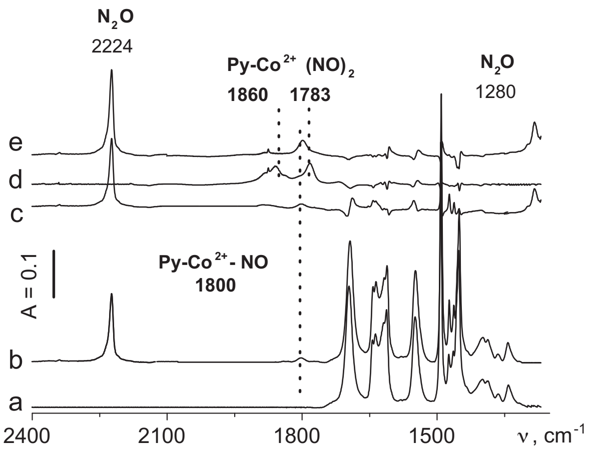

Fig. 1. *a* – spectrum recorded upon the sorption of pyridine at 440 K in CoZSM-5, followed by the evacuation at the same temperature, *b* – spectrum recorded upon the sorption of NO at room temperature in CoZSM-5 with preadsorbed pyridine, *c* – difference spectrum $c = b - a$, *d* – difference spectrum of NO sorbed at 170 K in zeolite CoZM-5 with preadsorbed pyridine, and *e* – difference spectrum recorded upon heating to room temperature of CoZSM-5 with pyridine and NO coadsorbed at 170 K (spectrum *d*).

When NO was sorbed in zeolite CoZM-5 with preadsorbed pyridine at low temperature 170 K (Fig. 1 spectrum *d*) very weak bands of $[Co(py)(NO)_2]^{2+}$dinitrosyls (1780 and 1860 cm^{-1}) developed indicating that at 170 K very small number of $[Co(py)]^{2+}$was able to bond two NO molecules. The frequencies of dinitrosyls bands are lower by 30–35 cm^{-1} than for dinitrosyls formed in CoZSM-5 without pyridine preadsorbed (1810 and 1895 cm^{-1} – spectrum not shown) due to N=O bond activation by π back donation. The subsequent evacuation results in the transformation of dinitrosyls to mononitrosyls (band at 1800 cm^{-1} – spectrum *e*).

The spectra recorded upon the sorption of NO in CoZSM-5 with preadsorbed pyridine show also the bands at 2224 and 1280 cm^{-1} assigned to N_2O [9,21] (Fig. 1, spectra *c* and *e*). The formation of N_2O can be evidence that NO in the presence of $[Co(py)]^{2+}$ adducts acts as oxidizer being reduced to N_2O. It should be noticed that NO sorbed in CoZSM-5 without preadsorbed basic molecules acts as reducer: Co^{3+} is reduced to Co^{2+} and NO is oxidized to NO^+. This was evidenced in by IR studies of Hadjiivanov et al. [9] as well as in our earlier investigation [21].

3.2. Sorption of NO in zeolite CoZSM-5 with preadsorbed ammonia

In this series of experiments NO was sorbed in CoZSM-5 with various amounts of ammonia preadsorbed. Fig. 2 shows the spectra of ammonia adsorbed species in the region 1700–1300 cm^{-1}. They exhibit the bands of ammonia interacting with Co^{2+} (1620 cm^{-1}) and of ammonium ions (1450 cm^{-1}).

Spectrum *c* was recorded upon the saturation with ammonia of all protonic sites and all Co^{2+} sites, whereas spectra *a* and *b* were recorded upon the sorption of smaller amounts of ammonia. The average number of ammonia molecules interacting with one Co ion was roughly estimated from the intensity of 1620 cm^{-1} band and its extinction coefficient. It was assumed that the values of extinction coefficients of IR bands of ammonia interacting with Al- and Co-Lewis sites are comparable, so more, that the band frequencies are the same. The value of extinction coefficient of 1620 cm^{-1} band of ammonia interacting with Al-Lewis acid sites determined in our previous study [22]. The average number of NH_3 molecules engaged

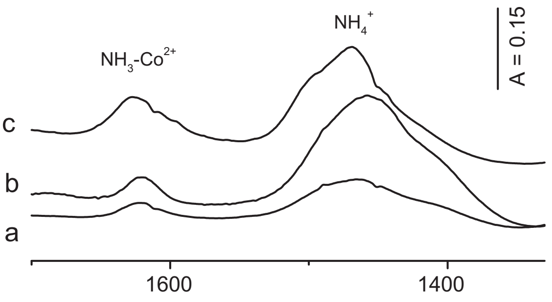

Fig. 2. The spectra of various amounts of ammonia sorbed in zeolite CoZSM-5. Spectra *a*, *b* and *c* correspond an average number of NH_3 molecules per Co^{2+}: 2.5, 4, and 6, respectively.

into interaction with Co^{2+} estimated from the spectra *a*, *b*, and *c* in Fig. 2 was 2.5, 4 and 6 NH_3/Co, respectively.

3.2.1. NO sorption in CoZSM-5 containing 2.5 NH_3/Co

The spectra recorded upon the sorption of increasing amounts of NO in zeolite CoZSM-5 containing in average 2.5 NH_3/Co are presented in Fig. 3. The presented spectra are difference spectra: the spectrum of zeolite with NH_3 but before NO sorption was subtracted from the spectra recorded upon NO sorption.

In the consideration presented below the number of NH_3 molecules coordinated to Co^{2+} is denoted as a symbol *n*. Even though the average number of NH_3 molecules interacting with Co^{2+} ions was estimated as 2.5 NH_3 per 1 Co^{2+}, there are Co^{2+} cations which coordinate bigger number NH_3 molecules and some others Co^{2+} cations engaged into interaction with smaller number NH_3 molecules. Moreover, some NO molecules replace NH_3 when forming $[Co(NH_3)_n(NO)_2]^{2+}$ adducts, hence the number of NH_3 molecules interacting with Co^{2+} cannot be given exactly.

The sorption of first doses of NO (bottom spectra) resulted in appearing of the band of NO interacting with Co^{3+} and also $[Co(NO)_2]^{2+}$ dinitrosyls bands (1815 and 1895 cm^{-1}). The frequencies of these bands are the same as if NO is sorbed in zeolite without ammonia, indicating that the first NO molecules react with Co^{2+} which do not coordinate ammonia. Subsequent NO doses (Fig. 3, top spectra) interact with $[Co(NH_3)_n]^{2+}$ adducts forming $[Co(NH_3)_n(NO)_2]^{2+}$ dinitrosyls. Both NO bands in such dinitrosyls are red shifted by 5–10 cm^{-1} from the positions typical of dinitrosyls without NH_3. This red shift similar (though smaller in comparison with preadsorbed pyridine) can be explained by π back donation of electrons from basic ammonia molecules *via* Co^{2+} to antibonding π* orbitals of NO molecules.

The results presented in Fig. 3 evidenced also that NO is more weakly bonded to Co^{2+} which coordinate NH_3 than to free Co^{2+}: NO reacts with $[Co(NH_3)_n]^{2+}$ in the next order upon reaction with free Co^{2+}. The same conclusion was also obtained in desorption experiment (Fig. 3, spectrum marked with an asterisk). The evacuation at room temperature removed the bands of dinitrosyls in $[Co(NH_3)_n(NO)_2]^{2+}$ complexes (1805 and 1892 cm^{-1}) without affecting the bands of dinitrosyls $[Co(NO)_2]^{2+}$ (1815, 1895 cm^{-1}).

The effect of NO sorption on the status and properties of preadsorbed ammonia will be now discussed. According the data presented in Fig. 3, the first doses of NO (bottom spectra) react with Co^{2+}free of NH_3, the spectrum of NH_3 bonded to Co^{2+} and of ammonium ions practically does not change (the difference spectra do not show any changes). On the other hand, when NO interacts with $[Co(NH_3)_n]^{2+}$ (Fig. 3, top spectra) the band of ammonia interacting with Co^{2+} at 1620 cm^{-1} decreases (this is seen as minimum in difference spectra), which is accompanied by the band of ammonium ions at 1450 cm^{-1} grow and a new band at 1645 cm^{-1} appearance. These effects can be explained as follows: some NO molecules react with $[Co(NH_3)_n]^{2+}$ complexes which have two free coordination positions and are able to coordinate two NO molecules forming $[Co(NH_3)_n(NO)_2]^{2+}$. Both NH_3 and NO bands are shifted from the positions typical if they are sorbed “solo”: NH_3 band is blue shifted (from 1620 to 1645 cm^{-1}) and the bands of NO are red shifted (by 5–10 cm^{-1}). Other NO molecules interact with $[Co(NH_3)_n]^{2+}$ complexes which have less than two coordination positions accessible. In this case, ammonia is substituted for NO-removed ammonia molecules reacts with acidic hydroxyls still not neutralized by ammonia forming new ammonium ions: the band at 1450 cm^{-1} grows.

3.2.2. NO sorption in CoZSM-5 containing 4 NH_3/Co

The spectra recorded upon the sorption of increasing amounts of NO in zeolite CoZSM-5 containing in average 4 NH_3/Co are presented in Fig. 4. At low NO loadings (Fig. 4, spectrum *a*) the 1750 cm^{-1} band is the only NO band. It can be assigned

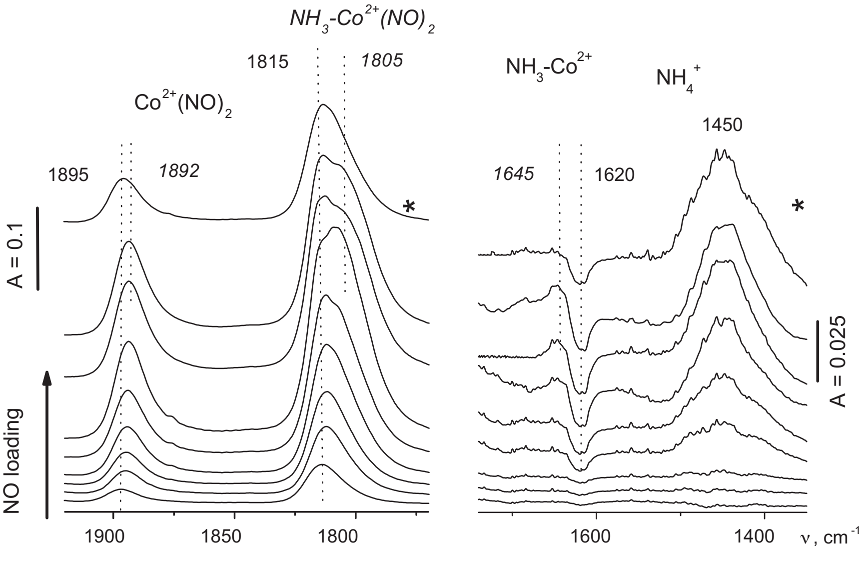

Fig. 3. The spectra recorded upon the sorption of increasing amounts of NO in zeolite CoZSM-5 containing 2.5 NH_3/Co. The spectrum marked with asterisk (*) was recorded upon the evacuation at room temperature. The presented spectra are difference spectra: the spectrum of zeolite with NH_3 but before NO sorption was subtracted from the spectra recorded upon NO sorption.

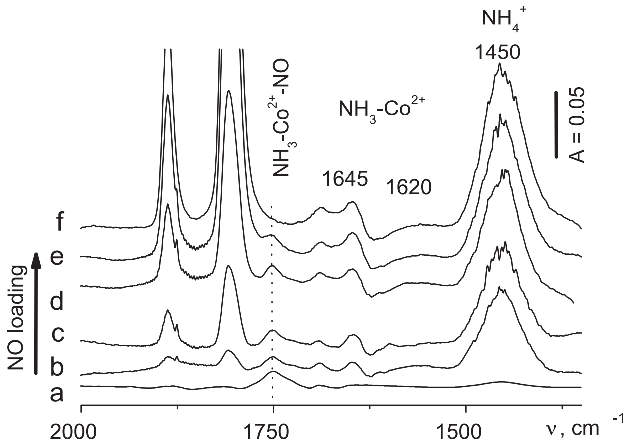

Fig. 4. The spectra recorded upon the sorption of increasing amounts of NO in zeolite CoZSM-5 containing 4 NH_3/Co. The presented spectra are difference spectra: the spectrum of zeolite with NH_3 but before NO sorption was subtracted from the spectra recorded upon NO sorption.

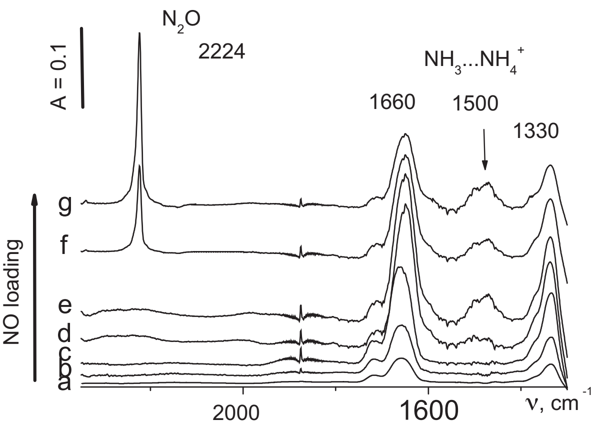

Fig. 5. *a–e* – spectra recorded immediately upon the sorption of increasing amounts of NO in zeolite CoZSM-5 containing 6 NH_3/Co (Co^{2+} coordinates maximum possible number of NH_3 molecules). The presented spectra are difference spectra: the spectrum of zeolite with NH_3 but before NO sorption was subtracted from the spectra recorded upon NO sorption. *f* – spectrum recorded upon 30 min contact time with NO. *g* – spectrum recorded upon 60 min contact time with NO.

to $[Co(NH_3)_4(NO)]^{2+}$ mononitrosyls. As mentioned, mononitrosyls have not been observed if NO was sorbed in CoZSM-5 at room temperature without ammonia. When NO is sorbed in CoZSM-5 with (in average) 4NH_3/Co only $[Co(NH_3)_4]^{2+}$ complexes with one coordination position unoccupied able to bond one NO molecule, therefore mononitrosyls are formed.

The NO band in such mononitrosyls is red shifted by 110 cm^{-1} in comparison with CoZSM-5 without ammonia [9,21]. This significant frequency shift may be attributed to the electron transfer of electrons from electron donor ammonia molecules *via* Co^{2+} to antibonding π^* orbitals of NO. This effect was found to be more important than that observed for pyridine preadsorbed ($\Delta\nu = 60\ cm^{-1}$) for the reason that Co^{2+} can bond only one bulky pyridine molecule but bonds several smaller ammonia molecules, therefore for ammonia the electron donation effect is multiplied. At higher NO loadings the mononitrosyl 1750 cm^{-1} band diminished, whereas two dinitrosyls bands (at 1810 and 1887 cm^{-1}) grew up. Likewise, as for lower ammonia loadings (see previous chapter) and for pyridine the bands of dinitrosyls are red shifted by 5–10 cm^{-1} in comparison with the spectrum of NO sorbed in zeolite without ammonia.

Similarly as for lower ammonia loadings (see previous chapter) NO molecules replaced some ammonia molecules from $[Co(NH_3)_4]^{2+}$. Removed ammonia molecules react with protonic sites forming new ammonium ions (the band at 1450 cm^{-1}). The 1620 cm^{-1} band of ammonia bonded to Co^{2+} shifts also to higher frequency due to the interaction of Co^{2+} with NO.

3.2.3. NO sorption in CoZSM-5 containing 6 NH_3/Co

In this series of experiments NO was sorbed in CoZSM-5 in which all the protonic sites were neutralized and all the Co ions coordinated maximum number of NH_3 molecules. As mentioned above, this maximum number was estimated to be equal to 6. It should be noted that in water solutions cobalt forms hexamine complexes in which coordination number is also equal to 6.

The spectra of NO sorbed in the zeolite saturated with ammonia are presented in Fig. 5 (spectra *a–e*). Similarly as for lower ammonia loadings, the NO sorption resulted in the appearance of the 1500 cm^{-1} band (in the region of ammonium ions deformation). According to our earlier study [23], this band is typical of dimmers: $NH_4^+\cdots NH_3$, which are formed by the reaction of ammonia with ammonium ions. This result suggests that NO replaced NH_3 from $[Co(NH_3)_6]^{2+}$ complexes forming $[Co(NH_3)_5(NO)]^{2+}$ while the NH_3 molecule released reacts with NH_4^+ ion (all the protonic sites are already neutralized by the ammonia) forming $NH_4^+\cdots NH_3$ dimmers.

$[Co(NH_3)_5(NO)]^{2+}$ complexes are widely known in the cobalt coordination chemistry [24–26]. They are formed in the reaction of hexamine complexes $[Co(NH)_6]^{2+}$ with NO at water solution even at 0 °C. The $[Co(NH_3)_5(NO)]^{2+}$ compounds are now known be formally NO^- complexes of Co(III). In such $[Co^{(III)}(NH_3)_5(NO^-)]^{2+}$ complexes the electron transfer from Co^{2+} to NO took place: Co^{2+} is oxidized to Co^{3+} and NO is reduced to NO^-. It is well-known that the Co(III) oxidation state is stabilized by NH_3 and other electrondonor amine ligands, as well as by CN^- in $[Co(CN)_5(NO)]^{3-}$ complexes [22–24]. The $[Co(NH_3)_5(NO)]^{2+}$ complexes are able to dimerize forming the hyponitrite dimmers $[(NH_3)_5Co–(O)N{=}N–O–Co(NH_3)_5]^{4+}$ [24–26]. Both complexes, i.e. monomers and dimmers, are diamagnetic which is an evidence that NO got negative charge forming nitroside anion NO^-. The fact that full electron transfer to NO occurred stands for a very important N=O bond activation by the donation of electron to π^* antibonding orbital.

As mentioned, it is known in coordination chemistry of cobalt, that $[(NH_3)_5Co–(O)N{=}N–O–Co(NH_3)_5]^{4+}$ dimmers are formed from $[Co(NH_3)_5(NO)]^{2+}$ monomers [24–26]. However, it seems that in our ZSM-5 zeolite there is not enough space to form such bulky species. Nevertheless, it is not excluded that in ZSM-5 hyponitrite fragments $[O–N{=}N–O]^{2-}$ can be formed by the addition of NO molecule from the gas phase to $[(NH_3)_5Co^{III}(NO^-)]^{2+}$ species according to the nitroside ion pathway proposed for the reaction of NO in zeolite CuZSM-5 [30]. In Cu^+–NO unit some electron density is transferred from zeolite framework *via* Cu^+ toward NO which gathers negative charge. This negative charge is accumulated on N atom which leads to the change of hybridization to sp^2. Cu^+-NO unit is prone to electrophilic attack of NO from gas phase leading to N–N bond formation. Finally N_2O as intermediate product of NO reduction to N_2 is produced. We suppose that similar situation may take place in our CoZSM-5. $[(NH_3)_5Co^{III}(NO^-)]^{2+}$ complexes in which N atom which did also gather electron density from NH_3 ligands *via* Co^{2+} may react with others NO molecule from gas phase forming $[(NH_3)_5Co^{III}(O–N{=}N–O)^-]^{2+}$ dimeric forms.

The results of presented above consideration will be now confronted with the IR data. According to the data presented in Fig. 5, the sorption of NO in CoZSM-5 saturated with ammonia results in appearing of two bands at 1330 and 1660 cm^{-1}. It is not excluded that these bands may be assigned to a hyponitrite species formed in our CoZSM-5. The frequency of the band at 1330 cm^{-1} is in the region of NO^- vibration [27,28]. Moreover, the 1660 cm^{-1} band is in the region of double bond vibration (1700–1600 cm^{-1}). The 1330 and 1660 cm^{-1} bands may be assigned to N–O single bond and N=N double bond in the hyponitrite structure.

The fact that electron transfer from Co^{2+} enriched in electrons by five ammonia ligands to NO ligand took place denotes that in this case (similarly as for CoZSM-5 with preadsorbed pyridine) NO acted as oxidant.

According to the data presented in Figs. 3 and 4, the hyponitrite species were not formed if NO interacted with $[Co(NH_3)_{2.5}]^{2+}$ and $[Co(NH_3)_4]^{2+}$, nitric oxide (II) took the form of mononitrosyls or dinitrosyls. It can be supposed that the hyponitrite species are formed only if Co^{2+} ions coordinating the maximum number of NH_3 ligands interact with NO. Only in this case Co^{2+} is so enriched in electrons that the electron transfer to NO may take place and hyponitrite species can be formed.

At longer contact time (Fig. 5, spectra *f* and *g*) the band of N_2O (2224 cm^{-1}) develops being evidence that, similarly as for preadsorbed pyridine, N_2O was produced from adsorbed NO forms. Parallel with the formation of N_2O, the bands of the hyponitrite species 1330 and 1660 cm^{-1} decrease suggesting that N_2O was formed from the hyponitrite species. What is more, N_2O was not formed in CoZSM-5 with smaller amount of ammonia preadsorbed, i.e. containing $[Co(NH_3)_{2.5}]^{2+}$ and $[Co(NH_3)_4]^{2+}$, in which the hyponitrite species were not formed (Figs. 3 and 4) supporting hypothesis that hyponitrite species (in which N–N bond already exists) may be precursor of N_2O formation in CoZSM-5 with preadsorbed ammonia.

The formation of N_2O from the hyponitrite Co species was also observed for cobalt complexes with various ligands e.g. CN^- [24,26,29]. The decomposition of the hyponitrite species was related to their instability and their tendency to lose nitrous oxide.

According to data presented in Fig. 1, N_2O was also formed if NO interacted with $PyCo^{2+}$ adducts in spite of the absence of hyponitrite bands (1330 and 1660 cm^{-1}). It is possible that in this case of pyridine, which transmitted less of electron density to NO ligand (*via* Co^{2+}) than six ammonia ligands the mechanism of N_2O formation was different.

4. Conclusions

(1) The interaction of NO with Co^{2+} in CoZSM-5 with preadsorbed pyridine and ammonia was followed. We studied CoZSM-5 with various amounts of ammonia preadsorbed: $NH_3/Co = 2.5$, 4 and 6.

(2) Without preadsorbed ammonia and pyridine molecules, NO sorbed at room temperature in CoZSM-5 formed dinitrosyls $[Co(NO)_2]^{2+}$, mononitrosyls $[Co(NO)]^{2+}$ were formed only at high temperatures (above 600 K). When NO was sorbed in CoZSM-5 with preadsorbed pyridine and ammonia, mononitrosyls $[Co(py)(NO)]^{2+}$, and $[Co(NH_3)_4(NO)]^{2+}$ were formed.

(3) The molecules NO interacting with Co^{2+} which bonds pyridine or ammonia molecules are strongly activated: the NO band shifts to lower frequencies by 60 and 110 cm^{-1}, respectively. This activation is realized by the transfer of electrons from basic molecules *via* Co^{2+} to antibonding π^* orbitals of NO. The activation is more important for ammonia than for pyridine. Co^{2+} is able coordinate only one bulky pyridine molecule but it can coordinate several small ammonia molecules, so for ammonia the electron donation multiplies.

(4) If NH_3 and NO molecules are coordinated to the same Co^{2+} ion, apart from NO molecule, the NH_3 molecule is also affected: the NH_3 bending band shifts to higher frequency by 25 cm^{-1}.

(5) The interaction of NO with Co^{2+}, which coordinates maximum possible number of NH_3 molecules ($NH_3/Co = 6$), results in substitution of one NH_3 for NO and the formation of $[Co(NH_3)_5(NO)]^{2+}$. In these complexes the electron transfer from Co^{2+} to NO takes place. The transfer of full electrons to antibonding π^* orbitals of NO results in very important NO activation. High likely $[Co(NH_3)_5(NO)]^{2+}$ complexes in our zeolite (similarly as in solutions) can form hyponitrite species: $[(NH_3)Co^{III}(O{-}N{=}N{-}O)^-]^{2+}$. It is possible that the bands at 1330 and 1660 cm^{-1} observed in our IR spectra can be assigned to a hyponitrite species (the band at 1330 cm^{-1} may be due to N–O bond, and 1660 cm^{-1} to double N=N bond).

(6) It is possible that the hyponitrite species $[(NH_3)Co^{III}(O{-}N{=}N{-}O)^-]^{2+}$, as well as $[Co(py)(NO)]^{2+}$ are precursors of of N_2O formation.

(7) The fact that NO accepts electron forming NO^- and finally N_2O indicates that NO acts as oxidant in the presence of $[Co(py)]^{2+}$ or $[Co(NH_3)_6]^{2+}$. However, when NO interacts with Co^{2+} without preadsorbed basic molecules, it acts as reducer: Co^{3+} is reduced to Co^{2+} and NO is oxidized to NO^+.

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