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FTIR spectroscopic study of low-temperature co-adsorption of NO and O_2 on H-ZSM-5: evidence of formation of [ONNO]$^+$ species

K. Hadjiivanov [a,*], A. Penkova [a], M. Daturi [b], J. Saussey [b], J.-C. Lavalley [b]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[b] *Laboratoire Catalyse et Spectrochimie, CNRS-ISMRA, Université de Caen, 6, bd Maréchal Juin, 14050 Caen Cedex, France*

Abstract

Coadsorption of NO and O_2 on H-ZSM-5 at room temperature leads to formation of NO$^+$ occupying cationic positions (2133 cm^{-1}) and adsorbed nitrogen oxides. At low temperature NO$^+$ reacts with NO, thus producing the unknown so far [ONNO]$^+$ surface complex (2000 and 1687 cm^{-1}). The latter is readily decomposed to NO$^+$ and NO. The assignment is supported by experiments involving ^{15}NO.
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1. Introduction

The chemistry of different NO$_x$ surface compounds is a subject of continuous interest. This is mainly due to two reasons: (i) the great importance of NO$_x$ conversion reactions for environmental catalysis [1,2] and (ii) the increasing utilization of NO as a probe molecule, alternative or complement to CO [3–10]. Probing different surfaces with NO is usually performed at ambient temperature. At low temperature NO tends to dimerize, which complicates the spectra and hinders the assignment of the registered bands. However, some examples on the high potential of NO as a probe at low temperatures have been provided recently [4,9,10].

A peculiarity of NO is its tendency to be easily oxidized by surface cationic sites or to disproportionate. That is why detailed knowledge of the nature of surface species resulting from partial NO oxidation is of definite interest.

Our knowledge of the nature of different nitrogen-oxo adsorption species has been significantly improved during the last decade. In particular, a large number of studies have been performed with metal-exchanged ZSM-5 zeolites [11–18], since these samples have demonstrated promising properties in the selective catalytic reduction of nitrogen oxides with hydrocarbons. There are many detailed investigations on NO + O_2 coadsorption on H-ZSM-5 but all of

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* Corresponding author. Fax: +3592-8705024.
E-mail address: kih@svr.igic.bas.bg (K. Hadjiivanov).

them have been performed at ambient temperature [19–21]. The main achievements can be summarized as follows:

- NO is practically not adsorbed on H-ZSM-5 at ambient temperature [19].
- Coadsorption of NO and O_2 leads to the formation of NO^+ according to the reaction [19]

$$2O–H^+ + N_2O_3 \leftrightarrow H_2O + 2O – NO^+ \qquad (1)$$
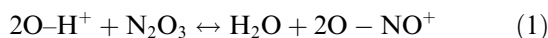
The NO^+ produced is characterized by a band at 2133 cm^{-1}. This band has almost the same position with different Me-exchanged ZSM-5 samples [12–18] and is usually observed at somewhat higher frequencies with other zeolites [22,23].

- At high oxygen concentration a reversibly adsorbed N_2O_3 (bands at 1875 and 1587 cm^{-1}) and N_2O_4 (1745 cm^{-1}) are formed [20] and a new species which has not been unambiguously assigned also appears. It absorbs at 2185 cm^{-1} and, according to Szanyi and Paffett [20], is produced at the expense of the NO^+ species absorbing at 2133 cm^{-1}.

To the best of our knowledge, there are no works reporting spectra of low-temperature $NO + O_2$ coadsorption on H-ZSM-5 or other H-zeolites.

The aim of this work is to study the low temperature $NO + O_2$ coadsorption on H-ZSM-5. We have demonstrated that NO^+ can react with NO, thus producing $(NO)_2^+$ species. For a better assignment of the spectra we have involved ^{15}NO in the experiments.

2. Experimental

The H–ZSM-5 material was supplied by Degussa and had a Si/Al ratio of 26.8.

The IR spectra were recorded on Nicolet Magna IR-550 and Nicolet Avatar 360 spectrometers at a spectral resolution of 2–4 cm^{-1} and accumulating 64–128 scans. Self-supporting pellets were prepared from the sample powder and treated directly in purpose made IR cells. The latter allowed measurement at room and low temperature and were connected to a conventional vacuum-adsorption apparatus. Prior to the adsorption

measurements, the samples were activated by heating for 1 h in oxygen at 623 K and 1 h evacuation at the same temperature. Nitric oxide was supplied by Air Liquide, France (99.9) and by Messer Griesheim, GmbH (>99.0). ^{15}NO was purchased by ONIA and had an isotopic purity of 98.5 at.%. Before adsorption oxygen was purified by passing through a liquid nitrogen trap.

3. Results and discussion

3.1. Co-adsorption of NO and O_2 at room and decreasing temperature

The IR spectrum of the activated H–ZSM-5 sample contains, in the v(OH) region, a sharp band at 3610 cm^{-1} which characterizes the O–H stretching modes of the so-called acidic zeolite hydroxyls. In addition, a weak band at 3743 cm^{-1} is also visible and is assigned to silanol groups [24].

Adsorption of NO at room temperature on the H-ZSM-5 sample does not lead to formation of any adsorption species. Only two very weak bands at 1830 and 1637 cm^{-1} are discernible in the difference spectra and assigned to a negligible amount of adsorbed N_2O_3 [25].

NO (665 Pa) and O_2 (133 Pa) were coadsorbed on the sample at ambient temperature. As a result, a band at 2133 cm^{-1} emerged (spectra not shown). This band was assigned to NO^+ occupying cationic positions in H-ZSM-5 [19]. In addition, the band due to zeolite acidic hydroxyls at 3610 cm^{-1} decreased in intensity. Bands due to molecularly adsorbed water (3699, ca. 3500 and 1630 cm^{-1}) as well as features characterizing H-bonded zeolite hydroxyls (2870, 2459 and 1354 cm^{-1}) also developed. These results are consistent with the proceeding of reaction (1).

Cooling of the sample in this atmosphere resulted in a shift of the 2133 cm^{-1} band to 2141 cm^{-1}, a high frequency shoulder at 2206 cm^{-1} being also clearly visible (Fig. 1, spectrum a). In addition, bands assigned to two kinds of adsorbed N_2O_3 (1964, 1908, 1591 and 1560 cm^{-1}) and NO_2 (1645 cm^{-1}) were registered [3]. The latter were superimposed with the water deformation modes.
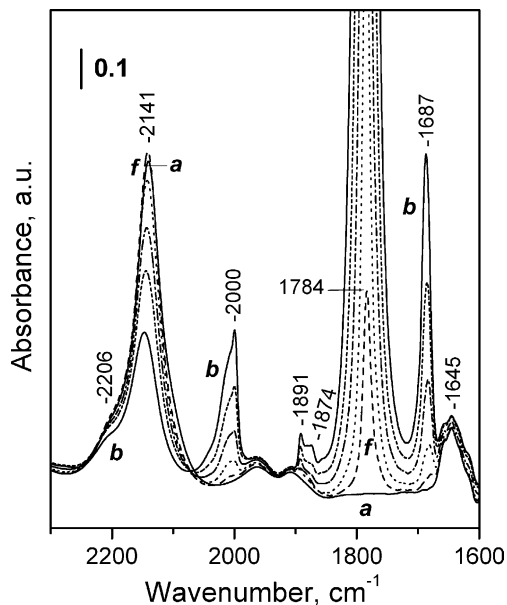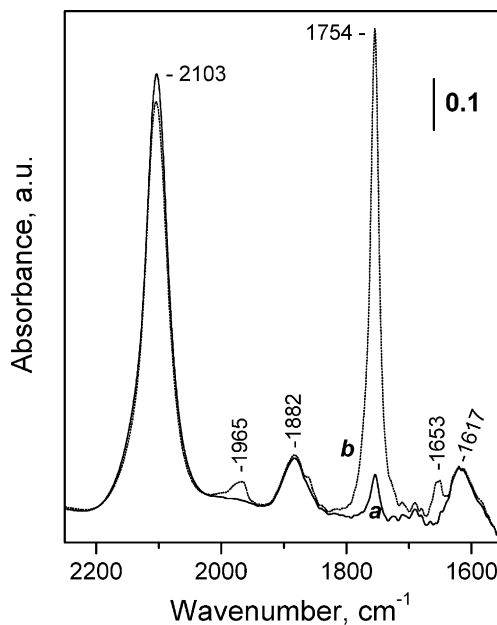
Fig. 1. FTIR spectra of NO and O_2 coadsorbed on H-ZSM-5. Introduction of NO (665 Pa) and O_2 (133 Pa) at ambient temperature and cooling to 100 K (a), subsequent introduction of NO (665 Pa) (b) and development of the spectra at the conditions of dynamic vacuum (c)–(f).

Introduction of NO (665 Pa initial pressure) led to drastic changes in the IR spectrum (Fig. 1, spectrum b). The band at 2141 cm^{-1} together with its higher frequency shoulder strongly decreased in intensity. A very intense band at 1784 cm^{-1} developed. In addition, two strong bands at 2000 cm^{-1} (with a high frequency shoulder) and 1687 cm^{-1} emerged. Two weak bands at 1891 and 1874 cm^{-1} were also produced. Evacuation of the sample resulted in a gradual intensity decrease of the bands at 2000, 1891, 1874, 1784 and 1687 cm^{-1} (Fig. 1, spectra b–f). Simultaneously, the 2141 cm^{-1} band was restored.

Separate experiments have shown appearance of bands at 1891 and 1874 cm^{-1} after low temperature NO adsorption. These bands are assigned to H-bonded NO and NO dimers. Their intensity here is very weak because the major part of the protons from the zeolite acidic hydroxyls have been replaced by NO^+. The strong band at 1784 cm^{-1} has also been detected after NO adsorption and attributed to the v_{as} modes of adsorbed *trans*-ONNO species. The respective symmetric vibra-

tions are IR inactive [25]. The bands at 2000 and 1687 cm^{-1} change in concert and their decrease in intensity follows the development of the band at 2141 cm^{-1}. The results indicate that these two bands characterize one species that is produced by interaction of NO^+ with NO. Moreover, the production of this species is reversible and its decomposition leads again to formation of NO^+.

3.2. Experiments involving ^{15}NO

In order to support the above assignment we performed experiments involving ^{15}NO. At first, ^{15}NO and O_2 were coadsorbed on the sample and the system was cooled to 100 K. As a result, an $^{15}NO^+$ band at 2103 cm^{-1} was dominating in the spectrum (Fig. 2, spectrum a). Weak bands due to $^{15}N_2O_3$ (1882 cm^{-1}), *trans*-$(^{15}NO)_2$ (1754 cm^{-1}) and $^{15}NO_2$ (1617 cm^{-1}) were also visible. Then ^{15}NO was added to the system. The band at 1754 cm^{-1}, due to *trans*-$(^{15}NO)_2$ dimers, strongly increased in intensity (Fig. 2, spectrum b). The band

Fig. 2. FTIR spectra of ^{15}NO and O_2 coadsorbed on H-ZSM-5. Introduction of ^{15}NO (665 Pa) and O_2 (ca. 65 Pa) at ambient temperature and cooling to 100 K (a) and after subsequent introduction of ^{15}NO (133 Pa) to the system (b).

at 2105 cm^{-1} slightly declined and two bands at 1965 and 1653 cm^{-1} emerged. These two bands correspond to the bands at 2000 and 1687 cm^{-1} registered in the experiments with ^{14}NO. On this basis, the ^{14}N–^{15}N isotopic shift factors can be calculated. They are 0.9825 and 0.9798 for the bands at 2000 and 1687 cm^{-1}, respectively. This is close to the ^{14}NO–^{15}NO isotopic shift factors, namely 0.98206 [3]. The small deviations indicate some coupling of the respective vibrations.

Some experiments involving ^{14}NO and ^{15}NO were also performed. As above, ^{15}NO and O$_2$ were coadsorbed and the system cooled. The ^{15}NO$^+$ band was registered at 2103 cm^{-1} and the band due to trans-(NO)$_2$, at 1754 cm^{-1} (Fig. 3, spectrum a). Then ^{14}NO (665 Pa) was added to the system. As a result, the ^{15}NO$^+$ band strongly decreased in intensity and was shifted to higher frequencies (typical of ^{14}NO$^+$), indicating a fast isotopic exchange (Fig. 3, spectrum b). A strong band at 1784 cm^{-1} with a shoulder at 1768 cm^{-1} appeared. Two intense bands at 2000 and 1687 cm^{-1} were also detected.
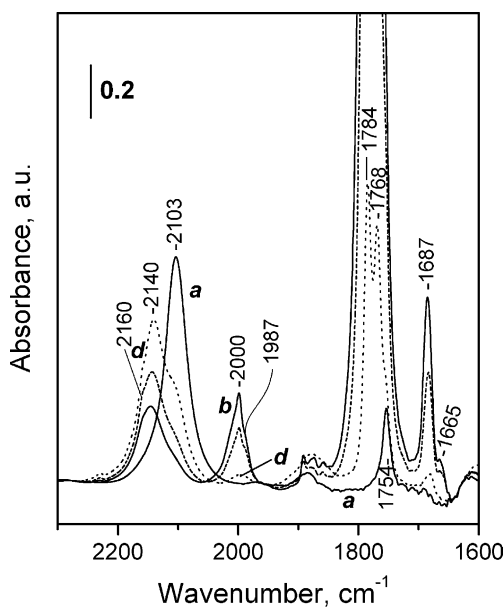

Fig. 3. FTIR spectra of ^{15}NO and O$_2$ coadsorbed on H-ZSM-5. Introduction of ^{15}NO (665 Pa) and O$_2$ (ca. 65 Pa) at ambient temperature and cooling to 100 K (a) after subsequent introduction of ^{14}NO (665 Pa) to the system (b) and development of the spectra at the conditions of dynamic vacuum (c,d).

Careful analysis of the spectra indicated that the band at 2000 cm^{-1} had a lower-frequency shoulder at 1987 cm^{-1} while the band at 1687 cm^{-1} demonstrated a shoulder at 1665 cm^{-1}. Under the conditions of the experiments we have an excess of ^{14}N in the nitrogen-oxo compounds, which indicates that the majority of the species have two ^{14}N atoms and some of them, one ^{14}N and one ^{15}N atom. Hence, the bands at 1987 and 1665 cm^{-1} originate from $[(^{14}NO)(^{15}NO)]^+$ species. Note that the similar situation was observed with the v_{as} modes of the trans-dimer of NO (Fig. 3, spectrum d).

The results allow us to assign the bands at 2000 and 1687 cm^{-1} to the v_s and v_{as} modes, respectively, of $[O^{14}N^{14}NO]^+$ species. Since both modes are IR active, the complex has a cis-configuration. Evidently, the positive charge in these complexes is delocalized. These species are easily decomposed to NO$^+$ and NO, which is consistent with the fast isotopic exchange observed in this study.

In order to check for eventual participation of OH groups in the reaction, we have examined the spectra in the O–H stretching region. Introduction of NO + O$_2$ mixture and cooling down to 100 K results in a strong decrease in intensity of the 3610 cm^{-1} band because of the formation of NO$^+$ occupying cationic positions (Fig. 4, spectrum a). Subsequent NO introduction leads to a small additional decrease in intensity of the band at 3610 cm^{-1} and development of a broad band at 3380 cm^{-1} (Fig. 4, spectrum b). These changes were registered after NO adsorption only and attributed to formation of H-bonded NO. In addition, two bands at 3764 and 3470 cm^{-1} develop (Fig. 4, spectrum b) and disappear after subsequent evacuation (Fig. 4, spectrum f). The same bands were found at lower frequencies (3698 and 3405 cm^{-1}, respectively) when ^{15}NO was used for the experiments. These results prove that the bands are not related to O–H stretching modes but are due to overtones/combination modes of N–O stretches. In particular, we assign the band at 3764 cm^{-1} to the ($v_s + v_{as}$), and that at 3470 cm^{-1}, to the ($2v_{as}$) modes, respectively, of the trans-(NO)$_2$ dimer. Thus, the results obtained prove that no OH group are involved in the formation of [ONNO]$^+$ from NO$^+$ and NO.
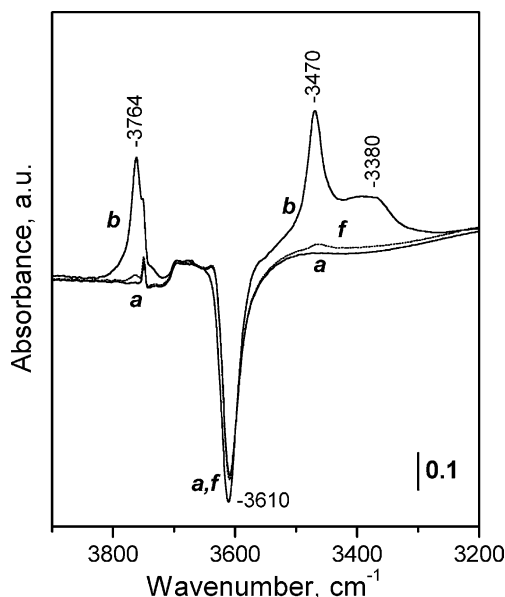
Fig. 4. FTIR difference spectra in the OH stretching region. The notations are the same as in Fig. 1.

A criterion of partial oxidation of NO when adsorbed at ambient temperature on H-ZSM-5 and Me-H-ZSM-5 zeolites, is the presence, in the IR spectra, of a NO^+ band at 2133 cm^{-1}. Our results indicate that this criterion is not valid when NO is adsorbed at low temperature. Because of the conversion of NO^+ to $[ONNO]^+$, the band at 2133 cm^{-1} is not expected to appear. Hence, at low temperatures a criterion for oxidation of NO should be the presence of bands at 2000 and 1687 cm^{-1}.

Acknowledgements

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