An FT-IR study of the adsorption and oxidation of N-containing compounds over Fe_2O_3/Al_2O_3 SCR catalysts

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Abstract

The interaction of NO, ammonia (NH_3), hydrazine (N_2H_4) and hydroxylamine (NH_2OH) on Fe_2O_3/Al_2O_3 model catalyst was studied. The data support the idea that hydrazine can be intermediate in the oxidation of ammonia to nitrogen, while hydroxylamine-type species, can be intermediate in the oxidation of ammonia to NO. On the contrary to those observed over Fe_2O_3/TiO_2 previously studied, hydroxylamine-type species are formed at relatively low temperature, indicating that Fe_2O_3/Al_2O_3 is less selective in SCR reaction with ammonia.
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1. Introduction

The surface chemistry of nitrogen-containing compounds is relevant with respect to several industrial processes. The preparation on industrial scale of aliphatic amines implies the conversion of the corresponding alcohols with ammonia over heterogeneous acid catalysts [1] while the synthesis of aliphatic and aromatic nitriles is performed by ammoxidation of the corresponding hydrocarbons over transition metal oxide catalysts [2].

In parallel with this, the use of ammonia as the reducing agent for NO_x in the so-called Selective Catalytic Reduction (SCR) process [3], according to the following reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$
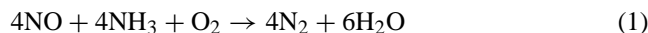
and the necessity to understand its mechanism implies more knowledge on the surface and catalytic chemistry of ammonia and other N-containing compounds. Actually, this process can also be performed using urea as the reducing agent [4].

The industrial catalysts for the SCR reactions with ammonia are generally based on V_2O_5–WO_3/TiO_2 or V_2O_5–MoO_3/TiO_2. However, many other transition metal oxide based systems are also active and could be proposed

for particular applications [5]. Among other, Fe_2O_3–based catalysts [6] such as α-Fe_2O_3 [7], γ-Fe_2O_3, $MgFe_2O_4$ [8], Fe_2O_3/SiO_2 [9,10], Fe_2O_3/TiO_2 [11–13], Fe_2O_3/TiO_2-pillared clays [14], Fe–ZSM5 [15], Fe–MOR [16], Fe–MFI [17] and Fe over activated carbon fibre [18] catalysts have also been investigated and found active and quite selective to N_2. Furthermore iron-based catalytic materials appear to be promising in relation to their low cost and environmental friendless. Moreover, some of these SCR catalysts are also active for SCR at low temperature and for the Selective Catalytic Oxidation (SCO) of ammonia to nitrogen:

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O \qquad (2)$$
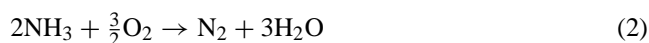
Recently a great interest in developing active SCR catalysts that work at low temperature, less than 523 K, that can be applied for a SO_2 free gas and/or in the so-called tail-end application, has been observed. Development of low temperature process can be represent an important economic and environmental benefit [5].

The so-called SCO process is now under deep investigation, because it allows to abate the ammonia slip after SCR reactors (if working with excess of ammonia), without introducing other reactant in the gas mixture and without producing further pollutants [19,20]. This reaction is competitive with the total oxidation of ammonia to NO:
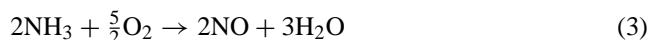
$$2NH_3 + \tfrac{5}{2}O_2 \rightarrow 2NO + 3H_2O \qquad (3)$$
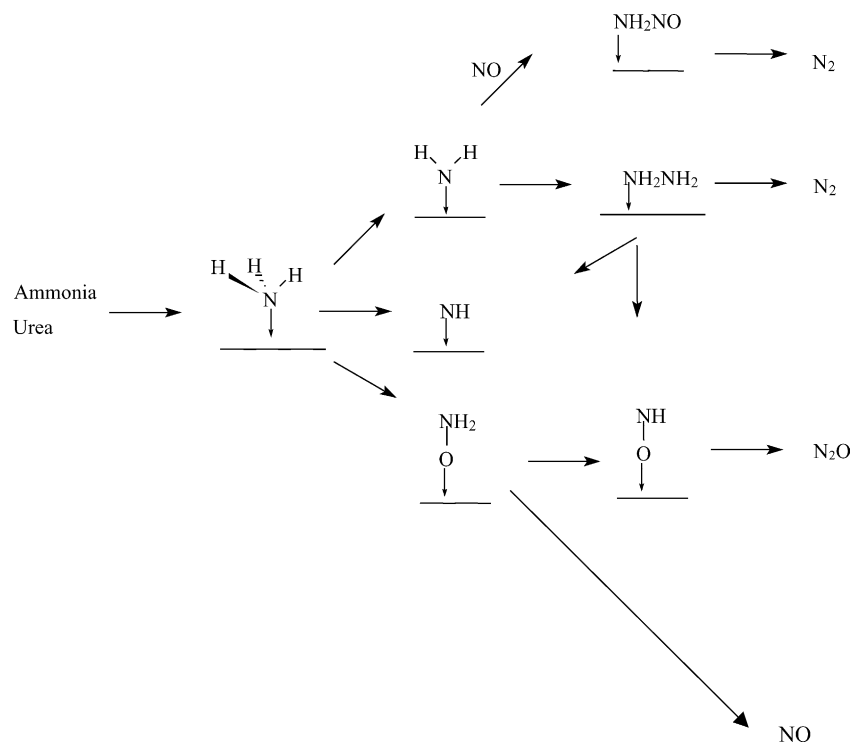
Scheme 1. Proposed pathway of the conversion of N-containing molecules over Fe_2O_3/Al_2O_3 catalysts.

Reactions (2) and (3) occur over several metal oxide catalysts, the former occurring mainly at lower temperatures, the latter at higher temperatures. Both have been observed on iron oxide-based catalysts such as Fe_2O_3 [21]. Actually different reaction mechanisms have been proposed for most of these reactions, the true pathways being still not unambiguously recognised (Scheme 1).

Metal oxides as alumina shows high stability and durability in the SCR of nitrogen oxides, in particular with hydrocarbons [22,23], so, as a further development of our studies concerning the chemistry of the reactants and the possible intermediates involved in the SCR reaction catalysed by metal oxides [13,24,25], we investigated by FT-IR the adsorption of different N-containing compounds over a model Fe_2O_3/Al_2O_3 catalyst.

2. Experimental

The catalyst (Fe_2O_3/Al_2O_3) has been prepared by impregnation of commercial Degussa Aluminium oxide C pigment (predominantly in phase θ) with iron nitrate followed by calcination at 673 K. The BET surface area of the resulting catalyst is, within experimental error, identical as that of the support ($100\,m^2/g$). The metal oxide loaded amount was near 6% Fe_2O_3/Al_2O_3 (w/w). This coverage is just below the theoretical monolayer, near 90%.

Hydrazine water solution (85%) and hydroxylamine chlorohydrate (purity 99%), were purchased from Carlo Erba (Milan, Italy). Ammonia and NO were taken from commercial cylinders from SIAD (Milan, Italy). NO was taken from a commercial cylinder at 5×10^6 Pa, after careful purification by freezing and vacuum distillation. Its purity was checked by FT-IR and only trace amounts of N_2O and NO_2 were detected.

FT-IR spectra were performed with a Nicolet Protegè 460 Fourier transform spectrometer ($4\,cm^{-1}$ resolution) using self-supporting pressed disks of the pure catalyst powders, previously pre-treated by calcination in the IR cell at 623 K for 2 h and outgassing at 623 K for 1 h. The IR cell is connected to a conventional gas-handling system. The spectrum of the activated catalyst has been subtracted.

3. Results and discussion

3.1. Adsorption of NO

The spectrum of the adsorbed species arising from contact of the Fe_2O_3/Al_2O_3 catalyst with NO gas at RT is reported in Fig. 1a.

According to previous studies [26,27], the interaction of NO with alumina is very complex and gives a number of different transformation species characterised by bands below $1800\,cm^{-1}$.

At higher frequency a sharp band at $1805\,cm^{-1}$, that resists evacuation at RT but disappeared after outgassing at higher temperatures (Fig. 1, spectra b–c) and a very weak
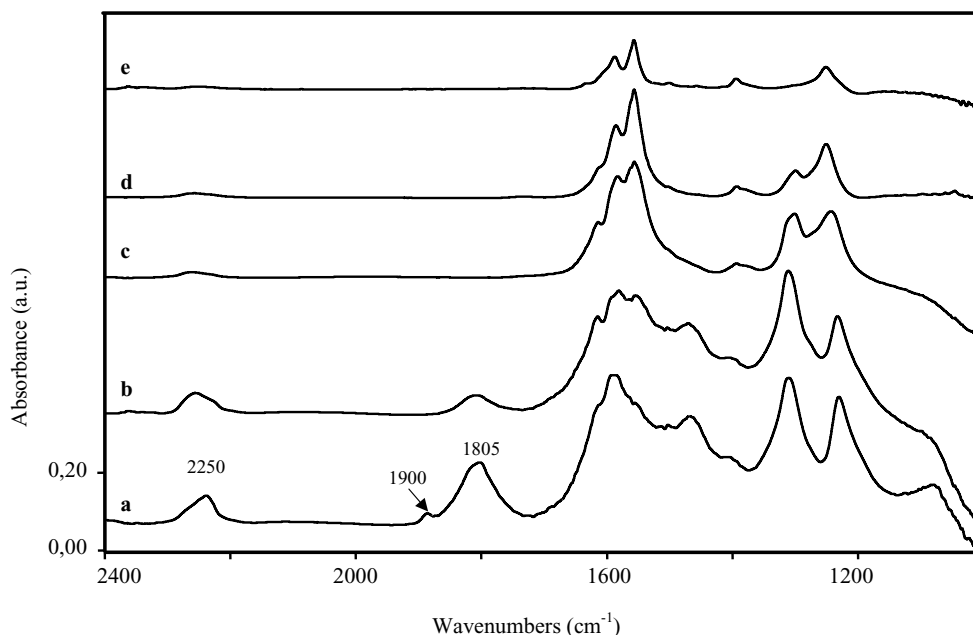
Fig. 1. FT-IR spectra of adsorbed species on Fe_2O_3/Al_2O_3 after contact with (a) NO (1330 Pa) and outgassing at (b) RT, (c) at 423 K, (d) 523 K and (e) 623 K.

absorption near $1900 \, cm^{-1}$, that completely disappear by outgassing, are observed. The position of the stronger band is shifted to lower frequencies as compared to that of NO gas ($1876 \, cm^{-1}$). This red shift of the NO stretching band of adsorbed nitrogen monoxide has been frequently observed [28] and characterises terminal surface nitrosyl species, probably bent, where the π-type backbonding from the d-orbitals of the adsorbing Fe^{2+} cation (partially filled) toward the π^* antibonding orbitals of NO predominates. On the contrary the frequency of weaker band can be due to NO weakly interacting with the surface, probably through a hydrogen bond with the alumina surface.

A weak couple of bands is also observed near $2250 \, cm^{-1}$. This couple of bands, that disappears by outgassing at increasing temperature, as previously discussed [29], can be assigned to *N*-bonded and *O*-bonded species of adsorbed N_2O either formed on the surface from NO or present as an impurity in the gas.

In the spectral region below $1800 \, cm^{-1}$ the complex absorption in the $1620–1450 \, cm^{-1}$ and $1300–1150 \, cm^{-1}$, thermally more stable (Fig. 1b and c), are due mainly to different forms of bridged nitrates although presence of adsorbed NO_2 cannot be excluded. These species should be produced by NO oxidation. The assignment is not straightforward. On alumina these bands has been assigned [27,29] to the partially superimposed asymmetric and symmetric stretching modes of chelating NO_2^- nitrito ions. However, alternative assignments to species formed by NO reduction like hyponitrite species (as in *cis*-$K_2N_2O_2$, $1304 \, cm^{-1}$ [30]) are more likely [29]. The formation of reduced species like hyponitrite ions is needed to justify the formation of NO_2 or nitrate on the surface of alumina, considered not reducible.

As reported by Kapteijn et al., for Mn/Al_2O_3 catalysts [31], NO disproportionation reaction can occur, for example, by the following hypotetical one: $3NO + O^{2-} = NO_2 + N_2O_2^{2-}$. These species are certainly formed also in the absence of Fe. However we cannot exclude the formation of a dinitrosyl species ON–Fe–NO that could transform into $N_2O_2^{2-}$ hyponitrite ion.

3.2. Adsorption of ammonia

The spectra of the adsorbed species arising from NH_3 adsorption over the Fe_2O_3/Al_2O_3 catalyst pre-activated by outgassing at 623 K are very complex and reflect the chemistry of the ammonia–alumina interactions, as reported by several authors [31–33] and agree to recent literature data [34].

In Fig. 2a the spectrum after contact at RT is reported. Bands can be found due to co-ordinate ammonia species (asymmetric deformation at $1624 \, cm^{-1}$, symmetric deformation in the region $1250–1120 \, cm^{-1}$) and to ammonium ions (shoulder at $1650 \, cm^{-1}$ and band at $1480 \, cm^{-1}$, symmetric and asymmetric deformation respectively), whereas further weak bands at 1910 and $1390 \, cm^{-1}$ can be observed. According to the sensitivity of the position of the $\delta_{sym}NH_3$ mode to the Lewis acid strength of the adsorbing cation [33,35] this spectrum can be interpreted as an evidence of the presence of cationic sites characterised by quite a strong Lewis strength, as predominant adsorbing sites.

The spectral feature significantly change by outgassing already at 423 K (Fig. 2, spectra b and c) showing a strong decrease of the intensity of the bands due to the co-ordinate ammonia and ammonium ions and the growing of new bands near $1550 \, cm^{-1}$ and in the region $1400–1350 \, cm^{-1}$. A
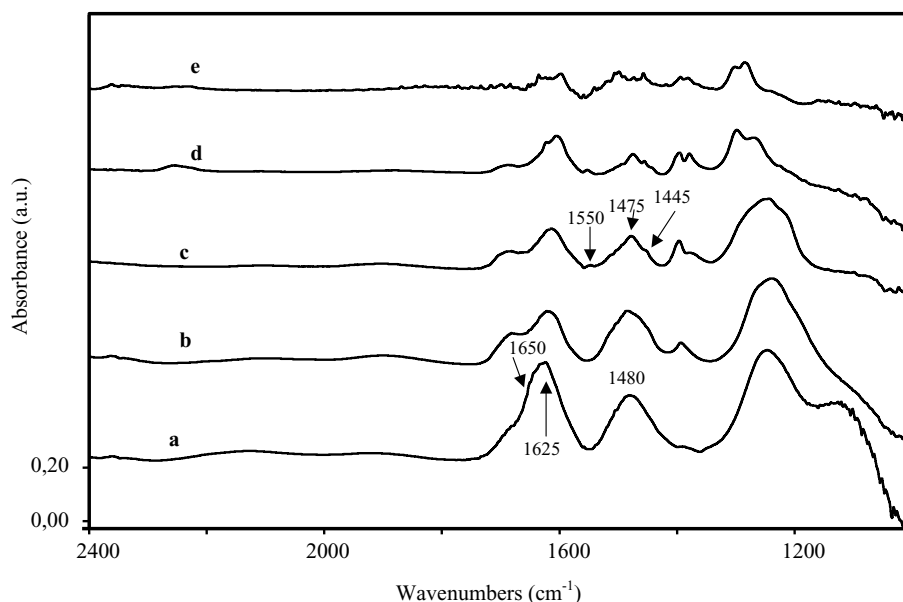
Fig. 2. FT-IR spectra of adsorbed species on Fe_2O_3/Al_2O_3 after contact with (a) ammonia (6650 Pa), and outgassing at (b) RT, (c) at 423 K, (d) 523 K and (e) 623 K.

similar behaviour was previously reported after ammonia adsorption over alumina-supported catalysts and on the support alone [34]. Although they fall in the region typical for the asymmetric deformation of ammonium cations, $\delta_{as}NH_4^+$, these band cannot be assigned to this mode because of its sharpness, that fully contrasts the typical width of the $\delta_{as}NH_4^+$ mode. Moreover, similar results have already been observed by some of us after ammonia adsorption over other surfaces, such as CrO_x/TiO_2 and MnO_x/TiO_2 [36] and CuO/TiO_2, $MgO\text{-}Fe_2O_3$ and $\gamma\text{-}Fe_2O_3$ [8], which are able to perform more or less selectively ammonia oxidation. However, a very weak band near $1550\,cm^{-1}$ has been observed after ammonia adsorption over other SCR catalysts. In particular an absorption at similar frequencies of an intermediate species was previously detected over vanadium-based model SCR catalyst after contact with ammonia and assigned to NH_2 amide species [25].

Evacuation at 523 K (Fig. 2d) causes a further decrease of the intensities of the adsorbed ammonia. Main absorption now appear at 1605, 1475, 1395, 1375, 1298 and $1270\,cm^{-1}$.

The bands at 1445 and $1475\,cm^{-1}$ apparently correspond to two different species, the one at $1445\,cm^{-1}$, is formed first but disappears only later. The band $1475\,cm^{-1}$ is formed and disappears quickly as well, due to a surface species intermediate with respect to the formation of other gas-phase species. The other bands will be discussed below in the following section.

Outgassing at increasing temperature causes the disappearance of all absorptions, although a very small bands can be detected near $1300\,cm^{-1}$.

Finally the band at $1910\,cm^{-1}$, as previously discussed, can be assigned to weakly bonded NO, indicating that a part of ammonia has been oxidised.

3.3. Adsorption of hydrazine

The spectra of the adsorbed species arising due to the contact of the surface of the catalyst with hydrazine vapour at RT and outgassing at increasing temperatures are shown in Fig. 3.

In the presence of hydrazine and water vapour (Fig. 3a) a strong absorption at $1645\,cm^{-1}$ (with a shoulder at lower frequency) and weaker broad bands near $1470\,cm^{-1}$ and near $1150\,cm^{-1}$ (broad) are detected. The spectrum observed is thus dominated by the features of hydrazinium ion, where the broad absorption at $1645\,cm^{-1}$ with shoulder near $1550\,cm^{-1}$ are due to $\delta_{as}NH_3$ and $\delta_{sym}NH_3$ of the $-NH_3^+$ group.

Evacuation at RT (Fig. 3b) and at increasing temperature causes relevant changes in the spectrum: (1) the intensities of the pair of bands assigned to hydrazinium ion strongly decrease; (2) a new weak band appears at $1230\,cm^{-1}$ while the band at $1175\,cm^{-1}$ first strongly increases in intensity and later decreases with respect to the component at $1230\,cm^{-1}$; and (3) other weak bands appear near 1475 (with shoulder at lower frequency), 1395 and $1375\,cm^{-1}$.

For liquid hydrazine and for metal–hydrazine complexes six infrared bands are observed in the $1800\text{--}1000\,cm^{-1}$ region [37,38]. These bands correspond to most of the bands we observe. In particular, the quite strong bands at $1605\,cm^{-1}$, with shoulder at lower frequency, (symmetric and asymmetric δNH_2 "scissoring" modes) and at 1230 and $1175\,cm^{-1}$ (N–N stretching and NH_2 rocking, respectively) likely belong to co-ordinated hydrazine species [38].

The spectra recorded after evacuation of adsorbed hydrazine at 423 K and increasing temperatures (Fig. 3, spectra c–e) show a very strong similarity with those observed
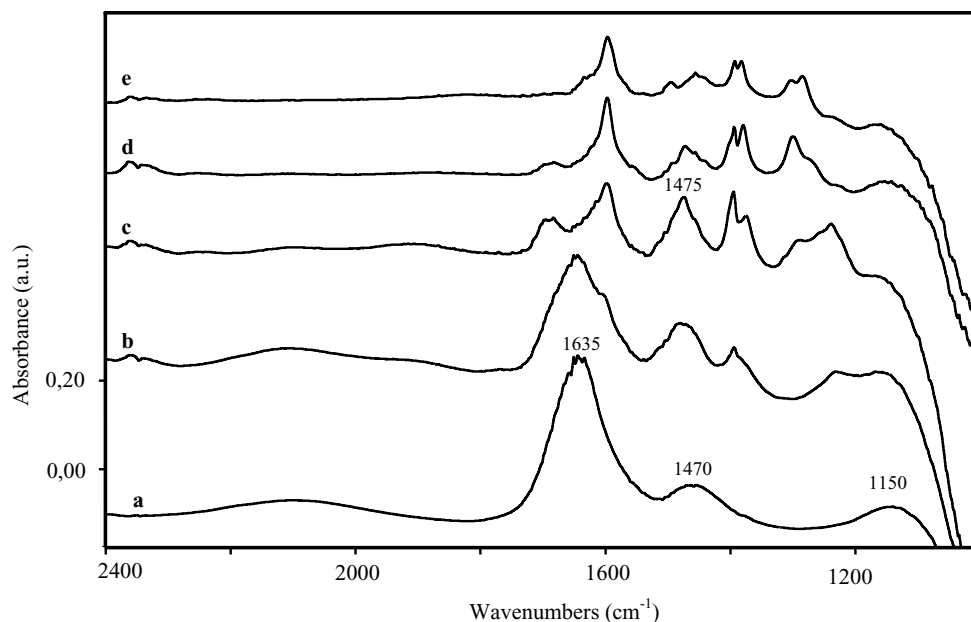
Fig. 3. FT-IR spectra of adsorbed species on Fe_2O_3/Al_2O_3 after contact with (a) hydrazine vapour and outgassing at (b) RT, (c) at 423 K, (d) 523 K and (e) 623 K.

after ammonia adsorption and transformation over the catalyst surface by heating at the same temperature. This suggests that actually adsorbed hydrazine can be also formed by adsorbed ammonia on the surface. Furthermore, the two weak bands observed at 1475 and 1445 cm^{-1} after both ammonia and hydrazine adsorption and heating, do arise neither from ammonia, nor from hydrazine adsorbed as such, and are certainly due to two different species because they behave independently from other.

3.4. Adsorption of hydroxylamine

The spectra of the adsorbed species arising after contact of the surface of the catalyst with hydroxylamine vapour at RT and outgassing at increasing temperatures are shown in Fig. 4. The strong band centred near 1645 cm^{-1} and the weaker band at 1150 cm^{-1} according to the lack of detection of OH absorption mode of molecular water, can be assigned to the NH_2 scissoring and wagging modes of
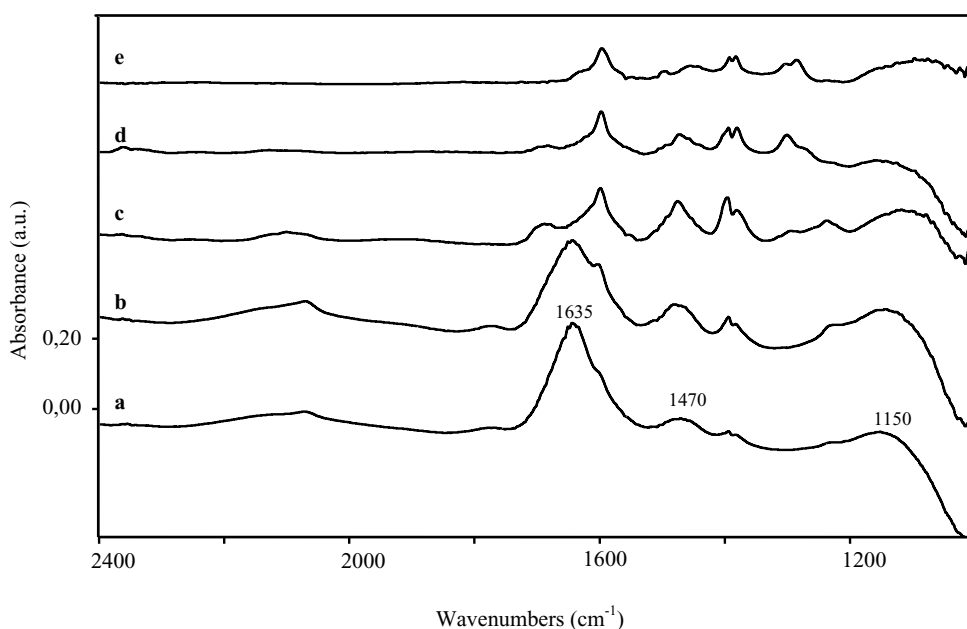

Fig. 4. FT-IR spectra of adsorbed species on Fe_2O_3/Al_2O_3 after contact with (a) hydroxylamine vapour (665 Pa) and outgassing at (b) RT, (c) at 423 K, (d) at 523 K and (e) at 623 K.

NH$_2$–O- species (a dissociated form of hydroxylamine) rather than to H$_2$O deformation. In fact, hydroxylamine is a weak acid ($K_a = 6.6 \times 10^{-9}$) and can dissociate easily on oxide surfaces. These bands nearly correspond to those observed for gaseous hydroxylamine and its liquid *O*-alkyl derivatives [39,40]. Together with these bands, a very weak band is also observed at 1770 cm^{-1}, resisting outgassing at RT and disappearing after outgassing above 423 K (Fig. 4, spectrum c). This band can be due to surface nitrosyl species and provides evidence for the easy conversion of hydroxylamine into NO. A weak feature near 1470 cm^{-1} is also observable, supporting the assignment of the band, observed at the same position from ammonia and hydrazine but after treatment at higher temperatures, to nitroxyl species HNO. Evacuation at increasing temperature also causes a lowering of the intensities and a slight shift of the frequencies of the bands of adsorbed hydroxylamine, evidencing bands, near 1500, 1450, 1365 and 1230 cm^{-1}, these bands certainly not belonging to hydroxylamine-like adsorbed species. Most of these bands are likely due to highly oxidised species like nitrates or nitrites.

4. Further discussion and conclusions

The experiments described above help us to propose a quite comprehensive picture of the adsorption behaviour of N-containing species on Fe$_2$O$_3$/Al$_2$O$_3$ SCR-type model catalysts. It is evident that ammonia coordinatively adsorbs as such on Lewis acid sites and is protonated on Brønsted sites present over the surface. The spectra clearly show the formation of at least two other species arising from ammonia after heating above 423 K, characterised by bands at 1475 and 1445 cm^{-1}. These bands are also formed from hydrazine, whose spectrum is almost superimposed to that of adsorbed ammonia. Features of the spectra suggest actually that hydrazine is formed from adsorbed ammonia above 523 K and that it can later evolve to molecular nitrogen (undetectable by IR), as discussed previously [13,36].

The study described above allowed us also to characterise adsorbed dissociated hydroxylamine-type species whose structure should be similar to that proposed by Bosch and Janssen [41] as intermediates from ammonia adsorption. Actually, the spectroscopic features of adsorbed hydroxylamine species are hardly distinguishable from adsorbed ammonia, so that we could not exclude their formation from ammonia. On the other hand, our data provide evidence for the very easy evolution of hydroxylamine-type species to NO, occurring already at RT over the present catalyst. However, the detection of NO from ammonia in our conditions is observed so, on contrary to that discussed by us for Fe$_2$O$_3$/TiO$_2$, in this case we cannot suggests that hydroxylamine-type species do not actually form in substantial amounts NH$_3$.

The data presented here suggest that ammonia adsorbed species can give rise selectively to nitrogen through a previous formation of hydrazine, which is formally the dimeric form of amide species whose formation from ammonia is quite substantiated from previous work of this laboratory [8,36]. In fact, hydrazine and ammonia appear to behave similarly, and hydrazine is easily oxidised to nitrogen by any oxidant [42].

However, hydroxylamine type species NH$_2$–O- are very likely intermediates for the production of NO from ammonia. They form from ammonia at relatively low temperature and can convert easily to NO. This could explain why NO is formed at low temperature. The formation of a weak band at 1475 cm^{-1} assigned to HNO species, can provide evidence for the formation of N–O bonds from ammonia. The formation of these species at relatively low temperature with respect to Fe$_2$O$_3$/TiO$_2$ can be related to the lower selectivity to nitrogen in SCR reaction with ammonia of Fe$_2$O$_3$/Al$_2$O$_3$.

On the contrary this catalytic system can be more promising in SCR with hydrocarbon, where a fundamental role is played by activation of NO in form of nitrite or nitrate ions over the surface. Interaction of NO with alumina is very complex and gives a number of different transformation species. Surface nitrosyl species, probably bent, and NO weakly interacting with the surface, probably through a hydrogen bond with the surface OH's are observed. N-bonded and O-bonded species of adsorbed N$_2$O either formed on the surface from NO or present as an impurity in the gas are present at low temperature. Finally, the complex absorption in the 1620–1450 cm^{-1} and 1300–1150 cm^{-1}, thermally more stable and produced by NO oxidation, are due mainly to different forms of bridged nitrates and of species formed by NO reduction like hyponitrite species, although presence of adsorbed NO$_2$ cannot be excluded.

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