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IR spectroscopic study of NO_x adsorption and NO_x–O_2 coadsorption on Co^{2+}/SiO_2 catalysts

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Adsorption of nitrogen oxides (NO, NO_2) and their coadsorption with oxygen on Co^{2+}/SiO_2 samples has been investigated by IR spectroscopy with a view to elucidating the mechanism of selective catalytic reduction (SCR) of NO_x with hydrocarbons. A Co^{2+}/SiO_2 sample synthesized by ion exchange is characterized by a highly dispersed cobalt and a very weak surface acidity: CO is adsorbed only at low temperature (100 K) forming Co^{2+}—CO carbonyls [$\nu(CO) = 2180$ cm^{-1}]. Adsorption of NO on Co^{2+}/SiO_2 leads to the formation of $Co^{2+}(NO)_2$ dinitrosyl complexes (1872 and 1804 cm^{-1}) which are decomposed upon evacuation. Adsorption of NO_2, as well as coadsorption of NO and O_2, produce NO_2 species weakly bound to the support (a band at 1681 cm^{-1}) and N_2O_4 (a band at 1744 cm^{-1} with a shoulder at 1710 cm^{-1}), the latter being adsorbed reversibly on both the support and the Co^{2+} ions. In the second case N_2O_4 is transformed into surface monodentate nitrates of Co^{2+} (a band at 1550–1526 cm^{-1}) and partly into bridged nitrates (a band at *ca.* 1640 cm^{-1}). The monodentate nitrates are stable with respect to evacuation up to 125 °C and act as strong oxidising agents: they are reduced by NO, even at room temperature, and by methane at 100 °C. In the latter case, organic nitro-compounds and isocyanate groups are registered as reaction products (probably intermediate compounds in SCR). The surface species obtained after NO and NO_2 adsorption on Co^{2+}/SiO_2 prepared from cobalt acetate (active SCR catalyst) are essentially the same as those observed with the ion-exchanged sample. No monodentate nitrates, however, are formed during NO_2 adsorption on a Co^{2+}/SiO_2 sample synthesized by impregnation with cobalt nitrate, which accounts for the lack of activity of this sample in the SCR.

1 Introduction

SCR is one of the most attractive possibilities for environmental protection from nitrogen oxides. The process has found industrial application with immobile NO_x sources, ammonia being used as a reducing agent.[1,2] However, a new technology has been discovered[3,4] and developed:[5–33] selective catalytic reduction of NO_x with hydrocarbons (HC-SCR). This process is very promising because it may be applied to motor vehicles and may permit the replacement of ammonia in immobile NO_x sources by hydrocarbons.

A characteristic feature of SCR is that it proceeds in the presence of oxygen. Under anaerobic conditions the catalyst activity is either low[4,5] or the nitrogen oxide is reduced to ammonia.[6] It is assumed that the role of oxygen is to keep the surface clean[5,7] and oxidized[6,8] and to convert NO to reactive surface compounds such as NO_2,[8,9] nitrites[10,12] or nitrates.[10,12,13]

Regardless of the fact that the key characteristics of HC-SCR are already known, there are still a number of problems that need elucidation. Thus, according to Delahay *et al.*[14] and Lentmaier *et al.*[15] the activity of the catalysts correlates with their Lewis acidity. Hadjiivanov *et al.*,[13] however, have established that Cu-ZSM-5 is characterized by a negligible surface acidity and suppose that this favours desorption of the SCR reaction products. Armor[16] has paid attention to the low acidity of Ga-containing catalysts. The mechanism of HC-SCR is also debatable. Some authors[5] are of the opinion that the process is based on NO decomposition to nitrogen and oxygen. The absence of correlation between the activities of the different catalysts in the SCR reactions and the NO decomposition is one of the main reasons for rejecting this mechanism. According to other concepts,[17,18] the formation of carbonaceous surface deposits or partially oxidized hydrocarbon derivatives interacting with NO is of special importance. However, these hypotheses contradict the zero order of HC-SCR with respect to NO and the high order of the reaction towards hydrocarbons.[9] Now, the opinion that oxidized NO ad-species are the active oxidizers in HC-SCR is gaining popularity.[8,10–13,19] This indicates that knowledge of the nature of surface compounds appearing on the catalysts during NO_2 adsorption and NO–O_2 coadsorption is of special importance for establishing the mechanism of the process. Unfortunately, investigations of the adsorption species of NO_2 are very restricted in number[13,17,20,34–38] and only a few studies consider surface compounds formed during NO–O_2 coadsorption.[12,13,20–22,29] However, in these cases the interpretations of the different authors are quite contradictory, as is typical of each new field of science. Thus, a band at 2133 cm^{-1} has been ascribed by different authors to NO_2,[20,39] $NO_2^{\delta+}$,[40,41] or NO_2^+.[18,37] Many authors[10–12,18,20,22,39,41,42] attribute bands stable towards evacuation in the region 1620–1550 cm^{-1} to nitrite complexes, while others[13,17,21,34–36,38,43–45] have noted that nitrites, as a rule, absorb at lower frequencies, and the bands observed should belong to surface nitrates.

An important stage in the development of SCR is the discovery of Armor *et al.*[23] that NO_x reduction on Co-ZSM-5 can be performed with methane. More recently, it was established that cobalt deposited on other supports,[20,24] as well as catalysts containing another active phase (*e.g.* Rh^+, Ni^{2+}, Mn^{2+} and Ga^{3+}, but not Cu^{2+} ions) are also active in this reaction.[5,16,25] Then the question arises: why is methane an effective reducing agent with some catalysts but feeble with others? According to Beutel *et al.*,[41] surface nitrites (IR band *ca.* 1526 cm^{-1}) appearing on Co-ZSM-5 and not on Cu-ZSM-5 are responsible for the oxidation of methane. Another interesting question associated with cobalt catalysts is the effect of the support on their activity. Armor *et al.*[25] reported that oxide-supported cobalt is not efficient in SCR with CH_4. Other investigations[26,27] have shown that both Al_2O_3 and SiO_2 can be successfully used as cobalt supports in SCR of

NO_x with C_3 hydrocarbons, but, unfortunately, the reduction with methane has not been studied. Inaba *et al.*[27] have found that the activity of CoO/SiO_2 catalysts in SCR with propene depends strongly on the method of preparation. Thus, they established that catalysts, prepared by impregnation with cobalt acetate, showed a good activity, whereas a sample prepared using cobalt nitrate was completely inactive. These authors concluded that highly dispersed cobalt ions are the active sites of the reaction. A similar conclusion has been arrived at by Hamada *et al.*[26] in studies of HC-SCR on CoO/Al_2O_3.

In this paper, an attempt was made to elucidate the effect of cobalt dispersion on the interaction of NO_x, O_2 and methane over silica-supported cobalt. We studied the adsorption of nitrogen oxides and their coadsorption with oxygen on a Co^{2+}/SiO_2 ion-exchanged catalyst with a high cobalt dispersion, and determined the stability of the observed adsorption species and their reactivity with respect to some reaction products (water), possible intermediates (CO) and the reagents of HC-SCR (NO, O_2, CH_4). Methane was chosen as a reducing agent because of the absence of data on its behaviour in SCR on Co^{2+}/SiO_2 catalysts. Some experiments were also carried out with two impregnated Co^{2+}/SiO_2 samples prepared, one from acetate (showing a good SCR activity), and the other from nitrate (totally inactive in SCR) using, in both cases, the procedure described by Inaba *et al.*[27]

2 Experimental

2.1 Sample preparation

Commercially available SiO_2 (aerosil) with a specific surface area of 336 m^2 g^{-1} was used as a support. A Co^{2+}/SiO_2 sample (denoted further on as Co_{ie}/SiO_2) was synthesized by ion exchange from a 0.75 M Co^{3+} solution. The latter was prepared by adding ammonia to a $Co(NO_3)_2 \cdot 6H_2O$ solution so as to achieve a final total ammonia concentration of 12.5 wt.%. During this reaction, the Co^{2+} ions were oxidized to Co^{3+}.[46] To increase the amount of reaction, 30% H_2O_2 [*ca.* 12 ml (g Co)$^{-1}$] was also added. Silica was dispersed in the Co^{3+} solution [0.2 (g SiO_2) ml^{-1}] and the mixture was stirred for 1 h. To ensure equilibrium with the initial cobalt concentration, the suspension was filtered and the precipitate was treated in a similar way. After a further 1 h the solid phase was filtered, abundantly washed with water and dried in air at 120 °C. The cobalt content in the sample was, according to chemical analysis data, 1.01 wt.%.

Two other Co^{2+}/SiO_2 samples were prepared, as described elsewhere,[27] by incipient wetness impregnation of silica: one with $Co(NO_3)_2$ and the other with $Co(CH_3CO_2)_2$. Both samples contained, nominally, 5 wt.% cobalt. These samples will be denoted as Co_{nitr}/SiO_2 and Co_{ac}/SiO_2, respectively.

2.2 Gases and reagents

AR oxygen (99.6, Merck), carbon monoxide (99.5, Merck) and methane (99.995, Messer, Griesheim) were additionally purified prior to adsorption by passing through a liquid-nitrogen trap. AR nitrogen oxide (99.0, Merck) was purified by fractional distillation. Nitrogen dioxide was synthesized by thermal decomposition of $AgNO_2$ as described earlier.[35] It was purified by addition of oxygen, its excess being evacuated after 24 h, while the NO_2 was frozen.

2.3 Methods

IR spectroscopy studies were carried out with a Specord M-80 apparatus at a spectral resolution of 1 cm^{-1}. Self-supporting pellets were prepared from the samples and heated directly in an IR cell. The latter was connected with a vacuum–adsorption apparatus with a residual pressure of 10^{-5} Torr. Before the adsorption measurements the pellets were activated by calcination for 1 h at 400 °C and evacuation for 1 h at the same temperature. Low-temperature CO adsorption was carried out in a specially constructed cell equipped with a dosing cock, allowing the introduction of definite adsorbate portions to the sample.

The specific surface area was measured by low-temperature nitrogen adsorption according to the conventional BET method.

Chemical analysis was performed by flame atomic absorption spectrophotometry using a PYE-UNICAM SP-1950 apparatus.

3 Results

The Co_{ie}/SiO_2 sample was investigated in detail, whereas the silica support and the impregnated catalysts were studied for comparison purposes.

3.1 SiO_2

3.1.1 Background spectrum and hydroxy group coverage. The IR spectrum of the activated SiO_2 support exhibits three broad bands within the 2000–1600 cm^{-1} region. According to data from the literature[6,13] they characterize overtones of lattice vibrations (1990 and 1626 cm^{-1}) and a combination frequency (1872 cm^{-1}). Self absorption determines the so-called 'cut-off' of the sample at *ca.* 1350 cm^{-1}: below this frequency the sample is opaque and no spectra of surface compounds can be detected. In the region of the OH-stretching modes there is a narrow band with a maximum at 3740 cm^{-1} which characterizes terminal groups of the Si—OH type.[47]

3.1.2 Adsorption of CO, NO and H_2O. Owing to the lack of Lewis acidity on silica,[48] CO is not adsorbed on the SiO_2 sample. Accordingly, adsorption of NO does not lead to formation of surface nitrosyl complexes. This is in agreement with the results of Ghiotti *et al.*[47] who have reported that NO is adsorbed on aerosil only at low temperatures. Under 5 Torr water vapour, the spectrum of SiO_2 exhibits an intense band at 1626 cm^{-1}, due to $\delta(H_2O)$ vibrations of molecularly adsorbed water. However, 10 min evacuation leads to the complete disappearance of this band and restoration of the initial spectrum.

3.1.3 Adsorption of NO_2. The admission of NO_2 (16 Torr) to an activated SiO_2 sample produces two main bands with maxima at 1686 and 1745 cm^{-1} (Fig. 1). Both bands decrease in intensity with the equilibrium pressure and disappear after evacuation. Note that the band at 1686 cm^{-1} is less sensitive to the pressure changes, *i.e.* it characterizes a more stable surface species. Subsequent NO_2 adsorption (16 Torr) causes the appearance of a spectrum almost identical with Fig. 1(a), *i.e.* the surface has not been modified by the adsorption–desorption of NO_2.

The band at 1745 cm^{-1} can be attributed to weakly adsorbed N_2O_4.[13,18,39,40,42] This molecule has antisymmetric NO stretching modes with two components: an intense in-phase band at 1758 cm^{-1} and a low-intensity band at 1709 cm^{-1} which corresponds to out-of-phase vibrations.[49] Indeed, our spectra also show a shoulder at *ca.* 1715 cm^{-1}. Li *et al.*[20] have assigned the pair of bands at 1751 and 1705 cm^{-1} to covalent N_2O_5. However, we think that this interpretation is not quite reliable because the bands at 1744 and 1710 cm^{-1} appear in an atmosphere of NO_2 (which is easily dimerized) and disappear almost completely after evacuation.

The band at 1686 cm^{-1} also characterizes a reversibly bound surface species and it seems logical to assign it to

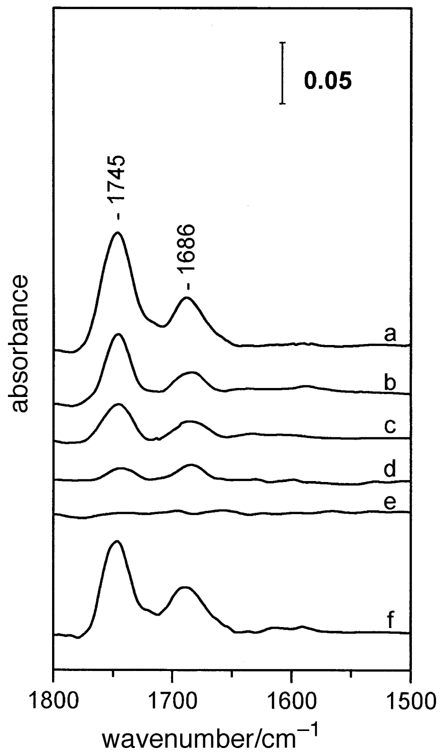


Fig. 1 IR spectra of NO_2 adsorbed on a SiO_2 support. Equilibrium pressure of 16 (a), 9 (b), 5 (c) and 3 (d) Torr NO_2, after evacuation (e) and after subsequent introduction of 16 Torr NO_2 (f).

adsorbed NO_2. The NO_2 vibrations in the gas phase are found at somewhat lower frequencies (1624 cm^{-1}).[50] It is known that NO_2 is characterized by the presence of a free electron situated on an antibonding orbit.[49] For that reason, ionization of the molecule leads to an increase in the N—O bond order and, as a result, to a rise in the ν_3 frequency up to 2392–2360 cm^{-1}. Similarly to the case of CO,[48] coordination of NO_2 accompanied by partial electron transfer would enhance the absorption frequency. Indeed, NO_2 adsorption on acid hydroxy groups of zeolites (showing an IR band at 3615 cm^{-1}) produces a surface compound which has been assigned by a number of authors to $NO_2^{\delta+}$,[40,41] or NO_2^{+},[18,37] and is characterized by a band at 2133 cm^{-1}. On the basis of the above analysis we have assigned the band at 1686 cm^{-1} to NO_2 adsorbed with partial charge transfer and probably with the participation of Si—OH groups.

3.2 Co_{ie}/SiO_2

3.2.1 Background spectrum and hydroxy group coverage. The activated Co_{ie}/SiO_2 sample is pale blue in colour and its IR spectrum scarcely differs from that of the support. This indicates that the terminal silanol groups have not participated in the ion exchange with the cobalt ions. Probably the active sites of the process are hydrogen-bonded hydroxy groups, which are desorbed under the conditions of sample activation.

3.2.2 CO adsorption. CO is one of the most used probe molecules for precise determination of the Lewis acidity.[48] Adsorption of CO (equilibrium pressure 32 Torr) at room temperature on an activated Co_{ie}/SiO_2 sample does not lead to new bands in the IR spectrum. This indicates that the cobalt ions are either not on the surface or are characterized by a very weak electrophilicity and form no complexes with CO at room temperature. In the latter case they may be Co^{2+} or Co^{3+} ions[51,52] because the Co^{+} and $Co^{\delta+}$ ions form stable carbonyls.[53] In order to establish whether, on the sample surface, there are cobalt ions, we studied low-temperature CO adsorption. It is known that at low temperatures very weak Lewis acid sites can be monitored by CO.[54] The introduction of a portion of CO (2 μmol), at *ca.* 100 K, to the pellet leads to the appearance in the IR spectrum of a symmetric band with a maximum at 2180 cm^{-1} (Fig. 2) which characterizes Co^{2+}—CO complexes.[53,55] The high frequency and low stability of the complexes indicate that, in this case, the character of the cobalt–carbon bond is mainly σ and/or electrostatic. The introduction of a second CO portion only enhances the band intensity without causing a frequency shift. After the third CO portion this band does not change, *i.e.* the adsorption sites have practically all been occupied. With increase in the amount of CO introduced into the cell, the spectrum also displays a shoulder with a maximum at 2156 cm^{-1} which, according to data from the literature,[54] is due to CO H-bonded to hydroxy groups. Gradual heating of the sample to room temperature results, initially, in the disappearance of the band of hydrogen-bound CO and then the band at 2180 cm^{-1} decreases in intensity, to disappear completely at room temperature. Here again no dependence of ν(CO) on coverage is observed, *i.e.* the band maximum remains unchanged at 2180 cm^{-1}. This implies absence of interaction between the adsorbed CO molecules and is evidence that the Co^{2+} sites are isolated. Thus, the CO adsorption experiments show unambiguously that, on the sample surface, (i) there are isolated Co^{2+} ions with a very weak electrophility and (ii) there are neither cobalt ions in a lower oxidation state nor metal cobalt.

3.2.3 Adsorption of NO. During NO adsorption (10 Torr), a pair of bands with maxima at 1884 and 1802 cm^{-1} appear in the IR spectrum of the Co_{ie}/SiO_2 sample (Fig. 3). According to data from the literature[18,20,22,38,40,42,44,47,48,54] these bands are due to the asymmetric and symmetric NO vibrations of dinitrosyl complexes of the type $Co^{2+}(NO)_2$. The decrease in the equilibrium pressure of NO is accompanied by a simultaneous drop in the bands' intensity, which does not

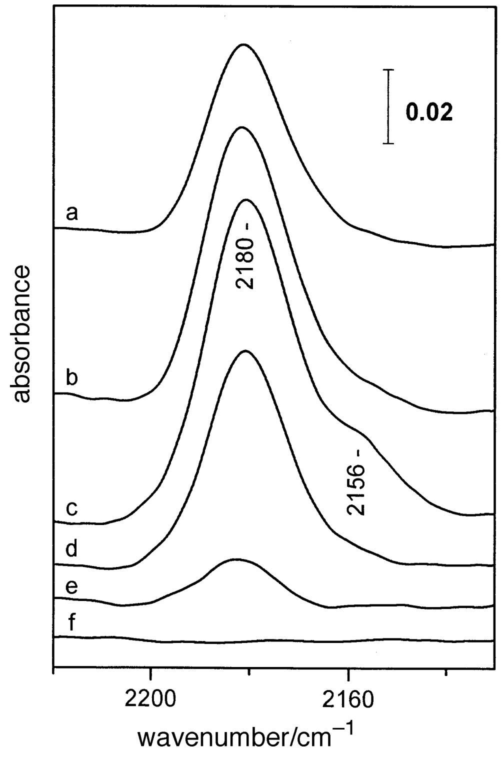


Fig. 2 IR spectra of CO adsorbed on Co_{ie}/SiO_2. Introduction of 2 (a), 4 (b), and 14 (c) μmol of CO at 100 K and time evolution of the spectrum during temperature increase (d)–(f).

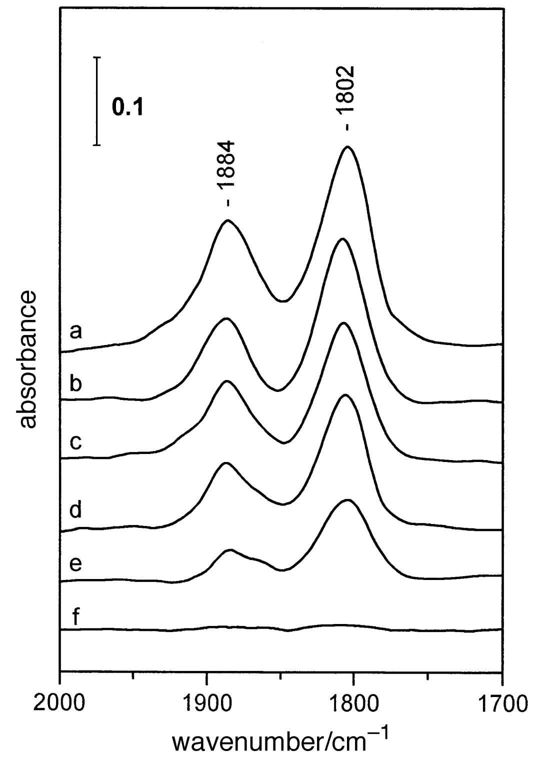


Fig. 3 IR spectra of NO adsorbed on Co_{ie}/SiO_2. Equilibrium pressure of 20 (a), 10 (b), 5 (c), 2.5 (d) and 1 (e) Torr of NO and after a brief evacuation (f).

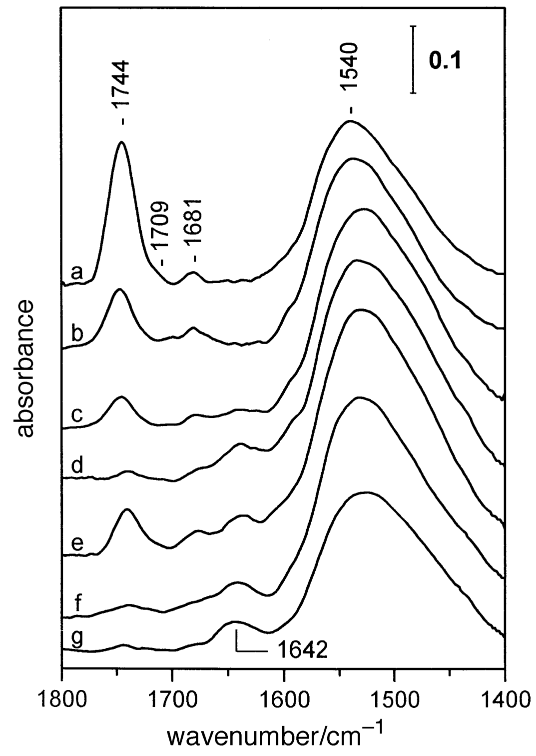


Fig. 4 IR spectra of NO_2 adsorbed on Co_{ie}/SiO_2. Equilibrium pressure of 16 (a), 9 (b), 5 (c) and 3 (d) Torr NO_2, increase in pressure to 16 Torr NO_2 (e) and after evacuation (f). Spectrum (g) is taken after subsequent introduction of 30 Torr NO into the IR cell.

affect the positions of the maxima. Both bands disappear after evacuation, which evidences the low stability of the dinitrosyls. A very weak feature at *ca.* 1865 cm^{-1} is visible at low equilibrium pressures, which might be attributed tentatively to the absorption of Co^{2+} mononitrosyls. This interpretation is in agreement with the weak electrophility of Co^{2+}, on our sample, which presupposes weak interaction with NO and the frequency of the nitrosyls formed being close to that of gaseous NO. Peculiarities of NO adsorption on our sample are the relatively low absorption frequencies and the low stability of the dinitrosyls. For the sake of comparison one may use the results of Li and Armor[20] who have established that dinitrosyls on Co-ferrierite (bands at 1900 and 1815 cm^{-1}) are stable, even after evacuation at 300 °C.

3.2.4 Adsorption of NO_2. Adsorption of NO_2 (equilibrium pressure 16 Torr) on the Co_{ie}/SiO_2 sample (Fig. 4) is accompanied by formation of the adsorption species characteristic of the SiO_2 support: the bands at 1744 cm^{-1} (with a shoulder at *ca.* 1710 cm^{-1}) and 1681 cm^{-1} have already been interpreted as being due to adsorbed N_2O_4 and NO_2. However, the band at 1744 cm^{-1} has a much stronger intensity than the analogous band observed on SiO_2 (note the different scales of Fig. 1 and 4), which indicates that, in addition to the support, part of the N_2O_4 occupies Co^{2+} ions. Moreover, the spectrum also contains an intense band with a maximum at 1540 cm^{-1}, which obviously characterizes compounds formed with the participation of cobalt ions. This band is attributed to monodentate nitrates. Additional support of this interpretation will be proposed in the Discussion section. It is worth noting that, after NO_2 adsorption, the sample acquires a purple nuance which may indicate either change in the coordination state of Co^{2+} ions or their oxidation to Co^{3+}.

The decrease in the NO_2 equilibrium pressure causes a drop in intensity of the bands at 1744 and 1681 cm^{-1}, while the 1540 cm^{-1} band intensity grows. In order to establish whether the development of this band is associated with a decrease in the NO_2 equilibrium pressure or is, rather, due to kinetic effects, NO_2 (16 Torr) was again admitted to the cell. As a result, the 1540 cm^{-1} band intensity exhibited a small additional increase, whereas the bands at 1744 and 1709 cm^{-1} displayed a much weaker intensity than those in the initial spectrum Fig. 4(a) and should perhaps correspond to N_2O_4 adsorbed on the support.

After a 10 min evacuation, the band at 1540 cm^{-1} is observed together with a low-intensity band at *ca.* 1640 cm^{-1}. The latter also characterizes an activated adsorption form and appears only after prolonged contact of the sample with NO_2. We assume this band to be due to bridged nitrates. The results obtained evidence that N_2O_4 adsorbed on Co^{2+} ions from the Co_{ie}/SiO_2 surface is transformed, with time, into new activated adsorption species which are stable with respect to evacuation at room temperature.

3.2.5 Coadsorption of NO and O_2. To elucidate the mechanism of SCR, it is important to study the surface compounds resulting from coadsorption of NO and O_2. From a thermodynamic viewpoint, NO is unstable in the presence of oxygen and should be completely converted into NO_2.[8] Since the oxidation of nitrogen oxide is a three-molecule reaction ($2NO + O_2$), this process is slow, especially at low NO concentrations.

The addition of 3 Torr oxygen to Co_{ie}/SiO_2 preliminary situated in an atmosphere of 20 Torr NO leads to the almost complete disappearance of the bands at 1884 and 1802 cm^{-1} characterizing $Co^{2+}(NO)_2$ dinitrosyls (Fig. 5). Simultaneously, a broad band with a maximum at 1550 cm^{-1} becomes visible. The admission of an additional amount of oxygen (32 Torr) to the sample leads to a *ca.* twofold increase in intensity of the band at 1550 cm^{-1} and a shift of its maximum to 1536 cm^{-1}. In addition, an intense band at 1744 cm^{-1}, due to adsorbed N_2O_4, appears, as well as a weak band with a maximum at 1640 cm^{-1}, which has already been associated with bridged nitrates. The 1744 cm^{-1} band intensity decreases a little with a concomitant slight increase in intensity of the 1536 cm^{-1}

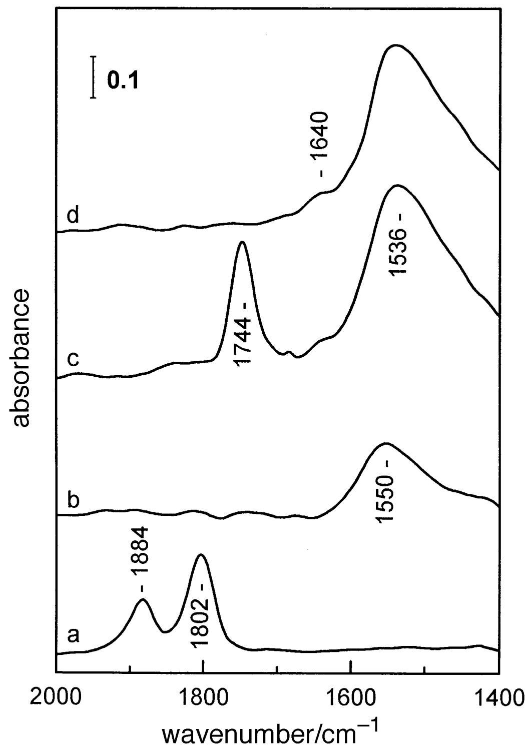


Fig. 5 IR spectra of NO (20 Torr) adsorbed on Co_{ie}/SiO_2 (a), after introduction of 3 (b) and 32 (c) Torr of O_2 into the IR cell and after evacuation (d)

band. After evacuation, the band at 1744 cm^{-1} disappears, while the remaining two bands do not change, *i.e.* the stable surface compounds being formed during NO–O_2 coadsorption are the same as those observed after adsorption of NO_2. It is interesting that blocking of the NO adsorption sites occurs on attaining about half of the maximum concentration of the surface nitrates, characterized by a band at 1550–36 cm^{-1}.

3.2.6 Coadsorption of NO_2 and O_2. In order to check possible formation of additional surface compounds in a strongly oxidizing medium, we have also studied the coadsorption of NO_2 and O_2 on the sample. The results do not differ from those on NO_2 adsorption.

3.3 Reactivity of the surface nitrates on Co_{ie}/SiO_2 (band at *ca.* 1540 cm^{-1})

The surface nitrates needed for the experiments have been obtained after coadsorption of NO and O_2 or adsorption of NO_2 on the Co_{ie}/SiO_2 sample, followed by evacuation.

3.3.1 Thermal stability. Evacuation at 100 or 125 °C induces no changes in the band at 1540 cm^{-1}. After a 10 min evacuation at 150 °C, however, the band decreases *ca.* twofold in intensity and disappears completely after evacuation at 200 °C, *i.e.* the monodentate nitrates are decomposed completely at this temperature.

3.3.2 Interaction with oxygen. Admission of oxygen (10 Torr) to a sample with preadsorbed surface nitrates leads to no changes in the spectrum. Changes have not been observed, either, after heating the sample at 100 °C under oxygen. The intensity of the nitrate bands, however, decreases after heating at 150 °C in an O_2 atmosphere, which is probably due to their partial decomposition. Bands characterizing new surface compounds have not been detected.

3.3.3 Interaction with NO. The interaction of the surface nitrates with NO is presented in Fig. 4(g). Admission of 30 Torr NO to a sample with preadsorbed nitrates leads to a significant decrease in intensity of the 1540 cm^{-1} band and to a shift of its maximum to 1526 cm^{-1}. No other surface compounds (in particular dinitrosyls) are formed. These results confirm that only part of the nitrates suffice to block NO adsorption on cobalt ions.

3.3.4 Interaction with methane. The interaction of the surface nitrates with methane is of great interest because CH_4 is a selective reducing agent of nitrogen oxides over zeolite supported Co catalysts. Interaction with methane (10 Torr) for 30 min at 100 °C with a sample containing preadsorbed nitrates leads to a drastic intensity drop of the band at 1535 cm^{-1} (Fig. 6). In addition, a series of new bands emerge. A weak band at 1625 cm^{-1} characterizes $\delta(H_2O)$ vibrations and evidences the presence of adsorbed water, obviously formed as a result of methane oxidation. A band at 1558 cm^{-1} can, on the basis of data from the literature,[12,17,33] be attributed to organic nitro-compounds. A weak and broad band with a maximum at 2207 cm^{-1}, assigned to surface isocyanates,[30,31,56] is detected in the higher-frequency region. These isocyanates are coordinated to cobalt ions, since isocyanates on silica manifest a band at considerably higher frequencies, namely at 2300 cm^{-1}.[56]

Since the surface nitrates are thermally stable at 125 °C, the results obtained show clearly that even at 100 °C, these compounds are reduced by methane. Both organic nitro-species and isocyanates are intermediates in this reaction.

3.3.5 Interaction with water. As water is an important SCR product, we have studied its effect on the surface nitrates. The admission of water vapour (5 Torr) to the Co_{ie}/SiO_2 sample causes the appearance of an intense band at 1626 cm^{-1} evidencing the presence of adsorbed water on the support, and possibly on the cobalt ions (Fig. 7). Moreover, the nitrate

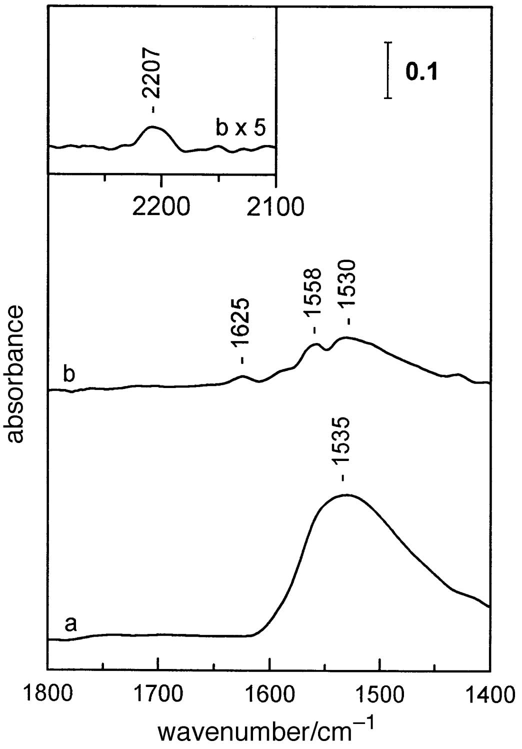


Fig. 6 IR spectra of surface species obtained after adsorption of NO_2 (15 min, 16 Torr, followed by evacuation) on Co_{ie}/SiO_2 sample (a) and after interaction with CH_4 (10 Torr) at 100 °C for 10 min (b)

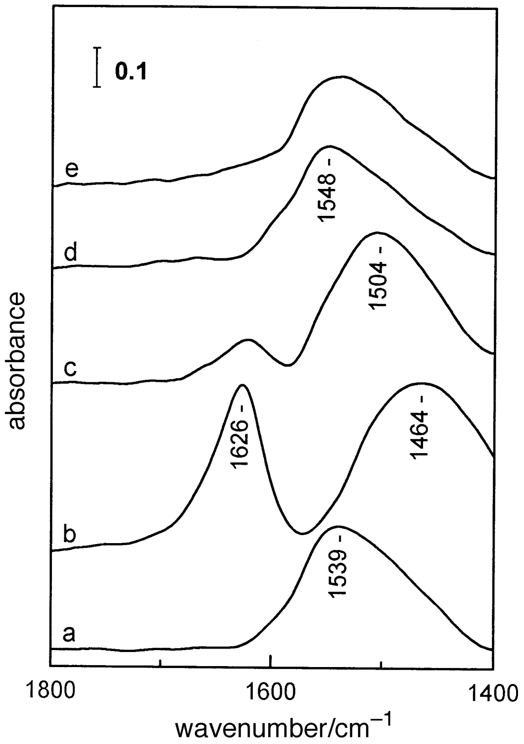


Fig. 7 IR spectra obtained after coadsorption of NO (15 Torr) and O_2 (5 Torr) on Co_{ie}/SiO_2 followed by evacuation (a), introduction of 5 Torr of water vapour (b), evacuation at room temperature (c) and at 100 °C (d) and after interaction with CO (10 Torr) at 100 °C for 10 min (e)

band at 1539 cm^{-1} is shifted to 1464 cm^{-1}. Evacuation of the sample at room temperature leads to a pronounced drop in the 1626 cm^{-1} band intensity (due to water desorption from the support) and a back shift of the band from 1464 to 1504 cm^{-1}. After evacuation at 100 °C, the band at 1626 cm^{-1} vanishes (due to water desorption from cobalt sites) and the initial spectrum is almost restored. The maximum of the nitrate band is at 1548 cm^{-1} and the intensity is slightly lower. These results show that the nitrates are, in general, stable under water vapour but adsorbed H_2O molecules strongly affect the position of their IR band. This observation is of importance for the identification of the monodentate nitrates in a humid atmosphere.

3.3.6 Interaction with CO. In order to check the oxidation properties of surface nitrates, we also studied their interaction with CO. It is known that CO is not a selective reducing agent in HC-SCR but probably belongs to the intermediate compounds of the reaction.[6,13] Carbon monoxide coming into contact with a sample having preadsorbed nitrates causes no changes in its IR spectrum. After 10 min heating at 100 °C (Fig. 7) the intensity of the band at 1548 cm^{-1} decreases slightly, which is an indication of interaction of a small fraction of the nitrates with CO.

3.4 Co_{nitr}/SiO_2: adsorption of NO_x

After activation, the colour of the Co_{nitr}/SiO_2 sample turns black, which suggests the formation of a separate cobalt oxide phase. NO adsorption leads to the appearance of a very weak band at 1802 cm^{-1} due to the ν_s(NO) of Co^{2+} dinitrosyls. The respective ν_{as}(NO) mode was not detected because of its low intensity and overlap with one of the silica background bands. The low intensity of the dinitrosyl bands evidences the poor cobalt dispersion on the sample.

Adsorption of NO_2 (16 Torr equilibrium pressure) on Co_{nitr}/SiO_2 leads to the formation of the already observed reversibly bound species, namely N_2O_4 (1744 and 1710 cm^{-1}) and NO_2 (1680 cm^{-1}). The strongly adsorbed compounds, however, differ totally from those observed with the Co_{ie}/SiO_2 sample: two bands with maxima at 1597 and 1380 cm^{-1} are visible after evacuation (Fig. 8). The band at 1380 cm^{-1} is typical of symmetric nitrates, whereas the band at 1597 cm^{-1} may be due either to water produced by replacement of surface Co—OH groups by nitrate anions, or to some kind of bidentate nitrates. A very broad feature in the 1550–1450 cm^{-1} region might evidence a negligible amount of monodentate nitrates on the sample surface. These results clearly demonstrate that no monodentate nitrates are characteristic of the surface of the Co_{nitr}/SiO_2 sample, *i.e.* the latter can be formed on highly dispersed Co^{2+} ions only.

3.5 Co_{ac}/SiO_2: adsorption of NO_x

After calcination, the sample colour turns from pink to blue, definitely deeper in colour than Co_{ie}/SiO_2. This colour is also preserved after activation. NO adsorption on Co_{ac}/SiO_2 leads to formation of the same nitrosyls observed with Co_{ie}/SiO_2, the respective bands having a higher intensity.

The spectra registered after NO_2 (16 Torr) adsorption on Co_{ac}/SiO_2 are very similar to those observed with the Co_{ie}/SiO_2 sample (see Fig. 8). The only differences are that (i) the bands due to surface nitrates (1526 cm^{-1}) and NO_2 (1676 cm^{-1}) are more intense with Co_{ac}/SiO_2, whereas (ii) bridged nitrates (1640 cm^{-1}) are not detected with this sample and (iii) the N_2O_4 band (1745 cm^{-1}) is almost absent from the spectrum. This is associated with the small free surface area of the silica support, resulting from the high cobalt concentration. This observation supports the previously made assumption that all of the N_2O_4 molecules adsorbed on dispersed cobalt ions are converted into monodentate nitrates.

The results obtained demonstrate that the Co_{nitr}/SiO_2 sample is characterized by a surface chemistry very different from that of the Co_{ac}/SiO_2 and Co_{ie}/SiO_2 samples.

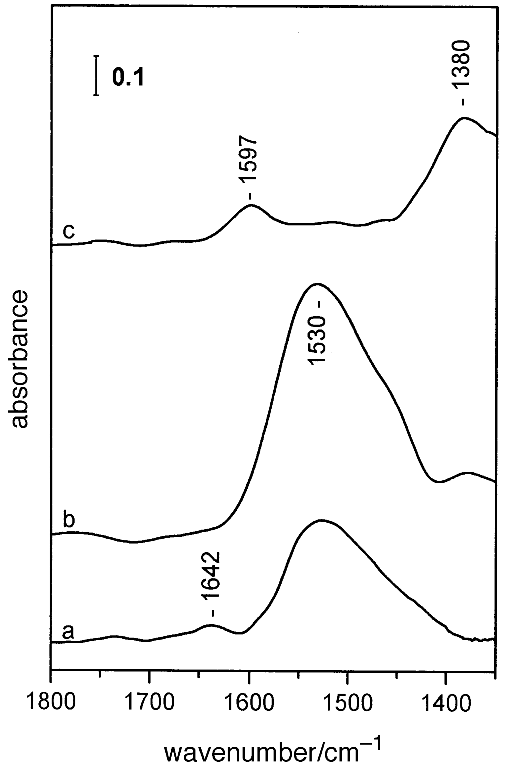


Fig. 8 IR spectra of the species obtained after NO_2 adsorption (16 Torr, 2 h, followed by evacuation) on Co_{ie}/SiO_2 (a), Co_{ac}/SiO_2 (b) and Co_{nitr}/SiO_2 (c)

Discussion

The compounds formed on our Co_{ie}/SiO_2 sample after NO_x adsorption are either reversibly or irreversibly adsorbed. The first type of species are dinitrosyls, appearing during NO adsorption, and weakly bound NO_2 and N_2O_4, observed in a NO_2 atmosphere. The dinitrosyls are directly coordinated to Co^{2+} ions. In the presence of oxygen these species are easily converted into surface cobalt nitrates. Note that NO_2 is adsorbed on the support alone because its adsorption is not suppressed by the formation of nitrates. Part of the N_2O_4, however, is located on the support, and the other part on the cobalt ions. Evidently, the NO stretchings of this molecule are not sensitive enough to be used for distinguishing between the adsorption sites. When adsorbed on the cobalt ions, N_2O_4 is transformed into surface nitrates.

The strongly adsorbed species are characterized by absorption bands at 1640 and 1540 cm^{-1}. Both types of compound are stable during evacuation and represent activated surface species formed with the participation of cobalt ions. Later, we shall concentrate on strongly bound NO_x adsorption forms.

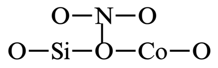
On the basis of the absorption frequency, the band at 1640 cm^{-1} might characterize NO_2 strongly bound to a cobalt ion. However, the band develops slowly, whereas $(NO_2)_{ads.}$ cannot be an activated adsorption species. Bands at *ca.* 1600 cm^{-1}, appearing after NO_2 adsorption on oxide surfaces, may also be due to water formed as a result of replacement of surface OH groups by nitrates.[35,36] This interpretation is not very probable in our case for two reasons: (i) water adsorbed on our sample manifests a band at 1626 cm^{-1} and (ii) the presence of adsorbed water should cause a significant shift of the band at 1540 cm^{-1} to lower frequencies, which is, in fact not observed.

Another peculiarity of the band at 1640 cm^{-1} is its low intensity, in spite of the sample treatment, which indicates that the formation of the corresponding surface compounds is limited by the sample structure. Taking into account the stability of the adsorption species and the high absorption frequency, we assign this band to bridged nitrates.[34–36,38] Indeed, pairs of cobalt ions have a very low concentration on our sample surface because the cobalt on it is highly dispersed. The lack of bridged nitrates on the surfaces of the NO_2-precovered Co_{ac}/SiO_2 and Co_{nitr}/SiO_2 samples confirms that the formation of such complexes requires a specific arrangement of the Co^{2+} ions.

The main type of activated compounds obtained during both NO_2 adsorption and NO–O_2 coadsorption on our Co_{ie}/SiO_2 and Co_{ac}/SiO_2 catalysts (characterized by dispersed cobalt) manifest a band at 1550–1526 cm^{-1}. Obviously, these species are formed with the participation of cobalt ions, since they are not found on the pure support. Consider now the basis of interpretation of the band at 1550–1526 cm^{-1}. Adelman *et al.*[10] have reported a similar band (1526 cm^{-1}) after coadsorption of NO and O_2 on a Co-ZSM-5 catalyst and ascribed it to surface nitrite compounds. Note that this interpretation is only based on the relatively low absorption frequency. However, inorganic nitro and nitrito compounds have much lower frequences.[44,49,50] The free nitrate ion is characterized by ν_3 at 1380 cm^{-1}, this vibration being split with decreasing symmetry lowering the symmetry.[50] Thus, bridged and bidentate nitrates are characterized by bands at 1650–1550 and 1300–1170 cm^{-1} while the monodentate nitrates have frequencies at 1530–1480 and 1290–1250 cm^{-1}.[57] Unfortunately, the lower frequency is within the range of the support's own absorbance and cannot be detected in our case. However, a number of authors have reported bands at *ca.* 1550 cm^{-1} together with bands at *ca.* 1250 cm^{-1}, after NO_2 adsorption on oxides, and have assigned them to surface nitrates.[13,18,34–36,38,40,45] In our case, this interpretation is strongly supported by the interaction of the surface compounds with NO. The nitrogen oxide might be oxidized by nitrates but not by nitrites since the formal oxidation number of nitrogen in NO and NO_2^- is 2 and 3, respectively.

An interesting peculiarity of the monodentate nitrates is the ability for two such anions to be bound to one cobalt cation. The formation of the second nitrate anion, however, is more difficult. During coadsorption of NO and O_2 (a substoichiometric amount), $Co(NO_3)_1$ surface nitrates are formed quickly. They are characterized by a relatively high absorption frequency (1550 cm^{-1}). In the presence of excess oxygen or during NO_2 adsorption, N_2O_4 is formed and slowly transformed into a second nitrate ion bound to the cobalt, the final compound being $Co(NO_3)_2$. In this case both nitrate ions manifest one band at lower frequencies: 1540–1526 cm^{-1}.

Additional information on the nitrate structures may be obtained from the results on their interaction with water. In principle, water adsorption would weaken the bonding of the nitrate ion with the surface. As a result, the absorption frequency of the nitrates would decrease. It has been established that water adsorbed on cobalt ions leads to a red shift of the nitrate ion band by *ca.* 35 cm^{-1}, this shift increasing by an additional 40 cm^{-1} in the presence of water adsorbed on the support. These results support the idea that the nitrates are bonded not only to cobalt but also to silicon ions:



$$\begin{array}{c} O{-}N{-}O \\ | \\ O{-}Si{-}O{-}Co{-}O \end{array}$$

Coordination of an NO_3^- anion to a cationic surface site requires either a simultaneous bonding of a positively charged particle in the vicinity (to prevent the zero charge), or oxidation of the cation. Since no other species have been formed simultaneously with the nitrates, it seems reasonable to propose that Co^{2+} ions are oxidized to Co^{3+} during NO_x adsorption:

$$Co^{2+}(NO)_2 + O_2 \rightarrow Co^{3+}{-}NO_3^- + NO \qquad (1)$$

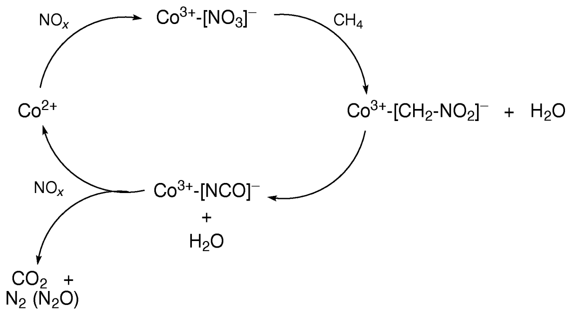
or

$$Co^{2+}{-}N_2O_4 \rightarrow Co^{3+}{-}NO_3^- + NO \qquad (2)$$

This supposition is supported by the colour change of the sample and the fact that Co^{2+} ions can be easily oxidized.

The results obtained show a significant difference in the mechanism of NO_x adsorption on cobalt and copper containing systems. Coadsorption of NO and O_2 on Cu-ZSM-5 leads to the successive formation of adsorbed N_2O_3, N_2O_4 and NO_3^-,[13] *i.e.* the nitrates are formed as a result of disproportionation of N_2O_4 adsorbed on Cu^{2+} ions. The quick formation of nitrates on Co^{2+}/SiO_2 is probably a result of the dimeric adsorption form of NO, in contrast to the monomeric adsorption form of NO on the Cu^{2+} ions from Cu-ZSM-5. The presence of $Co^{2+}(NO)_2$ compounds leads evidently to the instant formation of adsorbed N_2O_4 which, according to reaction (2), is rapidly converted into $Co(NO_3)_1$ species.

The monodentate nitrates are very strong oxidising agents. They are reduced by NO but are obviously in equilibrium with the gas mixture: in the presence of oxygen the equilibrium is shifted towards formation of surface nitrates. We are of the opinion that the results on the interaction of the monodentate nitrates with methane are important. This interaction proceeds even at 100 °C and two types of compounds, probably intermediate in HC-SCR, have been observed: organic nitro-compounds and isocyanates. Tanaka *et al.*[33] have also observed organic nitro-species as SCR intermediates. According to them, these compounds are converted to N_2 after oxidation by NO_x. Ukisu *et al.*[32] reported that isocyanates are formed at higher temperatures than organic nitro-compounds, which suggests that the latter species are converted into isocyanates. Thus, the following simplified scheme of the process can be proposed:



In the above scheme only the steps derived from our results are shown. To establish other intermediate states, *e.g.* to clarify how NCO^- is coupled with NO_x to evolve nitrogen, additional experiments are necessary.

Our results also explain the strong effect of the preparation method on the SCR activity of the supported cobalt catalyst. The idea that highly dispersed cobalt ions are responsible for the SCR proceeding, suggested by other authors,[27] has been confirmed by our experiments. Indeed, on the Co_{ac}/SiO_2 sample (characterized by highly dispersed cobalt and reported to be an SCR-active catalyst) we have observed, after NO_x adsorption, formation of monodentate nitrates. The latter species easily react with methane. Similar compounds have been reported by Adelman *et al.*[10] for Co-ZSM-5, which is a classic catalyst for CH_4-SCR and is, in principle, also characterized by dispersed cobalt ions. On the contrary, no monodentate nitrates have been detected on the surface of the Co_{nitr}/SiO_2 sample (exhibiting no SCR activity) where the cobalt is poorly dispersed. This accounts for the different SCR activity of oxide-supported cobalt catalysts, reported by different authors.[25,27]

Finally, our results suggest that (i) Co_{ac}/SiO_2 could be an efficient catalyst for selective reduction of NO_x, not only by higher hydrocarbons but also by methane, and (ii) Co_{ie}/SiO_2, prepared by ion exchange, could also be a good catalyst for this reaction.

5 Conclusions

The Co^{2+}/SiO_2 catalyst obtained by ion exchange (Co_{ie}/SiO_2) is characterized by the presence of isolated Co^{2+} ions which have a very low surface acidity: they form carbonyl complexes at a low temperature [$\nu(CO) = 2180\ cm^{-1}$].

Adsorption of NO on Co_{ie}/SiO_2 results in the formation of $Co^{2+}(NO)_2$ dinitrosyl complexes (1872 and 1804 cm^{-1}) which are decomposed after evacuation at room temperature.

Adsorption of NO_2 on Co_{ie}/SiO_2 (as well as coadsorption of NO_2 and O_2) leads to formation of NO_2 species located on the support (a band at 1681 cm^{-1}) as well as N_2O_4 species (bands at 1744 and 1710 cm^{-1}) on both the support and the Co^{2+} ions. In the second case, N_2O_4 is slowly transformed into monodentate (1540 cm^{-1}) and bidentate (1640 cm^{-1}) Co^{2+} surface nitrates.

Coadsorption of NO and O_2 on Co_{ie}/SiO_2 produces mainly monodentate and some bridged cobalt nitrates.

One surface Co^{2+} ion from Co_{ie}/SiO_2 can be bonded to two monodentate nitrate anions. The latter are stable during evacuation up to 150 °C. Under water vapour, the band at 1540 cm^{-1}, characteristic of monodentate nitrates, is shifted to 1464 cm^{-1} but returns to its initial position after evacuation at 100 °C.

The monodentate cobalt nitrates are supposed to be key species in the HC-SCR of NO_x. They are reduced at 100 °C with methane. Organic nitro-compounds and isocyanates are detected as intermediate products.

The surface chemistry of a Co^{2+}/SiO_2 sample prepared by acetate impregnation (active SCR catalyst) is quite similar to that of Co_{ie}/SiO_2 : surface monodentate nitrates are the principal irreversibly bound compounds formed upon NO_x adsorption. On the contrary, adsorption of NO_2 on Co^{2+}/SiO_2 prepared from nitrates (non-active SCR catalyst) leads to the formation of strongly bound symmetric (1380 cm^{-1}) and bidentate (1597 cm^{-1}) nitrates. No monodentate nitrates are formed on this sample. It is proposed that the ability of supported cobalt catalysts to form monodentate nitrates, favoured by a high cobalt dispersion, would determine their activity in the HC-SCR.

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