In situ DRIFTS study of NO reduction with CH_4 over PtCo-ferrierite catalysts

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The effect of platinum incorporated into Co-ferrierite catalyst on the selective catalytic reduction of NO_x with CH_4 was studied by means of *in situ* DRIFTS technique. NO adsorption on Co- and PtCo-ferrierite catalysts gave dinitrosyl and mononitrosyl species on Co^{2+} ions. The adsorption of $NO + O_2$ on Co-ferrierite yielded NO_2 ($NO_2^{\delta+}$) species and also nitrites and nitrates. Similar species were observed on PtCo-ferrierite, although chemisorbed NO_2 was much more stable since it persisted at reaction temperatures as high as 723 K. The spectra of the pre-reduced bimetallic PtCo-ferrierite catalyst exposed to the $CH_4 + NO + O_2$ reaction mixture showed bands at 2200–2100 cm^{-1}, which were similar to results for a Pt-free sample but slightly more intense. In addition, strong bands of nitrate, almost unchanged with temperature, were observed. A very stable Co^{2+}–NO_2 intermediate species was developed upon incorporation of Pt into the base Co-ferrierite catalyst.

Keywords: emission control, nitrogen oxides, selective catalytic reduction, methane, DRIFTS, PtCo-ferrierite

1. Introduction

The selective catalytic reduction (SCR) of NO_x by CH_4 on Co-loaded zeolites offers a promising alternative to ammonia-based technology for the removal of NO from exhaust gases since CH_4 is easier to handle and may also be present in the exhaust stream. The same applies for car engines in which the catalyst facilitates the development of lean-burn technology that could reduce fuel consumption to a significant extent. It is known that the reaction rate between NO and CH_4 increases strongly in the presence of O_2 [1–3]. Li and Armor were the first to report the exceptional ability of Co-zeolites to selectively reduce NO by CH_4 [1,2]. Since then, many works have aimed at increasing the resistance of these catalysts to deactivation in the presence of steam. Bimetallic catalysts have been proposed to solve the problems caused by water vapour [4]. In this sense, Ogura and Kikuchi [5] found that the incorporation of noble metals (Pt, Ir, and Rh) to In/H-ZSM5 zeolite enhances NO conversion in SCR with CH_4 under wet conditions. The same finding was reported by Gutierrez et al. [6] using PtCo-mordenite catalysts. Differences in activity have been ascribed to cation coordination and relative diffusivity in the zeolite channels, and it has been proposed that a certain type of zeolite would be required to position the cobalt cations providing a suitable electronic environment to carry out the selective reduction of NO with CH_4.

NO_2 formation is thought to be a necessary step for NO reduction and O_2 is required to develop this NO_2 species activating CH_4 [7]. Thus, NO and NO_2 adsorptions with CH_4, in the presence and absence of O_2, have been analyzed in detail by IR spectroscopy [1,7–9]. In a previous work, the promoter effect of platinum in a bimetallic PtCo-ferrierite catalyst during the reduction of NO with CH_4 under net oxidant conditions was observed [10]. Accordingly, this work was undertaken with the aim of uncovering the nature of surface species present on the surface of both monometallic Co-ferrierite and bimetallic PtCo-ferrierite catalysts. To this end, *in situ* DRIFTS experiments were carried out to identify the stationary species on the catalyst surface under oxidant conditions ($NO + O_2$ and $CH_4 + NO + O_2$) and to shed some light on the mechanism that results in N_2 production.

2. Experimental

2.1. Catalyst preparation

Powdered K-ferrierite $[(Na,K)_{3.7}(AlO_2)_{3.7}(SiO_2)_{32.3}]$ was used as the zeolite support. Monometallic Co-ferrierite was prepared by ion exchange using a dilute solution of 0.025 M $Co(NO_3)_2$. The zeolite was suspended in the solution (zeolite/solution ratio of 2 g/l) under vigorous stirring for 24 h at room temperature, keeping pH close to 5.5 throughout the exchange. Then, the liquid was decanted, and the solid was washed and dried in an oven at 393 K for 12 h. The dried sample was calcined in O_2 at 2 K/min up to 673 K for 2 h. Monometallic Pt-ferrierite was prepared by adding 2 g of the zeolite to 0.3 l of a $Pt(NH_3)_4(NO_3)_2$ aqueous solution of an appropriate concentration. Bimetallic PtCo catalysts were prepared from the monometallic Pt-ferrierite by a second exchange with a Co^{2+} solution, following the same

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procedure described above for Co-ferrierite. The experimental conditions of the exchange and drying steps were the same as above. Mono- and bimetallic samples containing platinum were calcined in O_2 at a rate of 0.5 K/min up to 623 K, keeping this temperature for 2 h. Metal loading, as determined by inductively coupled plasma spectrometry, was 1.6% Co for Co-ferrierite, and 1.4% Co and 0.47% Pt, respectively, for bimetallic PtCo-ferrierite.

2.2. DRIFT spectroscopy

Diffuse-reflectance infrared spectra were collected on a Nicolet-510 FTIR spectrophotometer working at a resolution of 4 cm^{-1} using a Harrick HVC-DRP environmentally-controlled cell. About 30 mg of the powdered sample was packed in a sample holder and pretreated *in situ* in the DRIFTS cell under a flow of He. Temperature was increased at a rate of 10 K/min up to 723 K and then maintained for 1 h. The sample was subsequently cooled to room temperature prior to exposure to the reactant mixture. The IR single-beam background spectrum of the pretreated ferrierite was recorded at a given temperature, and then subtracted from the single-beam spectrum of the sample in order to obtain the net IR spectrum. IR spectra were collected at each temperature by increasing the cell temperature and holding it at the desired temperature while collecting 256 scans.

3. Results and discussion

3.1. DRIFT spectroscopy (NO adsorption)

Figure 1 shows the IR spectra of NO adsorption on calcined (A) and H_2-reduced (B) Co-ferrierite at 673 K, exposed to a flow of 900 ppm NO/Ar in the 298–723 K temperature range. All the spectra were collected at the corresponding temperatures when constant peak intensity had been reached. Additionally, NO adsorbed on the K-ferrierite support was recorded as a reference. Three absorption bands were observed upon NO adsorption at room temperature: 1898 and 1813 cm^{-1}, which can be assigned to the symmetric and asymmetric stretching modes of a dinitrosyl adsorbed on Co^{2+} [7,11–13], and at 1940 cm^{-1}, which can be attributed to the stretching of a mononitrosyl, also adsorbed on Co^{2+} zeolites [7,11,12]. These two species were rather stable since no changes in peak intensities were observed upon purging the sample in a He flow for 1 h. Further insight into the thermal stability of nitrosyl species was obtained upon heating the sample under a NO/Ar flow. A slight shift of the bands toward lower wavenumbers, suggesting a weakening of the bond, was observed upon increasing temperature. In general, band intensities decrease with increasing temperature but this decrease depends on the nature of surface species. Thus, while the band of mononitrosyl species almost disappeared at 573 K, the most intense band of the dinitrosyl species was only removed upon heating at temperatures above 723 K.

The IR spectra of NO adsorbed on bimetallic calcined (A) and H_2-reduced (B) (623 K) PtCo-ferrierite catalysts in the temperature range from 298 to 723 K are shown in figure 2. The bimetallic catalyst exhibited the same three bands (1940, 1898, and 1813 cm^{-1}) responsible for the same species as for the Co-ferrierite sample. However, slight differences in stability were observed after platinum incorporation on the base Co-ferrierite catalyst. The mononitrosyl species were weaker, and even more so in the H_2-reduced samples (figure 2(B)). In contrast, the dinitrosyl species appeared to be more stable in the calcined than

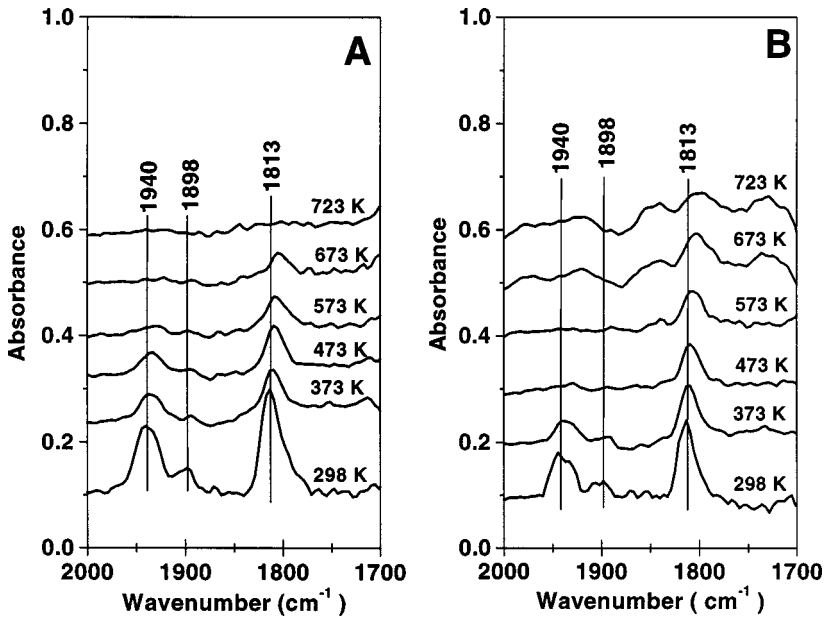

Figure 1. DRIFT spectra of Co-ferrierite calcined (A) and reduced (B) at 673 K in a flow of H_2. Both samples were pretreated in He at 723 K for 1 h and then exposed to a flow of NO/Ar mixture in the 298–723 K temperature range.

in the reduced bimetallic catalyst, alhtough they became weaker upon reduction in hydrogen. From these results it can be inferred that a certain interaction between both metals (Co and Pt) occurs in both the calcined and reduced state of the catalyst.

3.2. DRIFT spectroscopy in the $NO + O_2$ reaction mixture (NO oxidation)

Calcined (A) and H_2-reduced (B) Co-ferrierite samples were exposed to a flow of 900 ppm NO/Ar and 2% O_2 and the spectra were then recorded at each temperature upon 15 min on-stream stabilization. The spectra of samples exposed to the $NO + O_2$ mixture are shown in figure 3. A strong band at 2180 cm^{-1} can be observed, which splits into several overlapping bands (2270, 2199, 2170, and 2140 cm^{-1}) at increasing reaction temperatures. The same bands as those observed with NO alone were visible in the region from 2000 to 1700 cm^{-1}, although the dinitrosyl species became more vulnerable to oxygen than mononitrosyl species. The intensity of these bands decreased with increasing temperature, whereas the band at 1544 cm^{-1} followed the opposite trend. A negative band centred at

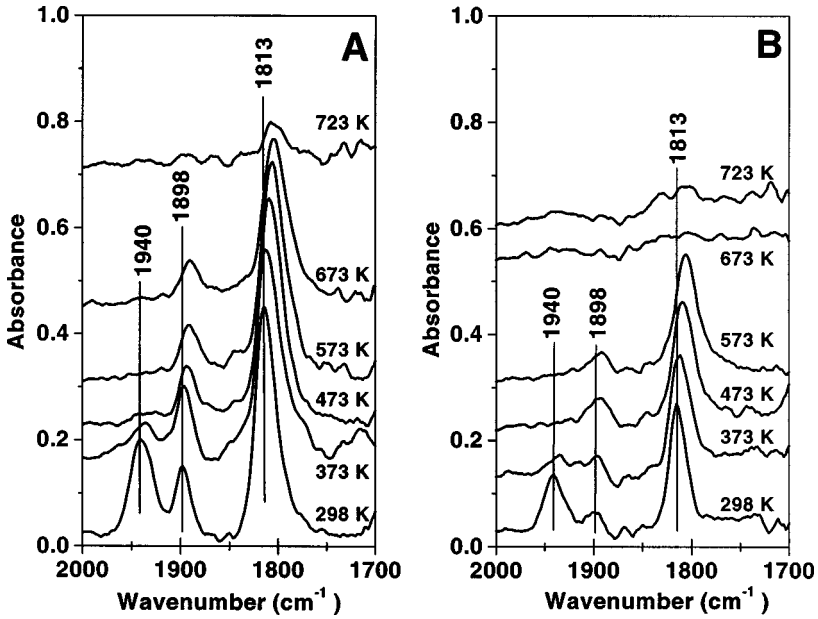

Figure 2. DRIFT spectra of PtCo-ferrierite calcined (A) and reduced (B) at 623 K in a flow of H_2, followed by purging in He at 723 K for 1 h, and then exposure to a NO/Ar mixture in the 298–723 K temperature range.

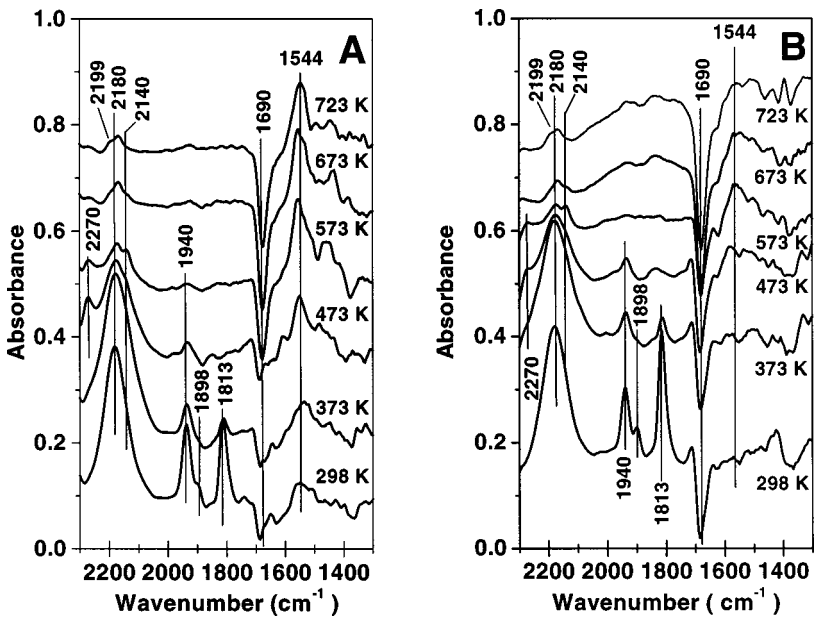

Figure 3. DRIFT spectra of Co-ferrierite calcined (A) and reduced (B) at 673 K in H_2, pretreated in He at 723 K for 1 h, followed by exposure to a flow of NO/Ar and 2% O_2 mixture in the 298–723 K temperature range.

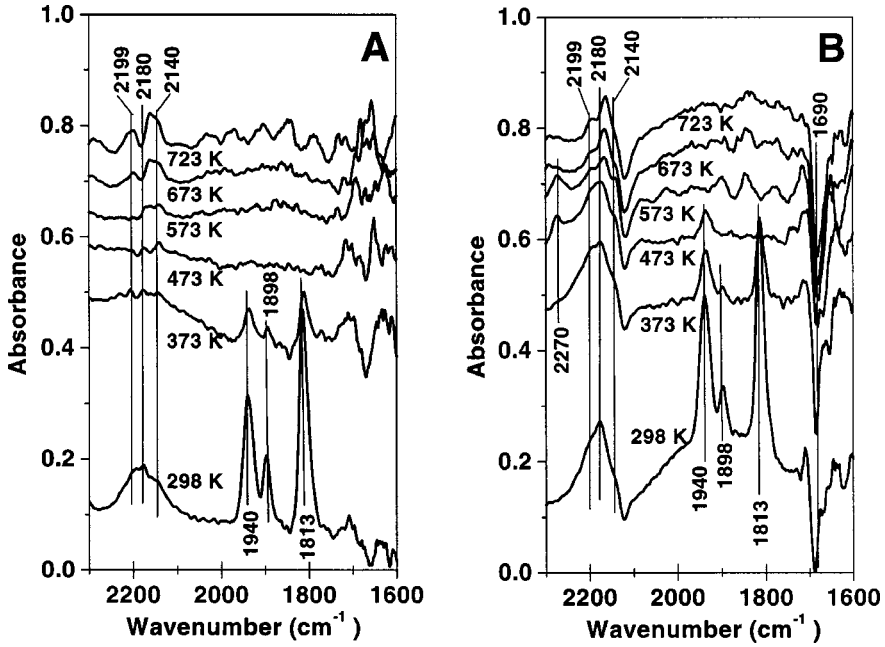

Figure 4. DRIFT spectra of PtCo-ferrierite calcined (A) and reduced (B) at 623 K in a flow of H_2 followed by purging in He at 723 K for 1 h and then exposure to a flow of NO/Ar and 2% O_2 mixture in the 298–723 K temperature range.

1690 cm^{-1} was also observed, suggesting a change of the zeolite substrate during the $NO + O_2$ interaction. No differences were observed after reduction treatment (see figure 3(B)).

The intensity of the broad band at 2180 cm^{-1} remained essentially unchanged up to 473 K, after which it decreased at higher temperatures. At 573 K, this broad band split into two components at ca. 2170 and 2140 cm^{-1} and a small shoulder at ca. 2199 cm^{-1}. At higher temperatures, only the band at 2170 and a shoulder at 2199 cm^{-1} were observed. A band ca. 2270 cm^{-1} was also detected. The band at 2140 cm^{-1}, and the shoulder at 2199 cm^{-1}, were quite similar to those recorded on HZSM-5 and CuHZSM-5 upon adsorption of NO_2, or NO adsorption followed by O_2 admission [14] or on CoZSM-5 [7], HZSM-5, NaZSM-5 [15–17], Fe-ZSM-5 [18] and H-mordenite [19]. Since the appearance of this band correlated with a decrease in the intensity of the acidic hydroxyls (3620 cm^{-1}), the band at 2140 and the shoulder at 2199 cm^{-1} should be assigned to $NO^{\delta+}$ or $NO_2^{\delta+}$. The band at 2170 cm^{-1}, which is stable at temperatures as high as 723 K, could originate from the bonding of NO_2 formed at room temperature in the presence of O_2 with Co^{2+} ions, as reported in literature [7,15].

When the reaction temperature was increased up to 573 K, the band of mononitrosyl species [Co^{2+}(NO)] was very weak, the band of dinitrosyl species [$Co^{2+}(NO)_2$] disappeared, and a band at 1544 cm^{-1}, very likely arising from nitrates [14,15,18], was developed. The high stability of this new band was quite apparent and it persisted up to 723 K. Further support for the influence of co-adsorbed species on the extent and stability of NO (or NO_2) species was gained by performing sequential adsorption experiments. By feeding NO first and then adding O_2, or by feeding NO first and then switching to O_2, similar bands as those described above were generated. However, by flowing O_2 first and then adding NO, NO did not chemisorb and no NO_2 was detected. These results allow us to conclude that on Co^{2+} ions O_2 adsorption is stronger than NO adsorption.

It is known [20] that Pt-exchanged ZSM-5 is very active for NO conversion, although it is also completely unselective to N_2, using methane as a reducing agent in the presence of oxygen, yielding NO_2 as a major reaction product.

The spectra of the bimetallic PtCo-ferrierite sample calcined and reduced when exposed to $NO + O_2$ mixture are shown in figure 4 (A) and (B), respectively. At room temperature, the bands of mononitrosyl and dinitrosyl species are clearly observed together with the band around 2180 cm^{-1}. At 473 K, this band splits into two small bands at 2140 and 2170 cm^{-1}, and intensity increases with temperature. At 673 K, a new band at 2199 cm^{-1}, together with a weak one at 2270 cm^{-1} were observed. Comparison of the spectra shown in figures 3(A) and 4(A) reveals that NO_2 (and $NO_2^{\delta+}$) species are much more stable in bimetallic PtCo-ferrierite than in its Pt-free counterpart. Substantial differences are observed in the NO_2 bands in the reduced PtCo-ferrierite. The bands at 2199, 2180 and a shoulder can be discerned and intensities do not change to a great extent with the reaction temperature. It may be inferred that the presence of Pt develops Co^{2+} locations in which NO_2 is strongly adsorbed. Furthermore, the dinitrosyl species is absent at 473 K whereas the mononitrosyl still persists. In this case, the region corresponding to the nitrite and nitrate region (1600–1300 cm^{-1}) was not recorded owing to the strong noise superimposed in the spectra.

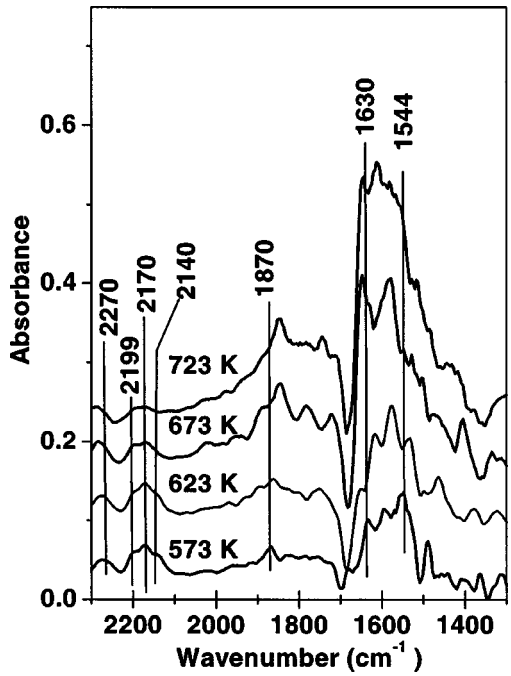

Figure 5. DRIFT spectra of Co-ferrierite reduced at 623 K in a flow of H_2 followed by purging in He at 723 K for 1 h and then exposure to a flow of $NO/CH_4/O_2$ reactant mixture in the 573–723 K temperature range.

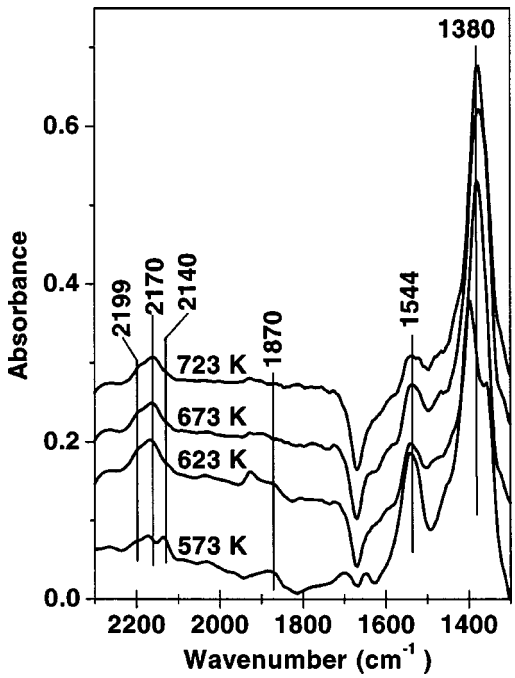

Figure 6. DRIFT spectra of PtCo-ferrierite reduced at 623 K in a flow of H_2 followed by purging in He at 723 K for 1 h and then exposure to a flow of $NO/CH_4/O_2$ reactant mixture in the 573–723 K temperature range.

3.3. DRIFT spectroscopy in the reaction mixture $CH_4 + NO + O_2$ (NO_2 reduction)

Figure 5 shows the DRIFTS spectra under the reaction mixture (CH_4+NO+O_2) at temperatures from 573 to 723 K over the prereduced Co-ferrierite sample. Upon reduction at 623 K, bands at 2270(w), 2199(w), 2172(w), 2140(w), 1870(w), 1630(s), and 1544(s) cm^{-1} are observed. The broad bands at 1544 and 1630 cm^{-1}, which shift to higher wavenumbers and increase in intensity upon increasing reaction temperature, can be assigned to nitrite and nitrate species bonded with Co^{2+} (Co^{2+}–NO_2), in agreement with Aylor et al. [7]. The weak band at 1870 cm^{-1}, which shifts to 1845 cm^{-1} and increases in intensity above 623 K, could be assigned to N_2O_3 species [7]. The weak and broad band at ca. 2170 cm^{-1}, which displays shoulders at lower (2140 cm^{-1}) and higher (2199 cm^{-1}) wavenumbers, is in keeping with with other literature reports for isocyanate [7,8,21,22] or even cyanide [12] species. Although such an assignment cannot be ruled out, the close similarity between the spectra in figures 3 and 5 indicates that similar NO_2 species are present both under oxidant ($NO + O_2$) and under the reaction conditions ($CH_4 + NO + O_2$).

The DRIFTS spectra of surface species on pre-reduced bimetallic PtCo-ferrierite are shown in figure 6. In the 2200–2100 cm^{-1} interval these spectra are similar to that of the Pt-free sample, although slightly more intense. The association of these bands is similar to Co-ferrierite catalysts (see figure 5). In addition, nitrate bands at 1544(m) cm^{-1} and a new band around 1380(vs) cm^{-1}, almost unchanged with temperature, are also observed. This latter band has been previously observed by Sun et al. [13], who associated it with some NO_2 intermediate structures developed in the presence of reactants resulting from the interaction with Co^{2+} cations bonded to the zeolite framework oxygen. The lower frequency of NO_2 intermediates is an indication of the strong interaction between Co^{2+} cations and the NO_2 species on PtCo-ferrierite. NO_2 species in the adsorbed state react with CH_4 – presumably in the gas phase – leading to some kind of intermediate [$NOCH_x$], which has a very short lifetime and decomposes very rapidly into the N_2 and CO_2 products, the rate-determining step being the formation of NO_2, which is the only species detected by DRIFTS in $NO + O_2$ or $NO + CH_4 + O_2$ reactions:

$$NO + CH_4 + O_{2(g)} \rightarrow NO_2(NO_2^{\delta+})_{(s)} + CH_{4(g)} \rightarrow [NOCH_x]_{(s)} \rightarrow N_{2(g)} + CO_{2(g)}$$

Nitrates are also detected at high temperatures. They are readily formed on calcined catalysts and monometallic Co-ferrierites. Thus, platinum incorporation into the base Co-ferrierite and pre-reduction of the catalyst inhibit the formation of nitrate structures, which in turn promote the formation of NO_2 intermediate species, which are responsible for the better performance in this reaction.

4. Conclusion

Co^{2+} ions in Co-ferrierite appear to be located in two different positions; namely, isolated ions stabilized in the cavities of the zeolite, and another less-dispersed phase, probably as CoO/Co_2O_3. With gaseous NO, isolated Co^{2+} sites form dinitrosyl species (bands at 1898 and 1813 cm^{-1}), whereas clustered Co^{2+} ions adsorb NO as

mononitrosyl species (band at 1940 cm^{-1}). In the bimetallic PtCo system, the incorporation of platinum leads to an increase in the proportion of isolated Co^{2+} ions, which in turn chemisorb NO strongly. In the presence of oxygen, NO is oxidized into NO_2, which then interacts on the surface of the catalyst. NO_2 chemisorption is stronger on the reduced surface than on the oxidized catalyst. The incorporation of Pt into the base Co-ferrierite and H_2-reduction enhance NO_2 coverage, which is clearly visible in the temperature region in which the $CH_4 + NO + O_2$ reaction occurs. NO_2 species are also accompanied by nitrite and nitrate structures, as revealed by the appearance of bands in the 1700–1300 cm^{-1} region. A very stable Co^{2+}–NO_2 intermediate species is promoted by Pt in PtCo-ferrierite.

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