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FTIR of adsorbed species on Co-H-MOR and Co-Na-MOR under $CH_4 + NO + O_2$ stream: Catalytic activity and selectivity

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ABSTRACT

The selective catalytic reduction (SCR) of NO with CH_4 in the presence of excess O_2 was studied on Co-H-MOR and Co-Na-MOR prepared from H-MOR and Na-MOR, respectively, by cobalt ion-exchange and containing nearly the same Co percentage (66 and 61%) but very different H^+ and Na^+ amounts.

Catalyst characterization was performed using NO as a probe at room temperature, and by means of *in situ* FTIR study at the reaction temperature (573–773 K) in the presence of flowing reactant mixtures of various compositions ($[CH_4] = 0$ or 4000 ppm, $[NO] = 0$ or 4000 ppm, $[O_2] = 0$ or 20,000 ppm, balance He). In one selected case, the *operando* FTIR-GC methodology was used.

The activity for SCR was nearly the same on the two catalysts, whereas the selectivity was higher on Co-H-MOR than on Co-Na-MOR.

NO adsorption at room temperature did not show major differences in the type of cobalt species present on the two samples, being nearly all cobalt present as isolated Co^{2+} with two coordinative vacancies. The *in situ* FTIR characterization under reaction conditions identifies Co^{2+}-mononitrosyls. We suggest that this mononitrosyl is a key species for the catalytic activity in the SCR reaction. Conversely, the *in situ* FTIR study under reaction conditions evidenced major differences between the surface nitrogen-oxo species (NO_y, oxidation number of nitrogen >2) formed on the two samples, specifically NO^+ on Co-H-MOR-66, and Co^{2+}-monodentate nitrates on Co-Na-MOR-61. We suggest that Co^{2+}-monodentate nitrate favors the CH_4 combustion, accounting for the finding that the S_{SCR} selectivity of Co-Na-MOR-61 is lower than that of Co-H-MOR-66.

1. Introduction

Co-exchanged zeolites (MFI, FER, MOR) are active for the selective catalytic reduction (SCR) of NO with CH_4 as reductant in the presence of excess O_2 [1–15]. Whereas some have invoked isolated Co^{2+} as the active site for this SCR reaction [3,9,12–14,16–18], others have suggested a role for a multinuclear cobalt oxo-alike species, of unspecified chemical composition [19–25].

In an earlier study of this reaction, we found that the catalytic activity of Co-MFI [9] and Co-MOR [14,26] was proportional to the cobalt content. In agreement with the previous conclusion reached with Co-H-MFI and Co-Na-MFI [9], comparing the catalytic activity of Co-H-MOR with that of Co-Na-MOR, we confirmed that the specific reaction rate per Co^{2+} depended neither on Brønsted acid nor on sodium ion amounts [14]. Brønsted acid sites or sodium ions were present in the samples as residual species after the exchange with cobalt of H-MOR or Na-MOR. On both H-MOR and Na-MOR, protons were also produced by hydrolysis of exchanged $Co^{2+}(H_2O)_n$ during the thermal treatment at 773 K, subsequent to the exchange process [26].

In our previous investigations on Co-H-MOR and Co-Na-MOR [14,26], we mainly focused on the dependence of catalytic activity for SCR on cobalt content, paying less attention to the selectivity aspects. In the present investigation, to study the role of Brønsted acid and Na^+ ion amounts in determining the selectivity of Co-MOR samples for the SCR reaction, we compared the activity and selectivity of two samples prepared from Na-MOR or H-MOR by cobalt ion-exchange and containing the same Co percentage (about 60%). These two samples were portions of those we previously used as catalysts for the SCR of NO with CH_4 in the presence of excess O_2 and characterized by FTIR using CO [14,26] or NO [27] as probe molecules. The characterization by CO at room temperature has shown that the cobalt active for this reaction was present mostly as isolated Co^{2+} species [14,26]. In this paper, (i) we compared Co-H-MOR with Co-Na-MOR using NO as a probe at room temperature, and (ii) we studied the surface species formed in the presence of flowing reactant mixtures of various compositions at the reaction temperature by means of *in situ* FTIR

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spectroscopy and, in one selected case, by means of the *operando* FTIR-GC methodology.

2. Experimental

2.1. Catalysts

Co-exchanged mordenite samples were portions of those previously used as catalysts for NO-SCR with CH_4 in excess O_2 [14]. Starting materials were Na-MOR (Si/Al = 9.2, Tosoh Corporation) and H-MOR (Si/Al = 9.2, Tosoh Corporation). The transition metal impurity level of the MOR matrices was analyzed by means of ICP-OES (Varian Vista-MPX CCD Simultaneous) and yielded Fe = 37 ppm, Ni = 2 ppm, Cu = 3 ppm, and Co = 2 ppm on Na-MOR, and Fe = 95 ppm, Ni = 20 ppm, Cu = 3 ppm, and Co = 2 ppm on H-MOR.

Co-exchanged samples were prepared following the same preparation procedure. They were ion-exchanged at 350 K, under continuous stirring for 6 h, by contacting 1.5 g of mordenite with 50 mL of a 0.02 M cobalt acetate aqueous solution. After the exchange procedure, samples were thoroughly washed with distilled water, dried overnight at 383 K, and calcined in air at 773 K for 5 h. The sodium and the cobalt content of wet samples (equilibrated at ca. 79% relative humidity over a saturated solution of NH_4Cl) were determined by atomic absorption (Varian SpectrAA-30). Samples are labelled as Co-H-MOR-66 or Co-Na-MOR-61, where H, or Na specifies the zeolite used in the preparation (H-form or Na-form), and 66 or 61 specifies the analytical Co-exchange percentage, expressed as % 2Co/Al.

2.2. Catalytic experiments

The catalytic activity was measured in a flow apparatus at atmospheric pressure. The apparatus included a feeding section where four gas streams (He, 3% NO in He, 2% CH_4 in He, 10% O_2 in He) were regulated by means of independent mass flow controller-meters (MKS model 1259, driven by a four-channel unit MKS model 247 c) and mixed in a glass ampoule before entering the reactor. Gas mixtures were purchased from RIVOIRA and used without further purification. The reactor was made of quartz with an internal sintered frit of about 12 mm diameter supporting the powdered catalyst (0.100 g). Reactants and products were analyzed by gas-chromatography (Varian Quad Micro-GC CP-2003, equipped with two columns: (i) 10 m Molsieve 5A BF, for detecting N_2, and CO, and (ii) 10 m Poraplot Q, for detecting CH_4, CO_2, N_2O). All experiments yielded satisfactory carbon balance. A fresh portion of catalyst was treated in a flow of 2% O_2/He mixture, while the reactor was heated from room temperature to 773 K in about 45 min and then isothermally at 773 K for 1 h. After this treatment, the reactor was bypassed and the temperature adjusted to the desired value. Catalysis was run with equimolar mixtures of NO and CH_4 containing 4000 ppm (v/v) of either reactant, O_2 = 2%, with He as balance. The reaction temperature and mixture composition were changed without intermediate activation treatment. The total flow rate was maintained at 50 cm^3 STP/min, and space velocity (GHSV) was 15,000 h^{-1}, based on the apparent sample density of 0.5 g cm^{-3}.

To compare catalytic activity and selectivity of the various catalysts, we assumed the following set of reactions to take place on all catalysts:

$$CH_4 + 2NO + O_2 = N_2 + CO_2 + 2H_2O \quad (1)$$

$$CH_4 + 2NO + 3/2O_2 = N_2O + CO_2 + 2H_2O \quad (2)$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (3)$$

$$CH_4 + 3/2O_2 = CO + 2H_2O \quad (4)$$

The NO conversion was calculated from $N_2 + N_2O$ molecules produced in Eqs. (1) and (2). The CH_4 conversion was calculated from CO_2 + CO molecules produced in Eqs. (1)–(4).

The percent S_{SCR} selectivity (NO reduction rather than CH_4 combustion) was calculated as: $S_{SCR} = 100[(N_2 + N_2O)/(CH_4 \text{ converted})]$.

2.3. In situ and operando FTIR experiments

The FTIR spectrometer (Perkin Elmer 2000), equipped with a MCT detector, operated at a resolution of 4 cm^{-1}. The powdered samples were pelletted (pressure, 2×10^4 kg cm^{-2}) in self-supporting disks of ca. 10 mg cm^{-2} and put in a stainless-steel IR reactor cell. The IR cell, equipped with CaF_2 windows, allowed to record spectra of samples heated up to 773 K, under gas stream.

The flow apparatus for the *in situ* FTIR and *operando* FTIR-GC experiments consisted of a feeding section, a reaction section and a analysis section. The feeding section and the analysis sections were the same we have previously used for catalytic measurements. Samples were activated at 793 K under He/O_2 flow for 1 h, followed by He flow for 15 min. Samples were therefore cooled to the desired temperature under He flow, and thereafter exposed to mixtures of various compositions ([CH_4] = 0 or 4000 ppm, [NO] = 0 or 4000 ppm, [O_2] = 0 or 20,000 ppm, balance He, total flow 50 cc/min). In the *operando* FTIR-GC experiment, reactants and products were analyzed by the on-line Micro-GC. In this experiment, IR reactor cell was fed with a NO + CH_4 + O_2 mixture having the same composition as that we used in catalytic experiments.

Spectra recorded after heating samples in the He stream at a given temperature (blank experiments at 298–773 K) were subtracted from those obtained after heating in the reactant mixture stream at the same temperature.

FTIR characterization of OH species and that of adsorbed NO (AIR LIQUIDE/SIO, 99.0%) were performed in a conventional IR silica-cell, which allowed thermal treatments in vacuum or in a controlled atmosphere. Before recording spectra at room temperature, samples were heated with O_2 (SOL, 99.9%) at 773 K for 1 h and evacuated at the same temperature for 1 h.

3. Results and discussion

3.1. Characterization of Brønsted acid sites in Co-H-MOR-66 and Co-Na-MOR-61

In the OH stretching region, the comparison of the FTIR spectra of Co-H-MOR-66 and Co-Na-MOR-61 with those of the corresponding matrices (Fig. 1), shows that (i) in Co-H-MOR-66 the band intensity of Brønsted acid sites (band at ν_{OH} at 3610 cm^{-1}) was far higher than that expected from the Co-exchange extent, and (ii) in Co-Na-MOR-61 an unexpected Brønsted acid site band (band at ν_{OH} at 3610 cm^{-1}) appeared. Because Brønsted acid sites (–Si–OH–Al–) were absent in Na-MOR (Fig. 1), their presence in Co-Na-MOR-61 was apparently due to the introduction of Co^{2+}. This unexpected formation of Brønsted acid sites in Co-Na-MOR-61 and the fact that the band intensity of Brønsted acid sites in Co-H-MOR-66 was far higher than that expected from the Co-exchange extent can be rationalized along the same lines we have previously proposed [14]. Namely, the $Co^{2+}(H_2O)_n$ species exchanged with (–Al–ONa–Si–) sites of Na-MOR, or with (–Al–OH–Si–) sites of H-MOR, yielding (–Si–O^-–Al–) and [–Al–$O^-Co^{2+}(H_2O)_n$–Si–]. On heating in O_2 at 773 K, a fraction of the [–Al–$O^-Co^{2+}(H_2O)_n$–Si–] species underwent hydrolysis thereby causing the formation of Brønsted acid sites, (–Si–OH–Al–), and [–Al–$O^-Co(OH)^+$–Si–]. In both Co-Na-MOR-61 and Co-H-MOR-66, the amount of Brønsted acid sites can be calculated as ($I_{Co\text{-}MOR}/I_{H\text{-}MOR}$), where $I_{Co\text{-}MOR}$ is the integrated

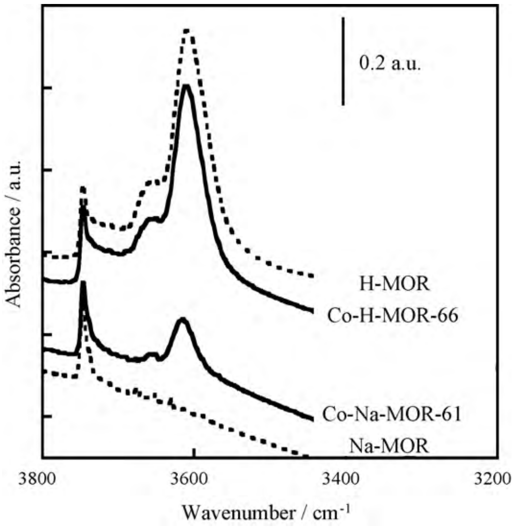

Fig. 1. FTIR spectra of Co-exchanged MOR and corresponding MOR matrices in the OH stretching region. Before recording spectra at room temperature, samples were heated in O_2 at 773 K for 1 h and evacuated at the same temperature for 1 h.

intensity of the 3610 cm^{-1} band in Co-Na-MOR-61 and Co-H-MOR-66, respectively, and $I_{H\text{-}MOR}$ that of the same band in the H-MOR sample. The H^+/Al ratios are reported in Table 1. From the H^+/Al ratio, determined by FTIR, and from the Na^+/Al ratio, determined by atomic absorption analysis, we calculated the H^+/Na^+ ratio (Table 1). The latter value was 220 times lower in Co-Na-MOR than in Co-H-MOR-66.

3.2. *Catalytic activity and selectivity of Co-H-MOR-66 and Co-Na-MOR-61*

In the temperature range 423–773 K, Na-MOR was nearly inactive for the SCR of NO with CH_4 in the presence of excess O_2. In the same temperature range, H-MOR was slightly active for this reaction, and highly selective. On this sample, the S_{SCR} selectivity increased with temperature from 70 to 90% (data not shown). Both Co-H-MOR-66 and Co-Na-MOR-61 were much more active than the corresponding matrices, yielding N_2 and CO_2 as main products, and N_2O and CO as by-products, in a negligible amounts. NO conversion on Co-H-MOR-66 equalled that on Co-Na-MOR-61 (Fig. 2a), CH_4 conversion was lower on Co-H-MOR-66 than on Co-Na-MOR-61 (Fig. 2b), and therefore S_{SCR} selectivity higher on Co-H-MOR-66 than on Co-Na-MOR-61 (Fig. 2c).

3.3. *Characterization of cobalt by adsorption of NO at RT*

3.3.1. *FTIR study of NO adsorption*

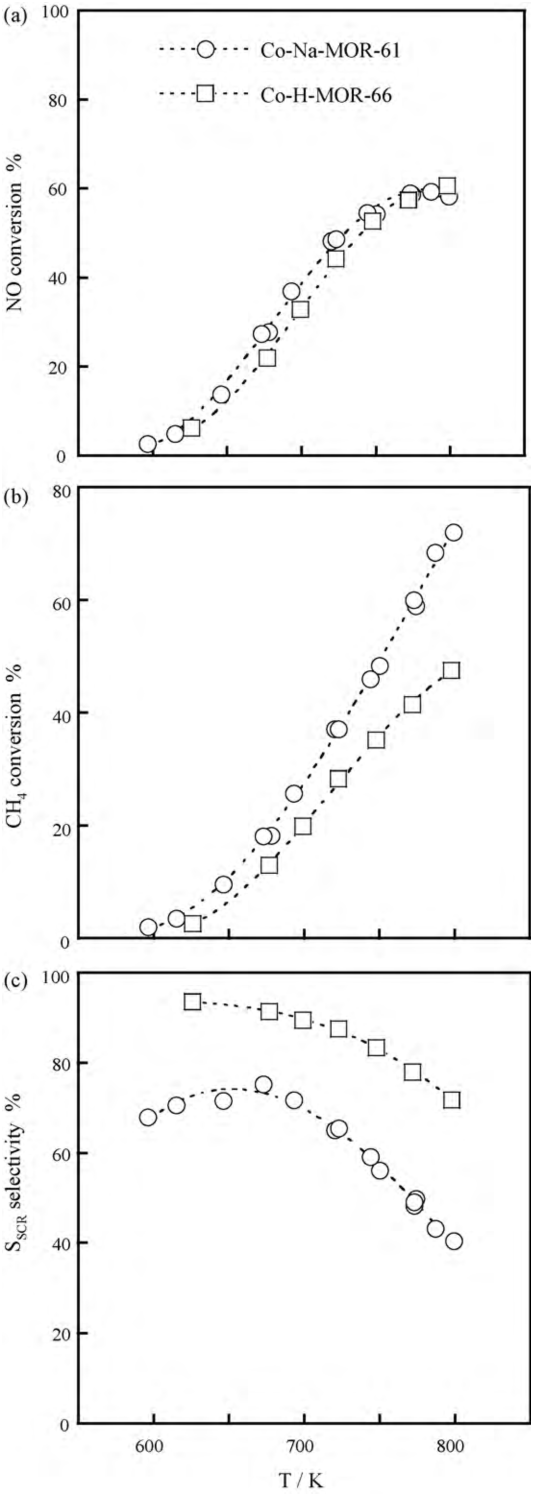

Fig. 2. Percent NO conversion (section a), CH_4 conversion (section b) and S_{SCR} selectivity (section c) as a function of temperature on Co-H-MOR-66 and on Co-Na-MOR-61. Reactant mixture: [NO] = 0.4%, [CH_4] = 0.4%, [O_2] = 2%, balance He (total flow = 50 cc STP/min, GHSV = 15,000 h^{-1}).

Table 1
Catalysts and their features.

Catalyst	2Co/Al[a]	Na^+/Al[a]	H^+/Al[b]	H^+/Na^+
Na-MOR		0.97	0.0	
H-MOR		0.00	1.0	
Co-Na-MOR-61	0.61	0.40	0.14	0.35
Co-H-MOR-66	0.66	0.01	0.77	77

[a] The sodium and the cobalt content was determined by atomic absorption.

[b] The amount of Brønsted acid sites was determined from the ratio between the integrated intensity of the Brønsted acid site band (3610 cm^{-1}) in Co-MOR, and that of the same band in H-MOR. In H-MOR, we assumed that H^+ content equalled Al content (H^+/Al = 1.0).

On both Co-H-MOR-66 and Co-Na-MOR-61 samples, NO adsorption at RT yielded bands at 1812, 1860 and 1900 cm^{-1}, a composite absorption at about 1940 cm^{-1}, and a broad absorption in the 2300–2050 cm^{-1} region, the latter having a different shape in Co-H-MOR-66 (Fig. 3a) and Co-Na-MOR-61 (Fig. 3b). As the equilibrium pressure was increased from 0.01 to 80 Torr, the intensity of all bands increased, whereas the intensity of the 1940 cm^{-1} band progressively decreased. At about 1920 cm^{-1}, an

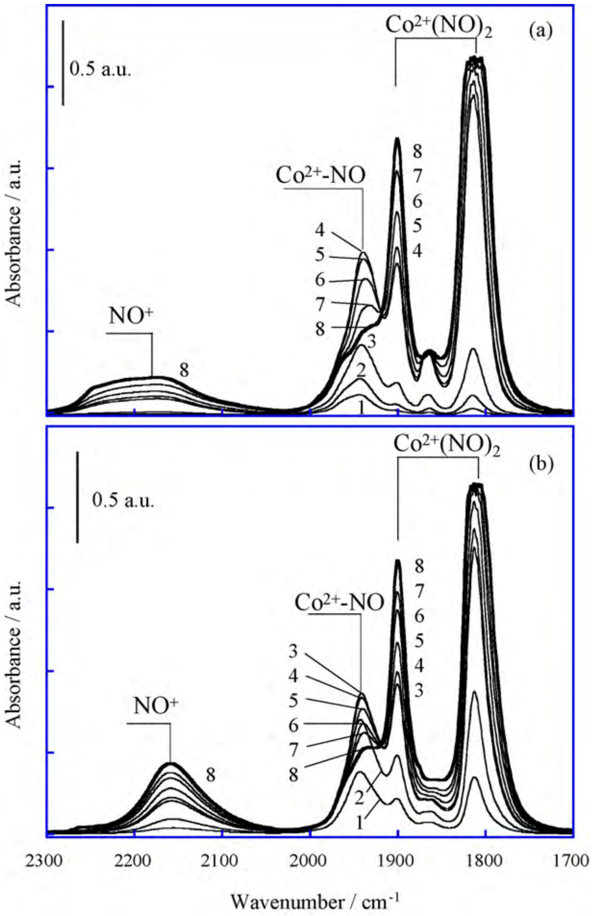

Fig. 3. FTIR spectra of NO adsorbed at RT at various equilibrium pressures (P_{NO}). Section a: Co-H-MOR-66, P_{NO} = 0.01 Torr (spectrum 1), 0.02 Torr (spectrum 2), 0.07 Torr (spectrum 3), 0.12 Torr (spectrum 4), 0.24 Torr (spectrum 5), 1.5 Torr (spectrum 6), 22 Torr (spectrum 7), 80 Torr (spectrum 8). Section b: Co-Na-MOR-61, P_{NO} = 0.01 Torr (spectrum 1), 0.08 Torr (spectrum 2), 0.12 Torr (spectrum 3), 0.20 Torr (spectrum 4), 1.0 Torr (spectrum 5), 4.5 Torr (spectrum 6), 15 Torr (spectrum 7), 80 Torr (spectrum 8).

isosbestic point was identified, indicating that the species absorbing at 1940 cm^{-1} had transformed into a species absorbing at 1900 cm^{-1} (Fig. 3a and b).

Bands in the 2000–1700 cm^{-1} region have been previously observed on various Co-zeolites [9,28–36], and assigned to mononitrosyls and dinitrosyls of cobalt. By consensus [9,28–36], the band at about 1900 cm^{-1} is the symmetric stretching mode of $Co^{2+}(NO)_2$ and that at 1812 cm^{-1} the asymmetric stretching mode of this dinitrosyl. The asymmetry and broadness of these two bands strongly suggest the concomitant presence of various $Co^{2+}(NO)_2$. The complex absorption centred at about 1940 cm^{-1} is typical of Co-mononitrosyls, whose cobalt oxidation state remains debatable. The broad band contains an intense component arising from Co^{2+}-NO and might also mask a Co^{3+}-NO component [9,28–36]. The complex absorption in the range 2300–2050 cm^{-1} arise from NO^+ species adsorbed on various matrix sites [31,37,38]. Collectively, the FTIR of adsorbed NO shows that various $Co^{2+}(NO)_2$ formed, Co^{2+}-NO and, possibly, Co^{3+}-NO. This high heterogeneity in the cobalt nitrosyl species is consistent with the broad FTIR bands we observed after NO adsorption.

The room temperature characterization with NO evidenced that the same cobalt species are present in both Co-H-MOR-66 and Co-Na-MOR-61, confirming the analogous result previously obtained with CO [14].

3.3.2. Volumetric adsorption of NO

On Co-H-MOR-66, the NO/Co ratio, evaluated from total NO adsorption at RT, was NO/Co = 1.8 ± 0.2. The NO/Co value indicates that a large fraction of cobalt adsorbed two NO molecules, yielding $Co^{2+}(NO)_2$. Being the intensity of dinitrosyl bands in Co-H-MOR-66 spectra nearly the same as that in Co-Na-MOR-61, we assume that nearly the same fraction of cobalt in Co-Na-MOR-61 adsorbed two NO molecules also.

3.4. FTIR of surface species formed in flow experiments under reaction conditions

Because of their reactivity with CH_4, adsorbed nitrogen-oxo species (NO_y, oxidation number of nitrogen >2) arising from NO + O_2 have been considered essential for the SCR of NO with CH_4 or other hydrocarbons on various catalysts [7,8,18,39–42]. The co-adsorption of NO and O_2 on Co-zeolites yielded stable nitrates of various structures, as evidenced by means of *in situ* FTIR characterization [43]. Among these nitrates, a monodentate species adsorbed on isolated Co^{2+} has been identified [29,44,45]. This monodentate nitrate reacts with CH_4 in the same temperature region in which catalysts are active (373–473 K), and therefore this nitrate has been considered a key compound in determining the activity for SCR with methane [29,44,45]. In a recent paper, by means of the DRIFT-MS operando technique, Lónyi et al. [46] suggested that NO^+ and the above-mentioned Co^{2+}-nitrates are key species in the NO reduction with methane. Hereafter, we will focus on the nature of NO_y species and on their reactivity with CH_4.

3.4.1. Species formed with NO + O_2 at increasing temperature

The FTIR spectra of H-MOR and Na-MOR under NO + O_2 flow at 373 K (Fig. 4a and b) showed (i) a composite band at about 2170 cm^{-1}, arising from NO^+ species, and (ii) an intense absorption in the 1650–1300 cm^{-1} region, which was previously observed and assigned to nitrates of various structures [43]. Nitrate bands at 1630 and 1610 cm^{-1}, more intense in H-MOR than in Na-MOR, arose from covalent bridged species adsorbed on matrix sites; nitrate bands at 1420 and 1380 cm^{-1}, detected in Na-MOR only, arose from ionic species interacting with Na^+ ions, as previously reported by Campa et al. [44]. On both H-MOR and Na-MOR, increasing the temperature from 373 to 723 K, the intensity of all bands progressively decreased. On H-MOR, NO^+ and bridged nitrates were somewhat more stable than on Na-MOR, being still present at 723 K.

At 373 K, on Co-H-MOR-66 and Co-Na-MOR-61 (Fig. 4a and b), in addition to the bands arising from species adsorbed on the matrix sites, FTIR spectra consisted of (i) a band of Co^{2+}-NO species at about 1940 cm^{-1}, and (ii) intense bands of nitrates centred at about 1525 and 1320 cm^{-1}. These latter two bands have been observed on various Co-zeolites and assigned to the vibration modes of covalent monodentate nitrates on isolated-Co^{2+} [29,44,45], as also suggested by the fact that their intensity was proportional to the isolated-Co^{2+} content in the zeolite [44]. The relative amount of surface species formed in Co-H-MOR-66 differed from that in Co-Na-MOR-61. In particular, Co^{2+}-NO, NO^+ and bridged nitrates on matrix sites in Co-H-MOR-66 were more abundant than in Co-Na-MOR-61, and Co^{2+}-nitrates types in Co-H-MOR-66 were more numerous than in Co-Na-MOR-61, indicating higher heterogeneity (compare section a with section b of Fig. 4).

Increasing the temperature from 373 to 773 K, on Co-H-MOR-66 and Co-Na-MOR-61 the intensity of bands progressively decreased. The stability of surface species on Co-H-MOR-66 differed from that on Co-Na-MOR-61. In particular, on Co-H-MOR-66, Co^{2+}-nitrates were the most labile species, becoming

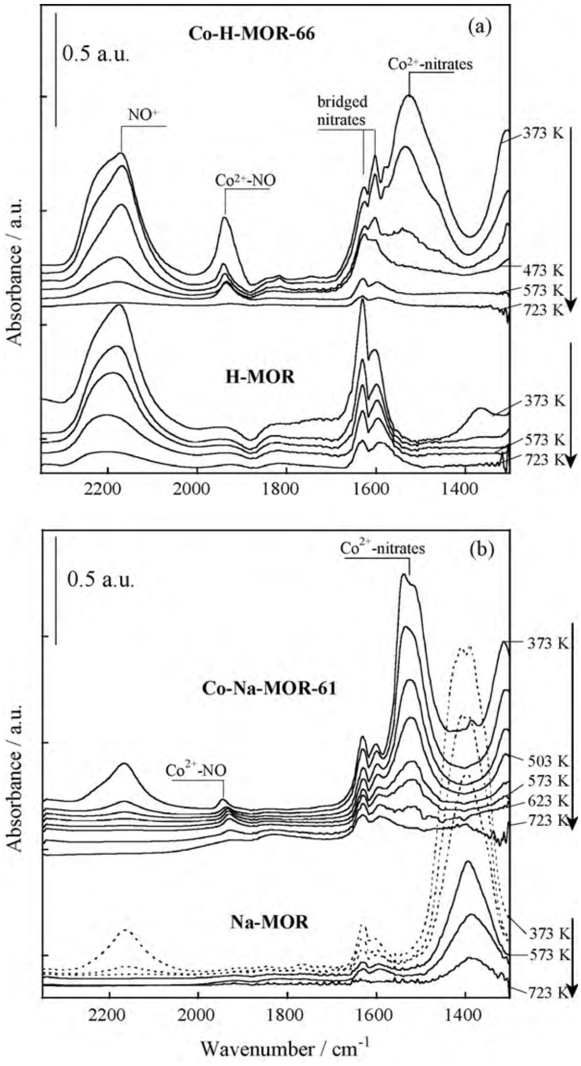

Fig. 4. Surface species formed under NO + O_2 flow at increasing temperature. Section a: Co-H-MOR-66 and H-MOR. Section b: Co-Na-MOR-61 and Na-MOR. On all samples, FTIR spectra at 373 K were recorded after heating them in NO + O_2 flow for 30 min. Samples were heated at increasing temperature from 373 to 723 K (heating rate = 10 K/min) and FTIR spectra were recorded at various temperatures, as indicated. Reactant mixture: [NO] = 0.4%, [O_2] = 2%, balance He (total flow = 50 cc STP/min).

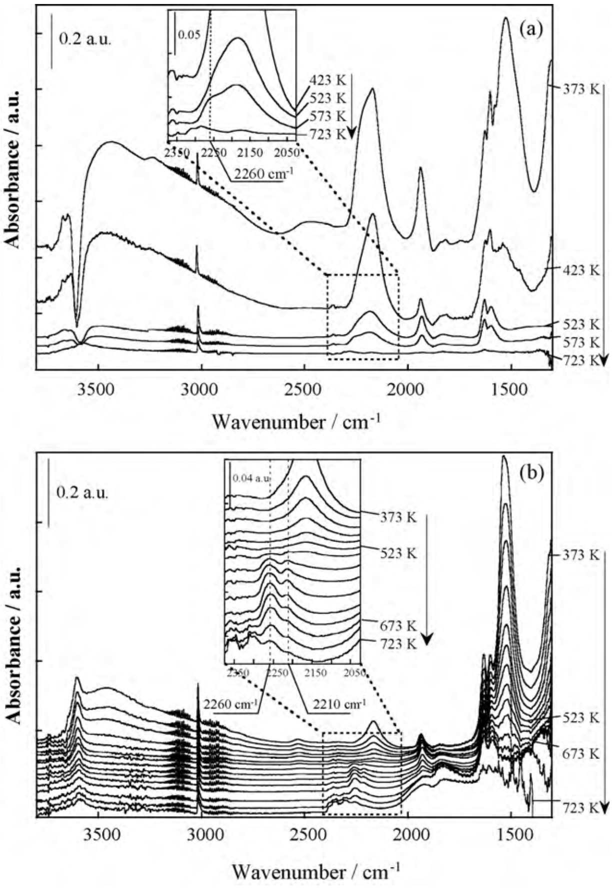

Fig. 5. Surface species formed under NO + O_2 + CH_4 flow at increasing temperature. Section a: Co-H-MOR-66. Section b: Co-Na-MOR-61. FTIR spectra at 373 K were recorded after heating samples in NO + O_2 + CH_4 flow for 30 min. Samples were heated at increasing temperature from 373 to 723 K (heating rate = 10 K/min) and FTIR spectra were recorded at various temperatures, as indicated. The insets report an exploded view of the 2375–2000 cm^{-1} region. Reactant mixture: [NO] = 0.4%, [CH_4] = 0.4%, [O_2] = 2%, balance He (total flow = 50 cc STP/min). On Co-H-MOR-66 (section a), at 573 K a GC-analysis of reactants and products was performed in parallel ("operando" experiment).

undetectable above 473 K, whereas NO^+, Co^{2+}-NO and bridged nitrates were still well detectable (Fig. 4a). Conversely, on Co-Na-MOR-61, NO^+ and sodium nitrates were the most labile species, becoming undetectable above 503 K, whereas Co^{2+}-NO and Co^{2+}-nitrates were undetectable above 623 K and bridged nitrates on matrix sites were still detectable at 723 K (Fig. 4b).

At the temperature at which Co-MOR samples started to be active in catalysis (573 K), the comparison between Co-H-MOR-66 and Co-Na-MOR-61 evidenced that the presence of Co^{2+}-NO and bridged nitrates on both samples, whereas NO^+ formed on Co-H-MOR-66 only, and monodentate Co^{2+}-nitrates on Co-Na-MOR-61 only (Fig. 4a and b). The absence of the monodentate Co^{2+}-nitrate (band at 1525 cm^{-1}) in Co-H-MOR-66 at the temperatures at which this catalyst is active allow to rule out that this species is a key intermediate in the SCR reaction.

The comparison between Co-H-MOR-66 and H-MOR evidenced that the presence of Co^{2+}-NO species on Co-H-MOR-66 is essential to guarantee high activity for SCR, the presence of the Co^{2+}-NO species being the only difference between the two samples.

3.4.2. Species formed with NO + O_2 + CH_4 at increasing temperature

The FTIR spectra of Co-H-MOR-66 and Co-Na-MOR-61 under NO + O_2 + CH_4 flow at 373 K showed the same bands observed under NO + O_2, namely those arising from Co^{2+}-NO and NO_y species, and new bands at 3017 and 1304 cm^{-1} arising from gaseous CH_4 (Fig. 5a and b). As the temperature increased, the amount of Co^{2+}-NO and NO_y species progressively decreased (Fig. 5a and b). Above 523 K, new weak bands in the 2260–2200 cm^{-1} region appeared, possibly arising from intermediates formed by the reaction of NO_y with CH_4 (insets in Fig. 5). Bands in this wavenumber region have been observed on various oxide systems in the presence of C_xH_y + NO + O_2 mixtures of various composition [18,25,43,46,47] and assigned to isocyanate and/or nitrile species. Both these species have been proposed as intermediates in the SCR of NO with CH_4, as precursors of N_2 and CO_2 [18,25,46]. Above 673 K, all these surface species on Co-H-MOR-66 and Co-Na-MOR-61 were hardly detectable, possibly because at this high temperature the high reaction rate caused their surface concentration to decrease. In parallel, increasing the temperature from 673 to 723 K a band at 2360 cm^{-1} from the product gaseous CO_2 increased in intensity (Fig. 5). On H-MOR and Na-MOR, under the same temperature and flow conditions, no intermediates were detected (data not shown).

The only difference between bands of intermediates on Co-H-MOR-66 and Co-Na-MOR-61 was that on Co-H-MOR-66 one band at 2260 cm^{-1} formed (Fig. 5a), whereas on Co-Na-MOR-61 two bands at 2260 and 2210 cm^{-1} formed (Fig. 5b). The band at 2260 cm^{-1} can be assigned to isocyanate species on Co^{2+}, Co^{2+}-NCO, as proposed for similar bands previously observed in the same spectral region [48,43]. The second band at lower wavenumber can arise from nitrile species, –CN, or from –NCO species adsorbed on cobalt, whose band wavenumber was influenced by the basic character of Na^+. This second hypothesis is supported by the fact that –NCO species interacting with K^+ absorbed at a lower wavenumber than those interacting with transition metal ions [49], and that Co^{2+}-NCO species on Co/SiO_2 (2207 cm^{-1}) occurred at lower wavenumber than those on Co-MFI (about 2260 cm^{-1}) [43], being silica more basic than MFI.

3.4.3. Reactivity with CH_4 of species formed with NO + O_2

To gain a better insight on the formation of intermediates, we studied the reaction with CH_4 of Co^{2+}-mononitrosyls and NO_y formed upon saturating samples with NO + O_2. We studied this reaction as a function of time at 573 K. At this temperature, (i) the amount of the spectator species was low, (ii) NO_y species on Co-H-MOR-66 differed from those on Co-Na-MOR-61, and (iii) the catalytic activity was high enough to yield products in an amount still detectable by the Micro-GC apparatus, as demonstrated in an operando experiment performed on Co-H-MOR-66 at 573 K in NO + O_2 + CH_4 stream. In this operando experiment (see spectrum at 573 K in Fig. 5a), the NO reduction rate r_{NO} was 6.6×10^{15} molecules s^{-1} g^{-1}, at 573 K. The measured r_{NO} value from the operando experiment lies on the same Arrhenius plot (log r_{NO} vs. $1/T$) obtained from the conventional catalytic experiments (Fig. 6).

After saturating the surface with NO + O_2 flow at 573 K for 30 min, FTIR spectra of Co-H-MOR-66 showed (i) Co^{2+}-NO (1940 cm^{-1}), (ii) NO^+ species (2250–2050 cm^{-1} region), and (iii) bridged nitrates on the matrix (1630 and 1590 cm^{-1}) (Fig. 7a, spectrum at t = 0 min). After the same treatment, FTIR spectra of Co-Na-MOR-61 showed (i) Co^{2+}-NO (1940 cm^{-1}), (ii) monodentate Co^{2+}-nitrates (1525–1320 cm^{-1}), (iii) NO^+ in traces (2200–2150 cm^{-1} region), and (iv) bridged nitrates (1630 and 1590 cm^{-1}) (Fig. 7b, spectrum at t = 0 min).

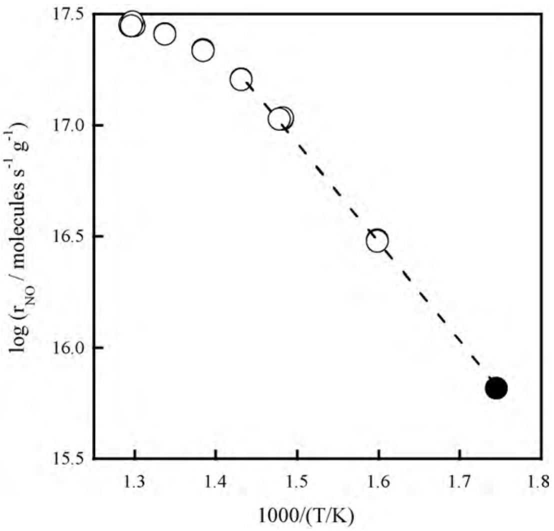

Fig. 6. Arrhenius plot of Co-H-MOR-66. Rate of NO reduction (r_{NO}/ molecules s^{-1} g^{-1}) was measured in flow catalytic tests (○) and in an *operando* FTIR-GC experiment (●). In both cases, the reactant mixture was: [NO] = 0.4%, [CH_4] = 0.4%, [O_2] = 2%, balance He (total flow = 50 cc STP/min). The corresponding FTIR spectrum in the *operando* FTIR-GC experiment is reported in Fig. 5a, spectrum at 573 K.

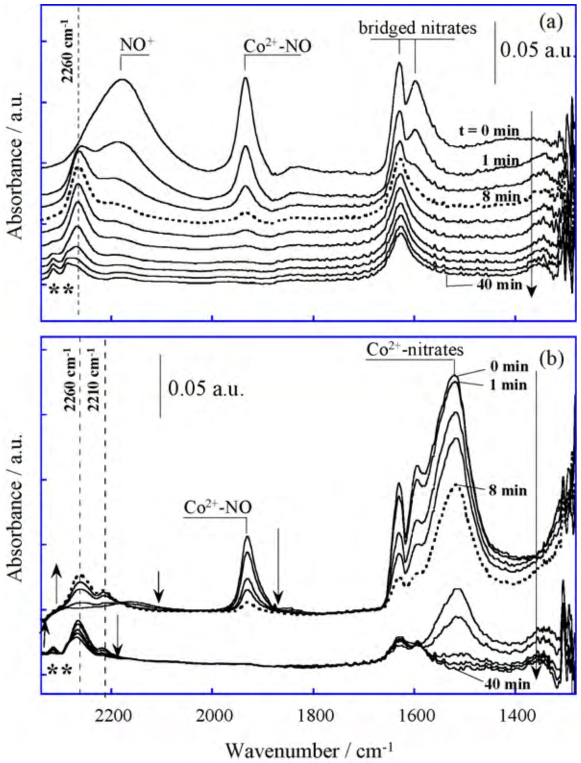

Fig. 7. Reaction with CH_4 of the surface species formed by exposing samples to NO + O_2 flow for 30 min at 573 K. Section a: Co-H-MOR-66. Section b: Co-Na-MOR-61. FTIR spectra at 573 K were recorded after heating samples in NO + O_2 flow for 30 min (t = 0 min). Samples were thereafter exposed to CH_4 flow ([CH_4] = 0.4%, balance He, total flow = 50 cc STP/min) for increasing times, as indicated.

After flowing CH_4 for 1 min, the –NCO bands formed at 2260 and at 2210 cm^{-1}, the latter on Co-Na-MOR-61 only (t = 1 min, in Fig. 7a and b). On both Co-MOR samples, as the extent of reaction with CH_4 increased, the NO_y bands decreased and those of the –NCO increased, the latter bands reaching their maximum intensity after 8 min (Fig. 7a and b). After 8 min, on Co-H-MOR-66 Co^{2+}-NO and NO^+ were present in traces (Fig. 7a). After the same time, on Co-Na-MOR-61 Co^{2+}-NO were present in traces, Co^{2+}-nitrates were present in a considerable amount (Fig. 7b). To clarify whether Co^{2+}-NO and NO_y surface species desorb at 573 K or react with CH_4, we studied the desorption of surface species as a function of time under He stream at 573 K. The comparison of the spectra at 573 K under CH_4 stream with those under He stream showed that on both Co-H-MOR-66 and Co-Na-MOR-61 Co^{2+}-NO and NO_y desorbed faster under the CH_4 stream than under the He one (spectra not shown). The reaction with the CH_4 stream suggests that Co^{2+}-NO and all NO_y surface species might participate to the SCR reaction.

After longer reaction times ($t > 8$ min), –NCO species decreased on both Co-MOR samples, and very weak bands at 2315 and 2286 cm^{-1} appeared and increased with reaction time (bands at 2315 and 2286 cm^{-1} are marked with an asterisk in Fig. 7a and b). A similar doublet has been previously observed adsorbing CH_3CN at RT on Co-H-MOR [50] and assigned to the interaction of the –CN group of acetonitrile with Co^{2+}. This doublet which formed on both Co-H-MOR-66 and Co-Na-MOR-61 after flowing CH_4 for a long time ($t > 8$ min) possibly arose from the interaction of gaseous CH_4 with adsorbed –NCO. In fact, by replacing CH_4 with He, the band at 2260 cm^{-1} was partially restored and the doublet at 2315 and 2286 cm^{-1} decreased. The interconversion between the two species yielded an isosbestic point at 2278 cm^{-1} (spectra not shown).

After 40 min, in addition to residual absorption from –NCO and –CN, a band at 1620 cm^{-1} on Co-H-MOR-66 and two peaks at 1620 and 1590 cm^{-1} on Co-Na-MOR-61 were the only bands still present, possibly arising from adsorbed H_2O and/or carbonates (Fig. 7a and b).

On the whole, the results reported in the previous paragraph compared with those reported in the present one show that surface species formed under $CH_4 + NO + O_2$ flow and those formed by reacting with CH_4 surface species arising from pre-adsorption of $NO + O_2$ are nearly identical, indicating that the two experimental approaches are equivalent.

Collectively, under reaction conditions, Co^{2+}-NO species of the same type (band at 1930 cm^{-1}) and amount are present on both Co-H-MOR-66 and Co-Na-MOR-61. This fact, taken together with the fact that the two samples have the same NO conversion activity suggests that these Co^{2+}-NO are key species for NO conversion. Conversely, in the same temperature region, monodentate Co^{2+}-nitrates are absent in Co-H-MOR-66, and NO^+ species are absent in Co-Na-MOR-61, indicating that monodentate Co^{2+}-nitrate and NO^+ are not key species for NO conversion. The presence of monodentate Co^{2+}-nitrates on Co-Na-MOR-61, and its absence on Co-H-MOR-66, might explain the lower selectivity of the former than that of the latter.

4. Conclusions

The equal NO conversion activity of Co-H-MOR-66 and Co-Na-MOR-61 suggests that specific Co^{2+}-NO observed under reaction conditions are key species for NO conversion. The different selectivity of the two samples can be ascribed to the different NO_y surface species formed during the reaction. Specifically, depending on the H^+/Na^+ ratio, NO^+ formed on Co-H-MOR-66, and Co^{2+}-monodentate nitrates on Co-Na-MOR-61. The presence of Na^+ in Co-Na-MOR-61 pushes electrons toward cobalt, causing the Co^{2+}-monodentate nitrate species to stabilize. This monodentate nitrate favors the CH_4 combustion, accounting for the finding that the S_{SCR} selectivity of Co-Na-MOR-61 is lower than that of Co-H-MOR-66.

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