

The SCR of NO with CH₄ over Co-, Co,Pt-, and H-mordenite catalysts

F. Lónyi^a, J. Valyon^{a,*}, L. Gutierrez^b, M.A. Ulla^b, E.A. Lombardo^b

^a*Institute of Surface Chemistry and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri u. 59-67, Hungary*

^b*Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL-CONICET), Santiago del Estero 2829, 3000 Santa Fe, Argentina*

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Abstract

The catalytic reduction of NO with methane was studied operando in the presence and absence of oxygen in the reaction mixture over Co-, Co,Pt-, and H-mordenite (CoM, CoPtM, HM) catalysts using the coupled methods of diffuse reflectance infrared Fourier-transform spectroscopy and mass spectroscopy (Operando-DRIFTS-MS). The reaction temperature was in the 573–773 K range, and the GHSV for nitric oxide was varied between 6000 and 60,000 h⁻¹. In general, the Co-containing mordenite catalysts were more active than the HM. Over each catalyst two major surface intermediates were identified such as nitrosonium ion (NO⁺) and ammonia. The NO⁺ cations were shown to balance the negative charge on the zeolite framework. The NH₃ molecules were bound either coordinately to Lewis-acid site Co²⁺ ions or were protonated on Brønsted acid sites and retained by the zeolite as NH₄⁺ cations. The prevailing route of N₂ formation was found to involve the reaction of NO⁺ and NH₃ or NH₄⁺ surface species. It was shown that the surface concentration of the intermediate ammonia governed the rate of NO conversion. If O₂ was present in the feed gas it competed with the NO in the oxidation of methane and the surface intermediate ammonia. As a result, the steady-state concentration of the ammonia intermediate and the overall NO conversion to N₂ decreased. Additional routes of N₂ formation were revealed over the CoM and CoPtM catalysts. The cobalt facilitated the formation of NO⁺ and surface nitrate (NO₃⁻). Also nitrile (CN) and isocyanate (NCO) surface species were detected. The NO₃⁻ could be rapidly reduced by methane to intermediate NH₃ and, thereby, it increased the rate of NO conversion significantly. Nitrogen forming reactions can pass also through CN and NCO intermediates; however, the share of these reaction routes in the overall N₂ generation process was minor.

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1. Introduction

The selective catalytic reduction of nitrogen oxides (NO_x-SCR) by hydrocarbons in the presence of large oxygen excess seems to be a feasible process to reduce NO_x emission [1–4]. The discovery that also the cheap and abundantly available methane can be used as selective reducing agent over some catalysts was an important milestone in the field [5–7]. This promising deNO_x technology, using methane, can be especially beneficial to control the NO_x emission of natural gas fuelled boilers and engines [1].

The need for more active and selective catalysts initiated a number of studies to understand the mechanism of the reaction [4,8–15]. In order to describe the possible reaction pathways,

the reaction surface intermediates and the nature of the active sites must be identified. The controversial results published by different authors indicate the complexity of the problem [2,4,10,14].

In general, it is postulated that the reduction of NO with methane in oxidative atmosphere (CH₄/NO-SCR) takes place through the interaction between surface NO_x species with methane to form surface intermediates, which then decompose into the reaction products [4,10,12,14,16–20]. However, the structure of these species is ambiguous.

Nitrite–nitrate complexes were proposed as surface NO_x species by several authors [16,17]; however, Sadovskaya et al. [18] stated the specific participation of two nitrite species: NO₂^{δ+} and NO₂^{δ-} for Co-ZSM-5 catalyst. In contrast, Resini et al. [14] proposed that the reaction proceeds through a kind of surface nitrate via a redox mechanism over Co²⁺/Co³⁺ active sites. Lobree et al. [10] substantiated surface nitrile (CN) species as important reaction intermediate.

* Corresponding author. Tel.: +36 1 438 1132; fax: +36 1 438 1142.

E-mail address: valyon@chemres.hu (J. Valyon).

The formation of nitromethane (CH_3NO_2) was also suggested to precede the conversion of NO to N_2 [12,19,20]. The nitromethane was shown to decompose giving ammonia, which was converted then to N_2 in reaction with O_2 , NO or NO_2 [12,20]. According to Chen et al. [4], the prevailing reaction path involves the reaction of either ammonia or amine intermediate with both NO and NO_2 . The coupling of N-atoms proceeds in the reaction between two surface intermediates, where one of them contains nitrogen atom in 3+ and the other in 3- oxidation states. This notion is supported by the results of the experiments using reactants with labeled nitrogen [4,20]. In catalysts, such as, Co-ZSM-5, Fe-ZSM-5, or Pd-ZSM-5, the transition metal was suggested to play the crucial role of initiating the reduction of NO to NH_3 [4].

Several authors proposed transition metal at exchange position in the zeolite structure as active sites, whereas metal oxide clusters would catalyze the oxidation of CH_4 by O_2 [21–24]. On the other hand, [15] Chupin et al. claimed that microaggregates composed by cobalt and oxygen were the active sites for $\text{CH}_4/\text{NO-SCR}$, while the isolated cobalt cations acted predominantly as adsorption sites for NO. Those CoO-like clusters were originated from Co^{2+} in α and β sites of the mordenite structure. However, Shimizu et al. [13] sustained that a bifunctional catalyst is required; the catalyst having a suitable combination of Brønsted acid sites and cations at exchange positions. This view is also supported by Adelman and Sachtler [25,26]. Besides, the existence of two coordinative vacancies of isolated Ni^{2+} ions in Ni-H-ZSM5 and their important role for $\text{CH}_4/\text{NO-SCR}$ were reported by Mihaylov et al. [27]. This kind of sites appeared to be responsible of the simultaneous coordination of NO_3^- anion and CH_4 molecule (or a CH_x radical) forcing their interaction.

In order to obtain better information about the surface phenomena occurring during the reaction process for $\text{CH}_4/\text{NO-SCR}$, it is important to explore the nature of the adsorbed species, reactants, products and possible intermediates simultaneously with their respective evolutions while the catalyst is working. One of the most plausible techniques for this application is the operando diffuse reflectance infrared Fourier transformed spectroscopy–mass spectroscopy (operando DRIFTS-MS). This system contains a special IR cell, which can act as a reactor and its downstream flow can be analyzed by a coupled on-line detection device (MS) [28].

The present study is a contribution to the understanding of the SCR mechanism of NO by CH_4 over Co-, Co,Pt-, and H-mordenite (M) catalysts taking advantage of the operando DRIFTS-MS method. We focus the investigation on the mechanism for the formation of NO^+ and NO_3^- species, the interaction between methane and NO_3^- and/or NO_2 , the dynamics of the major intermediates, nitrosonium ion (NO^+) and ammonia, in the presence and absence of O_2 . A reaction pathway is proposed to explain the significantly higher activity of the Co-containing mordenites with respect to the activity of the H-mordenite in the $\text{CH}_4/\text{NO-SCR}$ reaction.

2. Experimental

2.1. Catalyst preparation

H-mordenite (HM), Co,Na-mordenite (CoM), and Co,Pt,Na-mordenite (CoPtM) samples were prepared from a Na-mordenite (NaM), obtained from Zeolyst International (Product ID: CBV 10A, Si/Al = 6.5). A NaM sample was ion exchanged three times using 2 M NH_4NO_3 solution, then it was filtered, washed with deionized water and dried. The H-form (HM) was obtained by in situ thermal decomposition of the NH_4^+ -form (see below). The CoM and CoPtM catalysts were prepared by the method described previously [23,24,29]. Briefly, the zeolite NaM was ion exchanged using $\text{Co}(\text{CH}_3\text{COO})_2$ solution then filtered, washed and dried at 393 K. The CoM catalyst was obtained by heating the Co-exchanged sample up to 673 K in O_2 flow at a rate of 2 K min^{-1} . The temperature rise was interrupted at 393 and 493 K each time for 1.5 h and finally kept at 673 K for 8 h. The CoPtM was prepared from an aliquot portion of the Co-exchanged sample applying a second ion exchange using a $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solution. The doubly exchanged solid was heated in O_2 flow at a rate of 0.5 K min^{-1} up to 623 K and kept at this temperature for 2 h.

The Co, Pt and Na contents of the preparations were determined by atomic absorption spectroscopy. The CoM catalyst contained 2.8 wt% Co and 2.45 wt% Na. The Co, Pt, and Na content of the CoPtM catalyst was 2.7, 0.54, and 1.75 wt%, respectively. The Co/Pt atomic ratio in the CoPtM sample was 15.

2.2. Operando DRIFTS-MS experiments

The spectral analysis of the catalyst surface during the catalytic reaction was carried out using a Nicolet 5PC spectrometer equipped with a COLLECTORTM II diffuse reflectance mirror system and a high temperature/high pressure DRIFTS reactor cell (Spectra-Tech, Inc.). The reactor cell was connected to a quadrupole mass spectrometer (MS) for real-time MS analysis of the DRIFTS reactor effluent.

The sample cup of the cell was filled with about 20 mg of powdered sample. Prior to the experiments, catalyst samples were pre-treated in situ as follows: the HM was obtained by heating up the NH_4^+ -form in a diluted O_2 flow (10% O_2/He , $30 \text{ cm}^3 \text{ min}^{-1}$) to 773 K at a rate of 10 K min^{-1} and kept at the final temperature for 1 h. The CoM sample was heated up to 723 K at a rate of 5 K min^{-1} in a flow of 10% O_2/He ($30 \text{ cm}^3 \text{ min}^{-1}$) and kept at this temperature for 1 h. The CoPtM sample was first pre-treated as the CoM sample; then it was cooled to 298 K in He-flow and heated up again to 623 K at a rate of 5 K min^{-1} in flowing H_2 in order to reduce the Pt. Finally, each catalyst sample was purged with He at 773 K for 15 min and cooled to the lowest applied reaction temperature, i.e., usually to 573 K.

The background spectrum of the catalyst powder was taken at the same selected reaction temperatures in He-flow. This spectrum was subtracted from the corresponding spectrum collected with reactant mixture, flowing through the reactor

cell. The activated catalyst was contacted with a flow of a gas mixture, containing either 4000 ppm NO/He, or 4000 ppm NO/2% O₂/He, or 4000 ppm CH₄/2% O₂/He, or 4000 ppm NO/4000 ppm CH₄/He, or 4000 ppm NO/4000 ppm CH₄/2% O₂/He. In all cases, the GHSV for nitric oxide varied between 6000 and 60,000 h⁻¹ and the temperature between 573 and 773 K. Further on, these gas mixtures are to be mentioned without referring to the concentrations and the presence of balance He. The low feed rates, needed to get the specified GHSV for the small amount of catalyst in the DRIFTS reactor, was obtained by splitting the flow of the gas mixture before the DRIFTS cell and permitting only a fixed fraction to pass through the cell. In those experiments when O₂ was removed from the reactant mixture the concentration of the balance He was increased to keep the NO and CH₄ partial pressures of the gas mixture unchanged.

3. Results and discussion

3.1. Surface species formed from NO or from NO/O₂ mixture

Infrared spectra of surface species formed from NO or NO/O₂ mixture over CoM and CoPtM are shown in Figs. 1 and 2, respectively. From the adsorption of NO at 573 K strong infrared absorption bands were obtained, identified as bands of mononitrosyl (CoM: 1937 cm⁻¹; CoPtM: 1935 cm⁻¹) and dinitrosyl (CoM: 1897 and 1805 cm⁻¹; CoPtM: 1902 and 1807 cm⁻¹) groups, bound to Co²⁺ ions (Figs. 1A and 2A, spectra a) [10,19,30]. At higher temperatures (673 and 773 K), the partial conversion of NO to N₂ was detected by MS, while no dinitrosyl bands could be traced by DRIFTS. The mononitrosyl bands appeared with lower integrated absorbance

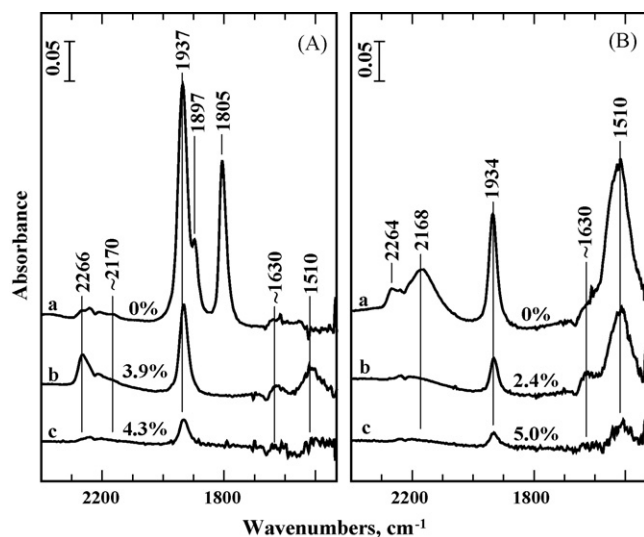


Fig. 1. DRIFT spectra of surface species formed over CoM catalyst under continuous flow of (A) 4000 ppm NO in He and (B) 4000 ppm NO + 2% O₂ in He at GHSV = 60,000 h⁻¹ and *T* = 573 K (spectrum a), 673 K (spectrum b), and 773 K (spectrum c). Each spectrum was collected after 5 min time on stream. The values shown in percent indicate the NO conversion to N₂ under the given reaction conditions.

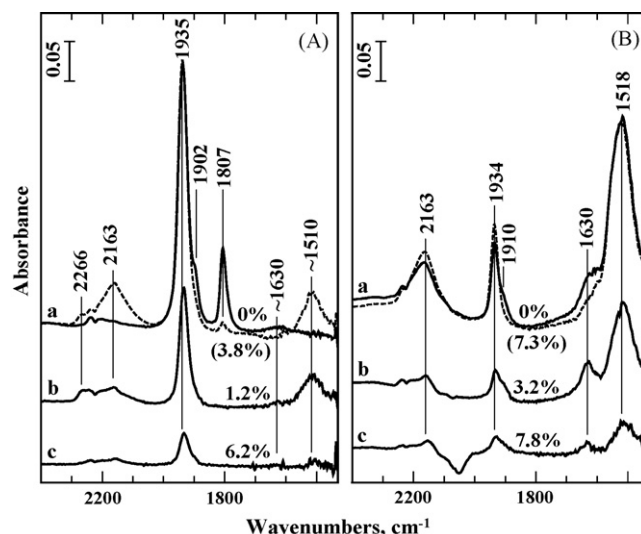


Fig. 2. DRIFT spectra of surface species formed over CoPtM catalyst under continuous flow of (A) 4000 ppm NO in He and (B) 4000 ppm NO + 2% O₂ in He at GHSV = 60,000 h⁻¹ and *T* = 573 K (spectrum a), 673 K (spectrum b), and 773 K (spectrum c). Dotted lines indicate spectra collected at GHSV = 6000 h⁻¹. Each spectrum was collected after 5 min time on stream. The values shown in percent indicate the NO conversion to N₂ under the given reaction conditions.

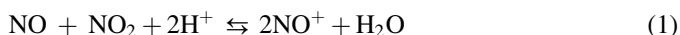
than at 573 K. New absorption bands developed at about 1510 and 1630 cm⁻¹, at 2170–2163 cm⁻¹ and at 2266 cm⁻¹ (Figs. 1A and 2A). When the GHSV of the reactant NO was decreased from 60,000 to 6000 h⁻¹ the NO conversion became measurable also at 573 K over the CoPtM catalyst. Simultaneously, the infrared peaks at 2163 and at 1510 cm⁻¹ gained, while the dinitrosyl bands lost integrated absorbance (Fig. 2A, dashed line). The mononitrosyl band at 1935 cm⁻¹ did not change. These results strongly suggest that the dinitrosyl species are the transition states of the NO conversion to N₂ and O₂, and moreover, that the appearance of the new surface species is related to the NO conversion. Obviously, the formation of the mentioned new species is more pronounced in the presence of O₂ over both catalysts (Figs. 1B and 2B).

As far as the new bands are concerned, previous studies reported the development of similar IR bands from adsorption of NO or NO/O₂ gas mixture on CoY and CoZSM-5 catalysts. The bands in the 2130–2270-cm⁻¹ region were assigned to nitrosonium ions, NO⁺, bound to the zeolite at different framework locations. The bands in the 1500–1650-cm⁻¹ region were attributed to NO_x⁻ species, particularly to differently-bound nitrate, NO₃⁻, species. The band at around 1630 cm⁻¹ was assigned to the δ(H₂O) bending mode of adsorbed water [30–32].

The stability of the surface species obtained from adsorption and conversion of NO at 573 K (Fig. 2A and B, dashed lines) was tested. A He flush at 573 K was found to eliminate the NO⁺ band, but it could not remove the bands from the 1500 to 1650 cm⁻¹ region. However, when the temperature jumped to 773 K, all the bands disappeared from the spectrum, while the MS measurement showed the appearance of NO and O₂ in the He flow in about equal amounts. The latter results support that the band at about 1518-cm⁻¹ can stem from surface NO₃⁻.

Obviously, the NO_3^- is more strongly bound than the NO^+ . This observation is in agreement with earlier results [30–32].

The mechanism of NO^+ and NO_3^- ion formation, which probably depends on the type of catalyst, is a matter of discussion [30–34]. It has been shown [31] that Brønsted acid sites participate in the reaction, generating NO^+ ions (Eq. (1)). Eq. (1) provides explanation for the appearance of the $\delta(\text{H}_2\text{O})$ band at 1630 cm^{-1} and also for the easy NO desorption, occurring possibly in the reverse process of Eq. (1):



The possibility that NO_3^- ions could be generated with the participation of superoxide ions, formed in the presence of oxygen, was also considered (Eq. (2)) [4].



It was also shown that on some catalysts, for instance, on multivalent cationic forms of some zeolites or on $\text{WO}_3\text{-ZrO}_2$ mixed oxide the simultaneous NO^+ and NO_3^- formation by dissociative chemisorption (Eq. (3)) can be energetically favored [33–35].



The bands of the ionic species were found to have about the same intensity ratio at different coverage (Figs. 1B and 2B), suggesting that formation of NO^+ and NO_3^- from NO/O_2 mixture are concurrent coupled processes both on the CoM and CoPtM catalysts. Under the applied conditions NO_2 can always be formed in the equilibrium proportions from Eq. (4):

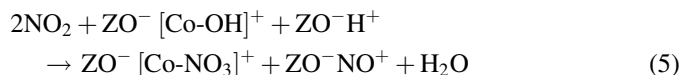


Besides, it is well-known that the presence of Pt^0 favored Eq. (4).

It is important to note that NO_2 was never observed in the gas phase during the experiments, suggesting that NO_2 , if formed, disproportionates and gives surface bound ionic species (Eq. (3)). In the absence of oxygen, NO_2 is obtained if the catalyst can oxidize NO and if the catalyst induces NO conversion either to N_2O and NO_2 or, at higher temperatures, to N_2 and O_2 [35]. The dinitrosyl species are possible intermediates of the two reactions [10]. In the latter case, the O_2 and the unconverted NO can form NO_2 through Eq. (4). Nevertheless, it is not surprising that the formation of NO^+ and NO_3^- is more pronounced from a NO/O_2 reaction mixture than from NO alone (Figs. 1 and 2).

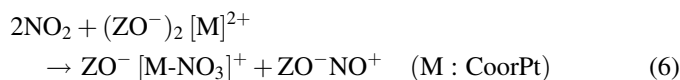
During the thermal dehydration of the Co-zeolite $[\text{Co-OH}]^+$ and bridged Brønsted acid OH groups are generated by the heterolytic dissociation of H_2O on the Co^{2+} ions [24]. In contact with NO or NO/O_2 negative ν_{OH} bands were observed at 3610 and 3654 cm^{-1} (not shown). These negative bands are attributed to the partial consumption of the bridged and the Co^{2+} -linked hydroxyls, respectively. In view of these findings, we rationalize the simultaneous formation of NO^+ and NO_3^-

over the Co-containing zeolites according to Eq. (5):



where ZO^- represents one of the negative charges on the zeolite framework. Eq. (5) is analogous to Eq. (3) but points out that water is also formed in the process.

A similar reaction can also take place on the cation exchanged sites according to:



The cation exchanged sites where the dinitrosyl species were adsorbed in the absence of oxygen would be responsible for NO^+ and NO_3^- formation as O_2 was added.

3.2. Surface species formed from CH_4/O_2 mixture

Under the applied reaction conditions nothing else but the products of full oxidation were obtained from the catalytic reaction of methane with oxygen over the CoM and CoPtM catalysts. The surface species on the working catalysts gave overlapping infrared bands between 1450 and 1750 cm^{-1} (Fig. 3). The strongest band at 1630 cm^{-1} stems from the adsorbed combustion product H_2O ($\delta(\text{H}_2\text{O})$ vibration), while the bands at 1664 , 1595 , and 1560 cm^{-1} can be attributed to carbonate species formed from product CO_2 [36]. At short contact time ($\text{GHSV} = 60,000\text{ h}^{-1}$), the methane conversion remained low over both catalysts (Fig. 3). However, at longer space time ($\text{GHSV} = 6000\text{ h}^{-1}$) the conversion reached 10.2

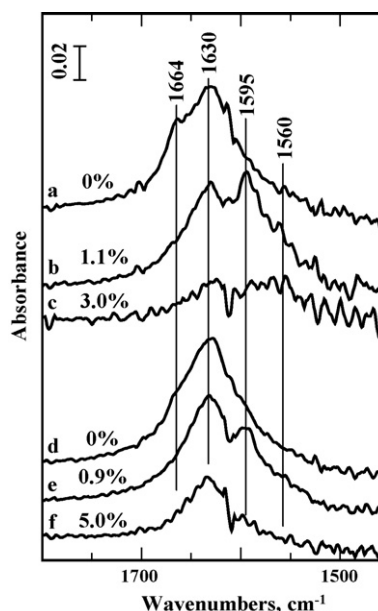


Fig. 3. DRIFT spectra of surface species formed under continuous flow of 4000 ppm CH_4 + 2% O_2 in He at $\text{GHSV} = 60,000\text{ h}^{-1}$ over CoM (spectra a–c) and CoPtM (spectra d–f) at $T = 573\text{ K}$ (a and d), 673 K (b and e), and 773 K (c and f). Each spectrum was collected after 5 min time on stream. The values shown in percent indicate the CH_4 conversion to the oxidation products CO_2 and H_2O under the given reaction conditions.

and 26.4% over the CoM and CoPtM catalysts, respectively (the corresponding spectra are not shown). Because of the presence of Pt, the activity of the CoPtM catalyst is significantly higher for the methane oxidation than the activity of the CoM catalyst.

3.3. Surface species formed from NO/CH₄ mixture in presence and absence of O₂

3.3.1. H-mordenite

A strong asymmetric infrared band, centered at 2225 cm⁻¹, developed when NO/CH₄/O₂ was flowed over the HM catalyst (Fig. 4). In agreement with previous studies [31,37,38] reporting about the rise of a similar band from adsorption of NO/O₂ or NO₂ on H-zeolites, the band at 2225 cm⁻¹ was assigned to the stretching vibration of nitrosonium, NO⁺, ion. We found that nitrosonium ions and water were formed together. The water formation is clearly indicated by the appearance of three broad bands, the so called ABC triad, around 2900, 2400, and 1700 cm⁻¹ (not labeled). The triad stems from the residual Brønsted acid OH groups perturbed by H-bound water (Fig. 4, spectrum a) [38,39]. A weak δ(H₂O) band also appeared at ~1630 cm⁻¹. Eq. (1) describes the possible surface reaction. In the process NO⁺ ions must become charge balancing cations of the zeolite [31].

Two overlapping negative bands can be distinguished in the ν_{OH} region at 3610 and 3570 cm⁻¹ (Fig. 4), which have been assigned to the consumption of the acidic OH-groups in the mordenite main channels and in the side pockets, respectively, in the reaction according to Eq. (1) [40]. The stronger negative band at 3570 cm⁻¹, relative to that at 3610 cm⁻¹, suggests that primarily the hydroxyl groups in the side pockets were involved in the process, i.e., established H-bond with the water that was formed in the reaction, or a fraction of the acidic hydrogen

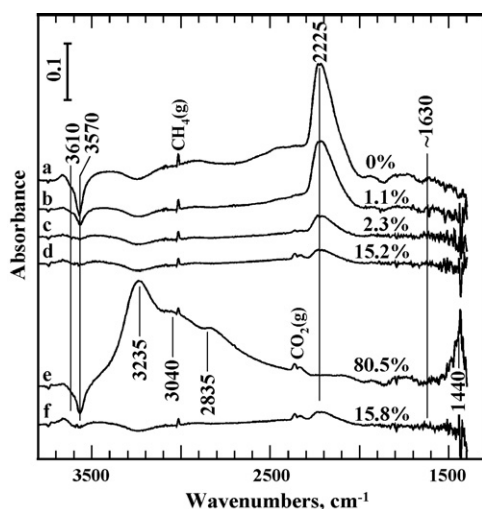


Fig. 4. DRIFT spectra of surface species formed over HM catalyst during the CH₄/NO-SCR reaction. Spectra were measured at 573 K (a), 673 K (b), and 773 K (c–f) and at GHSV = 60,000 h⁻¹ (a–c) and 6000 h⁻¹ (d–f). Reactant mixture contained 4000 ppm NO + 4000 ppm CH₄ + 2% O₂ in He, except for spectrum e, where O₂ was replaced by equal amount of He carrier gas. Spectra were collected after 5 min time on stream. The values shown in percent indicate the NO conversion to N₂ under the given reaction conditions.

atoms were replaced by NO⁺. From the absorbance drop of the OH-bands, we estimated that about 7% of the Brønsted acid hydroxyl groups were involved in the mentioned interactions at 573 K.

The asymmetry of the NO⁺ band suggests that it comprises bands at slightly different frequencies. The stronger component band is at the high frequency side (Fig. 4). This can indicate that the substitution of some of the protons for NO⁺ is favored. The preferable locations of NO chemisorption must be the side pockets [37,38]. The increasing temperature (573–773 K), as expected, reversed the reaction of Eq. (1) [37]. At higher temperatures, the NO⁺ band became weaker while the band of the acidic hydroxyls gradually restored (Fig. 4, spectra a–d). In the given temperature range, the NO conversion increased from zero to 2.3%. When the GHSV of the reactant was decreased from 60,000 to 6000 h⁻¹ at 773 K, the conversion increased to 15.2% (Fig. 4, spectrum d). A lower steady-state NO⁺ concentration corresponds to a higher NO conversion to N₂. The space-time dependence of the NO⁺ coverage substantiates that one of the reaction intermediates can be the NO⁺ species.

When O₂ was removed from the reactant mixture, the conversion of NO increased dramatically from 15.2% up to 80.5% over the HM sample and three broad bands developed at 3235, 3040, and 2835 cm⁻¹ (Fig. 4, spectrum e). These bands are characteristic features of the NH₄⁺-form zeolites, obtained, for instance, from adsorption of NH₃ on H-zeolite [37]. The δ_{NH} vibration of the NH₄⁺-cation must be at about 1450 cm⁻¹ [41]. During reaction, a similar band is clearly visible at 1440 cm⁻¹ on the spectrum of the HM catalyst (Fig. 4, spectrum e).

3.3.2. Co- and Co,Pt-mordenite

Before the onset of the NO conversion, similar surface species were formed on the catalysts from the NO/CH₄/O₂ and the NO/O₂ gas mixtures (cf. Figs. 5 and 6, spectra a, and Fig. 1B and 2B). The stretching band of the Co-mononitrosyl was near 1934 cm⁻¹, while the NO⁺ and NO₃⁻ species gave rise to bands in the 2170–2163 cm⁻¹ frequency region and at about 1516 cm⁻¹, respectively. The δ(H₂O) band of adsorbed water also appeared at 1630 cm⁻¹. In contrast to the spectra obtained for the HM catalyst, broad spectral features were observed in the 3500–3000 cm⁻¹ frequency range for the Co-, and CoPtM catalysts (Figs. 5 and 6, spectra a–d). The broad band comes from water, physically adsorbed on Lewis acid site metal cations [39]. The development of the negative ν_{OH} absorption bands at 3654 and 3610 cm⁻¹ support the involvement of the [Co-OH]⁺ and the zeolite Brønsted acid sites in the formation of NO⁺ and NO₃⁻ species and the adsorbed water (Figs. 5 and 6). Because of the presence of the broad water band these negative bands appear less clearly than in the corresponding spectra of the HM catalyst. The formation of NO⁺ and NO₃⁻ can proceed by the disproportionation of NO₂ according to Eq. (5).

The found decrease of the integrated absorbance of the bands shows that concentration of the adsorbed species, developed from the contact of the catalyst and the flowing gas mixture, decreased significantly when the temperature was raised. The change can represent the temperature dependence of the adsorption equilibrium. However, the concentration of

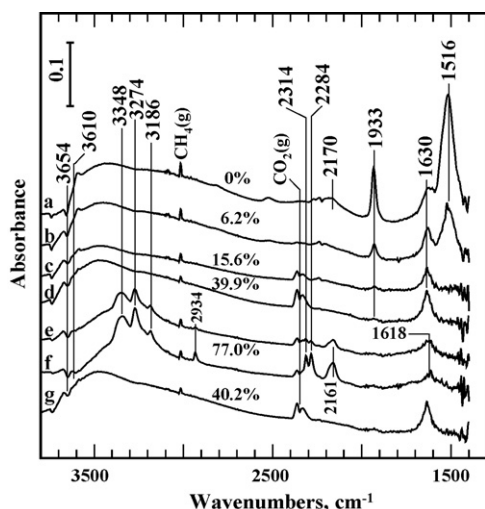


Fig. 5. DRIFT spectra of surface species formed over CoM catalyst during the CH₄/NO-SCR reaction. Spectra were measured at 573 K (a), 673 K (b), and 773 K (c–g) and at GHSV = 60,000 h⁻¹ (a–c) and 6000 h⁻¹ (d–g). Reactant mixture contained 4000 ppm NO + 4000 ppm CH₄ + 2% O₂ in He, except for spectra e and f, where O₂ was replaced by equal amount of He carrier gas. Spectra were collected after 5 min (a–e, g) or 30 min time on stream (f). The values shown in percent indicate the NO conversion to N₂ under the given reaction conditions.

those species, which are reaction intermediates, must depend also on the kinetic parameters of the proceeding reactions and the residence time. It was found, for instance, that the concentration of the NO⁺, and NO₃⁻ surface species, developing from the contact of the NO/O₂ mixture and the catalyst, significantly decreased with increasing temperature, while the level of NO conversion remained low (Figs. 1B and 2B). However, a much lower concentration of the same surface species was obtained from the contact of the corresponding catalyst and NO/CH₄/O₂ mixture at the same temperature because of the higher NO conversion in the presence of the reducing agent (Figs. 5 and 6).

Upon substitution of the O₂ component for He in the NO/CH₄/O₂ flow, reacting at 773 K over the CoM catalyst, new

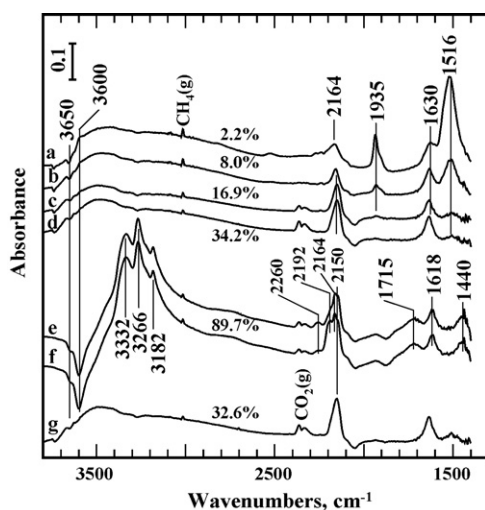


Fig. 6. DRIFT spectra of surface species formed over CoPtM catalyst during the CH₄/NO-SCR reaction. The details are same as given for Fig. 5.

bands developed in the spectrum at 3348, 3274, and 3186 cm⁻¹ (Fig. 5, spectrum e). The new bands gained in intensity in time (Fig. 5, spectrum f). Using CoPtM catalyst in the experiment similar but stronger bands developed at 3332, 3266, and 3182 cm⁻¹ (Fig. 6, spectra e and f). The appearance of these bands was accompanied by a dramatic increase in the conversion of NO over both catalysts. The frequency of the new bands corresponds to the characteristic ν_{NH} frequencies of NH₃, coordinately bound to Lewis acid sites [42,43], i.e., to NH₃, bound to Co²⁺ sites. It can also be seen, particularly in the spectra obtained for the CoPtM catalyst that these relatively sharp bands appear superimposed on broader bands. The ν_{NH} region of the DRIFT spectra obtained from the conversion of NO/CH₄ over the CoM, CoPtM, and HM catalysts at 773 K are shown in Fig. 7. The sharper bands of the coordinately bound NH₃ at 3332, 3266, and 3182 cm⁻¹ seem to be superimposed on broader bands at 3235, 3040, and 2835 cm⁻¹. The latter bands are attributed to NH₃, chemisorbed on protonic sites, i.e. to NH₄⁺-cations. The δ_{NH} region of the spectra provides supports for the above band assignments (Figs. 5 and 6). The band observed at 1618 cm⁻¹ corresponds most probably to the δ_{NH} band of coordinately bound NH₃ [41]. It is to be noted, however, that the δ_{NH} band can overlap with the δ(H₂O) band of adsorbed water. The δ_{NH} band of the NH₄⁺ ion is clearly visible at ~1440 cm⁻¹ (Fig. 6, spectra e and f). These results strongly suggest that NH₃ is commonly formed on the catalysts, studied in the absence of O₂ and accumulates on the catalyst surface by binding coordinately to Lewis acid Co²⁺ sites and forming NH₄⁺-cations on the Brønsted acid sites. Under reaction conditions, the accumulation proceeds until the steady-state

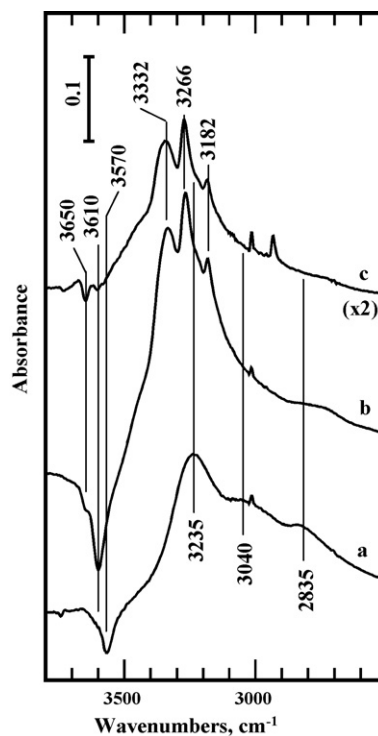


Fig. 7. DRIFT spectra in the ν_{OH} and ν_{NH} regions collected after 5 min time on stream under continuous flow of 4000 ppm NO + 4000 ppm CH₄ in He at 773 K and GHSV = 6000 h⁻¹ over HM (a), CoPtM (b), and CoM (c) catalysts.

concentration of the species is reached. Only NH_4^+ species were generated over the HM catalyst, which contains almost exclusively Brønsted acid sites [24].

Upon removal of O_2 from the reaction mixture, a band emerged also at 1715 cm^{-1} in the spectrum of the CoPtM catalyst (Fig. 6, spectra e and f). Previous NO-SCR studies assigned this band to $\nu_{\text{C}=\text{O}}$ vibration of carbonyl species [11,35,44]. The admixing of O_2 in the NO/ CH_4 flow quickly removed the adsorbed NH_3 and the carbonyl species from any of the catalysts (Fig. 4, spectrum f; Figs. 5 and 6, spectra g). Results suggest that the surface-bound NH_3 is highly susceptible to oxidation in the presence of NO and O_2 .

In addition to the above mentioned bands, nitrile (CN^-) and isocyanate (NCO^-) bands could be observed at characteristic absorption frequencies in the $2300\text{--}2160\text{ cm}^{-1}$ spectral range [45]. While NH_3 species were formed also over the HM sample, nitriles or isocyanates were generated only over the Co-containing catalysts (Figs. 5 and 6). Over the CoM sample surface species were obtained from the NO/ CH_4 mixture, giving a pair of bands at 2314 and 2284 cm^{-1} . These bands closely resemble those, obtained before from the adsorption of acetonitrile over zeolite Fe/ZSM-5 [46]. Thus, we assigned the observed bands to the ν_{CN} vibration of adsorbed acetonitrile or, more generally, to bands of an adsorbed saturated aliphatic nitrile type surface species. The latter assignment is supported by the ν_{CH} band at 2934 cm^{-1} (Fig. 5, spectra e and f). The assignment of the asymmetric absorption band at about 2160 cm^{-1} is dubious at present. It can be attributed either to nitrile or isocyanate species (Fig. 5) [45]. Since these species could be quickly removed in reaction with O_2 , they could be considered also as active intermediate species of the NO-SCR reaction (Fig. 5, spectrum g).

At the onset of the SCR reaction over the CoPtM catalyst a band developed at about 2150 cm^{-1} . This band hardly changed, while the conversion depended on the presence or absence of O_2 in the reaction mixture (Fig. 6, spectra c–e). The species, giving rise to this band, is not known at present. Since it developed in the frequency region of the ν_{CN} and ν_{NCO} vibrations, it is tentatively assigned to a kind of nitrile or isocyanate species. Whatever this surface species is, it must be a spectator species of the reaction.

Upon removal of O_2 from the NO/ CH_4/O_2 flowing mixture, bands developed at 2260 , 2192 and at about 2164 cm^{-1} . The latter two bands gained intensity in time (Fig. 6, spectra e and f). Re-addition of O_2 to the reaction mixture resulted in a quick elimination of these bands (Fig. 6, spectrum g). The assignment of these bands seems to be well established. Similar bands were obtained from the conversion of the NO/ CH_4 mixture and from the reaction of CH_3NO_2 , considered as a possible intermediate on the NO-SCR reaction, and O_2 over a Co-ZSM-5 catalyst [10,47]. The bands were assigned to different $\text{Al}^{3+}\text{-NCO}$, $\text{Si}^{4+}\text{-NCO}$, $\text{Co}^{2+}\text{-NCO}$, and $\text{Co}^{2+}\text{-CN}$ species. We attribute the small band at 2260 cm^{-1} to $\text{Al}^{3+}\text{-NCO}$, i.e. to isocyanate species attached to the zeolite framework, the band at 2192 cm^{-1} to $\text{Co}^{2+}\text{-NCO}$ species, and the band at about 2164 cm^{-1} to a second type of $\text{Co}^{2+}\text{-NCO}$ species or to $\text{Co}^{2+}\text{-CN}$ species. Obviously, these nitrile and isocyanate species are different

from those formed over the CoM catalyst. It should be mentioned that the 2164 cm^{-1} band is at the absorption frequency of the NO^+ species (Fig. 2, band at 2163 cm^{-1}). However, NO^+ species gave much weaker and broader bands even at much lower NO conversion. Therefore, the assignment of this stronger band to NO^+ species, generated at high NO conversion, would be unreasonable. The nitrile and isocyanate surface species react with O_2 , suggesting that these species can be active surface intermediates of the NO-SCR reaction (Fig. 6, cf. spectra f and g).

3.4. Transient responses of the CH_4/NO -SCR reaction on the change of the O_2 concentration

The real-time change of the CH_4 , NO, O_2 and N_2 concentrations in the reactor effluent are given in Fig. 8A. The IR spectrum of the CoPtM catalyst (Fig. 8B) was recorded at the times on stream, marked in Fig. 8A. The presence or absence of O_2 affects the chemistry on the catalyst surface and, thereby, the NO conversion. On the sudden removal of O_2 from the reaction mixture, while both the partial pressure and the flow rate of the reactants were maintained, the conversion of NO sharply increased from 32.8 to 91.5%. In contrast, the CH_4 conversion decreased from 48.1 to 23.8% gradually. Similarly,

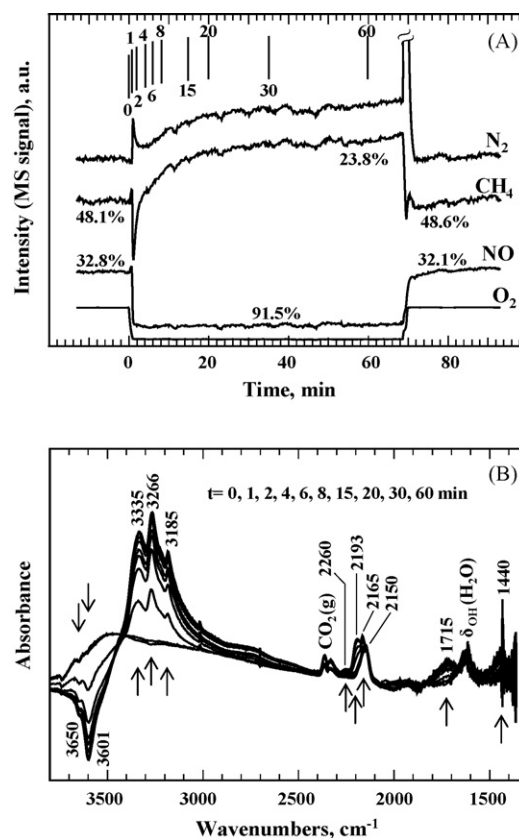


Fig. 8. Operando DRIFTS-MS examination of the transient response upon replacement of O_2 for He in the reaction mixture of 4000 ppm NO + 4000 ppm CH_4 + 2% O_2/He during CH_4/NO -SCR reaction on CoPtM catalyst at 773 K and GHSV = 6000 h^{-1} : (A) MS signals of CH_4 , NO, and O_2 reactants and N_2 and (B) the development of the DRIFT spectra. The values shown in percent indicate the NO and CH_4 conversion under the given reaction conditions.

a gradual concomitant increase was detected in the N_2 concentration. Steady-state surface and effluent compositions were reached in about 10 min. Notice the development of the ν_{NH} bands in the $3400\text{--}2800\text{ cm}^{-1}$ region, the δ_{NH} band at about 1440 cm^{-1} and the $\nu_{C=O}$ band of the carbonyl species at about 1715 cm^{-1} (Fig. 8B). In the initial period after O_2 removal, a quick accumulation of surface NH_3 and carbonyl moieties occurred, as indicated by the increasing integrated absorbance of the corresponding bands. These species were shown to form more rapidly over CoPtM than over CoM catalyst (cf. Figs. 5 and 6). It must be noticed that the concentration of adsorbed NH_3 parallels the N_2 concentration in the product mixture (Fig. 8A). This result suggests that NH_3 is a key intermediate of the NO-SCR reaction with methane.

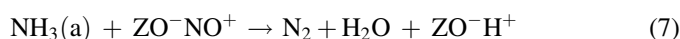
The re-addition of O_2 induced a large surge in the N_2 MS signal as shown in Fig. 8A, and also in the signals of H_2O and CO_2 (not shown). Then, the concentration of N_2 and the conversion of NO quickly reached the steady-state values recorded at the very beginning of the experiment. This change was accompanied by the disappearance of the NH_3 and carbonyl infrared bands in about 30 s (not shown in Fig. 8B for clarity). These results suggest that adsorbed NH_3 is highly reactive and is quickly oxidized by O_2 to N_2 and H_2O . The absorption band of the carbonyl species changes together with the NH_3 bands. The surface carbonyl must be the intermediate of the methane oxidation to CO_2 .

As expected, nitrile (CN^-) and/or isocyanate (NCO^-) bands appeared at 2260 , 2193 and 2165 cm^{-1} , when the oxygen was removed from the reacting mixture. Interestingly, these bands appeared more than 15 min later than the ν_{NH} bands. The relevant spectral region is shown enlarged in Fig. 9. An additional band of a spectator species, already discussed in relation to Fig. 6, appeared at 2150 cm^{-1} . The nitrile and isocyanate species, which were slowly generated upon removal of O_2 from the reacting gas stream (Fig. 9, spectra a–h) and were quickly eliminated when O_2 was added back into the gas

stream (cf. Fig. 9, spectra i and j), could be substantiated as reaction intermediates.

3.5. Mechanistic considerations

Formation and accumulation of ammonia on the catalyst surface can be readily detected not only over the Co-containing catalysts but also over the HM catalyst, if the NO/ CH_4 reactant mixture does not contain excess amount of oxidizing agent such as oxygen (Figs. 4–6). The other commonly formed surface species was NO^+ . The adsorbed ammonia and the NO^+ were substantiated as key intermediates of the NO-SCR reaction. The formation of N_2 involves the interaction of these intermediates according to Eq. (7). In the reaction, NO^+ is annihilated and Brønsted acid sites are restored to maintain the balance of the positive and negative charges on the catalyst.



This proposed mechanism is in agreement with that suggested by Chen et al. [4]. Accordingly, the nitrogen is formed in the reaction of species containing N-atoms in 3+ and 3– formal oxidation states. The formation of NH_3 intermediate can be obtained in the direct reaction of NO and methane or in the more facile reaction between NO_2 and methane. The different possible reaction routes to get NO_2 were discussed before. The applied spectroscopic method is not able to detect all the intermediates or transition states of the process of ammonia formation. Previous studies substantiated that nitromethane (CH_3NO_2) was one of the intermediates [12,20]. It was shown that nitromethane readily decomposes above 523 K to give CO_2 and NH_3 and the latter is further converted to N_2 at temperatures above 623 K if NO and O_2 are also present [12]. Moreover, the reaction between $CH_3^{14}NO_2$ and $^{15}N^{18}O/O_2$ mixture was shown to give $^{14}N^{15}N$ [20]. Actually, these observations pointed out those mechanistic details of the N–N bond formation that was declared later by Chen et al. [4].

The focus of the present work was to clarify the role of excess oxygen in the CH_4/NO -SCR reaction. The conversion of NO was found to be much higher in the absence than in the presence of O_2 , which is in agreement with the results of Burch and Scire [48] and Bell and coworkers [49]. In the steady state, the NH_3 formation and consumption have to proceed with equal rate. O_2 competes with NO and NO_2 for the oxidation of methane. Moreover, it competes also with NO^+ in the oxidation of the active intermediate NH_3 . The lower NH_3 coverage in the presence of oxygen suggests that the rate of NH_3 formation governs the rate of N_2 generation. It follows from the reaction stoichiometry (Eq. (8)) that the NH_3 oxidation with intermediate NO^+ results in twice as much N_2 formation than the same reaction with O_2 . Therefore the negative effect of O_2 on the NO conversion can be explained by the participation of the O_2 in the consumption of the slowly generated intermediate NH_3 . The NO conversion could be enhanced by the presence of O_2 , if the NH_3 formation was fast and the rate of NH_3 oxidation governed by the rate of N_2 formation. The conditions, where O_2

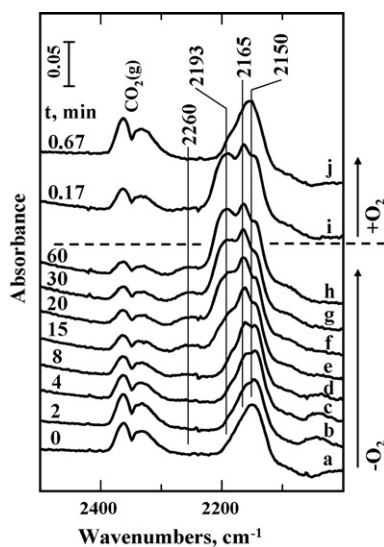
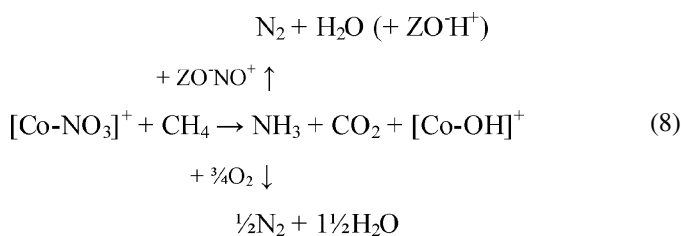


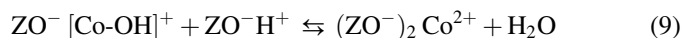
Fig. 9. The ν_{CN} region of the spectra shown in Fig. 8B obtained after removal of O_2 (spectra a–h) from and re-addition of O_2 (spectra i and j) into the reactant mixture.

could enhance the activity obviously did not prevail in our studied systems. In contrast, over a different catalyst and under different reaction conditions of the NO-SCR reaction with methane, Li et al. [5] observed that oxygen had a positive effect over the activity. Nevertheless, clarifying the role of O₂ in the CH₄-SCR of NO under different reaction conditions and catalysts deserves further investigation.

It seems to be important that NO⁺ was formed over all the studied zeolite samples but surface NO₃⁻ was formed only over the Co-containing catalysts according to the reactions of Eqs. (5) and (6). Although the surface NO₃⁻ is a thermally stable species even in the presence of adsorbed water [33], it has been found that it can readily react with methane or other hydrocarbons at relatively low temperature (<523 K) giving N₂ and CO₂ as major reaction products [9,32]. It was also reported that only monodentate nitrates show reactivity towards methane [32]. The participation of surface NO₃⁻ in the NO-SCR reaction is obvious (Figs. 5 and 6). Considering that surface NO₃⁻ species were formed according to Eqs. (5) and (6), we propose that the formation of N₂ may also proceed according to Eq. (8).



Thus, the possibility of the formation of NO₃⁻ on the Co-zeolites opens a reaction route to the more rapid NH₃ generation. The catalytic cycle is closed by the facile oxidation of ammonia, in which process the active sites of NO₂ disproportionation are regenerated (Eqs. (5) and (6)). Most of the product water is released by the catalyst, however, a fraction of the water, depending on the reaction temperature, remains bound to the surface, where it can generate hydroxyl groups by dissociation over the divalent exchange cations. Two hydroxyls of different characters, acidic and basic, create an active ensemble with a Co²⁺ cation. If the reaction



is shifted to the right side, for instance at high reaction temperature, the formation of the NO₃⁻ and NO⁺ intermediates must proceed predominantly according to the reaction of Eq. (6).

The generation of NO₂ and, thereby, that of NO₃⁻ is promoted by the presence of O₂. However, over H-mordenite the NO₂ disproportionation cannot proceed. Thus, O₂ only inhibits the NO-SCR, as discussed above, but its promoting effect cannot appear at all. This explains why the H-mordenite shows comparable activity to the Co-containing samples in the absence of O₂ in the reaction mixture, while the Co-mordenites show significantly higher activities in the presence of O₂ in the reaction mixture (Figs. 4–6).

Results substantiate that isocyanate and nitrile species are less important surface species in the NO-SCR reaction over the catalysts studied. Such species were not generated on the HM at all but appeared on the CoM and CoPtM samples, provided that no O₂ was admixed to the NO/CH₄ mixture. Interestingly, different isocyanate and nitrile species appeared over the different catalyst, i.e., over CoM and CoPtM. If they were important intermediates as suggested earlier [10], one would expect to get significantly different catalytic activities for the CoM and CoPtM catalysts carrying different isocyanate and nitrile species. Yasuda et al. [50] came to the conclusion that nitrile and isocyanate species formed in the NO-SCR reaction with methane over Co-ZSM-5 catalyst were most likely spectator by-products of the NO reduction. We also observed the formation of a spectator nitrile species over CoPtM sample, however, other nitrile and isocyanate species, observed over both Co-containing catalysts, were found to react with oxygen. In the reaction, these species can be converted into N₂ and CO₂ [10] and, therefore, to some extent may contribute to the NO conversion.

In sum, the above results substantiate that the prevailing reaction route in the NO-SCR reaction with methane passes through intermediates containing N-atoms in N³⁺ and N³⁻ oxidation states, namely NO⁺ and adsorbed NH₃. The latter is formed in the reaction of NO, NO₂ or NO₃⁻ and methane, where NO₂ or NO₃⁻ are believed to be better oxidizing agents of the methane than the NO.

4. Conclusions

NO⁺ and NH₃ are commonly formed surface species that are conceivably key reaction intermediates of NO-SCR with CH₄ over Co-, Co,Pt-, and H-mordenite catalysts. The rate governing step is the reaction of NH₃ formation. The NH₃ species are more rapidly formed over the Pt-containing Co-mordenite catalyst than over the others. The adsorbed NH₃ is more susceptible to oxidation to N₂ by NO/O₂ mixture than by either NO or O₂ only.

It follows from the stoichiometry of NH₃ oxidation that the reaction with NO results in a higher NO conversion to N₂ than the reaction with O₂. The favorable reaction path involves the reaction between surface NO⁺ and NH₃ leading to N₂, water and the restoration of the protonic sites of the zeolite. In the Co-containing samples formation of NO⁺ is accompanied by the formation of equal amount of NO₃⁻ attached to the Co²⁺ cations. It is proposed that surface NO₃⁻ further reacts with methane, which results in the formation of surface NH₃ and CO₂ and [Co-OH]⁺ sites. This new reaction pathway explains the significantly higher activity of the Co-containing mordenites with respect to that of H-mordenite in the CH₄/NO-SCR reaction in the presence of oxygen.

H-mordenite does not produce nitrile (CN) or isocyanate (NCO) surface species, while different NCO and CN is formed on Co- and Co,Pt-mordenite catalysts. Results suggest that at least some of these reaction intermediates react with oxygen, representing a different but subordinate route to N₂ formation.

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