The activation of NO and CH₄ for NO-SCR reaction over In- and Co-containing H-ZSM-5 catalysts

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ABSTRACT

The catalytic oxidation of NO to NO_2 (NO-COX) and the selective catalytic reduction of NO to N_2 by methane in the presence of excess oxygen (NO-SCR) was studied over zeolite In,H-, Co,H-, and Co,In,H-ZSM-5 catalysts. The catalysts were characterized by temperature-programmed H_2 reduction (H_2-TPR) and operando DRIFT spectroscopy. The cobalt was present in the catalysts predominantly in Co-oxide clusters, whereas the charge of the zeolite framework was balanced by H^+ and cationic indium species. The Brønsted acid sites promoted the NO-COX reaction; however, the Co-oxide clusters were much more active in this reaction. In absence of indium the catalysts were inactive in the NO-SCR reaction. The NO/NO_2 mixture formed in the NO-COX reaction was shown to further react with the $InO^+/(InOH)^{2+}$-zeolite resulting in the simultaneous formation of $InNO_3$ and NO^+ species. The Co-oxide clusters increased the rate of NO_2 generation and, thereby, the $InNO_3/NO^+$ formation. It was substantiated that an N-containing organic intermediate was obtained in the reaction of methane and nitrate group. Nitrogen was generated in the reaction between the obtained intermediate and the NO^+. The catalytic cycle must have been closed by the oxidation of In^+ to $InO^+/(InOH)^{2+}$ by the reactant mixture.

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1. Introduction

A number of studies showed that In-zeolites have significant activity in the NO-SCR reaction with methane [1–5], which reaction has great practical importance especially in the abatement of NO_x emission of boilers and engines fuelled by natural gas [1,6–8]. The reaction was suggested to proceed *via* redox mechanism. The active sites were described as In^+/InO^+ redox couples. During the NO-SCR reaction the oxidation state of the indium ion alternates between +1 and +3, while each ion keeps balancing one negative charge on the zeolite framework [9]. The activity could be enhanced by promoting the catalyst with a second metal, such as, Pt, Ir, Fe, Mn or Co [3,4,10–13]. The addition of cobalt gave especially good results [12,13]. The promoters were shown to increase the rate of the NO oxidation by O_2 ($2NO + O_2 \leftrightarrows 2NO_2$). It was suggested that this reaction was a crucial part of the reaction sequence, in which the NO was reduced to N_2 [2,3,14,15]. However, the origin of the considerable NO-SCR activity of some non-promoted catalysts, such as the In,H-zeolites, remained unclear. Resini et al. [16,17] even questioned that NO_2 had any role in the reactions that finally result in the conversion of NO to N_2. In lack of sufficient evidence for the possible reaction intermediates conflicting ideas were forwarded for the mechanism of N_2 formation [9,16,18–20].

The present study shows that NO and NO_2 must contact simultaneously with the In,H-zeolite to get active surface intermediate for the selective N_2-forming oxidation of methane in the presence of excess oxygen. Thus, regarding the NO-SCR reaction, it is favourable if catalyst promotes also the NO oxidation to NO_2 by O_2 because this reaction is kinetically hindered at the reaction temperature. Evidences are presented that Brønsted acid sites of In,H-zeolite can speed up the NO-COX reaction, although the catalyst containing cobalt oxide additive is much more active in this reaction.

2. Experimental

Zeolite In,H-ZSM-5 catalyst was prepared by the method of reductive solid state ion exchange (RSSIE). The zeolite H-ZSM-5 was our synthetic product having a Si to Al_F ratio of 33.0, where Al_F represents the framework aluminium content. It was mixed with In_2O_3 (Aldrich; 99.99%) applying intense co-grinding. The mixture was treated in H_2 flow at 773 K for 1 h, then cooled to room temperature in He flow and finally oxidized in O_2 flow at 673 K. The In/Al_F ratio of the obtained ZSM-5 catalyst was 0.33 (1.7 wt % In). Zeolite Co,H-ZSM-5 sample was prepared by applying a procedure similar to that described in Refs. [12] and [13]: H-ZSM-5 powder was mixed with cobalt acetate powder ($Co(CH_3COO)_2\cdot4H_2O$,

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Aldrich) applying intense co-grinding. The mixture was heated up at a rate of 10 K min^{-1} in a He flow (30 cm^3 min^{-1}) to 823 K and kept at this temperature for 2 h. The Co/Al$_F$ ratio of the sample was 0.125 (0.34 wt% Co). Bimetallic Co,In,H-ZSM-5 catalyst, containing as much In and Co as the above samples, was prepared from the In,H-ZSM-5 sample by Co-introduction following the above described procedure.

The oxidation state of the indium and cobalt cations was investigated by H$_2$-TPR method. A flow-through quartz microreactor (I.D. 4 mm) was used. About 150 mg of catalyst sample (particle size: 0.25–0.5 mm) was placed into the reactor and was pretreated in a 30 cm^3 min^{-1} flow of O$_2$ at 773 K for 1 h. The sample was purged then with N$_2$ flow at 773 K, cooled to room temperature in the same flow and was contacted then with a 30 cm^3 min^{-1} flow of 10% H$_2$/N$_2$ mixture. The reactor temperature was ramped up at a rate of 10 K min^{-1} to 1073 K, while the effluent gas was passed through a dry-ice trap and a thermal conductivity detector (TCD). The temperature and the corresponding H$_2$ concentration of the gas flow were recorded.

Catalytic measurements were carried out using a flow-through microreactor. About 100 mg of catalyst (particle size: 0.25–0.5 mm) was pre-treated in a 30 cm^3 min^{-1} flow of 10% O$_2$/He at 773 K for 1 h, then the sample was purged with pure He and cooled to 573 K. The catalytic activities were determined at temperatures between 573 and 873 K. The reaction was initiated by switching the He flow to a flow of 4000 ppm NO/4000 ppm CH$_4$/2% O$_2$/He mixture. The total flow rate of the reaction mixture was 100 cm^3 min^{-1} throughout the catalytic experiments corresponding to about a GHSV of 30,000 h^{-1} (calculated using a catalyst bulk density of 0.5 g cm^{-3}). The composition of the reactor effluent was monitored by on-line MS (VG ProLab, Fisher Scientific) having a quantitative analysis program. The instrument was calibrated with gas mixtures of known compositions. To avoid the difficulty coming from the overlapping $m/z = 28$ signal of N$_2$ and CO the total conversion of NO (X_{NO}) and conversion of NO to N$_2$ ($X_{NO \to N2}$) was calculated from the following equations:

$$X_{NO} \ (mol\%) = \frac{[NO]^0 - [NO]}{[NO]^0} \cdot 100\% \tag{1}$$

$$X_{NO \to N_2} \ (mol\%) = \frac{[NO]^0 - [NO] - [NO_2] - 2[N_2O]}{[NO]^0} \cdot 100\% \tag{2}$$

where [NO]^0 is the initial concentration of NO (4000 ppm), whereas [NO], [NO$_2$] and [N$_2$O] are the concentrations of the corresponding components in the reactor effluent. The conversion of methane was calculated from the methane concentration of the feed and the effluent. The catalytic oxidation of NO to NO$_2$ by oxygen (NO-COX) was carried out as the SCR reaction above, except that methane was omitted from the reactant mixture.

The surface species obtained from the NO-SCR reaction were studied *operando* by diffuse reflectance infrared Fourier transformation (DRIFT) spectroscopy using a Nicolet 5PC spectrometer, equipped with a COLLECTOR^{TM} II diffuse reflectance mirror system and a high-temperature/high-pressure DRIFT spectroscopic reactor cell (Spectra-Tech, Inc.). Concentrations of the reactants and products in the cell effluent were continuously monitored by on-line MS (VG ProLab, Fisher Scientific). The sample cup of the cell was filled with about 20 mg of powdered sample. Prior to the NO-SCR experiments, catalyst samples were pre-treated in situ in a 30 cm^3 min^{-1} flow of 10% O$_2$/He at 773 K for 1 h, then purged with He and cooled to 573 K. The activated catalyst was contacted with a flow of 4000 ppm NO/2% O$_2$/He or 4000 ppm NO/4000 ppm CH$_4$/2% O$_2$/He at temperatures in the range of 573–823 K. Further on, for simplicity, these gas mixtures are referred to as NO/O$_2$ and NO/CH$_4$/O$_2$ mixtures, respectively. The GHSV was ~30,000 h^{-1}. The
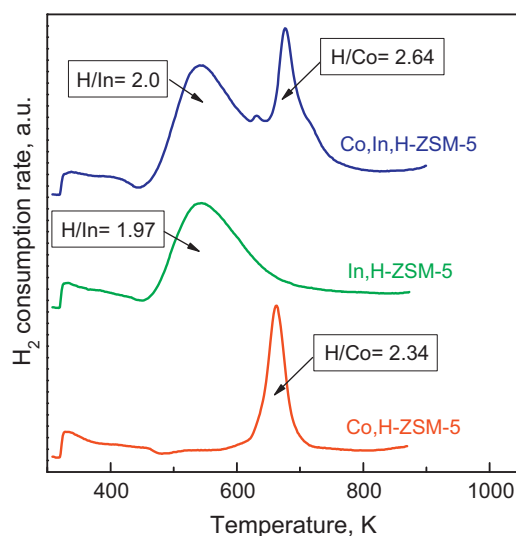

Fig. 1. Temperature-programmed reduction (H$_2$-TPR) of Co,H-ZSM-5, In,H-ZSM-5 and Co,In,H-ZSM-5 catalysts.

experimental set-up allowed abrupt switching between the reactant mixtures. The system reached a new steady state in about 4–8 min, as shown by the stabilized MS peak intensities. The spectrum of the catalyst powder was taken at every selected reaction temperature in contact with the reaction mixture and, in separate experiment, also in He-flow. Difference spectra were calculated by subtracting the latter spectrum from the corresponding spectrum of the catalyst and the reaction mixture in the cell.

3. Results and discussion

3.1. Oxidation states of cobalt and indium

H$_2$-TPR curves of monometallic (Co,H- and In,H-ZSM-5) and bimetallic (Co,In,H-ZSM–5) catalysts are shown in Fig. 1. A single peak appears on the TPR curve of the In,H-ZSM-5 at about 573 K. Earlier reports confirmed that the RSSIE generates In$^+$ cations that are oxidized by O$_2$ to In^{3+}, giving species [InO]$^+$ [21,22]. In the TPR experiment a 2e reduction was attained (H/In = 1.97) suggesting that the extra-framework oxygen ligand of the indium was removed and the In$^+$ state was recovered (Fig. 1). This result shows that our In,H-ZSM-5 preparation contains [InO]$^+$ as cations, which are the most often suggested active sites of NO-SCR over In-zeolites [2–5,10,15]. The corresponding reduction peak appeared also on the TPR curve of the Co,In,H-ZSM-5 sample indicating that the second metal (Co) did not influence the reduction of the In species (Fig. 1).

The Co,H-ZSM-5 sample gave reduction peak around 660 K. According to earlier TPR studies the cobalt reduction at this relatively low temperature corresponds to reduction of metal oxide clusters, such as CoO or Co$_3$O$_4$, which are most probably located on the outer surface of the zeolite crystallites [16,17,23,24]. The theoretical H/Co atomic ratio for the full reduction of CoO and Co$_3$O$_4$ (CoO·Co$_2$O$_3$) is 2.0 and 2.66, respectively. The H/Co values of 2.34 and 2.64 obtained for the reduction of Co,H-ZSM-5 and Co,In,H-ZSM-5, respectively, suggest that the cobalt oxide species in the catalysts is predominantly Co$_3$O$_4$.

3.2. Activity, selectivity and the role of active sites

The reduction of NO to N$_2$ by methane was found to proceed only in the presence of O$_2$. However, the selectivity of the NO conversion over Co,H-ZSM-5 and the In,H-ZSM-5 samples were drastically
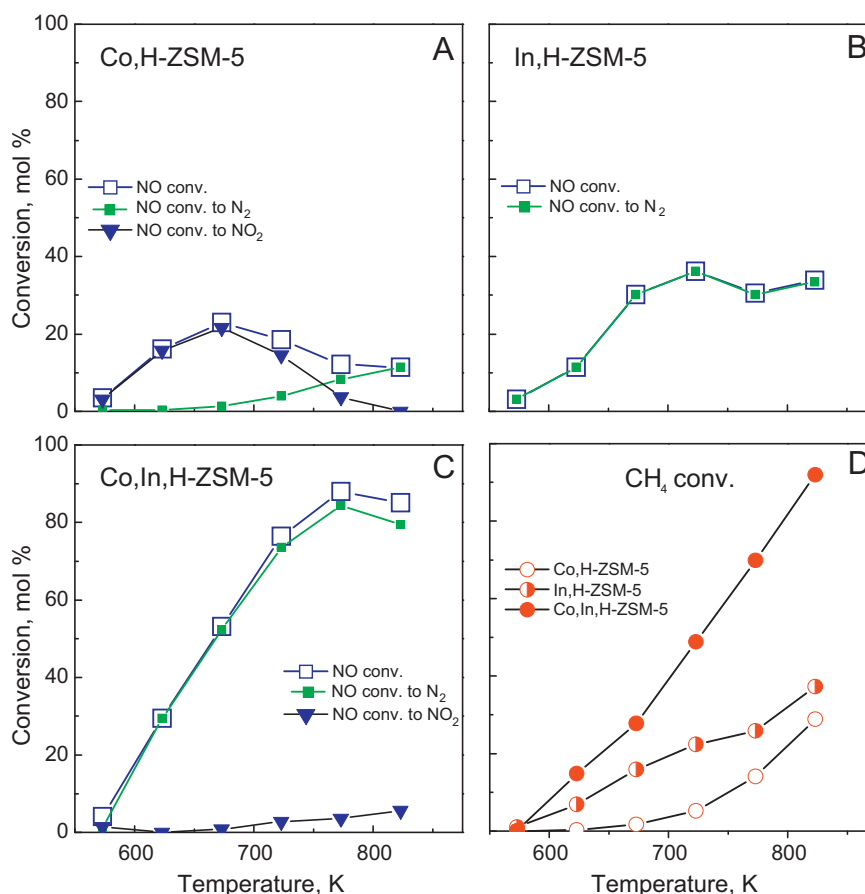
Fig. 2. The conversion of NO in the NO-SCR reaction over (A) Co,H–ZSM-5, (B) In,H–ZSM-5, (C) Co,In,H–ZSM–5 and (D) the conversion of CH_4 in the same reaction over the same catalysts. The reactant flow was 4000 ppm NO/4000 ppm CH_4/2% O_2/He gas mixture, the GHSV was 30,000 h^{-1}.

different. On former catalyst the NO was mainly converted to NO_2 (Fig. 2A) and N_2 product appeared only at reaction temperature over 700 K. This latter nitrogen formation is most probably related to the high-temperature gas phase reaction between NO_2 and CH_4 [25]. Despite the presence of methane in the reactant mixture the temperature dependence of NO conversion (Fig. 2A) closely resembles that usually obtained for NO oxidation by O_2 [16,17,26]. The cobalt oxides, that were shown to be present in the Co,H-ZSM-5 sample, are known to catalyze the NO-COX reaction [17,26,27]. In agreement with earlier observations the results shown in Fig. 2A suggest that the NO-COX reaction is kinetically controlled at temperatures below about 673 K, whereas it becomes limited by the thermodynamic equilibrium at temperatures above about 673 K [17,26]. In contrast to the Co,H-ZSM-5 and in line with the expectations [2,3,9,13] the In,H-ZSM-5 catalyst selectively converted NO to N_2 in the whole applied temperature range (Fig. 2B).

The activity of the Co,In,H-ZSM-5 catalyst (Fig. 2C) suggested substantial interplay of the two types of active sites, namely the Co-oxide (predominantly Co_3O_4) and $[InO]^+$ species. On one hand, the activity significantly increased in the presence of cobalt oxide relative to the activity of the In,H-ZSM-5 catalyst in the whole applied temperature range. On the other hand, compared to the Co,H-ZSM-5 catalyst the selectivity was obviously different. Over the bimetallic catalyst, containing cobalt oxide species of high NO oxidation activity, only a negligible amount of NO_2 appeared as product below about 700 K (cf. Fig. 2A and C). At higher temperatures some NO_2 was obtained, but the selectivity for N_2 formation remained high (>95%). These results strongly suggest that the NO_2 obtained from the reaction of NO and O_2 on the cobalt oxide sites was rapidly consumed in N_2-forming reaction, which latter reac-

tion was effected by cationic indium sites. It should be mentioned that the catalytic properties of a Co,In,H-ZSM-5 catalyst, containing exchangeable Co^{2+} cations, was similar to those of the In,H-ZSM-5 catalyst (not shown).

Conversion of methane under NO-SCR conditions is shown as function of the reaction temperature in Fig. 2D. In the selective catalytic NO reduction the molar conversion of methane must be half of that of NO ($2NO + CH_4 + O_2 = N_2 + 2H_2O + CO_2$). If its conversion exceeds the molar equivalence of the formed N_2 then the methane is also consumed in reaction with oxygen only ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$). Over the In-containing catalyst samples the direct methane oxidation with O_2, here referred to as methane combustion side reaction, becomes competitive with the NO-SCR only at reaction temperatures above 700 K (Fig. 2D). We have shown earlier that the undesired methane combustion becomes competitive with the NO-SCR reaction if the oxidation of In^+ sites to $[InO]^+$ sites proceeds much more by O_2 than by NO [9]. The 4e reduction of molecular O_2 can favourably proceed on two neighboring In^+ sites [9]. At low indium density the 2e oxidation of single In^+ ions must occur more easily by NO than by O_2. The low methane combustion activity of the In-containing samples below about 700 K (Fig. 2D), therefore, is attributed to the relatively low In^+ site density ($[Si + Al_F]/In \approx 100$) in these samples.

It follows from above results that the NO-SCR catalysts advantageously have a catalytic function, which speeds up the NO oxidation to NO_2 by oxygen. This reaction is evidently catalyzed by Co-oxide clusters in our Co-containing catalysts. But the origin of the similar activity, which is substantiated as prerequisite of the NO-SCR activity, is not clear over the In,H-zeolite catalyst. Therefore, we studied the conversion of NO to NO_2 in the presence of excess
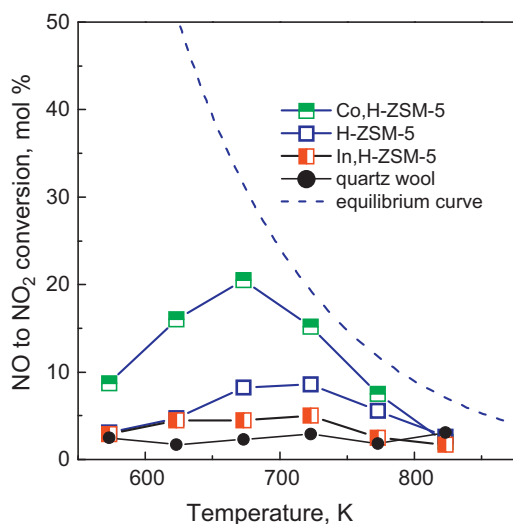
Fig. 3. The conversion of NO to NO$_2$ by O$_2$ over Co,H-ZSM-5, H-ZSM-5, In,H-ZSM-5 catalysts and inert quartz wool. The reactant flow was 4000 ppm NO/2% O$_2$/He gas mixture, the GHSV was 30,000 h^{-1}. The dashed curve shows the equilibrium concentration of NO$_2$.
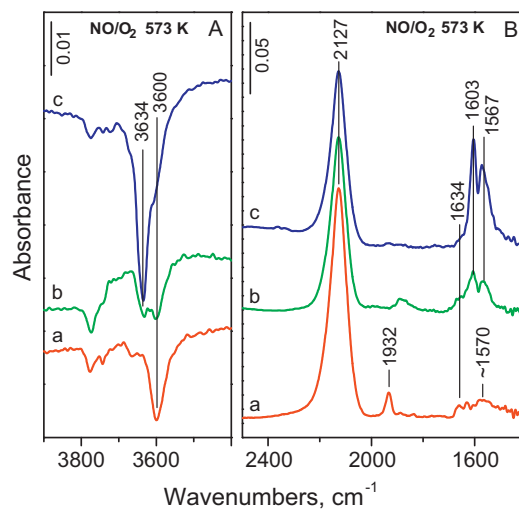

Fig. 4. DRIFT spectra obtained from the contact of the catalyst (a) Co,H-ZSM-5, (b) In,H-ZSM-5 and (c) Co,In,H-ZSM-5 with a continuous flow of 4000 ppm NO/2% O$_2$/He gas mixture at 573 K and GHSV 30,000 h^{-1}; part (A): ν_{OH} region, part (B): the spectra of the surface species.

oxygen and absence of methane over zeolite H-, Co,H- and In,H-ZSM-5 catalysts and without catalyst (over inert quartz wool) for comparison. The results are shown in Fig. 3. The thermodynamics of the process allows high conversion of NO to NO$_2$ especially below about 700 K (see the dashed equilibrium curve in Fig. 3). However, without catalyst (bottom curve) the conversion of NO was very low (1–2%). This clearly suggests that the NO oxidation reaction is kinetically controlled and catalyst is needed to increase the reaction rate. Among the catalysts the Co,H-ZSM-5 containing cobalt oxide clusters, showed the highest activity. The H-form and the In,H-form ZSM-5 samples were also active in the reaction (Fig. 3). Note that the conversion starts to decrease on each catalyst over about 673 K because approaching the equilibrium composition the NO conversion cannot increase further (Fig. 3, equilibrium conversion curve). The In,H-ZSM-5 contains less Brønsted acid sites than the H-form because about one third of the H-form protons were replaced by indium cations. The significantly higher activity of the zeolite H-ZSM-5 relative to the In,H-ZSM-5 catalyst indirectly suggests that the reaction proceeds rather over Brønsted acid sites than cationic indium sites. This result is in line with earlier suggestions that the NO-COX reaction proceeds on the Brønsted acid sites of the zeolites, whereas NO-SCR reaction rather proceeds on the indium sites [1,28,29]. Because the SCR reaction does not proceed without O$_2$ in the reactant mixture and considering that the In,H-ZSM-5 sample has NO-COX activity it is rational to think that the oxidation of NO to NO$_2$ is required for the NO-SCR reaction to proceed. Therefore, in line with earlier studies [2,3,14,15] we conclude that NO$_2$ is an important intermediate of the NO-SCR reaction.

3.3. Activation of NO and CH$_4$ for NO-SCR under reaction conditions

In the presence of CH$_4$ no NO$_2$ but N$_2$ appeared as reaction product if the mono or bimetallic catalyst contained indium, suggesting that besides NO$_2$ in the reactant mixture extra-framework indium lattice cations are responsible for the appearance of the NO-SCR activity. In order to understand how NO and NO$_2$ was activated for the N$_2$-generating reaction over the indium sites operando DRIFT spectroscopic investigations were carried out. Difference spectra were generated (*vide supra*) to get the operando DRIFT spectra of the catalyst in contact with NO/O$_2$ flow (Fig. 4).

At 573 K negative ν_{OH} band(s) appeared at 3634 and/or 3600 cm^{-1} (Fig. 4A), indicating that hydroxyl groups were consumed by a process resulting in the appearance of vibration bands in the frequency range of 1400–2400 cm^{-1} (Fig. 4B). The lower frequency ν_{OH} band (3600 cm^{-1}) is assigned to the stretching vibration of the bridging (Brønsted acid) OH-groups of the zeolite, whereas the higher frequency band (3634 cm^{-1}), which appeared in the spectra of the In-containing samples only, stems most probably from OH-groups bound to In^{3+} cations (Fig. 4A b,c) [9]. The OH-bands appearing in the range of 3630–3690 cm^{-1} are usually attributed to OH-groups formed from the adsorption of polarized or heterolytically dissociated H$_2$O in the electrostatic field of cations, such as Co^{2+}, Fe^{2+}, or Cu^{2+} [30–32]. In a recent publication, however the formation and stabilization of In$_4$(OH)$_4^{8+}$ units was substantiated in the sodalite cages of Y-zeolite having a Si/Al$_F$ ratio of 1.7 [33]. Considering the significantly lower framework aluminum concentration in our In,H-ZSM-5 sample (Si/Al$_F$ = 33), formation of similar, but monomeric species such as (InOH)$^{2+}$ seems to be more likely. The formation of these species, giving the OH-band at 3634 cm^{-1}, can be rationalized by the equilibrium reaction of neighboring InO$^+$ and H$^+$ cations [InO$^+$ + H$^+$ ⇆ (InOH)$^{2+}$]. Theoretical calculations might be able to justify the feasibility of this process. Note that the reduction of the (InOH)$^{2+}$ to In$^+$ would result in the same hydrogen consumption (2H/In) as observed in Fig. 1.

The band at 2127 cm^{-1} is assigned to ν_{NO} band of NO$^+$ nitrosonium ions [9,34], whereas the pair of bands at 1603 and 1567 cm^{-1} is attributed to NO$_3^-$ species (Fig. 4B b,c) [9,35]. Under similar conditions no nitrate groups were formed on the zeolite H-ZSM-5. The weak band at ~1570 cm^{-1} (Fig. 4B a) suggests that only minor amount of nitrate could have been formed on the Co,H-ZSM-5 sample [36]. The negligible nitrate formation on the sample containing Co predominantly in oxide clusters is in line with the findings that formation of nitro- or nitrate species proceeds on isolated Co-ions in ion exchange positions [17,18,36]. The band at 1932 cm^{-1} is usually assigned to mononitrosyl ligands of Co^{3+} ions, which ions are probably carrying also oxygen ligand(s) [36,37]. The δ(H$_2$O) band at 1634 cm^{-1} indicates that in the interaction of the catalysts and the NO/O$_2$ mixture water was also formed (Fig. 4B). These findings evidence, that the nitrate formation is related to the presence of indium cations in the catalysts.

As discussed in our previous study [9] we distinguish two possible processes of NO$^+$ formation. According to the one, first described
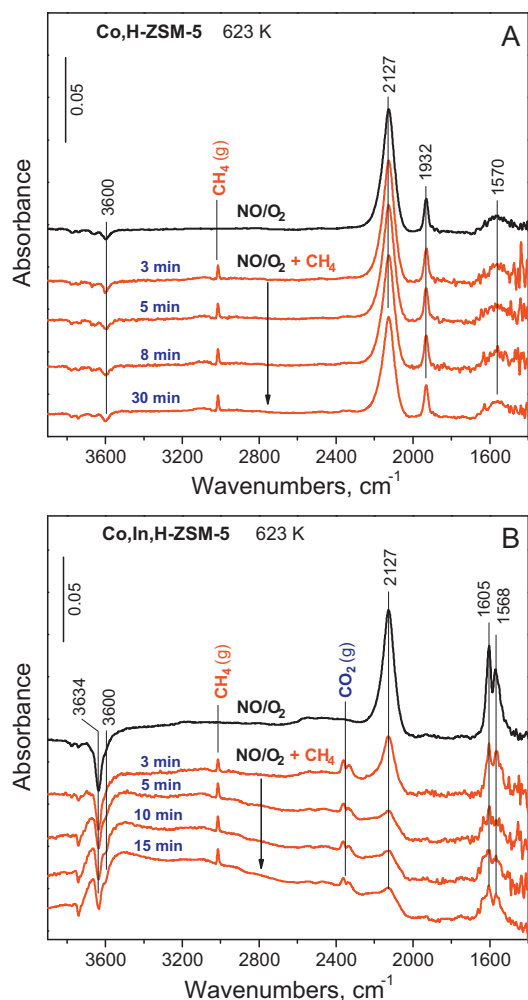
Fig. 5. Operando DRIFTS examination of the transient response of the catalyst on the change of the reactant composition. Catalysts (A) Co,H–ZSM-5 and (B) Co,In,H–ZSM-5 were contacted with the gas flow of 4000 ppm NO/2% O_2/He at GHSV 30,000 h^{-1} and 623 K. The first spectrum was recorded after the steady state was established (uppermost spectrum). Then the flow was abruptly changed to a flow of 4000 ppm NO/4000 ppm CH_4/2% O_2/He. Spectra were recorded after the indicated time on the stream. From each spectrum the spectrum of the catalyst in He at 623 K was subtracted and the difference spectrum is shown.

by Hadjiivanov et al. [34], NO^+ cations and H_2O are formed with the involvement of the Brønsted acid sites (Eq. (3)).

$$NO + NO_2 \overset{H^+Z^-}{\rightarrow} [NO^+Z^- + HNO_2] \overset{H^+Z^-}{\rightarrow} 2NO^+Z^- + H_2O \qquad (3)$$
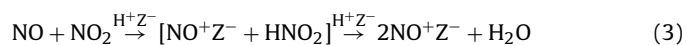
where Z^- represents a segment of the zeolite lattice, carrying a single negative charge.

Over the $[InO]^+Z^-$ species of zeolites, in a reaction similar to the initial step Eq. (3), NO^+ and $InNO_3$ is formed (Eq. (4)) [9].

$$NO + NO_2 + [InO]^+Z^- \rightarrow NO^+Z^- + In^+NO_3^- \qquad (4)$$
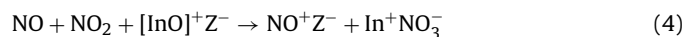
Assuming that the compensating In cation is in the form of $(InOH)^{2+}$, an analogue process can be written according to Eq. (5).

$$NO + NO_2 + [InOH]^{2+}Z_2^- \rightarrow NO^+Z^- + In^+NO_3^- + H^+Z^- \qquad (5)$$
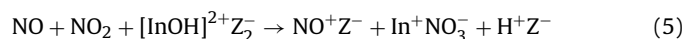
The results in Fig. 4 suggest that the surface reaction of Eq. (3) prevails on the Co,H–ZSM-5 sample, whereas both the reactions of Eq. (3) and Eq. (4)/(5) proceed on the In,H–ZSM-5 sample. The negative band at 3634 cm^{-1} suggests that $(InOH)^{2+}$ species become annihilated while all the products of Eqs. (3) and (4) or (5) are formed.

The zeolite-bound cobalt oxide was not active in the NO-SCR reaction by methane but it was able to catalyze the oxidation of NO to NO_2 by O_2. (Figs. 2A and 3). However, in absence of InO^+/$(InOH)^{2+}$ cations the nitrate formation is not significant (Fig. 4). Because the Brønsted acid sites also catalyze the NO oxidation the appearance of $InNO_3$ was detected even in the absence of cobalt oxide catalyst additive. The comparison of the spectra obtained for the In,H- and the Co,In,H–ZSM-5 catalysts shows that the presence of cobalt promotes the more extensive participation of the InO^+/$(InOH)^{2+}$ species in the reaction giving zeolite-bound NO^+ and zeolite-confined possibly near-to-molecular $InNO_3$. The more rapid supply of NO_2 because of the catalytic effect of the cobalt oxide was reflected by higher NO_3^- concentration in the Co,In,H–ZSM-5 than in the In,H–ZSM-5 catalyst (Fig. 4).

Above results clearly show that the in absence of InO^+/$(InOH)^{2+}$ species only NO^+ but no nitrate is obtained in the reaction with NO/O_2 mixture. In the presence of cationic indium species, especially together with cobalt oxide, however, the nitrate and the NO^+ must be formed together. In harmony with earlier findings [9,15,20,36] the operando DRIFTS results, shown in Fig. 5, confirm that the surface NO_3^- initiate the N_2 formation reaction by reacting with methane and forming an active intermediate. Because the concentration of this intermediate remained below the detection level due to its rapid conversion to SCR products N_2, CO_2 and H_2O (detected by MS and/or IR) we can only substantiate that it was nitromethane. This study shows that the formation and presence of surface NO^+ is necessary but not sufficient to initiate NO-SCR. The NO^+ is unable to activate methane (Fig. 5A) but rapidly reacts with the intermediate generated from the methane in reaction with the zeolite-bound indium nitrate. This is evidenced by the parallel consumption of the nitrate (bands at 1605 and 1568 cm^{-1}) and the surface NO^+ (band at 2127 cm^{-1}) in the transient period that follows the change of the NO/O_2 flow for $NO/CH_4/O_2$ flow (Fig. 5B). The charges of within the zeolite lattice remain balanced if In^+ takes over the role of the consumed NO^+. The maintenance of activity requires that In^+ should be oxidized by NO or NO_2 to InO^+. If NO is the oxidant this process contribute to the NO-SCR reaction $(In^+ + NO \rightarrow InO^+ + \frac{1}{2}N_2)$.

The cobalt ions in Co-zeolites were suggested to play the same role in the NO-SCR reaction as the indium cations do [17,36]. However, if the cobalt is predominantly in oxide clusters the formation of zeolite-bound nitrate is negligible (Fig. 4B a). This explains the low NO-SCR activity of our Co,H–ZSM-5 sample (Fig. 2A).

The activation of methane is generally considered as the rate determining step of the NO-SCR reaction [38–40] and, therefore, it follows from above arguments that the higher rate of the reaction, bringing about both nitrosonium cations and active nitrate species (Eq. (4) or (5)), should result in a higher reaction rate in the NO-SCR reaction with methane. Indeed, the presence of catalyst additive cobalt oxide speeds up the NO_2 formation by accelerating the reaction of NO and O_2 (Fig. 4), increases the formation rate of NO^+/NO_3^- pairs, the rate of methane activation and, as a result, the rate of the NO-SCR reaction (Fig. 2B and C).

4. Conclusions

Under favoured conditions of NO-SCR reaction (<700 K) the NO_2 formation from NO and O_2 is a kinetically controlled. Thus, the active NO-SCR catalysts must have surface sites that facilitate NO oxidation. The Brønsted acid sites of the ZSM-5 catalysts showed NO-COX activity but the catalysts modified by cobalt oxide were much more active in this reaction. In presence InO^+/$(InOH)^{2+}$ sites the NO_2, together with NO, forms NO^+/NO_3^- species. The nitrate species can activate methane and thereby initiate the NO-SCR reaction. The NO^+ that is formed on each studied catalysts is not able

to activate methane. The active intermediate, obtained in the reaction of methane and nitrate is rapidly consumed in an N_2-forming reaction with NO^+. Thus, both NO^+ and NO_3^- are essential NO-SCR intermediates. The intermediate formed in the methane activation step had a concentration, too low to permit its exact chemical identification. Generation of zeolite occluded molecular $InNO_3$ without the simultaneous formation of NO^+ could permit to study the reaction products of the NO_3^- and methane, i.e., the possible activated intermediate of the NO-SCR reaction. This work is in progress.

Acknowledgements

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