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Aspects of reducing agent and role of amine species in the reduction of NO over H-ZSM-5 in oxygen excess

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ABSTRACT

In this study the selective catalytic reduction (SCR) of NO has been investigated over H-ZSM-5 with three different reducing agents. Comparison of the reaction mechanisms using propane, ammonia and isopropylamine has been performed using in situ DRIFTS step-response experiments. The same type of surface NH species, likely organic amines, is formed in the presence of either propane or isopropylamine as reducing agent. For NH_3, on the other hand, NH_4^+ is the dominating NH surface species during reaction. Furthermore, in the case of propane, the nature of the NO_x-source, i.e. NO or NO_2, is crucial for the reaction. With NO_2, the reaction likely proceeds fast via direct reduction, while for NO, oxidation to NO_2 is required initially. In either case NH species play a vital role in the SCR reaction and organic amines are possible key-intermediates in the SCR with saturated hydrocarbons over H-ZSM-5.

1. Introduction

Combustion engines contribute significantly to the consumption of fossil fuels and consequently to the anthropogenic emissions of CO_2. The awareness of climate changes and the connection between CO_2 accumulated in the atmosphere and global warming [1] emphasizes the need to reduce the fuel consumption. Combustion in excess oxygen, like in diesel- and lean-burn engines, significantly increases the fuel efficiency and hence contributes to reduced CO_2 emissions. However, the lean environment obstructs NO_x reduction in the conventional three-way catalyst and new innovative solutions for NO_x reduction in excess oxygen are required. Selective catalytic reduction of NO by hydrocarbons (HC-SCR) is one potential technique for reducing NO_x emissions in diesel exhausts and among numerous investigated materials, zeolites have shown promising properties as HC-SCR catalysts.

Since the HC-SCR concept first was investigated by Iwamoto et al. [2] and Held et al. [3] the reaction mechanism has been extensively studied and debated. For zeolite materials there are several possible reaction pathways suggested in the literature. In general three main groups can be identified [4,5]. These are: catalytic decomposition of NO to N_2, oxidation of NO to NO_2, which subsequently is reduced to N_2 by hydrocarbons likely through organic intermediates, and partial oxidation of hydrocarbons forming oxygen and/or nitrogen containing intermediate species, which subsequently reduce nitrogen oxides to nitrogen. In more detail the mechanism has, for instance, been discussed over Fe/MFI catalysts in terms of NO oxidation, and formation of a C, O, H and N containing deposit [6,7]. Moreover, nitrogen oxides and organic compounds have been proposed to react and form nitromethane, from which isocyanic acid (HNCO) may be formed [8]. Ammonia is then suggested to form by hydrolysis of the HNCO and then further react with the nitrogen oxides to form ammonium nitrite and finally N_2. The HC-SCR reaction has also been investigated by the reaction of NO with higher nitro paraffins [9,10], and the mechanism that emerged from these studies involves formation of isocyanate species, likely formed via the aci-form over Brønsted acid sites. The N_2 formation is then suggested to proceed either by hydrolysis of isocyanate forming amine species (and/or ammonia) followed by an SCR reaction or by a reaction between NO_2 and the deposited isocyanate species.

The SCR reaction is dependent on the oxygen and hydrocarbon concentrations and cannot take place in the absence of oxygen [11]. A general view concerns the oxidation of NO to NO_2 as an initial and necessary step for the reaction to occur. Furthermore, the $NO:NO_2$ ratio has been reported to be crucial in NH_3-SCR over H-ZSM-5, where the NO oxidation is found to be rate determining when $NO:NO_2 > 1$ [12]. Tronconi and co-workers [13–16] have systematically studied the NH_3-SCR reaction over vanadium-based catalysts in a wide range of temperatures and $NO:NO_2$ ratios. The highest NO_x reduction efficiency was found for a 1:1 $NO:NO_2$ ratio. The authors have suggested that the reaction proceeds via NO_2 dimerization and disproportion to nitrous and nitric acid, with

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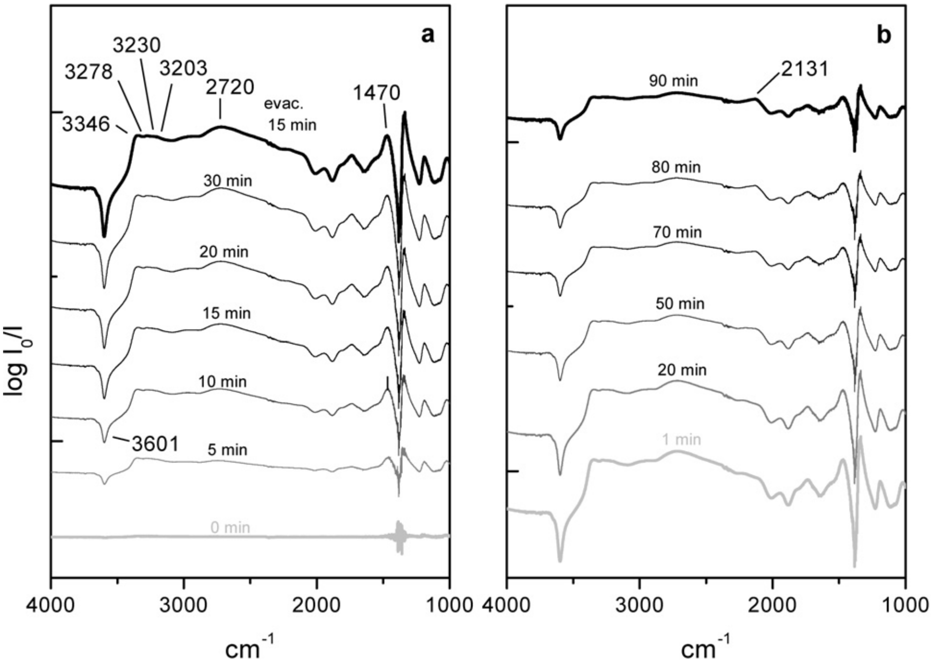

Fig. 1. DRIFT spectra from H-ZSM-5 40 zeolite taken after 0–30 min during NH_3 adsorption and 15 min after evacuation (a), and 0–90 min after exposure to 1000 ppm NO + 10% O_2 (b).

subsequent formation of ammonium nitrite, which readily decomposes to N_2 and water, and formation of ammonium nitrate. Then, NO is suggested to act as reductant converting nitrates to nitrites, which finally decompose to N_2.

We have previously focused on the reaction pathway for lean NO_2 reduction by propane over H-ZSM-5 [17–19]. The formation of NO^+ on the zeolite surface and the activation of propane, forming carbenium ions which subsequently form alkenes have been indicated as possible key steps in the reaction. These two types of species have been proposed to react forming isocyanates, which are likely hydrolyzed to amine species that can react with NO^+ and/or NO_2 forming N_2. The formation of amine intermediates has previously been studied for the reaction between NO_2 and isopropylamine [17,20]. In this work NO is used as NO_x-source and the picture that emerges in the comparison between NO and NO_2 deepens the information on the reaction pathway for HC-SCR over acidic zeolites. Furthermore, since amine species seem to be involved in the reaction mechanism it is interesting to compare the HC-SCR with the SCR using ammonia or organic amines as reducing agent. In the present investigation we have studied the selective catalytic reduction of NO over H-ZSM-5 with propane, isopropylamine and ammonia, as reducing agent. The attention is focused on the reaction mechanism, in particular the formation and role of the amine species in the SCR reaction.

2. Experimental

The catalyst used in this study was H-ZSM-5 (Akzo Nobel Catalysts BV) with a SiO_2/Al_2O_3 molar ratio of 40. Textural data, acidic characterization and preparation of the sample have been reported previously [17].

In situ FTIR (Fourier Transform Infrared) spectroscopy measurements were carried out using a BioRad FTS 6000 spectrometer equipped with a Harrick Praying Mantis DRIFT reaction cell [21–23]. The experimental procedure has previously been described in detail [17]. Briefly, feed gases were mixed from O_2, NO, NH_3, C_3H_8 and Ar (balance) and introduced to the DRIFT cell via individual mass flow controllers (Bronkhorst Hi-Tech). The sample was initially pre-treated in nitrogen dioxide and oxygen (1000 ppm NO_2 and 10% O_2, Ar, 500 °C, 40 min) followed by oxygen (10% O_2 in Ar, 500 °C, 1 h) and then evacuated in pure Ar at a total flow rate of 200 ml/min. Background spectra (40 scans at a resolution of 1 cm^{-1}) were collected under Ar exposure. Fresh samples were used for all experiments.

In the first experiment, ammonia adsorption was carried out at 350 °C. The sample was exposed to 1000 ppm NH_3 in Ar until saturation (about 30 min) and then flushed with pure Ar for 15 min. The sample was thereafter exposed to 1000 ppm NO and 10% O_2 at a constant temperature of 350 °C. Step-response experiments were performed using NH_3 or propane as reducing agent at 350 and 450 °C, respectively. These experiments were performed in three steps: Step 1, the sample was exposed to 1000 ppm NO and 10% O_2; Step 2, the reducing agent (1000 ppm NH_3 or 1500 ppm C_3H_8) was added to the feed; Step 3, when the reaction in Step 2 reached steady state, the supply of NO was turned off, leaving the sample only exposed to NH_3 (or 1500 ppm C_3H_8) and 10% O_2. In Step 3 the conditions in Step 2, when the reaction had reached steady state, were used as background.

Similar step-response experiments were also performed using isopropylamine (with an approximate concentration of 5000 ppm) as reducing agent, at 450 °C. The experimental set-up was the same as for the previous experiments with the exception of one additional Ar flow, which was saturated with isopropylamine before introduction to the reaction cell [17].

3. Results and discussion

In the sections below we describe the evolution of surface species upon introduction of different reducing agents. The main issue is to compare the mechanisms for propane, isopropylamine and ammonia SCR in order to identify similarities and differences, with a special emphasis on the role of amine species.

3.1. Ammonia as reducing agent

Fig. 1a shows the DRIFT spectra recorded during exposure of H-ZSM-5 to ammonia at 350 °C. Positive peaks appear at 3346, 3278, and 1470 cm^{-1}, which are attributed to asymmetric and

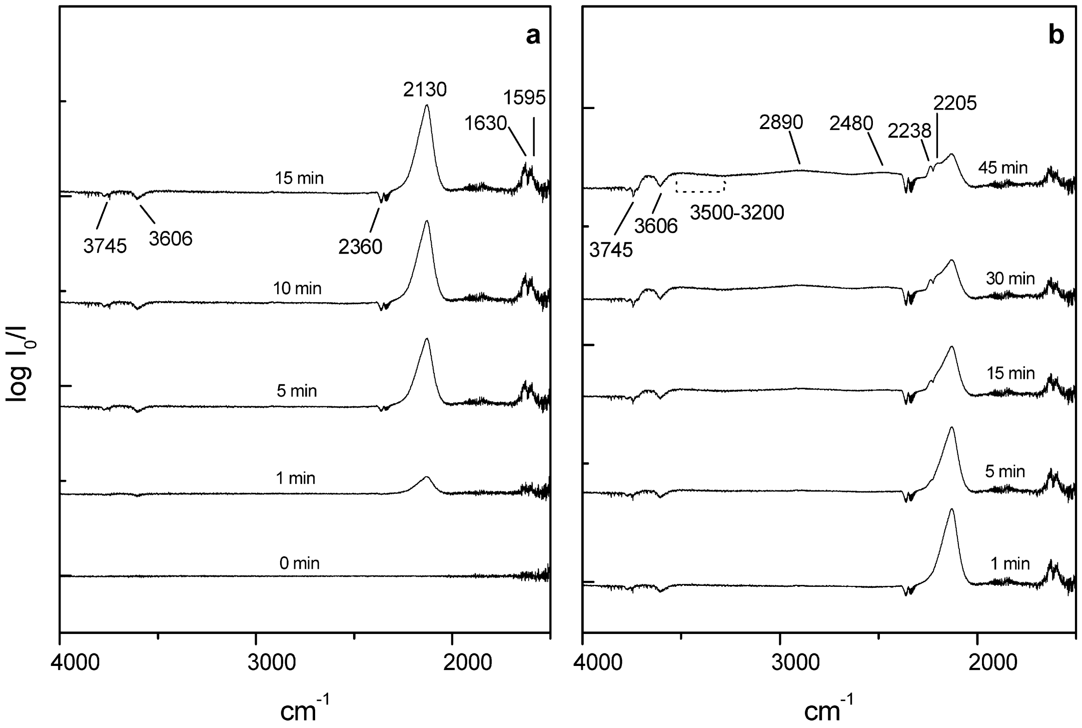

Fig. 2. DRIFT spectra of step-response experiments at 350 °C, over H-ZSM-5 40 zeolite, using NH_3 as the reducing agent. Step 1: 1000 ppm NO, 10% O_2 in Ar (a); Step 2: 1000 ppm NO, 1000 ppm NH_3, 10% O_2 in Ar (b).

symmetric NH stretching and bending vibrations, respectively, of NH_4^+ at the Brønsted acid sites of the zeolite [17,24–28]. The assignment of the peak at 1470 cm^{-1} is here somewhat uncertain since there are possible bands or overtones of bands in the spectra related to perturbed vibration frequencies of the zeolite framework, which makes peak assignment difficult in the region below 2000 cm^{-1} [17,28–31]. The presence of NH_4^+ species at the Brønsted acid sites is also strongly supported by the pronounced negative peak that appears at 3601 cm^{-1}, which is assigned to blockage of the OH stretching vibrations of the Brønsted acid sites (Si(OH)Al) [24]. Bands at 3230, 3203, and 2720 cm^{-1} are also observed. These are most likely due to NH stretching vibrations of NH_4^+ [17,28,32] and in the latter case also to weakly bound NH_3 [24,28]. During the ammonia adsorption the presence of trace amounts of water cannot be excluded, and the broad feature observed in the region of 3500–2200 cm^{-1} may be related to OH stretching vibrations of water present at the Lewis acid sites in the zeolite sample [28,31,33].

When the sample subsequently is exposed to NO and O_2 (Fig. 1b), NO reacts with adsorbed ammonia. The decrease of the peaks at 3346, 3278 and 1470 cm^{-1}, and the increase of the 3601 cm^{-1} band strongly suggest that NH_4^+ ions formed on Brønsted acid sites participate in the SCR reaction. In parallel to the decrease of the bands associated with ammonium ions and ammonia, a peak at 2131 cm^{-1} becomes visible after 50 min. According to Hadjiivanov and co-workers [34] the 2131 cm^{-1} peak is assigned to NO^+ species present at the Brønsted acid sites in the zeolite.

Step-response experiments performed at 350 °C with NO as the NO_x-source and NH_3 as the reducing agent, are presented in Figs. 2a and 2b. During the first step (Fig. 2a: 1000 ppm NO and 10% O_2) one peak is observed at 2130 cm^{-1}, corresponding to the NO stretching vibration of adsorbed NO^+ ions [34]. Peaks are also observed at 1630 and 1595 cm^{-1}, which can be assigned to surface nitrate species and/or weakly adsorbed NO_2 formed from NO in the presence of oxygen [35]. However, in the low-frequency region, overlapping vibrations of the zeolite framework makes the peak assignment somewhat difficult. Since weak negative peaks are observed around 3606 and 3745 cm^{-1}, which are assigned to OH stretching vibrations originating from Brønsted acid sites and silanol groups, respectively, it is probable that the NO^+ species are present at the Brønsted acid sites. The double negative peak around 2360 cm^{-1} is attributed to CO_2 in the gas phase, due to changes in the background concentration of CO_2 during the experiment.

When the sample subsequently also is exposed to NH_3 (Fig. 2b: 1000 ppm NO, 1000 ppm NH_3, and 10% O_2) the 2130, 1630 and 1595 cm^{-1} peaks decrease. In parallel new adsorption bands grow: two peaks at 2238 and 2205 cm^{-1} are observed and may be assigned to N_2O [36]. Two broad peaks centered around 2890 and 2480 cm^{-1} appear, probably originating from OH stretching vibrations of water, hydrogen bonded to Lewis acid sites in H-ZSM-5 [28]. The broad shoulder in the region of 3500–3200 cm^{-1} can be assigned to NH stretching vibrations of NH_4^+. The absence of highly resolved peaks in this region could be ascribed to the fast reaction of NH_3 with surface NO_x- and/or NO species. The peaks at 3606 and 3745 cm^{-1} gradually becomes more negative during the sequence with NH_3. This is indicative of blocking of the Brønsted acid sites by adsorbed species, most likely NH_4^+ ions, which bind stronger to the Brønsted sites than NO^+.

3.2. Propane as reducing agent

The corresponding step-response experiments for H-ZSM-5, with propane as the reducing agent, at 450 °C, are shown in Figs. 3a and 3b. Upon exposing the H-ZSM-5 sample to O_2 and NO (Fig. 3a) several peaks appear, in accordance with the previous experiment shown in Fig. 2a. These peaks are accordingly assigned to adsorbed NO^+ species (2130 cm^{-1}), silanol groups (3745 cm^{-1}), Brønsted acid sites (3605 cm^{-1}) and adsorbed NO_2 and/or nitrate species (1630 and 1595 cm^{-1}).

When the sample subsequently also is exposed to propane (Fig. 3b: 1000 ppm NO, 1500 ppm C_3H_8, and 10% O_2), several peaks

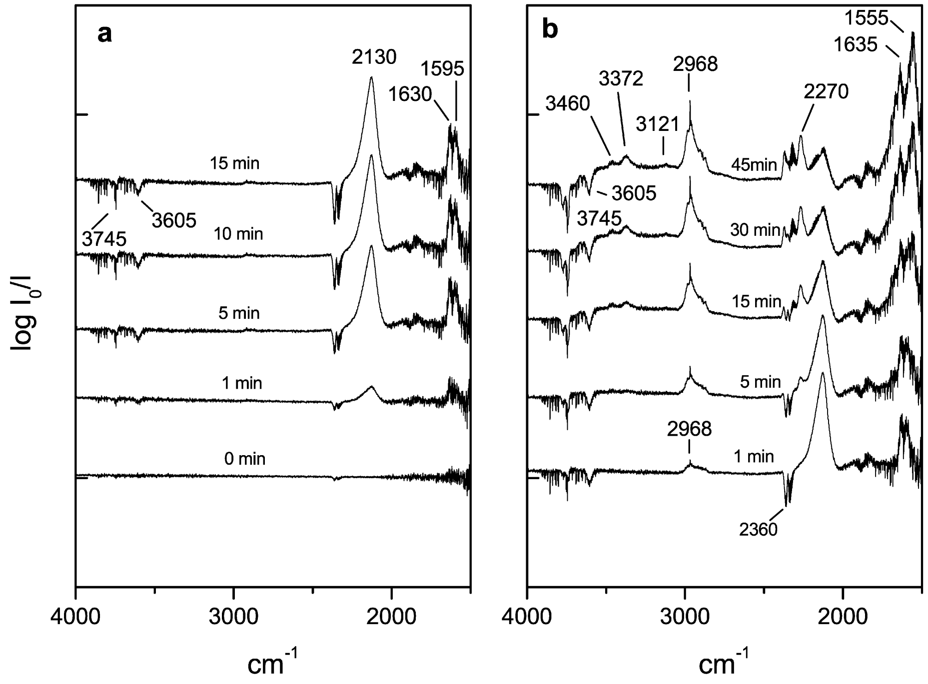

Fig. 3. DRIFT spectra of step-response experiments at 450 °C, over H-ZSM-5 40 zeolite, using C_3H_8 as the reducing agent. Step 1: 1000 ppm NO, 10% O_2 in Ar (a); Step 2: 1000 ppm NO, 1500 ppm C_3H_8, 10% O_2 in Ar (b).

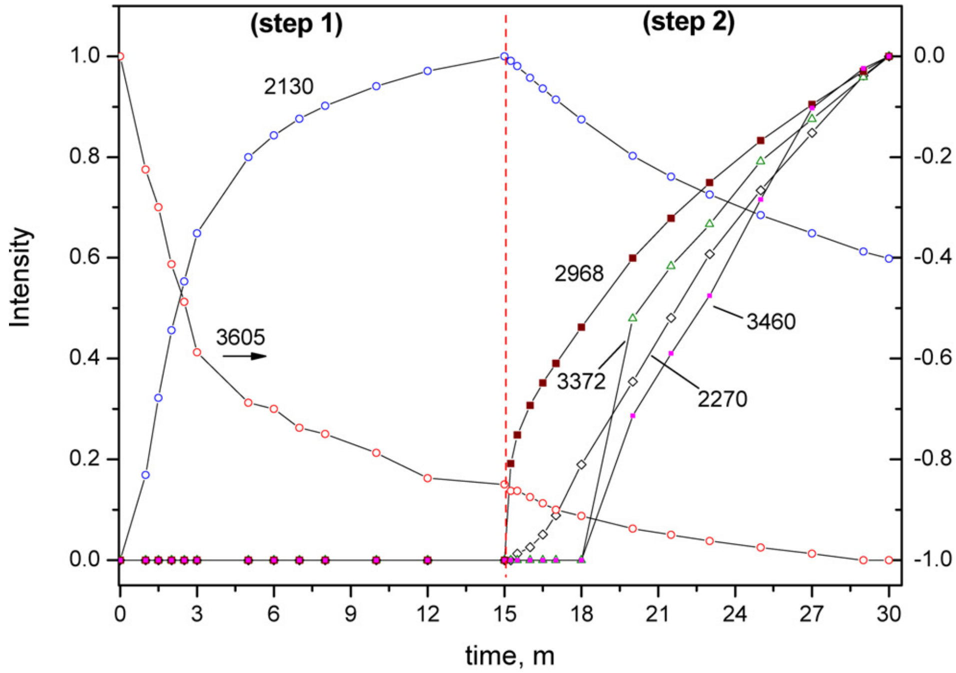

Fig. 4. Evolution of surface species adsorbed on H-ZSM-5 40 zeolite in presence of 1000 ppm NO, 10% O_2 in Ar (Step 1) and 1000 ppm NO, 1500 ppm C_3H_8, 10% O_2 in Ar (Step 2).

appear. The NO^+ peak decreases slightly with time, and a peak at 2270 cm^{-1} appears almost immediately. This peak is assigned to isocyanate (–NCO) species bound to Al and/or Si in the zeolite framework [7,37]. The strong band with two peaks at 1635 and 1555 cm^{-1} increases with time and may be due to formation of surface carbonates [38] and/or acetates [39]. Several peaks are observed in the 3000–2800 cm^{-1} region, which are assigned to CH stretching vibrations. The peak at 2968 cm^{-1} in particular can be attributed to adsorbed and/or gas-phase propane [39,40]. A peak around 3121 cm^{-1} starts to grow slowly after 5 min. This peak is likely due to CH stretching vibrations of unsaturated hydrocarbons [7,39]. Two peaks at 3460 and 3372 cm^{-1}, probably related to NH stretching vibrations, are observed after 5 min, indicating amine species present on the sample surface. The negative peak around 3605 cm^{-1} gradually becomes more negative during the sequence with propane. This is indicative of blocking of the Brønsted acid sites by adsorbed species, most likely hydrocarbons and/or amine species. The double peak around 2360 cm^{-1}, attributed to CO_2 in the gas phase, becomes positive and increases with time, due to oxidation of propane.

Fig. 4 shows the evolution of surface species during the first two steps. During Step 1, the specular increase of the NO^+ species

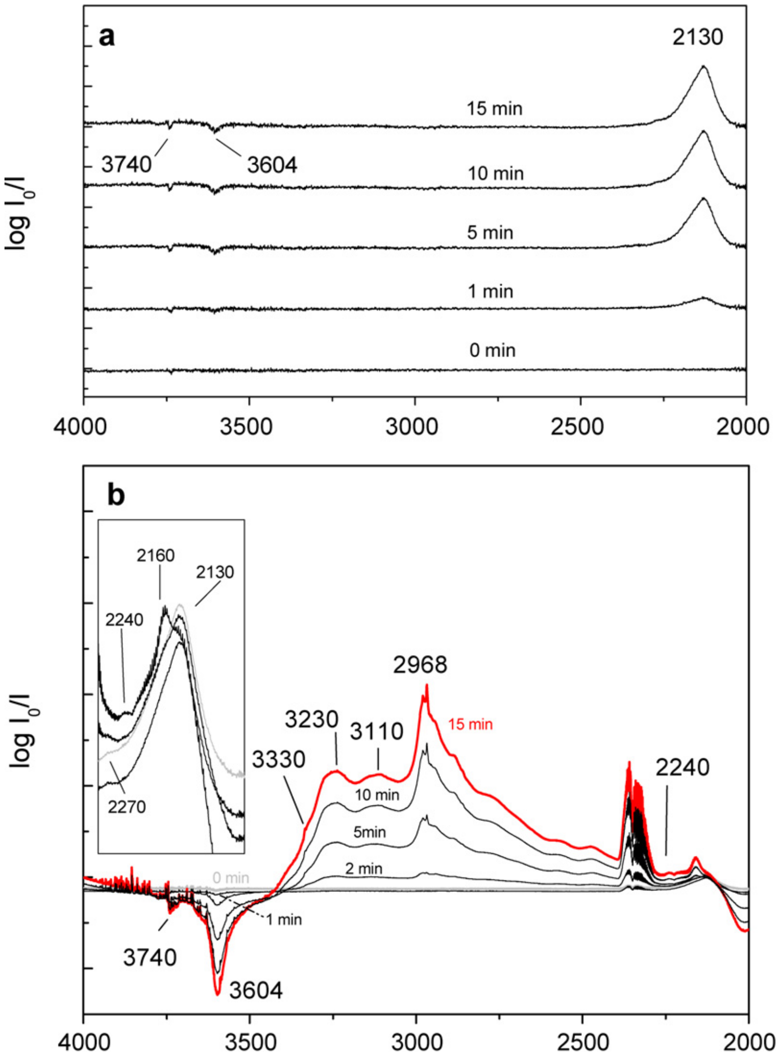

Fig. 5. DRIFT spectra of step-response experiments at 450 °C, over H-ZSM-5 40 zeolite, using isopropylamine as the reducing agent. Step 1: 1000 ppm NO, 10% O_2 in Ar (a); Step 2: 1000 ppm NO, isopropylamine, 10% O_2 in Ar (b).

and the decrease of Brønsted acid sites with time, confirm that the NO^+ species are adsorbed on the Brønsted sites. During Step 2, when the sample also is exposed to propane, formation of isocyanate species can be seen, likely as a consequence of reaction between NO^+ species and hydrocarbon-derived species. It is interesting to note that, as the reaction proceeds, amine species appear after an initial delay of about 5 min. This strongly supports formation of amine species by hydrolysis of the isocyanate species previously formed.

3.3. *Isopropylamine as reducing agent*

Step-response experiments with isopropylamine as the reducing agent for NO are shown in Figs. 5a and 5b. Upon exposing the H-ZSM-5 sample to O_2 and NO (Fig. 5a: 1000 ppm NO and 10% O_2) several peaks appear, in accordance with the previous experiments shown in Figs. 2a and 3a, which also demonstrates the good reproducibility of the experiments. The peaks are accordingly assigned to adsorbed NO^+ species (2130 cm^{-1}), silanol groups (3740 cm^{-1}) and Brønsted acid sites (3604 cm^{-1}). During Step 2 the sample is subsequently also exposed to isopropylamine (Fig. 5b), and several peaks appear. The peak at 2968 cm^{-1} is attributed to CH stretching vibrations and the peak at 3110 cm^{-1} most likely originates from CH vibrations from unsaturated hydrocarbons [7,39]. The peak at 3230 cm^{-1}, with a shoulder around 3330 cm^{-1}, is probably due to NH stretching vibrations and the negative peaks at 3604 and 3740 cm^{-1} indicate blocking of the Brønsted acid sites and silanol groups, presumably by adsorbed hydrocarbon and/or amine species. The inset in Fig. 5b shows the spectra during the first 5 min of isopropylamine exposure: after one minute a peak at 2270 cm^{-1} appears, which is assigned to isocyanate (–NCO) species bound to Al and Si in the zeolite framework. A peak at 2240 cm^{-1} is observed after 5 min and may be assigned to N_2O [36]. Another peak at 2160 cm^{-1} appears after 5 min and may result from adsorbed CO interacting with the surface hydroxyl groups in H-ZSM-5 [41,42].

3.4. *Comparison of the reaction mechanisms using the three reducing agents*

Fig. 6 shows the evolution of surface species when the zeolite is exposed to the different reducing agents after the NO supply is turned off. The background spectra, which are subtracted from the resulting spectra in Figs. 6a–6c, are collected during complete reaction conditions i.e. 1000 ppm NO, 10% O_2 and the reducing agent, respectively.

In Fig. 6a (background at complete reaction conditions) the results in presence of 1000 ppm NH_3 and 10% O_2 can be seen. Upon removal of NO from the feed, the NO^+ peak disappears and after 15 min a negative shoulder at 2130 cm^{-1} becomes evident. Posi-

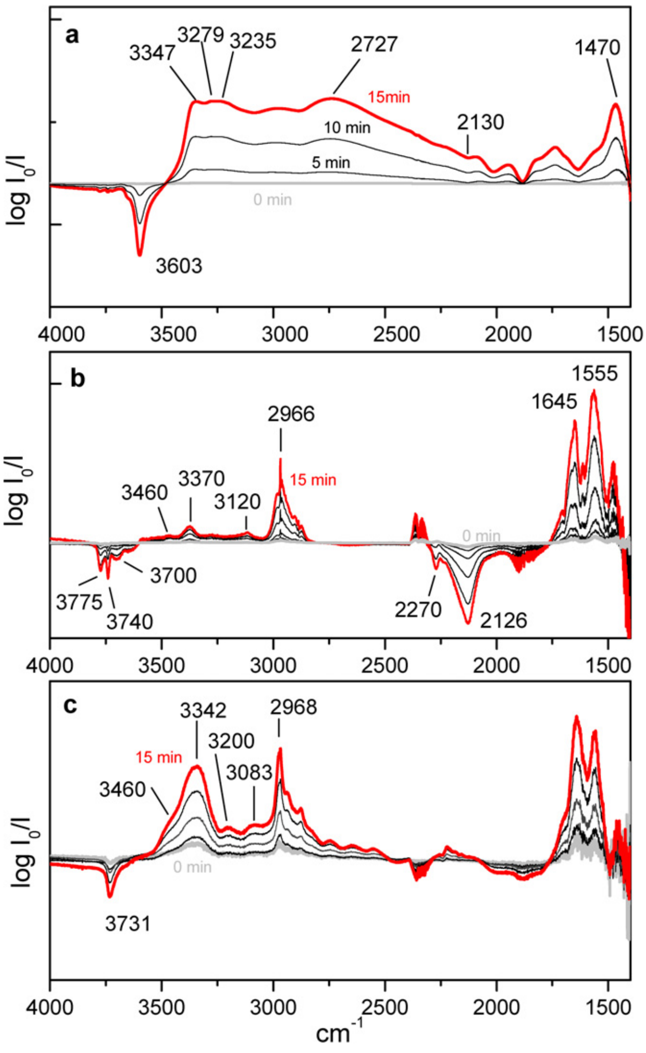

Fig. 6. Evolution of surface species adsorbed on H-ZSM-5 40 zeolite in presence of 10% O_2 and reducing agent in Ar, after removal of NO from the feed. Complete reaction conditions are used as background. (a) 1000 ppm NH_3 and 10% O_2 in Ar, (b) 1500 ppm C_3H_8 and 10% O_2 in Ar and (c) isopropylamine and 10% O_2 in Ar.

tive peaks related to NH_4^+ (3347, 3279, 3235 and 1470 cm^{-1}) and also to weakly bound NH_3 (2727 cm^{-1}) appear. Furthermore, the peaks assigned to Brønsted acid sites at 3603 cm^{-1} gradually becomes more negative during the sequence.

In Fig. 6b (background at complete reaction conditions) the results in presence of 1500 ppm C_3H_8 and 10% O_2 can be seen. When the NO supply is turned off, negative peaks develop at 2126 and 2270 cm^{-1}, corresponding to the consumption of NO^+ and NCO species and positive peaks appear at 3460, 3370 and 3120 cm^{-1}, related to NH stretching vibrations and CH stretching of unsaturated hydrocarbons, respectively. In the CH vibration region the magnitude of the peak at 2966 cm^{-1} increases and simultaneously negative peaks at 3775, 3740 and 3700 cm^{-1} gradually become more negative. This is indicative of blocking of silanol groups and/or terminal aluminum hydroxyl groups. A strong band with two peaks at 1645 and 1555 cm^{-1} increases with time and indicates formation of carbonates and/or acetates [38,39].

By carefully observing the NO^+ and isocyanate peaks, some conclusions may be drawn. When both NO, propane and oxygen are present in the feed (Fig. 3, Step 2) isocyanate species are formed and NO^+ species are consumed. At the end of the step the –NCO peak is relatively high compared to the NO^+ peak. Thus, it is conceivable that NO^+ species react to form isocyanate surface species. The NH vibrations observed at 3460 and 3372 cm^{-1} seem to correlate with the hydrolysis of the isocyanate species to form some type of amine species. When the NO supply is turned off (Fig. 6b), the negative peak corresponding to removal/consumption of the NO^+ species appears immediately. A negative peak at 2270 cm^{-1} develops after 2 min and gradually becomes more negative with time, however slowly in comparison with the NO^+ peak, i.e. the consumption of NO^+ species seems to be faster than the consumption of NCO species. At the same time peaks in the NH stretching region appear. Hence, it seems likely that the NO^+ species, present at the surface, still react to form isocyanates, which consequently are hydrolyzed forming amine species.

In Fig. 6c the results in presence of isopropylamine and 10% O_2 can be seen (background at complete reaction conditions). When the NO supply is turned off several peaks develop. In the CH stretching region the magnitude of the peak at 2968 cm^{-1} increases. At the same time a peak at 3342 cm^{-1}, with a shoulder at 3460 cm^{-1}, and bands centered at 3200 and 3083 cm^{-1} increase. These are probably due to NH stretching vibrations of amine species. The negative peak around 3731 cm^{-1} gradually becomes more negative during the sequence with isopropylamine.

An interesting observation is that the peak at 3342 cm^{-1}, with a shoulder at 3460 cm^{-1} increases faster than the bands centered at 3200 and 3083 cm^{-1}. Indeed these frequencies (3342 and 3460 cm^{-1}) are related to those species that are likely strongly involved in the complete reaction. Peaks at 3347 and 3370 cm^{-1} are also observed in the presence of ammonia (Fig. 6a) and propane (Fig. 6b). In the case of ammonia the peaks evolving in the NH stretching region, when NO is turned off, are likely due to NH_4^+. Furthermore, the Brønsted acid sites are blocked, probably by adsorbed NH_4^+ species. For propane and isopropylamine, on the other hand, the NH stretching peaks, which evolve upon removal of NO from the feed, do not seem to correlate with the Brønsted acid sites. Instead, the peaks associated with OH groups on Si and terminal Al decrease, which indicates that the species adsorbed are different from the ones adsorbed using ammonia as reducing agent. Takasuka and Terui [43] assign bands in the region 3395–3365 cm^{-1} to asymmetric NH stretching vibrations of saturated primary amines. Bands at 3470 and 3360 cm^{-1} have also been attributed to asymmetric and symmetric NH stretching vibrations of methylamine [44]. Furthermore, bands at 3520 and 3445 cm^{-1} have previously been assigned to Si–NH_2 surface groups [44–46]. It is thus probable that the species that evolve upon removal of NO, using propane or isopropylamine in the reaction, are –NH_2 species adsorbed on organic and/or surface Si groups. This result indicates that organic amine species are possible intermediates in the SCR reaction with saturated hydrocarbons as reducing agent, over H-ZSM-5.

In a previous study [17], NO_2 was used as NO_x-source with propane as reducing agent over H-ZSM-5, and during reaction conditions formation of unsaturated hydrocarbons and/or amine species (3130 cm^{-1}) was observed. Furthermore, Wallin et al. [12] studied the selective catalytic reduction of NO_x with NH_3 over H-ZSM-5. It was concluded that for NO:NO_2 ratios exceeding one the rate determining step for the reaction is most likely the NO oxidation to NO_2. Hence, using NO_2 as NO_x-source likely results in a rapid reaction with ammonia and/or amine species on the sample surface, even if these species are organic amines and/or derived from adsorbed hydrocarbons. This might explain why Ingelsten et al. [17] only observed a small shoulder in the NH stretching region (3400–3200 cm^{-1}), while the peak due to unsaturated hydrocarbons and/or amine species (3130 cm^{-1}) increased during reaction with NO_2 and propane. It is conceivable that NO_2 facilitates a partial oxidation of the hydrocarbon (manifested by the 3130 cm^{-1} peak), which can then react forming isocyanate- and amine species. Since NO_2 and amine species react rapidly the amine species will be consumed almost instantly and only a minor indication of these species is seen on the sample surface during reaction conditions. Using NO as NO_x-source, on the other hand, requires most likely oxidation of NO to NO_2, which is a slower reaction [12]. However, the surface NO^+ species seem to form, in the presence of oxygen, regardless of NO_x-source [34]. In accordance with previous studies [18,47], the results presented above show that it is probable that isocyanate species are formed by reaction between NO^+ species and hydrocarbon-derived species on the sample surface, using propane as reducing agent. The isocyanate species are then likely hydrolyzed forming amine species. In the case with NO as NO_x-source, the amine species will accumulate on the sample surface since further reaction to N_2 probably requires oxidation of NO to NO_2. Furthermore, the formation of partially oxidized hydrocarbons, as was seen for the NO_2–propane reaction, is less pronounced in the reaction with NO (only a small peak is seen) since NO_2 probably is needed for this reaction to a significant extent.

4. Concluding remarks

The same type of NH species, likely organic amines, is formed for either propane or isopropylamine as reducing agent in the (selective) reduction of NO over H-ZSM-5. On the contrary, for NH_3, NH_4^+ is the dominating NH surface species during reaction. The difference in where these groups are formed strongly suggest that they are different, since NH_4^+ likely is formed on more acidic (Brønsted) sites compared to the organic amines. Moreover, the choice of NO_x-source, i.e. NO or NO_2, is crucial for the reaction. Using NO_2, the reaction likely proceeds fast via direct reduction of NO_2 to N_2, while for NO, oxidation to NO_2 is likely required before reduction takes place. In either case NH species play a vital role in the SCR reaction and organic amines are possible key-intermediates in the SCR with saturated hydrocarbons over H-ZSM-5.

Acknowledgments

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