Catalysis Letters Vol. 106, Nos. 1–2, January 2006 (© 2006)
DOI: 10.1007/s10562-005-9184-5

Mechanistic study of lean NO_2 reduction by propane over HZSM-5 in the presence of water

Hanna Härelind Ingelsten[a,b,*], and Magnus Skoglundh[a,b]

[a]*Competence Centre for Catalysis, Chalmers University of Technology, Göteborg SE-412 96, Sweden*
[b]*Applied Surface Chemistry, Chalmers University of Technology, Göteborg SE-412 96, Sweden*

Received 30 June 2005; accepted 19 September 2005

This study focuses on the mechanism of lean NO_2 reduction by propane in the presence of water, over an acidic zeolite (HZSM-5). Fourier Transform Infrared spectroscopy measurements with NO_2 and propane in excess oxygen show formation of surface bound NO^+, isocyanate, unsaturated hydrocarbons and traces of amine species. Upon addition of water the isocyanate species disappear and amine species are formed. Hence, it seems likely that the isocyanate species are hydrolysed to amine species, which are possible reaction intermediates in the HC-SCR reaction over HZSM-5.

KEY WORDS: HZSM-5; lean NO_x reduction; propane; FTIR.

1. Introduction

Since the HC-SCR concept was first investigated by Iwamoto *et al.* [1] and Held *et al.* [2] the reaction mechanism has been intensively studied and debated. For zeolite materials there are several possible reaction pathways suggested in the literature. In general three main groups can be identified [3,4]. That is catalytic decomposition of NO to nitrogen, oxidation of NO to NO_2, which is then reduced by the hydrocarbon likely through organic intermediates, and partial oxidation of the hydrocarbon forming oxygen- and/or nitrogen-containing intermediate species, which subsequently reduce nitrogen oxides to nitrogen. The SCR reaction is dependent on the oxygen and hydrocarbon concentrations and cannot take place in the absence of oxygen [5]. A general view concerns the oxidation of NO to NO_2 as an initial and necessary step for the reaction to occur, which of course emphasises the role of oxygen. However, in the present case, NO_2 is used as the NO_x, source in the reaction, yet the oxygen concentration seems crucial. An optimum in oxygen concentration is shown for NO_2 reduction by iso-butane over HZSM-5 zeolites [6]. This optimum can be related to the hydrocarbon activation, i.e. the oxygen is necessary for the activation but compete with NO_2 for the activated species. The C/NO_2 ratio, for the same system, also shows an optimum in NO_x reduction [6]. The decrease in NO_x reduction at higher ratios is supposed to be due to carbonaceous deposits blocking the active sites.

Chen *et al.* [7,8] discuss the reaction mechanism for HC-SCR over Fe/MFI in terms of NO oxidation and chemisorption, and formation of a deposit containing C, O, H and N atoms. Isotope labelling shows that one N atom in the formed N_2 origins from the NO and the other from the deposit. Formation of a heteronuclear N_2 molecule has also been reported by, for instance, Sun *et al.* [9,10] and Li *et al.* [11] for ammonia-SCR. The reaction pathway is suggested to include formation of ammonium nitrite as a reaction intermediate, Yeom *et al.* [12] put a similar discussion forward for the HC-SCR reaction, The nitrogen oxides and the organic molecules are proposed to react and form nitromethane, from which isocyanic acid (HNCO) may be formed via the aci-form of the molecule. Ammonia is then suggested to be formed by hydrolysis of the HNCO and then further react with the nitrogen oxides to form ammonium nitrite and N_2. However, this reaction route seems to require a relatively basic catalyst since the aci-anion of nitromethane is less likely to be formed over acidic materials [13]. The HC-SCR reaction has also been investigated by the reaction of NO_x with a nitro-paraffin, e.g., [14,15], and the mechanism that emerges involves 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.

In a previous paper [16] we discuss the reaction pathway for lean NO_2 reduction by propane over HZSM-5 zeolites. The most important steps seem to be the formation of NO^+ species on the surface and the activation of the propane through interaction with

* To whom correspondence should be addressed.
E-mail: hannahi@chalmers.se

the Brønsted acid sites forming carbenium ion adsorbates, which subsequently form alkenes. These two types of species are proposed to react forming isocyanate species, which can be hydrolysed to amine species that eventually react with other NO^+ species, or with NO_2 in the gas phase, forming N_2. However, during the experiments an accumulation of isocyanate species on the sample surface is observed, which may be related to the water formation in the reaction, i.e. the hydrolysis of isocyanate species will eventually decrease as the water formed in the reaction is consumed. The objective of this work is to further investigate the reaction mechanism for lean NO_2 reduction by propane over a HZSM-5 zeolite in the presence of water.

2. Experimental

The catalyst used in this study is a HZSM-5 zeolite (Akzo Nobel Catalysts BV) with a SiO_2/Al_2O_3 molar ratio of 40. Textural data, acidic characterisation and preparation of the sample may be find in ref [16].

In situ FTIR (Fourier Transform Infrared) spectroscopy measurements were carried out using a BioRad FTS 6000 spectrometer in diffuse reflection (DRIFT) mode [17,18]. The experimental procedure is described in detail previously [16], however in short the gases, Ar (99.995%), O_2 (99.95%), NO_2 (5000 ppm in Ar), C_3H_8 (10% in Ar), O_2 (2% in Ar) and H_2 (4% in Ar), were introduced via mass flow controllers (Bronkhorst Hi-Tech) to the DRIFT cell and water was produced by oxidation of hydrogen over a noble metal catalyst placed in front of the DRIFT cell. Step-response experiments where water (2000 ppm) was added and removed from the reaction gas mixture (1000 ppm NO_2, 800 ppm C_3H_8 and 10% O_2, balanced with Ar) were performed at 450 °C.

3. Results and discussion

The FTIR measurements are performed in the region above 2000 cm^{-1} since below 2000 cm^{-1} the background noise level is significant, probably related to perturbed vibration frequencies of the zeolite framework [19–21], which makes peak observation and assignment difficult in this area.

When NO_2, propane and oxygen are introduced to the HZSM-5 sample several peaks appear (figure 1). The 2132 cm^{-1} peak can most probably be attributed to NO^+ species [22] and the peak at 2259 cm^{-1} with a shoulder at 2280 cm^{-1} is likely due to isocyanate (–NCO) species bound to Al and Si in the zeolite framework, respectively [8,23–30], and/or nitrile species [7,8,23,26,27]. The intensity of the isocyanate peaks increase with time, i.e. the species seem to be accumulated on the sample surface. In the C–H stretching region (3000–2800 cm^{-1}) [26,27,31] peaks appear at 2880 and 2968 cm^{-1}, in particular the latter peak can be assigned to propane, loosely bound on the surface and/or present in the gas phase [32]. Two peaks appear at 3139 and 3169 cm^{-1}, which can be due to C–H stretching vibrations of unsaturated hydrocarbons [8,26] and/or N–H stretching vibrations of amine species or ammonia [8,33,34]. Furthermore, a peak is observed around 3330 cm^{-1}, probably related to N–H stretching vibrations [8,26,27, 35,36], indicating amine species present on the sample surface. Absorption peaks are also found at 3745 and 3610 cm^{-1}, which are assigned to OH stretching vibrations originating from silanol groups (Si–OH) and Si(OH)Al bridging hydroxyl groups (Brønsted acid sites), respectively [20–22, 27,37–40]. These peaks are negative, which is indicative of species blocking the sites, possibly hydrocarbons and/or amine species. It is likely that propane is activated over the Brønsted acid sites forming carbenium ion adsorbates and eventually alkenes [16,41].

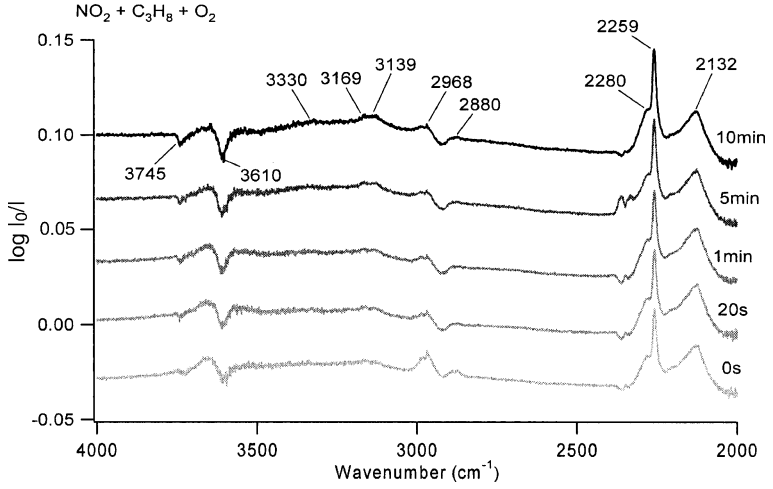

Figure 1. FTIR experiment with 1000 ppm NO_2, 800 ppm C_3H_8, 10% O_2 in Ar at 450 °C.

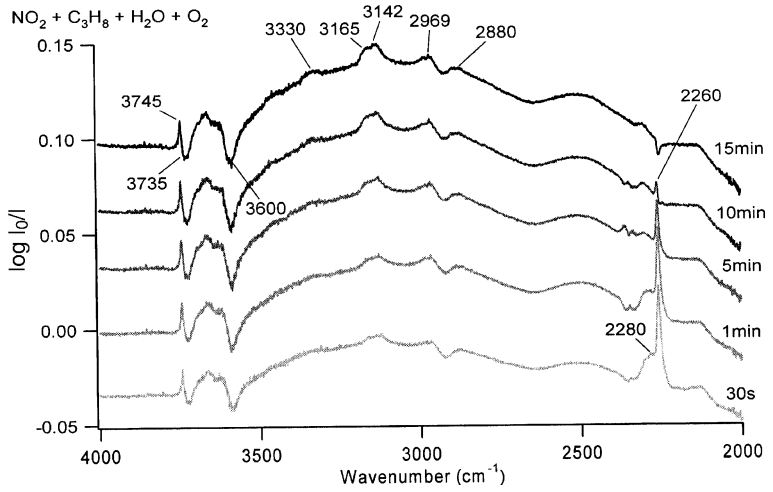

Figure 2. FTIR experiment with 1000 ppm NO_2, 800 ppm C_3H_8, 10% O_2 in Ar at 450 °C where 2000 ppm water is added at time 0 s. Light grey corresponds to direct after the gas switch and time is then increased until steady-state is reached, which is illustrated with black.

Introduction of water to the sample (figure 2) causes a rapid disappearance of the NO^+ species. This is likely caused by further reaction to –NCO species, as well as instability of the NO^+ species in the presence of water [22]. The isocyanate peaks decrease with time and eventually become negative, at the same time the N–H stretching peak, around 3330 cm^{-1}, and the peaks attributed to unsaturated hydrocarbons and/or amine species increase. During the sequence with water the Brønsted acid peak becomes more negative, i.e. the sites are blocked or consumed. These results support a hydrolysis reaction of the isocyanate species forming amine species and/or ammonia. For instance, Liu *et al.* [15] have studied the reaction of nitroethane over Cu-MFI under HC-SCR conditions and propose a reaction mechanism starting from the nitroparaffin via isocyanate species, which are likely formed through dehydrogenation of the aciform over Brønsted acid sites, and then further hydrolysed to amine species. Alternatively, ammonia can be formed from isocyanic acid (HNCO) which may react with NO_2 forming ammonium nitrite and eventually nitrogen [9–12]. However, this reaction route involves formation of N_2O_3 on the sample surface and even though we find a peak in the N=O region (1930–1880 cm^{-1}) [10] the symmetric and asymmetric stretching vibrations of NO_2, at 1590–1550 and 1305–1290 cm^{-1}, respectively [10], are not detected. Of course, disturbances from the zeolite framework are significant in this area (below 2000 cm^{-1}) and may influence the peak observations [19–21], thus it is possible that these peaks exists. On the other hand, Hadjiivanov *et al.* [22] state that the NO^+ species is the only stable NO_x surface species on HZSM-5 and Svedberg *et al.* [42] have investigated the NO_x storage ability on several materials and conclude that the amounts of stored NO_x on acidic samples is negligible above 300 °C. Therefore, based on the present results it is hence less likely that the ammonium nitrite route is the predominant reaction pathway under these conditions. For the same reason, formation of isocyanate from nitroparaffin may not readily occur over HZSM-5 zeolites. Moreover, it is reported that the aci-anion of nitromethane is less likely formed over acidic materials [13]. Instead isocyanate species are possibly formed by reaction of an alkene (formed from the alkane over Brønsted acid sites) and the NO^+ species over Brønsted acid sites. N-oxides (R-CNO) may thus be formed, which can be easily rearranged to isocyanate species (R-NCO) [25].

Turning off the water (figure 3) results in an immediate development of the NO^+ peak and eventually the isocyanate peaks (2259 and 2298 cm^{-1}) appear and seem to be accumulated throughout the sequence. The peaks assigned to unsaturated C–H and/or N–H vibrations have become one peak centred around 3155 cm^{-1}, which increases with time. It is likely that this peak eventually mainly reflects C–H vibrations, since the amount of water probably is insufficient for the hydrolysis reaction a while after the water has been turned off. The number of blocked Brønsted acid sites increases, which can be seen in an increasing negative peak at 3610 cm^{-1}. Unsaturated hydrocarbons and/or amine species are possibly formed on these sites, as manifested by the increase in the 3155 cm^{-1} peak, alternatively there is a loss of Brønsted acid sites.

It is hence most likely that amine species are formed in a hydrolysis reaction of isocyanate species and that the water produced from the propane, in the corresponding dry reaction, is not enough for a complete hydrolysis of the –NCO species to occur. We can thus conclude that the reaction route suggested in ref [16], where NO^+ species reacts with the activated hydrocarbon over the Brønsted acid sites forming isocyanate species, which are hydrolysed to amine species that can react with NO^+ species and/or NO_2 forming N_2, is a

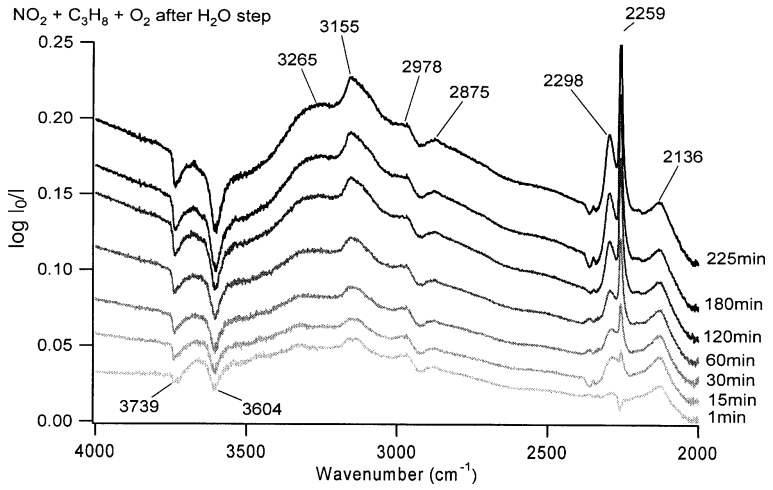

Figure 3. FTIR experiment with 1000 ppm NO_2, 800 ppm. C_3H_8, 10% O_2 in Ar at 450 °C where the water is turned off at time 0 s. Light grey corresponds to direct after the gas switch and time is then increased until steady-state is reached, which is illustrated with black.

possible pathway for the reaction to occur, over HZSM-5 zeolites.

Acknowledgements

The authors would like to thank Albemarle Catalysts BV for providing the zeolite. This work has been performed within the Competence Centre for Catalysis, which is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency and the member companies: AB Volvo, Volvo Car Corporation, Scania AB, GM Powertrain Sweden AB, Haldor Topsøe A/S, Perstorp AB, Albemarle Catalysts BV and The Swedish Space Corporation.

References

[1] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u and N. Mizuno, Shokubai (Catalyst) 32 (1990) 430.
[2] W. Held, A. Koenig, T. Richter and L. Puppe, SEA Paper 900496 (1990).
[3] Y. Traa, B. Burger and J. Weitkamp, Microporous Mesoporous Mater. 30 (1999) 3(and references herein).
[4] V.I. Parvulescu, P. Grange and B. Delmon, Catal. Today 46 (1998) 233(and references herein).
[5] M. Shelef, Chem. Rev. 95 (1995) 209.
[6] D.M. Zhao, *Catalysts for Aoutomotive Exhaust Cleaning – Aspects on TWC Deactivation and Lean NO_x* Reduction (Chalmers Reproservice, Göteborg, 2005).
[7] H.Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, J. Catal. 186 (1999) 91.
[8] H.Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, J. Catal. 180 (1998) 171.
[9] Q. Sun, Z.X. Gao, H.Y. Chen and W.M.H. Sachtler, J. Catal. 201 (2001) 89.
[10] Q. Sun, Z.X. Gao, B. Wen and W.M.H. Sachtler, Catal. Lett. 78 (2002) 1.
[11] M.J. Li, J. Henao, Y. Yeom, E. Weitz and W.M.H. Sachtler, Catal. Lett. 98 (2004) 5.
[12] Y.H. Yeom, B. Wen, W.M.H. Sachtler and E. Weitz, J. Phys. Chem. B 108 (2004) 5386.
[13] A.A. Kheir and J.F. Haw, J. Am. Chem. Soc. 116 (1994) 817.
[14] A.D. Cowan, N.W. Cant, B.S. Haynes and P.F. Nelson, J. Catal. 176 (1998) 329.
[15] I.O.Y. Liu, N.W. Cant, B.S. Haynes and P.F. Nelson, J. Catal. 203 (2001) 487.
[16] H.H. Ingelsten, D.M. Zhao, A. Palmqvist and M. Skoglundh, J. Catal. 232 (2005) 68.
[17] A. Hinz, M. Skoglundh, E. Fridell and A. Andersson, J. Catal. 201 (2001) 247.
[18] H.H. Ingelsten, Å. Hildesson, E. Fridell and M. Skoglundh, J. Mol. Catal. A 209 (2004) 199.
[19] R. Szostak, *Molecular Sieves* (Van Nostrand Reinhold, New York, 1989).
[20] M. Wallin, C.-J. Karlsson, A. Palmqvist and M. Skoglundh, Topics Catal. 30/31 (2004) 107.
[21] P.E. Fanning and M.A. Vannice, J. Catal. 207 (2002) 166.
[22] K. Hadjiivanov, J. Saussey, J.L. Freysz and J.C. Lavalley, Catal. Lett. 52 (1998) 103.
[23] K.I. Hadjiivanov, Catal. Rev. -Sci. Eng. 42 (2000) 71.
[24] S.A. Beloshapkin, E.A. Paukshtis and V.A. Sadykov, J. Mol. Catal. A 158 (2000) 355.
[25] A. Obuchi, C. Wogerbauer, R. Koppel and A. Baiker, Appl. Catal. B 19 (1998) 9.
[26] H.Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, Catal. Today 54 (1999) 483.
[27] F. Poignant, J.L. Freysz, M. Daturi and J. Saussey, Catal. Today 70 (2001) 197.
[28] M. Yamaguchi, J. Chem. Soc. -Faraday Trans. 93 (1997) 3581.
[29] F. Solymosi and T. Bansagi, J. Catal. 156 (1995) 75.
[30] S.K. Park, H. Choo and L. Kevan, Phys. Chem. Chem. Phys. 3 (2001) 3247.
[31] M. Xin, I.C. Hwang and S.I. Woo, J. Phys. Chem. B 101 (1997) 9005.
[32] T. Shimanouchi, *Tables of Molecular Vibrational Frequences Consolidated* Vol. 1(National Bureau of Standards, Washington, 1972) 1–160.
[33] E. Jobson, A. Balker and A. Wokaun, J. Chem. Soc. Faraday Trans. 86 (1990) 1131.
[34] N.Y. Topsoe, H. Topsoe and J.A. Dumesic, J. Catal. 151 (1995) 226.
[35] F. Poignant, J. Saussey, J.C. Lavalley and G. Mabilon, Catal. Today 29 (1996) 93.

[36] S.K. Park, Y.K. Park, S.E. Park and L. Kevan, Phys. Chem. Chem. Phys. 2 (2000) 5500.
[37] J. Szanyi and M.T. Paffett, J. Catal. 164 (1996) 232.
[38] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani and R.J. Willey, J. Catal. 179 (1998) 581.
[39] G. Boskovic, T. Vulic, E. Kis and P. Putanov, Chem. Eng. Technol. 24 (2001) 269.
[40] B.I. Mosqueda-Jimenez, A. Jentys, K. Seshan and J.A. Lercher, Appl. Catal. B 43 (2003) 105.
[41] F.C. Jentoft and B.C. Gates, Topics Catal. 4 (1997) 1.
[42] P. Svedberg, E. Jobson, S. Erkfeldt, B. Andersson, M. Larsson and M. Skoglundh, Topics Catal. 30–31 (2004) 199.