ELSEVIER

Catalysis Today 29 (1996) 93–97

CATALYSIS TODAY

In situ FT–IR study of NH_3 formation during the reduction of NO_x with propane on H/Cu-ZSM-5 in excess oxygen [1]

F. Poignant [a,*], J. Saussey [a], J.-C. Lavalley [a], G. Mabilon [b]

[a] *Laboratoire Catalyse et Spectrochimie, CNRS URA 0414, ISMRA-Université, 6 bd. Maréchal Juin, 14050 Caen Cedex, France*
[b] *Institut Français du Pétrole, B.P. 311, 92506 Rueil-Malmaison Cedex, France*

Abstract

IR experiments under flow of NO and propane on H/Cu-ZSM-5 evidence at 623 K the appearance of bands at 2248, 2157 and 2047 cm^{-1}, tentatively assigned through the use of ^{15}NO to nitrile, carbonyl ($CO–Cu^+$) and isocyano species respectively. Addition of O_2 suggests conversion of isocyano to isocyanato species (2208 cm^{-1}) which by hydrolysis leads to NH_3 formation, revealed by IR bands at 3366, 3290, 3192 and 1610 cm^{-1}.

Keywords: H/Cu-ZSM-5; FT–IR; NO_x reduction

1. Introduction

The mechanism of the reduction of NO_x with hydrocarbons in the presence of oxygen is not well established yet [1]. Propositions for the reactional process are numerous:

– decomposition of NO into $N_2 + O_2$ on the active sites, the hydrocarbon regenerating them by reacting with the oxygen produced [2].

– partial oxidation of the hydrocarbon by O_2 [3] or by NO_2 [4,5], the product formed reacting with NO.

– formation of an isocyanato species by thermal decomposition of a precursor $C_xH_yNO_z$, followed by reaction with NO to give N_2 [6].

– formation of a carbonaceous deposit on the surface as the active site [7].

In a recent study, we evidenced on Cu-ZSM-5 the formation of NH_3 during the reduction of NO by propane in excess oxygen [8]. The formation of NH_3 seemed to be linked with the presence of two types of adsorbed species characterized mainly by IR bands located at 2047 and 2248 cm^{-1}, respectively. The aim of the present work is to assign more precisely these two bands, to confirm the role of these species in the formation of NH_3 and especially to estimate the importance of this route in the mechanism of SCR of NO by propane.

2. Experimental

The H/Cu-ZSM-5 catalyst (Si/Al = 27) was prepared by ion exchange with a $Cu(NO_3)_2$ solution giving a copper content of 1.47 wt.-%. The design of the IR cell for in situ studies has already been reported [9]. It permits reactivity

---

[*] Corresponding author.

[1] This work was financially supported by the European Community, taking part in a Brite-Euram program.

SSDI 0920-5861(95)00285-5

experiments, combined with rapid collection of IR spectra of surface species (Nicolet Magna 750 FTIR spectrometer). Nitrogen oxides were analysed by FT–IR in a gas cell. The sample was pressed into self-supporting discs (ca. 15 mg cm^{-2}) and heated progressively to 623 K (2.5 K min^{-1}) under 5% O_2 in He and maintained for 3 h in these conditions. It was then exposed (flow rate = 25 cm^3 min^{-1}; GHSV = 50 000 h^{-1}) to different gas mixtures at 623 K.

Static experiments were performed in a classical IR cell. The sample was calcined then evacuated at 673 K before admission of the reactants (^{14}NO or ^{15}NO, C_3H_8: ca. 1 mmol/g cat) and the spectra further recorded at room temperature.

All the spectra of the adsorbed species were obtained by subtracting the spectrum of the activated wafer from the spectrum obtained after introduction of the reactants.

3. Results and discussion

3.1. Dynamic experiments

The IR spectrum of adsorbed species on H/Cu-ZSM-5 at 623 K under a stream of NO (2000 ppm) + C_3H_8 (2000 ppm) in helium shows the immediate formation of adsorbed CO species characterized by a band at 2157 cm^{-1} (Fig. 1a). With time on stream, bands at 2047 cm^{-1} then 2248 cm^{-1} and a broad massif in the region of ν_{CH} ethylenic vibrations appear, whereas the intensity of the band at 2157 cm^{-1} decreases. In the hydroxyl region, we note the appearance of a ν_{OH} band at 3597 cm^{-1}. Conversion of NO, which was initially 8%, decreases regularly and reaches ca. 3% after 40 min of reaction. From this moment, no further variation of the spectrum is observed. After a flush of pure helium at 623 K, the spectra of the adsorbed species remains unchanged (Fig. 2a). Pulses of oxygen (10 μl; 13.3 μmol/g cat) are then introduced in the inlet stream of helium. The IR spectra recorded after each pulse show a regular decrease of the bands at 2047 and 3597 cm^{-1} but above all, the simultaneous appearance of several bands in the vibration region of N–H bonds at 3366, 3290, 3192 and 1610 cm^{-1} (Fig. 2). A weak band by 2208 cm^{-1} can be evidenced from the second pulse (Fig. 2a–c) and its intensity remains constant until the fifth pulse of O_2. The band at 2248 cm^{-1} begins to disappear only from the third pulse. After the

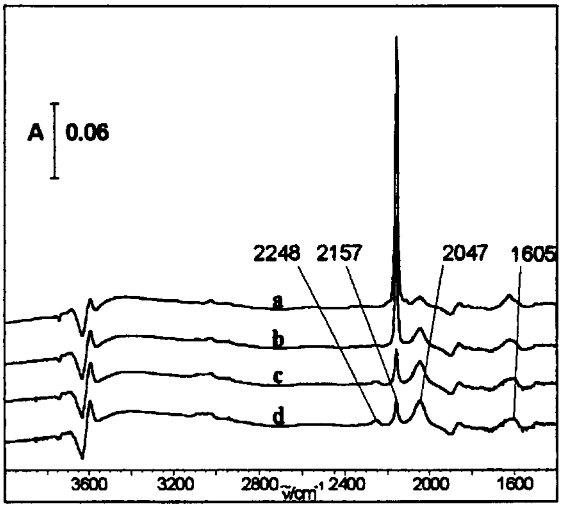

Fig. 1. IR spectra of adsorbed species on H/Cu-ZSM-5 at 623 K (a) NO + C_3H_8 in He after 7 min, (b) 18 min, (c) 30 min and (d) 40 min.

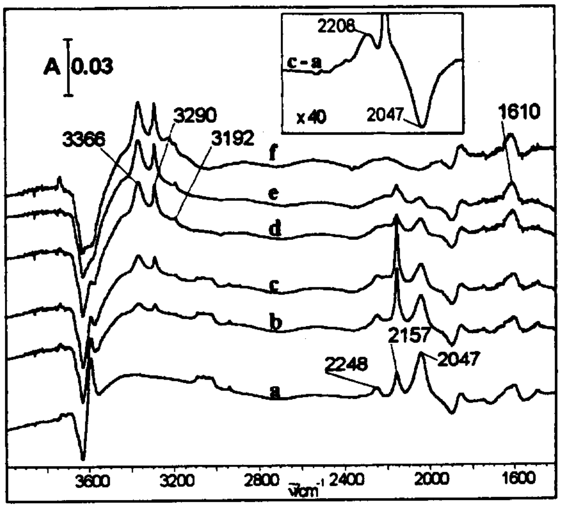

Fig. 2. IR spectra of adsorbed species on H/Cu-ZSM-5 at 623 K under He flow (a) 30 min after spectrum 1d, (b), (c), (d), (e) and (f) after 1, 2, 4, 5 or 6 pulses of O_2 (10 μl), respectively.

sixth pulse of O_2, the NH vibration region is modified by the appearance of one new band at 3225 cm^{-1} whereas the bands in the range 2000–2300 cm^{-1} have gone (Fig. 2f).

Other experiments, where pulses of oxygen have been replaced by pulses of NO or N_2O, did not evidence any reaction. Similarly, admission of pulses of H_2O did not alter the species associated with the band at 2047 cm^{-1} neither induced the emergence of ν_{NH} bands.

The first species formed on the catalyst is an adsorbed carbonyl; it is related to propane oxidation yielding CO. The catalyst contains Cu^+ and Cu^{2+} ions in cationic positions but the carbonyl species formed corresponds in fact to CO–Cu^+. This ν_{CO} vibration at 2157 cm^{-1} is higher than usual [10] but is characteristic for Cu^+ ions in cationic position [11]. Moreover, Cu^{2+} in cationic position in the H/Cu-ZSM-5 used does not give any ν_{CO} band characteristic for carbonyl species at temperatures above 298 K [12].

The intensity rise of the band at 3597 cm^{-1} is related to a partial reduction of the catalyst under a stream of $NO + C_3H_8$. This is due to the transformation of Cu^{2+} to Cu^+ ions which is accompanied by the formation of protons so as to maintain the charges balance of the zeolitic framework.

The second species detected is characterized by a band at 2047 cm^{-1}. The intensity of this band increases whereas the ν_{CO} intensity of the carbonyl species decreases. A linear correlation can be established between the appearance of the band at 2047 cm^{-1} and the disappearance of the carbonyl species but the interpretation is not univocal; whether the species is formed from the carbonyl or whether it is substituted to CO on Cu^+.

The regular consumption of the species related to the band at 2047 cm^{-1} with admission of pulses of O_2 shows that it is oxidised into a new species which could be associated to the band at 2208 cm^{-1} (Fig. 2a–c). We note the simultaneous appearance of bands at 3366, 3290, 3192 and 1610 cm^{-1} corresponding to NH_3 coordinated to Cu^+ [8]. Experiments of adsorption of NH_3 at different temperatures over H/Cu-ZSM-5 oxidised or reduced [26] show that at 623 K the ammonium form does not exist and that the coordinated form is present only on Cu^+. At this temperature, on oxidised catalyst, NH_3 must be totally oxidised.

The formation of NH_3 could originate from the hydrolysis of the oxidised species at 2208 cm^{-1} with water present on the catalyst or formed by oxidation of the catalyst ($2\ Cu^+ + 2\ H^+ + \frac{1}{2}O_2 \rightarrow 2Cu^{2+} + H_2O$) in accordance with the intensity decrease of the band at 3597 cm^{-1}.

Presence of at least three independent bands in the spectral region 2000–2350 cm^{-1} testifies to the formation of new species containing either two cumulative double-bonds (C=N, C=O or C=C) or one triple-bond (C≡N, N≡N or C≡C). The isocyanate species –N=C=O has often been put forward in the reactions of NO + CO over supported noble metals [13–18], over CuO–SiO_2 [19] or with NO, C_3H_6, O_2 over Cu/Cs–Al_2O_3 [6,20,21]. Hayes et al. [22] recently ascribed a band located at 2260 cm^{-1} observed during the reaction of $NO + C_3H_6$ over H/Cu-ZSM-5 to a nitrile species. In fact, assignment of bands in this range to adsorbed species with well defined structure is difficult because nitriles, isonitriles, carbodiimides, diazonium, cyanates, isocyanates, etc. all have strong IR absorption bands in this spectral region [23].

The band at 2047 cm^{-1} is ascribed to an adsorbed species which does not seem to have vibration bands in the ν_{CH} region. Its unreactivity towards H_2O and the fact that it needs to be exposed to O_2 to react suggest a cyano Cu–C≡N or isocyano Cu–N≡C type species. Moreover, the greater stability to oxidation of nitriles compared to isonitriles and the low value of the wavenumber of the band at 2047 cm^{-1} ($Cu(CN)_2$: $\nu_{CN} = 2125$ cm^{-1} [24]) direct the choice towards the isonitrile structure.

The weak band at 2208 cm^{-1} detected during oxidation of the species associated to the band at 2047 cm^{-1} could be ascribed to an isocyanate species on Cu^+. As a matter of fact, isocyanate species on metals are very unstable at these temperatures and their identification is most often assigned to an isocyanate formed on the metal support [16]. London and Bell [19] ascribed a band at 2200 cm^{-1} to copper isocyanate by comparison with the complex $Et_4N[Cu(NCO)_4]$ whose vibration $\nu_a(NCO)$ is at 2198 cm^{-1}. Solymosi and Kiss [25] in the dissociative adsorption of isocyanic acid HNCO over $Cu-SiO_2$ partially oxidised obtained a band at 2210 cm^{-1} assigned to CuNCO. Ukisu et al. [20], in the reaction of $NO + C_3H_6 + O_2$ over $Cu/Cs-Al_2O_3$, observed a band at 2254 cm^{-1} that they ascribe to copper isocyanate but the presence of alumina which gives stable isocyanates at these same wavenumbers does not certify this assignment. An argument for the identification of this species is the concomitant formation of NH_3 over the catalyst since hydrolysis of isocyanic acid or isocyanate complexes is known to produce unstable carbamic acid which decomposes into NH_3 and CO_2.

The species associated to the band at 2248 cm^{-1} seems much less sensitive towards O_2 and moreover, it can be correlated with a ν_{CH} band at 3065 cm^{-1}. The group responsible for the absorption at 2248 cm^{-1} could, thus, be hold by an olefinic group. But as in any performed experiments this band ever preceded the appearance of the one at 2047 cm^{-1}, it is unlikely that these two species take part to the same reactional process.

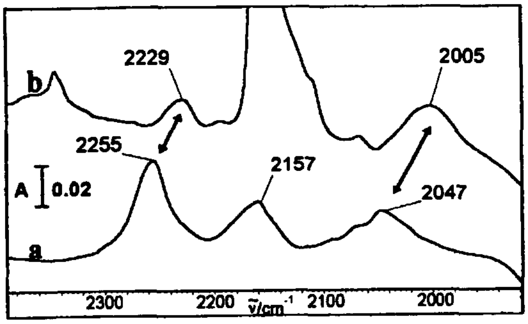

Fig. 3. IR spectra of adsorbed species on H/Cu-ZSM-5, (a) from $^{14}NO+C_3H_8$ after 15 min at 623 K and (b) from $^{15}NO+C_3H_8$ after 15 min at 623 K.

Table 1
Table of isotopic shifts $^{14}N \rightarrow {}^{15}N$ calculated and observed (cm^{-1})

	$\Delta\nu_{cal}$ [23]	$\Delta\nu_{obs}$ [23,27]
Cyano (–CN)	30	ca. 30
Isocyano (–NC)	38	ca. 38
cyanato (–OCN)		18
Isocyanato (–NCO)	10	ca. 10
Fulminato (–CNO)		37
Diazo, azido (–NN)		73

3.2. Static experiments

In order to confirm the assignment of the bands situated at 2047 and 2248 cm^{-1} we have undertaken experiments with $^{15}NO + C_3H_8$. The species associated with the band at 2047 cm^{-1} is much more difficult to generate in static conditions than the one at 2248 cm^{-1}. The spectrum of the adsorbed species with $^{14}NO + C_3H_8$ compared to $^{15}NO + C_3H_8$ is shown in Fig. 3. Thus, one can correlate the band at 2255 cm^{-1} to a band at 2229 cm^{-1} (with ^{15}NO), i.e., an isotopic shift of 26 cm^{-1} whereas the one at 2047 cm^{-1} seems to be associated to a broad band centred near 2005 cm^{-1} (with ^{15}NO) giving an isotopic shift of ca. 42 cm^{-1}. These experiments confirm that these two species contain only one nitrogen atom and that it is not located within a group of two cumulative double-bonds since the coupling met in the latter species disperses the mass effect on the vibrations ν_a and ν_s and decreases a lot the isotopic shift. Comparison of the isotopic shifts obtained in our experiments to those in Table 1 confirms that the vibration at 2047 cm^{-1} can correspond to an isonitrile species whereas the one at 2248 cm^{-1} is closer to a nitrile species.

4. Conclusion

The mechanism of the SCR of NO with C_3H_8 in the presence of O_2 is probably made up with several parallel and consecutive reactions. The relative importance of one or the other of these reactions depends on the operating conditions and on the nature of the catalyst.

In the present work, the first stage of the process which allows the formation of the $Cu^{I}NC$ species is not elucidated yet. The immediate appearance of CO in the beginning of the reaction, which further decreases simultaneously with the appearance of the isonitrile species leads to think that over H/Cu-ZSM-5, the reaction NO + CO would rather yield isonitrile species rather than isocyanate species habitually observed over noble metals. In fact, this isonitrile species stable without O_2 locks the process. An approximate determination of the amount of this species from the ammonia obtained after addition of O_2 shows that the catalyst at this stage would contain at least 30 μmol/g cat of this species. This fact suggests that this route is not secondary in the whole process.

We showed in a recent work [8] that if one introduces 0.5% of O_2 in a C_3H_8 + NO stream consecutively to the formation of this species, the IR spectrum presented the same NH bands in flow mode. The NO conversion initially nil reached 64% after 12 min on stream. With rising the concentration of O_2, the NH_3 bands become very weak and the conversion passes through a maximum (78%) with 2% of O_2 in the feed. In these conditions, the NH_3 species and the one related to the band at 2047 cm^{-1} have totally disappeared. This suggests the CuNC species formed takes part in the reduction process of NO and must lead in its final stage to a mechanism close to that proposed for the SCR of NO by NH_3. An evaluation of the relative importance of this process compared to other mechanisms can only be done through a correlation between the quantity of these adsorbed species and the conversion of NO in transient flow mode experiments.

References

[1] R. Burch and S. Scire, Appl. Catal. B, 3 (1994) 295.
[2] Y. Li and W.K. Hall, J. Phys. Chem., 94 (1990) 6145.
[3] C.N. Montreuil and M. Shelef, Appl. Catal. B, 1 (1992) L1.
[4] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett., 15 (1992) 297.
[5] J.O. Petunchi and W.K. Hall, Appl. Catal. B, 3 (1994) 239.
[6] Y. Ukisu, S. Sato, G. Muratmasu and K. Yoshida, Catal. Lett., 11 (1991) 177.
[7] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B, 2 (1993) 303.
[8] F. Poignant, J. Saussey, J.C. Lavalley and G. Mabilon, J. Chem. Soc., Chem. Commun., (1995) 89.
[9] J.F. Joly, N. Zanier-Szydlowski, S. Colin, F. Raatz, J. Saussey and J.C. Lavalley, Catal. Today, 9 (1991) 31.
[10] G. Ghiotti and F. Boccuzzi, Catal. Rev. Sci. Eng., 29 (1987) 151.
[11] M.L. Shepot'ko, A.A. Davydov and A.A. Budneva, Kinet. Katal., 35 (1994) 612.
[12] T. Piéplu, F. Poignant, A. Vallet, J. Saussey, J.-C. Lavalley and G. Mabilon, Stud. Surf. Sci. Catal., 96 (1995) 619.
[13] M.L. Unland, J. Phys. Chem., 77 (1973) 1952.
[14] M.L. Unland, J. Catal., 31 (1973) 459.
[15] D.A. Lorimer and A.T. Bell, J. Catal., 59 (1973) 223.
[16] F. Solymosi, L. Völgyesi and J. Rasko, Z. Physik. Chem. (NF), 120 (1980) 79.
[17] F. Solymosi, L. Völgyesi and J. Sarkany, J. Catal., 54 (1978) 336.
[18] F. Solymosi and J. Rasko, Appl. Catal., 10 (1984) 19.
[19] J.W. London and A.T. Bell, J. Catal., 31 (1973) 96.
[20] Y. Ukisu, S. Sato, G. Muratmasu and K. Yoshida, Catal. Lett., 16 (1992) 11.
[21] Y. Ukisu, S. Sato, A. Abe and K. Yoshida, Appl. Catal. B, 2 (1993) 147.
[22] N.W. Hayes, W. Grunert, G.J. Hutchings, R.W. Joyner and E.S. Shpiro, J. Chem. Soc., Chem. Commun., (1994) 531.
[23] B.A. Morrow and I.A. Cody, J. Chem. Soc., Faraday Trans. 1, 71 (1975) 1021.
[24] R.A. Penneman and L.H. Jones, J. Chem. Phys., 24 (1956) 293.
[25] F. Solymosi and J. Kiss, Surf. Sci., 104 (1981) 181.
[26] F. Poignant, J. Saussey and J.C. Lavalley, in preparation.
[27] S. Pinchas and I. Laulicht, IR spectra of labelled compounds, Academic Press, New York, 1971.