NH_3 Formation during the Reduction of Nitrogen Monoxide by Propane on H-Cu-ZSM-5 in Excess Oxygen

Frédéric Poignant,[a] Jacques Saussey,*[a] Jean-Claude Lavalley[a] and Gilles Mabilon[b]

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

Substitution of a NO + C_3H_8 + He flow by O_2 + He at 623 K leads to the appearance on a H-Cu-ZSM-5 catalyst of three IR bands at 3366, 3290 and 3192 cm^{-1} assigned to NH_3 species as confirmed by NH_3 adsorption showing that ammonia is formed during the SCR of NO by propane in excess oxygen, suggesting that it could play the role of an intermediate.

Catalytic reduction of NO_x from emissions of diesel engines has become an urgent problem. NO_x reduction by hydrocarbons in excess oxygen appears the most efficient process. However the catalyst, generally copper-based,[1] is not efficient enough yet. Study of the reaction mechanism and active sites must allow one to improve its efficiency. It is the reason why we have undertaken the study of the adsorbed species present either in the steady state or in the transient state, using an IR cell working as a reactor.

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 mass%. The design of the IR cell has already been reported.[2] It permits reactivity experiments, combined with rapid IR spectroscopic recordings of surface species (Nicolet Magna 750 FTIR spectrometer). The GC collection was performed with a Delsi chromatograph on line. Nitrogen oxides were analysed by FT-IR in a gas cell, also directly connected to the IR cell-reactor, with a Nicolet 5SX spectrometer. NO reduction was measured as the ratio %C = $[NO^0 - (NO + NO_2)]100/NO^0$, NO^0 being the inlet NO concentration. The sample was pressed into self-supporting discs (*ca.* 10 mg cm^{-2}) and prior to reaction it was 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 = 50000 h^{-1}) to different gas mixtures at 623 K. 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.

The *in situ* 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 characterized by a band at 2157 cm^{-1} [Fig. 1(*a*)]. With time on stream, bands at 2047 cm^{-1} then 2248 cm^{-1} and a broad complex one in the region of ν_{CH} ethylenic vibrations appear, whereas the intensity of the band at 2157 cm^{-1} decreases. In the hydroxy 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.

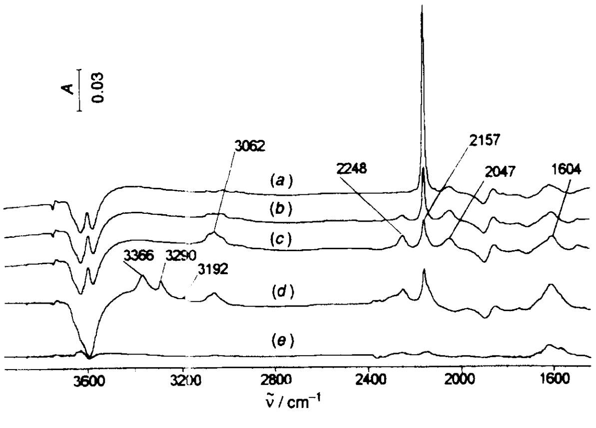

Fig. 1 IR spectra of adsorbed species on H–Cu–ZSM-5 at 623 K under flow: (*a*) NO + C_3H_8 + He after 4 min, (*b*) after 15 min, (*c*) after 42 min, (*d*) substitution by O_2 + He after 1 min, (*e*) after 5 min

Substitution of the (NO, C_3H_8, He) flow by O_2 (18% in He) drastically changes the IR spectrum of the species adsorbed on the catalyst [Fig. 1(*d*)]. The 2047 cm^{-1} band disappears immediately and the intensity of that at 2248 cm^{-1} rapidly decreases but the most interesting fact is the appearance of three bands at 3192, 3290 and 3366 cm^{-1} with the last two being particularly strong. Another one near 1610 cm^{-1} seems to add to a band at 1604 cm^{-1} initially present under NO + C_3H_8. The 3597 cm^{-1} band also disappears with the introduction of oxygen in the flow in such a way that after 5 min on stream (O_2, He), nearly all the bands disappear [Fig. 1(*e*)].

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 at cationic sites but the carbonyl species formed corresponds in fact to CO–Cu^+. This ν_{CO} vibration at 2157 cm^{-1} is higher than usual[3] but is characteristic for Cu^+ at a cationic site.[4] Moreover, Cu^{2+} at a cationic site in the H–Cu–ZSM-5 used does not give any ν_{CO} band characteristic for carbonyl species.[5] The 2157 cm^{-1} band intensity is stronger than that observed when adsorbing CO on the activated catalyst. This increase of Cu^+ ions corresponds to a reduction of a few copper sites under the (NO + C_3H_8, He) flow. This fact is confirmed by the growth of the 3597 cm^{-1} band which shows that the transformation of Cu^{2+} into Cu^+ occurs with formation of protons (ν_{OH} at 3597 cm^{-1}) so as to maintain the charges balance of the zeolitic framework. The presence of two bands in the range 2000–2300 cm^{-1} testifies to the formation of new species containing cumulative double-bonds (C=N, C=O and C=C) or triple-bonds (C≡N, C≡C). Isocyanate species –N=C=O have already been characterized in the reaction of NO + CO on CuO[6] or with NO, C_3H_6, O_2 on Cu–Cs/Al_2O_3,[7] although Hayes *et al.*[8] recently ascribed a band at 2260 cm^{-1} during the NO + C_3H_6 reaction on H–Cu–ZSM-5 (without O_2) to a nitrile species –C≡N. In fact, assignment of bands in this range to adsorbed species with well defined structure is difficult because cyanides, isocyanides, cyanates, isocyanates,fulminates, isofulminates and carbonyl all have a strong IR absorption bands in the spectral region between 2300 and 2000 cm^{-1}.[9] The attribution for the 2047 cm^{-1} band is not straightforward and cannot be realised without the use of ^{13}C and ^{15}N isotopes. Admission of oxygen induces the immediate disappearance of the 2047 cm^{-1} band whereas concomitantly the bands at 3366 (ν_3) 3290 (ν_1) and 3192 cm^{-1} appear. Their wavenumber is characteristic of NH vibrations. To confirm such an assignment, a flow of ammonia (8000 ppm in He) was passed over the fresh H–Cu–ZSM-5 at 623 K. The spectrum obtained asserts well the presence of these three bands (Fig. 2). They are accompanied by a band at 1614 cm^{-1} corresponding to the $\delta_{asym}(NH_3)$ vibration (ν_4) of NH_3 coordinated to copper ions. This experiment confirms the formation of NH_3 species over the catalyst.

In order to determine if the coordinated ammonia species formed are intermediates of the selective catalytic reduction (SCR) of NO with C_3H_8, we attempted to generate them in steady state (Fig. 3). On a catalyst activated under O_2–He we introduced the reactants as described previously, *i.e.* C_3H_8 (2000 ppm) + NO (2000 ppm). Then, 0.5% O_2 is introduced in the (NO, C_3H_8, He) flow. The band at 2047 cm^{-1} strongly decreases whereas the one at 2248 cm^{-1} does not change. On the other hand, in the 3400–3100 cm^{-1} region, one can see weak NH_3 bands at 3366 and 3291 cm^{-1}, the expected band at 3192 cm^{-1} being too small to be detected [Fig. 3(*a*)]. The conversion of NO, initially nil, reaches 64% after 12 min on stream. When the oxygen concentration is increased to 1%, the NH bands become weaker still [Fig. 3(*b*)] but the conversion of NO increased to 76% after 20 min on stream. With 2% O_2, the conversion passes through a maximum of 78%. At this value, NH_3 species and those characterized by bands at 2047 and 2248 cm^{-1} have totally disappeared but new ones in the 1600–1400 cm^{-1} region appear due to carboxylate species originating from partial oxidation of propane [Fig. 3(*c*)]. The fact that the NH_3 bands disappear from the spectrum at oxygen percentages close to the maximum of conversion tends to show that the NH_3 formed participates in the process of reduction of NO with C_3H_8. According to Unland,[10,11] substantial amounts of NH_3 are produced in the reaction of (NO, CO, H_2O) mixtures over noble metals and this fact is related to the hydrolysis of isocyanate species formed on the catalyst. He proposed a mechanism that results in the formation of NH_3 through hydrolysis of isocyanate species. This mechanism may be compatible with the reduction of NO by hydrocarbons. The ammonia formed would further react with NO to yield N_2 according to the process of the SCR of NO_x with NH_3.[12] Additional experiments are necessary to appreciate the relative importance of this mechanism in the process studied.

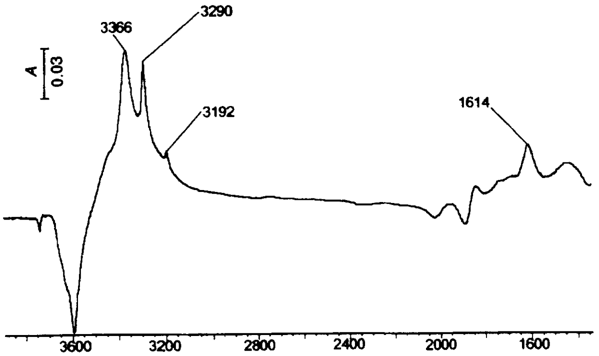

Fig. 2 IR spectrum of adsorbed species under flow of ammonia at 623 K

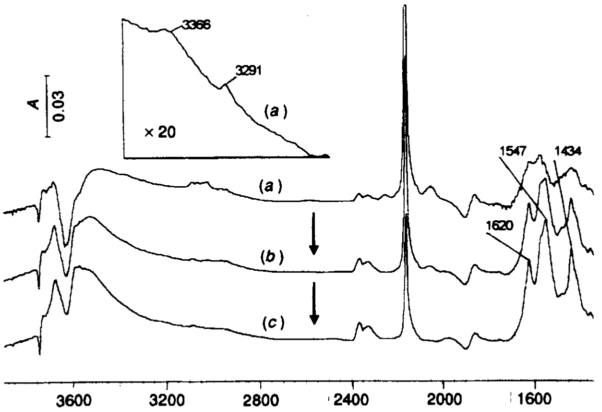

Fig. 3 IR spectra of adsorbed species under flow of NO + C_3H_8 + O_2 in He at 623 K (*a*) 0.5% O_2, (*b*) 1% O_2, (*c*) 2% O_2

Received, 14th October 1994; Com. 4/06293K

References

1 M. Iwamoto and H. Hamada, *Catal. Today*, 1991, **10**, 57.
2 J. F. Joly, N. Zanier-Szydlowski, S. Colin, F. Raatz, J. Saussey and J. C. Lavalley, *Catal. Today*, 1991, **9**, 31.
3 G. Ghiotti and F. Boccuzzi, *Catal. Rev.-Sci. Eng.*, 1987, **29**, 151.
4 M. L. Shepot'ko, A. A. Davydov and A. A. Budneva, *Kin. Katal.*, 1994, **35**, 612.
5 T. Piéplu, F. Poignant, A. Vallet, J. Saussey, J.-C. Lavalley and G. Mabilon, to be published.
6 J. W. London and A. T. Bell, *J. Catal.*, 1973, **31**, 96.
7 Y. Ukisu, S. Sato, A. Abe and K. Yoshida, *Appl. Catal. B*, 1993, **2**, 147.
8 N. W. Hayes, W. Grunert, G. J. Hutchings, R. W. Joyner and E. S. Shpiro, *J. Chem. Soc., Chem. Commun.*, 1994, 531.
9 B. A. Morrow and I. A. Cody, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1021.
10 M. L. Unland, *J. Catal.*, 1973, **31**, 459.
11 M. L. Unland, *J. Phys. Chem.*, 1973, **77**, 1952.
12 T. Komatsu, M. Nunokawa, I. S. Moon, T. Takahara, S. Namba and T. Yashima, *J. Catal.*, 1994, **148**, 427.