Possible intermediates in the selective catalytic reduction of NO_x: differences in the reactivity of nitro-compounds and *tert*-butyl nitrite over γ-Al_2O_3

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Nitromethane decomposes over alumina to give various surface species such as isocyanates and its oxidation by O_2 yields significant amounts of ammonia; on the other hand, *tert*-butyl nitrite decomposes to give only surface nitrate species and mostly oxides of nitrogen are formed by reaction with O_2.

Several authors have suggested that the selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons proceeds *via* organic nitro or nitrite intermediates over various catalysts such as promoted ZSM5[1–3] or Pt/SiO_2.[4] For the latter material, Tanaka *et al.* reported that the oxidation of both nitromethane and *n*-butyl nitrite gave products similar to those of the SCR of NO_x.[4] The gas phase decomposition and oxidation of nitromethane and its reactivity have previously been studied in connection with the NO_x-SCR over different catalysts such as Co-ZSM5, H-ZSM5, Na-ZSM5, SiO_2 or Al_2O_3.[5,6] The adsorption of this molecule on Al_2O_3, one of the most active single metal oxides for SCR reactions, has also been studied by Yamaguchi.[7] While organic nitro or nitrite species have not usually been differentiated in their involvement in the SCR reaction, our present work reports significant differences in the adsorption and reaction/oxidation of nitromethane and *tert*-butyl nitrite over Al_2O_3. These differences stress the need to consider differently the role of these compounds in the modelling of SCR reactions over alumina.

The catalytic experiments were carried out in a quartz flow microreactor (4 mm internal diameter) using 200 mg of Al_2O_3 (Alcan AA400, 150 $m^2\ g^{-1}$) previously calcined for 6 h at 973 K . The reactant gases used were O_2 (BOC 99%) and Ar (Air Products, high purity grade). Nitromethane (Fluka, puriss $\geqslant$ 99.0%) and *tert*-butyl nitrite (Fluka, assay $\geqslant$ 90%) were fed using a saturator flushed by the O_2 stream, which was then added to the Ar stream. The total rate of flow was 100 $cm^3\ min^{-1}$ with 1.5% O_2 in the gas mixture. The saturator was kept at room temperature and at 273 K for the experiments using nitromethane and *tert*-butyl nitrite, respectively. The products of reaction were analysed using a gas-cell (Foxboro®) fitted in a FTIR spectrophotometer (Nicolet 550®), 64 scans with a resolution of 1 cm^{-1} were usually collected. The diffuse reflectance FTIR measurements (DRIFTS) were carried out *in situ* using a finely ground sample (*ca.* 30 mg) of Al_2O_3 and the spectra were recorded after 128 scans at a resolution of 2 cm^{-1}. The catalytic experiments and the *in situ* measurements were both carried out at 573 K under steady state conditions. The nitromethane and *tert*-butyl nitrite were pre-adsorbed on the Al_2O_3 at room temperature for the *in situ* DRIFTS experiments.

Fig. 1(a) shows the DRIFT spectrum of the species formed from the adsorption of nitromethane on Al_2O_3 at room temperature and subsequently heated to 573 K in argon alone. The bands at 1376 cm^{-1} ($\nu^{sym}{}_{OCO}$), 1393 cm^{-1} (δ_{CH}), 1598 cm^{-1} ($\nu^{a}{}_{OCO}$), 2902 cm^{-1} (ν_{CH}) and 3003 cm^{-1} (combination band $\nu^{a}{}_{OCO} + \delta_{CH}$) can be assigned to a formate species; the vibration mode to which each band corresponds is given in parentheses.[8,9] The small band at 2092 cm^{-1} could be characteristic of a linearly adsorbed cyanide whereas the major band at 2228 cm^{-1} could be characteristic of an (inorganic) isocyanate group, a bridged cyanide or a nitrile species.[9,10] The adsorption of HCN on our Al_2O_3 showed in the spectral region 2000–2300 cm^{-1}, only a band at 2092 cm^{-1} whereas a band at 2228 cm^{-1} was observed when cyclohexyl isocyanate was adsorbed. Additional experiments have shown that the band at 2228 cm^{-1} derived from nitromethane was readily displaced by water at 573 K and NH_3 was observed in the gas phase. This high reactivity with water suggests that this band should be assigned to an isocyanate species rather than to a cyanide/nitrile species which are significantly less reactive towards water.[11,12] Other peaks were detected at 1447, 1681 and 3390 cm^{-1} which could tentatively be assigned to the ν_{NCO}, ν_{CO} and ν_{NH} of carbamic acid (NH_2CO_2H), respectively. Similar DRIFTS spectra to that observed with nitromethane were obtained with several other nitro compounds: nitroethane, 2-nitropropane and nitrobutane.

The DRIFT spectrum obtained from the adsorption of *tert*-butyl nitrite on Al_2O_3 at room temperature followed by heating to 573 K in Ar alone [Fig. 1(b)] was markedly different from that obtained using nitromethane. Only nitrate species, with characteristic bands at 1258, 1306 and 1554 cm^{-1}, were detected. Separate adsorption experiments over the same Al_2O_3 sample using NO, NO_2 and O_2 showed that the bands at 1258 and 1554 cm^{-1} were coupled, whereas the band at 1306 cm^{-1} was coupled with a band at 1580 cm^{-1}. This latter could not be observed here because it overlapped with the band at 1554 cm^{-1}. According to the literature, these bands correspond to two different types of bidentate nitrate species.[9] Some CH vibrations were also observed following the pre-adsorption of

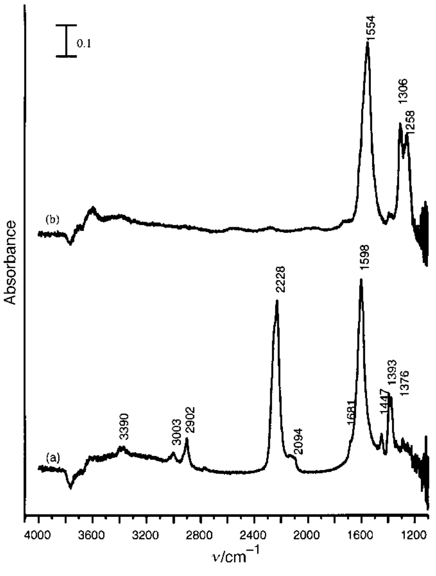

Fig. 1 DRIFT spectra at 573 K in argon of Al_2O_3 following pre-adsorption of (a) nitromethane and (b) *tert*-butyl nitrite at room temperature.

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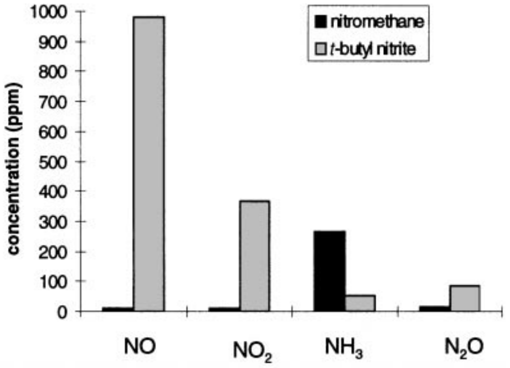

Fig. 2 Distribution of the products of reaction in the oxidation of nitromethane and *tert*-butyl nitrite at 573 K over Al_2O_3. Feed: 1.5% O_2 + 405 ppm nitromethane or 1700 ppm *tert*-butyl nitrite in Ar. Total flow 100 $cm^3 min^{-1}$.

the *tert*-butyl nitrite at room temperature. However, these CH bands were readily displaced with increasing temperature (under argon) and only the ad-NO_x species bands remained on the sample surface at 573 K. Details of these experiments will be given in a subsequent paper.

Fig. 2 shows the distributions of the main products of the oxidation of nitromethane and *tert*-butyl nitrite over alumina: NO, NO_2, N_2O and NH_3 were detected in both cases. Traces of HCN (not quantified) were also detected during oxidation of nitromethane and *tert*-butyl nitrite. Any N_2 formed could not be detected as it is inactive in the IR. The oxidation of nitromethane yielded a significant proportion (267 ppm) of NH_3, but NO (12 ppm), NO_2 (10 ppm) and N_2O (14 ppm) were formed only in much lower concentrations. In contrast, the oxidation of *tert*-butyl nitrite yielded oxides of nitrogen (*i.e.* NO: 983 ppm, NO_2: 366 ppm and N_2O: 87 ppm) as the main products of reaction whereas only traces of NH_3 (51 ppm) were observed.

The formation of NH_3 from the oxidation of nitromethane can be explained by the following reaction mechanism [eqn. (1)]:[5,6,12,13]

$$MeNO_2 \longrightarrow HNCO_{(ads)} + H_2O \longrightarrow NH_2CO_2H_{(ads)} \longrightarrow CO_2 + NH_3 \qquad (1)$$

The formation of the isocyanate species from the nitro-compound is believed to occur through the dehydration of the enol tautomer of nitromethane followed by isomerisation of the corresponding nitrile *N*-oxide. The intermediacy of carbamic acid in eqn. (1) is supported by the observation by DRIFTS of IR bands at 1448, 1681 and 3390 cm^{-1} which are compatible with its molecular structure. The reaction between the surface isocyanate species ($HNCO_{ads}$) and H_2O is probably fast enough on the Al_2O_3 surface to prevent the release of isocyanic acid (HNCO) to the gas phase, as no HNCO was detected during the catalytic oxidation experiment.

As described above, the adsorption of *tert*-butyl nitrite on Al_2O_3 gave rise to nitrate surface species [Fig. 1(b)], and so the formation of NO and NO_2 during the oxidation of this molecule was easily understandable. It has previously been reported that NO and NO_2 were formed in TPD experiments of nitrate species adsorbed on various catalysts.[14]

As has been often suggested,[1–3] organic nitro and organic nitrite compounds might both be intermediate species in the SCR of NO_x by hydrocarbons since their oxidation products were similar to those obtained in this reaction. However, the present work shows that their reactivity was quite different on alumina and hence that any reaction scheme for the SCR reaction must associate with them a specific role. This is of particular importance with regards to some recent results from our laboratory[15] which indicate that the formation of organonitrogen compounds may be a crucial step in the C_3H_6-SCR of NO over alumina. Among other reactions, it would be quite understandable if any ammonia (or, for that matter, any primary amine from which ammonia could be derived) formed from the decomposition of a nitro-type compound were to react with the NO_2 formed from the decomposition of a nitrite-type compound to yield N_2 as in a typical ammonia-SCR process.

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