A thermogravimetric study of NO_x adsorption and reduction over Cu-ZSM-5

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Thermogravimetric studies show that NO_2 is adsorbed over the surface of Cu-ZSM-5 at 300 °C and forms an intermediate with propene; this intermediate reacts with both NO_2 and O_2.

The most promising approach to the control of NO_x emissions in oxygen-rich exhaust gases is the reduction of NO to molecular dinitrogen by light hydrocarbons over a suitable catalyst. Metal-impregnated ZSM-5 has been shown to be active in this regard, with copper receiving most attention.

Many studies have been devoted to NO adsorption on Cu-ZSM-5.[1–3] When adsorption was carried out in the presence of oxygen, Adelman *et al.*[4] observed that temperature programmed desorption (TPD) resulted in the formation of the same quantities of NO and NO_2. A complex of N_2O_3 was suspected to form on the catalyst surface, and IR spectroscopic studies have shown numerous possible adsorbed species.[5–7]

The existence of a surface intermediate between NO/O_2 or NO_2 and the hydrocarbon has been demonstrated.[8] This intermediate is attacked by both NO_2 and O_2, with the former yielding mostly N_2 as product. In order to quantify the formation and destruction behaviour of this intermediate, a gravimetric approach has been adopted and is described here.

ZSM-5 catalyst was prepared by templated crystallisation at an Si/Al ratio of 27.5, and then 100% copper-exchanged (1.8% by mass on a dry basis). A series of tests involving the passage of different gases in sequence over the activated catalyst was performed at 300 °C in a thermobalance. A bed of activated catalyst was placed into the pan of a Linseis thermobalance and continuously flushed with 20 Nl h^{-1} of nitrogen. The temperature was then ramped up to 300 °C at a rate of 10 K min^{-1}. When the mass reading was stable, the gas composition was changed to include combinations of $NO–O_2–NO_2$ in nitrogen.

Fig. 1 shows the relative mass changes to about 100 mg of Cu-ZSM-5 after the injection of 1000 ppm of NO, followed by the addition of 10% oxygen and then a further 1000 ppm of propene. There is little change to the stabilised mass after the addition of NO only, but a significant increase when oxygen is present. Following the addition of propene, the differential mass falls to about half of the maximum.

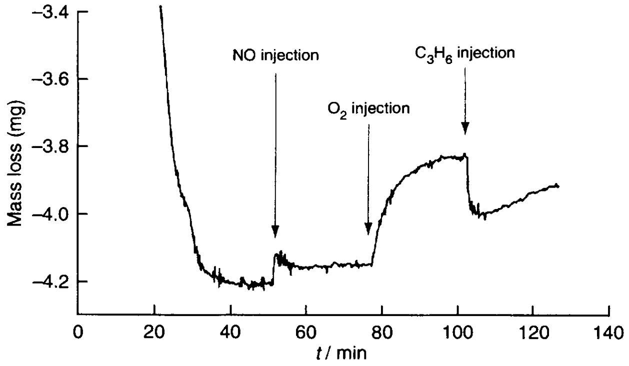

Fig. 1 Thermogravimetric study of NO adsorption at 300 °C over Cu-ZSM-5 (1000 ppm NO, 10% O_2, 1000 ppm C_3H_6, balance N_2)

Assuming that one molecule of gas is adsorbed per copper cation, only 4.3% of the copper sites are occupied by NO under inert-gas conditions but 28.1% under oxygen. Under reaction conditions, equilibrium calculations predict that virtually 100% of the NO would be present as NO_2. If NO_2 is the adsorbed species, 18.3% of the copper sites are occupied, which is consistent with the value found previously for NO_2 in a flow reactor[8] (19.1%). These results suggest that NO_2 is adsorbed rather than NO.

This was confirmed in a similar experiment carried out with NO_2 in place of NO, when the result shown in Fig. 2 was obtained. There is an immediate increase in the mass of 80 mg of catalyst as NO_2 is adsorbed, and no change following the addition of oxygen. However with the addition of propene, the mass returns almost immediately to the initial value but then begins to increase rapidly again.

In both cases the introduction of the hydrocarbon led to the rapid desorption of NO_x, a phenomenon which has also been found in the flow reactor.[8] The subsequent increase in mass, which is attributed to the formation of intermediate, occurs at a constant initial rate of approximately 2×10^{-4} mg mg^{-1} min^{-1} (see Fig. 3). After 100 min the rate begins to decrease and at

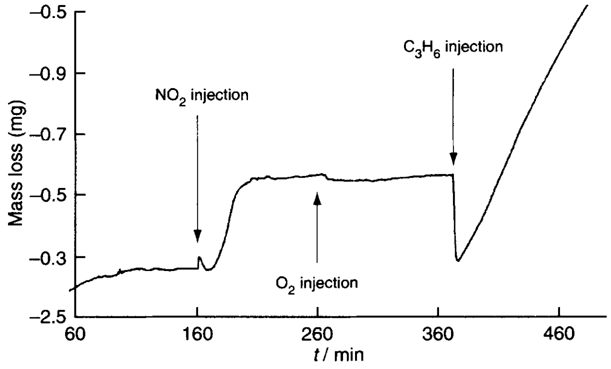

Fig. 2 Thermogravimetric study of NO_2 adsorption at 300 °C over Cu-ZSM-5 (3000 ppm NO_2, 10% O_2, 1800 ppm C_3H_6, balance N_2)

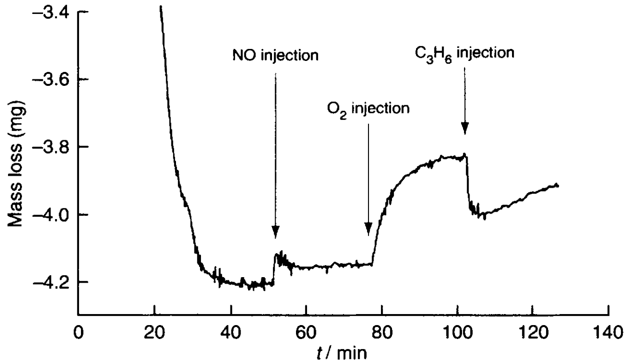

Fig. 3 Thermogravimetric study of intermediate formation over Cu-ZSM-5 at 300 °C (1000 ppm NO, 10% O_2, 1000 ppm C_3H_6, balance N_2)

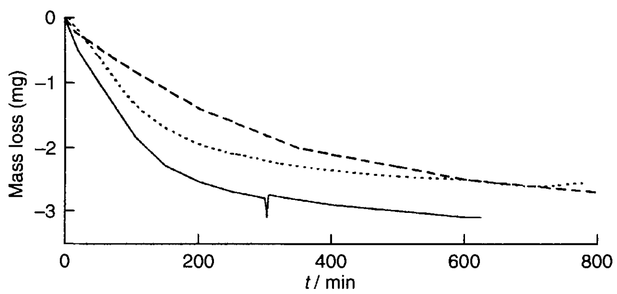

Fig. 4 Thermogravimetric study of intermediate consumption; (——) 1800 ppm NO, 10% O_2, balance N_2; (······) 3000 ppm NO_2, balance N_2; (– – –) 10% O_2, balance N_2

about 600 min the mass reaches a constant value equivalent to *ca.* 0.04 mg per mg of catalyst (in the presence of 1000 ppm NO and 1000 ppm propene).

The intermediate is attacked by both NO_2 and oxygen. The relative rates of consumption for the equilibrium mass of intermediate formed under the conditions applicable to Fig. 2 are shown in Fig. 4. It reacts only slightly more rapidly with 3000 ppm NO_2 than 10% oxygen, suggesting that the NO_2 is inherently more reactive. With a mixture of 10% O_2 and 1800 ppm NO, the rate is equivalent to the combined effect of O_2 and the NO_2 formed by oxidation of NO.

Thermogravimetry has confirmed that hydrocarbons strip from the surface any NO_2 adsorbed onto the active sites of Cu-ZSM-5. However the hydrocarbon adsorbate so formed is slowly complexed by gaseous NO_2 to form an intermediate. Both NO_2 and O_2 attack the NO_2–hydrocarbon intermediate in the course of the NO_x reduction reaction.

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