Activity of carbonaceous deposits in the selective reduction of nitrogen oxides

Jan Connerton, Richard W. Joyner* and Michael Stockenhuber

The Catalysis Research Laboratory, The Nottingham Trent University, Clifton Lane, Nottingham, UK NG11 8NS

Carbonaceous deposits, formed on the catalyst Cu/ZSM-5 by interaction at low temperature with propene, NO and oxygen, are characterised spectroscopically and shown to be able to carry out the selective catalytic reduction of NO; rates of reaction, which follow simple kinetics, are lower than in the absence of pre-deposited coke, and the results suggest an inverse correlation between catalyst Brønsted acidity and activity in NO_x reduction.

The selective reduction of nitrogen oxides by hydrocarbons in the presence of oxygen, using for example Cu/ZSM-5 catalysts, continues to attract attention.[1–5] Much interest now centres on the nature of the nitrogen-containing functionality in the reaction, with spectroscopic support emerging both for oxidised nitrogenous species such as nitro groups,[6,7] and also for reduced species, particularly cyanides.[7–12] Less attention has been paid to the characterisation of the hydrocarbon moieties which must be involved, although it is recognised that long-lived carbonaceous species can be formed within the pores of the zeolite, with possible mechanistic importance, as discussed by ourselves and others.[7,13] Here, we report on the nature and reactivity of hydrocarbon species deliberately deposited on Cu/ZSM-5 catalysts with different metal contents. We have previously shown that nitrogen is released from these deposits by reaction with oxygen[7] and now show that the deposits are also able to activate NO_x directly. The reactivity of the coke towards NO_x is also compared to the steady-state performance of these catalysts.

Catalysts have been prepared from H-ZSM-5 (Si/Al ratio 25) as described previously,[3] using conventional ion-exchange techniques. A range of catalysts from 50 to 130% nominal degree of exchange has been examined. Catalyst performance has been tested in a simple flow-through microreactor, equipped with a chemiluminescent analyser for nitrogen oxides (NOx Box, Signal Instruments Model 4000), and a gas chromatograph. Steady-state reaction conditions comprised 2% oxygen, 1200 ppm propene, 2000 ppm NO, balance helium and GHSV = 30 000 h^{-1}; the catalysts were initially activated by heating at 773 K for 1 h in 2% oxygen in helium. IR spectroscopy measurements were carried out in transmission mode using a specially constructed *in situ* vacuum cell which can be heated to >800 K, and an ATI RS1 Fourier transform spectrometer.

Before studying the behaviour of deposited coke, the steady-state performance of the catalysts was measured, starting at 773 K and gradually reducing the temperature. As in our earlier study,[7] coke was then deposited by exposing the catalyst of interest to the reaction mixture at 473 or 573 K. The IR spectrum of the deposit on a 54% copper exchanged catalyst is shown in Fig. 1. The bands at 2879, 2937 and 2971 cm^{-1} are typical of hydrocarbons adsorbed on acidic zeolites such as H-ZSM-5 and are due to C–H stretching vibrations. It is important to note that the band characteristic of the zeolite's Brønsted acidity (normally observed at *ca.* 3607 cm^{-1}) has been suppressed, indicating that these sites have played their expected role in hydrocarbon activation. The intense band at *ca.* 1600 cm^{-1} is assigned to C=C stretching vibrations in adsorbed aromatic molecules, and is characteristic of hydrocarbon deposits on zeolites.[9] It is superimposed on an overtone band associated with the zeolite lattice vibrations. The other important features of the spectrum are the band at 2250 cm^{-1}, which it is now accepted is due to cyanide species,[10–12] and bands at 3300 and 3375 cm^{-1}. These are nitrogen–hydrogen stretches which probably reflect the presence both of =NH and $-NH_2$ groups, which have not been reported before in this system. Their observation provides important evidence that the organic nitro groups, which are formed first in the sequence of reactions leading to release of nitrogen,[5] can undergo sequential reduction to cyanide [eqn. (1)].

$$-NO_2 \rightarrow -NH-OH \rightarrow -NH_2 \rightarrow =NH \rightarrow \equiv N \qquad (1)$$

The zeolite is unable to activate oxygen at the relatively low temperatures where the hydrocarbon deposit is formed. Coupled with the presence of readily activated propene, the result is an atmosphere which is more strongly reducing than is the case where steady-state reactivity is high, and where the reduction sequence may not progress as far as cyanide.[5]

The reactivity of the carbonaceous deposit in NO reduction in the absence of other hydrocarbons has been studied by exposing it to the same NO–oxygen concentration as was used for steady-state reaction, and heating from 473 to *ca.* 920 K at 10 K min^{-1}. The results of experiments with two different catalysts are shown in Fig. 2, which show the instantaneous concentration of NO_x ($NO + NO_2/N_2O_4$) at the reactor exit. In each case the deposit on the catalyst shows significant activity in NO_x reduction, but the maximum of activity for the catalyst with 100% copper exchange occurs at *ca.* 100 K lower temperature than for the catalyst with only 54% exchange. The amount of NO_x converted in each case is, however, rather similar, corresponding to *ca.* 25 mg NO (g catalyst)$^{-1}$. This is the same order of magnitude as that measured for deposited coke in our earlier study,[7] where 30 mg g^{-1} of coke was formed on an overexchanged catalyst tested at 10 000 h^{-1} GHSV. The kinetics of reaction between NO_x, oxygen and the carbonaceous deposits can be simply described. Fig. 2 also shows rates of reaction calculated by assuming first-order behaviour in both NO and hydrocarbon concentration, and zero order of reaction in oxygen (which is present in substantial excess throughout). There is very good agreement with experiment for such a simple model, particularly when it is realised that NO_2 is a reaction

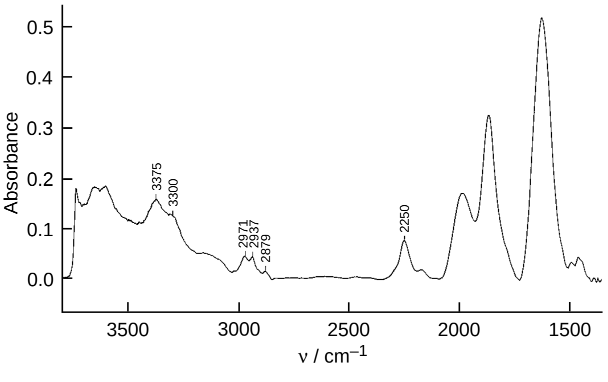

Fig. 1 IR spectrum of the carbonaceous deposit on a 54% Cu-exchanged catalyst; frequencies of bands discussed in the text are marked

intermediate.[5] In line with the changes in activity, the apparent activation energy of the reaction decreases from *ca.* 92 to 82 kJ mol^{-1} as the copper content of the zeolite is increased.

These results suggest that the presence of too many Brønsted zeolite acid sites inhibits the NO_x reduction reaction. It is known that relatively few Brønsted sites remain in the so-called 'overexchanged' catalysts which are the most active for NO_x reduction.[14] The present study shows that when the catalyst is pre-treated at low temperature in a way that allows the acid sites to have maximum influence in hydrocarbon activation, the result is to produce a hydrocarbonaceous deposit which is of lower activity in NO_x reduction at low temperature than that formed at steady state. Comparison of Fig. 1 with our earlier steady-state results (ref. 3, Fig. 1) shows that the steady-state process occurs more quickly at temperatures up to *ca.* 720 K. Equally, the deposit produced on the catalyst with lower copper content, and therefore higher residual Brønsted acidity, is even less active in NO reduction. There is thus an inverse correlation between Brønsted acidity and catalyst performance. It is still not clear whether the small amount of residual Brønsted acidity which remains in the most active Cu/ZSM-5 catalysts is necessary for the reaction to occur, since it is possible that the Lewis acidity associated with the Cu^{I} sites[14] is sufficient to activate the hydrocarbon species.

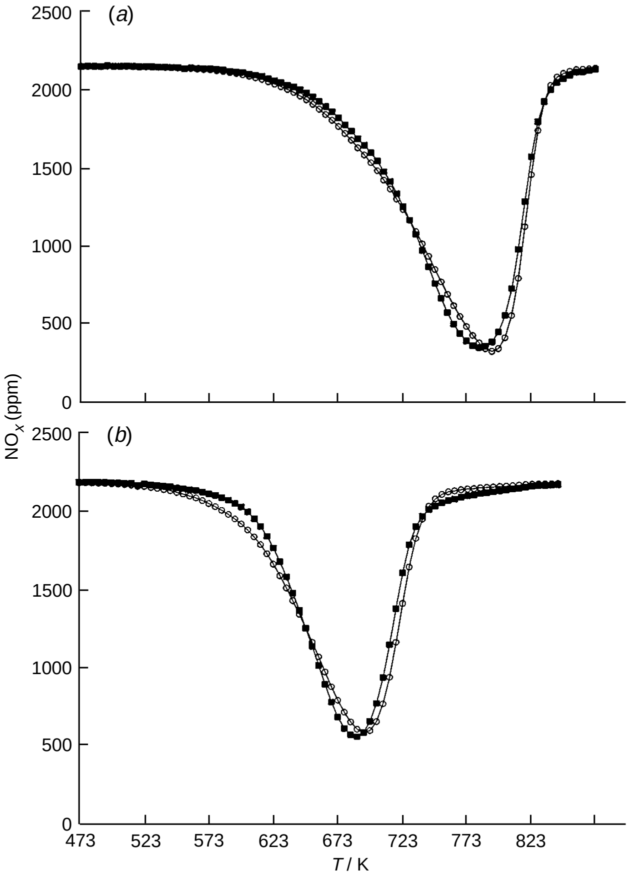

Fig. 2 (*a*) Observed and calculated NO_x concentration observed during heating at 10 K min^{-1} in NO–oxygen, after the formation of hydrocarbon deposits at 473 K on a 54% Cu-exchanged catalyst as described in the text. (■) Experimental, (○) calculated using the simple model described in the text. (*b*) As (*a*), but for a 100% Cu-exchanged catalyst.

We have had many useful discussions related to this with work with Dr Olga Tkachenko and the late Professor Efim Shpiro, of the Zelinsky Institute of Organic Chemistry, Moscow, and with Drs J. C. Frost, A. Diwell, A. P. Walker and colleagues, of Johnson Matthey Technology Centre. We thank Professor J. A. Lercher for the design of the *in situ* cell for IR spectroscopy developed in his research group. We are grateful to Johnson Matthey PLC for financial support and some analytical assistance, and to EPSRC for financial support.

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Received, 27th September 1996; Com. 6/06618F