New insights into the origin of NO_2 in the mechanism of the selective catalytic reduction of NO by propene over alumina

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The formation of NO_2 as a reaction intermediate in the selective catalytic reduction of NO by C_3H_6 in the presence of a large excess of O_2 over alumina is shown not to occur through the direct oxidation of NO by O_2.

Selective catalytic reduction (SCR) of NO_x by hydrocarbons has received much attention as a possible means to control the emissions from diesel and lean-burn engines. The work by Burch *et al.* has unveiled many of the features of the NO reduction over Pt-based materials.[1,2] Yet, the mechanisms of SCR reactions over alumina, one of the most active metal oxides for the SCR of NO by hydrocarbons,[3] and alumina promoted by metal oxides such as CoO_x remain unclear.[4] It has been suggested that when using propene as a reductant, the initial step of the SCR reaction is the oxidation of NO by O_2 to form NO_2 which in turn reacts with the reducing agent to form N_2.[5–7] The results of the experiments reported in this paper bring a new insight into the formation of NO_2 over alumina during the propene-SCR of NO, resulting in a necessary re-evaluation of the current theories on the reaction mechanism.

The γ-alumina used in these experiments was supplied by Alcan (AA400, 150 $m^2 g^{-1}$) and was calcined in air at 923 K for 6 h prior to use. The reactants (NO and C_3H_6) and products of reaction (CO_2, CO, NO_2, N_2O, NH_3) were analysed by FT-IR spectroscopy (7 m path length Foxboro® gas-cell fitted in a Nicolet® 550 FT-IR). No hydrogen cyanide nor any other products were detected in the experiments reported here. The N_2 concentration was calculated during steady state conditions on the basis of a 100% nitrogen balance on the other N-containing products detected. A quartz microreactor (4 mm internal diameter) was used for the catalytic tests, the catalytic bed being held in place by quartz wool plugs. No reaction was observed when the reactants were passed through the reactor in the absence of a catalyst bed. The results reported here were obtained at steady state conditions and were found to be reproducible.

Fig. 1(*a*) shows the NO_2 yield obtained during the oxidation of NO (500 ppm) by O_2 (2.5%) over alumina and Fig. 1(*b*) shows the calculated NO_2 yield obtained at the thermodynamic equilibrium of the reactions described by eqn. (1) as a function of temperature:

$$NO + \tfrac{1}{2} O_2 \leftrightarrow NO_2 \qquad (1)$$

As it has often been reported in the literature, the alumina catalyst exhibited very poor activity for the NO oxidation reaction with yields of NO_2 attaining equilibrium conversions only at temperatures above 900 K. Fig 1(*c*) shows the NO yield obtained during the decomposition of NO_2 to NO + $\tfrac{1}{2}$ O_2 (the reverse reaction of that discussed above) and Fig. 1(*d*) shows the calculated NO yield obtained at the thermodynamic equilibrium of the same reaction as a function of temperature. The activity of the alumina for the backward reaction of eqn. (1) was somewhat greater than that of the forward reaction but yet again the equilibrium limit was only reached at a temperature of about 900 K.

Fig. 2 shows the propene conversion [Fig. 2(*a*)] and yields of the different N-containing products of the reaction between NO (500 ppm), propene (500 ppm), and O_2 (2.5%) over alumina at 813 K and at varying *W*/*F*s (ratio of catalyst weight to feed flow rate). Fig. 3(*a*) shows the varying molar ratios of NO_2/NO obtained from the results of the experiments shown in Fig. 2. The NO_2/NO ratio at the thermodynamic equilibrium of reaction (1) at 813 K calculated using the initial concentration values of NO and O_2 is shown in Fig. 3(*b*). The conversion of propene [Fig. 2(*a*)] increased with increasing *W*/*F* values, reaching 100% conversion at *W*/*F* = 180 mg s cm^{-3}. The yield of N_2 [Fig. 2(*b*)] followed a similar trend to that of propene conversion, increasing steadily with increasing *W*/*F* values and then levelling off when all the propene was converted, *i.e.* at

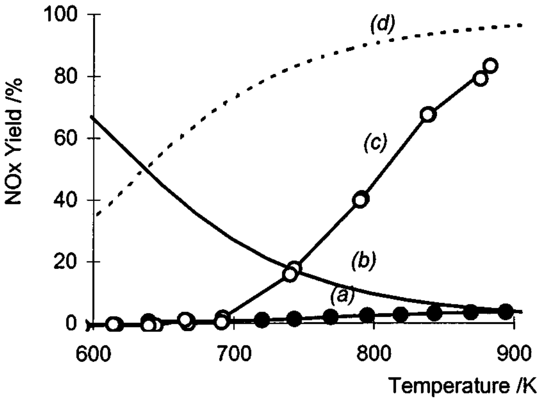

Fig. 1 *(a)* Experimental NO_2 yield (●) obtained during the oxidation of NO over γ-Al_2O_3 and (*b*) NO_2 yield limit (—) associated with the thermodynamic equilibrium of the reaction NO + $\tfrac{1}{2}$ O_2 ↔ NO_2 as function of temperature. *(c)* Experimental NO yield (○) obtained during the decomposition of NO_2 to NO + $\tfrac{1}{2}$ O_2 over γ-Al_2O_3 and (*d*) NO yield limit (---) associated with the thermodynamic equilibrium of the reaction NO + $\tfrac{1}{2}$ O_2 ↔ NO_2 as function of temperature. Feed: 500 ppm NO or NO_2 + 2.5% O_2 in Ar, *W*/*F* = 60 mg s cm^{-3}.

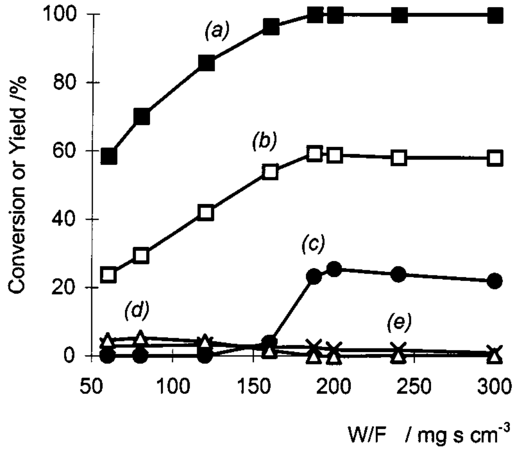

Fig. 2 Selective catalytic reduction of NO using propene over γ-Al_2O_3 at 813 K: (*a*) propene conversion (■), (*b*) N_2 yield (□), (*c*) NO_2 yield (●), (*d*) NH_3 yield (Δ) and (*e*) N_2O yield (×) as a function of the *W*/*F*. Feed: 500 ppm NO + 500 ppm C_3H_6 + 2.5% O_2 in Ar, 200 mg of alumina.

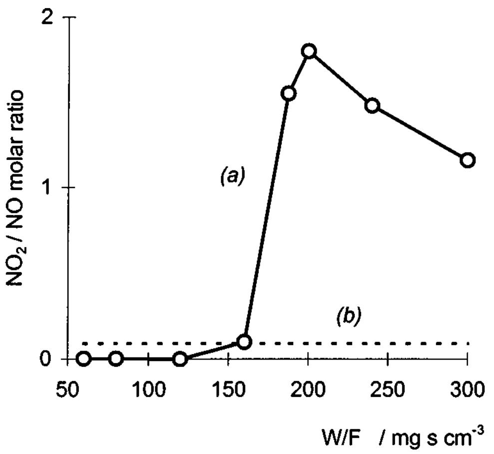

Fig. 3 Selective catalytic reduction of NO using propene over γ-Al_2O_3 at 813 K as a function of the *W*/*F*: NO_2 to NO ratio (*a*) experimental (○) and (*b*) at the thermodynamic equilibrium of the reaction NO + $\frac{1}{2}$ O_2 $\leftrightarrow$ NO_2 (---). Feed: 500 ppm NO + 500 ppm C_3H_6 + 2.5% O_2 in Ar, 200 mg of alumina.

W/*F*s greater than 180 mg s cm^{-3}. The striking feature of Fig. 2 is the sharp rise in the production of NO_2 [Fig. 2(*c*)] as soon as the conversion of propene reaches 100%. At propene conversions lower than 95%, the presence of NO_2 was not detected (*i.e.* $<$ 2.5 ppm). Upon completion of the conversion of propene, the NO_2 yield reached a value of approximately 25% (corresponding to 127 ppm of NO_2). With further increase in the values of *W*/*F*, the NO_2 yield gradually decreased. The gradual decrease in the concentration of NO_2 was accompanied by a similar increase in the concentration of NO (not shown in Fig. 2) while the concentrations of all the other products of reaction were either steady (N_2) or decreased (N_2O and NH_3). Interestingly, Fig. 3 shows that in the region of 100% propene conversion ($W/F \geqslant 180$ mg s cm^{-3}), the experimental values of the molar ratios of NO_2/NO were greater than 1. Hence, these values were more than 10 times greater than the value of the thermodynamic equilibrium ratio of NO_2/NO (*i.e.* 0.09) calculated at the same temperature. The same results were obtained whether the *W*/*F* was varied with increasing or decreasing values.

Further experiments carried out using the same reactant concentrations, at constant *W*/*F* (60 mg s cm^{-3}) and varying temperature also showed that, at the temperature of 100% conversion of propene, there was a sharp increase in the yield of NO_2. At 843 K, propene conversion was not complete and NO_2 was not detected; however, at 873 K propene was fully converted and NO_2 yields of 30% were obtained (this value again being well in excess of levels obtained from equilibrium calculations). The sharp increase in the NO_2/NO ratio at the temperature of 100% conversion of propene was the same regardless of whether the reaction temperatures were increased or decreased.

It is evident from the results of experiments described in this paper that NO_2 could not be observed when propene was present in the product streams. This can be explained by the work of a number of different authors,[4,6,7] who have shown that alumina is very active for the reduction of NO_2 by propene to form N_2. However, upon complete combustion of the propene, the NO_2 could not be reduced and was therefore detected in the reactor effluent. Fig. 2 and 3 show that the maximum NO_2/NO ratio occurred at a *W*/*F* value of 200 mg s cm^{-3}, and at higher *W*/*F*s the ratio decreased towards the equilibrium ratio. This was probably due to the slow decomposition of the NO_2 to NO and O_2 (in the absence of propene) which Fig. 1(*c*) shows can occur over the alumina catalyst. Surprisingly, the catalytic data reported on alumina in this paper and the corresponding thermodynamic calculations show that most of the NO_2 observed upon completion of propene conversion during the SCR of NO did not arise from the direct oxidation of NO by O_2 [eqn. (1)]. A mechanism involving the direct reaction of NO, O_2 and NO_2 could not exceed thermodynamic limits. Therefore, the current model of the alkene-SCR reaction over alumina-based catalysts needs to be re-evaluated.[5–7]

At least two alternative solutions could be proposed to explain the formation of the high concentrations of NO_2 observed. First, a mechanism involving consecutive steps could occur in which a nitro or a nitrite compound, *e.g.* nitromethane CH_3NO_2, is formed along with CO (or CO_2) from the reaction of propene, O_2 and NO [eqn. (2-1)]. Organic nitro or nitrite species have often been quoted as possible intermediates of SCR reactions.[8] The subsequent oxidation of this organo-NO_x species would yield NO_2 [eqn. (2-2)]

$$C_3H_6 + \tfrac{3}{2}\,O_2 + 2\,NO \longrightarrow 2\,CH_3NO_2 + CO \qquad (2\text{-}1)$$

$$CH_3NO_2 + \tfrac{7}{4}\,O_2 \longrightarrow NO_2 + CO_2 + \tfrac{3}{2}\,H_2O \qquad (2\text{-}2)$$

Overall, eqn. (2-1) and (2-2) combine to give:

$$C_3H_6 + 5\,O_2 + 2\,NO \longrightarrow 2\,NO_2 + 2\,CO_2 + CO + 3\,H_2O \quad (2\text{-}3)$$

This mechanism is supported by the fact that thermodynamic calculations show that the reactions given by eqn. (2-1) and (2-2) are strongly exergonic over the temperature range investigated here (*e.g.* $\Delta G°_{813K} = -298$ kJ mol^{-1} and -734 kJ mol^{-1}, respectively). Regarding a second possible mechanism, the oxygen needed to form the NO_2 could be supplied by another molecule of NO, *i.e.* in a disproportionation reaction, and not by the O_2. An example of mechanism of SCR of NO involving a disproportionation of NO to N_2 and NO_2 was proposed by Smits and Iwasawa .[9] These authors suggested that one of the roles of the hydrocarbon, NO and O_2 was to form a radical molecule R* (*e.g.* 1-nitro-*sec*-propyl) which in turn could propagate the disproportionation reaction:

$$4\,NO\,(+R^*) \leftrightarrow N_2 + 2\,NO_2\,(+R^*) \qquad (3)$$

The thermodynamics of the disproportionation reaction described by eqn. (3) essentially favour the right hand-side of the equation at temperatures below 600 °C (and are independent of the concentration of O_2) and therefore this mechanism could be responsible for the high yields of NO_2 observed. Hence, one of the possible role of the alumina (a known mild oxidiser) during alkene-SCR reactions would be to allow the formation of organic-nitro or nitrite species [eqn. (2)] and/or the formation of a hydrocarbon-based propagator [eqn. (3)]. Experiments using $N^{18}O$ and $^{16}O_2$ are planned and should give some evidence of the origin of the oxygen in NO_2 (*i.e.* by observing either $N^{18}O^{18}O$ or $N^{18}O^{16}O$) to determine which of the two models proposed is the most likely.

The conclusion of this work is that the formation of NO_2 during the propene-SCR of NO over alumina is not obtained by direct oxidation of NO by O_2 but that a more complex mechanism has to be considered.

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Notes and references

1 R. Burch and T. C. Watling, *Catal. Lett.*, 1997, **43**,19.
2 R. Burch, P. Fornasiero and T. C. Watling, *J. Catal.*, 1998, **176**, 204.
3 H. Hamada, *Catal. Today*, 1994, **22**, 21.
4 J. Yan, M. C. Kung, W. M. H. Sachtler and H. H. Kung, *J. Catal.*, 1997, **172**, 178.
5 H. Hamada, Y Kintaichi, M. Sasaki and T. Ito, *Appl. Catal.*, 1991, **70**, L15.
6 H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari and H. Tsuchida, *Catal. Today*, 1996, **29**, 53.
7 N. Okazaki, S. Osada and A. Tada, *Appl. Surf. Sci.*, 1997, **121/122**, 396.
8 C. Yokoyama and M. Misono, *J. Catal.*, 1994, **150**, 9.
9 R. H. H. Smits and Y. Iwasawa, *Appl. Catal. B*, 1995, **6**, L201.

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