Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 137 (2008) 146–156

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The use of copper catalysts for the selective reduction of NO with methanol

Julian R.H. Ross [*], Patricia Clancy

University of Limerick, National Technological Park, Limerick, Ireland

Abstract

A series of co-precipitated Cu–ZrO_2 catalysts which have previously been shown to be very effective for the steam reforming of methanol have been shown to be active and selective catalysts using methanol as reductant when tested in the presence of excess oxygen. They are also largely resistant to the presence of water and are only partially poisoned by the presence of SO_2. When no oxygen is admitted to the test gas, all the catalysts still convert NO using methanol as reductant but the product now contains other N-containing molecules. When the oxygen concentration was adjusted so that, together with the NO, it effectively balanced the methanol content of the feed gas, all the catalysts gave exceptionally high selectivities and conversions to N_2, effectively 100% in both cases.

Keywords: Selective NOx reduction; Methanol; Co-precipitated Cu–zirconia catalysts; Effect of reactant stoichiometry

1. Introduction

A wide variety of metals supported on different oxides have been studied for the selective reduction of NOx under lean-burn conditions. For example, we reported in paper given in the Zakopane meeting held in 1998 and then published in the open literature [1–3] that silver supported on alumina is an effective catalyst for the reduction of NO using propene as reductant. Meunier and co-workers [4] have recently reviewed much of the work in the area.

One of the first catalysts reported (simultaneously by Iwamoto et al. [5] and Held et al. [6]) to be effective and selective for the reduction of NO with hydrocarbons under lean-burn conditions was the Cu–ZSM-5 system. Iwamoto et al. investigated the use of Cu-exchanged ZSM-5 for the selective reduction of NO by propene [7] and this publication subsequently led to much work on the use of propene as a selective reductant.

Hamada et al. were the first to study the use of methanol, ethanol and propanol as selective reductants of NOx [8]. Much subsequent work has concentrated on the use of unpromoted alumina as catalyst using these oxygenated molecules as reductants but several papers have also reported the use of other metals, including copper. For example, Montreuil and Shelef compared the reduction activities of oxygen-containing compounds with those of alkenes and alkanes over a Cu–ZSM-5 catalyst at 482 °C [9]. The compounds tested included the three lowest aliphatic alcohols, methanol, ethanol and propanol, as well as acetaldehyde, acetone and an ether, 1,4-dioxane. Montreuil and Shelef found that none of the partially oxygenated reductants were as efficient in nitric oxide conversion as was propene itself, which gave a conversion of 39%. Methanol was completely inactive for nitric oxide reduction while the conversions of the remaining oxygen-containing compounds approximated to that of propene. When they used propene as a reductant and used a CuO/γ-Al_2O_3 catalyst instead of Cu–ZSM-5 material, they observed a conversion of only 1–2% and suggested that this proves that an excess of non-exchanged copper (as in the CuO/Al_2O_3 sample) does not affect the NO reduction to any significant extent. Nunes et al. characterised the behaviour of Cu–ZSM-5 in the presence of NO and methanol [10]. The material was active for NO decomposition and exhibited a high selectivity to N_2. The results indicated that the active species for the catalytic decomposition of NO is Cu^{2+} which can be reduced to Cu^+, forming Cu^+–NO_2 and Cu^+–$(NO)_2$ complexes. The

---

[*] Corresponding author.
E-mail address: julian.ross@ul.ie (J.R.H. Ross).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.10.115

pre-treatment conditions of these catalysts are therefore important to ensure decomposition activity. However, the results showed that methanol was inactive for the SCR of NO over this material since the molecule could not be activated on the NO adsorption sites to form species that are active for NO reduction.

Vassallo et al. studied the reduction of NO over H-, Co- and Cu-mordenite using CH_4, C_2H_4, and CH_3OH as reductants [11,12]. While Co- and H-mordenite proved active for all the reductants, Cu-mordenite was only active when CH_3OH or C_2H_4 was used. The authors observed maximum conversions at temperatures >500 °C for SCR with methanol over all the catalysts. Methane gave a lower level of conversion than methanol at all temperatures. In the absence of oxygen, deactivation of the catalyst occurred when methanol was the reducing agent, probably as a result of the formation of carbon deposits.

We have, for some time, been studying the use of promoted $Cu–ZrO_2$ catalysts for the steam reforming of methanol to produce hydrogen-rich mixtures without significant formation of CO [13]. Recently, we have examined the preparation of such catalysts by precipitation methods and found that a Cu–Y–Zr material was particularly active and stable [14]. We have now examined the use of these co-precipitated materials for the deNOx reaction under lean-burn conditions as well as without added oxygen over a wide temperature range and have found that the catalysts can have high activities and good selectivities to nitrogen, depending on the reaction conditions. This paper presents some of these results.

2. Experimental

The catalysts for which the results are given below were prepared by co-precipitation from solutions containing the appropriate metal nitrates (Cu, Zr, Zn, Ce, Al, Y, and La nitrates) using a solution of 1 M sodium carbonate at a constant pH of 7.0 and at temperature of 70 °C as described in detail in Ref. [14]. The resulting gel was filtered, washed and then dried overnight at 120 °C. The final catalyst was achieved after calcination at 650 °C for 6 h, ramping to this temperature at a rate of 5 °C/min. A sample of a commercial methanol synthesis catalyst ($CuO–ZnO–Al_2O_3$ in its freshly calcined form) was also examined for comparison. The compositions of the catalysts examined are given in Table 1; the first four, as well as the commercial sample, have relatively high Cu contents and the last four have significantly lower Cu contents. The total surface area of all the samples were in the range of 100–200 $m^2 g^{-1}$. In several cases, the samples were pre-reduced before testing; as reported elsewhere, the Cu areas of the reduced catalysts were of the order of 10 $m^2 g^{-1}$ [14].

Table 1
Formulations of the copper catalysts tested for SCR of NO with methanol

Catalyst	Composition (mol%)
CuZr	70/30
CuZnZrCe	70/18/6/6
CuZnZrAl	70/18/10/2
CuZnZr	66/17/17
BASF V1568 (CuZnAl)	Typically >60% Copper
CuZr	30/70
CuCeZr	30/10/60
CuYZr	30/20/50
CuLaZr	30/20/50

The catalysts were tested using a standard flow micro-reactor system in which the methanol and, where appropriate, water were introduced to the system via a syringe pump. The total flow rate of the reactant gases at all times was 100 $cm^3 min^{-1}$, this comprising for the standard experiments of 0–2% of O_2, 500 ppm of NO, 3600 ppm of CH_3OH, the balance being made up of helium. A catalyst weight of 150 mg was used in all experiments. The gas hourly space velocity was 12,000 h^{-1}, the corresponding value of W/F being 0.090 g s cm^{-3}. Samples from the gas chromatograph were taken at 15-min intervals. The reactant stream was also fed to a Nicolet Magna 550 FTIR spectrometer fitted with a gas cell to further ensure that all products of the reaction had been detected; the times of sample analysis were set to coincide with those used with the GC.

An experiment was also carried out using CO as the reductant. In this, the reactant concentrations were: 3500 ppm of CO; 500 ppm of NO and 0.4% of O_2. All the other conditions were maintained as given above. Experiments were also carried out in which water or SO_2 was added to the reaction mixture. Water concentrations in the range of 0.5–2% and SO_2 concentrations in the range of 80–150 ppm were used for experiments at 400 °C for all the catalysts with the exception of CuCeZr 30/10/60 which was tested at 350 °C and CuZr 70/30 tested at 550 °C. The catalyst stabilities were tested at 600 °C for a period of 48 h.

3. Results and discussion

3.1. Possible reactions

For a reaction mixture containing NO, CH_3OH and O_2, a number of reactions are thermodynamically possible, depending on the gas composition and the temperature. For example, in excess O_2, the NO can be converted to NO_2:

$$NO + 0.5O_2 = NO_2 \qquad (1)$$

or to N_2 by reduction with methanol (or some other molecule derived from methanol), formally depicted as:

$$NO + CH_3OH + O_2 = 0.5N_2 + CO_2 + 2H_2O \qquad (2)$$

The methanol can also be oxidised completely to CO_2 and H_2O:

$$CH_3OH + 1.5O_2 = CO_2 + 2H_2O \qquad (3)$$

More importantly, in relation to the experiments reported here in which the partial pressure of O_2 is close to the stoichiometric amount or even below, various other products are possible, these including formaldehyde, CO and H_2, depicted formally by the dehydrogenation steps:

$$CH_3OH = CH_2O + H_2 = CO + 2H_2 \qquad (4)$$

(These molecules may also be intermediate species in the reduction process depicted by Eq. (2).) If methanol is in excess (the combination being formally equivalent to the partial oxidation of methanol), hydrogen and CO_2 can also be formed by the steam reforming of methanol using the water formed in reaction (2):

$$CH_3OH + H_2O = CO_2 + 3H_2 \quad (5)$$

Methane is another possible product, formed by the methanation reaction:

$$CO + 3H_2 = CH_4 + H_2O \quad (6)$$

but this reaction is only likely to occur using metals such as Ni which give methanation; hence, its formation was not considered in the calculations reported below. Finally, the water-gas shift reaction may also occur:

$$CO + H_2O = CO_2 + H_2 \quad (7)$$

It should be noted that the catalysts tested in this work for the selective reduction of NO have previously been shown to carry out the steam reforming of methanol selectively according to Eq. (5) without significant contributions from the reverse water-gas shift reaction [14].

The concentrations of possible thermodynamically permissible products as a function of temperature above 200 °C for different partial pressures of O_2 were calculated using the thermodynamic program ‘‘HSC Chemistry’’ for the feed conditions typically used in this work: 500 ppm of NO, 3600 ppm of CH_3OH and 0–2% (0–20,000 ppm) of O_2, with a balance of inert (in this case He). The results are shown in Supplementary Material, Fig. 1. With 2% O_2, well in excess of the NO and methanol concentrations, all the methanol could react at all temperatures above 200 °C. N_2 was the only nitrogen-containing product allowed and no CO or H_2 was formed at any temperature. However, the situation was different if the partial pressure of oxygen was close to the stoichiometric value. (The exact amount of oxygen required for the stoichiometric reaction depends on whether the main carbon-containing product is CO or CO_2 and whether or not hydrogen is formed as a product.) When values of O_2 feed partial pressures of 0.4 or 0.5% were used, the equilibrium product gases contained CO in addition to the allowed products mentioned above for the 2% O_2 feed: N_2, CO_2 and H_2O. This can be seen in Fig. 1 which shows the calculated % equilibrium composition of CO as a function of temperature for a range of O_2 feed concentrations. Only for feeds containing 0.6% O_2 and above was no CO formed at any temperature. Hence, from these thermodynamic calculations, we can conclude that N_2 can be formed as the main N-containing product at all temperatures and that CO is a possible product only if the oxygen partial pressure approaches the stoichiometric amount needed to give N_2, CO/CO_2 and water as the main products. Only if there is kinetic control of any of the possible reactions we are likely to find any NO_2, formaldehyde or hydrogen. It should be noted that we have not in the calculations reported above considered other potential products such as ammonia, HCN, etc. We show below that such products are only found if the feed composition is sub-stoichiometric or zero.

3.2. Reaction of NO + CH_3OH + excess O_2 over ZrO_2

Fig. 2 gives the results of an experiment carried out over a pure ZrO_2 sample prepared in the same way as the co-precipitated catalysts were done and shows the NO and methanol conversions as a function of temperature. Methanol conversion occurred over the whole range of temperature studied, increasing with increasing temperature, but only reached 100% at very high temperatures. (This should be contrasted with results obtained with γ-Al_2O_3 (not shown) for which methanol conversion was almost complete at 400 °C.) The conversion of NO over the ZrO_2 reached about 30% at 300 °C and remained relatively constant at higher temperatures, the only product being N_2. At higher temperatures, the

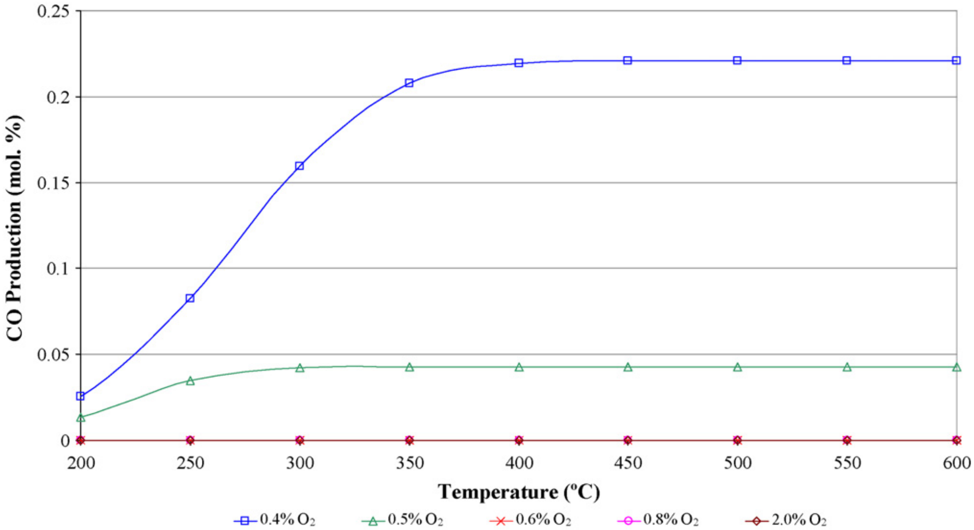

Fig. 1. Equilibrium diagram showing the % composition of CO in the gas mixture at various oxygen feed concentrations as a function of temperature. Feed composition: NO, 500 ppm; CH_3OH, 3600 ppm, O_2, 0.4–2% (see legend); balance inert.

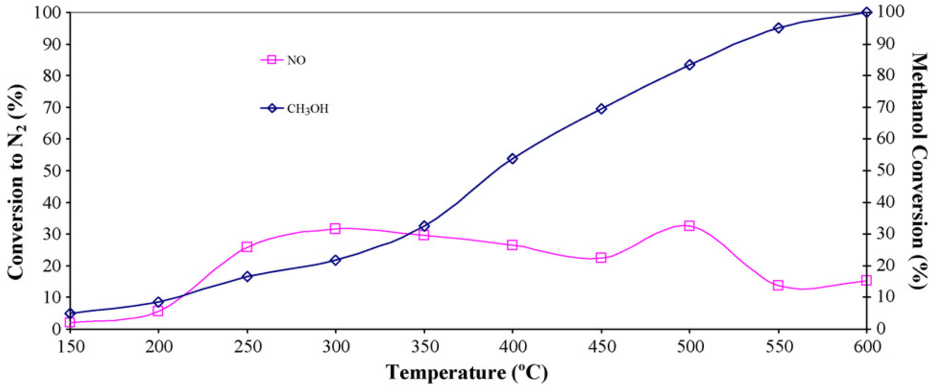

Fig. 2. SCR of NO with methanol over ZrO_2. Feed composition: O_2, 2%; NO, 500 ppm; CH_3OH, 3600 ppm; balance He.

methanol reaction gave predominantly CO_2 and H_2O as products.

3.3. Reaction of NO + CH_3OH + excess O_2 over Cu-containing catalysts

Figs. 3 and 4 show the NO conversions to N_2 as a function of reaction temperature for experiments with 2% O_2 for all the catalysts as a function of temperature, from 300 to 650 °C; Fig. 3 shows the results for the high-Cu content materials and Fig. 4 shows those for the low Cu contents. The results for the Cu–Zr sample (Fig. 3) are similar to those for the ZrO_2 alone (Fig. 2), the low temperature peak being slightly lower and that at higher temperatures being slightly higher. All the other samples shown in Fig. 3 contain ZnO and give higher conversions of the NO in the lower temperature region. The highest conversion of NO to N_2 was that given by the CuZnZrCe sample at about 400 °C, this being slightly higher than the sample without Ce. The results for the low-Cu content samples are shown in Fig. 4. It can be seen that the Cu–Zr sample is more active than the equivalent sample with high-Cu content (Fig. 3) and also than the unpromoted support. The most significant result was obtained with the CuCeZr sample, this giving a conversion of NO to N_2 of just below 50% at 350 °C. It therefore appears that the co-precipitated catalysts promoted with Cu are generally slightly more active than the unpromoted zirconia support and that the optimum temperature window is strongly dependent on the catalyst composition, particularly on the nature of the promoter. These results compare favourably with the results reported by other researchers for the selective reduction of NOx with methanol [8–12].

3.4. Effect of variation of O_2 feed composition

The effect of oxygen concentration was examined using the most active sample of Fig. 3, the CuZnZrCe material, and the conversions to N_2 as a function of O_2 feed concentration is shown in Fig. 5. The points to the right-hand side of the figure correspond to data of the sort discussed in the previous paragraph for this material, giving conversions of NO to nitrogen of from 40 to 50%, the selectivity being 100%.

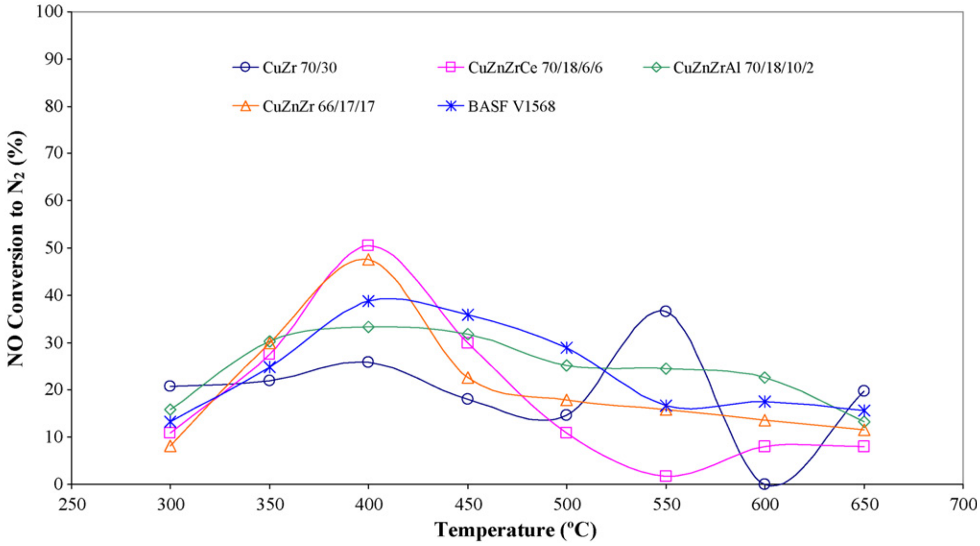

Fig. 3. The selective catalytic reduction of NO with methanol over the catalysts with high copper loadings. Feed composition: O_2, 2%; NO, 500 ppm; CH_3OH, 3600 ppm; balance He.

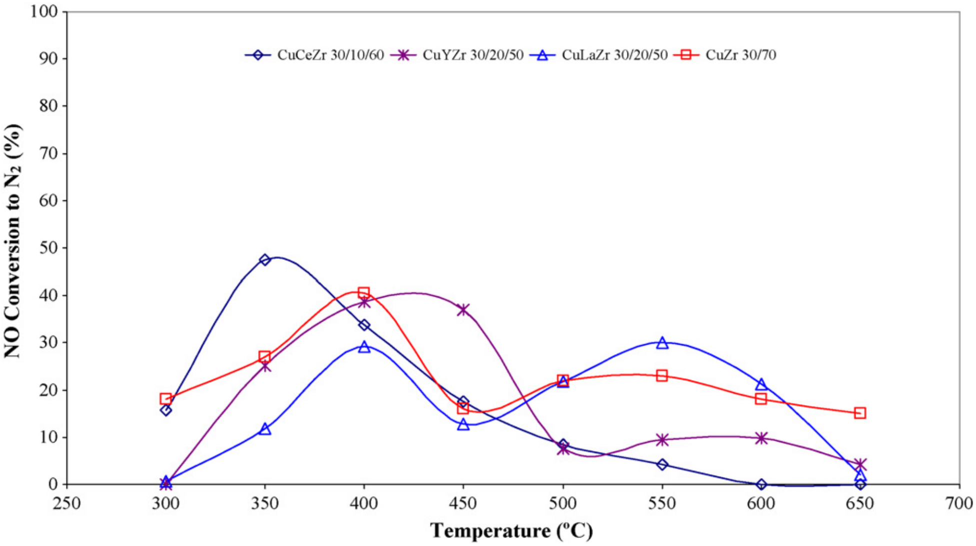

Fig. 4. The selective catalytic reduction of NO with methanol over the catalysts with low copper loadings. Feed composition O_2, 2%; NO, 500 ppm; CH_3OH, 3600 ppm; balance He.

However, at lower feed compositions of 0.6 and 0.8% O_2, the conversions of NO were somewhat lower, possibly due to partial reduction of the catalyst (see below) affecting the activity. For all these experiments, the only products were N_2, CO_2 and water.

When the feed concentration of oxygen was lowered to 0.4% O_2, the conversion to N_2 became 100%. Under these conditions, the feed composition was approximately stoichiometric and so, if the reaction approached thermodynamic equilibrium, CO might have been expected as a product (see Fig. 1). However, no CO was observed. Hence, it would appear that the reverse water-gas shift reaction (reverse of reaction (7)) does not occur under these conditions, as has been found for these catalysts in the case of the steam reforming of methanol [14]. This result seems to imply that the sequence of reaction of the methanol is indeed total oxidation followed by steam reforming (Eqs. (3) and (5)) rather than decomposition to CO and H_2 (Eq. (4)) or direct partial oxidation to CO and H_2O or CO_2 and H_2, both of which reactions, if occurring, would result in the presence of CO in the products; hence, the reduction of the NO must be brought about by hydrogen or some intermediate surface entities involved in its formation (e.g. a formate or similar species) rather than by CO. The reactions occurring under stoichiometric conditions will be discussed further in Section 3.5.

When there was no oxygen in the feed (see Fig. 5), the conversion to N_2 was again much lower. However, the selectivity was now not 100% and various other products such as NH_3, and HCN were formed. The results obtained in the absence of oxygen will be discussed further below (Section 3.6).

3.5. Behaviour under near-stoichiometric conditions

Fig. 6 shows the conversion to N_2 as a function of the reaction temperature for five of the catalysts for the reaction conditions which correspond to the maximum in Fig. 5. This feed composition is such that there is nominally just slightly

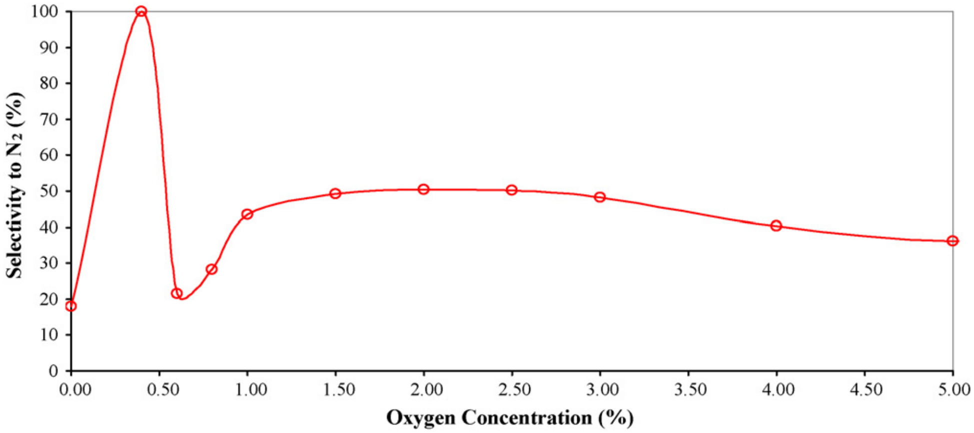

Fig. 5. The variation in selectivity to N_2 with increasing oxygen concentration over CuZnZrCe at 400 °C (673 K). Feed composition: NO, 500 ppm; CH_3OH, 3600 ppm; balance He.

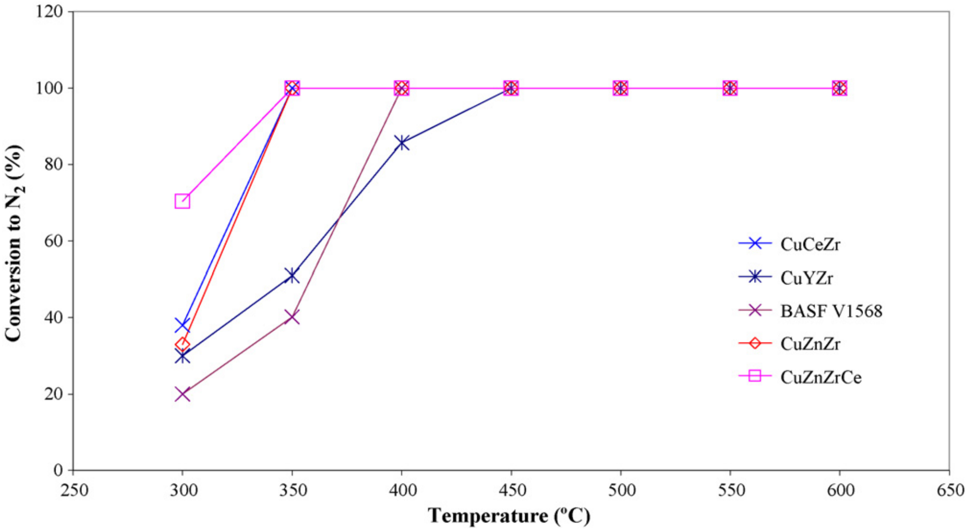

Fig. 6. Comparison of catalysts for SCR of NO with CH_3OH over the temperature region 300–650 °C. Feed composition: O_2, 0.4%; NO, 500 ppm; CH_3OH, 3600 ppm; balance He.

more oxygen than that necessary to bring about complete conversion of the NO to N_2 (Eq. (2)) as well as complete combustion of the methanol to give CO_2 and H_2O (Eq. (3)). For each of the catalysts, the selectivity to N_2 was 100% over the whole temperature range; however, the conversions of NO were less than 100% for all the catalysts at 300 °C, these rising to 100% at higher temperatures. During each set of experiments, the catalysts appeared to change during the reaction, each having assumed a red/brown colour when removed from the reactor. This colour change appears to have been caused by the reduction of the Cu of the catalysts during the reaction. An experiment was therefore carried out with the CuCeZr material to examine the deNOx reaction over a pre-reduced sample. Without pre-reduction (Fig. 6), this sample gave 100% conversion to N_2 only above 450 °C; however, following reduction in a flow of H_2 at 450 °C (see Supplementary Material, Fig. 2), this sample gave 100% conversion to N_2 at all temperatures in the range of 300–600 °C.

To see whether the results shown in Fig. 6 were just a peculiarity of the reaction conditions shown or whether the same behaviour would be obtained for different near-stoichiometric conditions, an experiment was carried out to show the effect of methanol concentration, now using a feed containing 2% O_2. The results are depicted in Fig. 7; this shows the selectivities to N_2 and the NO conversions as a function of the concentration of methanol in the feed. At low methanol concentrations, corresponding to the conditions of Figs. 3 and 4, the NO conversion was lower than 100% but the selectivity to N_2 was 100%. However, as the methanol concentration approached stoichiometric, both the conversion and selectivity were 100%. Again, no CO was observed among the products. Hence, the stoichiometry of the reaction mixture is all-important in determining the reactivity of the system. Fig. 8 shows the results of an experiment equivalent to that shown in Fig. 6 but now using the conditions of the cross-over of Fig. 7; the results are now shown as concentrations of NO, N_2 and CO_2 as a function of reaction temperature. As in Fig. 6, the catalyst does not give complete conversion of the NO at 300 °C but the conversion reaches 100% at 350 °C. Hence, in situ reduction of the catalyst is required to deliver the 100% yields of nitrogen in the selective reduction process. It would appear that the CuZnZrCe material is particularly effective at the lower

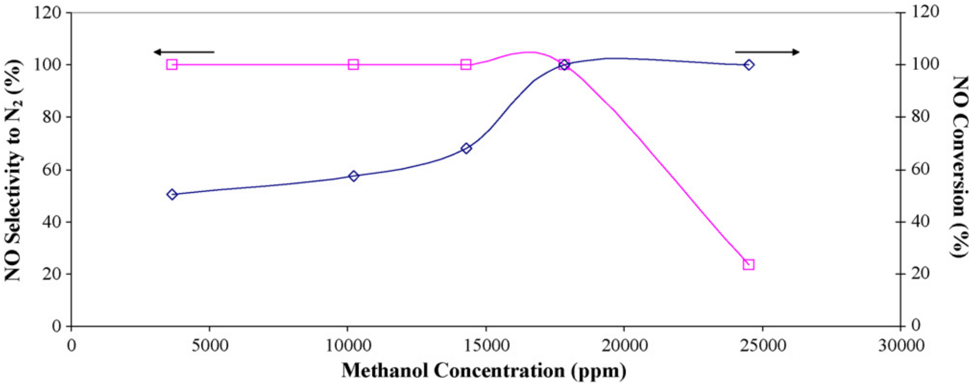

Fig. 7. The effect of increasing the concentration of methanol at constant oxygen partial pressure for reaction at 400 °C with the CuZnZrCe catalyst. Feed composition: oxygen, 2%; NO, 500 ppm; balance He.

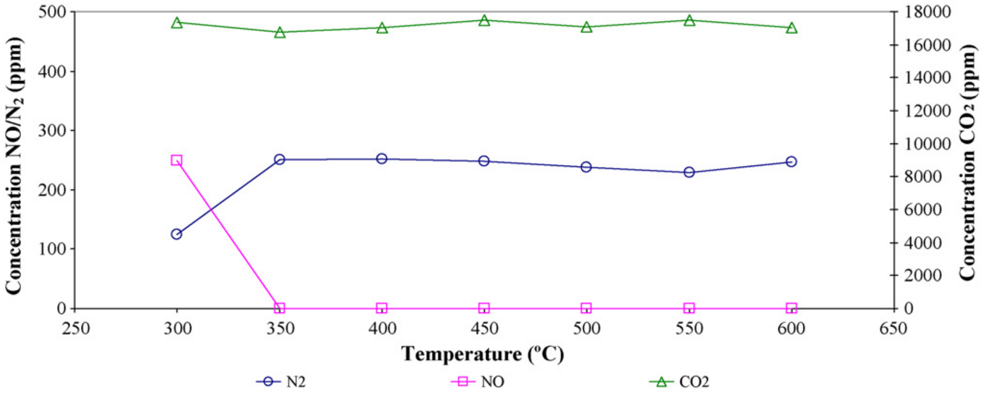

Fig. 8. Reduction of NO with methanol as a function of temperature at the feed composition corresponding to the cross-over point shown in Fig. 7. Feed composition: methanol, 17800 ppm (1.78%); NO, 500 ppm; O_2; 2%; balance He.

temperatures not because of having different sites but because it was more easily reduced under reaction conditions. Although this limitation can be removed by a pre-reduction step, it is still probably desirable to have a catalyst that can be reduced by the reaction mixture rather than relying on a separate procedure.

It appears from the results presented above that near-stoichiometry of the reaction mixture is necessary to achieve 100% reduction of the NO. As no CO, unreacted methanol or unreacted oxygen could be detected (within experimental error) in the effluent of the reactor when operating under these conditions, it would appear that the conditions are almost exactly stoichiometric. Hence, the fact that the figures do not tally exactly with the stoichiometries of Eqs. (2) and (3) must be put down to imprecision in the measurement of the methanol introduced to the feed rather than to the presence of other undetected products.

It is well established that the presence of oxygen is beneficial for the operation of selective deNOx catalysts with propene as reductant; for example, Iwamoto and Hamada [15] showed that the activity in the presence of oxygen over a Cu–Z-152 catalyst was much higher than in the absence of oxygen. We are aware of only one publication in which the effect of operating a deNOx catalyst at or near the stoichiometric ratio of reductant to NO and oxygen has been reported in detail. Montreuil and Shelef [9] examined the use of a series of different oxygen-containing reductants for NOx reduction over Cu–ZSM-5 and compared the results obtained with those obtained with the same catalyst using propene as reductant; they then compared the effect of the oxygen content of the reaction mixture for reduction using propene and propanol. With propene, the conversion of NO was improved by the addition of oxygen, rising to a roughly constant level at and above the stoichiometric ratio; the conversion of propene rose steadily with increasing oxygen content. In contrast, with propanol as reductant, the conversion of NO without oxygen in the gas phase was much higher than with propene without oxygen but the conversion decreased significantly with an increase in oxygen content, particularly at values below the stoichiometric ratio. In neither case was there any remarkably different behaviour of the type reported in this paper at or near the stoichiometric ratio. As noted in the introduction section, Montreuil and Shelef also examined the use of methanol as reductant over their Cu–ZSM-5 catalyst and found that it was totally inactive for NO reduction, the methanol being totally oxidised by the oxygen present at higher temperatures. We must conclude that the behaviour at near-stoichiometric conditions reported here is a property of the Cu–ZrO_2 co-precipitated catalysts examined in this work. What this property is not clear and requires further work.

3.6. Behaviour in the absence of oxygen

As noted in Section 3.4 in connection with Fig. 5, the behaviour in the absence of O_2 was completely different. The conversion of the NO was much lower than at the maximum and the selectivity towards N_2 was now much less that 100%. Fig. 9 shows the selectivity to N_2 as a function of reaction temperature for five of the catalysts and also for unpromoted ZrO_2. The selectivity to N_2 was relatively high at low temperatures but it decreased, reaching a minimum between 400 and 450 °C for most of the samples, before rising once more. It would appear that the low temperature results are associated with the oxidic forms of the catalysts as there was evidence that the catalysts were again reduced in situ at the higher temperatures of operation; hence, if the catalysts had been pre-reduced, the product slate as a function of reaction temperature described below might have been different. The details of the experimental results obtained are given in Supplementary Material, Fig. 3. The predominant secondary nitrogen-containing product was NH_3 for all the catalysts other than the unpromoted ZrO_2 sample which gave predominantly N_2O as secondary product. HCN was obtained as a subsidiary product with the BASF V1568, CuZnZrCe and CuZnZr materials and so its formation seems to be associated with the presence of the Zn. CO was also formed with all the catalysts; the water-gas shift reaction appeared to be in equilibrium under these conditions (see Supplementary Material, Fig. 4).

That the various subsidiary products were probably formed from the methanol or derived surface species was shown by an experiment with the CuCeZr sample at 300 °C shown in

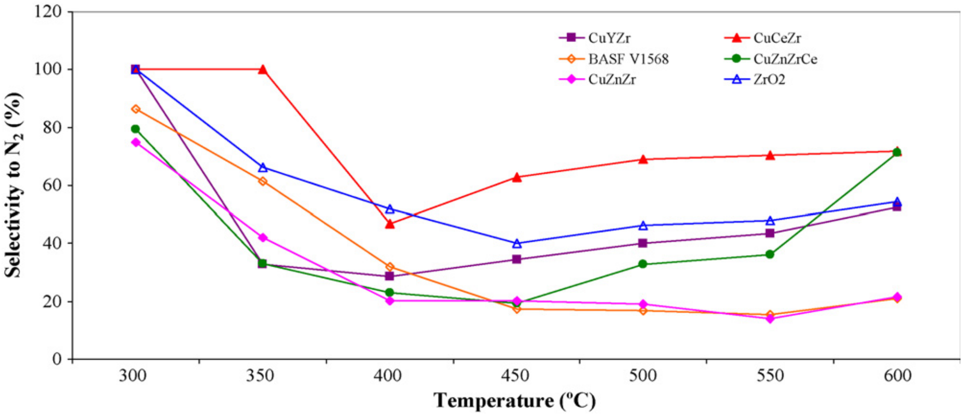

Fig. 9. Comparison of selectivities to N_2 in the absence of oxygen over the different catalysts. Feed composition: NO, 500 ppm; methanol, 3600 ppm; balance He.

Fig. 10. Here, the reaction mixture comprised CO and NO, with CO in excess. For just less than 50 min of operation, not only was the NO completely converted to N_2 but the CO was also completely converted, probably because of CO bringing about reduction of the catalyst with the formation of CO_2. Thereafter, the conversion of CO was lower, now corresponding to the stoichiometry of the reaction:

$$NO + CO = 0.5N_2 + CO_2 \tag{8}$$

There was no evidence for the formation of other products.

3.7. Effect of water vapour on the behaviour of the selective reduction reaction

Fig. 11 shows the results of an experiment in which the effect of the addition of water on the behaviour of the CuZnZrCe sample was examined under oxygen excess conditions; for comparison, results obtained in the absence of water are also shown. It can be seen that the effect of water was very small, the N_2 conversion being decreased by only a small amount over the whole range of temperature; indeed, at lower temperatures, the water had a slight beneficial effect. Similar results were obtained for a number of the other materials. (see Supplementary Material, Figs. 5 and 6). It would appear that the water therefore only has a slight poisoning effect on the active sites of the oxidic form of the catalyst.

When the effect of water was examined under close to stoichiometric conditions, the situation was different. Fig. 12 shows the results of an experiment with the CuZnZrCe material operating at 400 °C in which water was injected after 160 min of steady-state operation giving 100% conversion of NO to N_2. After the addition of water, there was a steady decrease in the NO conversion, from 100% to a level below 40%. However, when the water was removed, the conversion climbed steadily back to the original value of 100%. It is probable that this result is due to the fact that the water re-oxidises the reduced catalyst

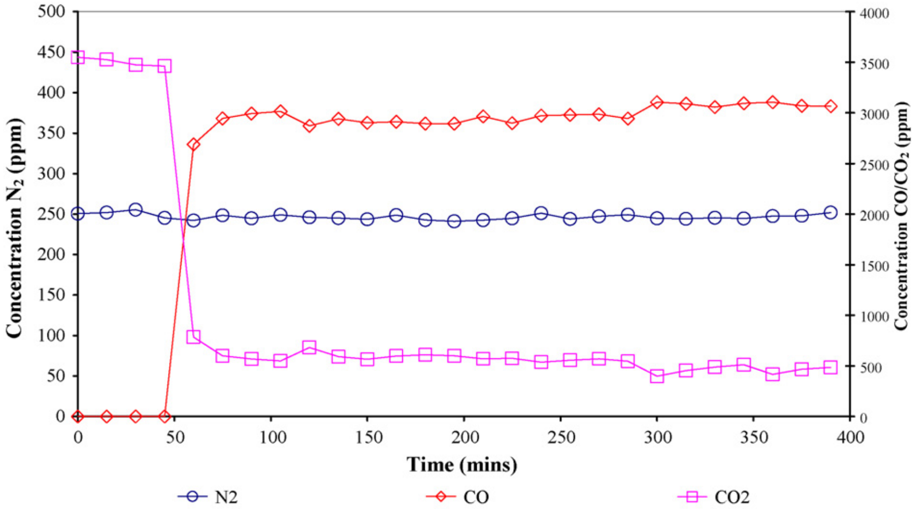

Fig. 10. The reaction of CO and NO without added oxygen over the CuCeZr catalyst as a function of time at 300 °C. Feed composition: CO, 3500 ppm; NO, 500 ppm; balance He.

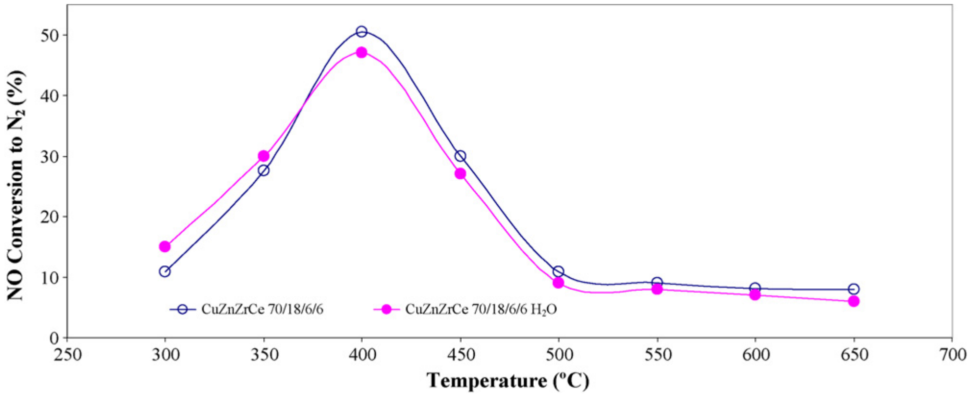

Fig. 11. Effect of water on the activity of the CuZnZrCe catalyst for the SCR of NO as a function of temperature. Feed composition: NO, 500 ppm; oxygen, 2%; methanol, 3600 ppm; water 0 or 2%; balance He.

sample to give a CuO-type surface and the conversion is similar to the peak value shown in Fig. 11 for operation under oxidising conditions. Further work is necessary to confirm these conclusions.

3.8. Effect of the addition of SO_2

One of the problems of operating selective deNOx catalysts under lean-burn conditions is that the materials are rapidly poisoned by the presence of SO_2 in the exhaust gases. The catalysts whose behaviour is described above were therefore tested for their tolerance to small amounts of SO_2 in the feed. Fig. 13 shows typical results for the CuZnZrCe material at conditions corresponding to the peak position shown in Fig. 11 (and also those in Fig. 3). It can be seen that there is little effect on the conversion to N_2 for about 2 h but that the conversion then drops to a new steady-state value of about 30%, this being maintained for the remainder of duration of the experiment. No experiments have yet been carried out to examine the possible regeneration of this catalyst. (Similar results were obtained for the other catalysts and the data are shown in Supplementary Material, Figs. 7 and 8.)

3.9. Stability under operating conditions

Fig. 14 shows the results of an experiment carried out under the same conditions as used in Figs. 12 and 13 but without any additions of water or SO_2 to test the durability of the CuZnZrCe catalyst under oxygen excess conditions over a long period of operation (50 h). It can be seen that there is little or no decrease in conversion with time, the value remaining at the same level within experimental error for the whole period of operation. It would therefore appear that the catalyst has very good stability when operated in the absence of water or SO_2.

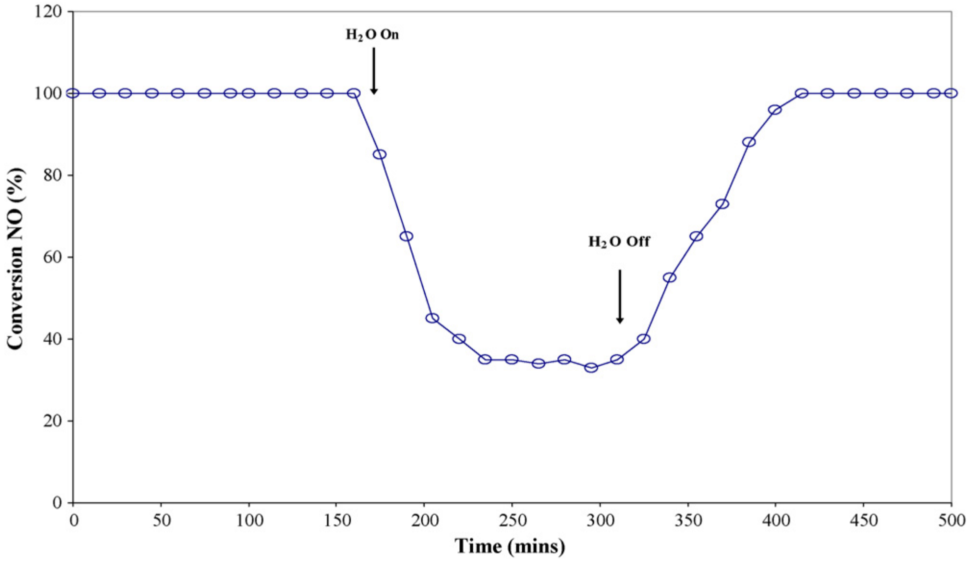

Fig. 12. Effect of water on the activity of the CuZnZrCe catalyst at 400 °C as a function of time showing the effect of the introduction of 2% H_2O to, and its subsequent removal from, the reaction mixture. Feed composition: NO, 500 ppm; oxygen, 0.4%; methanol, 3600 ppm.

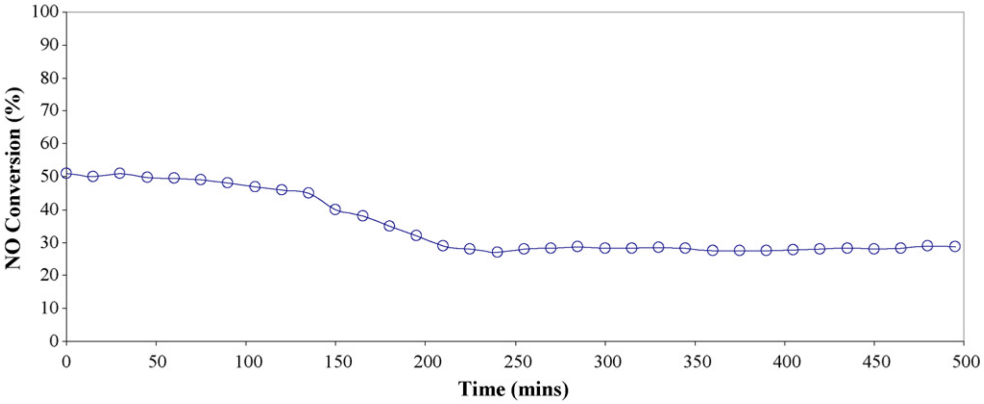

Fig. 13. The effect of SO_2 on the activity of the CuZnZrCe catalyst as a function of time of reaction. Feed composition: NO, 500 ppm; oxygen, 2%; methanol, 3600 ppm; SO_2, 80 ppm.

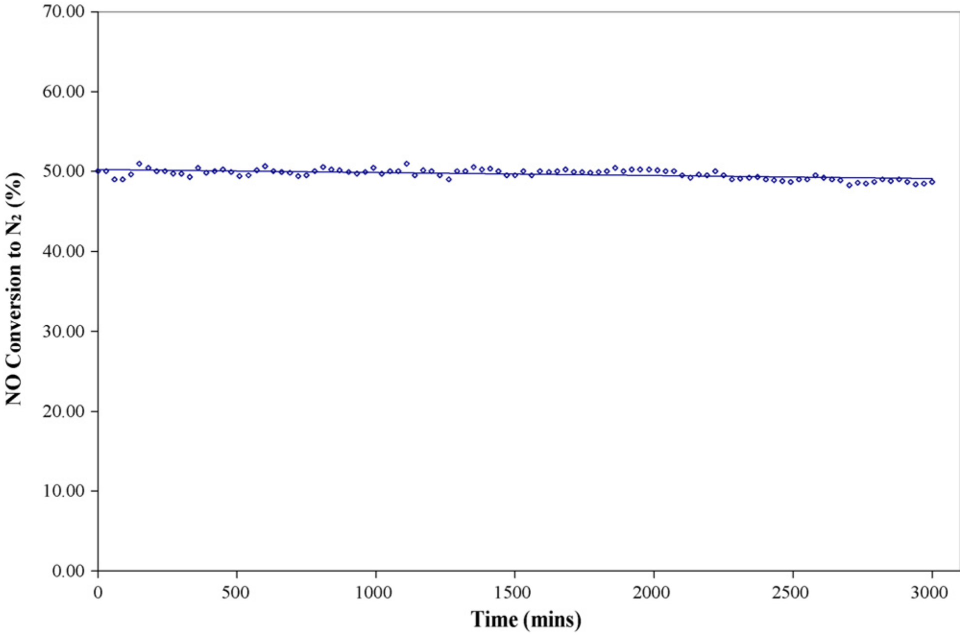

Fig. 14. The effect of time of reaction at 400 °C on the activity of the CuZnZrCe catalyst. Feed composition: NO, 500 ppm; CH_3OH, 3600 ppm; oxygen, 2%; balance He.

4. Conclusions

The promoted co-precipitated Cu–ZrO_2 catalysts prepared in this work are all effective selective deNOx catalysts using methanol as reductant when tested in the presence of excess oxygen. Under these conditions, they appear to be largely resistant to the presence of water and to be only partially poisoned by the presence of SO_2. In general, the results obtained with these materials compare very favourably with results reported by other authors using methanol as reductant. However, direct comparison is difficult as the conditions in this work are different (higher space velocity) from those reported in the literature. When no oxygen was admitted to the test gas, the catalysts could all still convert NO when methanol was used as reductant but the product now contained other N-containing molecules; the catalysts could also be used for the reduction with CO in the absence of O_2.

When the feed composition was adjusted such that the concentration of the methanol (as reductant) effectively balanced the NO and O_2 contents (oxidants) of the feed gas, the catalysts gave exceptionally high selectivities and conversions to N_2, approximately 100% in both cases. The activity was now more susceptible (but reversibly) to the presence of water vapour. The effect of SO_2 was not examined under these conditions. Further work is necessary to examine a number of aspects of the operation of these types of catalysts under stoichiometric conditions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2007.10.115.

References

[1] F.C. Meunier, J.P. Breen, V. Zuzaniuk, J.R.H. Ross, J. Catal. 187 (1999) 493.

[2] F.C. Meunier, J.R.H. Ross, Appl. Catal. B: Environ. 24 (2000) 23.

[3] F.C. Meunier, V. Zuzaniuk, J.P. Breen, J.R.H. Ross, Catal. Today 59 (2000) 287.

[4] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B: Environ. 39 (2002) 283.

[5] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo, N. Mizuno, Skokubai 32 (1990) 430.

[6] W. Held, A. Koenig, T. Richter, L. Puppe, SAE Paper 900496 (1990).

[7] M. Iwamoto, N. Mizuno, H. Yahiro, Stud. Surf. Sci. Catal. 75 (1992) 1285.

[8] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, T. Yoshinari, Appl. Catal. A: Gen. 88 (1992) L1.

[9] C.N. Montreuil, M. Shelef, Appl. Catal. B: Environ. 2 (1992) L1.

[10] M.C. Nunes Amorium de Carvalho, F. Barboza Passos, M. Schmal, Appl. Catal. A: Gen. 193 (2000) 265.

[11] J. Vassallo, M. Lezcano, E. Miro, J. Petunchi, Catalysis, automotive pollution control III, Stud. Surf. Sci. Catal. 96 (1995) 697.

[12] J. Vassallo, E. Miro, J. Petunchi, Appl. Catal. B: Environ. 7 (1995) 65.

[13] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521.

[14] P. Clancy, J.P. Breen, J.R.H. Ross, Catal. Today 127 (2007) 291.

[15] M. Iwamoto, H. Hamada, Catal. Today 10 (1991) 57.