An investigation of the mechanism of the selective catalytic reduction of NO on various metal/ZSM-5 catalysts: reactions of H_2/NO mixtures

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Several metal/ZSM-5 catalysts (Pt, Rh, Co and Cu/ZSM-5) were studied for the reduction of nitric oxide by a reducing agent which does not contain carbon, such as H_2, in the absence of oxygen. It has been found that these catalysts are very active towards the above reaction with H_2 even at relatively low temperatures, with a reactivity in the order: Pt/ZSM-5 > Rh/ZSM-5 > Co/ZSM-5 > Cu/ZSM-5. Between the above catalysts Co/ZSM-5 was the most selective to nitrogen with a formation of ammonia much lower than that observed on Pt/ZSM-5, Rh/ZSM-5 and Cu/ZSM-5 even at higher hydrogen partial pressures. A comparison between hydrogen, methane and ethane as the reducing agent has been made. In all cases the catalytic activity is higher using hydrogen rather than ethane or methane, the latter being the least active reductant. All data are consistent with a simple redox mechanism of NO reduction, and exclude the participation of carbonaceous deposits or carbon-containing species in the reaction mechanism.

Keywords: zeolites; reduction; nitrogen oxides; hydrogen; platinum; rhodium; cobalt; copper; pollution abatement

1. Introduction

Despite the fact that in recent years a lot of research has been undertaken on the selective catalytic reduction of NO with hydrocarbons under oxidising conditions, there is still little agreement about the detailed mechanism. Some researchers have suggested that the reaction proceeds through NO decomposition, followed by removal of adsorbed oxygen by the hydrocarbon reducing agent [1–3]. Other workers stress the importance of NO_2, formed in the gas phase, as a reaction intermediate [4–7]. Alternatively, the formation of reactive partially oxidised species

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[8–11], or an isocyanate (–NCO) intermediate [12,13], or some type of active coke [14–16] formed from the hydrocarbon, have been considered to be important.

Recently we have found that some metal-containing ZSM-5 zeolites (Rh, Pt and Co/ZSM-5) are more active towards the selective reduction of NO with ethane and methane in the absence of oxygen than in the presence of oxygen, whereas Cu/ZSM-5 was found to be active only in the presence of oxygen [17]. To explain this behaviour we suggested that the reaction on supported zeolite catalysts is mainly a redox process, in which NO decomposition occurs on reduced metallic or metal ion sites (the relative activity of each of these depending strongly on the choice of the metal), followed by the removal of the adsorbed oxygen by reduction with the hydrocarbon, thus regenerating the active sites for NO decomposition.

In order to provide further information on this mechanism, and to address specifically the contentious issue of the possible participation of carbonaceous deposits in the reaction mechanism, we have undertaken this work on the same set of metal/ZSM-5 catalysts described in the previous paper [17], but using hydrogen, which, of course, does not contain carbon, as a reducing agent.

The use of hydrogen as a reducing agent for NO has been discussed in the literature for about twenty years. Several noble metals supported on alumina (Pt, Pd, Rh, Au) have been found to be active for NO reduction [18–22]. Activity and selectivity to nitrogen were found to be strongly dependent on several factors, such as: the reaction temperature [19]; the choice of the support [20]; the metal content and its dispersion [21]. However, interest in the NO/H_2 reaction soon diminished when it was realised that all these catalysts were strongly poisoned by small amounts of oxygen in the gas stream. Moreover, hydrogen cannot be considered to be a very selective reductant: in fact a substantial quantity of undesirable by-products (such as NH_3 and N_2O) can be formed under certain experimental conditions. More recently there has been renewed interest in the NO/H_2 reaction especially on palladium and palladium–molybdenum on alumina catalysts, which have been found to be the most selective to nitrogen [23,24].

In our case we wish to emphasise that the purpose in using hydrogen as a reductant has been to better understand the complex reaction mechanism of NO reduction on zeolite-based catalysts, rather than to suggest that this would represent a viable practical process.

2. Experimental

All the metal-exchanged ZSM-5 zeolites were the same as those used in our earlier work [17] and have been prepared by ion exchange. The metal salts used for the exchange were the nitrate salt for Rh/ZSM-5, acetates for Co/ZSM-5 and Cu/ZSM-5, and $Pt(NH_3)_4Cl_2$ for Pt/ZSM-5. The silica/alumina ratio of the ZSM-5 zeolite was 31. Catalytic experiments were carried out in a pyrex glass tubular reactor, containing 100 mg of sample. Before catalytic tests the samples were always calcined in air at 500°C for 1 h. Before use, all catalysts were pelletized, crushed and sieved. The 250–600 micron fraction was always used. The reaction mixture contained 1000 ppm of NO and 1000–7000 ppm of hydrogen diluted with nitrogen to a total flow rate of 200 $cm^3\ min^{-1}$ (GHSV = 60 000 based on an apparent catalyst bulk density of 0.5 g/cm^3). This mixture was obtained by blending three different gas mixtures (NO/H_2, H_2/Ar and N_2). The analysis of the reaction products was performed continuously by using a chemiluminescence NOx analyzer (Signal 4000 series) for NOx and NO detection. A Perkin Elmer Sigma 4B gas chromatograph fitted with a TCD detector and a Porapak QS column was used to analyse for N_2O. The NO conversion has been evaluated as the percentage of NO converted to reduced products (variously N_2, N_2O, NH_3, see below).

We have found that hydrogen quenches the signal in the chemiluminescence NOx analyser, especially at high hydrogen concentrations (4000–7000 ppm). For this reason we found it necessary in some experiments to modify the analytical procedure to remove hydrogen prior to admitting the effluent gases to the detector. This was achieved by introducing air into the reaction mixture exiting from the catalytic reactor. This oxygen-rich gas was then passed through a Pt/Al_2O_3 catalytic convertor maintained at 400°C, which was shown to convert the excess hydrogen to water, thus eliminating the quenching problem in the chemiluminescence analyser. Blank experiments were performed to confirm that the Pt/Al_2O_3 catalyst did not affect the results for the NO reduction experiments on the zeolite-based catalysts. (This would be very unlikely to be a problem in any case since once NO had been converted to N_2, the N_2 would not be reoxidised on the Pt/Al_2O_3 catalytic convertor, and since the NOx analyser could determine NO and NO_2, any unreduced NO, which might be oxidized to NO_2 by the Pt/Al_2O_3 catalyst would be easily detected as total NOx, i.e. NO + NO_2.)

3. Results

It should be recalled (see Experimental) that hydrogen can interfere with the NOx analysis. However, when the reaction mixture contains <1000 ppm H_2 and the consumption of H_2 is high, i.e., at high NO conversions, the extent of the problem is very small. This is the case for all the experiments using low concentrations of hydrogen which are described below.

The total NO conversion to reduced products, i.e., to N_2, NH_3 and N_2O, as a function of the reaction temperature for all the metal/ZSM-5 catalysts, using 1000 ppm of H_2, is reported in fig. 1. The reactivity of the different systems is in the order: Pt/ZSM-5 > Rh/ZSM-5 > Co/ZSM-5 > Cu/ZSM-5 > H-ZSM-5. On Pt/ZSM-5 the reaction starts at about 50°C and reaches complete NO conversion at 100°C. In the case of Rh/ZMS-5 the conversion begins to increase at 150°C, reaching 100% at 250°C. On Co/ZSM-5 these temperatures are shifted about 100°C higher (starting point at 250°C and total conversion at 420°C). For the Cu/ZSM-5

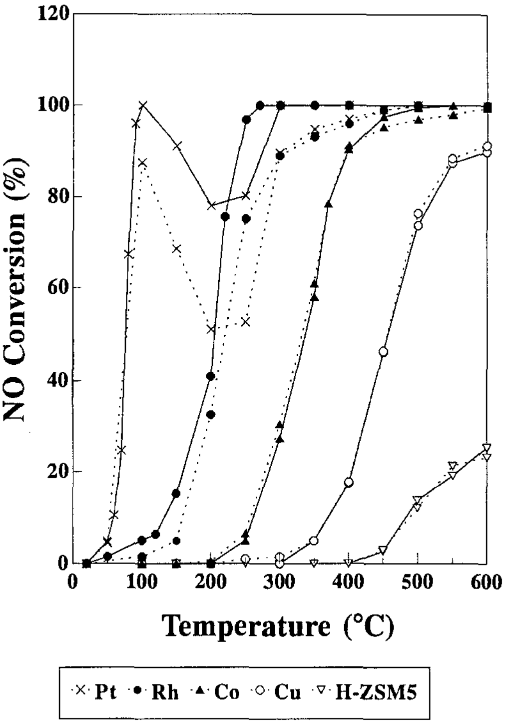

Fig. 1. Comparison between total NO conversion (full line) and NO conversion to $N_2 + N_2O$ (dotted line) as a function of reaction temperature on various metal/ZSM-5 tested. [NO]: 1000 ppm; [H_2]: 1000 ppm.

the conversion becomes detectable at 350°C and only reaches 90% at 600°C. The H-ZSM-5 support alone shows practically no activity below 400°C and reaches just 25% NO conversion at 600°C. A similar trend in NO conversion has already been reported on *alumina-supported* noble metals by Kobylinski and Taylor [19]. They found for hydrogen the following order of reactivity: Pd > Pt > Rh > Ru.

It should be noted that under our experiment conditions no NO_2 is ever detected from the zeolite-based catalysts, which is not too surprising given that the reaction mixture only contains H_2 and NO, although this clearly counts against any significant role for NO_2 in the NO reduction reaction. N_2O is sometimes formed, but only in low concentrations and at low temperatures (below 250°C).

The decrease in the total NO conversion observed on Pt/ZSM-5 between 150 and 250°C (see fig. 1) can be attributed to the lack of available hydrogen because of the simultaneous formation of ammonia under these conditions. (The formation of ammonia was confirmed by the intense brown colouration obtained by flowing the effluent gas stream through Nessler's reactant.) The formation of ammonia requires a higher stoichiometric quantity of hydrogen according to the reactions [19]

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{1}$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{2}$$

$$2NO + H_2 \rightarrow N_2O + H_2O\,. \tag{3}$$

As the reaction temperature is further increased the amount of ammonia detected decreases and so the conversion of NO increases again. Because the other catalysts are less active than the Pt/ZSM-5, the formation of ammonia is not observed to the same extent and so the conversion of NO rises smoothly with increasing temperature. Since the formation of ammonia quite probably requires first the dissociation of NO to N and O atoms, it is reasonable to add the amount of NH_3 formed to the amount of ($N_2 + N_2O$) formed in order to calculate the total NO conversion to reduced products. The overall results in fig. 1 (full line), therefore, indicate the high activity which can be obtained for these ZSM-5 based catalysts in the NO/H_2 reaction.

Any ammonia produced in the NO/H_2 reaction will be reoxidized by the Pt/Al_2O_3 catalytic converter when this is placed at the inlet to the chemiluminescence analyser. Consequently it is possible to obtain an approximate analysis for the amount of NH_3 formed by comparing the total amount of NOx analysed with the catalytic converter absent or present. In fig. 1 the NO conversion to $N_2 + N_2O$ (dotted line), calculated as explained above, is also shown as a function of the reaction temperature for the reaction with 1000 ppm of hydrogen. (The quantity of ammonia produced on each catalyst can be estimated from the difference between the corresponding total NO conversion and NO conversion to $N_2 + N_2O$ curves.)

Fig. 1 shows that for Pt/ZSM-5 the NO conversion to $N_2 + N_2O$ reaches over 80% at only 100°C, then goes through a minimum of ca. 50% at about 200°C before increasing again to 100% at higher temperatures. A poor selectivity to nitrogen at low temperatures has been also reported on Pt/alumina by Shelef et al. [18]. At temperatures above 300°C, however, fig. 1 shows that with 1000 ppm of hydrogen, the formation of ammonia is not important on Pt/ZSM-5 or on Rh/ZSM-5.

It is also clear from fig. 1 that on Co/ZSM-5, Cu/ZSM-5 and H-ZSM-5 alone, practically no ammonia is formed at any temperature in the range where there is some NO reduction activity. Moreover, considering that N_2O formation is also very small over this same temperature range (undetectable by our method of analysis), these catalysts are in fact very selective for NO reduction to nitrogen.

Figs. 2a–2d show the conversion to $N_2 + N_2O$ as a function of the reaction temperature on the different catalysts for different hydrogen contents. It is found in all cases that an increase in the hydrogen concentration leads to the formation of more ammonia, with a corresponding relative decrease in the conversion to $N_2 + N_2O$. This is in accord with other previous work on different types of catalyst [19]. It is interesting to note how at higher temperatures with Rh/ZSM-5, in contrast to Pt/ZSM-5, NH_3 formation decreases again, as indicated by the upswing in the NO conversion curve at high temperatures. This may be due to a higher activity

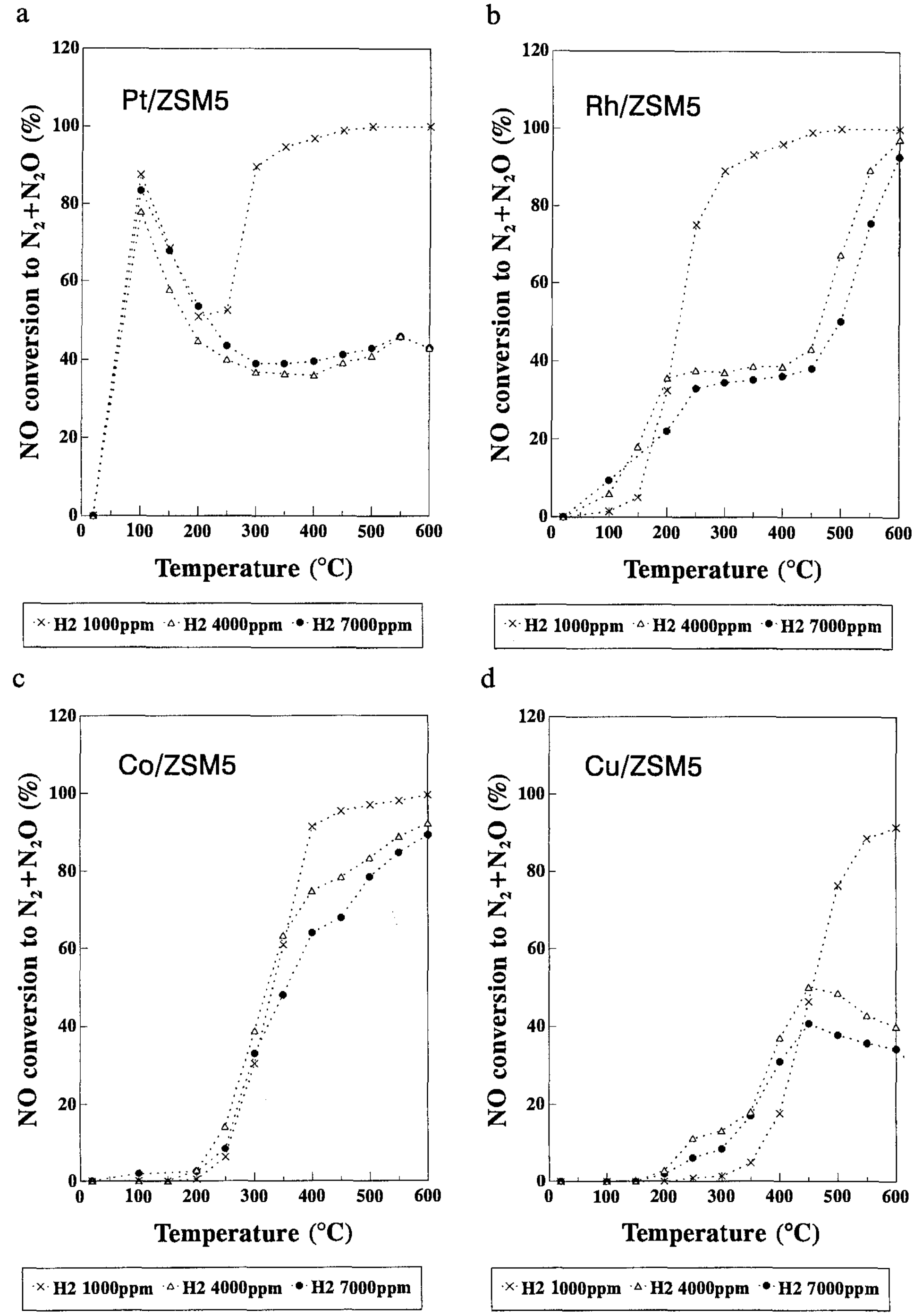

Fig. 2. Influence of hydrogen concentration on NO conversion to $N_2 + N_2O$ as a function of reaction temperature on Pt/ZSM-5 (a), Rh/ZSM-5 (b), Co/ZSM-5 (c) and Cu/ZSM-5 (d). (×), 1000 ppm of H_2; (△), 4000 ppm of H_2; (●), 7000 ppm of H_2. [NO]: 1000 ppm; [H_2]: 1000–7000 ppm.

for NH_3 decomposition on Rh as compared with Pt, or possibly to a further reaction of NH_3 with NO to form N_2 on the Rh-containing catalyst [19]. On Co/ZSM-5, even at higher H_2 contents, the quantity of ammonia formed is much lower than that observed on Pt/ZSM-5, Rh/ZSM-5 or Cu/ZSM-5.

The order of reactivity observed in this work on these metal/ZSM-5 catalysts in the NO/H_2 reaction with 1000 ppm of hydrogen (Pt/ZSM-5 > Rh/ZSM-5 > Co/ZSM-5 > Cu/ZSM-5) may be compared with the results previously reported by us for the corresponding reactions of NO with methane or ethane in the absence of oxygen [17]. Figs. 3a–3d show a comparison between the three reductants for each of the metal/ZSM-5 catalysts. In all cases we observed a much higher activity with hydrogen as compared with ethane or with methane, the latter being the least active reductant. For Pt/ZSM-5 and Rh/ZSM-5 total conversion of NO is reached about 200°C lower with hydrogen than with ethane and about 250°C lower than with methane. On Co/ZSM-5, the temperature difference is, respectively, about 150 and 200°C. In the case of Cu/ZSM-5 (fig. 3d), while with ethane or methane the NO conversion remains low until close to 600°C, hydrogen is able to reduce NO above 350°C. In any case Cu/ZSM-5 is clearly the least active among all the catalysts we have investigated in the absence of oxygen.

It seems clear that the higher conversions obtained with hydrogen at lower temperatures (in the absence of oxygen) can be simply related to its much higher activity, as compared with ethane and especially methane, in removing adsorbed surface oxygen.

4. Discussion

The main purpose of this research was to check out the possible role of carbonaceous residues in the selective reduction of NO on zeolite-based catalysts. As already outlined in the Introduction this has been a contentious issue for some time. In recent publications [2,17] we have argued that there is no unambiguous evidence that such carbon-containing species play any particular role in the selective NO reduction reaction. Indeed, we have clearly shown that under realistic reaction conditions the maximum activity for the NO to N_2 reaction occurs on a Cu/ZSM-5 catalyst within a few seconds of introducing the hydrocarbon reductant, propene in that case [2]. We have further shown that the decline in the activity after switching off the propene supply is independent of the time of exposure to the full reaction mixture. We have concluded that these results are inconsistent with any significant role for surface residues of carbon-containing species.

In a more recent publication [17] we have shown that in the absence of oxygen both ethane and methane can be very selective reductants for NO. However, in the absence of oxygen Cu/ZSM-5 is a poor catalyst whereas Co/ZSM-5, for example is an extremely effective catalyst. Since it seems likely that carbon deposition would be comparable in both catalysts we have taken this as further evidence that such

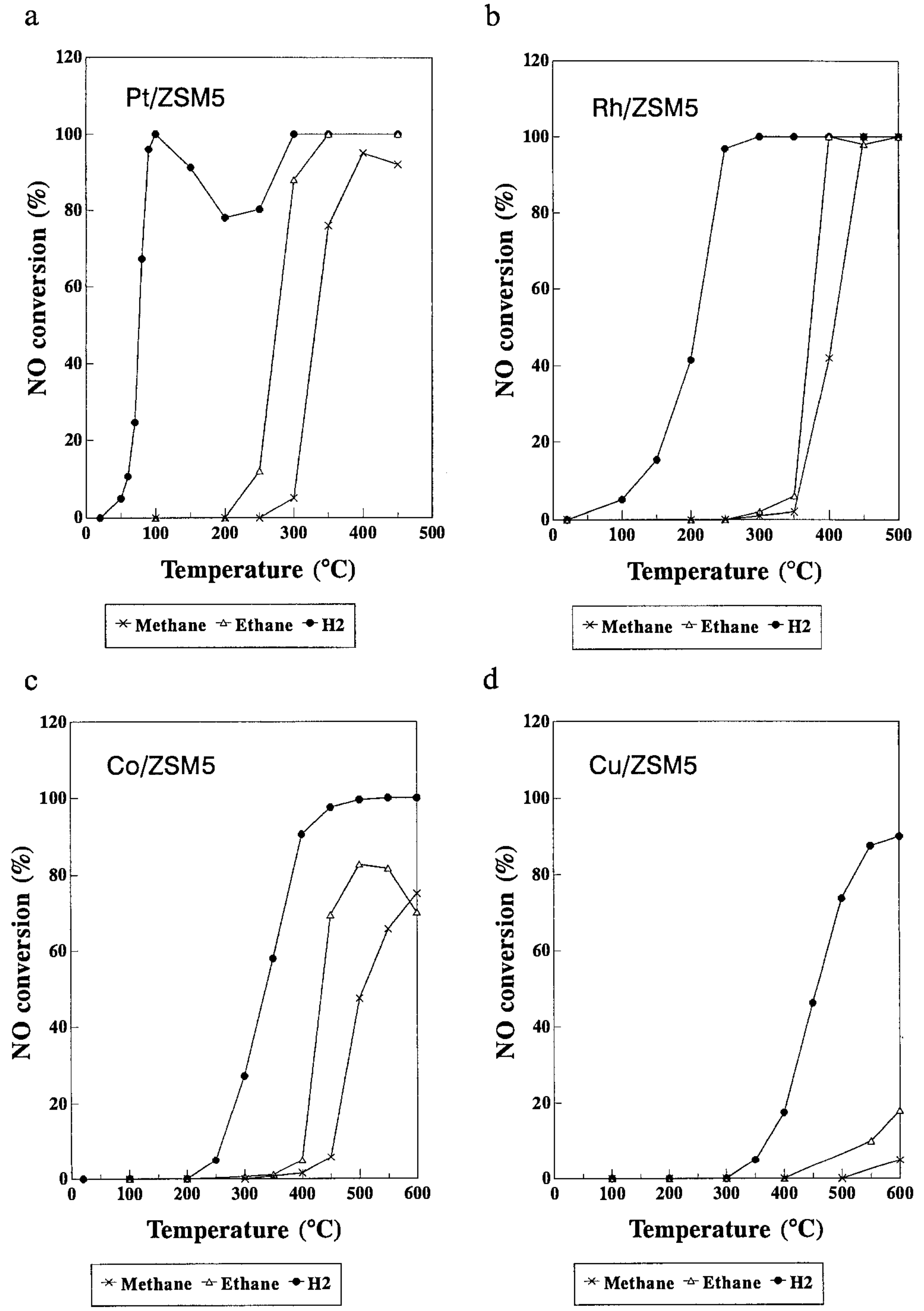

Fig. 3. Comparison between usage of methane, ethane and hydrogen as reducing agent on total NO conversion as a function of reaction temperature on Pt/ZSM-5 (a), Rh/ZSM-5 (b), Co/ZSM-5 (c) and Cu/ZSM-5 (d). (×), methane; (△), ethane; (●) H_2. [NO]: 1000 ppm; [reducing agent]: 1000 ppm.

carbon-containing species are not important in the NO reduction reaction. Instead we have argued that the reaction involves a simple redox cycle: the reductant converts the metal ion into a (reduced) active state; dissociative adsorption of NO releases N_2 into the gas phase and leaves behind adsorbed oxygen atoms; the reductant recreates the active site by removing these oxygen atoms.

On this basis, replacing the hydrocarbon reductant by a non-carbon-containing compound, such as hydrogen, should allow us to eliminate any effect from carbon. Moreover, if a simple redox mechanism is operative it would be expected that since hydrogen is a much more effective reductant of metal ions than most hydrocarbons, the maximum activity for NO reduction would occur at comparatively low temperatures.

It is apparent that the information presented in this paper is entirely consistent with our simple redox mechanism. The results obtained with hydrogen as the reducing agent show clearly that these metal/ZSM-5 catalysts are very active indeed for the conversion of NO to reduced products. Therefore for these catalysts, a reductant which contains carbon is not essential at least under these conditions. Consequently, no specific carbonaceous deposits or carbon-containing species need to be invoked in NO reduction even when hydrocarbons are used as reducing agents.

Of course the present work refers to oxygen-free conditions and it is pertinent to ask whether this information is relevant to the reaction mechanism under "lean-burn" conditions where there is excess oxygen in the gas stream. Hydrogen cannot be tested as a reductant for NO in the presence of oxygen because it reacts preferentially with oxygen, possibly because the dissociative adsorption of oxygen is faster than the dissociative adsorption of NO. However, we believe the present work is relevant to this question for two reasons. First, in the presence of oxygen the amount of carbon-containing material which will be present at steady state on a catalyst surface must be much less than would be present under oxygen-free conditions. Therefore, if there is no apparent need for a carbon-containing deposit in the absence of oxygen there seems even less likelihood that such species will be important under oxygen-rich conditions.

The second reason why we consider that carbon-containing deposits are not especially important in the selective reduction of NO in the presence of oxygen comes from our previously reported [17] observation that with ethane as a reductant the activity of Co/ZSM-5 actually decreases very sharply when oxygen is introduced into the reaction mixture. At that time we could not determine whether this effect was due to the removal of a very active carbon-containing deposit or to some other effect. Taken together with the results in the present paper, it now seems clear that the loss of activity when oxygen was introduced was not due to the removal of active carbon.

In conclusion, metal/ZSM-5 catalysts can be very active for the reduction of NO by H_2 even at relatively low temperatures. The results are consistent with a simple redox mechanism in which NO adsorption and decomposition on active (reduced) sites (each metal has its own most active oxidation state) leads to the formation of gaseous nitrogen and adsorbed oxygen. This step is followed by the removal of the oxygen by the reducing agent, restoring the (reduced) active site.

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