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NO_2 formation over Cu-ZSM-5 and the selective catalytic reduction of NO

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The extent of the selective catalytic reduction (SCR) of nitric oxide to dinitrogen in the presence of excess oxygen is enhanced by the oxygen on several zeolite-based catalysts and using different reductants. When the catalyst is Cu-ZSM-5 and the reductant is a hydrocarbon, an NO_2 intermediate has been suggested by several investigators. This work shows that at short residence times, with excess reductant and in the absence of oxygen, the NO_2 itself is reduced only back to NO. Thus, for the selective reduction of NO_2 to N_2 (N-pairing) strongly oxidizing conditions are required, same as for the complete reduction of NO. In the presence of excess oxygen the activity of Cu-ZSM-5 in the $NO + O_2$ reaction to form NO_2 parallels the SCR in every respect. It is higher over Cu-ZSM-5 than on Cu/Al_2O_3 or on H-ZSM-5. The copper-containing zeolite is also active in the decomposition of NO_2 back to NO and O_2 while the other catalysts are much less active. The inhibiting effect of water on the $NO + O_2$ catalytic reaction is also parallel to the effect on SCR. This evidence strengthens the notion of an NO_2 intermediate.

Keywords: nitric oxide; Cu-ZSM-5 catalysts; hydrocarbon; reduction

1. Introduction

The selective reduction of nitric oxide by hydrocarbons over Cu-containing zeolites in a large excess of oxygen has been under intense investigation during the last three years, driven by the promise of large scale applications for the control of oxides of nitrogen [1,2]. It was noticed early [2] that the presence of oxygen is a necessary condition for the occurrence of the selective reduction to dinitrogen over the most frequently studied catalyst – a copper-exchanged ZSM-5 zeolite having a SiO_2/Al_2O_3 ratio of 30–40. The oxygen in reductants such as alcohols, aldehydes, ketones and ethers also engenders the selective reduction when excess oxygen is absent in the reacting gas stream [3].

There have been several suggestions for the role of the oxygen in activating the desired selective reduction: (a) the nitrogen-containing molecule being reduced is not the monoxide but rather the dioxide formed by the reaction with oxygen; (b) the excess oxygen gasifies the rapidly forming carbonaceous deposits which block the surface, keeping the latter clean; (c) the oxygen prevents excessive reduction of the divalent copper cations. A recent paper asserts that the oxygen is involved in all of the above. Specifically, it was shown that NO_2 is a stronger oxidizing entity than NO, as could be expected and that NO_2 is better at maintaining the copper in the preferred *cupric* oxidation state. The experiments were run at a GHSV of 4400 h^{-1} [4]. The authors deduced that under the prevailing experimental conditions the system

$$2NO + O_2 \rightleftharpoons 2NO_2 \tag{1}$$

is in equilibrium. It was mentioned that the kinetics which determine the approach to this equilibrium will be influenced by the conditions.

Apart from the effects noted above it is possible that the NO_2 is a prerequisite for the necessary pairing of the nitrogens as it is known that the dimerization to N_2O_4 or the coupling with NO to N_2O_3 is more likely than the dimerization of NO [5].

In order to specify the role of the NO_2 still more precisely we tried to ascertain whether in a reacting mixture containing NO_2 and a hydrocarbon, propylene or propane, in the absence of oxygen, the selective reduction to dinitrogen takes place, contrary to the case with NO, which might directly confirm the intermediacy of the nitrogen dioxide. Further, we wanted to establish whether the pre-equilibration of reaction (1) takes place in the gas phase or is it, at short residence times such as prevail in practice, a catalytic process taking place on specific surface sites.

2. Results

The samples used in this work were H-ZSM-5 having a SiO_2/Al_2O_3 ratio of 30 from PQ Corp., a Cu-ZSM-5 from UOP having SiO_2/Al_2O_3 ratio of 32 with 2.41% Cu, and 2% Cu supported on γ-Al_2O_3 having a surface area of 95 m^2/g. Particular attention was paid to the accuracy of the determination of the oxides of nitrogen. For this purpose the chemiluminescence NO_x analyzer, including the catalytic attachment for the reconversion of NO_2 to NO was carefully recalibrated. The reagent grade reactants were diluted by nitrogen carrier gas containing <10 ppm of O_2.

The flow rate was 8.0 ℓ/min over 1.5 g of powdered solid sample ($\sim$ 1.0 ml). This amount of powdered catalyst will occupy a volume of $\sim$ 10 ml when washcoated on an industrial or automotive monolithic support. Hence, while under our conditions the residence time (<0.01 s) is that corresponding to a GHSV of ~ 500000 h^{-1}, under "real use" conditions it will be that corresponding to a GHSV smaller by about an order of magnitude.

Table 1 shows that at the temperature of 410°C, used in our previous work [6] the replacement of NO by NO_2, without oxygen in the gas mixture, results only in the reduction of the NO_2 *back to NO*. Under the strongly reducing conditions,

Table 1
Reduction of NO_2 over Cu-ZSM-5 with and without oxygen

Run No.	In (ppm)		Out (ppm)	
without oxygen				
1	NO_2 494	C_3H_6 1492	NO_2 5	C_3H_6 1420
	NO 18		NO 505	
2	NO_2 503	C_3H_8 1520	NO_2 9	C_3H_8 1458
	NO 15		NO 483	
with 3.8% oxygen				
3	NO_2 494	C_3H_6 1490	NO_2 26	C_3H_6 70
	NO 20		NO 215	
4	NO_2 525	C_3H_8 1480	NO_2 4	C_3H_8 730
	NO 12		NO 110	

prevailing when the results of table 1 were accurate, there is no pairing of the nitrogen atoms. This indirectly implies that an oxidized state of the copper, most likely Cu^{2+}, may be needed for the selective reduction to dinitrogen. It has been noted that propylene easily reduces cupric ions in the absence of excess oxygen [7]. In the presence of a large excess oxygen there is little difference in the behavior of the two forms of nitrogen oxides as noted in ref. [4]. This is so whether the reductant is propylene, which, in our experience, leads to a copiously sooted surface, or propane, which leaves the surface without visually discernible deposits. Thus, owing to the multiple effect of the oxygen both on the catalytic surface and on the composition of the gas phase the direct involvement of NO_2 in the formation of dinitrogen cannot be studied under reducing conditions in the absence of excess oxygen.

The NO_2 used throughout this work contained 2–4% NO, as seen in table 1. The material balances in runs 1 and 2 are quite good when it is realized that 9 and 10 molecules of NO_2 are reduced to NO by a molecule of propylene and propane, respectively. Runs 3 and 4, in the presence of excess oxygen, indicate a very high conversion of NO_2 to dinitrogen, ca. 55 and 80% for propylene and propane, respectively.

The activities of the copper-exchanged sample, the same one used to obtain the data in table 1, and of the $Cu/\gamma\text{-}Al_2O_3$ sample in the SCR of NO by propylene in excess oxygen are given, for reference purposes, in figs. 1 and 2. The approach to equilibrium of reaction (1) in a flow rate approximating realistic practical conditions is shown in fig. 3 for the forward direction in an empty quartz tube, H-ZSM-5, and Cu-ZSM-5. As seen in fig. 3, in the empty quartz tube the residence time is too short for any formation of nitrogen dioxide. The forward direction of process (1) in the gas phase is second order in NO and therefore quite slow at low concentrations. The metal-less H-ZSM-5 shows some small activity in NO_2 formation above

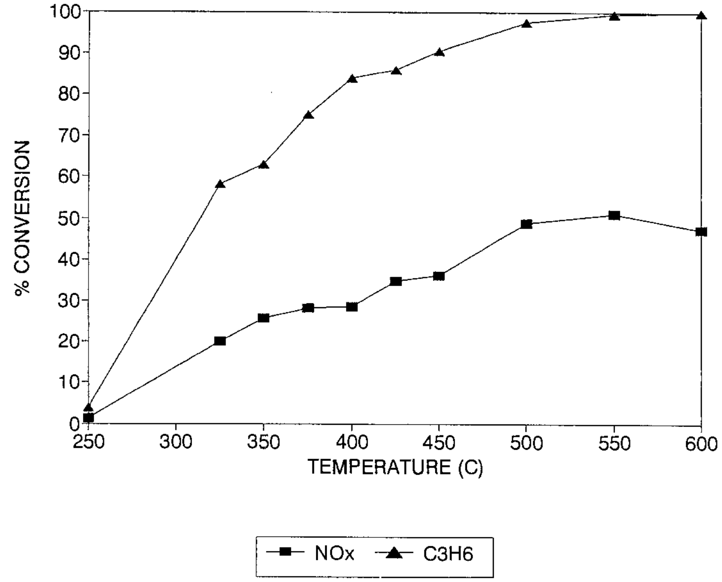

Fig. 1. Selective catalytic reduction of NO by C_3H_6 over Cu-ZSM-5. Inlet concentrations: NO 500 ppm, C_3H_6 1500 ppm, O_2 4.9%; flow rate 8 ℓ/min, catalyst volume 1 cm^3, weight 1.5 g.

250°C and in the reverse reaction above 350°C. The Cu-ZSM-5 on the other hand is quite active in moving the gas-phase composition towards equilibrium even at the low residence times used in the experiment. The formation of NO_2 begins at 200°C and peaks <400°C.

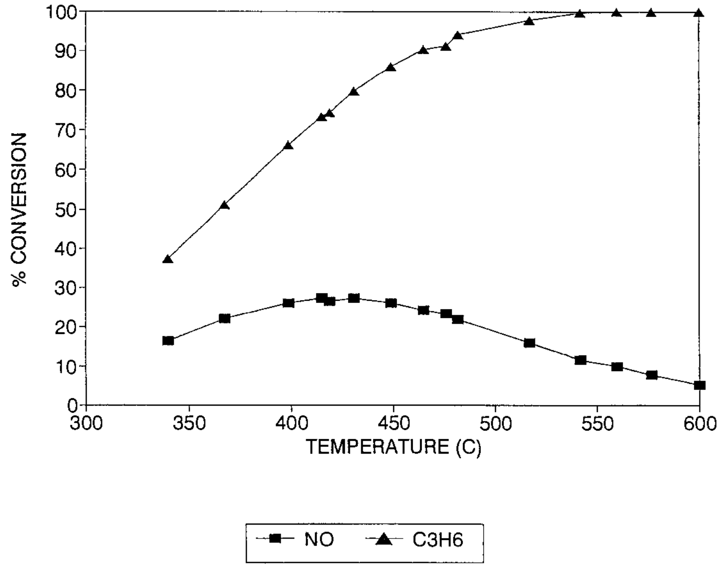

Fig. 2. Selective catalytic reduction of NO by C_3H_6 over Cu/γ-Al_2O_3. Inlet concentrations: NO 500 ppm, C_3H_6 500 ppm, O_2 3%; flow rate 3 ℓ/min, catalyst weight 1 g.

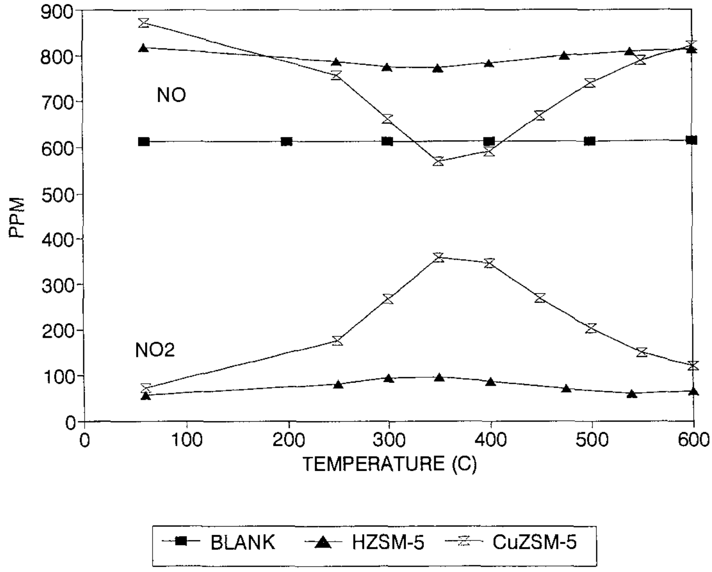

Fig. 3. The formation of NO_2 in the NO + O_2 reaction in an empty quartz tube and over H-ZSM-5 and Cu-ZSM-5. Inlet concentration of O_2 4.9%; flow rate 8 ℓ/min, catalyst weight 1.5 g.

In fig. 4 the NO_2 formation in a stream containing 4.9% oxygen is shown as the NO_2/NO ratio for H-ZSM-5, Cu/Al_2O_3 and Cu-ZSM-5 (the last catalyst was used at two space velocities). It is seen that at the short residence times used, the equilibrium is being approached only at >400°C and that the Cu-ZSM-5 is much

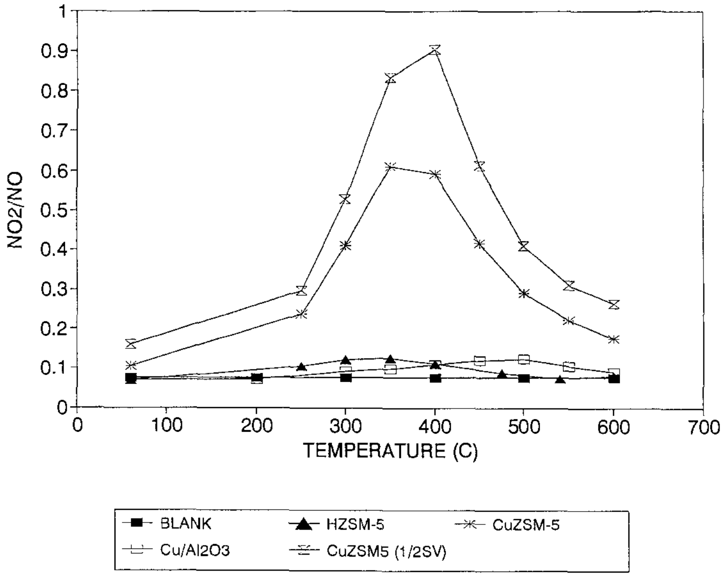

Fig. 4. The NO_2/NO ratio as a function of temperature attained under conditions of fig. 3. Note one run over Cu-ZSM-5 at a flow rate of 4 ℓ/min (1/2 GHSV of other runs).

more effective in this process than the other catalysts. Halving the space velocity over Cu-ZSM-5 strongly enhances the NO_2/NO ratio in the investigated temperature range. We can safely conclude that under short residence times a catalyst is needed to bring about the formation of NO_2 (or decomposition back to NO and O_2) and that the active catalytic sites are the copper ions in Cu-ZSM-5. The Cu/Al_2O_3 catalyst is much less effective.

Fig. 5 presents the process of eq. (1) from the reverse direction. Again, in the empty tube, not shown, there was no decomposition of NO_2 to NO and O_2 below 600°C. The metal-less H-ZSM-5 showed traces of activity at the higher temperatures while Cu-ZSM-5 was quite active and substantially more so than the alumina-supported copper oxide. The activity order of the examined catalysts is the same whether process (1) is approached from the left or right.

The effect of water on the catalytic process of eq. (1) over Cu-ZSM-5 is shown in fig. 6 where one of the curves from fig. 4 is reproduced along with an analogous experiment in a similar gas flow containing 10% H_2O. It is seen from the figure that the presence of water strongly inhibits the catalytic activity in the reaction between NO and O_2, parallel to its well-documented [2] inhibition of the SCR on the same catalyst. This is shown directly in fig. 7 by comparing the effect of water on the NO + O_2 reaction and SCR at two different temperatures. The relative suppression of the activity by the water is quite close for both reactions at the two widely different temperatures.

The results of this work indicate that at realistic flow conditions in automotive applications the copper catalytic sites in the ZSM-5 zeolite promote the formation

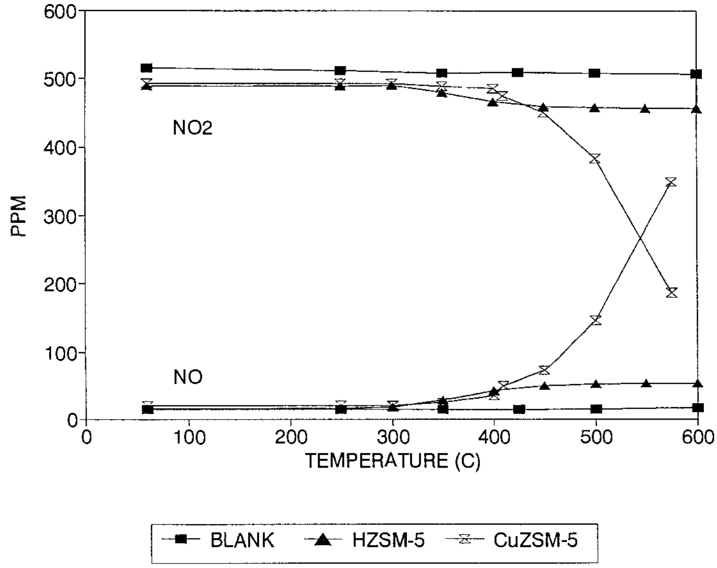

Fig. 5. Decomposition of NO_2 to NO and O_2 at the flow conditions of fig. 3.

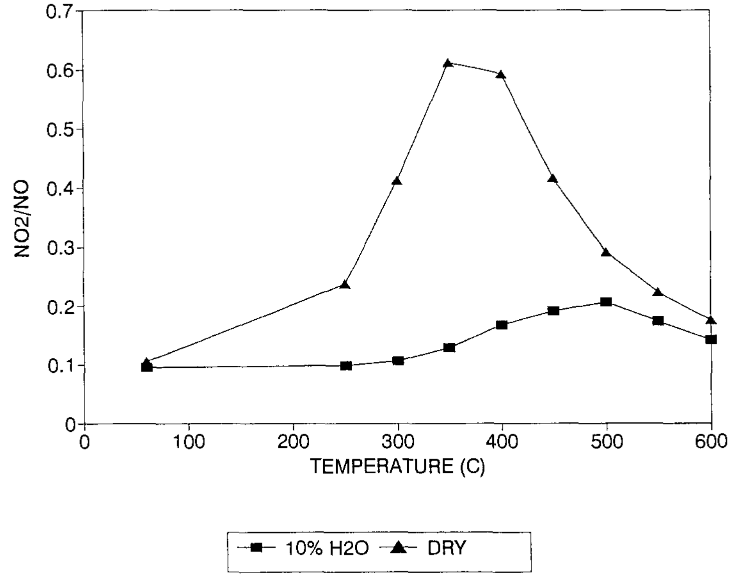

Fig. 6. Effect of water vapor on the NO_2/NO ratio over Cu-ZSM-5 at the conditions of fig. 3.

of NO_2 and this parallels the SCR activity. If the formation of NO_2 is indeed a *prerequisite* for the selective reduction of NO by hydrocarbons, catalysts active in the latter have also to be active in the former. The reverse may not be always true since it is likely that NO_2 formation is a *necessary but not a sufficient condition* for the

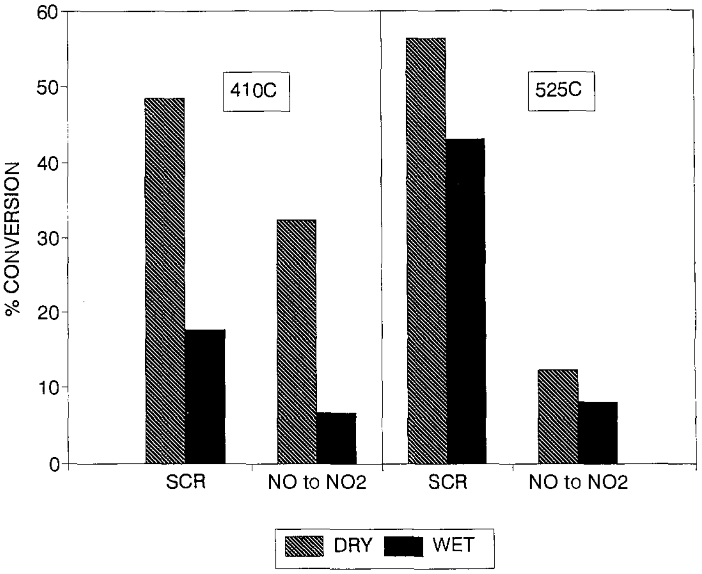

Fig. 7. Comparison of the effect of water on SCR (conditions of fig. 1) and $NO + O_2$ catalytic reaction (conditions of fig. 3) over Cu-ZSM-5.

SCR of NO. The activation of the hydrocarbons most likely requires acidic sites, and the absence of these may make useless a catalyst which otherwise is active in the equilibration of nitrogen oxides with oxygen. These results do not yet constitute proof of NO_2 intermediacy in the SCR process. They are merely congruent with such a view. It should be noted that the enhancement of SCR of nitric oxide by excess oxygen is widely documented: it is observed also when the reductant contains a nitrogen atom, NH_3, both on Pt [8] and on the commercial vanadia/titania catalysts [9].

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