The role of NO_2 in the reduction of NO by hydrocarbon over Cu-ZrO_2 and Cu-ZSM-5 catalysts

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The reduction of NO_x with propene or propane in the presence of 1 or 4% O_2 was studied at low conversions over a 7.4 wt% Cu-ZrO_2 and a 3.2 wt% Cu-ZSM-5 catalyst. The rates of N_2 production were compared in experiments using only NO or a mixture of NO and NO_2 in the feed. They were also compared with the rates of NO_2 reduction to NO under the same conditions, and of NO oxidation to NO_2 in the absence of hydrocarbon. It was found that the reduction of NO_2 to NO was very fast, consistent with literature data. The data were best explained by a reaction scheme in which the hydrocarbon was activated primarily by reaction with adsorbed NO_2 to form an adsorbed oxidized N-containing hydrocarbon intermediate, the reaction of which with NO was the principal route to produce N_2 under lean NO_x conditions.

Keywords: NO_x reduction, NO_2 in; Cu-ZSM-5, lean NO_x reduction on; Cu-ZrO_2, lean NO_x reduction on; NO oxidation

1. Introduction

The catalytic reduction of NO by hydrocarbon in a large excess of oxygen is a potentially important reaction in emission control for lean burn engines, and there have been many investigations in recent years to search for better catalysts for this reaction, or to elucidate the nature of the active sites and the reaction mechanism. Regarding the reaction mechanism, it is of current interest to elucidate whether NO or NO_2 is the direct source of N in the formation of N_2. The uncertainty in the direct source of N arises because of the potential ability of the catalyst to convert NO to NO_2, which many catalysts do readily [1]. Thus, it is possible that NO reduction proceeds via first the oxidation of NO to NO_2 and then reaction of NO_2 with hydrocarbon to form N_2:

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$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \tag{1}$$

$$NO_2 + \text{hydrocarbon} \rightarrow \rightarrow \tfrac{1}{2}N_2 + xCO_2 + yH_2O \tag{2}$$

In this scheme, the involvement of NO is only through the formation of NO_2. However, to date, no definitive experimental evidence is available to confirm or disprove this mechanism.

In a number of studies with Cu-ZSM-5, it was observed that O_2 up to concentrations of a few percent promotes the reduction of NO by hydrocarbons [2–6]. Although this promotion effect could be explained by the formation of NO_2 when O_2 is present, it can be explained also by the ability of oxygen to prevent catalyst coking [4] or to keep the Cu ions from being reduced to Cu metal [2]. As stated by Shelef et al. [5], the potential multiple roles of O_2 make determining the role of NO_2 difficult.

The rates of production of N_2 in the reduction of NO or NO_2 in the presence of oxygen have been compared on Cu-ZSM-5 using isobutane [6], propene [5], propane [5,7] or methane [8] as the reductant. In all cases, little difference was observed, although Petunchi and Hall reported that, at any temperature where the conversion of isobutane was less than 100%, the conversion to N_2 and the corresponding isobutane conversion were slightly higher when NO_2 was used than when NO was used [6]. They used this evidence to support the model that NO_2 is essential for the formation of N_2, and attributed the similar rates of production of N_2 from NO or NO_2 to the ability of Cu-ZSM-5 to achieve rapid equilibrium between NO, O_2, and NO_2. Unfortunately, the composition of the gas exiting the reactor was not measured in that study to ascertain whether the NO–O_2–NO_2 equilibrium was indeed achieved. Furthermore, if equilibrium was achieved much faster than N_2 production, it would not be possible to distinguish from the data which is the direct source of N_2.

Shelef et al. [5] measured the ability of H-ZSM-5, Cu-ZSM-5, and Cu/Al_2O_3 to oxidize NO to NO_2 and found that Cu-ZSM-5 is a much more effective catalyst than the other two. This paralleled the NO_x reduction activity over these catalysts. In addition, H_2O was found to suppress the NO oxidation reaction, similar to its suppression of the NO_x reduction reaction. However, as cautioned by the authors, although the similarity in these behaviors suggests that the formation of NO_2 is an important step in the NO reduction reaction, it remains unproven.

An NO_2 type intermediate (NO_2 or NO_3) was suggested to be important by Ansell et al. [9]. These authors adsorbed NO on a fresh and a precoked Cu-ZSM-5 sample. Upon desorption, only NO and O_2 were desorbed from the fresh sample, presumably from an adsorbed NO_2 species, whereas a species of mass 28 (which contained CO and presumably also N_2) was desorbed from the precoked sample. They suggested that the lean NO_x reduction mechanism involves a NO_2 species which reacts with carbonaceous deposits to form N_2. However, it is not clear whether there is significant carbonaceous deposit on the catalyst or whether this is the predominant route for N_2 formation under standard operating conditions [10].

Contrary to Cu-ZSM-5, on catalysts that are less effective in catalyzing the equilibration of NO + O_2 with NO_2, the rate of N_2 formation is substantially higher in the reduction of NO_2 than NO, even in the presence of O_2. This has been observed on Na-ZSM-5 [11], Ce-ZSM-5 [11], ZrO_2 [12], Ga_2O_3 [12], Al_2O_3 [13], and H-ZSM-5 [13]. In these cases, the role of NO_2 in initiating the NO_x reduction reaction, as well as in preventing deactivation of the catalysts by coking have been demonstrated. Nonetheless, it is still not resolved whether the predominant pathway in N_2 production involves NO.

It appears that one might be able to contribute to resolving the question of the importance of an NO_2 intermediate in the reduction of NO over Cu-containing catalysts by comparing quantitatively the rates of N_2 formation from NO and from NO_2, and by comparing these rates with the rate of NO oxidation to NO_2 under conditions where the equilibration of NO and NO_2 is far from being complete, that is, at low conversions. This can be achieved by complete analyses of the compositions of the exit gas stream of the reactor. Here we report the results of such experiments performed over Cu-ZSM-5 and Cu-ZrO_2, two active catalysts for lean NO_x reduction [3,14].

2. Experimental

The oxidation of NO was conducted in a conventional U-tube fused silica reactor. The exit gas of the reactor was sent to a 20 cm long gas cell for infrared spectroscopic analysis. The activity of the reaction system to oxidize NO to NO_2 in the absence of a catalyst was determined over the temperature range studied. A maximum conversion of 3.2% was obtained at the highest temperature and oxygen partial pressure employed (350°C and 4% O_2, with 0.1% NO). The NO_x reduction reaction was conducted on another conventional flow system with a U-tube fused silica reactor. The exit gas of the reactor could be sampled by on-line gas chromatography as described previously [14] and by infrared spectroscopy by passing the gas through the gas cell. Upstream from the reactor was another U-tube fused silica reactor containing 1 g of 5 wt% Co/Al_2O_3 catalyst at 300°C. When desired, the stream of O_2 and NO was passed over this Co/Al_2O_3 catalyst which oxidized the NO to NO_2. This reactor could be bypassed if a feed of NO and O_2 was desired. In the bypass mode, the conversion of NO to NO_2 for this system without a catalyst was 3% or less.

A Mattson Galaxy FTIR 5000 spectrometer, equipped with liquid N_2 cooled MCT detector was used at a resolution of 4 cm^{-1} for gas analysis. The assignment of the IR peaks to different species was as follows: 1845 and 1903 cm^{-1} to NO; 2209 and 2234 cm^{-1} to N_2O; 1601 and 1629 cm^{-1} to NO_2; 2342 and 2361 cm^{-1} to CO_2; 1443, 1473, 1638, 1665, 1814, 1839, and 2857–3103 cm^{-1} to C_3H_6; and 1362–

1506, 2874–2980 cm^{-1} to C_3H_8. An IR spectrum of 1000 ppm NO in He showed a trace amount of N_2O, which remained unchanged after mixing the gas with O_2. The integrated NO absorption peak intensity was found to be linear from 0 to 10 000 ppm NO. The error in the NO concentration was estimated to be ±20 ppm. The absorption coefficient for NO_2 was approximately 13 times higher than for NO, and its concentration could be determined quite accurately.

The 7.4 wt% Cu-ZrO_2 catalyst was prepared by coprecipitation of the nitrates of Cu and Zr with urea, as described previously [14]. Its surface area was 138 m^2/g. The 3.2 wt% Cu-ZSM-5 with a $Si/Al = 35$ was supplied by General Motors Corporation [15]. The 5 wt% Co/Al_2O_3 was prepared by impregnating γ-Al_2O_3 (Aldrich, 155 m^2/g) with an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich), and the 0.33 wt% Pt/Al_2O_3 was prepared by impregnating the Al_2O_3 with $Pt(NH_3)_2(NO_3)_2$ (Alfa) to incipient wetness, followed by drying overnight at 100°C. The Co/Al_2O_3 catalyst was calcined in 10% O_2 in He at 450°C for 0.5 h, and the Pt/Al_2O_3 catalyst was calcined in air at 400°C for 1.5 h followed by H_2 reduction at 500°C for 2 h.

In the data presented, the competitiveness factor was defined as the ratio of the rate of hydrocarbon consumed to produce N_2 (equivalent to rate of production of N_2) to the rate of total hydrocarbon consumption. In the case where NO_2 was consumed but NO was produced, the competitiveness factor was calculated as

$$\text{compet. factor} = \frac{2[(NO_{2,\mathrm{in}} - NO_{2,\mathrm{out}}) - (NO_{\mathrm{out}} - NO_{\mathrm{in}})]}{n(\mathrm{reductant}_{\mathrm{in}} - \mathrm{reductant}_{\mathrm{out}})}\,. \tag{3}$$

In the case where practically only NO was present in both the feed and the exit stream, the competitiveness factor was calculated as

$$\text{compet. factor} = \frac{NO_{\mathrm{in}} - NO_{\mathrm{out}}}{n(\mathrm{reductant}_{\mathrm{in}} - \mathrm{reductant}_{\mathrm{out}})}\,. \tag{4}$$

In these equations, the subscripts in and out refer to the concentrations in the factor feed and in the exit stream, respectively, and n is the number of oxygen atoms needed to convert the reductant to CO_2 and H_2O, which is 9 for propene and 10 for propane.

3. Results and discussion

3.1. OXIDATION OF NO TO NO_2

The conversions of NO to NO_2, corrected for the conversion due to the blank reactor, in a mixture containing 4% O_2 and 0.1% NO over a 7.4 wt% Cu-ZrO_2 and a 3.2 wt% Cu-ZSM-5 over the temperature range of 20–350°C are shown in figs. 1 and 2. The W/F values for these data were 1.25–2.5 g min/ℓ (space velocity 110000–54000 h^{-1}) for Cu-ZrO_2 and 0.125–2.5 g min/ℓ (space velocities 220000–

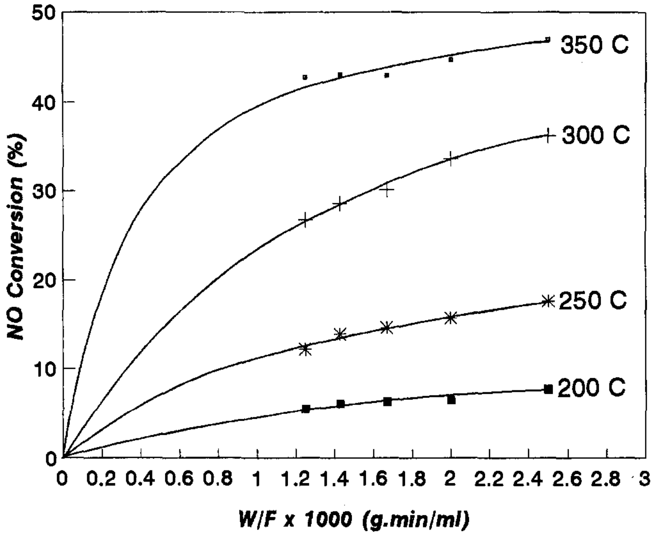


Fig. 1. Conversion of NO to NO_2 over a 7.4 wt% Cu-ZrO_2 catalyst. Feed contained 1000 ppm NO and 4% O_2.

11000 h^{-1}) for Cu-ZSM-5, using 0.025 to 0.125 g of catalysts and 50–200 cm^3/min. The calculated equilibrium conversions and a comparison of the conversions for a mixture that contained 1 or 4% O_2 are shown in table 1. Under these conditions, the conversions of NO were less than the thermodynamic equilibrium values and higher for higher oxygen partial pressure. For the same W/F, the NO conver-

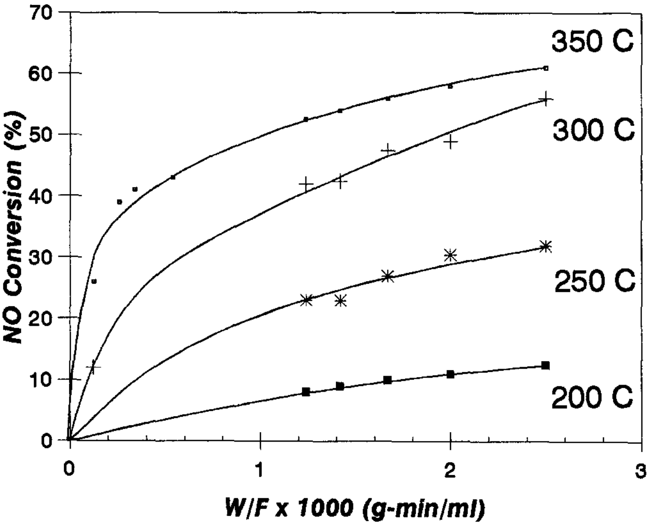


Fig. 2. Conversion of NO to NO_2 over a 3.2 wt% Cu-ZSM-5 catalyst. Feed contained 1000 ppm NO and 4% O_2.

Table 1
Oxidation of NO to NO_2 over Cu-ZSM-5 and Cu-ZrO_2 catalysts

Temp. (°C)	Conversion of NO to NO_2 [a]					
	equilibrium [b]		3.2% Cu-ZSM-5 [c]		7.4% Cu-ZrO_2 [c]	
	1% O_2	4% O_2	1% O_2	4% O_2	1% O_2	4% O_2
200	96	98	5.6	12	4.1	7.7
250	87	93	18	32	11	18
300	68	81	34	56	20	36
350	44	61	41	60	32	47

[a] Feed contained 1000 ppm NO.

[b] Calculated using equation from ref. [18].

[c] 0.25 g catalyst, 100 ml/min total flow rate. SV for Cu-ZSM-5 was 11000 h^{-1}, for Cu-ZrO_2 54000 h^{-1}.

sions were higher over Cu-ZSM-5 than Cu-ZrO_2. However, the Cu-ZSM-5 catalyst was not the most active one tested. Under the same experimental condition, Co/Al_2O_3 and Pt/Al_2O_3 were more active (table 2). The data in this table also showed that Cu-containing catalysts were more active than the corresponding catalyst without the Cu component. These results were similar to those of Shelef et al. who found little conversion over H-ZSM-5 but significant conversion over Cu-ZSM-5 [5]. When a much higher W/F was used, equilibrium conversion of NO to NO_2 could be achieved with both Cu-ZSM-5 and H-ZSM-5 [1], and presumably also with other catalysts.

3.2. NO_x REDUCTION

7.4 wt% Cu-ZrO_2

NO_x reduction by propene or propane in the presence of 1 or 4% O_2 in the feed was studied over the same sample of Cu-ZrO_2. The results are shown in table 3.

Table 2
Extent of NO oxidation to NO_2 over various catalysts at 300°C [a]

Catalyst	% NO to NO_2	SV (h^{-1})
blank	3.2	–
ZrO_2	12	54000
7.4% Cu-ZrO_2	33	54000
33% Cu-ZrO_2	44	54000
Na-ZSM-5	16	11000
3.2% Cu-ZSM-5	55	11000
0.33% Pt/Al_2O_3	65	95000
5% Co/Al_2O_3	79	95000
calc. equilibrium	81	–

[a] Catalyst weight: 0.25 g; flow rate: 100 ml/min; 0.1% NO; 4% O_2.

Table 3
Lean NO_x reduction and NO oxidation over 7.4 wt% Cu-ZrO_2

Cu-Zr	Exp.	Feed composition (ppm)				Exit composition (ppm)			% NO to NO_2 [b]	% NO to N_2	% C_3 conv.	% compet.
		O_2	C_3	NO	NO_2	N_2O	NO	NO_2				
250°C	1	40000	0	1000	0	–	850	150	15	–	–	–
C_3H_6	2	40000	1000	1000	0	30	790	< 20	–	18	34	6.9
	3	40000	1000	230	770	40	780	< 20	–	18	37	13
	4	10000	0	1000	0	–	890	110	11	–	–	–
	5	10000	1000	1000	0	30	750	< 20	–	30	36	7.7
	6	10000	1000	470	530	40	730	< 20	–	28	36	17
330°C	7	40000	0	1000	0	–	700	300	30	–	–	–
C_3H_8	8	40000	1000	1000	0	–	840	< 20	–	6.6	30	5.3
	9	10000	0	1000	0	–	840	160	16	–	–	–
	10	10000	1000	1000	0	–	900	< 20	–	10	20	5.0
	11	10000	1000	470	530	–	900	< 20	–	12	24	8.3

[a] Catalyst weight: 0.25 g; flow rate: 200 ml/min, SV: 11000 h^{-1}.

[b] Total conversion of NO to NO_2 over the catalyst and by the apparatus (1 or 3%, depending on the % O_2)

With the small amount of catalyst used, in the absence of reductant (experiments 1, 4, 7 and 9), NO was oxidized to NO_2 with a conversion far from thermodynamic equilibrium. The conversion of NO was increased when the feed contained propene. At 250°C and using 4% O_2, the NO conversion to NO_2 was 15% in the absence of propene (exp. 1). When propene was present (exp. 2), the NO conversion increased to 18%, and the product was N_2. Practically no NO_2 was detected. A similar increase in NO conversion and a change in the product was observed using 1% O_2 (exps. 4 and 5).

When propane was used as the reductant, a higher reaction temperature was required to achieve the same NO conversion as with propene, consistent with the fact that propane is a less active reductant. The lower activity of propane also resulted in the fact that the conversion of NO to N_2 by propane was lower than the corresponding conversion of NO to NO_2 in the absence of the reductant (exp. 7 versus 8, and 9 versus 10).

If the feed was a mixture of NO_2 and NO (exps. 3, 6 and 11), the NO_x conversion to N_2 was practically the same as when NO alone was used. Very interestingly, the nitrogen-containing gases in the exit stream of the reactor also contained only N_2 and NO and very little NO_2. That is, NO_2 was reduced effectively to NO, resulting in a gas composition that contained much more NO than the thermodynamic equilibrium composition. The efficient reduction of NO_2 to NO has been observed in similar experiments over Cu-ZSM-5 catalysts [5,7] and Ce-ZSM-5 [11].

The data in table 3 strongly suggest that over Cu-ZrO_2, NO reduction does not proceed via eqs. (1) and (2), which is first the formation of gaseous NO_2 followed by reduction of NO_2 to N_2. If eqs. (1) and (2) were applicable, the following sequences would be expected:

(1) Using a feed of NO, the N_2 production rate due to reduction by hydrocarbon is slower than or equal to the rate of NO oxidation to NO_2 in the absence of hydrocarbon, unless this latter reaction is promoted by hydrocarbon.

(2) The N_2 production rate due to reduction by hydrocarbon is higher for a feed of NO_2 than a feed of NO, provided that equilibrium for NO oxidation to NO_2 is not attained.

(3) The N_2 production rate would show a dependence on O_2 partial pressure parallel to that for NO oxidation to NO_2.

The data shown in table 3 for propene as the reductant are contradictory to these predictions. First, the rate of reduction of NO to N_2 was faster than the rate of oxidation of NO in the absence of propene (exp. 1 versus 3, and 4 versus 5). It is unlikely that propene greatly promotes NO oxidation to NO_2 because when NO_2 is in the feed, it is reduced rapidly by propene to NO such that the exit gas does not contain NO_2 at all. Secondly, the rates of N_2 production were virtually the same whether NO or NO_2 was used as the feed (exp. 2 versus 3, and 5 versus 6). Although one might argue that the rapid reduction of NO_2 to NO made the gas composition nearly identical, independent of the feed composition, this argument would also imply that at any time, there is practically no NO_2 in the gas phase, making it unlikely that gaseous NO_2 must be formed before N_2 can be produced.

Finally, the predicted dependence of N_2 production on O_2 partial pressure is contradictory to the observation (exp. 2 versus 5, and 3 versus 6). Instead of increasing with increasing O_2 partial pressure, the observed rate of N_2 production decreased. Since the propene conversion changed little, this decrease was not due to increased combustion of propene which would lower significantly the reductant concentration.

The data for propane reduction (exps. 9–11) were similar to the data for propene reduction. In particular, the rates of formation of N_2 were similar whether NO or a mixture of NO_2 and NO were in the feed (exp. 10 versus 11), increasing oxygen partial pressure decreased the rate of N_2 production (exp. 8 versus 10), although it increased the rate of NO oxidation to NO_2 (exp. 7 versus 9), and the reduction of NO_2 to NO by propane was much faster than the production of N_2. Thus, a similar conclusion can be drawn that N_2 formation is not by reduction of NO_2 only. As mentioned earlier, the lower reactivity of propane accounts for the slower rate of NO_x reduction to N_2 than the rate of NO oxidation to NO_2 in the absence of the hydrocarbon.

The values of competitiveness factors for experiments using NO_2 were close to twice those using NO at high conversions to N_2 and lower than that at low conversions. This is consistent with the observation that NO_2 was rapidly converted to NO, and at high conversions, the majority of the N_2 was produced by the same reaction pathways whether a mixture of NO_2 and NO or only NO was in the feed. The factor of two was a result of the definition used (eqs. (3) and (4)). At low conversions, the fact that the ratio of the competitiveness factors was less than a factor of two, and that the N_2 production rates were similar using either feed suggest that the rapid reduction of NO_2 to NO did not result in a significant increase in the concentration of the surface intermediates important for N_2 production, but was mostly accompanied by combustion of the hydrocarbon.

3.2 wt% Cu-ZSM-5

Table 4 shows the data for the Cu-ZSM-5 catalyst. There are trends shown by these data similar to those for the Cu-ZrO_2 catalyst. These trends include: (i) in the experiments using a mixture of NO, NO_2, and hydrocarbon in the feed, the exit gas stream contained much more NO and much less NO_2 than in the feed (exps. 14, 17, and 20). The concentration of NO at the exit was much higher than the equilibrium concentration; (ii) with 4% O_2 in the feed, the rate of production of N_2 was only slightly higher when a mixture of NO_2 and NO was used in the feed than when NO alone was used (exp. 13 versus 14, 16 versus 17); and (iii) under certain conditions, the rate of N_2 production was higher than the rate of NO oxidation to NO_2 (exps. 18 and 19).

The similarities between Cu-ZSM-5 and Cu-ZrO_2 strongly suggest that a similar conclusion regarding the direct source of N for N_2 formation applies. That is,

Table 4
Lean NO_x reduction and NO oxidation over 3.2. wt% Cu-ZSM-5 [a]

CU-ZSM-5	Exp.	Feed composition (ppm)				Exit composition (ppm)			% NO to NO_2 [b]	% NO_x to N_2	% C_3 conv.	% compet.
		O_2	C_3	NO	NO_2	N_2O	NO	NO_2				
300°C	12	40000	0	1000	0	–	850	150	15	–	–	–
C_3H_8	13	40000	1000	1000	0	–	890	< 20	–	5.4	3.4	32
	14	40000	1000	230	770	–	570	340	–	6.5	6.3	29
350°C	15	40000	0	1000	0	–	710	290	29	–	–	–
C_3H_8	16	40000	1000	1000	0	–	720	< 20	–	24	21	13
	17	40000	1000	230	770	–	690	< 20	–	27	29	21
	18	10000	0	1000	0	–	890	110	11	–	–	–
	19	10000	1000	1000	0	10	870	< 20		15	5.4	24
	20	10000	1000	470	530	20	770	< 20	–	26	16	29

[a] Catalyst weight: 0.025 g; flow rate: 200 ml/min; SV: 22000 h^{-1}.

[b] Total conversion of NO to NO_2 over the catalyst and by the apparatus (1 or 3% depending on the % O_2).

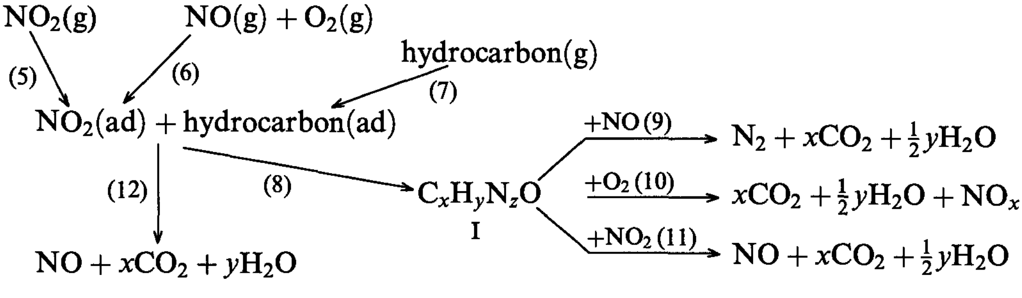
N_2 formation does not have to proceed via formation of gas phase NO_2 first. Regarding this point, experiment 14 was particularly informative. The experiment was conducted under the regime of differential conversion such that even the rapid reaction of reduction of NO_2 to NO by propane was far from completion, and there was a significant partial pressure of NO_2 in the exit gas. Thus, in this experiment, the partial pressure of NO_2 was substantial throughout the entire catalyst bed. However, even under such a condition, the rate of N_2 production was only marginally higher than that when NO was used in the feed. This set of data strongly suggests that, similar to Cu-ZrO_2, NO reduction at 300°C on Cu-ZrO_2 does not need to proceed via the formation of gas phase NO_2 first. This conclusion is supported also by the data of experiments 16 and 17.

The values of the competitiveness factor showed the same trend as for Cu-ZrO_2. As the conversion to N_2 increased, the ratio of the values for experiments using both NO_2 and NO to those using only NO increased and approached a factor of two.

There are also interesting differences between the data for Cu-ZrO_2 and for Cu-ZSM-5. Unlike Cu-ZrO_2, the rate of N_2 production on Cu-ZSM-5 was consistently higher, sometimes by a significant amount (exp. 19 versus 20), when NO_2 was used in the feed than when only NO was used. The conversion of propane was significantly higher when NO_2 was used (exp. 14 versus 13, 17 versus 16, and 20 versus 19), and when the O_2 partial pressure was higher (exp. 16 versus 19, and 17 versus 20).

Reaction scheme

The data reported here and those in the literature can be explained with the following reaction scheme:



In this scheme, adsorbed NO_2 can react with adsorbed hydrocarbon through two pathways. The path believed predominant (eq. (12)) does not lead to N_2 formation as the adsorbed NO_2 is reduced to NO by the adsorbed hydrocarbon. The path responsible for N_2 formation (eq. (8)) results in the generation of an N-containing surface intermediate (I). Species I is further oxidized by NO_2 and/or O_2 to form other intermediates, which eventfully react with NO to produce N_2. In addition, species I can be oxidized by oxygen to CO_2 (eq. (10)). The data in this study did not provide any indication regarding the nature of the species I. In a separate report, we showed with in situ IR isotope labeling experiments that adsorbed CN and NCO species are formed that react with NO to form N_2 [16]. The nature of adsorbed hydrocarbon in eq. (8) that reacts with adsorbed NO_2 is not known either. Chemisorption of propene occurs readily [17], probably as π-allyl on Cu ions. Chemisorption of propane is weak [17], and the molecule is more inert. Thus, activation of propane requires higher temperatures. Its activation by gas phase reaction is also possible, particularly at high temperatures [8].

This scheme explains the data for lean NO_x reduction on Cu-containing catalysts that are active in the oxidation of NO to NO_2. For these catalysts, adsorbed NO_2 is readily formed whether NO_2 or a mixture of NO and O_2 is present in the gas phase. Thus, species I can be formed without much difficulties. Since the gas phase composition is practically all NO in most experiments, the observed rate of production of N_2 is the same, independent of whether NO or NO_2 is used in the feed. On catalysts such as H-ZSM-5, Ce-ZSM-5, ZrO_2 and Ga_2O_3 that are less active in the oxidation of NO to NO_2, the N_2 production rate is higher using NO_2 than NO because of higher surface coverages of adsorbed NO_2, thus, higher rate of formation of species I. Of course, the rates of the other steps could also be different and contribute to the observed overall differences in N_2 production rate.

This scheme explains the multiple roles of NO_2, and the different dependence of NO reduction activity on O_2 partial pressure on different catalysts. For catalysts that deactivate due to coking, NO_2 helps maintain the activity by removing the surface carbonaceous species, resulting in an impression that NO_2 is the reagent for N_2 production. For catalysts that do not oxidize NO readily to NO_2, addition of NO_2 to the feed, or the use of higher O_2 partial pressure increases N_2 production activity because of the higher surface coverage of NO_2 for the formation of intermediate I.

It should be mentioned that there is an alternate scheme to produce N_2 [11], which is:

$$NO_2(ad) + \text{hydrocarbon}(ad) \rightarrow C_xH_yN_zO(ad) \xrightarrow{+NO_2(ad)} N_2 + xCO_2 + yH_2O \tag{13}$$

We believe that this is less likely than the scheme presented above. Eq. (13) is not supported by the change in the competitiveness factor with conversion discussed earlier. In addition, we have shown that the surface CN and NCO species on Cu-ZrO_2 react with pulses of NO to produce N_2 in the same way as pulses of NO_2 [16]. The similarity can be interpreted with the rapid conversion of NO_2 to NO over the catalyst. Thus, there is no evidence that NO_2 reacts with surface intermediate I to produce N_2.

4. Conclusion

The data in this study showed that under the commonly employed experimental conditions where the space velocity is reasonably high, the oxidation of NO to

NO_2 over a 3.2 wt% Cu-ZSM-5 and a 7.4 wt% Cu-ZrO_2 does not reach equilibrium. In particular, in the presence of propene or propane reductant, the reduction of NO_2 to NO is very rapid, such that the gas composition is rapidly depleted of NO_2. By comparing the rates of NO oxidation to NO_2 and the rates of N_2 formation when NO or NO_2 is used in the feed, it is concluded that on both catalysts, the reduction of NO does not need to proceed via the formation of gas phase NO_2. Thus, the similar rates of N_2 production observed in lean NO_x reduction independent of whether NO or NO_2 is in the feed is not due to rapid formation of equilibrium amount of gas phase NO_2. Instead, it is due to the rapid reduction of NO_2 to NO. These data and those in the literature can be explained with a scheme in which a surface N-containing hydrocarbon intermediate is formed by reaction of adsorbed NO_2 with adsorbed hydrocarbon. Subsequent reaction of this intermediate with NO produces N_2. In addition to the production of the surface intermediate, NO_2 also oxidizes surface hydrocarbon species to CO_2 and H_2O, while itself being reduced to NO.

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