Nitrogen production efficiency for acetaldehyde and propionaldehyde in lean NO_x reduction over anatase titania

Anguelina P. Kozlova, Hiu-Ying Law, Mayfair C. Kung*, and Harold H. Kung**

Department of Chemical Engineering, Northwestern University, Evanston, IL 60208-3120, USA

Received 12 January 2004; accepted 5 April 2004

The nitrogen formation efficiencies, defined as the number of nitrogen molecules formed for every reductant molecule consumed were determined for acetaldehyde and propionaldehyde in the reduction of NO_2 under lean conditions over anatase TiO_2. The efficiency increased with increasing NO_2/reductant in the feed, reaching 0.61 ± 0.05 for NO_2/acetaldehyde between 1.5 and 3.0 and 0.85 ± 0.08 for NO_2/propionaldehyde between 3.8 and 5.7. Simultaneously, the CO/CO_2 ratio as well as the small concentration of N_2O in the product stream increased. The results suggested that at higher NO_2/reductant ratios, the reaction between the reductant and adsorbed NO_2 accounted for a large majority of the reaction. The results were consistent with the IR results, which showed that surface nitro groups reacted readily with acetaldehyde. The implications of these results on the NO_2 reduction mechanism were discussed.

KEY WORDS: titania; NO_x; reduction; acetaldehyde; propionaldehyde.

1. Introduction

Reduction of NO_x emission from diesel engine exhaust has been a subject of intense study in the past decade. This is in part due to the implementation of more stringent emission regulation, and in part due to the promising discovery of catalysts by Held *et al.* [1] and Iwamoto *et al.* [2] that can reduce NO_x using a low concentration of hydrocarbon. The investigations to-date have yielded significant understanding of the reaction and new, interesting catalytic systems, but there is yet no satisfactory catalyst for commercialization.

There are many technical requirements for commercialization, which include long-term durability, high NO_x conversion at the diesel exhaust temperature, tolerance to poisonous impurities, cost, and efficiencies in reductant utilization. The last factor relates to fuel penalty. In brief, a major driver to use diesel engines is their higher efficiency in converting fuel into power than gasoline engines. In the diesel exhaust, there is insufficient hydrocarbon to reduce NO_x in the stream stoichiometrically. Thus, the conceptual design of a device using this technology involves injection of hydrocarbon or other reductants (such as urea) into the exhaust stream. Since none of the injected hydrocarbon is used for power generation, its consumption is fuel penalty and decreases the advantages of diesel engine. Therefore, efficient utilization of the hydrocarbon for NO_x conversion to dinitrogen is an important requirement of the catalyst. Accordingly, one can define a nitrogen production efficiency, which is the number of N_2 molecules formed for every molecule of reductant consumed, as a measure of the effectiveness of both the reductant and the catalyst.

The nitrogen production efficiency is determined by the relative ratio of the productive utilization of the reductant versus the nonproductive combustion reaction, which is the reaction of the reductant with oxygen. Previously, we have determined the nitrogen production efficiencies of acrolein and acetaldehyde over alumina, and found them to be similar for the two reductants, reaching a value of about 0.8 at high NO_x/reductant ratios in the feed [3]. In both cases, at low NO_x/reductant ratios, the efficiencies were higher for the reduction of NO_2 than NO. The observed similar production efficiencies for acrolein and acetaldehyde were interpreted as an indication that the two reductants operate along the same reaction pathway.

Subsequently, we have determined the nitrogen production efficiency of acetaldehyde and propionaldehdye with NO_2 over titania. These reactions were studied because a promising strategy for NO_x abatement of diesel exhaust is the use of nonthermal plasma assisted catalysis. In the plasma reactor, NO is oxidized to NO_2 and propene to oxygenates; acetaldehyde being a major product [4,5]. Titania was studied because it has reasonably good activity at intermediate temperatures and is resistant to sulfur poisoning [6]. Other works have shown that, in general, there is potential for oxides in NO_x reduction that is worth exploring [e.g. 7, 8, 9]. Here we report the result of the study.

---

*To whom correspondence should be addressed.
E-mail: m-kung@northwestern

**To whom correspondence should be addressed.
E-mail: hkung@northwestern.edu

1011-372X/04/0600–0211/0 © 2004 Plenum Publishing Corporation

2. Experimental

The anatase titania sample (surface area of 200 m^2/g as indicated by the supplier) was obtained from Sachtleben Chemie, GmbH. It was used without further treatment. The feed mixture of the desired composition was prepared by mixing He (UHP grade), O_2 (UHP grade), 0.097% NO_2 in He, 0.998% acetaldehyde in He, and 0.998% propionaldehyde in He, all obtained from Matheson. The concentrations of the hydrocarbon gases were checked by complete combustion over a Pt catalyst. Water was introduced by passing a stream of He through a heated water saturator. Experiments were carried out with a U-shaped, fused silica, tubular reactor. The temperature was measured with a thermocouple placed outside the reactor at the position of the catalyst. Typically, 0.1 g of the catalyst was used, packed between two quartz wool plugs. The concentration of oxygen was 6% and water 7% in the feed, and the total flow rate was 100 mL min^{-1}. Sometimes, 0.2 g of catalyst and a total flow rate of 200 mL min^{-1} were used for the same space velocity. The catalyst was first heated to the reaction temperature in a flow of O_2 and H_2O in He. After the desired temperature was reached, the reaction feed was introduced.

The products were analyzed by an online gas chromatograph using a Molecular Sieve 5A (for N_2 and CO) and a Porapak Q (for O_2, CO_2, N_2O, H_2O, CH_3CHO, C_2H_5CHO, and other hydrocarbons) column from Alltech. A chemiluminescence analyzer was used to determine the NO and NO_2 concentrations.

In the results reported, conversions were calculated from the concentrations in the exit and the inlet of the reactor. $\%N_2$ yield was defined as $(2(N_{2,out})/NO_{x,in})100\%$. The reductant conversion was determined from the difference in the inlet and exit concentrations.

Temperature-programmed reduction (TPR) was conducted using a Hewlett Packard 5890 gas chromatograph equipped with a TCD detector. In a typical experiment, 200 mg of a sample was first heated in a flow (70 mL/min) of pure oxygen at 300 °C for 30 min. After cooling to room temperature in O_2, the system was purged with Ar for 20 min. TPR was carried out by heating the sample at 10 °C/min to 950 °C in a 5% H_2-Ar mixture flowing at 30 mL/min. Infrared spectra were collected with a Mattson Galaxy 5000 spectrometer using an *in situ* cell. All the spectra were collected at the reaction temperature of 300 °C.

3. Results

Figure 1 shows the N_2 yield as a function of temperature. Over the anatase sample, a maximum N_2 yield was observed at about 300 °C. Consequently, all other experiments were conducted at this temperature. No N_2O was detected when the ratio was below unity. At higher ratios, the N_2O/N_2 ratio in the exit increased to about 12%.

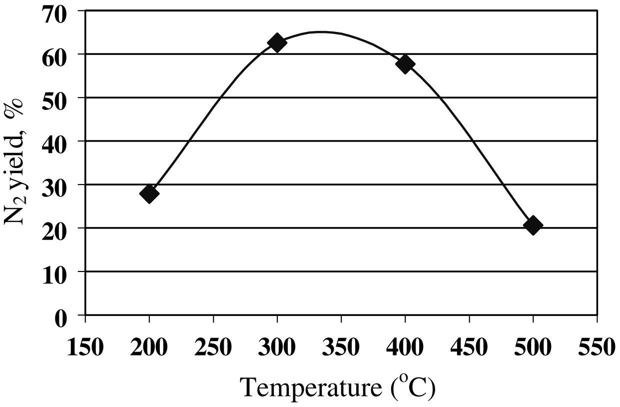

Figure 1. NO_2 conversion over TiO_2. Feed composition: 280 ppm NO_2, 270 ppm acetaldehyde, 6%O_2, 8%H_2O, balance He. Total flow rate = 100 cc/min; catalyst = 0.1 g.

The N_2 yield and acetaldehyde conversions were determined for various concentrations of NO_2 and acetaldehyde in the feed. A summary of the results is shown in table 1. From these data, the nitrogen production efficiencies for acetaldehyde were calculated and plotted in figure. 2a as a function of NO_2/C_2H_4O in the feed. The efficiency increased with increasing NO_2/C_2H_4O ratio until a maximum value was reached at about 0.61 ± 0.05. As the NO_2/C_2H_4O ratio increased, the CO/CO_2 ratio in the reactor effluent also increased to reach a value higher than 5 (figure. 2b). The opposite trend was seen for NO concentration in the exhaust, which decreased steadily with increasing NO_2/C_2H_4O ratio in the feed (table 1). The reactivity of acetaldehyde in the presence and absence of NO_2 was compared, and the results, shown in table 2, indicated that NO_2 in the feed enhanced the oxidation of acetaldehyde.

A similar set of experiments was conducted using propionaldehyde as the reductant. A summary of the results is shown in table 3. The corresponding nitrogen production efficiencies and the CO/CO_2 ratios in the effluent are plotted in figures 3a and b, respectively as a function of NO_2/propionaldehyde in the feed. Similar to the case for acetaldehyde, the efficiency increased with increasing NO_2/C_3 ratio, reaching a maximum value of about 0.85 ± 0.08, whereas the CO/CO_2 ratio increased to about 2. Table 4 compares the oxidation of propionaldehyde in the presence and absence of NO_2. The presence of NO_2 did not affect the oxidation of propionaldehyde. However, in the absence of NO_2, there was a small carbon imbalance, suggesting deposition of carbonaceous species on the catalyst.

The TPR of TiO_2 showed that reduction of TiO_2 occurred only at temperatures above 450 °C. Thus, at the reaction temperature of 300 °C, there should be little reduction of the catalyst. From the total consumption of hydrogen up to 950 °C, it was estimated that the

Table 1
Product distribution as a function of feed composition in the reaction of acetaldehyde (AA) and NO_2 over TiO_2 at 300 °C in the presence of 6%O_2 and 8% H_2O

Feed NO_2/AA	AA ppm	NO_2 ppm	Exhaust NO/NO_x	N_2 ppm	NO ppm	N_2O ppm	NO_2 ppm	AA ppm	CO ppm	CO_2 ppm	Conv. %	
											NO_2	AA
0.58	310	180	0.81	44	79	0	19	161	162	110	46	48
0.89	304	272	0.88	85	104	0	14	130	220	132	57	58
1.03	266	273	0.86	91	84	8	14	95	213	96	62	64
1.16	235	272	1.00	85	105	0	0	57	252	141	60	76
1.33	282	374	0.51	161	53	0	50	20	364	93	72	94
1.48	321	474	0.72	197	89	15	34	21	450	162	74	93
1.60	486	776	0.18	200	70	20	316	127	467	120	49	74
1.94	319	620	0.14	153	46	7	276	86	347	69	48	72
2.50	317	791	0.08	139	42	19	513	75	347	66	30	76
3.02	319	963	0.09	150	63	18	631	66	347	64	28	79

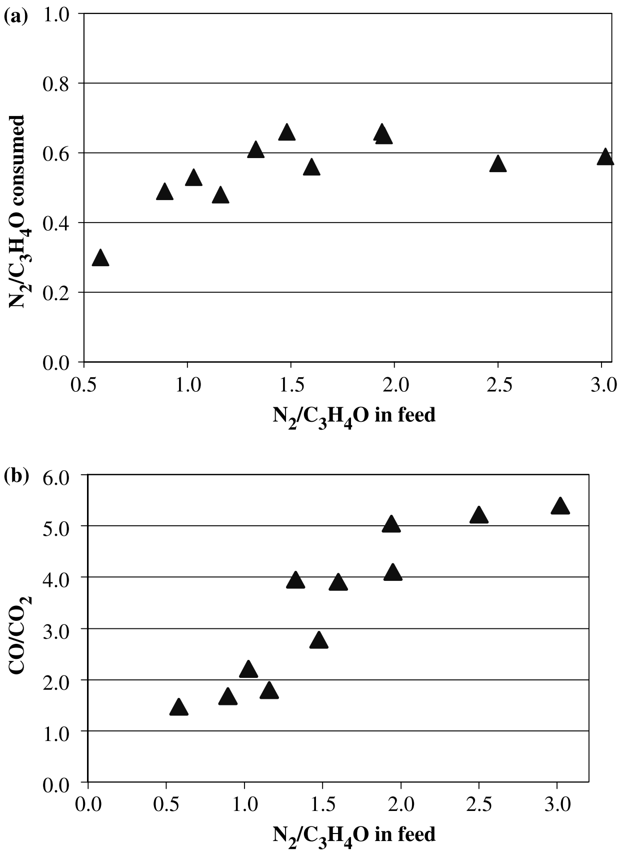

Figure 2. (a) $N_2/C_2H_4O_{consumed}$ as a function of NO_2/C_2H_4O in the feed. Reaction conditions indicated in table 1. (b) CO/CO_2 as a function of NO_2/C_2H_4O in the feed. Reaction conditions indicated in table 1.

Table 2
Comparison of acetaldehyde reaction, with and without NO_2, over TiO_2 at 300 °C

Feed	AA conversion %	CO $_{out}$, ppm	CO/CO_2
Without NO_2	54.9	130	1
370 ppm NO_2	92.7	364	4

O_2 = 6%, H_2O = 7%, acetaldehyde = 280 ppm, balance He.

amount of reducible Ti (Ti^{4+} to Ti^{3+}) was 3.1% of total Ti in the sample.

The IR spectra collected for this sample at 300 °C are shown in figure 4. Spectrum 4a shows the TiO_2 after 300 °C oxygen pretreatment. The impurity peaks at 1417 and 1352 cm^{-1} could not be removed by the oxidative pretreatment. In the literature, the 1352 cm^{-1} peak had been ascribed to nitrates on the cell window [10]. However, since this spectrum was obtained by subtracting the spectrum of an empty cell (25 °C), any contribution from the cell window should have been corrected, although it is possible that NO_2 from decomposition of nitrates upon heating to 300 °C deposited on the window.

The sample was then exposed to a flow of 310 ppm NO_2, 6.5% O_2, balance He for 40 min at 300 °C and then purged with He for 15 min. The spectrum of this sample (spectrum 4b), referenced to spectrum 4a showed a negative change for the 1417 cm^{-1} peak, suggesting removal of this species. The 1352 cm^{-1} peak shifted and gave rise to an apparent peak at 1359 cm^{-1}. In addition, new absorbance peaks appeared at 1605, 1583, and 1243 cm^{-1}. These peaks diminished upon exposure of the sample to 520 ppm acetaldehyde and 9% O_2 in He for 2 min, as shown in spectrum 4c (referenced to spectrum 4b). Separately, we determined using an empty sample cell that it took about 30 min for full exchange of the gases in the cell. Thus, the actual concentration of acetaldehyde that the sample was exposed to in this experiment was substantially less than 520 ppm, since 2 min was not nearly enough to fully exchange the gases in the cell. Thus, the adsorbed NO_x species were very reactive towards low concentrations of acetaldehyde.

4. Discussion

In lean NO_x reduction by hydrocarbon over oxides, it is commonly accepted that the activation of both hydrocarbon and NO are critical in determining the

Table 3
Product distribution as a function of feed composition in the reaction of propionaldehyde (PA) with NO_2 over TiO_2 at 300 °C in the presence of 6% O_2 and 8% H_2O

Feed NO_2/PA	PA ppm	NO_2 ppm	Exhaust NO/NO_x	N_2 ppm	NO ppm	N_2O ppm	NO_2 ppm	PA ppm	CO ppm	CO_2 ppm	Conver. %	
											NO_2	PA
2.55	421	1075	0.91	234	569	25	55	11	568	433	42	97
2.77	398	1102	0.69	209	403	26	185	12	551	411	47	97
2.84	388	1100	0.80	239	456	29	117	8	543	335	48	98
3.81	223	852	0.45	217	226	22	277	7	416	220	41	97
3.99	229	914	0.46	182	238	19	276	2	422	217	44	99
4.07	226	919	0.51	189	244	21	234	3	434	237	48	99
4.55	229	1042	0.37	191	243	20	419	2	451	218	37	99
4.77	247	1178	0.35	199	271	24	494	3	477	249	35	99
5.68	223	1267	0.32	172	288	24	611	1	420	215	29	100

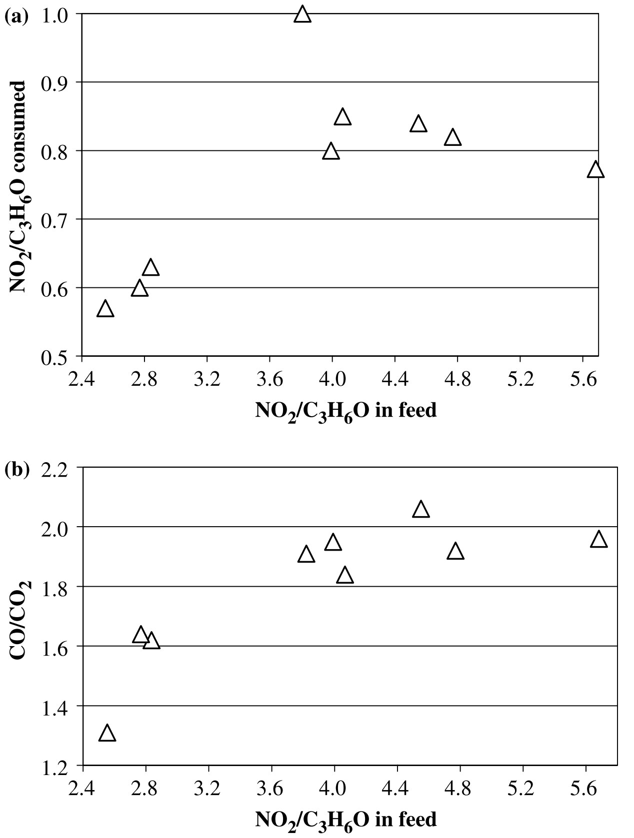

Figure 3. (a) $N_2/C_3H_6O_{consumed}$ as a function of NO_2/C_3H_6O in the feed. Reaction conditions indicated in table 4. (b) CO/CO_2 as a function of NO_2/C_3H_6O in the feed. Reaction conditions indicated in table 4.

Table 4
Comparison of propionaldehyde reaction in the presence and absence of NO_2 at 300 °C

Feed	PA conv. %	CO_x formed, ppm	CO/CO_2
Without NO_2[a]	84	238	0.8
852 ppm NO_2[b]	94	416	1.9

[a] 213 ppm propionaldehyde, 5.7% O_2, 7% H_2O.
[b] 223 ppm propionaldehyde, 6.3% O_2, 7% H_2O.

rate of reaction between them. For the hydrocarbon reductants, it has been observed that compounds containing functional groups, such as aldehydes and alkenes, are more active (reaction starting at lower temperatures) and effective (higher nitrogen production efficiency) than the corresponding alkanes [11]. For example, using the same reaction feed for comparison, reduction by propene occurs at lower temperatures and is more effective than propane [12], and reduction by oxygenates occurs at even lower temperatures [13]. The low nitrogen production efficiency of light alkanes may in part be due to the high temperatures needed to activate them. At the high temperatures, the reaction intermediates become quite susceptible to degradation by combustion, leading to significant nonproductive degradation reactions.

Ideally, every atom in a reductant molecule should be consumed by reaction with NO_x, reducing the latter to dinitrogen. For acetaldehyde and propionaldehyde in the reduction of NO_2, the most desirable reactions are:

$$CH_3CHO + \frac{5}{2}NO_2 \rightarrow 2CO_2 + 2H_2O + \frac{5}{4}N_2 \quad (1)$$

$$C_2H_5CHO + 4NO_2 \rightarrow 3CO_2 + 3H_2O + 2N_2 \quad (2)$$

Thus, the maximum nitrogen production efficiencies are 1.25 for acetaldehyde and 2 for propionaldehyde. On the other hand, if the reaction product contains exclusively CO and no CO_2, the corresponding reactions become:

$$CH_3CHO + \frac{3}{2}NO_2 \rightarrow 2CO + 2H_2O + \frac{3}{4}N_2 \quad (3)$$

$$C_2H_5CHO + \frac{5}{2}NO_2 \rightarrow 3CO + 3H_2O + \frac{5}{4}N_2 \quad (4)$$

and the nitrogen production efficiencies are 0.75 and 1.25, respectively. For acetaldehyde on TiO_2, at NO_2/C_2H_4O ratios higher than 1.3, CO accounts for over 80% of the carbon oxide products (figure 2b), whereas for propionaldehyde, CO accounts for about 65% (figure 3b). Thus, the overall reactions 3 and 4 are dominant to reactions 1 and 2.

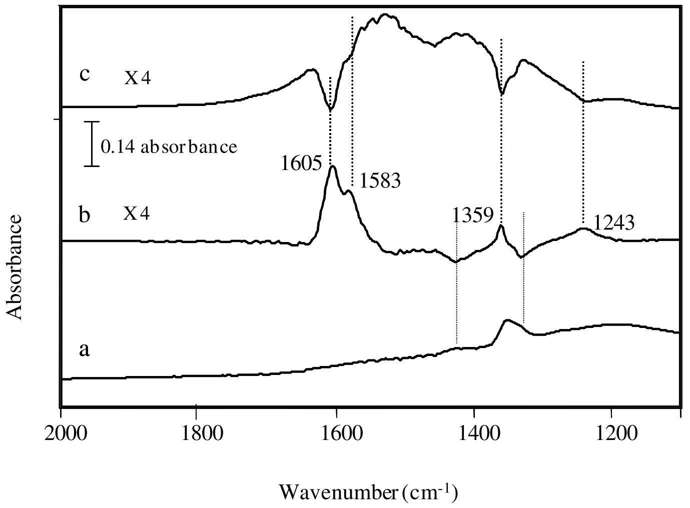

Figure 4. IR spectra (a) TiO_2, (b) NO_2 adsorbed at 300 °C (c) sample b after 2 min exposure to acetaldehyde.

The observed nitrogen production efficiencies are about 0.61 and 0.85, respectively for acetaldehyde and propionaldehyde, lower than the theoretical maximum values. Thus, there are some undesirable, nonproductive reactions that consume the reductant reaction intermediates in these experiments.

There are two general types of nonproductive reactions of the reductants. One is reaction with oxygen, and the other is reaction with NO_2 to form NO or N_2O instead of N_2. The contribution of reactions with oxygen can be estimated from the observed stoichiometry of the overall reactions. For example, for acetaldehyde, from the concentrations of CO and CO_2 (and assuming that corresponding amounts of H_2O are formed) in the product, the number of oxygen atoms needed to convert that amount of acetaldehyde to these products can be calculated. At the same time, from the concentrations of NO_2, NO and N_2O in the effluent, the number of oxygen atoms supplied by the reaction of NO_2 (there was very little NO in the feed) can be found. When the ratio of these two numbers equals to unity, there is no contribution from reactions with oxygen.

The ratios of these two numbers for the acetaldehyde experiments are shown in the last column in table 5, and the corresponding ratios for propionaldehyde are shown in table 6. It can be seen from table 5 that the contribution from reactions with oxygen decreases with increasing NO_2/acetaldehyde in the feed. This is expected, since the surface coverage of NO_x increases with higher NO_2 concentration in the feed. Consequently, a larger fraction of the surface hydrocarbon would react with adsorbed NO_x. The data show that for feed NO_2/acetaldehyde ratios higher than unity, reaction with adsorbed NO_2 represents 90% or more of the reaction of acetaldehyde. This implies that under these conditions, the surface of titania is almost all covered by the organic intermediates and adsorbed NO_y species, and there is very little adsorbed oxygen, in spite of its high concentration in the gas phase.

Table 5
Oxygen source for the oxidation of acetaldehyde

NO_2/AA in feed	[O] from NO_2 rxn[a]. ppm	[O] for CO[b] ppm	[O] for CO_2[c] ppm	[O] for CO + CO_2 ppm	[O] from NO_2/ [O] for CO_x
0.58	254	243	275	518	0.5
0.89	443	330	330	660	0.7
1.03	461	320	240	560	0.9
1.16	449	378	353	731	0.6
1.33	697	546	233	779	0.9
1.48	892	675	405	1080	0.9
1.6	891	701	300	1001	0.9
1.94	664	521	173	693	1.0
2.5	619	521	165	686	1.0
3.02	680	521	160	681	1.1

[a] $(4N_2 + NO + 3N_2O)_{exhaust}$ = [O] that came from the reaction of NO_2.
[b] $C_2H_4O + 3[O] = 2CO + 2H_2O$.
[c] $C_2H_4O + 5[O] = 2CO_2 + 2H_2O$.

Table 6
Oxygen source for the oxidation of propionaldehyde

NO_2/PA	[O] from NO_2[a] ppm	[O] for CO[b] ppm	[O] for CO_2[c] ppm	[O] for CO + CO_2 ppm	[O] from NO_2/[O]for CO_x
2.55	1505	852	1083	1935	0.8
2.77	1239	827	1028	1854	0.7
2.84	1412	815	838	1652	0.9
3.81	1094	624	550	1174	1.0
3.99	966	633	543	1176	0.9
4.07	1000	651	593	1244	0.9
4.55	1007	677	545	1222	0.9
4.77	1067	716	623	1338	0.9
5.68	976	630	538	1168	0.9

[a] $(4N_2 + NO + 3N_2O)_{exhaust}$ = [O] that came from the reaction of NO_2
[b] $C_3H_6O + 5[O] = 3CO + 3H_2O$.
[c] $C_3H_6O + 8[O] = 3CO_2 + 3H_2$.

The results of the IR experiments are consistent with the high reactivity of adsorbed NO_2. Exposure of the sample to NO_2 generated peaks at 1608 and 1583 cm^{-1} and 1243 cm^{-1} (figure 4) that can be assigned to bidentate nitrate [10]. This nitrate species is quite stable as it remained after 40 min purging at 300 °C. However, exposure of this nitrate species to acetaldehyde resulted in large decreases in these peak intensities. In addition, the acetaldehyde is completely transformed as the characteristic peak of C=O of adsorbed acetaldehyde (~ 1680 cm^{-1} [14]) was not observed. There is no evidence for the formation of crotonaldehyde that was reported that on TiO_2 (ν (C=O) at 1655 [15] and ν(C=C) at 1628 cm^{-1} [14]). In fact, the major carbon species on the surface are carboxylate groups, since there was no ν(C—H) band detected.

A similar conclusion applies to propionaldehyde. At high NO_2/propionaldehyde ratios in the feed, a large majority of the reductant reacts with adsorbed NO_y species instead of oxygen. In this case, higher NO_2/reductant ratio in the feed is necessary for the ratio of the number oxygen atoms supplied by the reduction of NO_2 to N_2, NO, and N_2O to the total number of oxygen atoms consumed in the oxidation of propionaldehyde to reach a limit of 90%.

There are a number of proposals on the mechanism of dinitrogen formation, as described in a review by Sadykov *et al.* [16]. The hydrocarbon reductant may first be converted to an organic nitro compound, which is then converted to an oxime [17] or oximic acid [18]. Eventually, an organic amine or cyanide is formed, which reacts with a nitro or nitrosyl group to from dinitrogen. The results here, that the nitrogen production efficiencies are higher than 0.5, suggest that the pathway to form dinitrogen requires no more than one organic reductant molecule. That is, the formation of the N–N bond cannot be by a reaction between an organic amine formed from one reductant molecule and an organic nitro compound from another, because then the nitrogen formation efficiency would be no higher than 0.5.

The higher nitrogen formation efficiency for propionaldeyde than acetaldehyde also implies that the alkyl portion of the molecule is the more likely group responsible for nitrogen formation than the aldehyde functional group. If we assume the limiting case that: (1) the aldehyde (CHO) group is exclusively oxidized to carboxylate which then decomposes to CO_2 by a nonproductive pathway, such as reducing NO_2 to NO, and (2) N_2 is formed by a productive pathway between the alkyl group and NO_2, the resulting theoretical nitrogen production efficiency can be evaluated by considering the overall reaction of CHO (equation 6) and the alkyl group (equation 7) separately. The value for acetaldehyde would be 0.875 if CO_2 is formed as in equation 5. It should be noted that the arbitrary assumption of formation of an equal amount of CO and CO_2 in reaction 6 is inconsequential to the calculation of the production efficiency, since it does not affect the ratio of NO_2 to CH_3 reacted.

$$2CH_3 + \frac{7}{2}NO_2 \rightarrow 2CO_2 + 3H_2O + \frac{7}{4}N_2 \qquad (5)$$

$$2CHO + 2[O] \rightarrow CO_2 + CO + H_2O \qquad (6)$$

$$\frac{N_2}{CH_3CHO} = \frac{7/4}{2} = 0.875$$

Alternatively, if CO is the product of reaction between the alkyl group and NO_2 instead of CO_2, then equation. 7 applies instead of equation 5, and the corresponding nitrogen production efficiency becomes 0.625.

$$2CH_3 + \frac{5}{2}NO_2 \rightarrow 2CO + 3H_2O + \frac{5}{4}N_2 \qquad (7)$$

$$\frac{N_2}{CH_3CHO} = \frac{5/4}{2} = 0.625$$

The corresponding equations for propionaldehyde are equations 8 and 9 if CO_2 is the product in the reaction of the ethyl group, and 9 and 10 if CO is the product. The production efficiencies are 1.625 and 1.125, respectively:

$$2C_2H_5 + \frac{13}{2}NO_2 \rightarrow 4CO_2 + 5H_2O + \frac{13}{4}N_2 \qquad (8)$$

$$2CHO + 2[O] \rightarrow CO_2 + CO + H_2O \qquad (9)$$

$$\frac{N_2}{C_2H_5CHO} = \frac{13/4}{2} = 1.625$$

$$2C_2H_5 + \frac{9}{2}NO_2 \rightarrow 4CO + 5H_2O + \frac{9}{4}N_2 \qquad (10)$$

$$\frac{N_2}{C_2H_5CHO} = \frac{9/4}{2} = 1.125$$

The observed production efficiency is about 0.61 for acetaldehyde, which is close to the value of 0.625 predicted using equations 6 and 7, and the CO/CO_2 concentration ratio at the reactor exit is high. Thus, for this reductant, the result is consistent with a reaction pathway in which the methyl group is used completely for nitrogen formation. For propionaldehyde, however, the experimental nitrogen production efficiency is about 0.85. This suggests that only a portion of the ethyl group is effective for nitrogen production. It is more effective than the methyl in acetaldehyde in terms of the number of nitrogen molecules produced per alkyl group consumed, but less effective in terms of per carbon atom consumed.

The increasing CO/CO_2 ratio with increasing NO_2 concentration in the feed is interesting. One would expect that with a higher surface coverage of NO_2, oxidation of the reductant would be more complete because NO_2 is a more reactive oxidant than O_2. Then, there should be a higher concentration of CO_2 in the effluent. The observed trend is opposite to this. It suggests that when the NO_2 concentration is high, CO_2 is not formed primarily by further oxidation of CO. In addition, the amount of CO_2 formed is less than the amount of acetaldehyde reacted. Assuming no further reaction of CO_2, this implies that less than one CO_2 molecule is formed for every acetaldehyde reacted. This, in turn, implies that decarboxylation of a surface carboxylate (such as one formed by oxidation of adsorbed acetaldehyde) is not the pathway for the formation of CO_2. In fact, it implies that CO_2 is not a stoichiometric product in any step in the N_2 formation pathway. Thus, it may be a secondary product by the oxidation of CO with adsorbed oxygen.

5. Conclusion

TiO_2 anatase catalyzes the low temperature selective NO_x reduction by aldehydes very efficiently. At 300 °C at NO_2/acetaldehyde ratio above unity and NO_2/prionaldehyde ratio above 2.8, 90% of the oxygen used in the oxidation of the oxygenates originated from NO_2. The high coverage of the surface by nitrates at this temperature is the probable reason that the combustion pathway is unimportant.

Acknowledgment

We like to thank Dr. Bernd Proft of Sachtleben Chemie for the anatase TiO_2 sample. This work was supported by the EMSI program of the National Science Foundation and the U.S. Department of Energy Office of Science (CHE-9810378) at the Northwestern University Institute for Environmental Catalysis.

References

[1] W. Held, A. Konig, T. Richter and L. Puppe, SAE paper 900496 (1990).

[2] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Sundo, and N. Mizuno, Shokubai (Catalyst) 32 (1990) 430.

[3] J.H. Lee, A. Yezerets, M.C. Kung and H.H. Kung, Chem. Commun. (2001) 1404.

[4] B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin, E.N. Balko, K.E. Voss, C.Z. Wen, M.C. Kung, and H.H. Kung, SAE paper no. 98FL577 (1998).

[5] A.G. Panov, R.G. Tonkyn, M.L. Malmer, C.H.F. Peden, A. Malkin and J.W. Hoard, SAE 2001-01-3513.

[6] P. Forzatti and L. Lietti, Heterogeneous. Chem. Rev. 3 (1996) 33.

[7] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li and H.H. Kung, Catal. Today 26 (1995) 169.

[8] H.H. Kung and M.C. Kung, Catal. Today 30 (1996) 5.

[9] M.C. Kung, P.W. Park, D.-W. Kim and H.H. Kung, J. Catal. 181 (1999) 1.

[10] K. Hadjiianov, V. Bushev, M. Kantcheva and D. Klissurski, Langmuir 10 (1994) 464.

[11] A. Yezerets, Y. Zheng, P.W. Park, M.C. Kung and H.H. Kung, Stud. Surf. Sci. Catal. 130 (2000) 629.

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

[13] H. Hamada, Y. Kintaichi, T. Yoshinari, M. Tabata, M. Sasaki and T. Ito, Catal. Today 17 (1993) 111.

[14] W. Rachmady and M.A. Vannice, J. Catal. 207 (2002) 317.

[15] H. Idriss, K.S. Kim and M.A. Vannice, J. Catal. 139 (1993) 119.

[16] V.A. Sadykov, V.V. Lunin, V.A. Matyshak, E.A. Paukshits, A. Ya. Rozovskii, N.N. Bulgakov and J.R.H. Ross, Kinet. Catal. 44 (2003) 379.

[17] H.-Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, Catal. Today 54 (1999) 483.

[18] N.W. Cant and I.O.Y. Liu, Catal. Today 63 (2000) 133.

[19] M. Haneda, N. Bion, M. Daturi, J. Saussey, J.-C. Lavalley, D. Duprez, and H. Hamada, J. Catal. 206 (2002) 114.