

N₂O DECOMPOSITION CATALYZED IN THE GAS PHASE BY SODIUM

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INTRODUCTION

The concentration of N₂O in the atmosphere is observed to be increasing at a rate of 0.18% to 0.26% annually. This increase in the N₂O concentration is presumably the result of one or more human activities, though the activities responsible have not been identified with certainty. Whatever the source of the N₂O its increase in the atmosphere is a matter of concern both because N₂O is a greenhouse gas and because it has a major and unfavorable influence on the ozone layer (1,2,3).

Until recently it was believed that in additions to its problems with NO, NO₂, and SO₂ emissions pulverized coal firing also had a severe problem with N₂O emissions. Weiss and Craig (4), Pierotti and Rasmussen (5), Hae et al (6), and C. Castaldinin et al (7), have all reported measurements of N₂O emissions by pulverized coal fired utility boilers (8). N₂O levels of approximately 25% of the NO emissions were found. If one accepted this 25% correlation between N₂O and NOx emissions, the observed increase in N₂O concentration could be accounted for with reasonable accuracy as coming from pulverized coal firing (5). Thus in addition to its problems with NO, NO₂ and SO₂ emissions pulverized coal firing appeared to be an unacceptable technology because of its N₂O emissions.

Lyon and coworkers (9) have, however, shown that when samples of combustion gases are allowed to stand for periods of hours, chemical reactions occur which form N₂O. Since the studies mentioned above all involved taking samples for later analysis, they were all subject to this artifact and it was possible that the N₂O which was apparently present in gases from pulverized coal firing was in fact absent. Later measurements of N₂O emissions for numerous pulverized coal fired utility boilers and other large combustion systems confirmed this expectation, i.e. none of the long established combustion technologies were found to produce significant quantities of N₂O (10). Given N₂O is unstable at extremely high temperatures and that all the long established combustion technologies involve extremely high temperatures, this result is not surprising.

For the much lower temperatures involved in fluid bed combustion, however, N₂O production is quite high (11) and this may be a barrier to extending the industrial use of this technology.

N₂O emissions are also a problem in the NOxOUT and RAPRENOx technologies for controlling NOx emissions, but not in the Thermal DeNOx process. In the latter NH₃ is injected into hot flue gas, and NO is reduced by the

$\text{NH}_3 + \text{NO}$ reaction. In RAPRENOx, however, HNCN is injected, the NCO radical can be formed, and N_2O can be formed via the $\text{NCO} + \text{NO} = \text{N}_2\text{O} + \text{CO}$ reaction. Since the urea injected in the NOxOUT process decomposes to equimolar amounts of NH_3 and HNCN this technology also has a problem with N_2O production.

This paper reports the discovery of a promising new method of controlling the emissions of N_2O . This discovery has been demonstrated on a 0.9 MBTU/hr natural gas fired research combustor and has been examined by computer modeling.

APPARATUS, EXPERIMENTAL PROCEDURES AND COMPUTER MODELING PROCEDURES

Experiments were done in a 15.2 centimeter diameter by 2.4 meter long refractory lined tunnel furnace which has been described in detail elsewhere (12).

Computer modeling experiments were done using the reaction mechanism shown in Table 1 with the PC version of Chemkin. While this program is nominally limited to gas phase species, the presence of liquid phase materials such as Na_2CO_3 was easily handled by assuming a fictional gas phase species with thermodynamic properties such that at equilibrium it produced the same gas phase species in the same amounts as does the vaporization of the liquid phase material.

EXPERIMENTAL RESULTS

A series of experiments was done in which the effects of various additives on the reduction of NO by urea injection was examined. Figure 1 shows the results of an experiment comparing NO reduction by urea and by urea mixed with monosodium glutamate (MSG). The urea-MSG mixture achieves a deeper reduction of NO over a wider temperature range than did pure urea. While results similar to this were obtained with other mixtures of urea with organic compounds, as shown in Figure 2 the addition of MSG was also found to greatly decrease the production of N_2O .

Figure 3 shows the effect on N_2O production during NO reduction by urea of adding Na_2CO_3 and Na_2SO_4 .

Figure 4 shows the results of an experiment in which solid Na_2CO_3 was injected into the post combustion gases at a point at which their temperature was 2150°F and N_2O was injected at a downstream point for which the temperature was 1800°F . Not only do these results show that Na_2CO_3 injection is an effective method for N_2O removal, they show that in some manner the Na_2CO_3 acts as a catalyst for N_2O removal, many N_2O molecules being removed for each injected Na_2CO_3 .

Figure 5 shows computer modeling calculations which will be discussed later and experimental data for the temperature dependence of Na_2CO_3 catalyzed N_2O decomposition. It is interesting to note that within experimental error the rate of N_2O decomposition is independent of whether 50 or 100ppm Na_2CO_3 is used to catalyze the decomposition.

Figure 6 shows the effect of SO_2 on the Na_2CO_3 catalyzed decomposition of N_2O . While the presence of SO_2 does to some extent reduce the ability of Na_2CO_3 to catalyze the decomposition of N_2O , even high ratios of SO_2 to Na_2CO_3 are not able to completely inhibit this catalyzed reaction.

COMPUTER MODELING RESULTS

At high temperatures the thermodynamically most favorable path for Na_2CO_3 vaporization is the reaction $\text{Na}_2\text{CO}_3 = 2\text{Na} + 1/2\text{O}_2 + \text{CO}_2$. Figure 7 shows the calculated equilibrium for this reaction. The rate of the reaction between sodium atom and N_2O has been measured by a number of investigators and is relatively well established as are all of the other reactions shown in Table 1 with the exception of $\text{Na} + \text{Na}_2\text{O} = \text{NaO} + \text{NaO}$. Since this reaction is analogous to a number of reactions which are known to be extremely rapid, it is assumed to occur with a rate equal to the three body collision rate.

In doing these calculations it was also assumed that the vaporization of Na_2CO_3 achieves equilibrium instantaneously.

The predictions of this computer model agree with experiment in that the model shows that Na_2CO_3 can cause rapid N_2O decomposition, that this N_2O decomposition is catalytic, and that it occurs only above a threshold temperature which the model approximately predicts.

In qualitative terms this reaction mechanism also explains the fact that SO_2 inhibited Na_2CO_3 catalyzed N_2O decomposition, i.e. SO_2 reacts readily with Na_2CO_3 converting it to nonvolatile Na_2SO_4 . Once the Na_2CO_3 becomes coated with a layer of Na_2SO_4 its ability to exert its vapor pressure would be reduced.

CONCLUSIONS

The injection of sodium carbonate has been shown to be an effective method of preventing the emission of N_2O in combustion systems. This decomposition is catalytic but occurs in the gas phase. Computer modeling studies suggest that in this catalytic gas phase decomposition the reactions $\text{Na} + \text{N}_2\text{O} = \text{NaO} + \text{N}_2$ and $2\text{NaO} = 2\text{Na} + \text{O}_2$ are important.

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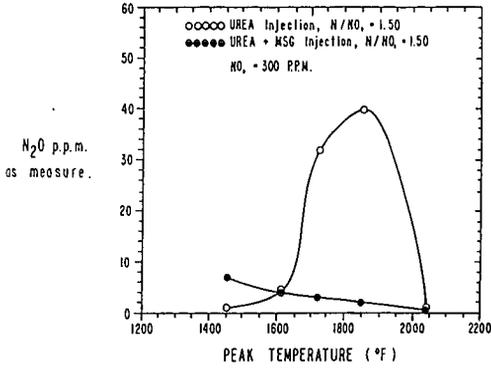


Figure 2

N₂O Reduction

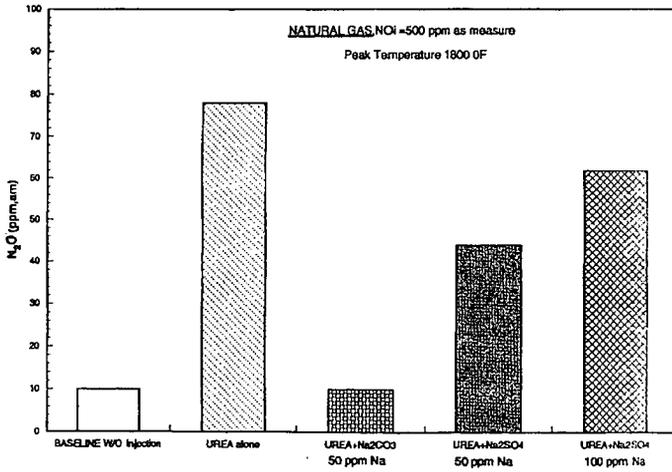


Figure 3

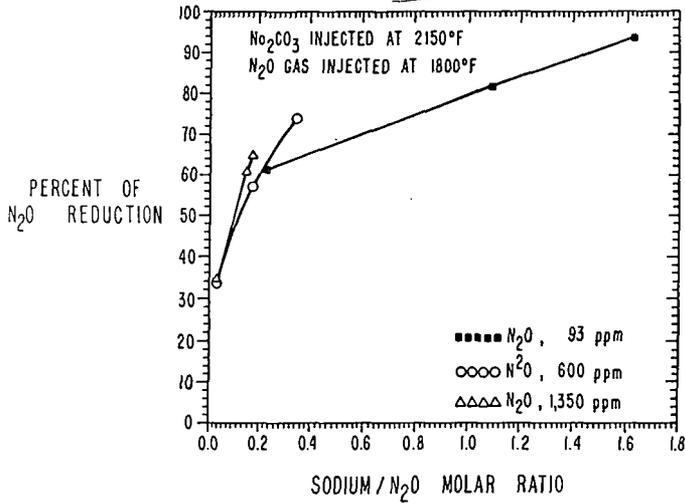
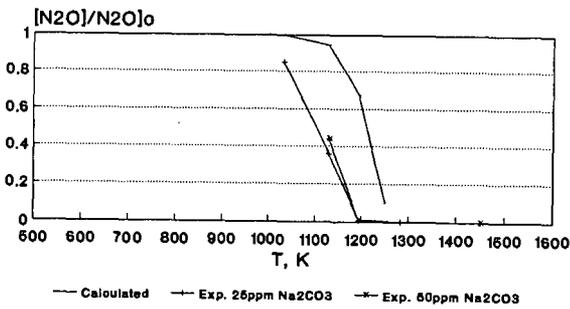


FIG. 4

Temperature Dependence of Na_2CO_3
Catalyzed Decomposition of N_2O



Calculations done for $[\text{N}_2\text{O}]_0 = 100\text{ppm}$,
 $t = 0.1\text{sec}$, 3.8% O_2 , 8.1% CO_2 , 16.2% H_2O
 $[\text{Na}] = \text{equilibrium for } \text{Na}_2\text{CO}_3$

Figure 5

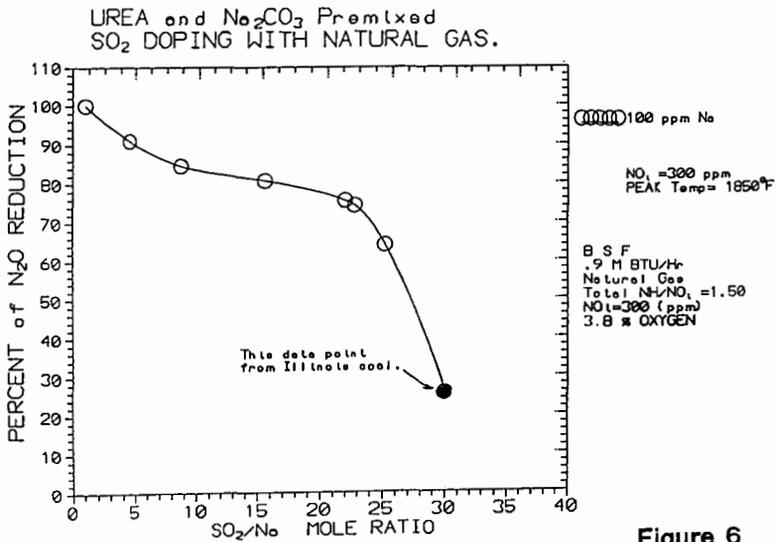


Figure 6

Equilibrium Calculation for
 $\text{Na}_2\text{CO}_3 = 2\text{Na} + 1/2\text{O}_2 + \text{CO}_2$

