

# The Heterogeneous Formation of N<sub>2</sub>O over Bulk Condensed Phases in the Presence of SO<sub>2</sub> at High Humidities

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**Abstract.** In view of the uncertainty of the origin of the secular increase of N<sub>2</sub>O, we studied *heterogeneous processes* that contribute to formation of N<sub>2</sub>O in an environment that comes as close as possible to exhaust conditions containing NO and SO<sub>2</sub>, among other constituents. The N<sub>2</sub>O formation was followed using electron capture gas chromatography (ECD-GC). The other reactants and intermediates (SO<sub>2</sub>, NO, NO<sub>2</sub> and HONO) were monitored using gas phase UV-VIS absorption spectroscopy. Experiments were conducted at 298 and 368 K as well as at dry and high humidity (approaching 100% rh) conditions. There is a significant *heterogeneous rate of N<sub>2</sub>O* formation at conditions that mimic an exhaust plume from combustion processes. The simultaneous presence of NO, SO<sub>2</sub>, O<sub>2</sub> in the gas phase and condensed phase water, either in the bulk liquid or adsorbed state has been confirmed to be necessary for the production of significant levels of N<sub>2</sub>O. The stoichiometry of the overall reaction is:  $2\text{NO} + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{SO}_4$ . The maximum rate of N<sub>2</sub>O formation occurred at the beginning of the reaction and scales with the surface area of the condensed phase and is independent of its volume. A significant rate of N<sub>2</sub>O formation at 368 K at 100% rh was also observed in the absence of a bulk substrate. The diffusion of both gas and liquid phase reactants is not rate limiting as the *reaction kinetics* is dominated by the rate of N<sub>2</sub>O formation under the experimental conditions used in this work. The simultaneous presence of high humidity (90–100% rh at 368 K) and bulk condensed phase results in the *maximum rate and final yield* of N<sub>2</sub>O approaching 60% and 100% conversion after one hour in the presence of amorphous carbon and fly-ash, respectively.

**Key words:** N<sub>2</sub>O formation, heterogeneous reactions, synthetic exhaust/flue gas, soot, fly-ash, calcite, sulfuric acid solutions, high relative humidities.

## 1. Introduction

Nitrous oxide is known to be extremely inert in the troposphere, being present today at low background concentrations of 310 to 320 ppb at sea level. The recent interest in nitrous oxide emissions began when a significant increase in its atmospheric concentration was observed (0.25–0.31% increase per year, Bard, 1993). We have investigated the possibility whether or not N<sub>2</sub>O may be generated in a slow secondary reaction of combustion exhaust gases in the presence of airborne particulate such as soot, sulfuric acid aerosol and fly-ash which are all byproducts of combus-

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tion originating from energy production processes or transportation. The interest in the present work stems from the fact that in contrast to the more well defined albeit variable biogenic origin of  $N_2O$ , mainly from natural processes in oceans and soils, the anthropogenic sources are not well characterized. It is thought that the increase of the  $N_2O$  concentration in the atmosphere may be attributed mainly to human activities such as the use of fertilizers, combustion of fossil fuel, biomass burning, and industrial production of adipic and nitric acids (Berges *et al.*, 1993; Bouwman *et al.*, 1995; Thiemens and Trogler, 1991). The contribution of mobile and stationary combustion sources is highly uncertain and emission of power plants remains controversial since a  $N_2O$  sampling artifact was discovered in 1988 casting doubt on the importance of combustion processes as a source of  $N_2O$  (Muzio and Kramlich, 1988). However, the reactions that led to the formation of  $N_2O$  in sampling containers may occur in exhaust plumes as well and could contribute significantly to the nitrous oxide budget (Khalil and Rasmussen, 1992).

The goal of the present laboratory study was to investigate if heterogeneous chemical processes of combustion exhaust gases taking place on the above mentioned bulk condensed phase surfaces contributed to formation of  $N_2O$  under experimental conditions that come as close as possible to exhaust gases containing NO and  $SO_2$ , among other constituents. Prior to the present laboratory study we have pointed out the elementary oxidation mechanism of NO in aqueous solution resulting in HONO which is a key ingredient in the subsequent chemistry of  $SO_2$  oxidation (Pires *et al.*, 1994). Our efforts are directed at understanding the complex chemistry which will enable us to predict or simulate  $N_2O$  formation using laboratory data to describe heterogeneous and homogeneous chemical processes that take place in realistic environmental situations. A detailed mechanistic study on the heterogeneous formation of  $N_2O$  over liquid sulfuric acid solutions has been published recently (Pires *et al.*, 1996). The present work investigates the role of additional condensed phase surfaces such as soot, fly-ash and calcite on the rate of heterogeneous formation of  $N_2O$ .

## 2. Materials and Methods

$N_2O$  formation was studied in a static aluminum reactor coated with halocarbon wax to minimize unwanted wall reactions. Nitrous oxide from a high relative humidity (rh) environment has been sampled by gas chromatography using electron capture detection (ECD-GC), both in the presence and absence of condensed phase surfaces (solid or liquid). The reactants and intermediates were monitored by gas phase UV-VIS absorption spectroscopy using a CCD camera as detector. The octagonal aluminum cell has an internal volume of 1 liter and is fitted with two quartz windows located on parallel faces with an optical path of 15.5 cm. The cell is shown in Figure 1 together with the analytical devices.

Before each run the cell was connected to the vacuum manifold in order to reach a background pressure lower than 10 mTorr before the start of the experi-

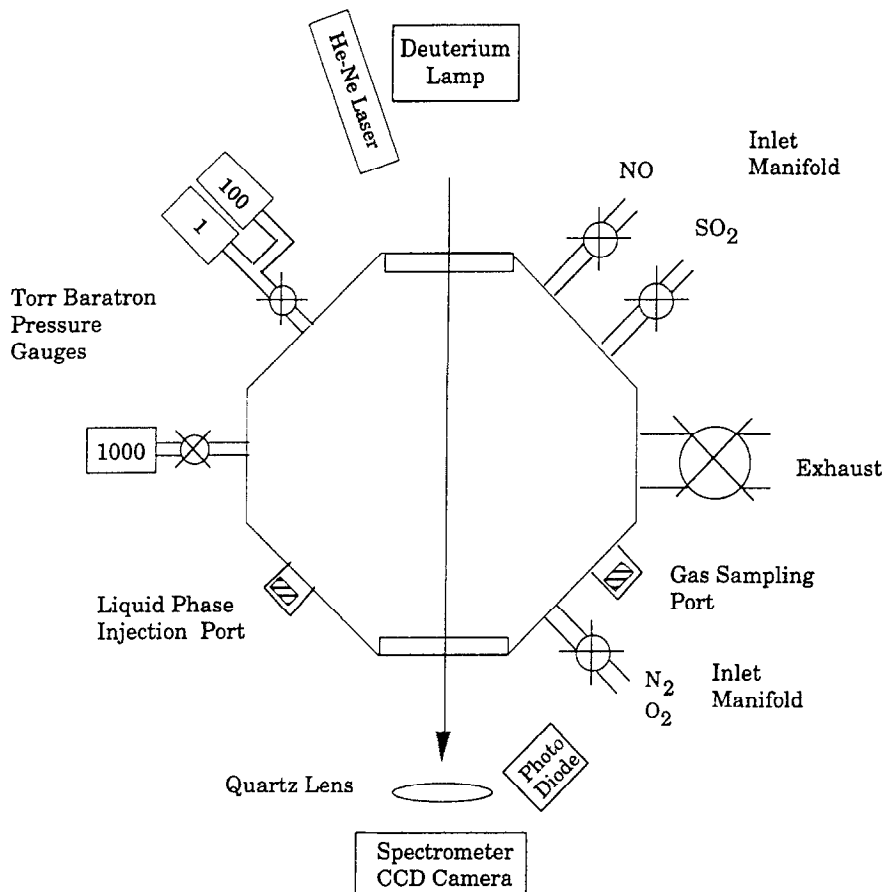


Figure 1. Atmospheric pressure cell (aluminum) for the study of the heterogeneous formation of nitrous oxide.

ment. Subsequently the reactant gases NO (> 99.9%, Carbagas), SO<sub>2</sub> (> 99.9%, Matheson Inc.) and O<sub>2</sub> (> 99.998%, Carbagas) are let into the cell through different flow-controlling valves from the gas storage line. The desired gas concentration is obtained by absolute pressure measurements using two manometers (1 and 100 Torr full scale). The absolute concentration and purity of both NO and SO<sub>2</sub> are confirmed by their respective UV absorption spectra at 226 and in the range 286–300 nm. The possible presence of some N<sub>2</sub>O contamination in the NO was tested for using ECD-GC detection, and we observed that the N<sub>2</sub>O concentration in the NO storage tank was < 0.05%, an amount that is negligible for the present experiments. The homogeneity of the mixture was checked in that the initial SO<sub>2</sub> absorption was constant over time in the aluminum reactor before injection of the liquid phase. The system is maintained at atmospheric pressure adding as a balance nitrogen (> 99.999%, Carbagas) that is purified by flowing it through an oxygen trap and

a 5 Å molecular sieve (used to eliminate N<sub>2</sub>O) prior to admission into the reaction cell.

For the experiments where solid phases (soot, fly-ash or calcite) were used as model substrates for atmospheric particulates the procedure used was the following: the samples were first put into a glass dish in the reactor prior to evacuation and subsequent *in situ* mixing of the gaseous reactants. The samples were weighed before the exposure to the gas mixture and the amount of the solid sample per cm<sup>2</sup> was calculated relative to the geometrical surface area of the dish. The physico-chemical characterization of these samples is presented below. For a detailed description of the procedure used in the study of the acidic solutions corresponding to sulfuric acid and aerosol mimics, see Pires, 1995. Most experiments were performed at standard gas phase concentration conditions: [SO<sub>2</sub>] = 3000 ppm, [NO] = 650 ppm in purified compressed air.

To check the possible variation of the reactivity of the soot material with changing surface functional groups, we exposed our samples to one atmosphere of 5–10% ozone in O<sub>2</sub> during a short period of time (30 s) prior to reaction. This oxidative treatment transformed the surface of the soot samples to becoming hydrophilic after ozone exposure. It has been shown that amorphous carbon reacts rapidly with O<sub>3</sub> producing water soluble acids (Smith *et al.*, 1988; Stephens *et al.*, 1986; Sergides *et al.*, 1987). Smith *et al.* (1988) suggest that the number density of carboxylic groups is significantly enhanced in hexane soot treated with O<sub>3</sub> reflecting an increase in the oxygen content and water solubility of these samples after treatment.

In the experiments carried out in the presence of water vapor the relative humidity (rh) was 100% at ambient temperature and 80 to 100% at temperatures up to 368 K. A detailed description of the experimental set-up and procedure may be found in the literature (Pires, 1995). For the experiments performed at low temperatures the N<sub>2</sub> flow was saturated with water vapor (or nearly so) by passing it first through water before injection into the reactor. To attain the expected relative humidity at 368 K a given amount of liquid water (0.5–2 ml) was injected into the heated cell using a syringe. To verify if the water was still in the vapor phase or already condensed on the quartz windows representing the coldest spot of the reaction cell we used a He-Ne laser emitting at 632.8 nm to check for scattering of laser radiation. We expected the variation of the transmitted light intensity to be attributed to water droplet formation in the cell, had there been any condensation. During the experiments we observed a small decrease in the transmitted laser intensity after complete evaporation of the liquid water injected into the reactor indicating a small extent of condensation of water vapor, probably on the quartz windows. We thus claim that there was almost certainly no formation of H<sub>2</sub>O droplets suspended in the gas phase. The possibility of independently controlling the temperature of both the reactor and the windows, the constant transmission of the He-Ne laser beam across the cell and the time-invariant gas phase absorption spectra of SO<sub>2</sub> in reference experiments all point towards the absence of important H<sub>2</sub>O condensation in the reactor, at least on the time scale of the experiments.

The statistical error in the measurement of N<sub>2</sub>O using ECD-GC and of NO<sub>2</sub>, SO<sub>2</sub> and HONO using gas-phase UV absorption is less than 15% (Pires *et al.*, 1995). Most series of measurements of this work were performed at least twice in order to ensure reproducibility of the results.

## 2.1. CHARACTERIZATION OF THE SOLID SURFACES USED IN THE HETEROGENEOUS STUDIES

Table I shows the physico-chemical characterization of the solid surfaces used in this work, namely three different kinds of fly-ash, soot and calcite samples. This Table also shows literature data for two fly-ash samples used by Dlugi and Güsten (1993) from a study on SO<sub>2</sub> oxidation for comparison. The description of these results is given for each sample and the analytical methods are presented as the case may arise.

### 2.1.1. Fly-Ash Samples

We have tested three different types of fly-ash produced by large coal-fired power plants in the USA and Brazil. The American fly-ash originates from the National Institute of Standards and Technology (NIST) and is a standard reference material (ref. 1633b). This sample was supplied by a coal-fired plant burning Pennsylvania and West Virginia coals and was selected as a typical bituminous coal fly-ash by NIST. This material was sieved through a nominal sieve opening of 90  $\mu\text{m}$  and was used as provided. The Brazilian fly-ashes were sampled in electrostatic precipitators of the Candiota and Charqueadas power plants (Teixeira, 1995) and were not sieved before use. The Brazilian coals have generally high mineral matter ( $\sim 45\%$ ) and low sulfur ( $< 3\%$ ) contents (Fiedler, 1987; Pires and Teixeira, 1992), in contrast to low ash and high sulfur contents observed in American coals (Smith, 1980). Keeping these differences in mind as well as considerations of the variation of the combustion processes used in the respective power plants where fly-ash was collected we expected significant differences between these samples. This fact is deemed important because it allows us to test N<sub>2</sub>O formation on fly-ash surfaces having different physico-chemical properties.

The morphology and size distribution of the NIST fly-ash and soot samples were studied by scanning electron microscopy (SEM) using a JEOL JMS-6300F microscope. We qualitatively confirmed the large size distribution by the existence of coarse particles (mean diameter approximately 10  $\mu\text{m}$ ) and fine particles with mean diameter  $< 1 \mu\text{m}$ . The fly-ash particles present a varied morphology with a significant fraction of so-called cenospheres which are typically hollow spherical particles found over a wide range of sizes (Smith, 1980; Fisher *et al.*, 1978). While the spherical particles originated from mineral matter in coal, shapeless particles are associated with the incomplete combustion of the organic coal matrix (Fisher *et al.*, 1978). The surface of a cenosphere particle presents a complex morphological

Table I. Physico-chemical characterization of the solid surfaces

Physico-chemical parameters	Fly-ashes		Literature <sup>b</sup>		Calcite <sup>c</sup>	Soot <sup>d</sup>		
	Analysed <sup>a</sup>		KI KII				Rubber	FW2
	NIST	Charqueadas	Candiota					
pH of leaching solution	~ 6	12	4-5	5-6.5	10.6	nd	nd	2.5
Internal surface ( $m^2 g^{-1}$ )	1.42	2.53	0.76	5-8	4.4-6.4	nd	61	460
Density ( $g cm^{-3}$ )	nd	nd	2.1	2.58	2.74	nd	1.8-1.9	1.8-1.9
Mean diameter ( $\mu m$ )	10.8	16.0	15.4	nd	nd	~2 mm	0.1	nd
Chemical composition (wt%)								
Al	15.05		10.1	17.2	14	0.3		
Fe	7.78	3.9	2.9	2	7.9	0.2		
Si	23.02		32.2	14.7	9.4	0.9		
Ca	1.51		0.6	2.5	4.7	39		
K	1.95		0.7	2.7	2.2	-		
Mg	0.482		0.4	1.3	0.92	0.15		
S	0.2075		0.39	nd	nd	-		
C	nd		0.25	3.9	7.8	12		

<sup>a</sup> Analysed coal fly-ashes are: a standard reference material from NIST and two Brazilian samples from the Charqueadas and Candiota power plants.

<sup>b</sup> Fly-ash literature data from the study of Dlugi and Güsten (1993).

<sup>c</sup> Calcite stones from Transmat, Switzerland, 97% wt  $CaCO_3$ .

<sup>d</sup> Soot samples: obtained from Degussa (FW2) and produced by burning rubber hose.  
nd - not determined.

structure called 'alphabet soup'. This structure is attributed to chemical segregation of Fe oxides present at a high concentration in this kind of particle (Fisher *et al.*, 1978; Andrade, 1985).

The particle size distribution of the NIST fly-ash sample was measured in a Horiba CAPA 700 particle analyzer. This equipment is based on the principle of liquid-phase sedimentation and optical transmission. The results obtained for the three fly-ash samples analyzed in this study are shown in Table I, expressed as mean diameter (> 50%) of the cumulative volume distribution. We observed that the NIST sample has a smaller mean diameter (10.8  $\mu\text{m}$ ) compared to values of  $\sim 15.5 \mu\text{m}$  for the Candiota and Charqueadas samples. This difference may be due to differences in the coal composition and combustion efficiency of the power plants where these fly-ashes were collected. In conclusion, these results seem to be in good agreement with literature studies about fly-ash morphology and size distribution (Ghosal and Self, 1995; Fisher *et al.*, 1978; Andrade, 1985).

The internal surface area of the sample was determined in a BET analyzer. We measured a surface area of 0.76, 1.42 and 2.53  $\text{m}^2 \text{g}^{-1}$  for the Candiota, Charqueadas and NIST samples, respectively. These values are small and in the range expected for this kind of material (Smith, 1980) while being slightly smaller than corresponding literature data (Dlugi and Güsten, 1993) presented in Table I. The variation of the internal surface area of fly-ash samples may be due to the differences of coal composition and combustion conditions.

The pH of a leaching solution in contact with fly-ash samples (Dlugi and Güsten, 1993; Teixeira, 1995) presents a wide range of acidity. The most 'acidic' fly-ash is the Candiota sample with a pH = 4 while the Charqueadas sample presented high alkaline behavior (pH = 12) (Teixeira, 1995). In comparison, literature fly-ashes presented weak acidic (pH  $\sim 6$ , KI, c.f. Table I) and basic (pH = 10, KII, c.f. Table I) characteristics. The pH of a leaching solution of the NIST sample was not mentioned and only a nominal measurement was performed resulting in pH  $\sim 6-7$ .

The chemical analysis of the major elements is shown at the bottom of Table I. We noted a relative large variation of the concentration of the major fly-ash constituents as observed in other studies. (Meij, 1994; Linak and Wendt, 1994; Pires, 1988). The reason for this may be complex (Smith, 1980) and is outside of the scope of this work.

### 2.1.2. Soot Samples

As a model for carbonaceous atmospheric aerosols we used soot particles produced by burning rubber. The rubber from a laboratory rubber hose was burned in air and the soot formed by incomplete combustion of organic matter was collected on plane glass dishes (5 up to 20  $\text{cm}^2$ ) which were weighed before and after deposition. The soot samples were collected a few minutes before an experiment (evacuation of the cell and mixing of gas reactants). Some experiments were also performed using a commercial soot sample, namely FW2 from Degussa. This sample has a large

surface area ( $460 \text{ m}^2 \text{ g}^{-1}$ ) when compared to soot from burnt rubber ( $61 \text{ m}^2 \text{ g}^{-1}$ ). The significant difference of surface areas between these two soot samples was used to test the importance of internal surfaces on the  $\text{N}_2\text{O}$  generation.

The morphology of the soot from burnt rubber was analyzed by SEM. The soot particles present a remarkable homogeneous morphology consisting of very fine individual particles (diameter  $< 0.1 \mu\text{m}$ ). These small particles form large aggregates which seem to present a typical structure. These results are in good agreement with the study of Sergides *et al.* (1987) who generated soot particles by controlled combustion of hexane.

The soot density and the pH of a leaching solution in contact with soot generated by burnt rubber were not determined. Therefore, the density was taken as  $1.8\text{--}1.9 \text{ g cm}^{-3}$  for both soot samples which is the value given in the literature for FW2. Using this value we calculated the thickness of the deposit to be between  $0.14$  to  $52 \mu\text{m}$  for soot weighing between  $0.5$  and  $188 \text{ mg}$ , respectively, and deposited on a  $20 \text{ cm}^2$  glass dish. This calculation was made using the assumption that the sample was homogeneously deposited on the glass support surface which was not the case for the low mass samples. They did not present a coherent deposit and in addition were associated with a large uncertainty in the layer thickness due to the gravimetric determination.

### 2.1.3. Calcite Sample

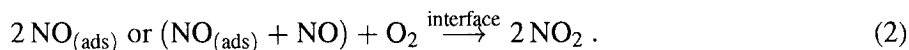
We performed a few experiments using coarse calcite rocks (diameter  $< 5 \text{ mm}$ ) with the aim to evaluate the role of building materials on  $\text{N}_2\text{O}$  formation, especially in highly polluted atmospheres such as encountered in large cities. The 'Oolithique Calcaire' samples were provided by Transmat, La Sarraz-Switzerland. The chemical characterization of this material is shown in Table I. It contains  $97\%$  wt  $\text{CaCO}_3$  with small quantities of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . In contrast to other solid surface materials, we did not undertake a complete physico-chemical characterization of the calcite sample because of the nature of this sample (coarse rocks) and the minor importance of  $\text{CaCO}_3$  in the particles emitted by combustion processes.

## 3. Mechanism of the Heterogeneous $\text{N}_2\text{O}$ Formation

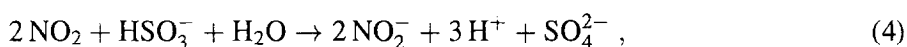
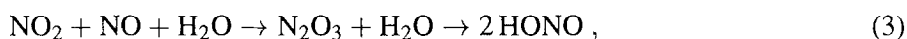
Based on experimental results recently presented by Pires and Rossi (1996) using sulfuric acid solutions ( $0.1 \text{ M}$ ) as a substrate we propose the following simplified mechanism for heterogeneous  $\text{N}_2\text{O}$  formation from exhaust gases of combustion. In the first few minutes after the start of the reaction  $\text{NO}$  is oxidized by  $\text{O}_2$  to  $\text{NO}_2$  mainly in the gas phase following the widely known termolecular rate law, that is second order in  $\text{NO}$  and first order in  $\text{O}_2$ . The presence of both  $\text{H}_2\text{O}$  and active surfaces significantly accelerate the  $\text{NO}_2$  production in a heterogeneous reaction at the gas-condensed phase interface:



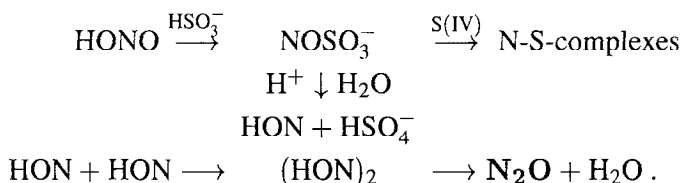




Subsequently, dissolved or adsorbed NO<sub>2</sub> will react with excess NO to obtain HONO (reaction 3) or with S(IV) (reaction 4) depending on the relative concentrations of dissolved NO and S(IV). The recently discovered reaction of NO<sub>2</sub> in the presence of sulfate resulting in N<sub>2</sub>O is slower by at least two orders of magnitude and therefore does not play a role in the present reaction system (Becker *et al.*, 1996). This was confirmed by observing identical N<sub>2</sub>O yields when H<sub>2</sub>SO<sub>4</sub> was replaced by HNO<sub>3</sub> as a condensed phase (Pires, 1995). NO<sub>2</sub> disproportionation (reaction 5) resulting in equivalent amounts of HONO and HNO<sub>3</sub> is apparently too slow to compete as nitrate could not be detected under our conditions.



The observation of gas phase NO<sub>2</sub> and HONO in the presence of the condensed phase represents a powerful clue to the overall reaction mechanism proposed above. Thus it is proposed that HONO may react with S(IV), probably HSO<sub>3</sub><sup>-</sup> under our conditions, to ultimately form N<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> through a complex reaction sequence following the Raschig mechanism shown below:



A similar mechanism is expected in the presence of active solid surfaces such as soot and fly-ash where reaction (2) may be accelerated and reactions (3) to (5) may occur in the presence of adsorbed H<sub>2</sub>O. It is important to recognize that we only monitor the relevant gas phase species in the course of this work in which we investigate the effect of the presence of active surfaces. Therefore only limited information regarding the detailed heterogeneous reaction mechanism may be deduced. In the next section the results obtained in the presence of particulate matter is presented and discussed.

## 4. Results and Discussion

### 4.1. EFFECT OF VAPOR PHASE AND CONDENSED WATER

The effect of the presence of both vapor phase and condensed water on N<sub>2</sub>O production was investigated and the results are shown in Figure 2. The rate of nitrous

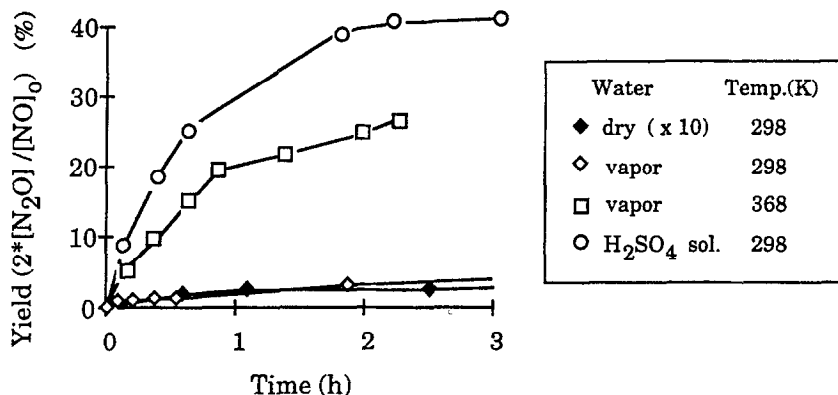


Figure 2. Effect of the presence of water on the temporal profiles of  $N_2O$  formation. The humid system was kept at approximately 100% rh at the specified temperature,  $[NO]_0 = 650$  ppm,  $[SO_2]_0 = 3000$  ppm and  $[O_2]_0 = 5\%$ . We used 20 ml of sulfuric acid solution (0.1 M) exposed in a dish of  $50\text{ cm}^2$  surface area (for further information see Pires, 1995). The ordinate of the curve corresponding to the dry experiments at ambient temperature was multiplied by 10.

oxide formation in the dry system is slower by a factor of 100, corresponding to a NO conversion of only 0.2% compared to the analogous humid system. Injection of water vapor at 368 K increases the initial rate and final yield by a factor of 30 to 60 compared to a dry system. These results show the importance of water for  $N_2O$  production as observed in other studies (Muzio and Kramlich, 1988; Linak *et al.*, 1990).

The results obtained by Linak *et al.* (1990) are similar to our results. These authors analyzed extracted flue gas samples using time dependent analysis of  $NO_2$ , NO,  $N_2O$  and  $SO_2$ . The samples were collected at three different degrees of dryness: humid samples (before refrigerator drier), partially dried samples (immediately after refrigerator drier) and desiccated samples (after additional drying by use of  $P_2O_5$  desiccant).  $N_2O$  is rapidly formed from an initial value of 4.2 ppm, corresponding to sample contamination, to a level approaching 200 ppm in one hour or so when condensed water was present. A drop in gaseous  $SO_2$  is observed indicating the importance of sulfur as well as moisture, in agreement with our results discussed previously. In addition, they observed that the consumption of  $SO_2$  seems to be dependent on the sample dryness, and NO data show rapid removal (possibly a reaction forming  $NO_2$ ) within 1 to 4 hours regardless of the moisture content of the samples. This fact corroborates the hypothesis that NO oxidation in the gas phase dominates the initial kinetics in this reaction system and that the active nitrogen reactant is either a direct or indirect product of this oxidation.

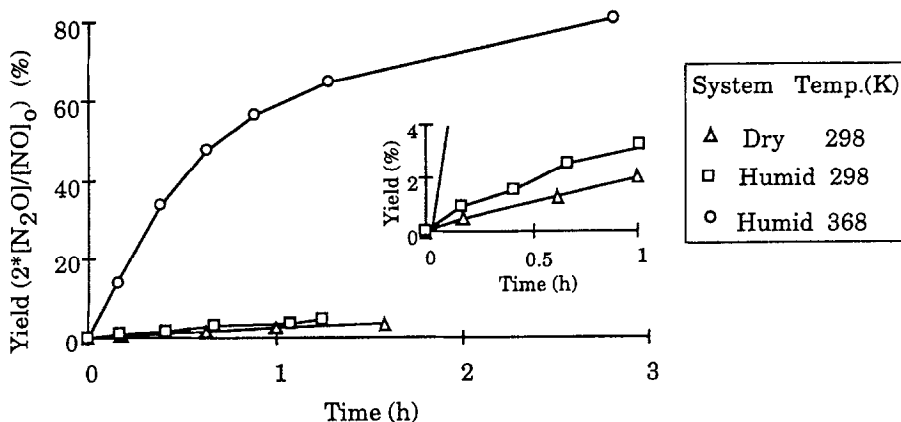


Figure 3. Effect of humidity and temperature on the temporal profiles of N<sub>2</sub>O formation in the presence of a soot surface at standard concentration conditions. All tests were performed using 1 mg of a soot sample collected on a glass support with a geometrical surface area of 20 cm<sup>2</sup>.

#### 4.2. EFFECT OF THE ACTIVE SOLID SURFACE

We have performed several experiments to test the reactivity of some solid surfaces, namely fly-ash, soot and calcite with respect to N<sub>2</sub>O formation. The description of the principal physico-chemical characteristics of these surfaces has been presented in Section 2.

##### 4.2.1. Soot Surfaces

We used a soot sample obtained by burnt rubber as a model for carbonaceous particles produced by combustion (see Table I for characterization). The presence of soot in the reactor remarkably changes the kinetics of the reaction system (insert Figure 3). We observe an increase of a factor of two in the initial rate with the addition of a 10 mg soot sample with an external surface area of 20 cm<sup>2</sup> compared to a dry system at ambient temperature. The increase of the relative humidity up to 100% at ambient temperature (298 K) slightly enhances the N<sub>2</sub>O formation (Figure 3). In addition, at high humidity (~90–100%) and at a temperature of 368 K in the presence of a similar soot sample we observed a strong increase of both the initial rate and the final yield of N<sub>2</sub>O compared to the corresponding dry/humid soot systems at 298 K. We observe the highest final N<sub>2</sub>O yield of 80% as well as the maximum initial rate of N<sub>2</sub>O formation in the presence of a soot surface under both high relative humidity and elevated temperature. This result is important because the conditions of the humid soot approach the conditions of the real case of exhaust or flue gas from combustion such as higher temperature, high humidity and the presence of active surfaces.

We observe that the burnt rubber soot used in our experiments has hydrophobic character, which was verified by testing the wettability of the soot sample. We

performed a few kinetic experiments using soot samples oxidized by ozone (see Section 2). However, we do not observe a significant change of  $N_2O$  formation in the presence of these  $O_3$ -treated samples when compared with 'hydrophobic', that is non-treated soot samples. This behavior is somewhat unexpected because hydrophilic carbonaceous particles are known to be more reactive than hydrophobic ones. However, as discussed by De Santis and Allegrini (1992), the reactivity of carbonaceous particles towards  $SO_2$  and  $NO_2$  strongly depends on the nature of the sample and there is no general conclusion regarding materials of different origin.

Figure 4A displays the effect of the sample mass on  $N_2O$  formation at standard concentration conditions in a dry system, corresponding to a sample with  $20\text{ cm}^2$  of geometric surface area. We did not observe any significant change on the rate of  $N_2O$  formation upon increasing the mass of the sample exposed to reactive gases 200 times. We just observed a slight decrease of  $N_2O$  production at very low sample mass ( $\sim 0.5\text{ mg}$ ) which may be considered a lower limit of reactivity for this soot material. This mass of soot is assumed to correspond to one formal monolayer of carbonaceous material of approximate thickness of  $0.1\ \mu\text{m}$ . However, these results may be somewhat inaccurate due to errors in the gravimetric measurements for such low sample weights and due to the possible inhomogeneity of the deposited material.

The concentration profiles of  $N_2O$ ,  $SO_2$  and  $NO_2$  obtained in the presence of a burnt rubber soot sample in dry (0% rh) and humid ( $\sim 100\%$  rh) systems at 298 K are shown in Figure 4B. As discussed above, we observe a slight increase of the  $N_2O$  yield in the presence of water vapor at ambient temperature compared to a dry system. We observed a similar rapid adsorption of  $SO_2$  at the beginning of the reaction for both dry and humid conditions. The  $SO_2(g)$  adsorbed onto the soot surface corresponds to 30% of  $[SO_2]_0$  and no additional adsorption was observed up to the end of the reaction after 3 hours. On the other hand, the  $NO_2$  concentration profiles change significantly in the presence of water vapor. We observe a rapid  $NO_2$  formation at the beginning of the reaction for both experiments. However, in the humid system  $NO_2$  rapidly disappears from the gas phase without concomitant formation of additional amounts of  $N_2O$ . In the dry system the  $NO_2$  maximum of 330 ppm occurs after 2 hours with a slightly decreasing concentration towards the end of reaction. The reaction between  $NO_2$  and soot resulting in  $NO$  is not enhanced in the presence of water vapor (Tabor *et al.*, 1994). Consequently,  $NO_2$  may be consumed by  $O_2$  oxidation which is enhanced in the presence of water vapor. This reaction neither increases  $SO_2$  adsorption nor enhances  $N_2O$  formation.

With the aim to verify the influence of the nature of the soot sample we performed a few experiments using a commercial sample with a large surface area (see Table I), namely FW2. Figure 5 presents the results obtained in these experiments. We do not observe any change in the initial rate of  $N_2O$  formation in the presence of a FW2 sample compared to the burnt rubber soot albeit the final yield of  $N_2O$  is larger in the presence of burnt rubber soot (6.5%) compared to the FW2 sample (4%). This result is interesting because a FW2 sample has an internal surface area

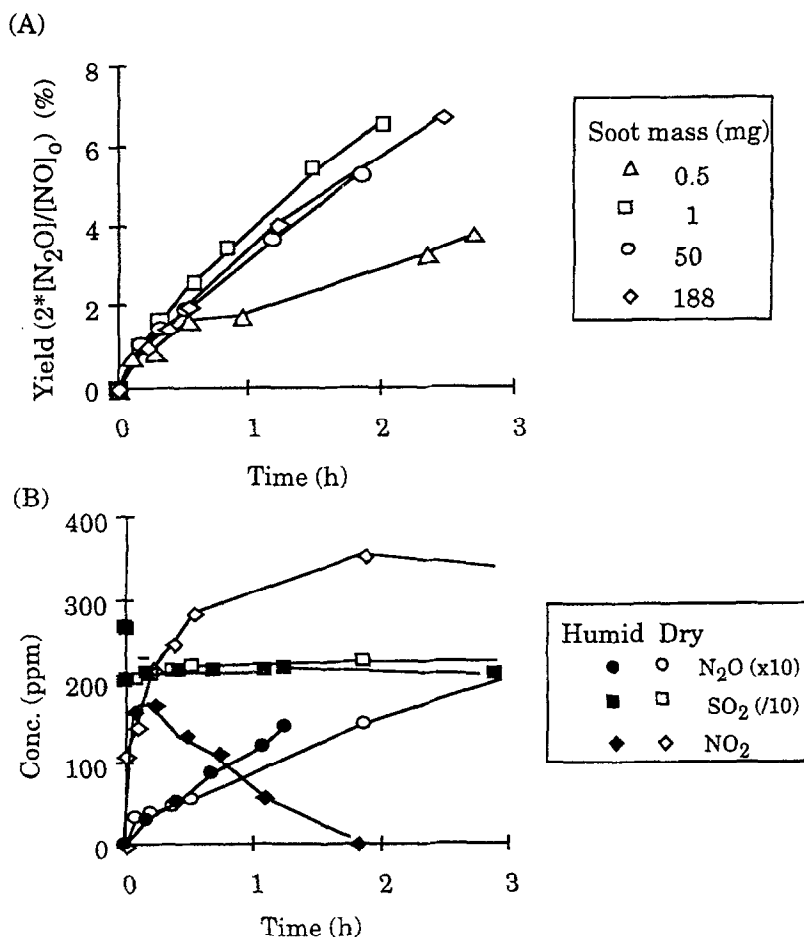


Figure 4. (A) Influence of the mass of the soot sample on the N<sub>2</sub>O yield in a dry system at 298 K and (B) concentration profiles of NO<sub>2</sub>, SO<sub>2</sub> and N<sub>2</sub>O in the presence of 50 mg of soot with a geometric surface area of 20 cm<sup>2</sup> in both a dry and a humid (~100% rh at 298 K) system.

8 times greater than burnt rubber soot. We used a slightly larger amount of FW2 powder (350 mg) compared to the burnt rubber soot experiment (~200 mg) which should not change the N<sub>2</sub>O yields as discussed above (Figure 4A). However, the high surface area of FW2 surprisingly does not enhance N<sub>2</sub>O formation under the experimental conditions used. This result may be due to an inherently lower reactivity of FW2 compared to burnt rubber soot which is offsetting the significantly larger internal surface area of the former.

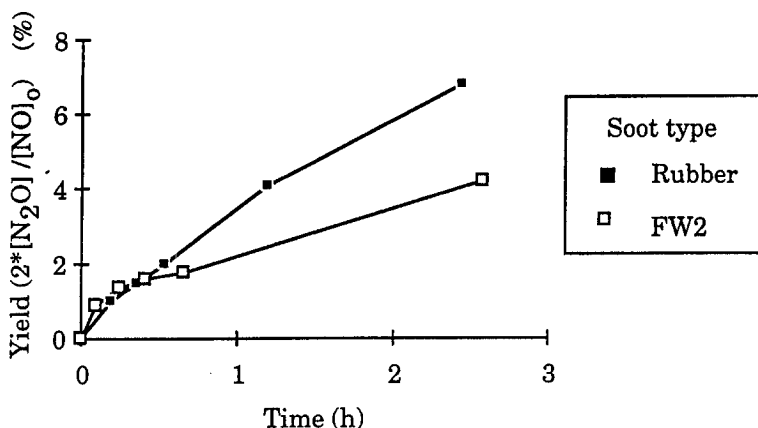


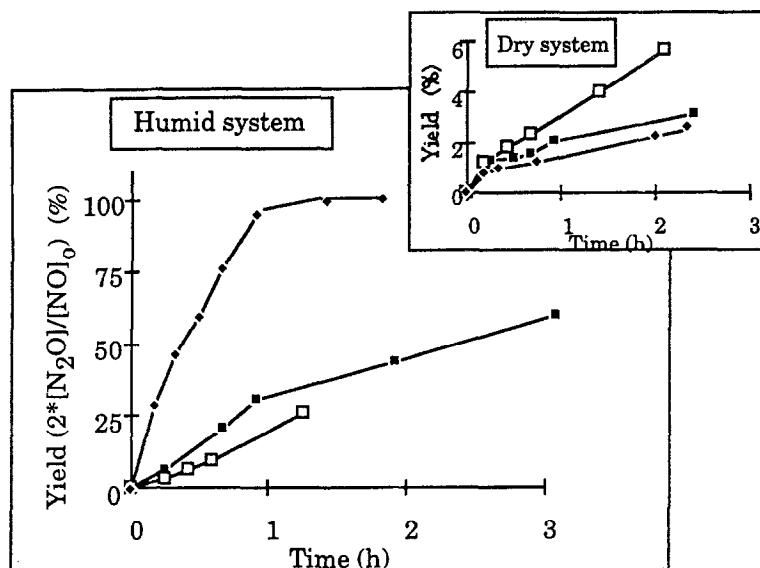
Figure 5. Effect of the type of soot surface on  $N_2O$  yield at standard concentration conditions,  $[NO]_0 = 650$  ppm,  $[SO_2]_0 = 3000$  ppm,  $[O_2]_0 = 5\%$  at 100% rh and 298 K. The soot samples were a burnt rubber material and FW2.

#### 4.2.2. Fly-Ash Surfaces

We carried out a series of experiments using three different fly-ash samples: *NIST* sample which is a reference material from National Institute of Standards and Technology (USA), *Candiota* and *Charqueadas* samples from two large Brazilian power plants. The characterization of these samples is presented in Table I.

Figure 6 shows the formation of  $N_2O$  in the presence of the three fly-ash samples in the absence/presence of water vapor. In dry systems (detail at the top of Figure 6) we observed a slow rate of  $N_2O$  formation on all samples, namely a small yield for the *NIST* and *Candiota* fly-ashes ( $\sim 3\%$ ) and a more important yield for the *Charqueadas* fly-ash (8%). This difference in reactivity is certainly not due to the different residual humidities of the samples as experiments were carried out with samples previously dried under vacuum during 2 hours at 373 K with identical results within experimental error.

On the other hand, the reactivity of fly ashes dramatically increases with humidity. Figure 6 shows the  $N_2O$  production under these conditions and we note that the *NIST* fly ash is more reactive than the Brazilian samples. The rate of formation of  $N_2O$  is between 4 and 9 times larger in the presence of the *NIST* sample when compared to the *Candiota* and *Charqueadas* samples, respectively. This phenomenon may be due to the difference in chemical composition of these samples. Dlugi and Güsten (1993) also observed a significant difference in reactivity with respect to  $SO_2$  oxidation for two fly-ashes from coal-burning power plants in Germany. These authors suggested that the difference of acidity of the samples is responsible for this effect, the acidic fly-ash being 10 times more reactive than the basic fly-ash with respect to  $SO_2$  oxidation. This effect may explain the different reactivity of fly-ash observed in this work. In our case, the slightly acidic fly-ash (*NIST*) displays the highest reactivity with respect to nitrous oxide formation under humid



Legend	Fly-ash	Rate ppm N <sub>2</sub> O/h	Yield (%)	
			2*[N <sub>2</sub> O]/[NO] <sub>0</sub>	2*[N <sub>2</sub> O]/[SO <sub>2</sub> ] <sub>0</sub>
Dry system (298 K)				
◆	NIST	2.6	0.7	0.2
■	Candiotia	3.2	3	8
□	Charqueadas	7.5	6	1.2
Humid system (368 K and r.h.100%)				
◆	NIST	460	100	28
■	Candiotia	118	60	16
□	Charqueadas	60	26	6

Figure 6. N<sub>2</sub>O formation in dry/humid systems in the presence of three different fly-ashes at standard concentration conditions. In all experiments 3.5 g of fly-ash sample were placed into a dish of surface area of 50 cm<sup>2</sup>. Humid systems were kept at 100% rh at the given temperature.

conditions with the 'acidic' Candiotia samples showing an intermediate reactivity and the 'alkaline' Charqueadas fly-ash being the least reactive. Thus, it seems that neutral to acidic fly-ashes are more effective in N<sub>2</sub>O formation when compared to basic fly-ashes. However, the reactivity of fly ash samples are not controlled only by their leaching pH values which only gives qualitative indications of the reactivity of the active sites present on the surface. Moreover, these results may be pertinent because alkaline fly-ashes are more frequently encountered than acidic ones (Smith, 1980).

The effect of the mass of the Candiotia sample on N<sub>2</sub>O formation is shown in Figure 7A. We did not observe any significant variation of the N<sub>2</sub>O production at

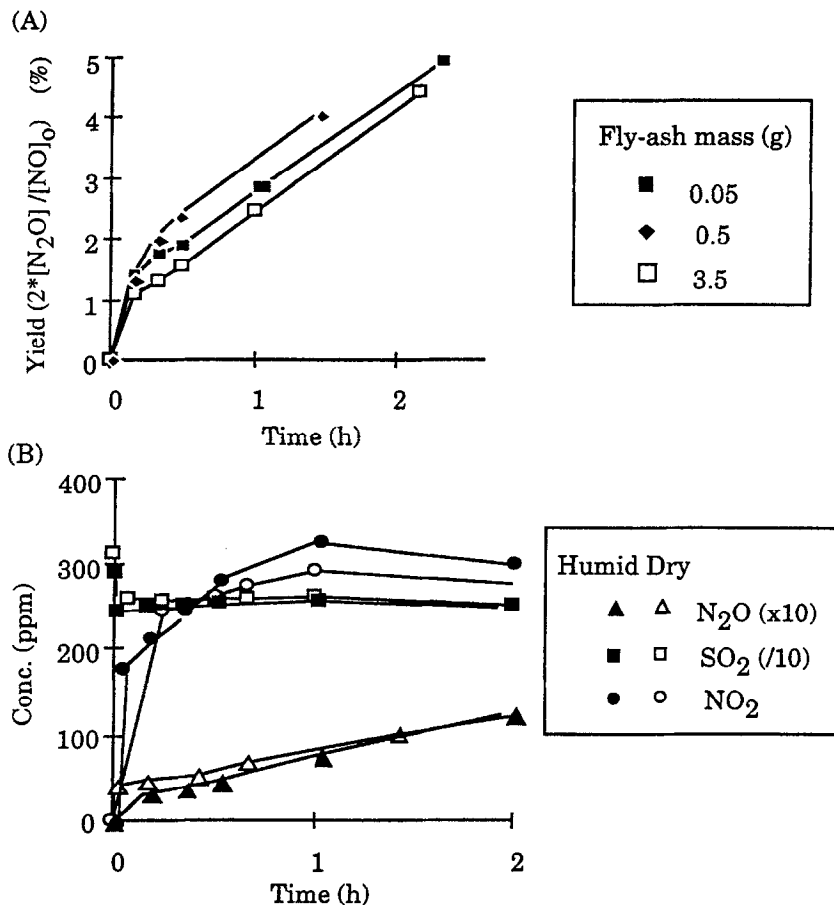


Figure 7. (A) Effect of the mass of the Candiota fly-ash sample on the  $N_2O$  formation in a dry system and (B) concentration profiles of  $NO_2$ ,  $SO_2$  (ordinate divided by 10) and  $N_2O$  (ordinate multiplied by 10) in the presence of 3.5 g of the same type of fly-ash in dry and humid ( $\sim 100\%$  rh at 298 K) systems. The experiments were carried out at standard concentration conditions on a geometrical surface area of  $50 \text{ cm}^2$ .

standard concentration conditions with a large increase of the fly-ash mass from 0.05 to 3.5 mg. This fact may be due to the existence of several monolayers of sample even for the experiment at the lowest mass. Unfortunately, it was impossible to obtain a coherent monolayer with this material due to the physical characteristics of the samples. In this case the observed reactivity of this sample may be taken as an upper limit to the true value.

The concentration profiles of  $N_2O$ ,  $SO_2$  and  $NO_2$  obtained in the presence of the Candiota fly-ash sample under dry (0% rh) and humid ( $\sim 100\%$  rh) conditions at 298 K are shown in Figure 7B. We observe the same profiles for all species in the presence or in the absence of water vapor. No significant changes in  $N_2O$  formation were observed in changing from a dry to humid environment.  $SO_2$  adsorption



(~17%) is rapid in the beginning of reaction without additional consumption afterwards under both conditions. Important amounts of SO<sub>2</sub> (2500 ppm) remain in the gas phase until the end of the reaction as observed in the soot experiments. Water vapor does not seem to be important to NO<sub>2</sub> adsorption on Candiota fly-ash in contrast to the soot experiments discussed above (Figure 4B). The maximum NO<sub>2</sub> concentration (280–300 ppm) was observed after 1 hour with no significant disappearance of this species from the gas phase until the end of the reaction after 3 hours under both dry and humid conditions. This fact indicates that the fly-ash sample may be less reactive than the soot sample with respect to NO<sub>2</sub> (Figure 4) in the presence of water vapor at ambient temperature.

We have tested the possible ‘poisoning’ of the surface of the fly ashes exposed to synthetic exhaust gases (SO<sub>2</sub>/NO/O<sub>2</sub>). These compounds may react irreversibly with the active site on the fly ash surface and consequently may decrease the sample reactivity with time. We observed this because the N<sub>2</sub>O rate of formation in the presence of fly ash showed a significant decrease once it had been exposed to the NO/SO<sub>2</sub> mixture. However, this ‘poisoning’ akin to the deposition of an involatile reaction product does not seem to be permanent because the samples exposed once to the reactive system could be reactivated by pumping during long periods (1–2 days) at ambient temperature. Consequently, sulfate formation may not be the real reason for the decrease of the rate of N<sub>2</sub>O formation on exposed samples. In any case, the reactivity of these reactivated samples was somewhat inferior (~30%) to the observed reactivity on fresh fly ash regarding N<sub>2</sub>O formation.

#### 4.2.3. *Calcite Surface*

We performed additional experiments using calcite coarse rocks under both dry and humid conditions with the aim to study the possible formation of N<sub>2</sub>O on building material (‘sandstone’). The degradation of historic buildings by atmospheric pollutants have been intensively studied and the present work may contribute to a better understanding of this complex system. The production of N<sub>2</sub>O on this kind of surface is shown in Figure 8A, where we observe significant rates of formation as well as final yields for N<sub>2</sub>O in the presence and in the absence of water. In the high humidity system (100% rh at 298 K) the formation of N<sub>2</sub>O is similar to its production on condensed sulfuric acid solutions (0.1 M) at standard conditions, also shown in Figure 8A. However, the effective surface area of these two condensed phases are different. Whereas the sulfuric acid solutions are characterized by their geometrical surface, the effective calcite surface must be larger by a factor of 2 or 3 compared to the geometrical surface of the glass dish used as a support (50 cm<sup>2</sup>). Consequently, the effective surface of the film (formed by water condensation) in the high humidity experiments on calcite may be larger than the aqueous surface used in the sulfuric acid experiments. Moreover, while the pH of adsorbed water on the calcite surface may considerably change with time, the sulfuric acid solution must be considered a buffer solution. Consequently, the comparison between these

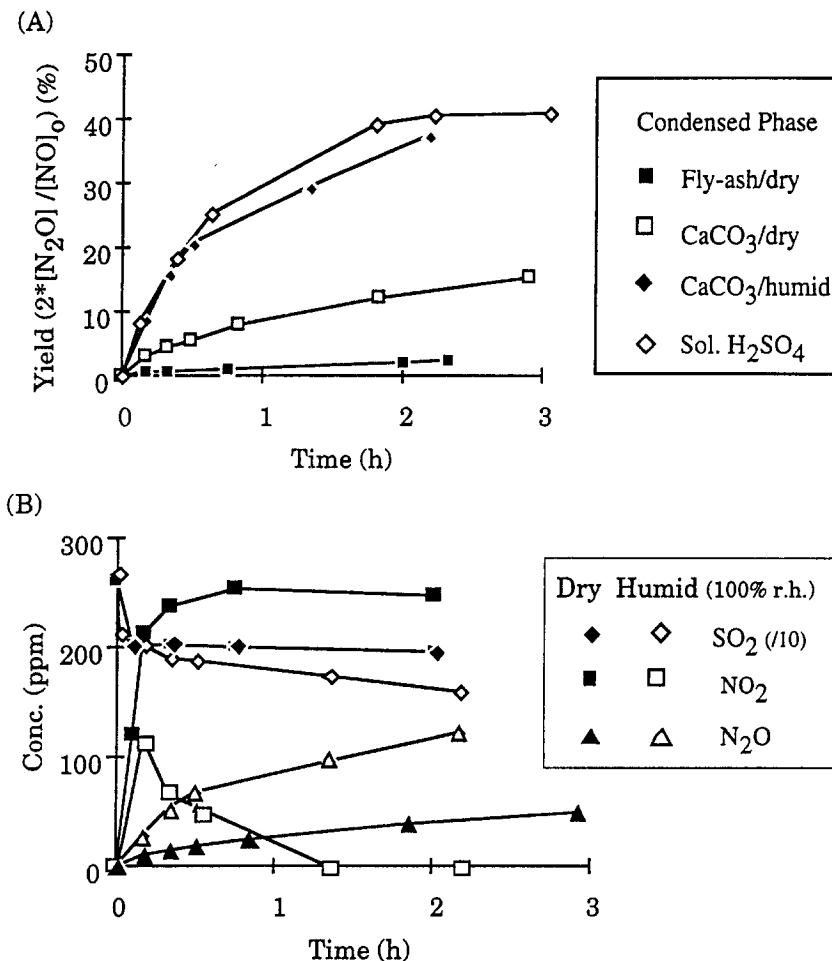


Figure 8. (A)  $\text{N}_2\text{O}$  yield and (B) concentration profiles of  $\text{SO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_2$  in the presence of a calcite surface in dry/humid systems at standard concentration conditions. The  $\text{SO}_2$  profiles in (B) were divided by 10.

two surfaces is difficult and should be made with caution. In addition, the  $\text{N}_2\text{O}$  production on the calcite surface, even in the absence of water, is two times larger than the rate of formation observed in the presence of other solid surfaces such as soot and fly ash under similar conditions. This fact may also be due to the different chemical nature of these samples.

The concentration profiles of  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{SO}_2$  as a function of time in the presence of calcite under dry (0% rh) and humid (~ 100% rh) conditions at 298 K are shown in Figure 8B. We observe the same concentration profiles using other solid surfaces under dry conditions. On the other hand, the concentration profiles change significantly in the presence of water vapor. We observe a more rapid transfer of  $\text{SO}_2$  and  $\text{NO}_2$  to the aqueous phase compared to a similar dry system.

The NO<sub>2</sub> produced by NO oxidation is completely consumed after 1 hour whereas the transfer of SO<sub>2</sub> from the gas to the condensed phase is still important even after 2 hours of reaction. The highest rate of disappearance of both NO<sub>2</sub> and SO<sub>2</sub> are observed over a calcite surface when compared to experiments using soot samples under similar concentration conditions. On the other hand, we remind the reader of the different behavior on fly-ash samples with respect to the NO<sub>2</sub> disappearance under humid conditions (Figure 7B).

The results obtained using the calcite surfaces suggest that N<sub>2</sub>O formation may not be occurring at specific active surface sites. However, reference experiments carried out either in the absence of any active surface within the reaction vessel or in the presence of the glass dish showed only an insignificant rate of N<sub>2</sub>O formation. These results suggest that the existence of active surface sites on the condensed phase substrate is necessary for appreciable N<sub>2</sub>O formation. Furthermore, these results point towards a possibly significant N<sub>2</sub>O formation occurring on surfaces made of calcite-containing building materials. However, the estimation of the importance of this source of N<sub>2</sub>O is difficult and outside the scope of this work. The very low concentration of the precursors (SO<sub>2</sub> and NO) in the atmosphere and the possible change of calcite reactivity with time due to attack by acids and physical degradation do not allow a direct correlation of the present experimental results with the environment.

In conclusion, we present a synopsis of the principal results obtained with different types of surfaces used in the presence/absence of water vapor in Figure 9. We note that the maximum initial rate as well as the final N<sub>2</sub>O yield was observed under conditions of the simultaneous presence of NIST fly ash and water vapor at high temperature (368 K) approaching quantitative conversion of NO to N<sub>2</sub>O. A generalization with respect to the fly ash behavior is not possible because the three samples studied show significant differences with respect to N<sub>2</sub>O formation. The reactivity of the fly ash seems to be related to the presence of acidic sites on the surface but it is probable that other parameters such as chemical composition and sample history may play an important role. The second highest initial rate as well as final yield of N<sub>2</sub>O formation are observed in the presence of soot at high humidity and temperature conditions (~100% rh at 368 K). The many systems studied present the following reactivity sequence with respect to rate and final yield of N<sub>2</sub>O formation:

fly ash (humid) > soot (humid) ≫ sulfuric acid solution ≈ calcite (humid)  
(298 K) > water vapor (368 K) > calcite (dry) > soot (dry) > fly ash (dry)  
≈ water vapor (298 K) ≫ dry system without condensed phase.

where 'humid' and 'dry' mean 90–100% rh at 368 K and 0% rh at 298 K, respectively, unless specified otherwise. It has to be pointed out, however, that the rates and yields of N<sub>2</sub>O have not been corrected for the contribution of the internal surfaces of the reactor. A typical result regarding a 'blank' run is shown in the third entry of the table below (Figure 9, vapor, 368 K). The blank runs at 368 K

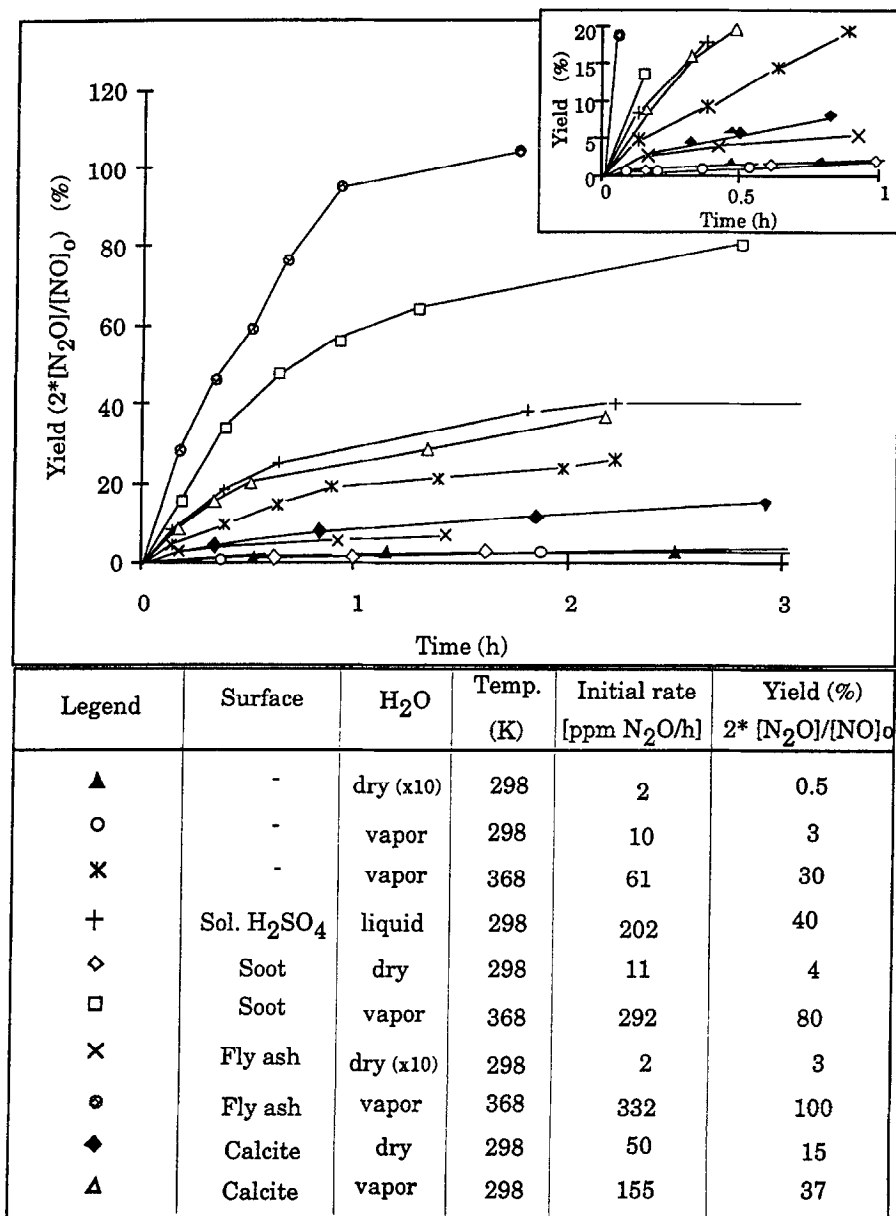


Figure 9. Effect of solid/liquid active surfaces in the presence/absence of vapor/liquid water on N<sub>2</sub>O formation at standard concentration conditions. All solid/liquid samples had a geometric surface area of 50 cm<sup>2</sup>, and the acid solution consisted of 20 ml of sulfuric acid at 0.1 M. The fly-ash used was a NIST sample and the soot originated from burning rubber.

and 100% rh result in final N<sub>2</sub>O yields of 25%, thus leading to corrections that are lower than 20% for the experiments involving soot and fly-ash.

These results point towards a potentially significant heterogeneous rate of N<sub>2</sub>O formation in exhaust gases emitted in combustion processes. The present data are obtained in laboratory experiments and provide the basis for potential applications to the environment. Based on results displayed in Figures 2 and 5 50% of the N<sub>2</sub>O yield at 368 K and 100% rh would take place in the first 20 minutes if there is sufficient particulate matter present in the exhaust plume. We estimate that this mode of formation of N<sub>2</sub>O may well represent a significant fraction of the anthropogenic portion of the global N<sub>2</sub>O source in view of the rate and efficiency with which nitrous oxide is generated. We are presently planning to undertake estimations of the source strength for N<sub>2</sub>O based on modeling calculations of combustion exhaust plumes taking into account new chemistry recently obtained from detailed mechanistic studies (Pires, 1995; Pires and Rossi, 1996).

## 5. Conclusion

The heterogeneous formation of N<sub>2</sub>O was studied in an atmosphere of controlled chemical composition in a static cell in the presence of several bulk liquid and solid condensed phases at atmospheric pressure, at two humidities (0 and 100% rh) and two temperatures (298 and 368 K). The nitrous oxide concentration was analyzed using gas chromatography coupled to electron capture detection (ECD-GC). The other reactants and intermediates (NO, SO<sub>2</sub>, NO<sub>2</sub> and HONO) were monitored using gas phase UV-VIS absorption spectroscopy.

The results obtained in these experiments are as follows: The maximum rate of N<sub>2</sub>O formation was observed at the beginning of the reaction for all experimental conditions. The N<sub>2</sub>O formation is favored in a humid compared to a dry system, both in terms of rate as well as final yield of nitrous oxide. The presence of condensed phase surfaces increases both the rate and the yield in a dry system. The simultaneous presence of high humidity (90–100% at 368 K) and condensed phase surfaces results in the *maximum rate and final yield of N<sub>2</sub>O* approaching 60 and 100% conversion after one hour in the presence of amorphous carbon and fly ash, respectively, leaving no room for nitrate formation or any other forms of nitrogen. In view of the large initial rate of N<sub>2</sub>O formation both in the presence of condensed phase substrates as well as high humidities at 368 K the expected secondary heterogeneous reactions involving NO oxidation in power plant plumes might be a potentially significant source for N<sub>2</sub>O on a global scale.

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