Catalytic and Gas–Solid Reactions Involving HCN over Limestone

Anker Jensen, Jan Erik Johnsson, and Kim Dam-Johansen
Dept. of Chemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

In coal-fired combustion systems solid calcium species may be present as ash components or limestone added to the combustion chamber. In this study heterogeneous reactions involving HCN over seven different limestones were investigated in a laboratory fixed-bed quartz reactor at 873–1,173 K. Calcined limestone is an effective catalyst for oxidation of HCN. Under conditions with complete conversion of HCN at O_2 concentrations above about 5,000 ppmv the selectivity for formation of NO and N_2O is 50–70% and below 5%, respectively. Nitric oxide can be reduced by HCN to N_2 in the absence of O_2 and to N_2 and N_2O in the presence of O_2. At low O_2 concentrations or low temperatures, HCN may react with CaO, forming calcium cyanamide, $CaCN_2$. The selectivities for formation of NO and N_2O from oxidation of $CaCN_2$ is 20–25% for both species. The catalytic activity of limestone for oxidation of HCN decreases with increasing degree of sulfation. Simultaneously the selectivity for formation of NO decreases while that for N_2O increases. The catalytic activity of sulfated limestone increases with decreasing SO_2 concentration, indicating a competition between SO_2 and HCN for sites on the surface. The results indicate that heterogeneous oxidation of HCN is important in calciners and fluidized-bed combustors with limestone addition or when burning coals with an ash with a high catalytic activity.

Introduction

Combustion of coal for production of electricity, heat, and process steam is a major contributor to the emission of environmentally harmful oxides of nitrogen (NO, NO_2, N_2O) (Bowman, 1992). In most modern coal combustion processes fuel nitrogen is the major source of nitrogen oxides. During devolatilization, the nitrogen in the fuel is split into volatile nitrogen and nitrogen in the char (Johnsson, 1994). The volatile nitrogen is released with the tar and gases such as NH_3, HNCO, and HCN (Baumann and Möller, 1991; Nelson et al., 1991, 1992, 1996; Kambara et al., 1993; Bassilakis et al., 1993; Niksa, 1995). Hydrogen cyanide may also be formed from secondary pyrolysis of the tar (Haussmann and Kruger, 1990) as confirmed by pyrolysis experiments using tar model compounds (Axworthy et al., 1978; Houser et al., 1980; Doughty et al., 1994; Doughty and Mackie, 1994). Hydrogen cyanide is the most important gaseous nitrogen species for high-rank coals, but the fraction of fuel nitrogen released as NH_3 increases with decreasing rank (Chen et al., 1982; Bose et al., 1988). The conclusion is that both NH_3 and HCN are important volatile nitrogen species in coal combustion and they are precursors for nitrogen oxides, as discussed below.

Gas-phase oxidation of NH_3 primarily yields NO and N_2, although minor amounts of N_2O have been reported (Hulgaard and Dam-Johansen, 1993; Kasuya et al., 1995; Caton et al., 1995). At high temperatures the products of gas-phase HCN oxidation are mainly NO and N_2, but in the temperature range 1,000–1,200 K, the operating range of fluidized-bed combustors (FBC), significant amounts of N_2O are formed (Hulgaard and Dam-Johansen, 1993; Khan et al., 1993).

When solids are present in the combustion chamber, heterogeneous pathways for conversion of volatile nitrogen may become important. Calcium species ($CaCO_3$, CaO, $CaSO_4$, CaS) are frequently present in combustion chambers, either due to addition of limestone (of which the main constituent is $CaCO_3$) or because the ash contains calcium. The calcium content may be high, especially in low-rank coal (lignite) ashes. It has been reported that calcium species may catalyze

---

Correspondence concerning this article should be addressed to A. Jensen.

a number of reactions related to formation and reduction of nitrogen oxides (Johnsson, 1994). Reactions related to the formation of nitrogen oxides are discussed below.

Oxidation of NH_3 catalyzed by calcined or partly sulfated limestone has been investigated by several investigators (Lee et al., 1985, 1987; Yasunaga and Furusawa, 1986; Iisa et al., 1991; de Soete and Nastoll, 1991; Shimizu et al., 1993; Lin et al., 1993, 1994; Bruun and Møller, 1994). For oxidation of NH_3 over calcined limestone it is generally found that NH_3 is oxidized to NO with a selectivity in the range 50–80%, which is higher than for the homogeneous reactions. The selectivity for formation of N_2O is much lower. Lin et al. (1994) reported values less than 1%, and Iisa et al. (1991) found a maximum selectivity of 16% for N_2O with 2,000 ppmv NO and 2,000 ppmv NH_3 in the inlet gas. The selectivity for NO formation and the catalytic activity decreases during sulfation of the limestone (Lin et al., 1994; Bruun and Møller, 1994), mostly because $CaSO_4$ has a lower catalytic activity than CaO and partly because the active surface area decreases due to filling of the pores, since the molar volume of $CaSO_4$ (46.0 cm^3/mol) is larger than that of CaO (16.9 cm^3/mol). The study by Lee et al. (1987) indicates that the lower selectivity for NO formation may be due to reduction of NO by NH_3 catalyzed by $CaSO_4$. Recently, Kiil et al. (1996) reported a model for the simultaneous sulfation of a limestone particle and oxidation of NH_3, which can describe qualitatively the decrease in NO selectivity with an increasing degree of sulfation.

Catalytic oxidation of HCN over calcium species has been investigated less than NH_3 oxidation. Calcined limestone has been reported to be an effective catalyst for oxidation of HCN (de Soete and Nastoll, 1991; Shimizu et al., 1992, 1993, 1994), and the reported selectivity for NO formation is typically in the range 40–70% when the O_2 concentration is above 5,000 ppmv. There is agreement that the selectivity for N_2O formation is low, less than 10%. Jensen et al. (1993) reported a study of HCN oxidation and simultaneous sulfation of the limestone. It was found that for six different types of limestone the catalytic activity and the selectivity for NO formation decreased by sulfation of the limestone. Simultaneously the selectivity for formation of N_2O increased from almost zero to about 10%. The influence of sulfation on HCN oxidation thus appears to be similar to the case of NH_3 oxidation.

The reactions just discussed are of potential importance for understanding the formation of nitrogen oxides in industrial combustion systems. In FBC limestone is added for sulfur capture and typically a Ca/S ratio of 2–3 is used to obtain sufficient sulfur capture (Zhang et al., 1992). Addition of limestone to FBC often results in a higher emission of NO and a lower emission of N_2O (Moritomi et al., 1991; Moritomi and Suzuki, 1992; Gavin and Dorrington, 1993; Åmand et al., 1993), indicating the importance of the reactions discussed earlier. A detailed discussion of the nitrogen chemistry in FBC with limestone addition can be found in Jensen et al. (1996). In the cement industry there has been a growing interest in low-NO_x calciners because more stringent legislation is expected (Syverud et al., 1994; Deussner, 1995; Jeschar et al., 1996). In calciners limestone is calcined in a gas–solid suspension and coal or coke is burned to produce the necessary heat. The operating temperature of calciners is similar to FBC, but the Ca/S ratio is much higher and the limestone is essentially unsulfated. Reburning is a method to reduce the emission of NO_x by injecting a reburning fuel after the primary combustion zone, forming a reducing zone where NO is reduced to N_2, NH_3, and HCN. Traditionally, gas has been used as reburning fuel, but coal has been considered for economical reasons. Burch et al. (1991) investigated lignite as a reburning fuel and suggested that HCN was converted to NH_3 over the fly ash in the reburning zone. In a subsequent study Chen and Ma (1996) reported significant reduction of NO over lignite char. This indicates that heterogeneous reactions may be important in lignite reburning, and suggests that catalytic oxidation of HCN or NH_3 over ash in the burnout zone is of importance, too.

The objective of this study is to investigate the reactions involving HCN and calcium species in the form of limestone in a fixed-bed quartz reactor in order to improve the understanding of how nitrogen oxides are formed and reduced in combustion systems where calcium species are present. Seven different limestone types have been investigated. The influence of temperature, HCN inlet concentration, O_2 concentration, sulfation of the limestone, and NO concentration on oxidation of HCN is reported.

Experimental Studies

The experiments were performed in the fixed-bed reactor made of quartz shown in Figure 1. The reactor was placed in an electrically heated three-zone oven that gave a good temperature control and a flat temperature profile in the reaction zone. The inner and bottom sections of the reactor were removable, and the solids were placed on the porous quartz plate and reinserted without changing the oven temperature. The main gas inlet was positioned in the bottom of the reactor (1), which functioned as a preheating section. A second gas stream could be introduced through the tube at the top of the reactor (2). With this arrangement, reactant gases could be kept separate until mixed, just above the solids placed on the porous quartz plate. The reactor temperature was measured below the porous quartz plate by a thermocouple shielded by a quartz tube (3). There was a steep temperature gradient in the outlet section in order to limit homogeneous reactions, and the gases left the reactor through the outlet (4) to flow to the analyzers. Two different diameters of the porous quartz plate supporting the solids were used, depending on the amount of limestone: large (16 mm) and small (8 mm). The gas residence time from the point where the primary and secondary gases mix and down to the porous quartz plate was 43 ms with the large (16-mm) quartz plate for a total gas flow of 2000 NmL/min. The residence was not significantly influenced by the presence of solids in the reactor because the bed is very shallow, only a few particle diameters high. Hydrogen cyanide entered the reactor through the inlet (2) together with a flow of N_2 to give a total flow of about 900 NmL/min. The other gases (N_2, NO, SO_2, O_2) were introduced through the main inlet in the bottom at a rate of 900–1,200 NmL/min. The flow rates of the individual gases were controlled by mass-flow controllers and the actual flow rates were measured by means of a bubble flowmeter. The gas analyzers were conventional continuous IR (CO, CO_2, N_2O), UV (NO, SO_2), and paramagnetic (O_2) analyzers from Hartmann & Braun, except for the N_2O analyzer, which was from Perkin-Elmer (Spectran 647). The NO and N_2O analyz-

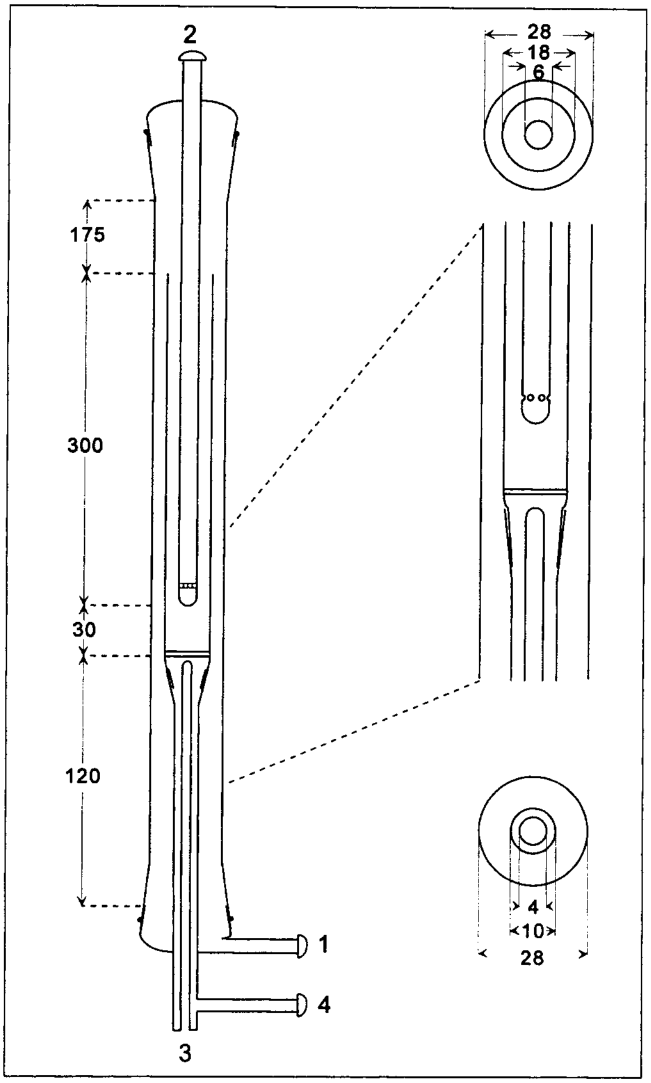

Figure 1. Fixed bed reactor for the study of heterogeneous reactions.

1 = Main inlet; 2 = secondary inlet; 3 = thermocouple; 4 = outlet to gas analyzers. All figures are in mm.

ers were cross sensitive to SO_2, and therefore SO_2 was removed by scrubbing the gas in a 1-M Na_2CO_3 solution in a bubble flask before the NO and N_2O analyzers. The N_2O analyzer was cross sensitive to H_2O, and excess water was removed in a condenser at 273 K after scrubbing for SO_2 removal. The analyzers were calibrated every day before starting experiments, by means of certified calibration gases. Hydrogen cyanide was measured by an on-line gas chromatograph (GC) equipped with a Flame Ionization Detector in some of the experiments. The column was a Porapak Q 80/100 mesh kept at 393 K. The GC made one measurement every 8.5 min, but it was necessary to make measurements 3–4 times to get a steady value, and therefore the GC results are only qualitative during transient experiments.

Seven limestones were tested in the present work and their chemical composition is given in Table 1, while the physical characteristics of the limestones are presented in Table 2. The data for limestones 1, 2, 4, and 5 are taken from Dam-Johansen (1987) and van der Lans (1994), whereas the data for limestones 3, 6, and 7 were measured in this study by Hg-porosimetry. The presence of CO_2 in the calcination procedure by Dam-Johansen (1987) and van der Lans (1994) may result in a lower BET surface area compared to the procedure used in this study, in which the limestone was calcined in N_2. The pore-size distribution of the calcined limestones 3, 6 and 7 was not bimodal, and consequently macro- and micropore sizes are not given for these limestones. Dam-Johansen and Østergaard (1991) classified the limestones according to their sulfur capture capacity. Stevns Chalk is a geologically young porous and soft limestone with a high sulfur capture capacity, whereas the other limestones are relatively soft, geologically young limestones with an intermediate sulfur capture capacity. Chichibu limestone (7) was used in an earlier study of limestone catalyzed HCN oxidation by Shimizu et al. (1992, 1993).

Before each experiment the limestone sample was calcined at temperatures of 1,073–1,173 K in an N_2 flow according to Reaction R1 until no more CO_2 was detected in the reactor outlet:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g). \tag{R1}$$

Most of the experimental results are presented as conversion of HCN, X_{HCN}, and selectivities for formation of NO and N_2O, ϕ_{NO} and ϕ_{N_2O}, respectively, defined by

$$X_{HCN} = \frac{\text{mol of HCN in} - \text{mol of HCN out}}{\text{mol of HCN in}} \tag{1}$$

$$\phi_{NO} = \frac{\text{mol of NO formed by HCN oxidation}}{\text{mol of HCN oxidized}} \tag{2}$$

Table 1. Chemical Composition of Limestones*

		Chemical Composition (wt. %)						
Limestone	No.	CO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Other
Faxe Bryozo	1	43.6	0.45	0.10	0.08	55.1	0.43	0.24
Stevns Chalk	2	43.6	0.36	0.07	0.04	55.2	0.29	0.44
Köping Fine	3	40.0	4.0	0.9	0.9	51.0	1.3	1.9
Faxe Bryozo Fe	4	43.4	0.55	0.11	0.58	54.8	0.31	0.25
Ignaberga	5	40.1	8.33	0.39	0.22	49.8	0.55	0.61
Gotland	6	41.5	3.33	1.27	0.65	50.7	1.37	1.18
Chichibu	7	43.3	0.60	0.80	0.30	54.3	0.67	0.03

*The composition of limestone 1, 2, and 4–6 from Dam-Johansen and Østergaard (1991). The composition of limestone No. 3, Köping Fine, from Mjörnell et al. (1991). The composition of No. 7, Chichibu, was recalculated from Shimizu et al. (1993).

Table 2. Physical Characteristics for Calcined Limestones*

Limestone	1**	2**	3†	4**	5**	6†	7†
Specific surface (m^2/g)	14.3	17.0	9.34	18.2	17.0	23.7	16.2
Macropore vol. (mL/g)	0.55	0.37	—	0.15	0.17	—	—
Micropore vol. (mL/g)	0.24	0.21	—	0.25	0.18	—	—
Total pore vol. (mL/g)	0.79	0.58	0.26	0.40	0.35	0.23	0.12
Macropore radius (nm)††	400	500	—	—‡	400	—	—
Micropore radius (nm)††	35	27.5	—	27.5	25	—	—
Particle density (g/mL)	0.90	1.09	1.32	1.20	1.54	1.49	1.54

*For limestones 1, 2, 4 and 5, the calcination was performed at 1123 K in a flow with 4 vol. % O_2 and 10 vol. % CO_2, Dam-Johansen (1987) and van der Lans (1994). For limestones 3, 6 and 7, the calcination was performed at 1,123 K in a flow of N_2.
**BET area.
†From Hg-porosimetry.
††The stated values are mean pore radii obtained from the pore-size distribution.
‡Not stated.

$$\phi_{N_2O} = \frac{2\cdot(\text{mol of } N_2O \text{ formed by HCN oxidation})}{\text{mol of HCN oxidized}}. \quad (3)$$

The calculated conversion of HCN was based on the measured outlet concentrations of CO and CO_2. The N_2O selectivity is calculated from Eq. 3 also when NO is present in the inlet gas, even though one of the N atoms in N_2O may come from NO in the inlet gas. All the results are presented as measured values, except if specifically stated otherwise.

Experimental Results

HCN oxidation over calcined limestone

Faxe Bryozo and Stevns Chalk were tested in the study of HCN oxidation over calcined limestone. The conversion of HCN in the empty reactor was first investigated to be able to interpret the results with limestone in the reactor with greater confidence.

Oxidation of HCN in the Empty Reactor. The reactor is designed to minimize homogeneous reactions, but some oxidation of HCN does take place in the empty reactor. Figure 2 shows the influence of temperature on HCN oxidation in the empty reactor. At each temperature level the influence of 175 ppmv NO was tested. The presence of NO did not influence the oxidation of HCN and the formation of CO and CO_2 significantly, and only one set of curves for HCN conversion and CO and CO_2 is shown. The conversion of HCN increases from about 7% at 873 K to 42% at 1,173 K. Without NO in the inlet gas, the NO and N_2O outlet concentrations reach 40 ppmv and 8 ppmv respectively, at 1,173 K. The N_2O outlet concentration is higher with NO in the inlet gas than without NO present, which is consistent with the homogeneous reaction (Glarborg and Miller, 1994):

$$NCO(g) + NO(g) \rightleftharpoons N_2O(g) + CO(g). \qquad (R2)$$

An increase in the CO outlet concentration (not shown in Figure 2) was also observed in the presence of NO, which supports that Reaction R2 was taking place. In most of the experiments with limestone the O_2 concentration was lower than that used in the experiments in Figure 2, and so the conversion in the empty reactor will be lower than shown in Figure 2. The reactions with nonlinear rate expressions are complex, and the results with limestone in the reactor have not been corrected for the reactions in the empty reactor.

Influence of Temperature. Figure 3 shows the outlet concentrations of CO_2, CO, NO, and N_2O as a function of temperature, with Stevns Chalk as catalyst. At each temperature level the effect of 175 ppmv NO on the inlet gas was investigated. The same data are plotted as conversion of HCN and selectivities for NO and N_2O in Figure 4. The catalytic effect of calcined Stevns Chalk, which appears from a comparison with the results from the empty reactor is significant (Figure 2). The conversion of HCN is 65% at 823 K, increasing to 100% at temperatures above 973 K, and the NO selectivity increases from about 25% at 823 K to 64% at 1,173 K. The NO selectivity is lower when NO is present in the inlet gas, but the difference is reduced with a rising temperature. The NO selectivities reported here are in fair agreement with the values reported by de Soete and Nastoll (1991) and Shimizu et al. (1993, 1994). Interestingly, significant amounts of N_2O are formed at low temperatures. A maximum of almost 17 ppmv is formed at 923 K, and with 175 ppmv NO present in the inlet gas, almost 30 ppmv is formed, which corresponds to selectivities of 12% and 23%, respectively. At high tempera-

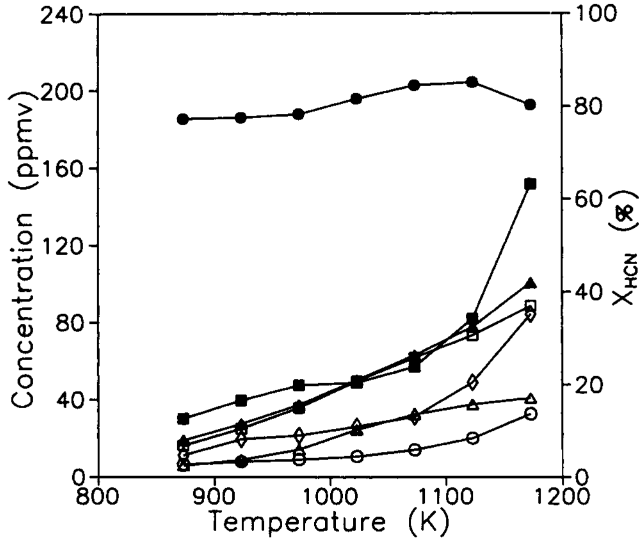

Figure 2. Influence of temperature and NO and HCN oxidation in the empty reactor.

Flow rate: 1748 NmL/min. Inlet concentrations: 290 ppmv HCN, 1 vol. % O_2, 0.0 and 175 ppmv NO. ○: CO; □: CO_2; △: NO; ◇: N_2O*10; ●: NO (175 ppmv NO in); ■: N_2O*10 (175 ppmv NO in); ▲: X_{HCN}.

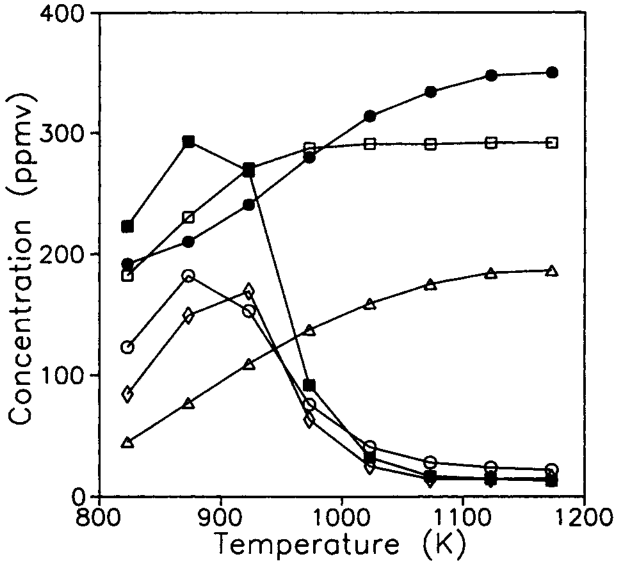

Figure 3. Influence of temperature and NO on HCN oxidation over calcined limestone.

Flow rate: 1748 NmL/min. Limestone: Stevns Chalk. Mass of uncalcined limestone: 0.2451 g. Particle diameter: 0.25–0.3 mm. Inlet concentrations: 290 ppmv HCN, 1 vol. % O_2, 0.0, and 175 ppmv NO. □: CO_2; ○: CO*10; △: NO; ◇: N_2O*10; ●: NO (175 ppmv NO in); ■: N_2O*10 (175 ppmv NO in).

tures, however, the N_2O selectivity is close to zero. It is known that N_2O decomposes over calcined limestone (Iisa et al., 1991; Shimizu and Inagaki, 1993; Hansen and Dam-Johansen, 1993; Johnsson et al., 1997). Calculation of the intrinsic N_2O selectivity was attempted by correcting for N_2O decomposition over the limestone, as described in detail elsewhere (Jensen, 1996). The corrected N_2O selectivity is shown in Figure 4 for the case with NO in the inlet gas. It can be seen that the intrinsic N_2O selectivity is significantly higher than the observed N_2O selectivity, indicating that N_2O decomposition over limestone is important. However, even the intrinsic selectivity decreases with increasing temperature, which is in agreement with the observations of Shimizu et al. (1993).

Influence of O_2 Concentration. Experiments were performed at 1025 K with Stevns Chalk to test the influence of O_2 and NO on HCN oxidation. Figure 5 shows the influence of O_2 with and without 520 ppmv NO in the inlet gas. In the absence of NO, the conversion of HCN increases from about 70% at 300 ppmv O_2 to 100% for O_2 concentrations above 1 vol. %. The selectivity for NO formation increases from 15% to 56% when the O_2 concentration increases from 300 ppmv to about 3 vol. %. The selectivity for N_2O formation increases from 2% at 300 ppmv O_2 to a maximum of 6–8% at 2,000 ppmv O_2 and then decreases with increasing O_2 concentration. The HCN conversion with NO present is slightly higher than without NO when the O_2 concentration is below 1 vol %. The selectivity for NO formation is negative at low O_2 concentration and lower than without NO in the inlet, indicating that NO is reduced by HCN. Part of the NO is reduced to N_2O as shown by the higher N_2O selectivity with NO in the inlet. Experiments without NO in the inlet gas were also performed with Faxe Bryozo at 1,015–1,167 K, and

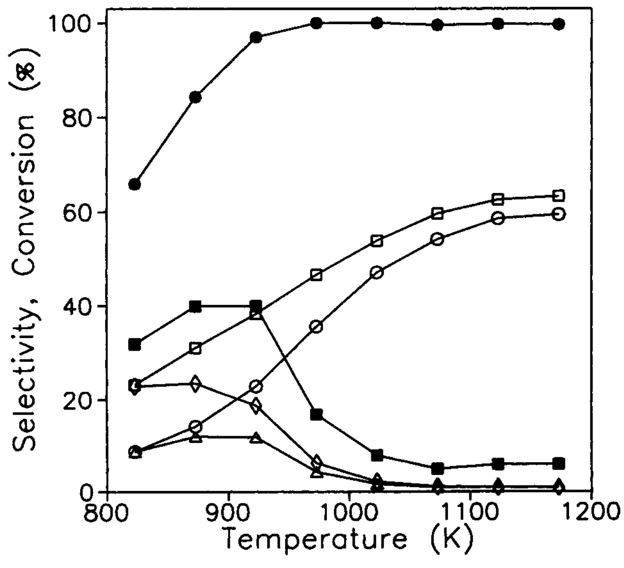

Figure 4. Influence of temperature and NO on HCN oxidation over calcined limestone.

Flow rate: 1,748 NmL/min. Limestone: Stevns Chalk. Mass of uncalcined limestone: 0.2451 g. Particle diameter: 0.25–0.3 mm. Inlet concentrations: 290 ppmv HCN, 1 vol. % O_2, 0.0 and 175 ppmv NO. □ NO; ○: NO (175 ppmv NO in); △: N_2O; ◇: N_2O (175 ppmv NO in); ■: N_2O (175 ppmv NO in) corrected; ●: HCN conversion.

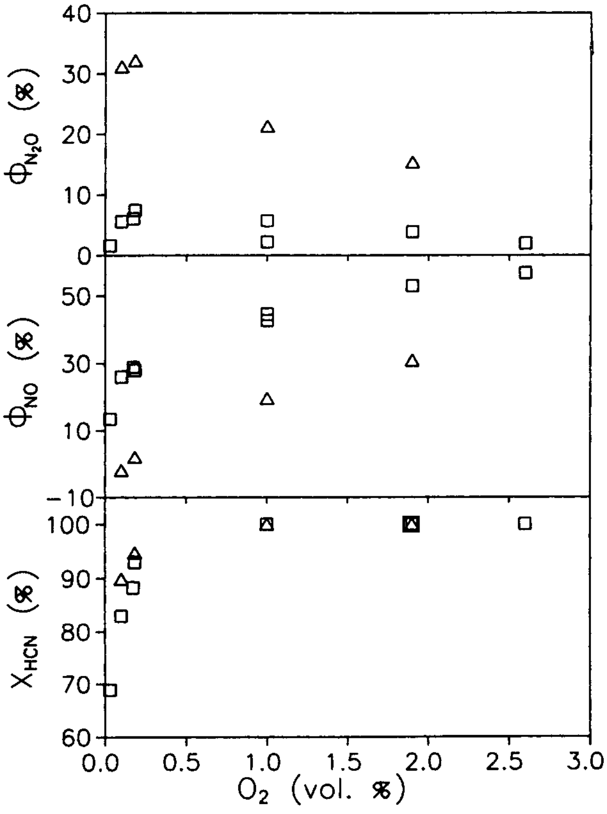

Figure 5. Influence of O_2 and NO on oxidation of HCN over calcined limestone.

Temperature, 1,025 K; flow rate, about 1,860 NmL/min; limestone, Stevns Chalk; mass of uncalcined limestone, 0.25 g; particle diameter, 0.25–0.3 mm; inlet concentration, 396–420 ppmv HCN; □, without NO; △, 520 ppmv NO.

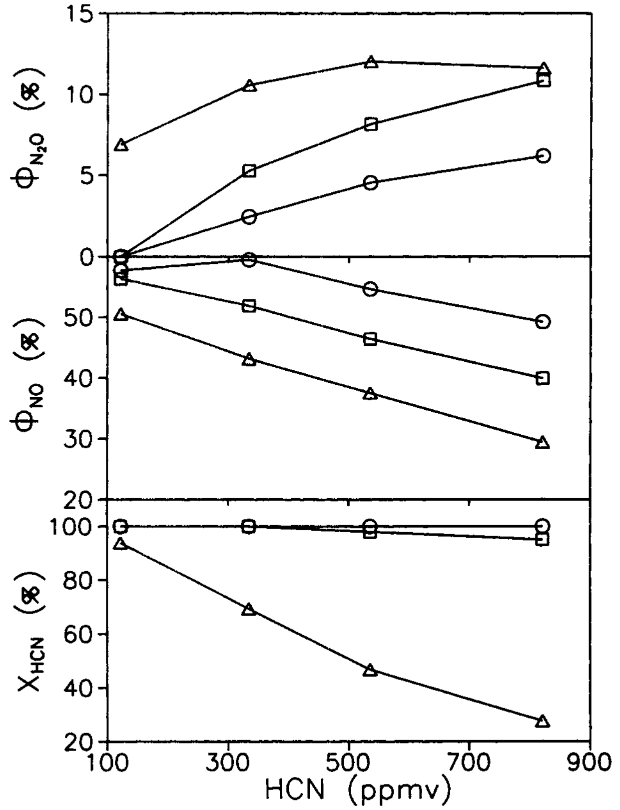

Figure 6. Influence of HCN concentration on HCN oxidation over calcined limestone.

Flow rate, 1,770–2,030 NmL/min.; limestone, Faxe Bryozo; mass of uncalcined limestone, 0.0656 g; particle diameter, 0.25–0.3 mm; inlet concentration of O_2, 0.52–0.59 vol. %; ○, 1167 K; □, 1,117 K; △ 1,015 K.

the results were similar to those obtained for Stevns Chalk (Jensen, 1996).

Influence of HCN Concentration. The influence of HCN inlet concentration was investigated for Faxe Bryozo at temperatures of 1,015 K, 1,117 K, and 1,167 K, and the results are shown in Figure 6. At 1,117 K and 1,167 K, the conversion of HCN is close to 100% for all HCN inlet concentrations. However, the HCN conversion decreases with an increasing inlet HCN concentration at the low temperature of 1,015 K, indicating that the reaction order with respect to HCN is less than 1. The NO selectivity increases with decreasing HCN inlet concentration and a rising temperature, the maximum selectivity being about 60%. The N_2O selectivity shows the opposite trend and reaches a maximum selectivity of 12% at 1,015 K and inlet concentrations above 500 ppmv HCN. Shimizu et al. (1993) observed the same influence of HCN inlet concentration using limestone 7 (Chichibu) of this study.

Formation and Oxidation of $CaCN_2$. In experiments with a high HCN concentration surrounding the limestone particles, that is, at low O_2 concentration, at low temperature and/or high HCN inlet concentration, a solid product was sometimes formed. This was especially severe in a preliminary study of the kinetics of HCN oxidation over calcined Faxe Bryozo (Klug and Michelsen, 1992), where the conversion of HCN was kept low. The formation of this solid product resulted in a transient decrease in the catalytic activity of the limestone throughout an experiment. The phenomenon appeared similar to coking of refinery catalyst particles, and sometimes the limestone turned black. During combustion of this residue CO, CO_2, NO, and N_2O was formed. An experiment was performed where HCN was passed through a bed of calcined limestone and the solid product subjected to IR analysis. The IR spectrum showed that the solid product was $CaCN_2$, calcium cyanamide. de Soete and Nastoll (1991) investigated the reaction between HCN and calcined limestone but did not report the formation of $CaCN_2$.

The oxidation of $CaCN_2$ at 1,023 K was investigated after it was formed by reacting HCN with calcined Stevns Chalk for a given time. When HCN was removed from the inlet gas, O_2 was added and the solid product burned off. In Figure 7 the outlet concentrations of CO_2, CO, NO and N_2O are shown vs. time for an experiment with inlet concentrations of 420 ppmv HCN and 0.5 vol. % O_2 in the two periods, respec-

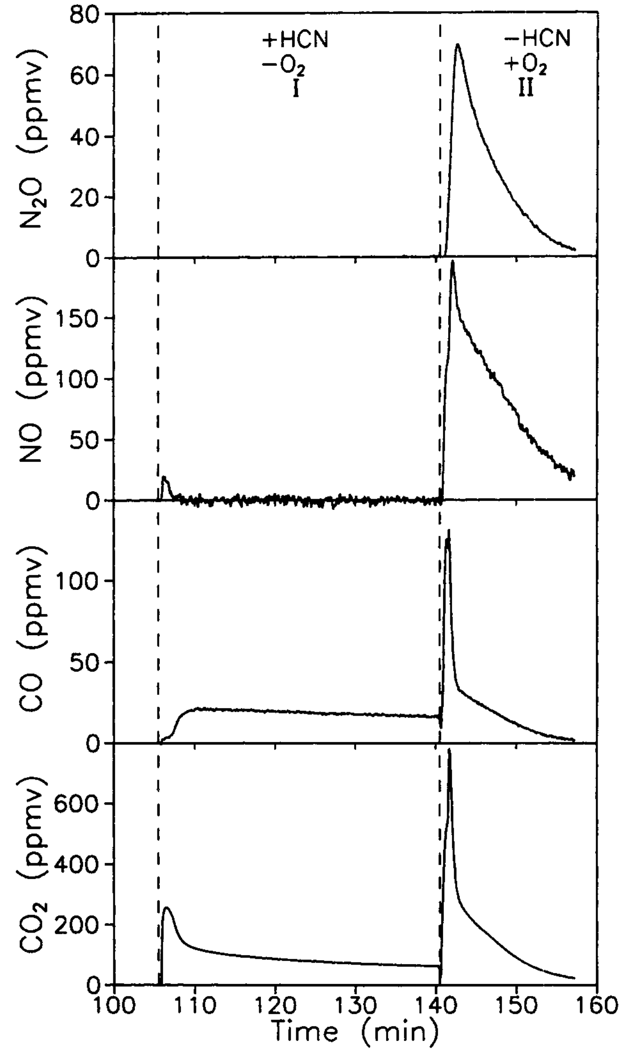

Figure 7. Reaction between calcined limestone and HCN with subsequent combustion of the reaction product.

Temperature, 1,023 K (limestone calcined at 1,123 K); flow rate, 1,783 NmL/min; limestone, Stevns Chalk; mass of uncalcined limestone, 0.2498 g; particle diameter, 0.25–0.3 mm; inlet concentrations, 420 ppmv HCN, 0.5 vol. % O_2.

tively. When HCN reacts with CaO, that is, in period I, the only gaseous products are CO and CO_2, with CO_2 as the main product. The formation of CO_2 indicates that $CaCN_2$ is formed, for example, according to the overall reaction (Reaction R3) (*Ullman's Encyclopedie*, 1985):

$$4HCN\,(g) + 2CaO\,(s) \rightleftharpoons 2CaCN_2\,(s) + C\,(s) + CO_2\,(g) + 2H_2\,(g). \quad (R3)$$

In period II HCN is removed and O_2 is introduced. In the oxidation period the products CO, CO_2, N_2, N_2O and NO are formed. The integral NO and N_2O selectivities from oxidation of $CaCN_2$, defined as mole N in NO or N_2O formed per mole N oxidized, were calculated from four experiments at 1,023 K with 0.5–1.0 vol. % O_2 in the oxidation period. The selectivities were found to be 20–22% for NO and 20–28 % for N_2O. In a single experiment $CaCN_2$ was burned in the presence of 1,000 ppmv O_2 and 550 ppmv NO. In this case the NO and N_2O selectivities were zero and 40%, respectively, indicating that part of the NO is reduced to N_2O. Further experimental work is required on this matter.

Reduction of NO by HCN. The reaction between NO and HCN over calcined Stevns Chalk was investigated (Figure 8). In period I between 180 and 207 min, there is 420 ppmv HCN and 280 ppmv NO in the inlet gas. Nitric oxide is reduced to about 20 ppmv and the CO and CO_2 concentrations are 40 ppmv and 200 ppmv, respectively. The oxygen in these two compounds corresponds to 220 ppmv O_2, which is more than released by reduction of NO. This indicates that some of the oxygen comes from CaO and that $CaCN_2$ is formed simultaneously. When changing from period I to period II at 207 min, hydrogen cyanide is removed from the inlet gas and the NO inlet concentration increases to 300 ppmv due to the lower total flow. There is a rapid decrease in the CO and CO_2 outlet concentrations, followed by a slower transient decrease. The NO outlet concentration is initially low and then increases slowly, indicating that NO is reduced by a reaction with $CaCN_2$ formed in the first period. The gaseous products are CO and CO_2 and a very small amount of N_2O is also formed. In period III, NO is removed from the inlet gas and the remaining $CaCN_2$ is burned off. It is interesting that N_2O is not formed by the reaction between NO and $CaCN_2$. Nitrous oxide is only formed in the presence of O_2, but the presence of NO enhances N_2O formation. This is similar to the formation of N_2O from char oxidation (Krammer and Sarofim, 1994; Mochizuki et al., 1992).

Discussion of HCN Oxidation over Calcined Limestone. Polyanchikov et al. (1976) proposed a reaction mechanism with 15 elementary reactions for formation of $CaCN_2$ by the reaction between HCN and CaO. The proposed mechanism involves adsorption of HCN on CaO and further reaction of adsorbed cyano species to finally form $CaCN_2$. The experimental results showed that $CaCN_2$ was formed under conditions with a high HCN concentration surrounding the limestone particles even with O_2 present. This indicates that the first step in oxidation of HCN is adsorption of HCN. Adsorbed HCN may react either along the path forming $CaCN_2$ or be oxidized. Once $CaCN_2$ is formed it may also be oxidized to gaseous products. Under conditions with a low HCN concentration the surface coverage of adsorbed cyano species is low, and consequently the rate of $CaCN_2$ formation and its subsequent oxidation is also low. Under these conditions the experimental results show that NO and N_2 are the main products, whereas insignificant amounts of N_2O are formed. Oxidation of $CaCN_2$, on the other hand, leads to significant formation of N_2O. These steps are shown in Figure 9. The steps should not be considered as elementary steps, except perhaps for the adsorption of HCN. The discussion indicates that the chemistry of HCN oxidation over calcined limestone is complex and consists of a system of both catalytic reactions and gas–solid reactions. Further discussion of the mechanism of HCN oxidation and a preliminary mathematical model based on the reaction steps in Figure 9 is presented elsewhere (Jensen, 1996).

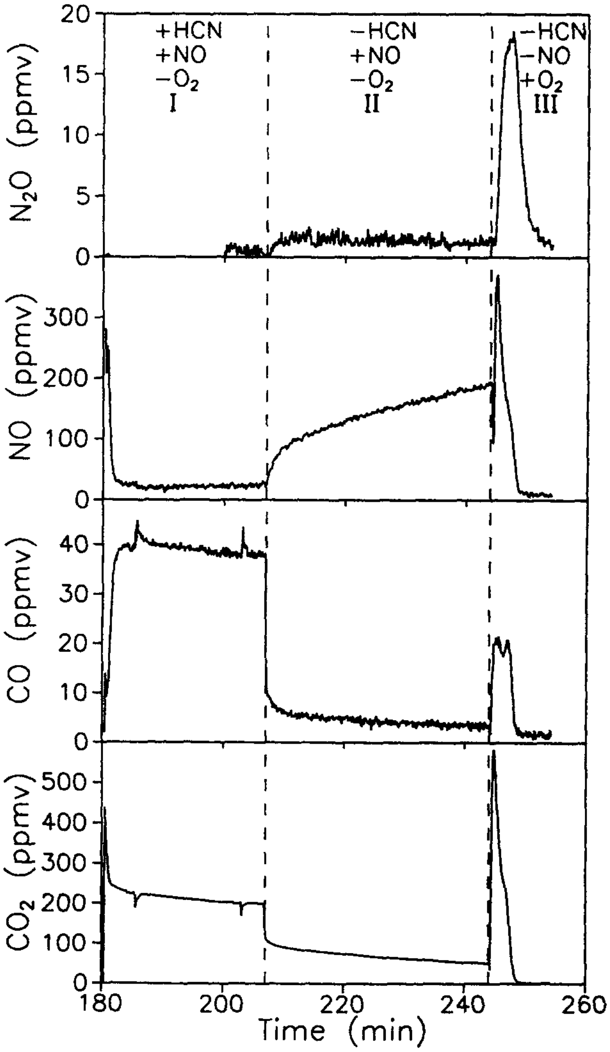

Figure 8. Reduction of NO by HCN and over $CaCN_2$.

Temperature, 1,123 K; flow rate, 1,940 NmL/min (with HCN); 1,792 NmL/min (without HCN); limestone, Stevns Chalk; mass of uncalcined limestone, 0.2492 g; particle diameter, 0.25–0.3 mm; period I, 420 ppmv HCN and 280 ppmv NO; period II, 300 ppmv NO; period III, 5,700 ppmv O_2.

Oxidation of HCN and simultaneous sulfation

The seven limestones in Table 1 were tested as catalysts to investigate the influence of limestone type on sulfation and

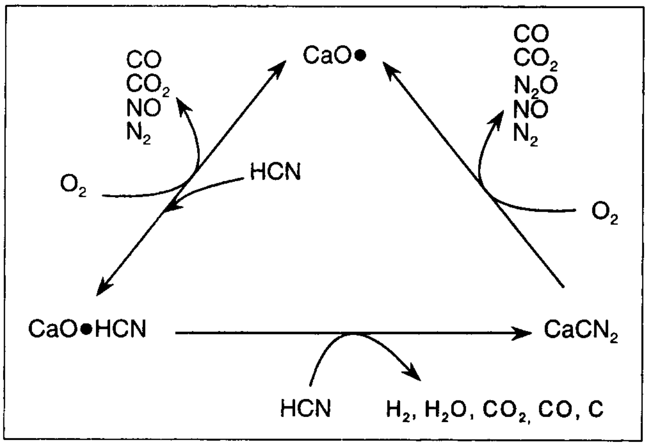

Figure 9. Qualitative mechanism for oxidation of HCN over calcined limestone.

oxidation of HCN. Faxe Bryozo and Stevns Chalk were tested more systematically for the influence of particle size and NO and SO_2 concentrations. Furthermore, the decomposition of sulfated limestone by HCN in the absence of O_2 was briefly investigated.

Oxidation of HCN in the Empty Reactor in the Presence of SO_2. It is known that the presence of SO_2 influences the homogeneous oxidation of HCN (Dam-Johansen et al., 1993) and consequently HCN oxidation in the presence of SO_2 was tested in the empty reactor. The conversion of HCN decreased from about 30% at zero SO_2 concentration to an asymptotic level of 17–19% for SO_2 concentrations above 400 ppmv. Similarly, the NO selectivity decreased from 32–36% to 14–22%, and less than 2 ppmv N_2O was formed throughout the experiments.

Description of an Experiment. The conversion of HCN in the empty reactor was measured before limestone was added to the reactor and calcined in a flow of N_2. Then a period with HCN oxidation over calcined limestone followed before SO_2 was introduced and the limestone was sulfated. In some experiments the effect of removing SO_2 from the inlet gas after sulfation of the limestone was investigated, and the flow rate of N_2 was immediately adjusted to keep the total flow constant. The outlet concentrations in a typical experiment are shown in Figure 10 as a function of time. The experimental conditions are given in the figure caption. Hydrogen cyanide was measured with the GC, except in the period when the empty reactor was tested. Oxidation of HCN in the empty reactor in the presence of SO_2 was tested from 5 to 55 min, period I. A slow transient decrease in the outlet concentrations is observed, probably due to reaction of HCN with adsorbed oxygen on the reactor walls. The limestone was calcined in period II from 55 min to 88 min, and no concentrations are shown for this period. In period III, oxidation of HCN over calcined limestone starts at 89 min. The conversion of HCN and the NO selectivity are about 80 and 62%, respectively, and the N_2O selectivity is almost zero. In period IV, SO_2 was added to the inlet gas and the limestone was sulfated. The outlet HCN concentration increased and the outlet concentrations of CO_2 and NO decreased, indicating that the rate of HCN oxidation decreased. On the other hand, the concentrations of CO and N_2O increased, partly because $CaSO_4$ has a lower catalytic activity than CaO for CO oxidation (Dam-Johansen et al., 1993), and N_2O decomposition (Shimizu and Inagaki, 1993; Johnsson et al., 1997). When SO_2 was removed after 208 min, period V, the rate of HCN oxidation increased, as seen from the decreasing outlet concentration of HCN and increasing CO_2 and NO outlet concentrations. Lin et al. (1994) investigated NH_3 oxidation over limestone 1 and 2 of this study during simultaneous sulfation. As discussed in the introduction, the catalytic activity decreased with increasing degree of sulfation, as observed for HCN oxidation in this study, but the activity of the completely sulfated limestone for NH_3 oxidation was almost negligible. Furthermore, Lin et al. (1994) found no change in the activity when removing SO_2 from the inlet gas, as opposed to this study where a significant effect is seen. The results indicate that the mechanisms for the catalytic oxidation of HCN and NH_3 are different.

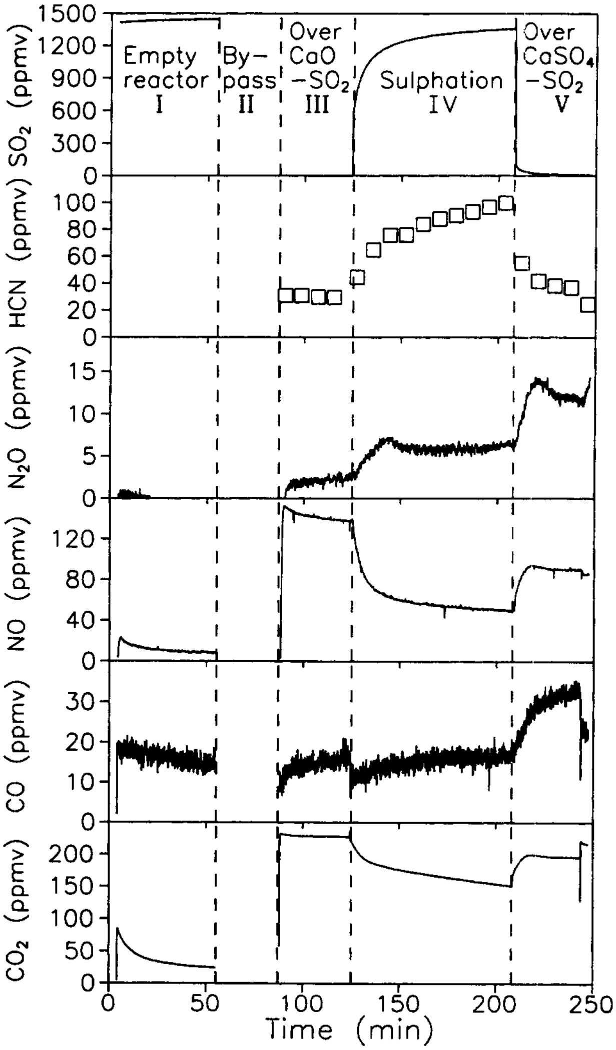

Figure 10. Example of an experiment with simultaneous sulfation of limestone and oxidation of HCN.

Temperature, 1,123 K; flow rate, 2,000 NmL/min; limestone, Stevns Chalk; mass of uncalcined limestone, 0.2501 g; particle diameter, 1.7–2.0 mm; inlet concentrations in period IV, 296 ppmv HCN, 1,460 ppmv SO_2, 4,800 ppmv O_2.

Influence of Limestone Type. Figure 11 shows the results of HCN oxidation over seven different limestones. The conversion of HCN decreases with increasing degree of sulfation, but for Stevns Chalk, limestone 2, the decrease is only from 98% to 92%. The selectivity for NO formation over the calcined limestones, that is, at zero degree of sulfation, is almost the same for all samples and in the range 50–60%. A small difference between different limestone types with respect to NO selectivity was also observed by Shimizu et al. (1994). Figure 10 shows that the rate of NO formation decreases during sulfation, which is expected since the rate of HCN oxidation decreases. Figure 11 shows that the NO selectivity also decreases with an increasing degree of sulfation. It is interesting that the NO selectivities from HCN oxidation over the sulfated limestones are all in the range of 22–26%. This suggests that $CaSO_4$ is responsible for the catalytic activity and not impurities in the limestones, because the level of impurities is different in the different types of limestone. The N_2O selectivity increases from almost zero to about 10% over the fully sulfated limestones. This value may be considered as the intrinsic selectivity for N_2O formation because the catalytic activity for N_2O decomposition over sulfated limestone is negligible (Shimizu and Inagaki, 1993; Johnsson et al., 1997).

Hansen and Dam-Johansen (1993) showed that for the reduction of NO by CO over limestone during sulfation the catalytic activity could be ranked according to the sulfur capture capacity of the limestones. This conclusion seems to hold only partly for HCN oxidation. The present results show that the loss of catalytic activity during sulfation is lowest for Stevns Chalk, which has the highest sulfur capture capacity. There is no clear relation between sulfur capture capacity and catalytic activity for the six other limestones. The small decrease in catalytic activity for Stevns Chalk is probably partly because pore blocking is less severe for this very porous limestone as shown by Dam-Johansen (1987). However, Lin et al. (1994) showed that Stevns Chalk loses most of its catalytic activity for oxidation of NH_3 upon sulfation. Therefore, pore blocking cannot be the only explanation for that observation, since this effect should be similar for NH_3 and HCN. A possible explanation could be that $CaSO_4$ is not a catalyst for NH_3 oxidation but an activity catalyst for HCN oxidation.

Influence of Particle Size. The influence of particle size is shown in Figure 12 for Stevns Chalk. The conversion of HCN is lower for the large particles, which indicates increasing external and internal mass-transfer limitations. Calculations indicate that the reaction rate is strongly limited by the rate of external mass transfer even for the small particle size at low degrees of sulfation. The catalytic activity decreases to a greater extent for the large particles during sulfation, which may be attributed to more severe pore blocking. The NO selectivity is apparently not influenced by the particle size; the

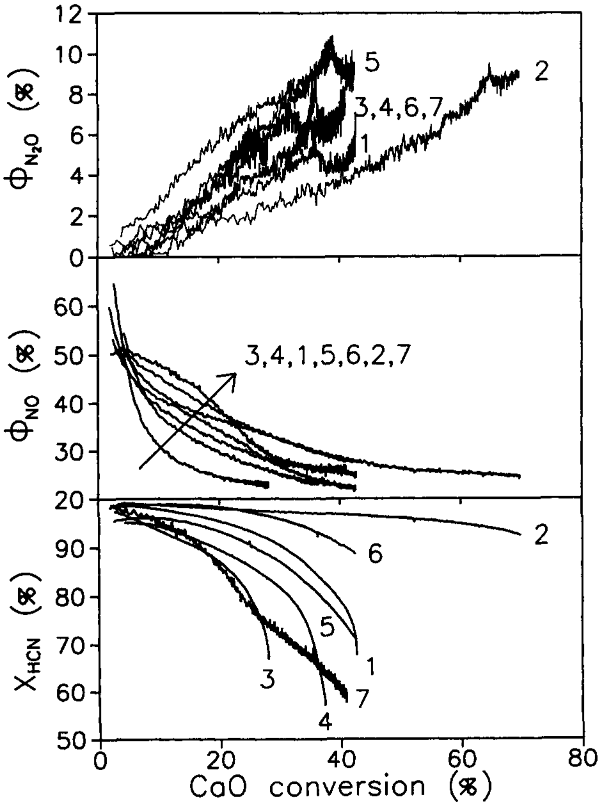

Figure 11. Oxidation of HCN over seven different limestones during simultaneous sulfation.

Limestone numbers refer to Table 1. Temperature 1,123 K; flow rate, 1,790 NmL/min; mass of uncalcined limestone, 0.25 g; particle diameter, 0.25–0.3 mm; inlet concentrations, 286 ppmv HCN, 1,430 ppmv SO_2, 4,300 ppmv O_2.

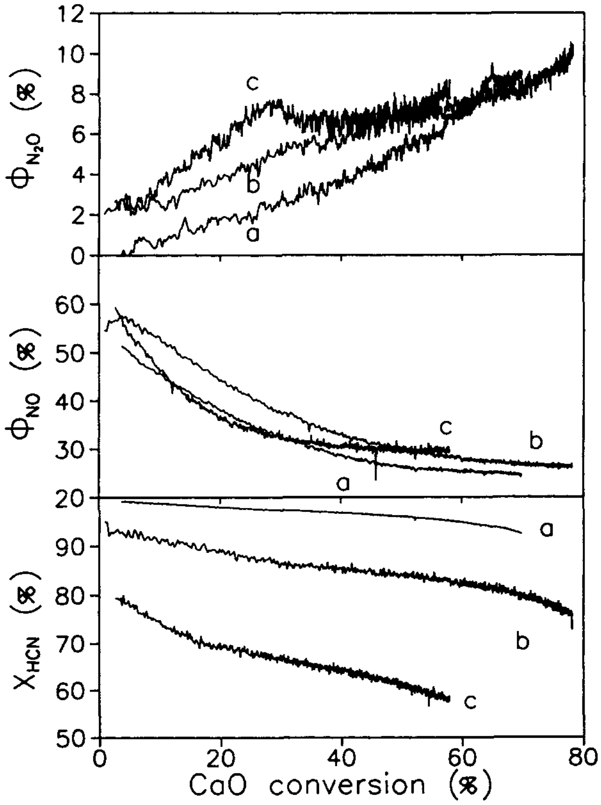

Figure 12. Influence of particle diameter on oxidation of HCN during simultaneous sulfation.

Temperature, 1,123 K; flow rate, 1,790–2,000 NmL/min; limestone, Stevns Chalk; mass of uncalcined limestone, 0.25 g; inlet concentrations, 290 ppmv HCN, 290 ppmv SO_2, 1,450 ppmv O_2, 4,300–4,700 ppmv. a: 0.25–0.30 mm; b: 0.85–1.0 mm; c: 1.7–2.0 mm.

differences are probably within the experimental uncertainty. The slightly higher N_2O selectivity for the large particles is possibly caused by a higher HCN concentration within the particle layer resulting in a higher N_2O production, either by HCN oxidation over CaO or by reduction of NO over $CaSO_4$, as will be shown later. Similar results were obtained for Faxe Bryozo (Jensen, 1996).

Influence of NO. The influence of 430 ppmv NO was tested with Stevns Chalk and Faxe Bryozo for three different particle sizes. The results for Stevns Chalk are shown in Figure 13. The presence of NO does not influence the conversion of HCN due to the relatively high concentration of O_2. In comparison with Figure 12, it appears that the NO selectivity is lower in the presence of NO. Furthermore, the selectivity for NO formation decreases with increasing particle size. The N_2O selectivity increases with increasing conversion of the limestone and the final level is 25–30%, that is, 2.5–3 times higher than in the absence of NO. The N_2O selectivity is higher for the large particles throughout most of the experiment. The lower NO selectivity and higher N_2O selectivity in the presence of NO indicates that NO participates in N_2O formation, most likely over $CaSO_4$. Similar results were obtained for Faxe Bryozo (Jensen, 1996).

Influence of SO_2. Experiments were carried out with a lower SO_2 concentration of about 540 ppmv, compared to 1,450 ppmv used in most of the experiments, to obtain a lower rate of sulfation. The results for Stevns Chalk and Faxe Bryozo are shown in Figure 14. Surprisingly, the conversion of HCN decreased only slightly with an increasing degree of sulfation. This is seen most clearly for Faxe Bryozo since for Stevns Chalk the decrease in conversion is low even at high SO_2 concentrations. In a similar experiment with Faxe Bryozo with 1,440 ppmv SO_2, the conversion of HCN decreased from almost 100% to 70% (see Figure 11). The NO selectivities at low SO_2 concentrations are slightly higher than at high SO_2 concentrations, but the N_2O selectivities are similar.

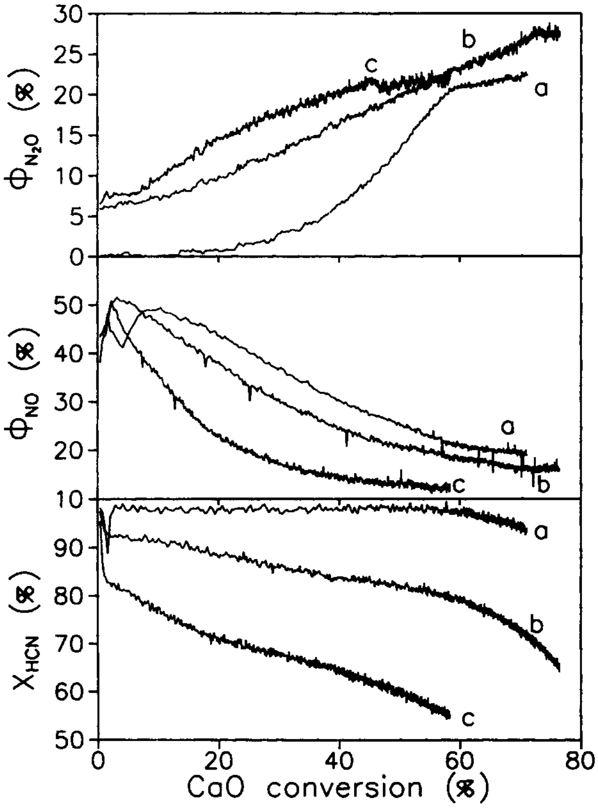

Figure 13. Effect of particle diameter and NO on HCN oxidation during simultaneous sulfation.

Temperature, 1,123 K; flow rate, 2,000 NmL/min; limestone, Stevns Chalk; mass of uncalcined limestone, 0.25 g; inlet concentrations, 290 ppmv HCN, 1,450 ppmv SO_2, 4,800 ppmv O_2, 430 ppmv NO. a: 0.25–0.30 mm; b: 0.85–1.0 mm; c: 1.7–2.0 mm.

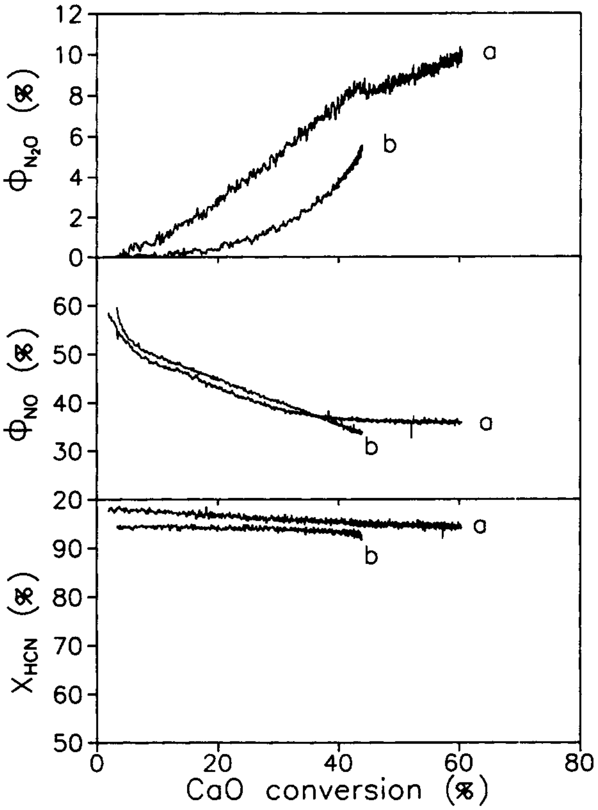

Figure 14. HCN oxidation during simultaneous sulfation at a low SO_2 concentration.

Temperature, 1,123 K; flow, 1,770 NmL/min; mass of uncalcined limestone, 0.25 g; particle diameter, 0.25–0.3 mm; inlet concentrations, 330 ppmv HCN, 540 ppmv SO_2, 5,400 ppmv O_2. a: Stevns Chalk; b: Faxe Bryozo.

The influence of the SO_2 concentration was further investigated using Faxe Bryozo. Nitrous oxide was not measured in these experiments. Initially, the oxidation of HCN over the calcined limestone was tested. The limestone was then sulfated at a high inlet SO_2 concentration of 1,950 ppmv until it was almost completely sulfated, and then the inlet SO_2 concentration was changed in the following steps: 1,950 → 1,450 → 1,000 → 500 → 0 → 500 → 1,950 ppmv SO_2. During these steps the outlet concentrations of the measured gases changed in a slow transient on each change of the SO_2 concentration (Jensen, 1996). This may indicate that some of the $CaSO_4$ has decomposed to CaO in the periods with a low SO_2 concentration and that resulfation of CaO takes place when the SO_2 inlet concentration is increased.

A summary of the influence of SO_2 on the conversion of HCN and NO selectivity is shown in Figure 15. There was a

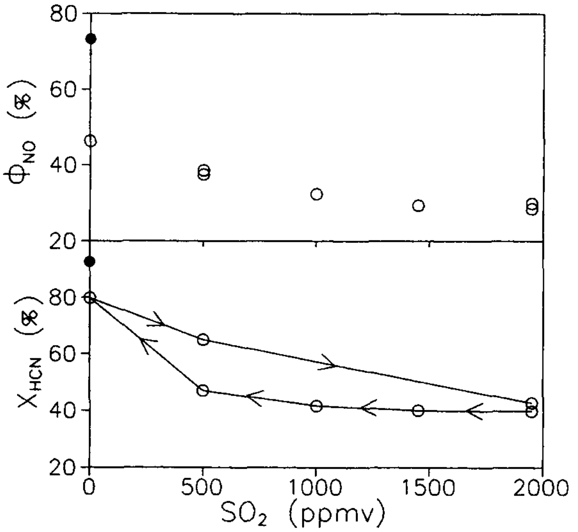

Figure 15. Influence of SO_2 concentration on oxidation of HCN over sulfated limestone.

Temperature, 1,123 K; flow rate, 1,881 NmL/min; limestone, Faxe Bryozo; mass of uncalcined limestone, 0.2494 g; particle diameter, 1–1.7 mm; inlet concentrations, 300 ppmv HCN, 5400 ppmv O_2. ● Before sulfation; ○: after sulfation.

high conversion of HCN and a high NO selectivity of 93 and 73%, respectively, over the calcined limestone. After sulfation of the limestone with an SO_2 concentration of 1,950 ppmv, the conversion of HCN decreased to about 40% and the NO selectivity to less than 30%. A decrease in the SO_2 concentration to 1,450 ppmv and then to 1,000 ppmv did not influence the HCN conversion or the NO selectivity significantly. When the SO_2 concentration was decreased to 500 ppmv, the HCN conversion and the NO selectivity increased to 47 and 38%, respectively, in a slow transient. When SO_2 was removed from the inlet gas, the conversion of HCN increased to almost 80% and the NO selectivity increased to 46%. When 500 ppmv SO_2 was introduced again, the HCN conversion and the NO selectivity decreased to 65 and 39%, respectively, in a slow transient. The NO selectivities obtained in the two experiments with 500 ppmv SO_2 are in agreement, but the conversion of HCN in the latter experiment was significantly higher than in the former. The differences in HCN conversion are probably due to the fact that steady state was not achieved. When 1,950 ppmv SO_2 was put on the conversion of HCN and the NO selectivity decreased to the level observed earlier. It is clear that the SO_2 concentration influences both the rate of HCN conversion and the NO selectivity, although the results are not easily interpreted quantitatively due to the influence of SO_2 on HCN oxidation in the empty reactor.

Decomposition of $CaSO_4$. In fluidized-bed combustors there are zones with very low concentrations of O_2 and high concentrations of CO and hydrocarbons present (Stubington and Chan, 1990; Lyngfelt et al., 1993). The presence of reducing zones has been shown to be of great importance for the capture of SO_2 by limestone (Hansen et al., 1993). The effect of removing both SO_2 and O_2 from the inlet gas but retaining HCN was tested in a few experiments to simulate reducing conditions. Figure 16 shows the results from an experiment with Faxe Bryozo Fe (4). The limestone was first sulfated for 85 min and the conversion of CaO to $CaSO_4$ was 37%. When SO_2 was removed after 162 min, period I, HCN was simultaneously added to the inlet gas, and in period II, after 176 min, O_2 was removed from the inlet gas. The decrease in the total flow by the removal of O_2 was not corrected for, and so the inlet concentration of HCN increased from 295 ppmv to 335 ppmv, and the CO_2 concentration increased from 255 ppmv to 300 ppmv. The CO concentration decreased at first and then increased when O_2 was removed. The NO concentration decreased quickly at first, but then more slowly. The N_2O concentration was low throughout the experiment and decreased further when O_2 was removed. There was a peak in the SO_2 outlet concentration that indicates the decomposition of $CaSO_4$. Since there was no O_2 in the inlet, all oxygen in the reaction products must come from the decomposition of $CaSO_4$. Both CaO and CaS may be products of the decomposition reaction as shown in Reactions R4 and R5:

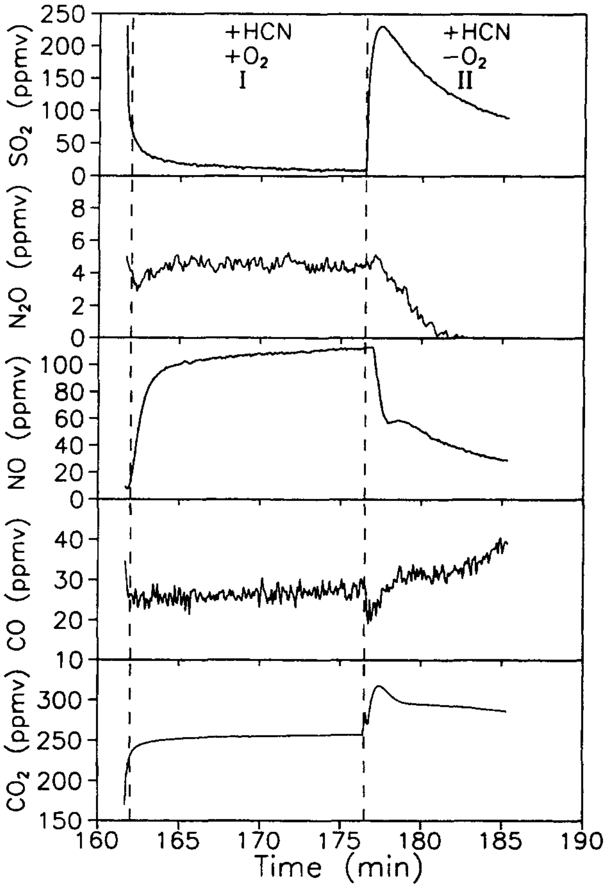

Figure 16. Decomposition of sulfated limestone ($CaSO_4$) by reaction with HCN in the absence of O_2.

Temperature, 1,123 K; flow rate in the presence of O_2 (period I), 2,000 NmL/min; flow rate without O_2 (period II), 1,760 NmL/min; limestone, Faxe Bryozo Fe; mass of uncalcined limestone, 0.2497 g; particle diameter, 0.3–0.355 mm; inlet concentrations in the presence of O_2, 295 ppmv HCN, 4,800 ppmv O_2; HCN inlet concentration without O_2, 334 ppmv.

$$\mathrm{HCN\ (g) + 2.5CaSO_4\ (s) \rightleftharpoons 2.5CaO\ (s) + 1/2H_2O\ (g) + CO_2\ (g) + 1/2N_2(g) + 2.5SO_2\ (g)} \quad \text{(R4)}$$

$$\mathrm{HCN\ (g) + 5/8CaSO_4\ (s) \rightleftharpoons 5/8CaS\ (s) + 1/2H_2O\ (g) + CO_2(g) + 1/2N_2(g).} \quad \text{(R5)}$$

These reactions are thermodynamically possible under the present conditions (Jensen, 1996). Figure 16 shows that at 180 min about 175 ppmv SO_2 is formed and therefore also 70 ppmv CO_2 according to the stoichiometry of Reaction R4. The actual CO_2 concentration at 180 min is about 300 ppmv, and consequently decomposition of $CaSO_4$ to CaS by Reaction R5 also takes place forming 230 ppmv CO_2. Similar results were obtained for Faxe Bryozo (Jensen, 1996).

Discussion of HCN Oxidation over Limestone During Simultaneous Sulfation. The experiments with simultaneous HCN oxidation and sulfation of limestone were carried out under conditions at which $CaCN_2$ is not formed, and $CaCN_2$ is left out of the following discussion.

During sulfation of the particles a layer of $CaSO_4$ builds up from the outer surface of the particle progressing inwards. The sulfation influences the reaction in two ways. The original catalyst CaO is converted to $CaSO_4$ and the pores of the limestone close because the molar volume of $CaSO_4$ is larger than that of CaO. The pore plugging reduces the surface area available for reaction and the effective diffusion coefficient for the gaseous reactant resulting in a lower reaction rate. Furthermore, it is usually found that the catalytic activity of $CaSO_4$ is lower than the catalytic activity of CaO (Jensen, 1996). The experimental results show that the catalytic activity of limestone decreases during sulfation, which is in line with the general observations discussed earlier. However, the influence of SO_2 on HCN oxidation is surprising because such effects have not been observed when NH_3 is oxidized over limestone during sulfation (Lin et al., 1994). The effect of SO_2 is discussed further below.

The catalytic activity of sulfated limestone decreases with an increasing SO_2 concentration up to about 1,000 ppmv and then reaches an asymptotic level. This behavior indicates a competition between HCN and SO_2 for active sites. The fact that by increasing the SO_2 concentration the catalytic activity decreases asymptotically to a nonzero level, which is higher than in the empty reactor, may be explained if there are two different types of active sites. On type 1 sites there is a competition between HCN and SO_2, which leads to a decrease in HCN conversion with an increasing SO_2 concentration. At an SO_2 concentration of 1,000 ppmv these sites are completely covered by SO_2, and HCN is no longer oxidized on these sites. On type 2 sites only HCN can adsorb, and so the oxidation of HCN on these sites is not influenced by SO_2. The selectivity for NO formation must be higher on type 1 sites than on type 2 sites since the NO selectivity increases when SO_2 is removed. The tests with decomposition of sulfated limestone showed that $CaSO_4$ can decompose to CaO and CaS in the presence of HCN when O_2 and SO_2 are absent. Furthermore, transient results reported elsewhere (Jensen, 1996) indicate that $CaSO_4$ decomposes to CaO in the presence of HCN when SO_2 is absent even in the presence of O_2, indicating that the type 1 sites are CaO. This interpretation is in agreement with the higher NO selectivity in the absence of SO_2. Further conclusions on the mechanisms of HCN oxidation over limestone during sulfation would require more detailed experiments.

Discussion

In this section the relative importance of homogeneous gas-phase oxidation of HCN and heterogeneous catalytic oxidation of HCN over calcined limestone in combustion systems is discussed based on the following simplified assumptions:

1. The reaction temperature is 1,123 K, relevant for calciners and fluidized-bed combustors.
2. The rate of the catalytic oxidation of HCN is controlled by external mass transfer because the reaction is extremely fast. As a lower limit for the mass transfer rate a Sherwood number of 2 is used.
3. The rate of the homogeneous oxidation of HCN is based on the mechanism of Glarborg and Miller (1994), and includes the following reactions:

$$\mathrm{HCN + O \rightleftharpoons NCO + H} \quad \text{(R6)}$$

$$\mathrm{HCN + O \rightleftharpoons CN + OH} \quad \text{(R7)}$$

$$\mathrm{HCN + O \rightleftharpoons NH + CO} \quad \text{(R8)}$$

$$\mathrm{HCN + OH \rightleftharpoons HOCN + H} \quad \text{(R9)}$$

$$\mathrm{HCN + OH \rightleftharpoons HOCN + H} \quad \text{(R10)}$$

$$\mathrm{HCN + OH \rightleftharpoons HNCO + H} \quad \text{(R11)}$$

$$\mathrm{HCN + OH \rightleftharpoons NH_2 + CO.} \quad \text{(R12)}$$

Only the forward reactions, that is, HCN destruction, are included.

Based on assumption 2 the rate of heterogeneous HCN oxidation is

$$r_{\text{het}} = \frac{12 \cdot \rho_v \cdot D}{d_p^2 \cdot \rho_p} \cdot C_{\text{HCN}} = k_{\text{het}} \cdot C_{\text{HCN}} \frac{\text{mol}}{\text{m}^3\ \text{gas} \cdot \text{s}}, \quad (4)$$

where ρ_v is the particle suspension density of limestone in the reactor; D is the molecular diffusion coefficient of HCN in N_2; d_p is the particle diameter; and ρ_p is the particle density, assumed here to be 1,000 kg/m^3 for CaO. The molecular diffusion coefficient of HCN in N_2 was estimated to be 1.68×10^{-4} m^2/s at 1,123 K (Reid et al., 1987).

From assumption 3, the rate of homogeneous HCN oxidation is the sum of the rates of Reactions R6–R12:

$$r_{\text{hom}} = (1 - \rho_v/\rho_p) \cdot \sum_{i=6}^{12} k_{\text{hom},i} \cdot C_R \cdot C_{\text{HCN}} = k_{\text{hom}} \cdot C_{\text{HCN}} \frac{\text{mol}}{\text{m}^3\ \text{gas} \cdot \text{s}}, \quad (5)$$

where $k_{\text{hom},i}$ is the rate constant for the ith homogeneous reaction, and C_R is the concentration of the radical, that is, O for reactions R6–R8 and OH for Reactions R9–R12.

For a quantitative assessment of the relative importance of homogeneous and heterogeneous reactions, a complete reactor model would be necessary. This is outside the scope of the present work. Instead a qualitative comparison will be made based on k_{het} and k_{hom} defined in Equations 4 and 5, respectively. To estimate the rate of the homogeneous reactions, the radical concentrations are needed. Based on calculations with a comprehensive model for a circulating FBC (CFBC), Goel et al. (1996) found a maximum concentration of about 230 ppmv OH and 100 ppmv O close to the bottom bed with a rapid decrease at higher levels. In the present calculations it will be assumed that the concentration of O and OH is the same. An upper limit of 100 ppmv is used for the radical concentration because more than 80% of the homogeneous destruction of HCN is by reaction with O radicals. Reaction R6 is the most important reaction of HCN with OH radicals, and about 16% of the HCN is destroyed by this reaction.

Figure 17 shows a plot of k_{het} and k_{hom} as a function of the solids density for different particle sizes and radical concentrations. Calciners typically operate with particles with diameters in the 50–100-μm range or less, and suspension densities of 0.1 kg/m^3 to 2 kg/m^3. It can be seen from Figure 17 that the heterogeneous oxidation of HCN is very important in this case due to the small particle size, and the homogeneous reactions are only important at the highest radical concentration of 100 ppmv. In CFBCs with limestone feed, the suspension density varies from about 500 kg/m^3 in the bottom to 10–20 kg/m^3 in the top of the riser, and the particle size is less than 1 mm. Figure 17 shows that in the bottom the heterogeneous reactions are important due to the high suspension density, while at the top the homogeneous reactions are not important due to the low radical concentrations when the volatiles' combustion is complete. The conclusion is that the heterogeneous destruction of HCN is important in calciners and the fluidized-bed combustor with limestone addition. Without limestone addition, heterogeneous HCN oxidation may still be important if the coal ash has a high catalytic activity. Under pulverized coal combustion/reburning conditions the temperature is higher than 1,123 K. Simulations of CO oxidation (2 vol. % CO; 4 vol. % O_2) at 1,400 K using a detailed kinetic model of Glarborg et al. (1997) indicate that the maximum concentrations of O and OH are above 1,000 ppmv, and at these levels HCN is destroyed very quickly. Since the solids concentration under pulverized coal/reburning conditions is even lower than in calciners, heterogeneous reactions are probably of low importance in these systems.

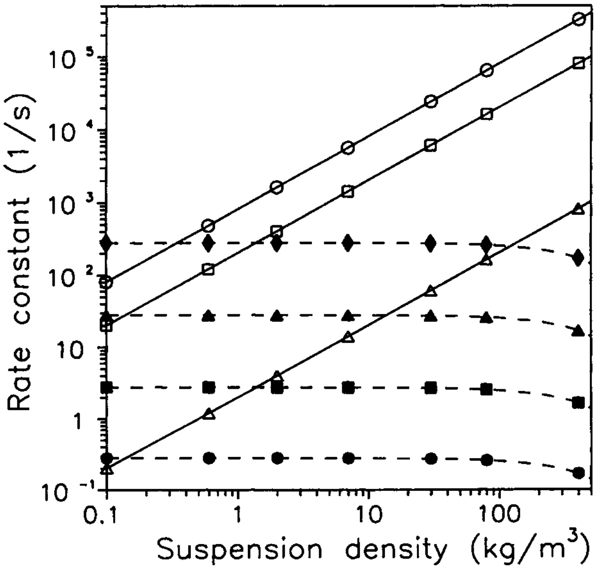

Figure 17. k_{het} and k_{hom} defined in Eqs. 4 and 5, respectively, as a function of the suspension density of calcined limestone at 1,123 K.

○: $d_p = 50$ μm; □: $d_p = 100$ μm; △: $d_p = 1{,}000$ μm; ●: $C_R = 0.1$ ppmv; ■: $C_R = 1$ ppmv; ▲: $C_R = 10$ ppmv; ◆: $C_R = 100$ ppmv.

Conclusions

The results obtained in this study may help to improve the understanding of the nitrogen chemistry in coal combustion processes where significant concentrations of solid calcium species, such as fluidized bed combustors and calciners, are present. It was shown that:

- HCN is oxidized catalytically over CaO or reacts with CaO in a gas–solid reaction to form $CaCN_2$ depending on the conditions. A high HCN concentration, a low O_2 concentration, and a low temperature favor the formation of $CaCN_2$. Once formed, $CaCN_2$ can be oxidized to CaO and gaseous products. The nitrogen in $CaCN_2$ is oxidized to N_2O and NO with selectivities of 20–28% and 20–22%, respectively, under the experimental conditions employed.
- The NO selectivity from HCN oxidation over calcined limestone increases with a rising temperature, an increased O_2 concentration, and a decreasing HCN concentration. The maximum NO selectivity is of the order of 50–70%. At low O_2 concentrations, or in the absence of O_2, NO is reduced by HCN over CaO and by a gas–solid reaction with $CaCN_2$. In the absence of O_2, only N_2 is formed by NO reduction, but with O_2 present, part of the NO is reduced to N_2O.
- The selectivity for N_2O formation from HCN oxidization over calcined limestone under conditions where $CaCN_2$ is not formed is below about 5%. At low temperatures the observed N_2O selectivity shows a maximum as a function of the O_2 concentration, under the present experimental conditions at about 300–1,000 ppmv O_2. A similar maximum is observed as a function of temperature at about 873 K. Under these conditions $CaCN_2$ is formed and there are indications that the maximum rate of N_2O formation occurs when $CaCN_2$ is simultaneously formed and oxidized at a significant rate. It was observed that the presence of NO in the inlet gas enhances N_2O formation.
- The catalytic activity of limestone for HCN oxidation decreases with an increasing degree of sulfation. The limestone with the highest sulfur capture capacity had the highest catalytic activity after sulfation.
- The catalytic activity of sulfated limestone depends on the SO_2 concentration, and it decreases to a nonzero level with an increasing SO_2 concentration. This indicates that HCN is oxidized on two different types of active sites. On type 1 there is competition between HCN and SO_2, and as a consequence the catalytic activity decreases with an increasing SO_2 concentration. On type 2 sites only HCN adsorbs and so the reaction rate on these sites is independent of the

SO_2 concentration. It is possible that the type 1 site is CaO, formed by reductive decomposition of $CaSO_4$ even in the presence of O_2.

- The selectivity for NO formation decreases with an increasing degree of sulfation of the limestone, and the selectivity for NO formation over the fully sulfated limestone is not significantly influenced by the type of limestone. When NO is added to the inlet gas, the NO selectivity decreases, showing that NO is reduced by HCN over $CaSO_4$. The selectivity for N_2O formation when HCN is oxidized increases with an increasing degree of sulfation and is higher in the presence of NO.
- $CaSO_4$ decomposes to CaO and CaS by a fast reaction with HCN in the absence of O_2 and SO_2.
- Simplified calculations indicate that the heterogeneous catalytic oxidation of HCN over calcined limestone is important in calciners and in fluidized-bed combustors with limestone addition or if the ash has a high catalytic activity. The importance of heterogeneous reactions for HCN destruction under pulverized coal combustion/reburning conditions is probably low.

Acknowledgment

This work is part of the research program CHEC (Combustion and Harmful Emission Control) funded by the Technical University of Denmark, the Danish Technical Research Council, Elsam, Elkraft, the Danish Energy Research Programme, the Nordic Energy Research Programme, and the European Union.

Literature Cited

Åmand, L.-E., B. Leckner, and K. Dam-Johansen, "Influence of SO_2 on the NO/N_2O Chemistry in Fluidized Bed Combustion: 1. Full-scale Experiments," *Fuel*, **72**, 557 (1993).

Axworthy, A. E., V. H. Dayan, and G. B. Martin, "Reactions of Fuel-Nitrogen Compounds Under Conditions of Inert Pyrolysis," *Fuel*, **57**, 29 (1978).

Bassilakis, R., Y. Zhao, P. R. Solomon, and M. A. Serio, "Sulfur and Nitrogen Evolution in the Argonne Coals: Experiment and Modeling," *Energy Fuels*, **7**, 710 (1993).

Baumann, H., and P. Möller, "Pyrolysis of Hard Coals Under Fluidised Bed Combustor Conditions," *Erdöl Kohle-Erdgas Petrochem.*, **44**, 29 (1991).

Bose, A. C., K. M. Dannecker, and J. O. L. Wendt, "Coal Composition Effects on Mechanisms Governing the Destruction of NO and Other Nitrogenous Species during Fuel-Rich Combustion," *Energy Fuels*, **2**, 301 (1988).

Bowman, C. T., "Control of Combustion-generated Nitrogen Oxide Emissions: Technology Driven by Regulation," *Int. Symp. on Combustion*, Combustion Inst., p. 859 (1992).

Bruun, M., and K. Møller, *Ammonia Oxidation over Limestone during Sulfation*, BSc Thesis, The Engineering Academy of Denmark, Lyngby (1994).

Burch, T. E., F. R. Tillman, W. Y. Chen, T. W. Lester, R. B. Conway, and A. M. Sterling, "Partitioning of Nitrogenous Species in the Fuel-Rich Stage of Reburning," *Energy Fuels*, **5**, 231 (1991).

Caton, J. A., J. K. Narney, C. Cariappa, and W. R. Laster, "The Selective Non-catalytic Reduction of Nitric Oxide Using Ammonia at up to 15% Oxygen," *Can. J. Chem. Eng.*, **73**, 345 (1995).

Chen, W. Y., and L. Ma, "Effect of Heterogeneous Mechanisms during Reburning of Nitrogen Oxide," *AIChE J.*, **42**, 1968 (1996).

Chen, S. L., M. P. Heap, D. W. Pershing, and G. B. Martin, "Fate of Coal Nitrogen during Combustion," *Fuel*, **61**, 1218 (1982).

Dam-Johansen, K., *Svovldioxidbinding på tør kalk*, PhD Thesis (in Danish), Dept. of Chemical Engineering, Technical Univ. of Denmark, Lyngby (1987).

Dam-Johansen, K., and K. Østergaard, "High Temperature Reaction Between Sulphur Dioxide and Limestone: I. Comparison of Limestones in Two Laboratory Reactors and a Pilot Plant," *Chem. Eng. Sci.*, **46**, 827 (1991).

Dam-Johansen, K., L.-E. Åmand, and B. Leckner, "Influence of SO_2 on the NO/N_2O Chemistry in Fluidized Bed Combustion: 2. Interpretation of Full-scale Observations Based on Laboratory Experiments," *Fuel*, **72**, 565 (1993).

de Soete, G. G., and W. Nastoll, "Catalytic Nitrogen Chemistry on CaO and $CaCO_3$ at Fluidized Bed Temperature Conditions," Ref. 39362, Institut Francais du Petrole (1991).

Deussner, M., "Clinker Burning with Reduced NO_x Emissions," *KHD Symp.*, p. 80 (1995).

Doughty, A., and J. C. Mackie, "Kinetics of Thermal Decomposition of the Diazines: Shock-Tube Pyrolysis of Pyrimidine," *J. Chem. Soc. Faraday Trans.*, **90**, 541 (1994).

Doughty, A., J. C. Mackie, and J. M. Palmer, "Kinetics of the Thermal Decomposition and Isomerization of Pyrazine (1,4 Diazine)," *Symp. Int. on Combustion*, Combustion Inst., p. 893 (1994).

Gavin, D. G., and M. A. Dorrington, "Factors in the Conversion of Fuel Nitrogen to Nitric and Nitrous Oxides during Fluidized Bed Combustion," *Fuel*, **72**, 381 (1993).

Glarborg, P., and J. A. Miller, "Mechanism and Modeling of Hydrogen Cyanide Oxidation in a Flow Reactor," *Combust. Flame*, **99**, 475 (1994).

Glarborg, P., M. U. Alzueta, K. Dam-Johansen, and J. A. Miller, "Kinetic Modeling of Hydrocarbon/Nitric Oxide Interactions in a Flow Reactor," Submitted to *Combust. Flame* (1997).

Goel, S., A. Sarofim, P. Kilpinen, and M. Hupa, "Emission of Nitrogen Oxides from Circulating Fluidized-Bed Combustors: Modeling Results using Detailed Chemistry," *Int. Symp. on Combustion*, Combustion Inst., p. 3317 (1996).

Hansen, P. F. B., and K. Dam-Johansen, "Limestone Catalyzed Reduction of NO and N_2O under Fluidized Bed Combustion Conditions," *Proc. Int. Conf. on Fluidized Bed Combustion*, L. Rubow and G. Commonwealth, eds., ASME, p. 779 (1993).

Hansen, P. F. B., K. Dam-Johansen, and K. Østergaard, "High Temperature Reaction Between Sulphur Dioxide and Limestone: V. The Effect of Periodically Changing Oxidizing and Reducing Conditions," *Chem. Eng. Sci.*, **48**, 1325 (1993).

Haussmann, G. J., and C. H. Kruger, "Evolution and Reaction of Coal Fuel Nitrogen during Rapid Oxidative Pyrolysis and Combustion," *Int. Symp. on Combustion*, Combustion Inst., p. 1271 (1990).

Houser, T. J., M. Hull, R. M. Alway, and T. Biftu, "Kinetics of Formation of HCN during Pyridine Pyrolysis," *Int. J. Chem. Kinet.*, **12**, 569 (1980).

Hulgaard, T., and K. Dam-Johansen, "Homogeneous Nitrous Oxide Formation and Destruction Under Combustion Conditions," *AIChE J.*, **39**, 1342 (1993).

Iisa, K., P. Salokoski, and M. Hupa, "Heterogeneous Formation and Destruction of Nitrous Oxide under Fluidized Bed Combustion Conditions," *Proc. Conf. on Fluidized Bed Combustion*, E. J. Anthony, ed., ASME, p. 1027 (1991).

Jensen, A., *Nitrogen Chemistry in Fluidized Bed Combustion of Coal*, PhD Thesis, Dept. of Chemical Engineering, Technical Univ. of Denmark, Lyngby (1996).

Jensen, A., J. E. Johnsson, and K. Dam-Johansen, "Formation of Nitric Oxide and Nitrous Oxide from Heterogeneous Oxidation of Hydrogen Cyanide at Fluidized Bed Combustion Conditions," *Proc. Int. Conf. on Fluidized Bed Combustion*, L. Rubow and G. Commonwealth, eds., ASME, p. 447 (1993).

Jensen, A., J. E. Johnsson, and K. Dam-Johansen, "Nitrogen Chemistry in FBC with Limestone Addition," *Int. Symp. on Combustion*, Combustion Inst., p. 3335 (1996).

Jeschar, R., R. Jennes, H. Kremer, and T. Kellerhoff, "Optimierung der Verbrennung im Calcinator einer Zementdrehofenanlage," *ZKG Int.*, **49**, 304 (1996).

Johnsson, J. E., "Formation and Reduction of Nitrogen Oxides in Fluidized-bed Combustion," *Fuel*, **73**, 1398 (1994).

Johnsson, J. E., A. Jensen, R. Vaaben, and K. Dam-Johansen, "Decomposition and Reduction of N_2O over Limestone Under FBC Conditions," *Proc. Int. Conf. on Fluidized Bed Combustion*, F. D. S. Preto, ed., ASME, p. 953 (1997).

Kambara, S., T. Takarada, Y. Yamamoto, and K. Kato, "Relation Between Functional Forms of Coal Nitrogen and Formation of NO_x Precursors during Rapid Pyrolysis," *Energy Fuels*, **7**, 1013 (1993).

Kasuya, F., P. Glarborg, J. E. Johnsson, and K. Dam-Johansen, "The

Thermal DeNO$_x$ Process: Influence of Partial Pressures and Temperature," *Chem. Eng. Sci.*, **50**, 1455 (1995).

Khan, T., Y. Y. Lee, and R. A. Brown, "Homogeneous Phase Formation of Nitrous Oxide from Hydrogen Cyanide in a Circulating Fluidized Bed Combustor," *Proc. Int. Conf. on Fluidized Bed Combustion*, L. Rubow and G. Commonwealth, eds., ASME, p. 441 (1993).

Kiil, S., S. K. Bhatia, and K. Dam-Johansen, "Modelling of Catalytic Oxidation of NH$_3$ and Reduction of NO on Limestone during Sulphur Capture," *Chem. Eng. Sci.*, **51**, 587 (1996).

Klug, C. F., and H. P. Michelsen, *Limestone Catalyzed Oxidation of HCN*, BSc Thesis, Engineering Academy of Denmark, Lyngby (1992).

Krammer, G. F., and A. F. Sarofim, "Reaction of Char Nitrogen during Fluidized Bed Coal Combustion—Influence of Nitric Oxide and Oxygen on Nitrous Oxide," *Combust. Flame*, **97**, 118 (1994).

Lee, Y. Y., A. Sekthira, and C. M. Wong, "The Effects of Calcined Limestone on the NH$_3$-NO-O$_2$ Reaction," *Proc. Int. Conf. on Fluidized Bed Combustion*, p. 1208 (1985).

Lee, Y. Y., S. M. S. Soares, and A. Sekthira, "The Effects of Sulfated Limestone on the NH$_3$-NO-O$_2$ Reaction," *Proc. Int. Conf. on Fluidized Bed Combustion*, J. P. Mustonen, ed., ASME, p. 1184 (1987).

Lin, W., J. E. Johnsson, K. Dam-Johansen, and C. M. Van den Bleek, "Interactions Between NO$_x$ Emission and Desulphurization in FBC," *Proc. Int. Conf. on Fluidized Bed Combustion*, L. N. Rubow and G. Commonwealth, eds., ASME, p. 1093 (1993).

Lin, W., J. E. Johnsson, K. Dam-Johansen, and C. M. Van den Bleek, "Interaction Between Emissions of Sulfur Dioxide and Nitrogen Oxides in Fluidized Bed Combustion," *Fuel*, **73**, 1202 (1994).

Lyngfelt, A., K. Bergqvist, F. Johnsson, L.-E. Åmand, and B. Leckner, "Dependence of Sulphur Capture Performance on Air Staging in a 12 MW Circulating Fluidized Bed Boiler," *Gas Cleaning at High Temperatures*, R. Clift and J. P. K. Seville, eds., Blackie, Glasgow, p. 470 (1993).

Mjörnell, M., B. Leckner, M. Karlsson, and A. Lyngfelt, *Proc. Int. Conf. on Fluidized Bed Combustion*, E. J. Anthony, ed., ASME, p. 655 (1991).

Mochizuki, M., J. Koike, and M. Horio, "The Mechanism of N$_2$O Formation from Fluidized Bed Char Combustion," *Proc. Int. Workshop on Nitrous Oxide Emissions*, p. 237 (1992).

Moritomi, H., Y. Suzuki, N. Kido, and Y. Ogisu, "NO$_x$ Emission and Reduction from Circulating Fluidized Bed Combustor," *Circulating Fluidized Bed Technology*, Vol. III, P. Basu, M. Horio, and M. Hasatani, eds., Pergamon Press, Oxford, p. 399 (1991).

Moritomi, H., and Y. Suzuki, "Nitrous Oxide Formation in Fluidized Bed Combustion Conditions," *Fluidization*, Vol. VII, The Engineering Foundation, New York p. 495 (1992).

Nelson, P. F., M. D. Kelly, and M. J. Wornat, "Conversion of Fuel Nitrogen in Coal Volatiles to NO$_x$ Precursors Under Rapid Heating Conditions," *Fuel*, **70**, 403 (1991).

Nelson, P. F., A. N. Buckley, and M. D. Kelly, "Functional Forms of Nitrogen in Coals and the Release of Coal Nitrogen as NO$_x$ Precursors (HCN and NH$_3$)," *Symp. (Int.) on Combustion*, Combustion Inst., p. 1259 (1992).

Nelson, P. F., C.-Z. Li, and E. Ledesma, "Formation of HNCO from the Rapid Pyrolysis of Coals," *Energy Fuels*, **10**, 264 (1996).

Niksa, S., "FLASHCHAIN Theory for Rapid Coal Devolatilization Kinetics. 6. Predicting the Evolution of Fuel Nitrogen from Various Coals," *Energy Fuels*, **9**, 467 (1995).

Polyanchikov, O. I., Yu. I. Krasnokutskii, S. N. Ganz, and V. D. Parkhomenko, "Study of the Mechanism of Calcium Cyanamide Production during the Reaction of Hydrogen Cyanide with Calcium Oxide," *Dnepropetr. Khim-Tekhnol. Inst. im. Dzerzhinskogo Dnepropetrovsk Zh. Prikl. Khim. (Leningrad)*, **49**, 1445 (1976).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1987).

Shimizu, T., and M. Inagaki, "Decomposition of N$_2$O over Limestone under Fluidized Bed Combustion Conditions," *Energy Fuels*, **7**, 648 (1993).

Shimizu, T., Y. Tachiyama, D. Fujita, K. Kumazawa, O. Wakayama, K. Ishizu, S. Kobayashi, S. Shikada, and M. Inagaki, "Effect of SO$_2$ Removal by Limestone on NO$_x$ and N$_2$O Emissions from a Circulating Fluidized Bed Combustor," *Energy Fuels*, **6**, 753 (1992).

Shimizu, T., K. Ishizu, S. Kobayashi, S. Shikada, and M. Inagaki, "Formation of NO$_x$ and N$_2$O Through Oxidation of NH$_3$ and HCN Catalyzed by Limestone," *J. Jpn Inst. Energy*, **72**, 189 (1993).

Shimizu, T., D. Fujita, K. Ishizu, S. Kobayashi, M. Miura, T. Togashi, and M. Inagaki, "Role of Limestone in Formation and Destruction of NO$_x$ and N$_2$O under Fluidized Bed Combustion Conditions," *Fluidization*, Chemical Industry Press, Beijing, p. 196 (1994).

Stubington, J. F., and S. W. Chan, "The Interpretation of Oxygen-Probe Measurements in Fluidised-Bed Combustors," *J. Inst. Energy*, **63**, 136 (1990).

Syverud, T., A. Thomassen, and Ø. Høidalen, "Reducing NO$_x$ at the Brevik Cement Works in Norway—Trials with Stepped Fuel Supply to the Calciner," *Zement-Kalk-Gips*, E92 (1994).

Ulmann's Encyclopedie of Industrial Chemistry, **A8**, 139 (1985).

van der Lans, R. P. L., *Solids Characterization* (Part One); *Limestones* (Part Two), CHEC Rep. No. 9411, Dept. of Chemical Engineering, The Technical Univ. of Denmark, Lyngby (1994).

Yasunaga, K., and T. Furusawa, "Effect of Particles on the Reaction Behaviors of NH$_3$ and NO," *Proc. Meet. of Chem. Engrs. Soc. of Japan*, Tokyo, p. 417 (1986).

Zhang, J. Q., W. E. Jones, I. T. Lau, and F. D. Friedrich, "Effects of Fuel Type and Operating Conditions on SO$_2$ Emission in Fluidized Bed Combustion," *Can. J. Chem. Eng.*, **70**, 998 (1992).

Manuscript received February 3, 1997, and revision received June 13, 1997.