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Selective non-catalytic reduction of NO$_x$ using ammonium sulfate

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Abstract

Ammonium sulfate (AS) is of interest as an additive in stationary combustion plants for the simultaneous control of NO$_x$ (through selective non-catalytic reduction, SNCR) and deposition and corrosion (through sulfation of alkali chlorides). The SNCR performance of ammonium sulfate was evaluated through experiments in a laboratory-scale flow reactor. Experiments with 5 and 10 wt.% aqueous ammonium sulfate solutions, corresponding to AS/NO ratios above one, yielded NO reductions up to 95% in a temperature interval of 1025 to 1075°C. The results indicated that sulfur from ammonium sulfate is mainly released as SO$_3$, even though SO$_2$ is detected in increasing concentrations at temperatures above 1000°C. Addition of KCl to the SNCR process was shown to promote reaction at lower temperatures,
extending the temperature window for reduction by 50°C. Furthermore, ammonium sulfate facilitated a high degree of KCl sulfation at or below 1000°C, demonstrating the potential of using ammonium sulfate to simultaneously reduce NOx and corrosion in full-scale combustion plants. The experiments were analyzed in terms of a detailed kinetic model. The SNCR experiments using ammonium sulfate were described satisfactorily by the model, although the NO reduction at the optimum was slightly underestimated. Also the sulfation of KCl was captured well, but the promoting effect of KCl on SNCR with ammonium sulfate was greatly underestimated. Possible reasons for this discrepancy was discussed.

Introduction

Combustion of alternative fuels such as biomass and waste is a competitive method for production of heat and electricity with a reduced CO2 impact. However, emission of nitrogen oxides (NOx) from combustion of such fuels continues to be a major environmental concern. Regulations on NOx emission limits have become increasingly stringent and continue to be a driving force for research and development of new and improved methods for NOx abatement.1,2 A commonly used technology for reduction of NOx emissions from stationary combustion sources is the selective non-catalytic reduction (SNCR) process.3 The SNCR process is classified as a post-combustion treatment of the flue gas, where chemical agents are sprayed into the flue gas in the post-combustion region to react with NO. The most common additives for the SNCR process are ammonia (NH3) and urea (CO(NH2)2), which can both react selectively with NO. The SNCR process with these additives has been demonstrated to achieve up to 70% NOx reduction in commercial power plants.3,4

The SNCR process is known to be strongly temperature dependent, with a narrow temperature window of effective NO reduction, typically located around 850-1100°C. The process has been studied extensively in the past and is considered a mature technology for NOx reduction in stationary sources.2,5 Previous studies have shown that important process
parameters for SNCR include temperature,\(^5\) residence time,\(^6\) injection rate of the chemical reducing agent,\(^7\) mixing of reagent with the flue gas,\(^8,9\) oxygen concentration,\(^6,10\) and presence of combustibles,\(^11-15\) Also the impact of alkali metals\(^16-25\) and SO\(_2\) has been investigated.\(^27-30\)

An additional challenge in combustion of biomass and waste fuels arises due to the content of chlorine inorganic matter (e.g., alkali and heavy metals) in the fuel.\(^31\) Alkali salts, particularly alkali chlorides, released during combustion can act as a glue to induce agglomeration of ash particles, and can thus generate highly sticky and corrosive deposits in the boiler.\(^32\) The partitioning of alkali metals in the boiler is a determining factor for the amount and composition of ash deposits, and has been studied extensively in the past.\(^31,33,34\) Build-up of deposits may increase the pressure drop, and eventually cause shutdown of the boiler. Furthermore, the deposits are typically highly corrosive and can cause rupture of heat transfer tubes in the boiler. Techniques for reducing deposition and corrosion in boilers operating with biomass and waste fuels are scarce. However, in previous studies it has been shown that addition of sulfur containing additives can facilitate sulfation of alkali chlorides and thereby reduce the extent of deposition and corrosion in the boiler.\(^35-40\) Sulfur may be added as elemental sulfur to the fuel,\(^41,42\) or through injection of SO\(_2\)\(^43\) or ammonium sulfate\(^42,44,45\) into the flue gas. Kassman et al.\(^42\) showed that ammonium sulfate was more efficient than elemental sulfur for the sulfation of gaseous KCl in a biomass fired circulating fluidized bed (CFB) boiler, indicating that SO\(_3\) is more efficient than SO\(_2\) for the sulfation of KCl.

Techniques for the simultaneous reduction of NO\(_x\) emissions, deposition and corrosion have recently come of interest. One possibility involves injection of additives that are active both in the SNCR process and in sulfating corrosive alkali metals. Ammonium sulfate (AS), (NH\(_4\))\(_2\)SO\(_4\), has been proposed as an additive, which upon decomposition yields NH\(_3\) for the reduction of NO and SO\(_2\)/SO\(_3\) for sulfating metals. Results for the use of AS as SNCR agent are reported for pilot-scale conditions,\(^46,47\) while its use for sulfation of alkali metals has been
studied in pilot and full-scale.\textsuperscript{42,44,48} These results provide an understanding of the overall behavior and the potential of the additive, but due to the complexities of flow and mixing in larger scale, they are less useful for kinetic model development and validation. In the present work, SNCR experiments using ammonium sulfate were conducted in a laboratory flow reactor as a function of temperature, AS/NO ratio, and residence time. Also, the impact of KCl on the SNCR process, as well as the sulfation of KCl by ammonium sulfate, was investigated. The results were interpreted in terms of a detailed chemical kinetic model for both the SNCR process and KCl sulfation using ammonium sulfate as additive.

**Experimental**

**Experimental setup**

A flow reactor setup was developed for the purpose of studying the SNCR process with the use of solvable additives. The setup, illustrated in Fig. 1, is comprised of 1) a homogeneous flow reactor, 2) a feeding system capable of pre-mixing a liquid stream of the reducing agent with a gas stream, and 3) gas analysis by Fourier-transform infrared spectroscopy (FTIR).

![Figure 1: Schematic illustration of the flow reactor setup.](image-url)
A closed cylindrical tank of approximately 1.5 L was used to store a 500 ml aqueous solution of the desired solvable additive, primarily ammonium sulfate. Circulation of cooling water was installed in an outer shell to avoid heating of the solution from the oven. A 24 V ultrasonic humidifier was used to generate a fine mist of the aqueous solutions. The droplet size distribution of the mist was recorded by a high-speed camera, and the average droplet size was determined as \( \sim 1 \, \mu m \) (see Supporting Information). The droplet size distribution was not influenced by the additive concentration. The droplets were transported to the reactor with a carrier \( \text{N}_2/\text{O}_2 \) gas flow.

A mixing unit was installed above the reactor, where the mist was mixed with gas reactants before entering the reactor. Two quartz flow reactors, both designed to obtain plug-flow in the laminar flow regime, were used in the experiments. The reactors were simple straight tubes with inner diameters of 0.6 and 2.1 cm, respectively. Reactants were mixed before heating. The reactor in use was placed in an electrically heated oven with three separate heating elements, which facilitated a uniform temperature profile over a length of 30 cm. Representative measured temperature profiles are shown in Supporting Information. The gas residence times in the isothermal zone were \( 151/T(K) \) s for the small reactor and \( 6686/T(K) \) s for the large reactor.

The concentrations of NO, NO\(_2\), SO\(_2\), H\(_2\)O, and HCl in the flue gas from the reactor were continuously monitored by on-line FTIR spectroscopy (MultiGas 2030). In selected experiments, CO, CO\(_2\), O\(_2\), and NO concentrations were monitored by on-line gas analyzers (NGA2000, Fisher-Rosemount). Due to the presence of NH\(_3\), SO\(_3\), and H\(_2\)O in the outlet stream, sulfurous acid and/or sulfuric acid can potentially be formed by condensation between approximately 115 and 170\(^\circ\)C.\(^4\) In order to avoid condensation of water and sulfur containing species, both the outlet tube and the FTIR was kept at 180\(^\circ\)C. Measurements of NH\(_3\) were uncertain due to potential downstream formation of ammonium sulfate or ammonium chloride in the presence of SO\(_3\) or HCl, respectively.
Estimation of the additive feeding rate

The additive was supplied to the reactor as micron sized droplets generated by a humidifier suspended in an aqueous solution of the additive. However, as the feeding rate of the additive to the reactor could not be actively controlled, it was necessary to make accurate determinations of the actual feeding rate. The NH₃ measurement was not considered reliable, due to uncertainties arising from adsorption, condensation or reaction in the outlet tube. Instead, the feeding rate of additive to the reactor was investigated by two methods, as described below.

In the first method, the feeding rate was estimated from the H₂O measurement by the FTIR gas analyzer, along with the known additive concentration in the aqueous solution. Water was transported to the reactor partly as aerosols (with additive), generated by the humidifier, and partly as water vapor (without additive), from evaporation. Evaporation of H₂O was facilitated by the gas flow in the tank, despite continuous cooling of the tank below 20°C. The relative contribution of aerosols and evaporated H₂O was determined experimentally by running with and without the humidifier turned on. The mist feeding rate was determined as 0.26 mg/s.

In the second method, the additive feeding rate was determined based on decomposition of a urea-water solution (UWS). A 5 wt.% UWS was reacted at 1200°C at varying O₂ and NO conditions, while using a gas flow through the tank similar to that of the H₂O quantification experiment. Urea is known to fully decompose into NH₃ and HNCO at high temperatures. In the presence of O₂ and further promoted by trace amounts of NO, HNCO is further oxidized to CO and CO₂. The feeding rate of urea to the reactor was determined from a carbon mole balance, assuming complete conversion of urea into CO/CO₂ at the highest O₂ and NO concentrations. The total mist flow rate based on this method was determined to be 0.23 mg/s.

The two methods, reported in more detail in SM, yielded comparable results for the mist feeding rate, with flow rates around 0.25 mg/s. The H₂O measurement method was used in
the experiments discussed below.

**EDX analysis**

Particles samples were collected on a fibrous filter downstream of the reactor under SNCR conditions using an aqueous solution of AS (5 wt.%) and KCl (2.5 wt.%). Three samples were collected in individual experiments at steady state temperatures of 850, 1000, and 1150°C, respectively. The samples were analyzed by Energy-dispersive X-ray (EDX) coupled with a scanning electron microscope (SEM) (Prisma E-SEM, manufacturer Thermofisher Scientific, Denmark), to evaluate the elemental composition of the samples. The SEM instrument was operated at an accelerating voltage of 20 kV.

The elemental composition analysis by EDX was conducted at multiple areas (typically 3-5 repeated areas for every sample), in order to ensure the repeatability of the results. The weight distributions of elements were well repeated at every area. Some uncertainty in the measurements can be expected, as the filter temperature was 160°C, possibly allowing a small degree of acid condensation which can affect the results.

**Modeling approach**

Simulations of the SNCR experiments were conducted in ANSYS Chemkin Pro, using a one-dimensional plug flow reactor configuration. At the inlet to the reactor, all reactants were assumed to be gaseous, following immediate evaporation of water aerosols upon entering the isothermal zone of the reactor. The measurements were obtained at steady state conditions and the gas temperature was assumed to be equal to the oven temperature.

The simulations were conducted with a detailed chemical kinetic model for reduction of NO by ammonium sulfate. The model was based on the extensive mechanism for nitrogen chemistry by Glarborg et al. In addition to the nitrogen chemistry, the model contained subsets for H₂/O₂, H₂S/O₂, alkali/sulfur/chlorine, and N/S interactions. In the
present work, a small subset for ammonium sulfate conversion was developed, as discussed below, and a subset for alkali/N interactions was adopted from Zamansky et al.\textsuperscript{17} The full model, including thermodynamic properties, is available as Supporting Information.

A decomposition reaction for ammonium sulfate,

\[
(NH_4)_2SO_4 \rightarrow 2NH_3 + SO_3 + H_2O
\]  

was included in the mechanism, with the rate constant \( k_1 = 9.2 \times 10^6 \exp(-13040/T) \) s\(^{-1}\) drawn from Wu et al.\textsuperscript{48} The low values for the pre-exponential factor and the activation energy indicate that the decomposition occurs in condensed state. The assumption that ammonium sulfate decomposes into NH\(_3\), SO\(_3\), and H\(_2\)O as the sole products, even at the highest temperatures studied, is supported by present experimental results, discussed below. However, it is not consistent with the findings of Wu et al.,\textsuperscript{48} who reported that the sulfur is mainly released as SO\(_2\) at temperatures above 900°C. Since the dissociation reaction conceivably occurs in condensed phase, it is possible that differences in droplet size and reaction conditions may affect the SO\(_2\)/SO\(_3\) ratio, but more work is required to resolve this issue.

The introduction of ammonium sulfate as an additive means that the sulfur oxide levels in the process are significant. Presumably there are interactions between the amine and the sulfur chemistry. The N/S subset was drawn largely from Glarborg,\textsuperscript{53} but extended in the present work. Dagaut and Nicolle\textsuperscript{29} proposed that formation of NH\(_2\)SO\(_2\) might be important for the interactions between amines and SO\(_2\). Consequently, a subset for NH\(_2\)SO\(_2\) was established and implemented in the model. The NH\(_2\)SO\(_2\) adduct is formed by recombination of NH\(_2\) and SO\(_2\),

\[
NH_2 + SO_2(+M) \rightarrow NH_2SO_2(+M) \]  

(R2)

The kinetic data for this reaction were adopted from the study of Gao et al.\textsuperscript{54} There is no information reported about consumption reactions for NH\(_2\)SO\(_2\) so a subset was established
with estimated rates (see SM). However, based on the thermodynamic properties of \( \text{NH}_2\text{SO}_2 \), calculated in the present work, the thermal stability of this species is too low for it to be important at temperatures relevant for SNCR.

For simulations with alkali addition, it was assumed that KCl sublimes instantaneously at the inlet for temperatures above 770°C. This assumption is supported by the study of Knudsen et al.,\textsuperscript{55} who investigated the release of K species from combustion of biomass in a fixed-bed reactor. They showed that all fuel chlorine was released to the gas phase above 800°C. A recent study by Simonsson et al.\textsuperscript{56} showed that alkali salts with low lattice energies (i.e., NaCl and KCl) rapidly dissociate when passing through a flame, which further supports the assumption of a fast KCl sublimation.

A complication in interpreting the flow reactor experiments with addition of potassium chloride is that KCl may react at the quartz reactor wall, forming potassium silicates and releasing HCl to the gas phase. The reaction between alkali chlorides and quartz sand has been studied in fluid bed experiments,\textsuperscript{57,58} but results are not conclusive. To assess the extent of reaction, reference experiments were conducted with a feed consisting of KCl, \( \text{H}_2\text{O} \), and \( \text{N}_2 \), with and without \( \text{O}_2 \). Selected results are shown in Fig. 2.

The results show significant formation of HCl, peaking at around 250 ppm at 800°C. The HCl yield is independent of the presence of \( \text{O}_2 \). Conceivably, the reaction of KCl with \( \text{SiO}_2 \) is limited by the sublimation rate or by kinetics of the gas-solid reaction below 800°C, and at higher temperatures by equilibrium or by deterioration of the reactor wall. The results are not fully repeatable, even though the trends and the temperature for the peak in HCl remain the same. This indicate that the condition of the reactor surface plays a role.

The loss of KCl at the reactor surface introduces an uncertainty in the reaction conditions. However, the results in Fig. 2 provides a measure of the extent of reaction. In the modeling, it has been assumed that these data are representative for the conditions with addition of KCl.
Figure 2: Yield of HCl from a feed consisting of KCl, H₂O, and N₂, with and without O₂. Gas flow rate 1 NL/min, with a reactor residence time of about 0.1 s. A 5 wt% KCl/water solution was used, resulting in an inlet KCl concentration of about 800 ppm. The inlet O₂ was 0 or 2%.

For simplicity, it is assumed in the modeling that the KCl + SiO₂ reaction is instantaneous, so the inlet composition contains a mixture of KCl and HCl according to the measurements in Fig. 2.

Results and discussion

The experimental and numerical results are presented and discussed in this section. The results include investigation of the SNCR performance of ammonium sulfate at varying AS/NO molar ratios, temperature, and residence time. The effect of KCl on NO reduction and the sulfation of KCl by ammonium sulfate, were also investigated. An overview of the experiments, which were all conducted at atmospheric pressure, is found in Supporting Information.
SNCR with ammonium sulfate

In this section, the experimental and numerical results for the SNCR process using ammonium sulfate with varying AS/NO molar ratio at two different residence times are presented. To the knowledge of the authors, this work represents the first laboratory-scale experiments, i.e., under controlled conditions, of the SNCR performance using ammonium sulfate as the reducing agent.

The impact of AS/NO ratio, temperature and residence time

Figure 3 shows the experimental and numerical results of SNCR with AS/NO molar ratios of 0.4, 1.0, and 2.0 at a short residence time of 151/T(K) s. The reported experimental data are given as average values of steady-state conditions at every temperature. The typical fluctuations in the measured concentrations during steady-state is around ±5 ppm. The onset of reaction was found to occur at around 900°C, with the highest NO reduction at around 1050°C for all investigated AS/NO ratios. Reductions of NO of up to 95% were achieved in a somewhat narrow temperature window for AS/NO ratios at or above 1.0. Increasing the AS/NO ratio to 2.0 did not cause a further improvement in the NO reduction, indicating that formation and consumption of NO has reached a steady-state at the optimum. Reducing the AS/NO ratio to 0.4 resulted in a strong decrease in the NO reduction. The present results are consistent with the results of Kassman et al., who reported a significant NO reduction using ammonium sulfate in a CFB boiler.

The onset of formation of SO₂ occurs around 900-1000°C. Above this temperature interval, the SO₂ concentration increases linearly with temperature, reaching levels corresponding to more than 50% conversion of AS to SO₂. The behavior is similar to that observed by Wu et al. for decomposition of ammonium sulfate in a tube reactor. However, the results are not directly comparable, because the experiments of Wu et al. were conducted in an inert
Figure 3: Comparison of modeling and experimental results of SNCR using a 2.5 wt.% (upper left), 5 wt.% (upper right), and a 10 wt.% (lower) AS/H$_2$O solution. The initial conditions with a 2.5 wt.% AS solution were: NO = 400 ppm, (NH$_4$)$_2$SO$_4$ = 160 ppm, O$_2$ = 1%, H$_2$O = 8%, balance N$_2$. The initial conditions with a 5 wt.% AS solution were: NO = 400 ppm, (NH$_4$)$_2$SO$_4$ = 430 ppm, O$_2$ = 1%, H$_2$O = 9.5%, balance N$_2$. The initial conditions with a 10 wt.% AS solution were: NO = 400 ppm, (NH$_4$)$_2$SO$_4$ = 908 ppm, O$_2$ = 1%, H$_2$O = 9.5%, balance N$_2$. The residence time in all experiments were 15l/T(K) s.

atmosphere. Under the present conditions, the O/H radical pool formed by the interaction of NH$_3$, O$_2$, and NO enhances reduction of SO$_3$ to SO$_2$.

The experimental results shown in Fig. 3 are described satisfactorily by the model. However, the onset for reaction occurs at around 25°C lower than predicted. Furthermore, NO is generally overpredicted at higher temperatures, presumably related to overestimation of the O/H radical pool. The onset for formation of SO$_2$ at 900-1000°C is captured well, but the SO$_2$ concentration is strongly overestimated above 1050°C; a further indication that the predicted chain branching is too strong. The overprediction of the reaction rate at high temperatures can presumably be attributed mostly to deficiencies in the amine subset of the kinetic model; similar discrepancies were reported in the review by Glarborg et al.\textsuperscript{2} for
SNCR with NH₃. However, also uncertainties in describing amine / sulfur oxide interactions may play a role.

Figure 4 shows sensitivity analyses for NO and SO₂ above the onset temperature of reaction (1000°C) and above the optimum temperature (1100°C) for the SNCR process using a 5 wt.% AS solution. At both temperatures, the predicted NO reduction is most sensitive to the branching fraction of the NH₂ + NO reaction,

\[
\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH} \quad \text{(R3a)}
\]

\[
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2 \text{O} \quad \text{(R3b)}
\]

where R3a is chain branching, while R3b is terminating. The chain branching reaction H + O₂ → O + OH shows up with a smaller sensitivity. Also prediction of SO₂ is very sensitive to the NH₂ + NO reaction, due to its influence on the radical pool. Generally, more radicals lead to a higher production rate of SO₂ via SO₃ + H = SO₂ + OH. This is consistent with the SNCR results (Fig. 3), which show an increase of SO₂ above 1000°C. Above the optimum temperature, the sensitivity of NO and SO₂ is reversed; here, the chain branching and propagating reactions that lead to an increase in the radical pool promotes the NO formation via NH₂ oxidation.

![Figure 4: Sensitivity coefficients for prediction of NO (left) and SO₂ (right) in the SNCR process using ammonium sulfate for the conditions of Fig. 3.](image-url)
The results of the sensitivity analysis shown in Fig. 4 indicate that the presence of sulfur oxides has an impact on the SNCR chemistry. SNCR experiments with NH$_3$, with and without addition of SO$_2$,\textsuperscript{28–30} indicate that SO$_2$ has only a small impact on the NO reduction, shifting the window for reaction slightly to higher temperatures. Presumably, SO$_3$ is a more active species than SO$_2$, but to our knowledge there are no studies of the effect of SO$_3$ on SNCR.

The reduction of NO was also investigated at longer residence times, but for lower AS/NO ratios. Figure 5 shows experimental and numerical results for SNCR using ammonium sulfate solutions of 2.5 wt.%, 5 wt.%, and 10 wt.% in a larger reactor with a residence time of $6686/T(K)$ s, corresponding to 3-5 s at the relevant temperatures. It was found that the long residence time shifted the temperature window significantly towards lower temperatures, in agreement with the findings of Liang et al.\textsuperscript{6} for NO reduction by NH$_3$. Due to the lower additive feeding rate, the NO reduction levels are lower than those shown in Fig. 3. The temperature for onset of reaction and the temperature for highest NO reduction are both satisfactorily predicted by the model for all three AS solution concentrations.

The impact of KCl on NO reduction

The influence of KCl on the SNCR process was investigated using an aqueous solution with 5 wt.% AS and 2.5 wt.% KCl. Figure 6 shows a comparison of SNCR results in the presence and absence of KCl. The addition of 390 ppm KCl was found to have a strong promoting effect on NO reduction at lower temperatures. It shifts the onset of reaction from approximately 900°C to 800°C and broadens the temperature window by 50-100°C. Also the formation of SO$_2$ is promoted at lower temperatures by addition of KCl.
Figure 5: Comparison of modeling and experimental results of SNCR, using varying AS in H$_2$O solutions. The inlet conditions were: NO = 400 ppm, O$_2$ = 1.3%, H$_2$O = 4.0%, balance gas N$_2$. The residence time was 6686/T(K) s.

Figure 6: Comparison of modeling and experimental results of SNCR using a 5 wt.% AS and a 5 wt.% AS + 2.5 wt.% KCl in H$_2$O solution. The inlet conditions without KCl were: NO = 400 ppm (NH$_4$)$_2$SO$_4$ = 430 ppm, O$_2$ = 1%, H$_2$O = 9.0%, balance N$_2$. The inlet conditions with KCl were: NO = 410 ppm, (NH$_4$)$_2$SO$_4$ = 430 ppm, KCl(g) = 390 ppm, O$_2$ = 1%, H$_2$O = 9.0%, balance N$_2$. The residence time was 151/T(K) s.

The results are in good agreement with observations reported in literature. A promoting effect of various Na/K additives (chlorides, carbonates, and hydroxides) on NO reduction has been demonstrated in SNCR experiments with both NH$_3$\textsuperscript{17-20} and urea\textsuperscript{21-26} as additives. The presence of alkali salts acts to widen the window for the process to lower temperatures,
typically by 50-100°C, while the performance at temperatures at and above the optimum is only slightly affected. Apparently potassium and sodium salts behave very similarly, and consistent results are obtained in reactors of scales varying from laboratory size to pilot scale. The present results are remarkable because the strong impact is observed despite the fact that a large fraction of KCl is converted either to potassium sulfate by reaction with SO₃ (see below) or to potassium silicates by reaction with the quartz reactor wall. However, literature results indicate that even small levels of alkali salts have an effect. Hao et al.²⁰ found that addition of 125 ppm KCl enhanced the NO reduction by 15% at 850°C, while Guo et al.¹⁹ showed that addition of 25 ppm Na₂CO₃ improved the NO reduction at 750°C from 20% to 70%.

Figure 6 shows that the present model strongly underestimates the promoting effect of KCl on NO reduction at lower temperatures. The failure to capture fully the observed enhancement of reaction by adding alkali salts is common for the reported modeling studies.¹⁷⁻¹⁹,²⁴ All the models, including the present one, have adopted the mechanism of enhancement from the work of Zamansky et al.¹⁷ It involves conversion of the added alkali salt to alkali hydroxide, here by the fast reaction KCl + H₂O ⇌ KOH + HCl, followed by the reaction sequence (here for potassium as the added alkali) KOH $\rightarrow^{O_2} KO_2$ $\rightarrow^M K$ $\rightarrow^{NO_2} KO$ $\rightarrow^{H_2O} KOH$. The most sensitive reactions are¹⁷,¹⁹

$$\text{KOH} + \text{O}_2 \rightarrow \text{KO}_2 + \text{OH} \quad \text{(R4)}$$

$$\text{KOH} + \text{M} \rightarrow \text{K} + \text{OH} + \text{M} \quad \text{(R5)}$$

$$\text{KO} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{OH} \quad \text{(R6)}$$

The sodium equivalent of reactions R5 and R6 have both been characterized experimentally; both Na + OH + M²⁹ and NaO + H₂O⁶⁰,⁶¹ are quite fast, with the latter proceeding close to collision frequency. Assuming that sodium and potassium gas-phase reactions have comparable rate constants,³⁵ there is limited uncertainty for $k_{5b}$ and $k_6$. Reaction R4 has not been
measured, but is represented in the mechanism in the reverse direction with a rate constant $k_{4b}$ also close to collision frequency. There is thus limited room for improving modeling predictions by increasing rate constants. Even though the thermodynamic properties of KOH and KO$_2$ (and the sodium equivalents) have been in discussion, current values$^{35,62,63}$ are believed to be quite accurate. Under the present conditions the KOH enhancement mechanism is further inhibited, because KOH is predicted only in very small concentrations, partly because KCl at lower temperatures is favored thermodynamically to KOH, and partly because a large fraction of the potassium is bound in sulfates and silicates.

For temperatures above 770°C, the sublimation rate of KCl is assumed to be fast due to the small droplet size ($\sim 1 \ \mu$m), in line with the results from Knudsen et al.$^{55}$ Still, it is desirable in future work to validate this assumption, e.g., by estimating the required time for complete sublimation of KCl for this droplet size at temperatures between 770-850°C. Since the present results do not provide evidence of KCl sublimation at the investigated conditions, it cannot be concluded whether the observed promoting effect of KCl on NO production is due to gas-phase interactions or to catalytic effects of KCl aerosols. Clearly, more work is required to understand and simulate the promoting effect of alkali salts on SNCR.

The model captures qualitatively the effect of KCl on the SO$_2$ yield, but again it underestimates the effect. A sensitivity analysis at 1000°C indicates that the predicted SO$_2$ is mainly sensitive to the reactions SO$_3$ + H $\rightarrow$ SO$_2$ + OH and KOSO$_2$(+M) $\rightarrow$ KO + SO$_2$(+M). The intermediate KOSO$_2$ is produced from association of K atoms with SO$_3$; K + SO$_3$(+M) $\rightarrow$ KOSO$_2$(+M). Thus, the addition of KCl presumably promotes the reduction of SO$_3$ to SO$_2$ both through its influence on the radical pool and by direct K/S interactions, but this influence is underestimated by the model.

**Sulfation of KCl by ammonium sulfate**

In order to investigate the degree of KCl sulfation by ammonium sulfate during SNCR operation, particle samples were collected on a filter downstream of the reactor at selected
stable SNCR operating conditions. Based on the observed impact of KCl on NO reduction (Fig. 6), it was chosen to collect samples at 850, 1000, and 1150°C to gain information about the degree of KCl sulfation well below the optimum, close to the optimum, and well above the optimum for NO reduction.

The elemental composition of the samples obtained by EDX analysis is shown in SM. Figure 7 shows a comparison between the experimental and predicted Cl/(Cl+S) molar ratio, which provides a measure of the degree of sulfation. The EDX results showed a high amount of S and low amount of Cl in the samples collected at 850 and 1000°C, while at 1150°C a high amount of Cl was detected. Thus, temperatures of up to 1000°C seem to favor KCl sulfation, while temperatures at or above 1150°C causes poor KCl sulfation. The significant extent of sulfation only below 1150°C was also observed in recent studies on aerosol emissions from biomass + SO₂ combustion or co-firing;⁶⁴,⁶⁵ as discussed below, the formation of alkali sulfates above this temperature is presumably thermodynamically constrained.

The EDX results were used to evaluate the capability of the model to describe the KCl sulfation by (NH₄)₂SO₄ under SNCR conditions. In these simulations, the inlet KCl concentration was scaled down from 390 ppm to 265 ppm, due to the observed reaction between KCl and the quartz reactor surface. The reduced inlet KCl concentration is not expected to have any impact on the overall trends in the alkali transformations, and the simulation results can thus still be compared qualitatively with the EDX results. The model predictions are in good agreement with the experiments, supporting the validity of this aspect of the model.

Figure 8 shows the transient results of the simulations at the temperatures of 850, 1000, and 1150°C. The alkali chemistry is seen to be very fast, with the majority of the transformations occurring within the first 0.2 cm of the reactor, corresponding to a residence time of about 0.5 ms. For a reactor temperature of 850°C, the predicted Cl/(Cl+S) molar ratio among the alkali salts in the heated zone was found to be reduced from 1.0 to 0.3. For
Figure 7: Comparison of experimental and predicted Cl/(Cl+S) molar ratios of collected particle samples from AS/KCl SNCR experiments. The inlet composition in the experiments was: NO = 400 ppm, (NH₄)₂SO₄ = 430 ppm, KCl(g) = 265 ppm, HCl(g) = 165 ppm, O₂ = 1%, H₂O = 9%, balance N₂. The residence time was 151/T(K) s.

At a reactor temperature of 1000°C, part of the KCl is still sulfated within the heated zone, although the predicted degree of sulfation is lower compared to 850°C, with a Cl/(Cl+S) ratio of 0.6. During the cooling period of the simulations at 850 and 1000°C, the remaining KCl is predicted to transform completely into K₂SO₄, which then nucleates to form aerosols. Thus, the simulations are in good agreement with the EDX results, which did not detect any Cl in the samples collected at reactor temperatures of 850 and 1000°C. At 1150°C, the model predicts a very low degree of sulfation within the heated zone. Part of the KCl is initially transformed into KH₂SO₄ and K₂SO₄, but is converted back to KCl before it reaches the cooling zone. After the cooling period, the main compound is predicted to be KCl in condensed form (the KCl dimer in the predictions), with small amounts of K₂SO₄. These results are also in good agreement with the EDX results, which shows high amounts of Cl and low amounts of S in the sample collected at 1150°C.

Figure 9 shows a reaction pathway analysis for K transformation during the SNCR process using the AS/KCl solution, conducted at 1000 and 1150°C. The gas-phase chemistry of K
Figure 8: Transient simulations of alkali transformations under SNCR conditions at 850°C (upper left), 1000°C (upper right), and 1150°C (lower). The inlet composition in the experiments was; NO = 400 ppm, \((\text{NH}_3\)\)\(_2\)\(\text{SO}_4\) = 430 ppm, KCl\((g)\) = 265 ppm, HCl\((g)\) = 165 ppm, O\(_2\) = 1%, H\(_2\)O = 9%, balance N\(_2\). The residence time was 151/T(K) s. Between 30-45 cm, the gas is cooled linearly from the reactor temperature to 300°C.

species is fast, and quickly reaches equilibrium upon entering the reactor. According to the model, the initial step in the gaseous \(\text{K}_2\text{SO}_4\) formation is an association reaction; KCl + \(\text{SO}_3\) (+M) → KSO\(_3\)Cl (+M). The alkali oxysulfur chloride complex further reacts in a sequence of shuffle reactions leading to formation of \(\text{K}_2\text{SO}_4\); KSO\(_3\)Cl + H\(_2\)O → KHSO\(_4\) + HCl, KHSO\(_4\) + KCl → \(\text{K}_2\text{SO}_4\) + HCl. Theoretical evaluations have indicated that KSO\(_3\)Cl and KHSO\(_4\) are sufficiently stable in the gas phase up to 1100°C to act as precursors for \(\text{K}_2\text{SO}_4\).\(^{35}\) As discussed above in relation to Fig. 8, the high temperature alkali reactions are very fast and partial equilibrium is achieved promptly. The partitioning of the alkali species in the isothermal region of the reactor is determined by equilibrium constraints, rather than
by rate limiting steps. Downstream, at the reactor outlet, the sulfation rate is determined
mostly by the cooling rate and by the rate of homogeneous nucleation, with only a small
sensitivity to the rate constants of the potassium reshuffling reactions shown in Fig. 9.

![Chemical Reaction Diagram]

Figure 9: Pathway analysis for gas-phase alkali transformation in the SNCR process using
ammonium sulfate. The analysis was conducted at a) 1000°C and b) 1150°C.

Since SO₃ is assumed to be a direct product from decomposition of ammonium sulfate, the
oxidation of SO₂ to SO₃ is not rate-limiting for the KCl sulfation in the present calculations.
However, the SO₂ concentration was found to increase linearly with temperature above 900°C
in the SNCR experiment with AS/KCl solution (see Figure 9). Thus, the KCl sulfation may
in reality be limited by reduction of SO₃ to SO₂ above 900°C.

At 1150°C, the alkali chemistry is notably more complex, and involves several recycle
sequences. KCl is mainly converted to KOH through the following reaction sequence; KCl +
H → K + HCl, K + O₂ (+M) → KO₂ (+M), KO₂ + OH → KOH + O₂. The intermediate
KO₂ is also formed through a sequence of association reactions with SO₂; K + SO₂ (+M)
→ KOSO (+M), O₂ + KOSO (+M) → KOSO₃ (+M), KOSO₃ (+M) → KO₂ + SO₂ (+M).
A small amount of K$_2$SO$_4$ is produced through a reaction sequence started by association of K with SO$_3$; K + SO$_3$ (+M) → KOSO$_2$ (+M), OH + KOSO$_2$ (+M) → KHSO$_4$ (+M), KHSO$_4$ + KCl → K$_2$SO$_4$ + HCl. However, under these conditions parts of the consumed KCl is replenished from reactions of K$_2$SO$_4$ with Cl and KOH with HCl. As a consequence, ammonium sulfate is not as efficient in the sulfation of KCl at 1150°C as compared to 1000°C.

Conclusions

The use of ammonium sulfate in the SNCR process was investigated in a laboratory-scale flow reactor setup, using a liquid feeding system for the supply of additive to the reactor. The SNCR performance was evaluated at (NH$_4$)$_2$SO$_4$/NO molar ratios of 1.1 and 2.3, which both demonstrated NO reductions up to 95% in a temperature interval of 1025-1075°C. Longer residence times shifted the optimum temperature window towards lower values. Addition of 390 ppm KCl was found to promote NO reduction, shifting the onset temperature of reaction towards lower temperatures by 100°C, while widening the operating window. A high degree of KCl sulfation could be obtained at temperatures of or below 1000°C, while the sulfation was significantly reduced at higher temperatures.

A detailed kinetic model was established to describe both NO reduction and sulfation of KCl by ammonium sulfate. The NO reduction was predicted satisfactorily by the model, with a small offset by 25°C in the predicted onset of reaction. However, the model overestimated NO, as well SO$_2$ formed from AS, at high temperatures, conceivably due to overestimation of chain carriers. The sulfation of KCl was captured well, but the promoting effect of KCl on SNCR with ammonium sulfate was greatly underestimated.

Supporting Information

The Supporting Information contains material about droplet size measurements, additive feed quantification, experimental overview, measured temperature profiles, urea SNCR ex-
periments, and EDX characterization of filter samples.

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