Influence of mixing, oxygen and residence time on the SNCR process

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HIGHLIGHTS

- Mixing comes into play only at higher temperatures within the temperature window.
- Oxygen has opposite influence on NO and N₂O at lower and higher temperatures.
- NO₂ yield is always enhanced by increasing O₂.
- Extending residence time shifts the optimum temperature to lower values until 1173 K.
- Our mechanism has good applicability for NOₓ reduction within tolerable uncertainty.

ABSTRACT

A laboratory-scale laminar flow reactor coupling chemical reaction and mixing process is used to study the influence of operating conditions (mixing, temperature, oxygen and residence time) on the selective non-catalytic reduction (SNCR) process, in terms of the variations in the concentrations of NO, NH₃, NO₂ and N₂O. As the results indicated, mixing process only comes into play at higher temperatures. At lower temperatures enriched O₂ enhanced NO reduction and N₂O yield, with more NH₃ being consumed. At higher temperatures, increasing O₂ inhibited NO reduction and suppressed N₂O formation, with the depletion of NH₃. NO₂ yield was always enhanced by increasing O₂, especially at lower temperatures. Extending residence time progressively shifts the optimum temperature for NOₓ reduction to lower values, but for a sufficiently long residence time, the optimum temperature finally settled at about 1173 K. The detailed mechanism developed in this work gave qualitative and quantitative agreement with our experimental data. Evaluation against several independent works illustrates its capability to predict cases with or without significant mixing process.

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1. Introduction

Oxynitride emission is one of the major sources of air pollution which affect environment seriously. In recent years, several strategies have been developed to accomplish reduction of the oxynitride emission, especially from thermal power plants. Among them, selective non-catalytic reduction (SNCR) technology is known to be a very promising approach because of low investment cost and attractive reduction efficiency.

Study on SNCR has been focused on chemical kinetics during the last decades [1–6]. NO reduction occurs only within a narrow temperature window between 980 K and 1380 K without any additives. Reduction efficiency up to 90% can be achieved with an optimum temperature of about 1240 K [7]. Database has firmly established that among various operating conditions, temperature is the leading one to determine the output of the SNCR process. In fact, the best reduction efficiency achieved so far in utility units is limited to about 40% [8,9], mainly due to the failure of the reductant to mix with NOₓ-loading flue gas perfectly. This fact indicates that transport phenomena play a strong role in the real SNCR process. For most of the previous studies, reactors working in one dimensional Plug Flow Reactor (PFR) or Perfect Stirred Reactor (PSR) model have been favored as the laboratory workhorse to obtain intrinsic kinetic data. While limited effort on non–premixed reactor has demonstrated that mixing comes into play only at higher temperatures [10,11], there is by far no experimental evidence presenting the systematic impact of changing mixing rate with well-defined laminar flow characteristics reported.

Several detailed mechanisms [12–16] have been proposed on SNCR. However, no available mechanism is able to perfectly represent the impact of a broad domain of operating conditions, probably due to the fact that many key intermediates and their roles in the “actual” mechanism have only recently (or never) been identified, therefore it is doubtful if the rate parameters have assumed
their ultimate values. In addition, may be because the earlier database focused solely on NO and NH₃, the reported predictions usually emphasized on the dynamics of these two species during the process, despite of the participating of the other N-containing gases such as NO₂ and N₂O in the whole reacting system.

In this paper, we work with a laminar flow PFR in which mixing intenseness could be regulated continuously, to study the effect of mixing rate, temperature, initial O₂ concentration, the residence time was depending on the aver-

eage temperature of all the gaseous species were controlled by mass flow controllers with an accuracy of ±2% to yield a total gas flow rate fixed to 2.06 L/min (at standard conditions), and the distance can be regulated so that residence time may be varied at will to determine extent of the reaction. In the study of the effect of temperature and initial O₂ concentration, the residence time was depending on the average temperature T according to the relationship t = 1024/T. Other-

wise, the residence time was adjusted from t = 128/T to t = 1024/T s at various temperatures to study its own effect.

While the partitioning of N₂ to reductant flow and simulated flue gas is adjusted to obtain various flow rate ratios between the two streams, thus the intenseness of the mixing can be regulated at will. Calculation shows that the mixing time gradually shrinks with increasing temperature, and this dependence varies with the flow rate ratio between the two streams. For six individual mixing rates we examined, the correlations for mixing time as a function of temperature (in Kelvin) are t = 47/T, 53/T, 60/T, 73/T, 89/T and 112/T, respectively.

NO, NH₃, NO₂ and N₂O, sampled by the water-cooled probe, were continuously quantified by a Gasmet Fourier Transform Infrared Spectroscopy (FTIR) analyzer with an accuracy of ±2%. O₂ was measured with an accuracy of ±0.3% by an electrochemical flue gas analyzer.

3. Modeling

As a reference calculation for a fully premixed system, a plug flow reactor model was used at first. In this stage, a low Mach number model provides a full description of the two dimensional reacting flow. Then, a simple approach of Zwiering [17] referred to as “maximum mixedness model” has been employed to model the mixing process of a jet (reductants) with a cross flow (simulated flue gas) in the SCNR process. The maximum mixedness model can offer a simplified assessment of the effect of mixing on the chemistry. The Zwiering approach together with the detailed mechanism has been used with some success to describe the effect of mixing on the natural gas reburning [18–20] and the SNCR [11,21–23] processes. In this work, the simulated flue gas is progressively incorporated into the reductants jet. So, it is assumed that the mass flow of the cross flow entrained into the reductants jet at a given time is considered to follow the equation:

\[-\frac{dm_{cross}}{dt} = km_{cross}\]  \hspace{1cm} (1)

and the mass flow of the jet flow follows the equation:

\[\frac{dm_{jet}}{dt} = km_{cross}\]  \hspace{1cm} (2)

where \(m_{cross}\) to the mass flow of the main cross flow, \(m_{jet}\) corresponds to the mass flow of the jet stream, and \(k\) to a fictitious constant accounting for mixing. With this assumption, which implies an exponential mixing rate, the mass flow of the reductants jet at a given time is expressed by the following equation:
\[ m_{\text{jet}}(t) = m_{\text{jet}}(0) + m_{\text{cross}, 0}(1 - \exp(-kt)) \]  

where \( m_{\text{jet}}(t) \) corresponds to the mass flow of the jet stream at any time, \( m_{\text{jet}}(0) \) corresponds to the mass flow at initial time. The constant \( k \) is calculated \( k = \ln(m_{\text{cross}, 0}/m_{\text{cross}, i})/t \)

The mixing time accounts for the segregation in the reactor due to macro- or micromixing. Thereby, an increase in the mixing time corresponds to a slower rate of mixing of the reactants. In this work, the mixing time has been taken as the time for which 90\% of the cross flow is mixed with the reductants jet, i.e., \( k = \ln(10)/t_{\text{mix}} \). At the moment of the mixing time, the concentration of reductants has diffused down to about 110\% of its final concentration. The mixing time is obtained from CFD (Computational Fluid Dynamics) calculations by integrating the flow field [11]. The chemical kinetic mixing time is obtained from CFD (Computational Fluid Dynamics) simulations by using the Sandia SENKIN program of CHEMKIN subroutines [24,25]. This program also solves the conservation equations for mass and energy. It can calculate homogeneous phase reaction of gases in reactors of diverse configurations, describing the evolution history of mole fractions of species. In addition, it can perform kinetic sensitivity analysis. Therefore, the SENKIN model is appropriate to research the homogeneous reaction mechanisms of NO\(_x\) reduction. The detailed mechanism developed in this work is listed in Appendix A. Our mechanism has been developed based on the framework of Rota [14], AA [15] and the KLIP [12,13,16] mechanisms.

### 4. Results and discussion

#### 4.1. Experimental results

The operating conditions are shown in Table 1. The initial concentrations of NO and NH\(_3\) were kept at 400 and 480 ppmv. The N\(_2\) was used as the carrier gas. To study the effect of mixing rate ranging from \( t_{\text{mix}} = 47/T \) to 112/T, the initial O\(_2\) concentration was kept at 3\%, in all other cases the mixing rate was always a function of temperature as \( t_{\text{mix}} = 112/T \).

#### 4.1.1. Effect of mixing time

The impact of the mixing rate on the NO reduction is depicted in Fig. 2. Discernible effect can only be observed at higher temperatures, especially when the temperature is above the optimal value for NO reduction. At any temperature the reduction is limited to some extent by extended mixing time, and again, the effect is more remarkable at higher temperatures. All these observations demonstrate that at temperatures roughly below the optimal value, the mixing rate, at least within the range we examined, is not the rate-limiter of the process.

#### 4.1.2. Effect of initial O\(_2\) concentration and temperature

In this section, we focus on the O\(_2\) concentration dependence of the SNCR process. The initial O\(_2\) concentration varies from 1\% to 6\% with an 1\% increment between series of runs, as well as different nominal isothermal temperatures determining the residence time according to the correlation \( t = 1024/T \). The variations of species NO, NH\(_3\), NO\(_2\) and N\(_2\)O as functions of both O\(_2\) concentration and temperature are depicted in Fig. 3a–d, respectively.

In Fig. 3a it appears that, in all of the cases NO begins to diminish from its initial value at about 1048 K through a minimum at roughly 1173 K, and then increases monotonously with elevated temperature. The temperature at which most extensive NO reduction can be achieved almost keeps constant for the O\(_2\) concentration range examined, although the final NO concentration shows a slightly positive response to the increasing initial O\(_2\) concentration. So, the optimum temperature here is 1173 K, and the maximum NO reduction efficiency is up to 96.5\%.

From Fig. 3a we also observe the complex relationship between the effects of O\(_2\) concentration and temperature on NO reduction. Below 1148 K, richer O\(_2\) atmosphere promotes NO reduction, which appears to be extremely sensitive to changes in initial O\(_2\) concentration, especially in the region around 1098 K, whereas at and above this threshold temperature growing O\(_2\) concentration seems to suppress NO reduction but less variation can be found among the qualitative sensitivity of NO reduction to initial O\(_2\) concentration. These features are in qualitative agreement with earlier work [4].

The effects on NH\(_3\) appear in Fig. 3b. Below 1198 K, higher temperatures and initial O\(_2\) give rise to enhanced NH\(_3\) consumption and the behaviors are qualitatively similar to that of NO. Above 1198 K, depletion of NH\(_3\) can be observed under any initial O\(_2\) concentration tested. The findings described above give useful suggestions to identify optimal operating conditions in utility units: for temperature region below some level, approximately 1148 K, raising initial O\(_2\) concentration and temperature is in favor of NO reduction as well as suppressing the amount of excessive NH\(_3\); the most extensive NO reduction occurs at about 1173 K; pushing temperature to higher values ensures complete depletion of NH\(_3\) but gradually lessens NO reduction, with initial O\(_2\) concentration playing a similar but relatively minor role.

It could be seen in Fig. 3c that in the range examined rising initial O\(_2\) concentration invariably enhances NO\(_2\) formation, and widens the temperature interval in which experimentally detectable amount of NO\(_2\) can be sensed. Under any O\(_2\) level, the

<table>
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<th>Parameters</th>
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<th>Value or formula</th>
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<tr>
<td>NO</td>
<td>ppmv</td>
<td>400</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>ppmv</td>
<td>480</td>
</tr>
<tr>
<td>O(_2)</td>
<td>Vol.%</td>
<td>1, 2, 3, 4, 5 and 6</td>
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</tr>
<tr>
<td>Total flow rate</td>
<td>NL min(^{-1})</td>
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</tr>
<tr>
<td>Temperature</td>
<td>K</td>
<td>998 K–1373 K</td>
</tr>
<tr>
<td>Residence Time</td>
<td>s</td>
<td>( t = 128 \times n/T, n = 1, 2 \ldots 8 ) (T in Kelvin)</td>
</tr>
<tr>
<td>Mixing Time</td>
<td>s</td>
<td>( t_{\text{mix}} = m/T, m = 47, 53, 60, 73, 89 ) and 112 (T in Kelvin)</td>
</tr>
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</table>

Fig. 2. Experimental evaluations of NO concentration with temperature for various values of the mixing time. Initial conditions are as follows: NO = 400 ppm, NH\(_3\) = 480 ppm. O\(_2\) = 3 vol\%, carrier N\(_2\). Residence time \( t = 1024/T \). The mixing time has been taken as the time for which 90\% of the cross flow is mixed with the reductants jet. The solid lines are drawn to guide the trends in data.
maximum NO2 yield can be reached essentially at the same temperature, which is approximately 1098 K. For temperature higher than 1248 K, NO2 does not diminish to the asymptotic value but shows a slight increase, especially for more enriched O2 atmosphere. From Fig. 3d it appears that as temperature rises, the N2O yield increases, reaching a maximum value and then diminishes. However, with reduced initial O2 concentration, the maximum value of N2O yield gradually shrinks and the downward trend after peak yield becomes less sharp, although the 6% O2 case seems like an exception. Consequently, it seems that below about 1198 K O2 plays a role to promote N2O formation while at and above the threshold temperature the situation gets reversed.

4.1.3. Effect of residence time

With temperature identified as the most sensitive factor in the SNCR process, the optimum temperature to achieve the most extensive NO reduction in the NO/O2/NH3 system continues to stimulate controversy and confusion. Previous experimental work usually reported different values with relatively shorter residence time. For example, an optimum temperature of about 1248 K was observed by Muzio [7], Rota [5] and Dagaut [6] with a residence time of about 0.1 s, while 1223 K was measured by Wenli [26] with a longer residence time of about 0.5 s. Particularly, one work [3] noted a trend that extended residence time may shift the optimum temperature to lower values. And in that work, residence time used was no longer than 0.227 s.

All the data in this section are prepared with 3% O2 initially. The results are shown in Fig. 4, from which it can be seen that initially extending residence time progressively shifts the optimum temperature to lower values, but for sufficiently long residence time the optimum temperature finally reaches an asymptotic value, consistent to the observation of Duo and Rojel [3,19]. We also find that the minimum NO concentration at the reactor outlet can be reduced as residence time being extended, although this impact becomes indiscernible if longer residence time is available. Also, at higher temperatures, the ultimate NO concentration is less sensitive to the variation in residence time than at lower temperatures, which may be attributed to the impact on the magnitude of rate coefficient by temperature, according to Arrhenius law.
4.2. Kinetic model and analysis

4.2.1. Kinetic model

SNCR chemical kinetics have been extensively studied with detailed mechanisms proposed, particularly by Miller and Glarborg [3,6,22,25,26]. In recent years, an important intermediate, NNH, has attracted continuous attention from researchers, but the length of its lifetime is quite controversial. Researchers [16] reviewed the studies on the lifetime of NNH, pointed that a lower value between $1 \times 10^{-9}$ to $2 \times 10^{-9}$ s may be a good estimate with respect to the thermal rotational states of NNH at 1000–1500 K, while theoretical studies indicate values between $4 \times 10^{-10}$ to $3.6 \times 10^{-8}$. However, the uncertainty in this prediction is still significant, the short NNH lifetime involved prohibits phenomenological description, and sophisticated theoretical analysis remains a daunting challenge. Adopting very short lifetime for NNH in mechanism seems to cause the predicted onset temperature to be less sensitive to the $O_2$ concentration in the range 4%-50% than observed experimentally [16]. Relatively longer lifetimes for NNH have been proposed as $1 \times 10^{-4}$ s [14], $1 \times 10^{-3}$ s [15,27] and about $1.5 \times 10^{-4}$ s [6,13,28], and fairly good agreements with experimental data are obtained, although these values might not represent fundamental significance. We adopt $2 \times 10^{-7}$ s for NNH, along with other modifications in our work. It should be noted that our NNH lifetime may carry little fundamental meaning, but our aim is to obtain better agreements with the available database in the literature. Using this value is also encouraged by previous modeling efforts [16,27] which indicated that a value of about $1 \times 10^{-7}$ may lead to the best agreement between predictions and experimental results. The value we adopt only works well with the mechanism we proposed. The discrepancy with theoretical values [16,29–31] may reflect the problems in reaction pathways and rate coefficients, which require further work.

While the available mechanisms have provided useful insights into the SNCR process, it is still difficult to quantitatively predict all the impact of a broad domain of various operating conditions. Because of the obstacle to yield every rate parameters either phenomenologically or analytically, and in line with the fact that most of the experimental data being reported without error bars, we try to make some fine-tuning on some relevant parameters based on the detailed mechanisms proposed to reconcile discrepancies between independent studies. The bulky body of our modifications is listed in Table 2. Refer to Supplementary data for all the coefficients.

4.2.2. Evaluations against literature database

In this section, evaluations against several independent datasets from a broad domain of operating conditions are made to corroborate the applicability of the proposed mechanism.

All the data [2,4,26] collected herein were derived from reactors working in such a manner that all the reactants (or at least NO and NH$_3$) are believed to fully premixed before being heated. Evaluation against data from such reactors will be presented to demonstrate the validity of the detailed mechanisms proposed. Evaluation against literature data affected by mixing process is impossible. Unfortunately, bulk of mixing-influenced literature data have to be omitted here. The dataset from Rojel [11] didn’t come with enough details regarding the diffusion streams’ configuration to enable calculation of the mixing time. Data from Ostberg derived from experiments in which NH$_3$ was injected laterally into the flue gas. The flow pattern had a strong tendency to turbulence and was incompatible with the mass transfer model we use here, which only applies to laminar concentric streams. Therefore, the evaluations presented here only serve to demonstrate the validity of chemistry aspect of our model.

Table 2

<table>
<thead>
<tr>
<th>No</th>
<th>Reactions (k = A $T^n$ exp(-E/RT))</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>7</td>
<td>NH$_3$ + NO = N$_2$ + H$_2$O 1.18E+16 $-1.2$ 0.0 This work</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>HNO + O$_2$ = NO + HO$_2$ 2.00E+13 $-0.0$ 25000.0 This work</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>NNH + H = N$_2$ + H$_2$O 5.00E+07 $-0.0$ 0.0 This work</td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>NNH + O$_2$ = N$_2$ + HO$_2$ 1.00E+07 $-0.0$ 0.0 This work</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 shows comparisons of experimental results reported by Lyon [2] on temperature window with predictions calculated with three mechanisms. Throughout the temperature range examined our mechanism agrees well with the data. The model shows good prediction for the onset, optimum temperature of NO reduction and the minimum NO concentration. The only discrepancy is less sensitivity of NO reduction to the rising temperature before maximum NO reduction is achieved, which is better predicted by the other two mechanisms.

Fig. 6 shows a comparison of experimental data by Kasuyab [4] with model results calculated with our mechanism. The K mechanism [16] predicted the observed wide variation in the initiation temperatures for the O$_2$ concentration range, although overestimated by a little, however, it predicts nearly identical initiations for initial O$_2$ concentration from 4% to 50%, at odds with the data. Our mechanism predicts relatively narrower variation in the initiation temperature, but agrees better with the data regarding the initiations for initial O$_2$ concentration from 4% to 50%.

It could be observed that our prediction yields higher outlet NO concentration in most of the cases for this dataset. For clarity we use the parity plot shown in Fig. 7 to show the comparison between predictions and data with O$_2$ from 1% to 20%. Aside from a few discrepancies appear at the lower limit of the temperature window, where very accurate agreement on the initiation of reduction can barely be achieved, all the data show more extensive reduction than do the predictions. Probably the reason lies in the uncertainties in the thermal history of the experiment. These data...
were collected with very short residence time, and the gases were sampled by an air-cooled probe. The apparatus was described as the same type as used in [3]. However, the exemplary thermal history showed in [3] indicates the gases travelled through the air-cooling tube, of length comparable to that of the reaction tube, with temperature dropped by no more than 200 K, so it is possible that reactions continued to occur in the probe. More important, for runs where nominal reaction temperature was well above the optimal reduction value, this problem means the gases spent extra residence time at temperatures in favor of NO reduction. The calculations do not account for this potential problem in line with the lack of clarification.

The comparison between data from Duo and our mechanism appears in Fig. 8. The predictions give results comparable to AA mechanism at high temperatures and slightly better agreement at lower temperatures. However, the KLIP mechanism agrees more closely to data prepared at temperatures lower than the optimal value.

**4.2.3. Evaluations against our experimental data base**

In this section, we evaluate the mechanism against our data affected by mixing process. To make clear, we present only the comparisons for several typical mixing times, initial O₂ concentrations and residence times.

Fig. 9 shows the effect of mixing time. Three work conditions of \( t_{\text{mix}} = 47/T, 73/T \) and \( 112/T \) for comparison are calculated. Although we didn’t perform pre-mixed experiment because of the character of our apparatus, calculated values for such case, i.e., mixing time reduced to nominally zero, also appear as a reference. The prediction indicates virtually no effect in the low temperature domain, while the data depict a very small variation. Much pronounced variation at high temperature domain is also predicted, although the calculated variation is more sensitive to the rising temperatures and extended mixing times than the data showed.

We afterward present predictions against our data regarding the effect of temperature and initial O₂ concentration in Fig. 10. Three initial O₂ concentrations of 1%, 3% and 6% are presented to the comparison.
In Fig. 10a, the model predicts the minimum temperature required to initiate remarkable NO reduction and the temperature at which most extensive reduction can be achieved, as well as its independence of O2 within experimental uncertainty. The model also illustrates the promotion and suppression of NO reduction in the two temperature regions by the presence of O2. Note that the reduced sensitivity of NO reduction to variation in initial O2 concentration at higher temperatures is also predicted accurately throughout. Similar qualitative and quantitative agreement is also given for NH3 in Fig. 10b.

As for NO2 there are some quantitative discrepancies between the measured and predicted yields shown in Fig. 10c. First, for low and intermediate O2 concentrations, the peak yields of NO2 are over-predicted by 50%–100%. Second, according to experimental data, the maximum NO2 yield can be achieved at essentially the same temperature whereas the prediction indicates a minor shift to higher temperatures with progressively reduced O2 available. It is hard to tell whether experimental uncertainty or the model itself is accountable to these discrepancies because the typical yield of NO2 is about one order of magnitude less than either NO or NH3, and the absolute differences between measured and predicted values are quite small. Notwithstanding, the prediction is quite close to the data for temperatures higher than 1173 K.

A similar scenario can be found with N2O in Fig. 10d. The predictions are almost within experimental uncertainty throughout. However, the prediction shows that, subject to reduced O2, the temperature to reach peak N2O yield shifts slightly to higher values, while the measured results depict a constant temperature except for the case with 1% O2.

The lines in Fig. 11 denote predicted values. The predictions qualitatively depict the variations of the ultimate NO concentration and the optimum temperature affected by the gradually extended residence time. Obviously, the predictions deviate from the measured values, especially for the runs with higher temperature or shortened residence time. However, the discrepancy is probably no direct indication of potential flaws in the chemistry aspect of the model, but of the treatments on the mass transfer details. In the actual apparatus, the simulated flue gas and the reductant are injected parallely into the reactor tube. The subsequent mixing is not very intense because the fluid flow is laminar in nature. Hence, mass transfer between the flue gas and the reductant is a finite-rate process. However, the model inherently assumes normally infinite rate mixing on any cross section,
rendering the mass transfer between the two streams modeled partially approach an infinite-rate step. This artificial “speed-up” of the mass transfer process in constantly represents a diluted O2 atmosphere where major reactions occur, especially in the entrance section with respect to the species concentration, to the reaction system in comparison to the authentic experimental conditions. Recall that we have affirmed with longer residence time the O2’s promotion on NO reduction at low temperature as well as its opposite effect at intermediate and high temperatures, so the deviation of the predictions from measured values at any temperature becomes self-explanatory. This interpretation also explains why the discrepancy appears to be more noticeable with higher temperature or lessened residence time. As we analyzed before, with increasing temperature the chemical time scale gradually shrinks, so the entrance section which is not perfectly modeled plays an increasing role in the whole process. For short-residence time, reaction occurs in the entrance section also becomes more dominant. This argument is important because reaction rates usually be inferred from integral conversion data by fitting the parameters in a reaction model, and during the fitting procedure, uncertainties in the treatment of mass transfer process which couples with chemical reactions translate directly into uncertainties in the modelling parameters.

According to the above comparisons and analysis, it can be seen that our mechanism has good applicability for NOx reduction and can offer reasonable prediction for cases where the mixing process can be ignored, but further study is still needed to confirm it.

5. Conclusion

The objective of this work was to study the effect of major factors such as mixing time, temperature, O2 concentration and residence time on the SNCR process in a PFR where the mixing process plays an important part. Meanwhile, a detailed mechanism has been proposed to quantitatively predict the dynamics of all N-containing species including NH3.

The major experimental results are as follows: the mixing process comes into play only at higher temperatures, i.e., higher than optimal temperature. At lower temperatures enriched O2 enhanced NO reduction and N2O yield, with more NH3 being consumed. At higher temperatures, increasing O2 inhibited NO reduction and suppressed N2O formation, with the depletion of NH3. NO2 yield was always enhanced by increasing O2, especially at lower temperatures. Extending residence time progressively shifts the optimum temperature for NOx reduction to lower values, but for a sufficiently long residence time the optimum temperature finally settled at 1173 K.

The detailed mechanism developed in this work gave qualitative and quantitative agreement with our experimental data of all N-containing gases. Evaluation against several independent works illustrates the mechanism’s capability to predict for cases with or without mixing process within tolerable uncertainty. However, evaluations against non-premixed reaction system with short residence time show the approach adopted to treat mass transfer overestimates the mixing rate, leading to opposite deviations in different temperature regions. However, this flaw is barely observed if a longer residence time is available.

Acknowledgements

This work was supported by The National Key Technology R&D Program of China (Contract 2011BAK06B04) and The National Energy Application Technology Study and Demonstration Project of China (Contact NY2013040303).