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Model discrimination and parameter estimation of NH_3-SCR for diesel NOx removal over Cu/Chabazite

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Highlights

- 176 runs under different feedstream composition, temperature and W/Q were carried out.
- A good fitting for NO and NH_3 is observed for calculated vs. experimental data graphs.
- Optimal estimated kinetic parameters for NH_3-SCR system reactions were obtained.
- Proposed model resulted of high statistical significance as deduced from variance analysis.

1. Introduction

Selective catalytic reduction of NOx gaseous mixtures is a complex system in which a multiple reaction network takes place. To advance in the development of more efficient NOx removal NH_3-SCR converters, with modern and powerful modeling and simulation tools, it is essential to describe the reaction pathway and estimate kinetic parameters with high statistical significance, under conditions simulating real operation in lean burn engine automobile application. Here we develop a global kinetic model that predicts main features of different NO/NO_2+NH_3 reactions under oxidizing environments.

2. Methods

In this work a global kinetic model for the reaction NH_3-$NO/NO_2/O_2$ on a Cu/zeolite catalyst has been proposed. The overall kinetic model of the NH_3-SCR reaction has been based on a selection of the reaction mechanism, consisting of the following reactions: (I) NH_3 oxidation, (II) NO oxidation, (III) standard SCR reaction, (IV) rapid SCR reaction, (V) slow SCR reaction, (VI) N_2O formation and (VII) N_2O decomposition. For the definition of the velocity equations it has been considered that ammonia participates in the reactions I, III, IV, V and VI once adsorbed on the acid centers of the zeolite, whereas the rest of the species does it directly from the gas phase.

The catalyst used is a 64 cpsi cordierite monolith washcoated with powdered Cu/chabazite supplied by ITQ (Valencia, Spain), by following the preparation procedure described elsewhere [1]. The actual chemical compositions of the powdered Cu/CHA zeolite resulted in Si/Al ratio of 10.6 and a loading of 3.9% Cu, which was used for kinetic experiments. The NH_3-SCR experiments were performed in a vertical downflow stainless steel reactor, inside which the Cu/CHA monolith was placed [2].

3. Results and discussion

176 experiments were designed with simulated $NO/NO_2/NH_3$ mixtures, under a wide range of feedstream composition, temperature and space time. The experimental outlet NO, NH_3, NO_2 and N_2O concentrations have been managed for kinetic parameter estimation. Figure 1 shows the outlet NO and NH_3 concentrations calculated with optimal estimated parameters vs. experimental data for different reaction series, assuring a good fitting for both components. On the other hand, Table 1 shows the optimal estimated kinetic parameters (frequency factors and activation energies) for each reaction included in the NO_x NH_3-SCR system. The activation energy values for standard SCR reaction, fast SCR reaction and slow SCR reaction have resulted in 91.5, 42.0, and 118 kJ mol^{-1}, respectively. The analysis of variance showed high statistical significance for the proposed model, with a determination coefficient of 0.952, and excellent F-test for a probability superior to 99%.

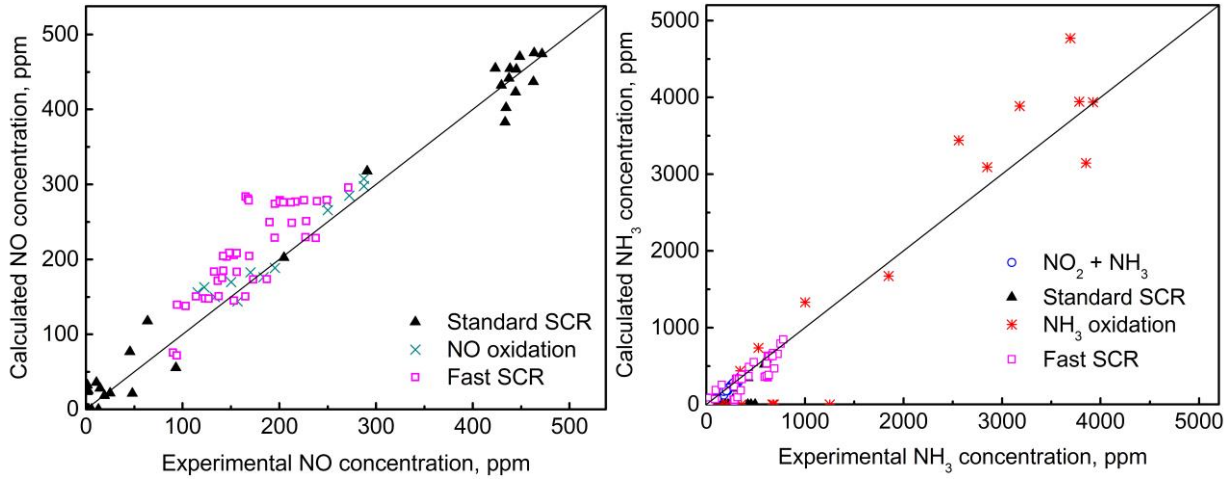

Figure 1. a) Outlet NO and b) NH_3 concentrations calculated from the proposed global model vs. experimental data.

Table 1. Reaction network, estimated parameters and confidence intervals.

Reactions	Frequency factors		Activation energy, kJ mol^{-1}	Confidence interval (95%)
	Value	Units		
1. $NH_3 + 3/4O_2 \rightarrow 1/2N_2 + 3/2H_2O$	1.59×10^{12}	$m^6\ g^{-1}\ h^{-1}\ mol^{-1}$	108.11	± 0.40
2. $NO + 1/2O_2 \rightleftarrows NO_2$	6.81×10^{5}	$m^{4.5}\ m^{-3}\ h^{-1}\ mol^{-0.5}$	12.39	± 3.01
3. $NH_3 + NO + 1/4O_2 \rightarrow N_2 + 3/2H_2O$	1.09×10^{12}	$m^9\ g^{-1}\ h^{-1}\ mol^{-2}$	91.45	± 1.58
4. $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$	9.40×10^{9}	$m^9\ g^{-1}\ h^{-1}\ mol^{-2}$	41.98	± 1.15
5. $4NH_3 + 3NO_2 \rightarrow 7/2N_2 + 6H_2O$	3.07×10^{12}	$m^6\ g^{-1}\ h^{-1}\ mol^{-1}$	118.10	± 29.21
6. $3NH_3 + 4NO_2 \rightarrow 7/2N_2O + 9/2H_2O$	4.48×10^{18}	$m^6\ g^{-1}\ h^{-1}\ mol^{-1}$	152.34	± 1.44
7. $2N_2O \rightarrow 2N_2 + O_2$	2.45×10^{28}	$m^6\ g^{-1}\ h^{-1}\ mol^{-1}$	257.92	± 6.16
K_{NH_3} *(NH_3 adsorption equilibrium)*	7.66×10^{-7}	$m^3\ mol^{-1}$	99.19[a]	-
$K^{eq.}_{NO}$ *(Reaction 2 equilibrium)*	8.61×10^{-4}	$m^{1.5}\ mol^{-0.5}$	57.28[a]	-

[a] In the case of NH_3 and NO, this value corresponds to the enthalpies of the adsorption process and the oxidation reaction, respectively.

4. Conclusions

In this work a global kinetic model for the reaction NH_3-$NO/NO_2/O_2$ on a Cu/zeolite catalyst has been proposed. A good degree of fit has been obtained between the model and the experimental results over a wide range of reaction conditions: temperature, spatial time (W/Q) and reactor feed composition. The proposed model has been able to follow with high precision the majority species (NO and NH_3) and is considered acceptable for the adjustment of the rest of the species, with statistic of high significance. The proposed model is considered valid for its implementation in the simulation phase and monolithic converters for the control of nitrogen oxides in exhaust gases of motors of poor or diesel mix, which is under development in the laboratories of the research group.

References

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[2] U. De-La-Torre, B. Pereda-Ayo, J.A. González-Marcos, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, Catal. Today, 296 (2017) 95–104.

Keywords
NH_3-SCR; Kinetic Model; Parameter Estimation; Cu/CHA