

# Reaction kinetics for removing NO by ethanol over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst

Mun Kyu Kim<sup>1</sup>, Pyung Soon Kim<sup>1</sup>, Sung Bong Kang<sup>1</sup>, Hyuk Jae Kwon<sup>1</sup>, In-Sik Nam<sup>1\*</sup>, Byong K. Cho<sup>2</sup>, Se H. Oh<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering/School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), San 31, Hyoja-dong, Nam-gu, Pohang, 790-784, Korea

<sup>2</sup>General Motors R&D and Planning Center, Warren MI 48090-9055, USA

## Summary

Reaction kinetics for OHC/SCR reaction system with ethanol over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst has been developed on the basis of the possible reactions observed under the variety of the feed gas conditions. Ethanolamine, acetaldehyde and ammonia have been identified as the primary reaction intermediates for the progress of OHC/SCR reaction. The rate expressions based upon LHHW mechanism were derived with the surface reaction as the rate determining step. The model with estimated kinetic parameters well describes the experimental data with respect to the reactor space velocity and temperatures as well as the C<sub>1</sub>/NO<sub>x</sub> feed ratio and water feed concentration.

## Keywords

Ag/Al<sub>2</sub>O<sub>3</sub>; Ethanol; Kinetics; Modeling

## Introduction

Deterministic reaction kinetics in view of the power law model has often been developed to describe the deNO<sub>x</sub> performance of the HC/SCR reaction system [1]. However, the model may not be relevant to predict the NO<sub>x</sub> reduction activity of the HC/SCR system with respect to the reactor operating conditions including the reaction temperature, concentration and reactor space velocity. Backman et al. developed a simple power model for the reduction of NO<sub>x</sub> by n-octane over a 1.91 wt.% Ag/Al<sub>2</sub>O<sub>3</sub> catalyst on the basis of the molecular adsorption of NO and CO as well as the dissociative adsorption of H<sub>2</sub> and O<sub>2</sub> onto the catalyst surface under isothermal and steady-state conditions in the presence of hydrogen [2]. Moreover, when ethanol was used as a reducing agent, a detailed surface reaction mechanism based upon a variety of irreversible reactions including the partial oxidation of ethanol to CH<sub>3</sub>CHO, CO or surface acetate, and N<sub>2</sub> formation by the reaction of the surface NCO formed with NO<sub>2</sub> over the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was proposed by Tham et al. [3]. However, the model hardly described the general trend of NO<sub>x</sub> and ethanol conversions with respect to the reaction condition and even cannot predict the formation of N<sub>2</sub> and NH<sub>3</sub>, two major products for the OHC/SCR reaction system.

In the present study, a kinetic study for removing NO by ethanol over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst has been conducted in

order to predict and optimize the deNO<sub>x</sub> performance of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst. Ethanolamine (HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), acetaldehyde (CH<sub>3</sub>CHO) and ammonia (NH<sub>3</sub>) have been identified as the critical reaction intermediates for the progress of the present NO<sub>x</sub> reduction reaction. A kinetic model for the OHC/SCR system using ethanol as the reductant has been developed and it may be an initial step and a guideline for developing detailed reaction kinetics over the HC/SCR process using E-diesel or bioethanol as the reductant.

## Experimental

The Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the incipient wetness method with aqueous solution of AgNO<sub>3</sub> (Kojima). The catalyst prepared was dried at 110 °C overnight and calcined in air at 550 °C for 5 h. The NO removal activity has been examined using a packed-bed flow reactor using a 3/8 inch o.d. quartz tube with respect to the reactor space velocities varied from 30,000 to 120,000 h<sup>-1</sup>. The conversions of the reactants and the formation of the byproducts were determined by FT-IR equipped with a 2 m gas-cell (Nicolet 6700, Thermo Electron Co.) and GC equipped with a TCD (HP 6890N, Agilent). A feed stream containing 400 ppm NO, 400, 800, 1600 ppm ethanol, 6 % O<sub>2</sub>, 0, 2.5, 10 % H<sub>2</sub>O and He balance was employed for the catalyst deNO<sub>x</sub> performance.

## Development of reaction kinetics

A kinetic model based upon the reaction pathways anticipated has been developed with the following assumptions: (i) all reaction steps are assumed to be a first-order reaction with respect to the reactants involved. (ii) all reactants beside  $N_2$  and  $CO_2$  adsorb onto the catalyst surface, (iii) oxygen adsorbs dissociatively, (iv) the surface reaction is described by a Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, (v) the surface reaction is a rate-determining step, (vi) major reaction intermediates are  $CO$ ,  $CH_3CHO$ ,  $NH_3$  and ethanolamine and (vii)  $NH_3$  is mainly formed from the oxidation of ethanolamine. Based upon these assumptions and observations, the reaction mechanism has been postulated as extensively listed in Table 1.

Table 1. Postulation of reaction mechanism

No.	Reactions	
(1)	$O_2 + 2S \leftrightarrow 2O \cdot S$	$K_1$
(2)	$NO + S \leftrightarrow NO \cdot S$	$K_2$
(3)	$C_2H_5OH + S \leftrightarrow C_2H_5OH \cdot S$	$K_3$
(4)	$NH_3 + S \leftrightarrow NH_3 \cdot S$	$K_4$
(5)	$CO + S \leftrightarrow CO \cdot S$	$K_5$
(6)	$CH_3CHO + S \leftrightarrow CH_3CHO \cdot S$	$K_6$
(7)	$H_2O + S \leftrightarrow H_2O \cdot S$	$K_7$
(8)	$N_2O + S \leftrightarrow N_2O \cdot S$	$K_8$
(9)	$HOCH_2CH_2NH_2 + S \leftrightarrow HOCH_2CH_2NH_2 \cdot S$	$K_9$
(10)	$2NO \cdot S + 4C_2H_5OH \cdot S + 9O \cdot S \rightarrow 2HOCH_2CH_2NH_2 \cdot S + 4CO_2 + 5H_2O \cdot S + 8S$	$k_{10}$
(11)	$2NO \cdot S + 2HOCH_2CH_2NH_2 \cdot S + 11O \cdot S \rightarrow 2N_2 + 4CO_2 + 7H_2O \cdot S + 8S$	$k_{11}$
(12)	$2HOCH_2CH_2NH_2 \cdot S + 13O \cdot S \rightarrow N_2 + 4CO_2 + 7H_2O \cdot S + 8S$	$k_{12}$
(13)	$HOCH_2CH_2NH_2 \cdot S + 5O \cdot S \rightarrow NH_3 \cdot S + 2CO_2 + 2H_2O \cdot S + 3S$	$k_{13}$
(14)	$2NO \cdot S + CH_3CHO \cdot S + 3O \cdot S \rightarrow N_2 + 2CO_2 + 2H_2O \cdot S + 4S$	$k_{14}$
(15)	$2NO \cdot S + 2CH_3CHO \cdot S + 5O \cdot S \rightarrow 2NH_3 \cdot S + 4CO_2 + H_2O \cdot S + 6S$	$k_{15}$
(16)	$C_2H_5OH \cdot S + 6O \cdot S \rightarrow 2CO_2 + 3H_2O \cdot S + 4S$	$k_{16}$
(17)	$C_2H_5OH \cdot S + 4O \cdot S \rightarrow 2CO \cdot S + 3H_2O \cdot S$	$k_{17}$
(18)	$C_2H_5OH \cdot S + O \cdot S \rightarrow CH_3CHO \cdot S + H_2O \cdot S$	$k_{18}$
(19)	$CH_3CHO \cdot S + 5O \cdot S \rightarrow 2CO_2 + 2H_2O \cdot S + 4S$	$k_{19}$
(20)	$CH_3CHO \cdot S + 3O \cdot S \rightarrow 2CO \cdot S + 2H_2O \cdot S$	$K_{20}$
(21)	$CO \cdot S + O \cdot S \rightarrow CO_2 + 2S$	$k_{21}$
(22)	$2NH_3 \cdot S + 3O \cdot S \rightarrow N_2 + 3H_2O \cdot S + 2S$	$K_{22}$
(23)	$2NH_3 \cdot S + 5O \cdot S \rightarrow 2NO \cdot S + 3H_2O \cdot S + 2S$	$K_{23}$
(24)	$2NO \cdot S + CH_3CHO \cdot S + 4O \cdot S \rightarrow N_2O \cdot S + 2CO_2 + 2H_2O \cdot S + 4S$	$k_{24}$
(25)	$2HOCH_2CH_2NH_2 \cdot S + 15O \cdot S \rightarrow 2NO \cdot S + 4CO_2 + 7H_2O \cdot S + 8S$	$K_{25}$

The steady-state rate equations for the removal of NO and the formation of the reaction intermediates and byproducts have been developed [4].

A set of 9 rate expressions developed for NO,  $C_2H_5OH$ ,  $N_2$ ,  $NH_3$ ,  $N_2O$ , ethanolamine, acetaldehyde,  $CO_2$  and CO in forms of the nonlinear ODE were solved by Gear's method [5]. The kinetic parameters were estimated by using nonlinear regression to minimize the sum of squares of the

difference between the experimental and predicted data. The parameters obtained from the literatures [6, 7], particularly the heats of adsorption are quite similar to those determined by the present study. A regression routine for the minimization of the sum of the squares uses the Marquart algorithm [8]. The computer subroutine program for the estimation of the parameters was prepared by using MATLAB<sup>®</sup> (version 6.1, The MathWorks, Inc.) [9].

## Results and Discussion

The model well predicts the general trends of the measured conversions of NO and  $C_2H_5OH$  as well as the formation of  $N_2$ ,  $NH_3$ , CO,  $CH_3CHO$ ,  $CO_2$ ,  $N_2O$  and  $HOCH_2CH_2NH_2$  with respect to the reactor space velocities varied from 30,000 to 120,000  $h^{-1}$  over the Ag/ $Al_2O_3$  catalyst. Furthermore, the effects of the  $C_1/NO$  feed ratio and water feed concentration on the deNOx performance of the present catalytic system have been also examined at the reactor space velocity of 60,000  $h^{-1}$ . The model is capable of predicting the trend of the catalytic deNOx performance, especially the NO conversion to  $N_2$  and the formation of  $NH_3$  over the Ag/ $Al_2O_3$  catalyst as a function of the  $C_1/NO$  feed ratio. Moreover, the model well predicts the general trends of the NO removal activity as well as the formation of  $NH_3$  over the Ag/ $Al_2O_3$  catalyst with respect to the water feed concentration.

## References

- (1) Ansell, G. P.; Bennet, P. S.; Cox, J. P.; Frost, J. C.; Gray, P. G.; Jones, A.-M.; Rajaram, R. R.; Walker, A. P.; Litorell, M.; Smedler, G. The development of a model capable of predicting diesel lean NOx catalyst performance under transient conditions. *Applied Catalysis B: Environmental* **1996**, 10, 183.
- (2) Backman, H.; Arve, K.; Klingstedt, F.; Murzin, D. Y. Kinetic considerations of  $H_2$  assisted hydrocarbon selective catalytic reduction of NO over Ag/ $Al_2O_3$ : II. Kinetic modelling. *Applied Catalysis A: General* **2006**, 304, 86.
- (3) Tham, Y. F.; Chen, J.-Y.; Dibble, R. W. Development of a detailed surface mechanism for the selective catalytic reduction of NOx with ethanol on silver alumina catalyst. *Proceedings of the Combustion Institute* **2009**, 32, 2827.
- (4) Kim, M. K.; Kim, P. S.; Nam, I.-S. **2009**. Selective catalytic reduction of NOx in diesel engine exhaust using partially oxidized fuel hydrocarbons. *Final Report for GM R&D*, POSTECH, Pohang, Korea.
- (5) Oh, S. H.; Cavendish, J. C. Mathematical modeling of catalytic converter. *AIChE Journal* **1985**, 31, 943.
- (6) Gajdos, M.; Hafner, J.; Eichler, A. Ab initio density-functional study of NO adsorption on close-packed transition and noble metal surfaces: II. Dissociative adsorption. *Journal of Physics: Condensed Matter* **2006**, 18, 41.
- (7) Shustorovich, E.; Bell, A. T. Oxygen-assisted cleavage of O-H, N-H, and C-H bonds on transition metal surfaces:

bond-order-conservation-Morse-potential analysis. *Surface Science* **1992**, 268, 397.

(8) Marquardt, D. W. An algorithm for least-square estimation of nonlinear parameters. *Journal of the Society for Industrial and Applied Mathematics* **1963**, 11, 431.

(9) Kwon, H. J.; Baik, J. H.; Kwon, Y. T.; Nam, I.-S.; Oh, S. H. Enhancement effect of water on oxidation reactions over commercial three-way catalyst. *Chemical Engineering Journal* **2008**, 141, 194.