Dynamic multinuclear sites formed by mobilized copper ions during the selective catalytic reduction of nitrogen oxides with ammonia

Rajamani Gounder,[a,*] **William F. Schneider,**[b] **Fabio H. Ribeiro,**[a] **W. Nicholas Delgass**[a], **Jeffrey T. Miller**[a], **Aleksey Yezerets,**[c] **Christopher Paolucci,**[b] **Sichi Li,**[b] **Hui Li,**[b] **Ishant Khurana,**[a] **Atish A. Parekh,**[a] **Arthur J. Shih,**[a] **Jonatan D. Albarracin-Caballero,**[a] **John R. Di Iorio**[a]

[a]*Charles D. Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA*

[b]*Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA*

[c]*Cummins Inc., 1900 McKinley Avenue, MC 50183, Columbus, IN 47201, USA*

**Corresponding author: Fax number: +1-765-494-0805, E-mail address: rgounder@purdue.edu*

Abstract: Isolated copper ions exchanged onto zeolites catalyze the selective catalytic reduction (SCR) of nitrogen oxides with ammonia and dioxygen. We present evidence that the SCR mechanism at low temperatures involves full coordination and solvation of copper ions by ammonia, and the dynamic formation of binuclear cuprous amine complexes to activate dioxygen during oxidation half-cycles. We discuss the consequences of ionic tethering of cationic copper complexes at anionic framework aluminum centers in zeolites. This enables the reversible formation of multinuclear sites from mobilized single ions and provides energetically-favorable pathways to use dioxygen in partial oxidation catalysis at low temperatures.

Keywords: copper-zeolite, NO_X SCR, ion mobility

1. Introduction

Copper-exchanged chabazite (Cu-CHA) zeolites are used commercially in diesel emissions control for the selective catalytic reduction (SCR) of nitrogen oxides (NO_X, x = 1, 2) with ammonia.[1] After Cu ion exchange and high temperature oxidation treatments, Cu-CHA zeolites contain site-isolated divalent Cu ions that balance two proximal framework Al centers and monovalent CuOH complexes that balance single Al centers. These exchanged Cu ions behave as redox active sites (Cu^{2+}/Cu^{+}) for low temperature (<523 K) NO_X SCR catalysis,[2-4] however, the mechanistic details describing how dioxygen (a four-electron oxidant) participates in the Cu-catalyzed SCR redox cycle are imprecisely understood. Here, we combine experimental and theoretical evidence to support the mechanistic proposal that ammonia solvation of copper ions away from the zeolite lattice confers localized active site mobility, which enables the formation of binuclear copper complexes that activate dioxygen during the low temperature catalytic SCR redox cycle.[5]

2. Experimental and Theoretical Methods

Cu-CHA zeolites (Si/Al = 5, 15, 25; Cu/Al = 0-0.5) were synthesized with isolated Cu ions at varying spatial density, and characterized by UV-Visible spectroscopy, infrared spectroscopy, X-ray absorption spectroscopy (XAS), and active site titration techniques to verify their site isolated nature; these synthesis and characterization details are reported elsewhere.[2] Kinetic measurements of SCR reactivity were measured in differential reactors under low temperature (423-523 K) standard SCR conditions (300 ppm NO, 300 ppm NH_3, 10% O_2, 5% CO_2, 2.5% H_2O, balance N_2). *Operando* and transient XAS (Cu K-edge) were collected at the Advanced Photon Source at Argonne National Laboratory. Details of DFT calculations, molecular dynamics simulations, and statistical simulations of Cu site distribution and pairing are reported elsewhere.[5]

3. Results and discussion

SCR rates increase quadratically with Cu density on Cu-CHA samples with dilute Cu loadings, in a kinetic regime characterized by high apparent O_2 reaction orders (0.7-1.0). In contrast, SCR rates increase linearly with Cu density on Cu-CHA samples with high Cu loadings, in a kinetic regime characterized by low apparent O_2 reaction orders (0.0-0.3). These kinetic data are consistent with the SCR oxidation half-cycle being rate-limiting at low Cu ion densities, and with the SCR reduction half-cycle being rate-limiting at high Cu ion densities.[5] *Operando* XAS was used to directly measure the distribution of Cu^{2+} and Cu^{+} oxidation states on Cu-CHA samples of varying Cu ion density, during steady-state catalysis. Cu ions were predominantly present as Cu^{+} on samples with low Cu ion density, and the fraction of Cu present as Cu^{+} decreased systematically with increasing Cu ion density (Fig. 1). These data provide direct confirmation that the SCR oxidation half-cycle is the rate-limiting process on Cu-CHA samples of low Cu ion density.

Next, Cu-CHA samples of varying Cu ion density were reduced to their Cu^{+} states, and the transient Cu^{+}-to-Cu^{2+} oxidation behavior was studied by XAS using either NO_2 or O_2 as the oxidant. NO_2 oxidized every Cu^{+} site on each Cu-CHA sample with first-order kinetics, consistent with a reaction that formed mononuclear Cu^{2+} nitrite species. In contrast, O_2 oxidized only a fraction of all Cu^{+} sites on each Cu-CHA sample, in a second-order kinetic process. Additionally, the fraction of Cu^{+} sites that were oxidized by O_2 increased systematically with increasing Cu ion density; this phenomena reflects the increased propensity of Cu ions to form pairs at higher spatial densities. We will discuss how experimental data were combined with insights from theory to support O_2-oxidation of two Cu^{+} sites to form a binuclear copper-oxygen complex.

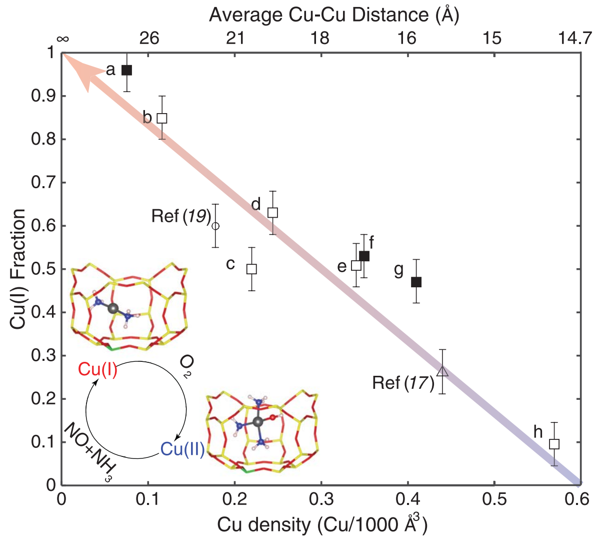

Figure 1. Distribution of Cu^{+}/Cu^{2+} oxidation states, measured *in operando* using XAS, during steady-state SCR catalysis (473 K) on Cu-CHA zeolites of varying Cu density. Inset shows a simplified redox cycle; O_2 only participates in the oxidation half.

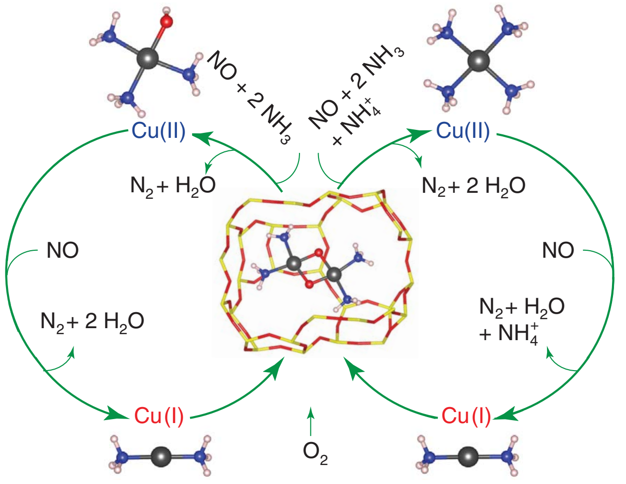

Figure 2. Proposed low-temperature SCR catalytic cycle. Reduction steps proceed on site-isolated Cu^{2+} ions residing near one (left-hand cycle) or two (right-hand cycle) framework Al centers with constrained diffusion of Cu^{+} ions into single cages and oxidation by O_2 (inner step).

4. Conclusions

These findings support a catalytic SCR redox mechanism (Fig. 2) in which the reduction half-cycle is catalyzed by a mononuclear Cu complex, while the oxidation half-cycle is catalyzed by a binuclear Cu complex.[5] Solvation of Cu ion sites by ammonia confers localized mobility, providing a mechanism for the dynamic interconversion of mononuclear and binuclear Cu active sites during steady-state catalysis. This catalytic phenomenon falls outside conventional descriptions of heterogeneous and homogeneous single-site behavior, and provides new pathways for dioxygen activation at mild conditions in redox catalysis.

References

1. C. Paolucci, J. R. Di Iorio, F. H. Ribeiro, R. Gounder, W. F. Schneider, Adv. Catal. 59 (2016) 1.
2. C. Paolucci, A. A. Parekh, I. Khurana, J. R. Di Iorio, H. Li, J. D. Albarracin Caballero, A. Shih, T. Anggara, W. N. Delgass, J. T. Miller, F. H. Ribeiro, R. Gounder, W. F. Schneider, J. Am .Chem. Soc. 138 (2016) 6028.
3. F. Gao, D. Mei, Y. Wang, J. Szanyi, C. H. F. Peden, J. Am. Chem. Soc. 139 (2017) 4935.
4. T. V. W. Janssens, H. Falsig, L. F. Lundegaard, P. N. R. Vennestrøm, S. B. Rasmussen, P. G. Moses, F. Giordanino, E. Borfecchia, K. A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P. Beato, ACS Catal. 5 (2015) 2832.
5. C. Paolucci, I. Khurana, A. A. Parekh, S. Li, A. J. Shih, H. Li, J. R. Di Iorio, J. D. Albarracin-Caballero, A. Yezerets, J. T. Miller, W. N. Delgass, F. H. Ribeiro, W. F. Schneider, R. Gounder*, Science, 357 (2017) 898.