

Two are Better than One: Mechanistic Insights Into the Cu-Chabazite Catalyzed Reduction of Nitrogen Oxides

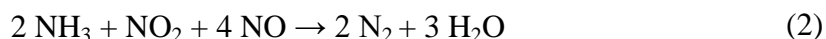
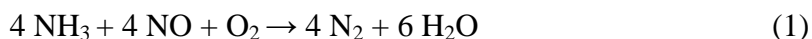
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Literature Seminar

October 24, 2017

In 2000, the Environmental Protection Agency (EPA) passed regulations mandating reduced emissions of nitric oxides (NO_x) from diesel engines by 2010.¹ In order to meet these restrictions, manufacturers began employing Cu-chabazite catalysts in the catalytic converters of their diesel vehicles.² These catalysts carry out a process called the selective catalytic reduction (SCR) of nitrogen oxides, which works in the oxygen-rich environment of diesel exhaust (equation 1).³ An advantage of these catalysts is that they depend on copper ion active sites rather than precious metals such as Pt or Pd thereby making them a more cost-effective option.⁴ Chabazite is a member of the zeolite class of aluminosilicates, and contains 4-, 6-, and 8-membered aluminosilicate rings. Because of the new commercial use of these catalysts, there have been increased efforts recently to elucidate the mechanism by which these catalysts operate.^{2,4}

Much of the work done thus far to determine the SCR mechanism has led to seemingly contradictory conclusions, but it is generally agreed upon that the catalyst exhibits single-site heterogeneous catalytic behavior, that is, the reaction occurs at *isolated* copper ions (which follow the Cu(II)-Cu(I) redox cycle) within the chabazite pores.² The reaction is thought to have the stoichiometries shown in equation 1 or equation 2, the only difference being that the rate of reaction is faster in the presence of excess NO_2 (equation 2).⁵



In diesel engines, ammonia is supplied to the catalyst by the thermal decomposition of urea (**Figure 1**). Urea, stored in a separate reservoir in the vehicle, is injected and mixed into the exhaust stream after oxidation, but prior to reduction. While in the stream, it undergoes thermal decomposition to form ammonia, which works with the catalyst to reduce nitrogen oxides.²

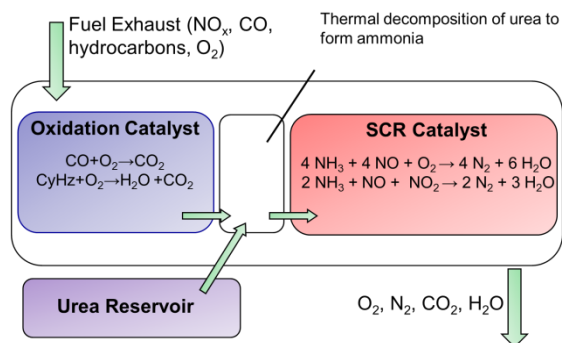


Figure 1. Schematic of a catalytic converter in a diesel engine

Janssens et al. have proposed the mechanism shown in **Figure 2**.⁵ In the first step, Cu(I) is oxidized by O₂ and NO (or, in the fast SCR cycle, by NO₂) to form a Cu(II) nitrate intermediate, which is then solvated by NH₃. The copper ammine nitrate species decomposes to give N₂ and H₂O and forms a Cu(II) hydroxide, Cu(OH)⁺; the latter is subsequently reduced by NO and NH₃ back to Cu(I), giving off two equivalents of H₂O and one equivalent of N₂ in the process.

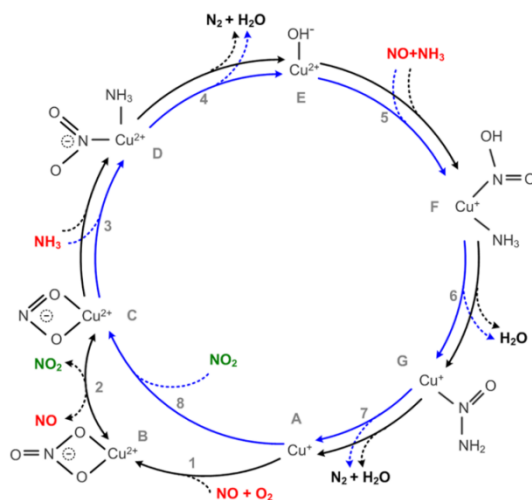


Figure 2. Cu-Chabazite SCR mechanisms proposed by Janssens et al.⁵

Although several intermediates in Janssens's mechanism were identified by means of *in situ* EPR, IR, and X-Ray absorption studies, this mechanism was unable to account for some of the more recent observations about the process.⁵ The most glaring of these inconsistencies is that the rate of NO_x reduction at low temperatures (150-200 °C) and low copper loadings exhibits second order kinetics with respect to copper.^{4,6} In contrast, Janssens's mechanism, which involves isolated copper ions as the catalytic centers, predicts that the rate of NO_x reduction should be first order with respect to Cu regardless of Cu loading.

In order to rationalize this observation and several others, Paolucci et al. and Gao et al. have proposed an alternative mechanism in which the active site is not a single copper atom, but rather a dinuclear copper complex and that this dinuclear complex is formed only when the copper centers can migrate through the chabazite pores and find another Cu (I) atom (A to B in **Figure 3**).^{4,6} Mobilization of the Cu(I) ions is enabled by solvation with ammonia to form a Cu(NH₃)₂⁺ species that are not bound to framework oxygen atoms. Two of these centers bind oxygen to form a Cu(II) di(μ-oxo) intermediate (E in **Figure 3**). If this hypothesis is correct, this catalyst is of an unusual type, having both heterogeneous and homogeneous character.

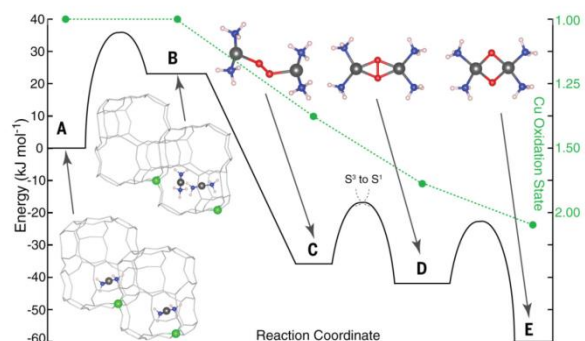


Figure 3. Cu oxygen-binding mechanism proposed by Paolucci et al.⁴

Paolucci's and Gao's study nicely explains the second-order behavior seen at low temperatures, but this Cu(II) di(μ -oxo) intermediate has been unable to be worked into a mechanism that makes chemical sense or is consistent with the stoichiometry in equation 1. Furthermore, it is inconsistent with the observation that, at high temperatures (>350 °C), the reaction is first order with respect to copper regardless of the Cu loading.⁶ Under these high temperature conditions, Cu may be immobilized because it is no longer sufficiently coordinated by ammonia, and instead is bound to the chabazite framework.² Additional mechanistic studies will be needed to fully elucidate the mechanism at these higher temperatures. Such studies will lead to better catalyst design and increase the catalyst's potential to catalyze other reactions.

References

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