PNNL-25688

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Final Report of a CRADA Between Pacific Northwest National Laboratory and Cummins, Incorporated (CRADA No. PNNL/283): "Enhanced High and Low Temperature Performance of NOx Reduction Catalyst Materials"

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September 2016

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Final Report of a CRADA Between Pacific Northwest National Laboratory and the Cummins, Incorporated (*CRADA No. PNNL/283*): "*Enhanced High and Low Temperature Performance of NOx Reduction Catalyst Materials*"

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Introduction

The NO_x Storage-Reduction (NSR; also known as lean-NO_x trap – LNT) technology is based upon the concept of storing NOx as nitrates in storage components, typically barium species, during a lean-burn operation cycle, and then reducing the stored nitrates to N_2 during fuel-rich conditions over a precious metal catalyst [1]. NOx Selective Catalytic Reduction (SCR), on the other hand, is accomplished by deliberately introducing the reductant urea into the engine exhaust to reduce NOx with the aid of a Cu(Fe)/zeolite catalyst [2]. These two technologies have been recognized as the most promising approaches for meeting stringent NOx emission standards for diesel vehicles within the Environmental Protection Agency's (EPA's) 2007/2010 mandated limits. For NSR, problems arising from either or both thermal and SO_2 deactivation must be addressed to meet durability standards. For SCR, SO_2 deactivation is less of an issue, but hydrothermal deactivation of the zeolite catalysts must be addressed.

With continuing R&D efforts in advanced powertrains, highly novel operating modes for internal combustion engines (ICEs) are being researched in order to meet the very stringent new demands for fuel efficiency (e.g., U.S. ''CAFE'' standards for fleet average miles/gallon are scheduled to increase significantly over the next 10–15 years). These new ICE engine operation modes, while highly fuel-efficient, result in much lower exhaust temperatures than current engines; temperatures so low that it is hard to imagine how the current catalytic emission control technologies will be able to function. For example, while steady-state operation of the NOx reduction technology at 150 °C may be required, current ‘‘light-off’’ temperatures for CHA-based zeolite catalysts are closer to 200 °C. Therefore, understanding low-temperature limitations in NOx reduction has become one of the most daunting challenges in R&D for developing new catalyst materials and processes that can effectively eliminate emissions at these quite low exhaust temperatures.

This project has two clear areas of focus: (1) The development of potassium-based high-temperature NSR materials, and studying the key causes of their deactivation as well as methods of regeneration. By comparing results obtained on “simple model” Pt-K/Al_2O_3 with “enhanced model” Pt-K/MgAlOx and Pt-K/TiO_2 materials, we have developed an understanding of the role of various additives on the deactivation and regeneration processes. Studies have also been performed on commercial catalyst samples that are being used in a Dodge Ram truck with a Cummins diesel emission control system. However, the results about these “commercial samples” will not be covered in this report for proprietary reasons. (2) For the Cu and Fe/Chabazite SCR catalysts, since these were only very recently developed and references from open literature and industry were nearly absent when we initiated our studies, our work began with zeolite synthesis and catalyst synthesis methodology development, followed by research on the low- and high-temperature performance, deactivation and regeneration of these materials. Again, most work reported here is based on our “model” catalysts that were synthesized in-house, and work performed on “commercial samples” will not be presented in this report. Following a brief description of our experimental approach, we will present a few highlights from some of the work performed in this CRADA, with more details about these results provided in lists of Publications, Invention Reports, and Presentations provided at the end of the report.

Objectives

Identify approaches to significantly improve both the high and low temperature performance, and the stability of catalytic NOx reduction technologies via a pursuit of a more fundamental understanding of:

- the various roles for the multiple catalytic materials;
- the mechanisms for these various roles;
- the effects of high temperatures on the performance of these catalyst component materials in their various roles;
- mechanisms for higher temperature NOx storage performance for modified and/or alternative storage materials;
- the interactions between the precious metals and the storage materials in both optimum NOx storage performance and long term stability;
- modes of thermal degradation of new generation CHA zeolite-based SCR catalysts.
- the sulfur adsorption and regeneration mechanisms for NOx reduction catalyst materials.

Accomplishments

- Complete characterization and NOx storage performance of base model Pt-K/Al_2O_3 high-temperature NSR materials.

- Complete characterization and NOx storage performance comparison between base model Pt-K/Al_2O_3 and advanced model Pt-K/MgAlOx high-temperature NSR materials.
- Complete characterization and NOx storage performance of model Pt-K/TiO_2 and Pt/$K_2Ti_6O_{13}$-based high temperature NSR catalysts with a variety of state-of-the-art methods.
- Methodology development in the synthesis of SSZ-13 and SAPO-34 materials.
- Methodology development in the synthesis of Cu/SSZ-13 and Cu/SAPO-34 catalysts, including solution ion-exchange, solid-state ion-exchange and one-pot synthesis.
- Complete low- and high-temperature performance for model Cu/SSZ-13 CHA zeolite based catalysts for ammonia SCR.
- Carry out performance and thermal durability studies of model Cu/SAPO-34 CHA zeolite based catalysts.
- Complete low- and high-temperature performance for model Fe/SSZ-13 CHA zeolite based catalysts for ammonia SCR.
- Complete comparative study between model Cu/SSZ-13 and Fe/SSZ-13 CHA zeolite based catalysts.
- Initiate Cu and Fe co-cation CHA and beta zeolite based SCR catalysts.
- 15 publications, 1 invention report, and 20 public presentations (6 invited) have resulted from this program from 2013 to the present.

Future Directions

- Finish Cu and Fe co-cation CHA and beta zeolite based SCR catalysts, especially on their deactivation mechanisms.
- Close up this CRADA in March, 2016 and initiate a new CRADA with Cummins/Johnson-Matthey; shift research focus toward SCR fundamentals and Passive NOx Adsorber (PNA).

Introduction

Two primary NOx after-treatment technologies have been recognized as the most promising approaches for meeting stringent NOx emission standards for diesel vehicles within the Environmental Protection Agency's (EPA's) 2007/2010 mandated limits, NOx Storage Reduction (NSR) and NH_3 selective catalytic reduction (SCR). Both have been commercialized in the United States for this application. Copper ion exchanged small pore zeolite catalysts with a chabazite (CHA) structure have recently been shown to exhibit both remarkable activity and very high hydrothermal stability in the NH_3 SCR process [3]. The NSR (also known as the lean-NOx trap, LNT, or NOx Absorber) technology is based upon the concept of storing NOx as nitrates over storage components, typically barium species, during a lean-burn operation cycle, and then desorbing and subsequently reducing the stored nitrates to N_2 during fuel-rich conditions over a precious metal catalyst [1]. However, with expected more stringent regulations, the continued viability of the NSR technology for controlling NOx emissions from lean-burn engines such as diesels will require at least two specific, significant and inter-related improvements. First, it is important to reduce system costs by, for example, ***minimizing the precious metal content*** while maintaining, even improving, performance and long-term stability.

A second critical need for future NSR systems, as well as for NH_3 SCR, will be significantly ***improved higher and lower temperature performance*** and stability. Furthermore, these critically needed improvements will contribute significantly to minimizing the impacts to fuel economy of incorporating these after-treatment technologies on lean-burn vehicles. To meet these objectives will require, at a minimum, an improved scientific understanding of the following things:

i) the various roles for the precious and coinage metals used in these catalysts;
ii) the mechanisms for these various roles;
iii) the effects of high temperatures on the active metal performance in their various roles;
iv) mechanisms for higher temperature NOx storage performance for modified and/or alternative storage materials;
v) the interactions between the precious metals and the storage materials in both optimum NOx storage performance and long term stability;
vi) the sulfur adsorption and regeneration mechanisms for NOx reduction materials;
vii) materials degradation mechanisms in CHA-based NH_3 SCR catalysts.

The objective of this CRADA project is to develop a fundamental understanding of the above-listed issues. Model catalysts that are based on literature formulations are the focus of the work being carried out at PNNL. In addition, the performance and stability of more realistic catalysts, supplied by the industrial CRADA partners, are being studied in order to provide baseline data for the model catalysts that are, again, based on formulations described in the open literature.

Approach

In microcatalytic reactor systems, catalyst performance is evaluated in two separate fixed bed reactors under both steady-state and transient operation conditions. We have established reaction protocols, which evaluate the performance of samples after various pretreat (hydrothermal aging) conditions. In this way, we could largely mimic performance of catalysts under on-road aging conditions.

Based on formulations and synthesis procedures described in the literature, PNNL has prepared model NH_3-SCR catalysts. Activity and performance stability measurements were performed. State-of-the-art catalyst characterization techniques such as XRD, Mössbauer, FTIR, NMR, EPR, TEM/EDS, BET/pore size distribution, and temperature programmed desorption/reaction (TPD/TPSR) were utilized to probe the changes in physicochemical properties of the PNNL-prepared model catalyst samples under deactivating conditions; *e.g.*, hydrothermal aging.

Results

Potassium-based high temperature NSR catalysts: preparation, characterization, NOx storage-reduction evaluation, deactivation and regeneration studies.

Commercialized LNTs mainly consist of noble metals Pt (Pd, Rh) and Ba supported on Al_2O_3 or $CeZrO_x$, which show excellent NO_x reduction activity, especially in the temperature range from 350 to 400 ºC. However, their efficiency becomes unsatisfactory for certain applications, such as for lean burn gasoline engines (GDI, gasoline direct injection) with exhaust temperatures as high as 400-500 ºC. At these temperatures, the stored NO_x phase, in the form of $Ba(NO_3)_2$, becomes unstable and tends to decompose. In this regard, developing lean NO_x trap catalysts with enhanced high temperature performance is very necessary. K-based LNTs show much higher NO_x storage capacities in the high temperature range (400 ºC and above) than Ba-based ones, due to the stronger basicity of K.

In studying K-based NSR catalysts, we started with a baseline support γ-alumina, and systematically investigated effects from Pt and K loadings, and thermal aging and regeneration [4]. From in situ XRD studies, it was discovered that both rhombohedral and orthorhombic KNO_3 phases are present on KNO_3/Al_2O_3 at room temperature. The relative population of the two phases depends on K loading. At ~150 ºC, these phases transform into a single rhombohedral phase accompanied with particle sintering. Further heating leads to KNO_3 melting and finally decomposition. KNO_3 is extremely mobile and is likely present as a liquid-like phase during high-temperature NO_x storage. By investigating K loading effects, it was further discovered that an optimum K loading exists for high temperature NO_x storage over $K/Pt/Al_2O_3$ samples. At low K loadings, the majority of KNO_3 is present as a surface layer. Similar to Ba-based LNTs, a strong interaction between these surface nitrates and Al_2O_3 promotes their decomposition. At high K loadings, in contrast to Ba-based LNTs where NOx storage is limited by diffusion, an observed decrease in NO_x uptake for $K/Pt/Al_2O_3$ is due to the blocking of Pt sites by mobile K species, leading also to a decrease in NO oxidation reactivity and effecting NOx storage performance.

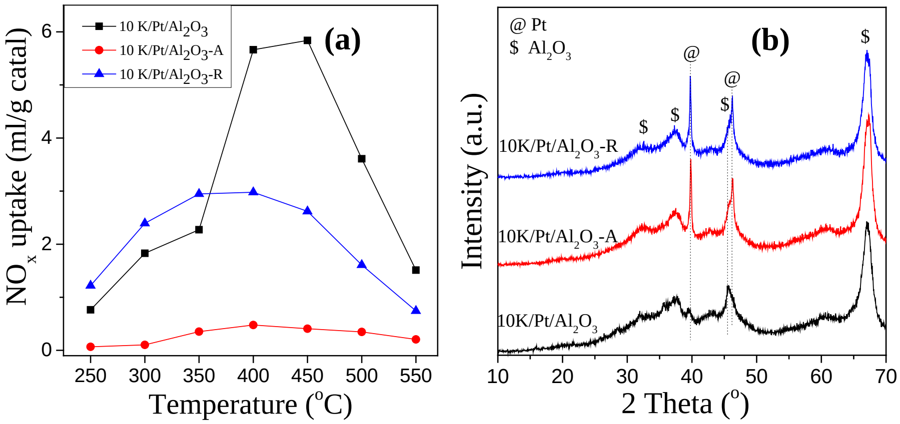

Figure 1: (a) NOx uptakes as a function of temperature on 10% K-Pt/Al_2O_3 samples following varying treatments (fresh–squares, aged–circles, and subsequently reduced–triangles). (b) XRD profiles for the 10% K-Pt/Al_2O_3 sample following varying treatments (A: aging; R: subsequent reduction of the aged (A) catalyst).

As shown in Figure 1(a), while the fresh K-Pt/Al_2O_3 catalyst has good NOx storage capacity between 400 and 500 °C; this capability greatly diminishes after thermal aging at 800 °C in air. After a reduction treatment, the NOx storage capacity partially recovers. XRD patterns shown in Figure 1(b) indicate significant Pt sintering during aging. TEM imaging results displayed in Figure 2 on fresh, aged and reduced samples allow the following conclusions to be made: during thermal aging of $K/Pt/Al_2O_3$ catalysts, some Pt species sinter to form large metallic Pt particles whereas a significant fraction interacts with K and remains finely dispersed. Upon reduction, these latter Pt species can be re-activated, resulting in a partial recovery of NO_x storage capacity.

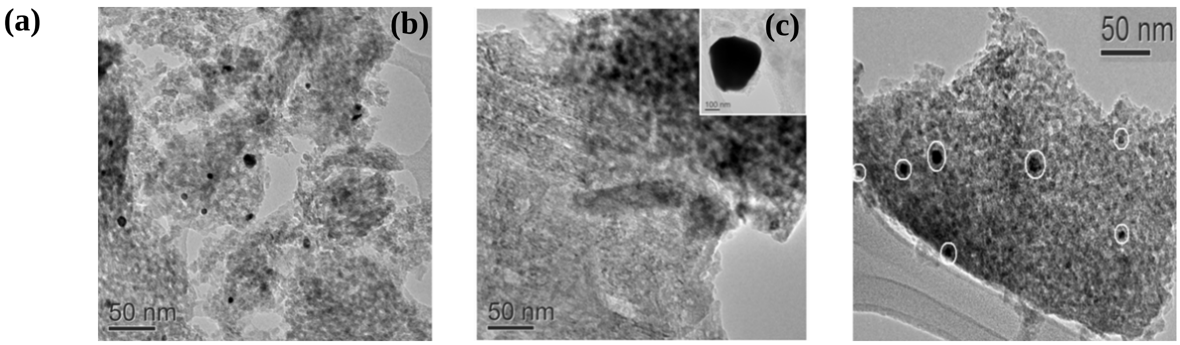

Figure 2: TEM images for the 10% K-Pt/Al_2O_3 sample following varying treatments: (a) fresh sample after reaction; (b) aged sample (insert: large Pt particle image); and(c) aged and reduced sample.

To mitigate issues associated with Pt sintering ‘Enhanced Model’ Pt-K/MgAlOx materials were prepared and tested for NOx storage [5]. Effects of support compositions, K/Pt loadings, thermal aging, and catalyst regeneration on NOx storage capacity were systematically investigated. The catalysts were characterized by XRD, NOx-TPD, TEM, STEM-HAADF, and in situ XAFS. The results indicate that MgAlOx mixed oxides have significant advantages over conventional γ-Al_2O_3 supports for LNT catalysts, in terms of high-temperature NOx trapping capacity and thermal stability. First, as a basic support, MgAlOx stabilizes stored nitrates (in the form of KNO_3) to much higher temperatures in comparison to mildly acidic γ-Al_2O_3. Second, MgAlOx minimizes Pt sintering during thermal aging, which is not possible for γ-Al_2O_3 supports. Notably, combined XRD, in situ XAFS, and STEM-HAADF results indicate that Pt species in the thermally aged Pt/MgAlOx samples are finely dispersed in the oxide matrix as isolated atoms. This strong metal−support interaction stabilizes Pt and minimizes the extent of sintering.

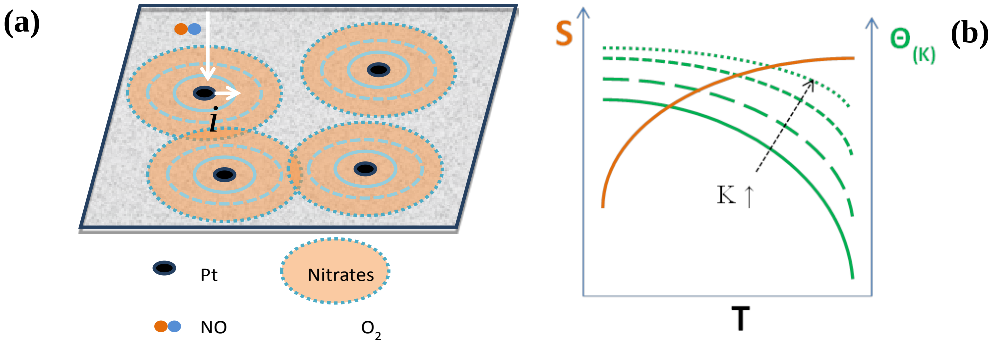

Figure 3: Physical model for NOx trapping (a) and illustration of the storage area S and nitrate coverage Θ(K) as a function of temperature and K loadings (b).

However, such strong interactions result in Pt oxidation via coordination with the support so that NO oxidation activity can be adversely affected after aging, which in turn decreases NOx trapping ability for these catalysts. Interestingly, a high-temperature reduction treatment regenerates essentially full NOx trapping performance. In fact, regenerated Pt-K/MgAlOx catalyst exhibits much better NOx trapping performance than fresh Pt-K/Al_2O_3 LNTs over the entire temperature range investigated here. In addition to thermal aging, Pt/K loading effects were systemically studied over the fresh samples. The results indicate that NOx trapping is kinetically limited at low temperatures, while it is thermodynamically limited at high temperatures. A simple conceptual model, shown in Figure 3, was developed to explain the Pt and K loading effects on NOx storage. An optimized K loading, which allows balancing between the stability of nitrates and exposed Pt surface, gives the best NOx trapping capability.

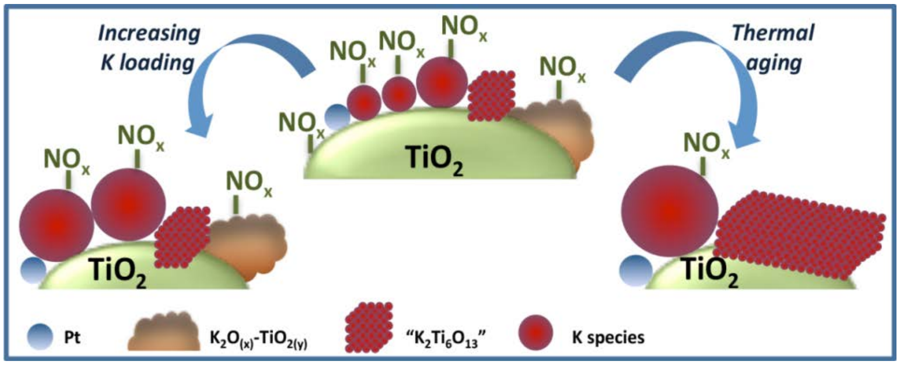

Figure 4: schematic description of the NOx storage process on Pt-K/TiO_2 and the formation of the $K_2Ti_6O_{13}$ phase during thermal aging.

Unfortunately, the volatile nature of the active K species, due to the low melting point (334 °C) of KNO_3, gives rise to technical challenges in avoiding loss of the active phase due to K volatilization, dissolution in water, and/or diffusion along with undesirable interactions with cordierite monolith supports. Therefore, overcoming of K stability concerns is mandatory to its applicability in LNTs formulations. To address this issue, Pt–K/TiO_2 LNT catalysts having different K loadings (2, 5, 10, 15, 20 wt%) have been synthesized, characterized and tested, along with a Pt/$K_2Ti_6O_{13}$ reference material [6]. The effects of K loading and thermal aging on NOx storage performance have been addressed, and the formation/decomposition of stored NOx species over Pt-free samples has been investigated by FT-IR, TPD and XRD techniques. NOx storage-reduction tests of Pt–K/TiO_2 catalysts indicate that 10 wt% K-loaded samples show the highest NOx storage capacity, registered at 300 °C. Both the temperature at which the maximum NOx storage capacity is attained and the NOx uptake yields are a function of the K-loading. A low K utilization in the NOx storage has been observed. Especially at high K contents (K = 20 wt%) this result can be attributed, in part, to the low surface area of the support material, and to the depletion of the K storage phase via reaction between K and TiO_2. In fact XRD analyses demonstrate that K and TiO_2 react already during the catalyst synthesis calcination process by forming a "$K_2Ti_6O_{13}$-like" potassium titanate at temperatures as low as 550 °C. This reaction is promoted by increasing the K content and calcination temperatures. Activity, XRD and FT-IR measurements have demonstrated that poorly crystalline potassium titanates have appreciable storage properties. Upon aging treatments, K incorporates into theTiO_2 structure, leading to the formation of potassium titanates: this increase in the stability of K, on the other hand decreases the NOx storage capacity. This raises questions concerning the capability of such systems to meet the durability requirements for vehicle emission control applications. The cartoon in Figure 4 describes the possible NOx storage mechanism and conversion of storage phases during application.

Methodology development for the synthesis of SSZ-13, SAPO-34 materials, and Cu/SSZ-13 and Cu/SAPO-34 SCR catalysts.

To better understand low- and high-temperature performance of Cu/CHA catalysts, it is mandatory to have model catalysts with various Cu loadings and Si/Al ratios. These are currently not available commercially. Therefore, a laboratory-scale synthesis method for SSZ-13 materials with different Si/Al ratios was developed at PNNL [7]. Composition of the gel is the following: 10SDA : 10NaOH : xAl_2O_3 : $100SiO_2$: $2200H_2O$, where x varies to allow preparation of samples with different Si/Al ratios. The gel is prepared by first dissolving NaOH (99.95%, Aldrich) in water and adding the SDA (TMAda-OH, Sachem ZeoGen 2825). Following which, $Al(OH)_3$ (contains ~54% Al_2O_3, Aldrich) and fumed silica (0.007 μm average particle size, Aldrich) were added sequentially under vigorous stirring until the gel was homogenized. The gel may be further aged at ambient temperature under stirring. The length of this aging period determines the extent of silica hydrolysis (i.e., the extent of oversaturation of the gel). Therefore, longer aging time typically leads to materials with smaller particle sizes. The gel was then sealed into a 125 ml Teflon-lined stainless steel autoclave with a stir bar in. Thereafter, the autoclave was placed in a sand bath on top of a hot plate stirrer to carry out hydrothermal synthesis at 160 °C for 96 h under stirring. Figure 5(a) presents XRD patterns of the synthesized materials (after SDA removal by calcination). Si/Al ratios adjacent to the patterns are obtained from ICP analysis. These materials are highly crystallized with no sign of the presence of amorphous phases. Figure 5(b) depicts ^{27}Al NMR spectra of the materials. Features at ~60 ppm are assigned to framework, tetrahedral Al (Al_f) and the much weaker features at ~0 ppm are attributed to extra-framework, octahedral Al. The latter can be viewed as Lewis acid defects, with relative intensity increasing with decreasing Si/Al ratio. Figure 5(c) presents the corresponding ^{29}Si NMR results, where features at -110, -104 and -99 ppm are attributed to Si(4Si, 0Al), Si(3Si, 1Al) and Si(2Si, 2Al), respectively. Similarly, PNNL also developed protocols for the synthesis of highly crystallized SAPO-34 materials with various Si contents [8].

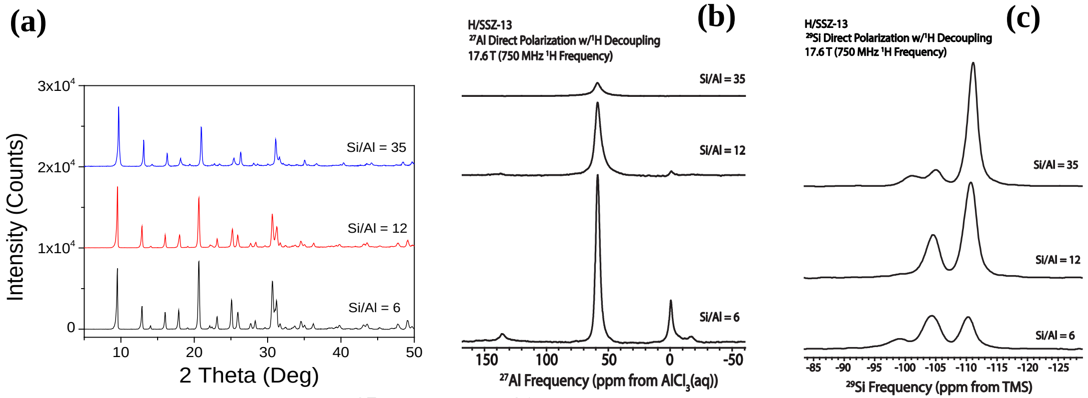

Figure 5: (a) XRD, (b) solid state ^{27}Al and (c) ^{31}Si NMR spectra for the H/SSZ-13 samples with Si/Al ratio = 6, 12 and 35. Samples were prepared by ion-exchanging Na/SSZ-13 samples to NH4/SSZ-13 followed by a calcination in air at 550 ℃. Note that small features in the ^{27}Al NMR spectra at -17 and 135 ppm, especially evident in the spectrum for the Si/Al = 6 sample, are spinning side bands.

Cu/SSZ-13 is readily generated via a traditional aqueous solution ion-exchange method that has been described in detail in recent publications. All soluble Cu salts can be used as the Cu sources. SSZ-13 in either (as-synthesized) Na form or NH_4 form can be used. Ion-exchange can be conducted at ambient temperature for longer time; or higher temperatures (e.g., 80 °C) for shorter time since higher temperatures facilitate Cu-ion migration. Repeated ion-exchange may be applied in order to generate high Cu-loaded catalysts. Cu/SAPO-34 can also be generated via a traditional solution ion-exchange method. Note that although SAPO-34 is typically synthesized in the H-form, to facilitate Cu^{2+} ion incorporation, it is still necessary to exchange it into the NH_4-form first. Two alternative Cu/CHA synthesis methods were developed at PNNL [9]. In a so-called solid state ion-exchange (SSIE) synthesis, heating up a CuO and SSZ-13/SAPO-34 mixture to an elevated temperature (800 °C) allows for the formation of extra-framework Cu^{2+}. This method is rather straightforward and allows facile Cu loading control. However, incomplete CuO reaction and partial damage of the zeolites at such high temperatures are the drawbacks. To avoid the potential SAPO-34 hydrolysis during aqueous solution ion-exchange, a one-pot method was developed at PNNL to synthesize Cu/SAPO-34. Using Cu-TEPA (tetraethylenepentamine) complex as a co-SDA (structure directing agent), PNNL has been able to prepare Cu/SAPO-34 catalysts with various Cu loadings and homogeneously dispersed Cu^{2+} ions. In this method, the gel composition is as follows: x Cu-TEPA: 0.6 SiO_2: 0.83 P_2O_5: 1 Al_2O_3: 3SDA: 60 H_2O (x = 0.0025, 0.006, 0.012, 0.038, 0.074, 0.148). The variation of x allows for the variation of Cu loading. After hydrothermal synthesis at 160 °C for 48 h under stirring, the solid powder was collected, dried and calcined at 550 °C in air to generate the Cu/SAPO-34 catalysts. Figure 1(a) depicts the structure of Cu-TEPA and Figure 1(b) presents temperature-programmed reduction (TPR) curves of the Cu/SAPO-34 catalysts.

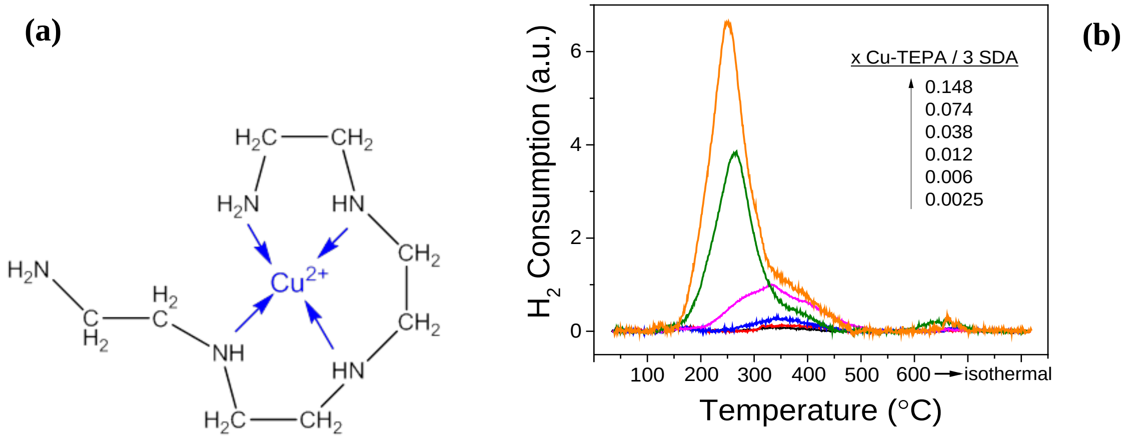

Figure 6: (a) structure of the Cu-TEPA complex, (b) temperature-programmed reduction (TPR) curves of the Cu/SAPO-34 catalysts.

As shown in Figure 6(b), Cu^{2+} ions are reduced to Cu^{+} between ~200 and 400 °C. In the low Cu-loaded catalysts, reduction is centered at ~350 °C, which shifts to ~250 °C at higher Cu loadings. The good symmetry of the TPR curves indicates that Cu ions in these catalysts are essentially homogeneously dispersed, critical for addressing important issues including the low- and high-temperature performance of these materials, and details on their deactivation mechanisms.

Factors that govern low- and high-temperature performance of Cu/CHA catalysts during the standard SCR reaction

It has become clear that there exist two types of isolated Cu-ions in Cu/SSZ-13: Cu^{2+} ions that charge-balanced by two Al tetrahedral sites, and $[Cu(OH)]^+$ ions that charge-balanced by one Al tetrahedral site. By varying Cu loadings and Si/Al ratios of Cu/SSZ-13, it is possible to generate model catalysts with one of two Cu-ions as dominant active centers. Using these model catalysts, standard SCR, NO/NH_3 oxidation kinetics were probed. By normalizing reaction rates, it is concluded that (1) both Cu^{2+}-2Al and $[Cu(OH)]^+$-1Al sites are SCR active, and they have similar activities; (2) below ~400 °C, both sites maintain excellent SCR selectivities, i.e., normalized SCR rates are much higher than NH_3 oxidation rates; (3) above ~400 °C, while Cu^{2+}-2Al sites still maintain excellent SCR selectivities, $[Cu(OH)]^+$-1Al sites lose SCR selectivities, i.e., normalized NH_3 oxidation rates approach SCR rates. From these experimental observations, it is readily concluded that (1) to enhance low-temperature NOx conversion, high Cu loading is preferred; (2) to maintain high-temperature SCR selectivity, low Cu loading is preferred. Also considering requirements for hydrothermal stability, it is suggested that for practical Cu/SSZ-13 catalysts, Si/Al ratios should be between 12 and 20 and Cu/Al ratios should be between 0.3 and 0.5 in order for optimized overall performance to be achieved. For Cu/SAPO-34 catalysts, the much weaker acidity of SAPO-34 compared to SSZ-13 indicated weaker interactions between Cu-ions with the SAPO-34 framework. This, in turn, suggests more facile Cu-ion agglomeration and CuOx formation. Therefore, for this catalyst, lower Cu loading (< 1 wt%) is recommended.

For Cu/SSZ-13 catalysts contain essentially only Cu^{2+}-2Al active sites, excellent SCR selectivities maintain even up to very high reaction temperatures (~600 °C and above). However in such catalysts, a large portion of Brønsted acid sites (-Al(OH)Si-) remain unprotected during hydrothermal aging, a situation that leads to severe hydrolysis and dealumination of the catalysts. In this case, we have discovered that by introducing alkali and alkaline earth cocations, these Brønsted acid sites can be neutralized. Catalysts thus prepared maintain excellent SCR selectivities and hydrothermal stability [10]. As shown in Figure 7, by adding 1.78 wt% Na to a Cu/SSZ-13 catalyst (Si/Al = 6, Cu = 0.98 wt%), the low temperature activity is moderately enhanced, presumably due to enhanced NH_3 storage by Na (as a Lewis acid). More importantly, ^{27}Al NMR results indicate substantial degradation of the catalyst without Na protection while for the catalyst with Na protection, essentially all Al maintain intact as framework tetrahedral sites.

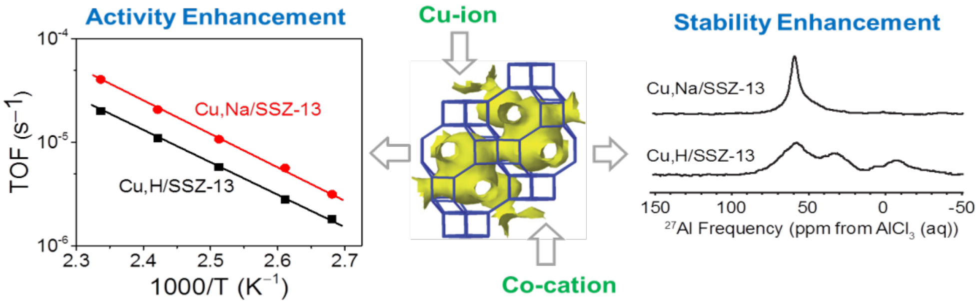

Figure 7: Arrhenius plots (left) for low-temperature standard NH_3-SCR and ^{27}Al solid-state NMR results (right) demonstrate that both SCR activity and hydrothermal stability of a low Cu-loaded Cu/SSZ-13 catalyst can be enhanced by the introduction of a Na^+ cocation.

Factors that govern low- and high-temperature performance of Cu and Fe/zeolite catalysts during the fast SCR reaction

The nature of the fast SCR reaction ($NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O$), i.e., no redox of Cu-ions by O_2 is part of the reaction mechanism, indicates that NO activation is via complexing with NO_2. As displayed in Figure 8, Cu/SSZ-13 displays much enhanced activity than H- and Na/SSZ-13 at low reaction temperatures. This demonstrate that low-temperature $NO + NO_2$ complexing reactions are facilitated by Cu^{2+} sites. At temperatures of 400 °C and above, advantages of the presence of Cu^{2+} sites are no longer obvious since the zeolite framework can catalyze the reaction already efficiently. However, NH_3 storage is still important to facilitate NOx conversion [2].

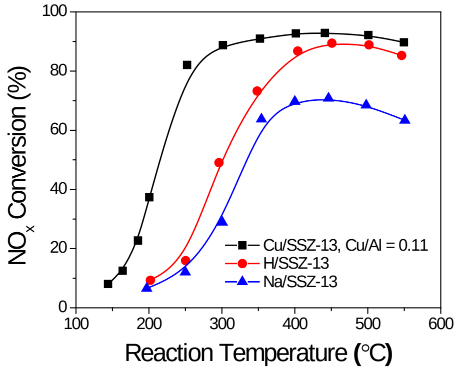

Figure 8: Light-off curves in fast SCR on Cu/, H/ and Na/SSZ-13 at Si/Al = 6. Reactant feed contains 175 ppm NO, 175 ppm NO_2, 350 ppm NH_3, 14% O_2, 2.5% H_2O balanced with N_2 at a GHSV of 800,000 h^{-1}.

At low reaction temperatures, model Fe/SSZ-13 and Fe/beta catalysts (Si/Al ≈ 12, Fe/Al ≈ 0.2) were prepared and hydrothermally aged at various temperatures before tested with fast SCR. As shown in Figure 9(a), even though the as-prepared catalysts have similar Si/Al ratios and Fe loadings, when a quasi-steady-state is reached at 200 °C, while NOx conversion reaches ~93% on Fe/beta, only ~23% NOx is converted on Fe/SSZ-13. From the NH_3-TPR results displayed in Figure 9(b), it is obvious that the remaining Brønsted acid sites bind more NH_3 molecules and with stronger binding for Fe/SSZ-13. As the strongly bound NH_3 stays as NH_4^+, a species that is much less reactive than weakly bound molecular NH_3, it is readily concluded that the lower activity for Fe/SSZ-13 is due to much more severe NH_4NO_3 inhibition, and NH_4^+ is responsible for NH_4NO_3 formation. To further prove this hypothesis, additional fast SCR measurements were conducted on Fe/SSZ-13 catalysts hydrothermally aged at various temperatures. From Figure 10(a), samples aged at 700 °C and above display substantially higher NOx conversion efficiency, suggesting that NH_4NO_3 inhibition is substantially mitigated for catalysts aged at these temperatures. As shown in Figure 10(b), solid-state ^{27}Al NMR spectra demonstrate loss of Brønsted acidity with hydrothermal aging. It is thus concluded that (1) low-temperature fast SCR does not require high Cu/Fe contents in catalysts; high NOx conversion efficiency can be sustained even at low isolated Cu/Fe concentrations. (2) NH_4NO_3 inhibition is a much more important criterion in affecting low-temperature fast SCR.

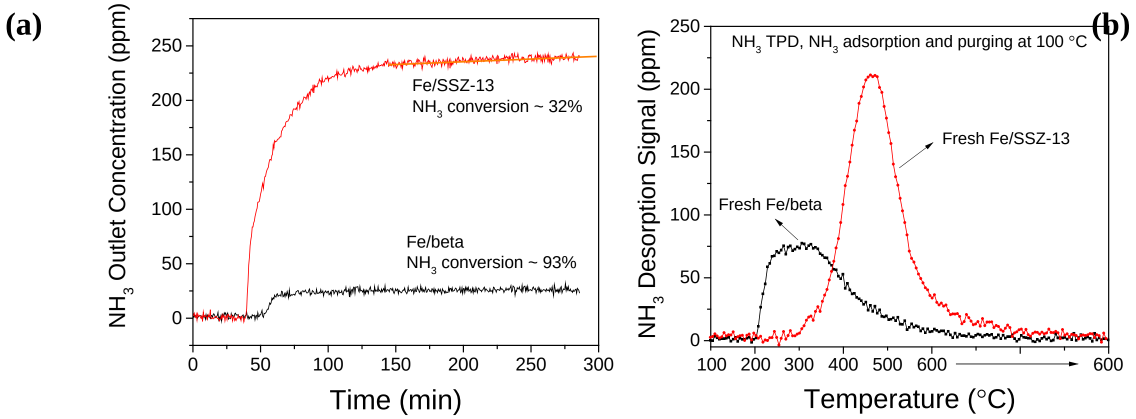

Figure 9: (a) Fast NH_3-SCR results on fresh Fe/SSZ-13 and Fe/beta catalysts at 200 ℃. Reactant feed contains 175 ppm NO, 175 ppm NO_2,350 ppm NH_3, 14% O_2, ~2.5% H_2O balanced with N_2 at a GHSV of 200,000 h^{-1}. (b) NH_3-TPD results on fresh Fe/SSZ-13 and Fe/beta catalysts.NH_3 adsorption and purging was conducted at 100 ℃.

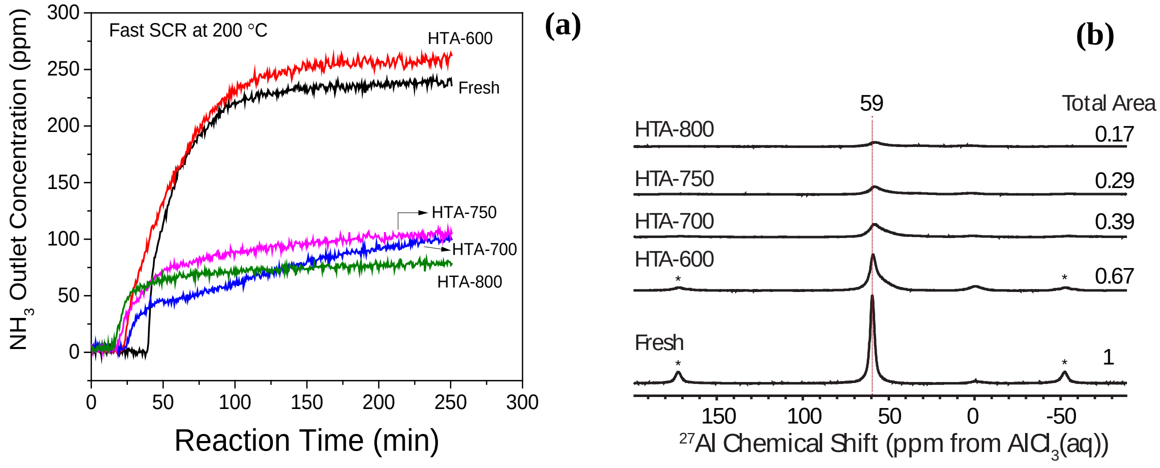

Figure 10: (a) Fast NH_3-SCR results on fresh and HTA Fe/SSZ-13 catalysts at 200 ℃. Reactant feed contains 175 ppm NO, 175 ppm NO_2,350 ppm NH_3, 14% O_2, ~2.5% H_2O balanced with N_2 at a GHSV of 200,000 h^{-1}. (b) ^{27}Al solid state NMR results for the samples.

Conclusions

PNNL and its CRADA partners from Cummins Inc. and Johnson Matthey have been carrying out a CRADA program aimed at understanding the fundamentals of limitations in low- and high-temperature performance of NOx reduction catalysts, and strategies in improving low- and high-temperature performance and stability of candidate NOx reduction technologies.

We have systematically investigated the advantages and limitations for K-based NSR materials. While the higher temperature performance can be improved as compared to Ba-based counterparts, the mobility of K must be considered and managed. Basic supporting material MgAlOx offers substantial advantages than alumina supports. A TiO_2 support, since it reacts with K to form phases with lower NOx storage capacities, may not offer long term stabilities.

We have developed methods to synthesize SSZ-13 and SAPO-34 materials with high crystallinity and tunable compositions at a laboratory scale. This greatly facilitated our capability in the synthesis of model Cu and Fe/zeolites that are otherwise difficult to purchase.

By utilizing a full array of modern spectroscopic and microscopic methods, and by conducting detailed reaction kinetics studies, we have been able to provide guidelines on Si/Al and Cu/Al ratios for the synthesis of Cu/CHA catalysts with optimized activity, selectivity and hydrothermal stability for standard SCR application. Using these guidelines, we further show in a case study that, by adding alkali and alkaline earth cocations to low-Cu loaded Cu/CHA, it is possible to create catalysts with excellent SCR selectivities at elevated reaction temperatures (≥ 500 °C) even after harsh hydrothermal aging.

For fast SCR, a detailed comparison between Fe/beta and Fe/SSZ-13 has been carried out. Under conditions where both catalysts have similar Fe loading, Si/Al ratio and NH_3 storage capacity, Fe/beta apparently displays better low-temperature activity. The lower acidity and higher pore openings for Fe/beta are likely responsible for the lack of NH_4NO_3 deposition, and therefore higher activities.

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Acronyms

BET: Brunauer-Emmett-Teller particle surface area and pore-size measurement method
CHA: chabazite zeolite
CRADA: cooperative research and development agreement
EDS: energy dispersive (X-ray) spectroscopy
EPA: Environmental Protection Agency
EPR: electron paramagnetic resonance
FTIR: Fourier transform infrared spectroscopy
ICE: internal combustion engine
LNT: lean-NOx trap (see also NSR)

NMR: nuclear magnetic resonance
NOx: nitrogen oxides (NO and NO_2)
NSR: NOx storage/reduction
PNA: passive NOx adsorber
PNNL: Pacific Northwest National Laboratory
SCR: selective catalytic reduction
STEM: scanning transmission electron microscopy
TEM: transmission electron microscopy
TGA: thermal gravimetric analysis
TPD/TPSR: temperature programmed desorption/temperature programmed surface reaction
TPR: temperature programmed reduction
XAFS: X-ray absorption fine structure
XANES: X-ray absorption near edge structure
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction