

Short communication

NMR studies of Cu/zeolite SCR catalysts hydrothermally aged with urea

Yisun Cheng^{a,*}, John Hoard^a, Christine Lambert^a,
Ja Hun Kwak^b, Charles H.F. Peden^b

^a Ford Innovation Center, Ford Motor Company, Dearborn, MI 48124, USA

^b Institute for Interfacial Catalysis, Pacific Northwest National Lab, Richland, WA 99352, USA

Available online 21 March 2008

Abstract

The effects of hydrothermal aging of Cu/zeolite urea-selective catalytic reduction (SCR) catalysts on their reactivity and material properties were assessed by performance tests and multiple characterization techniques that included ²⁷Al nuclear magnetic resonance (NMR) and X-ray diffraction (XRD). Three aging protocols were used that consisted of varying temperature during hydrothermal aging with or without exposure to aqueous urea solution. Differences in behavior were even found for samples hydrothermally aged immediately following exposure to the urea solution or if the sample was dried overnight before hydrothermal aging. The combination of urea and high-temperature exposure increased the deactivation of Cu/zeolite SCR catalysts beyond that observed by hydrothermal aging alone, with an immediate high-temperature exposure following wetting of the catalyst core with aqueous urea causing the most significant deterioration in performance. The impact of urea on SCR catalyst durability was also found to increase with the aging temperature. NMR analysis suggested that aging with urea resulted in relatively more dealumination of the zeolite for the SCR catalysts in this study.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Urea SCR; Cu/zeolite; Hydrothermal aging; Urea aging; NO_x reduction

1. Introduction

Selective catalytic reduction (SCR) of NO_x with aqueous urea and a catalyzed diesel particulate filter (CDPF) is considered as one of the emission control systems for diesel vehicles required to meet Federal Tier 2 and California LEVII emission standards [1]. Zeolite SCR catalysts, also used for stationary source NO_x emission control, have been widely studied for use on vehicles [2,3]. However, conditions such as temperature and flow rate are very different between the stationary and vehicle sources. Among these differences is that the SCR catalysts may have to sustain high temperatures associated with CDPF regeneration on vehicles. In addition, because of concerns about delivery and on-vehicle storage of the SCR reductant, aqueous urea solutions are used as the NH₃ source. It has been found that Cu/zeolite SCR catalysts that are engine-aged with urea injection deactivate in a more complicated manner than hydrothermal aging alone [4]. In

addition to the well-known aging factors, such as high temperature exposure and poisoning, urea is a new aging factor that SCR catalysts have to contend with on vehicles. Urea injected into the exhaust stream decomposes into ammonia and isocyanic acid (HNCO) then HNCO further hydrolyses to ammonia in the exhaust gas or on the surface of the SCR catalyst. However, the lower range of exhaust temperatures from vehicle diesel engines fall below the temperatures required for efficient urea decomposition. Thus, an important question to ask is whether the un-decomposed or partially decomposed urea impacts the performance and/or stability of the SCR catalysts on the vehicle.

In this short communication, the impact of urea along with high temperature hydrothermal conditions on Cu/zeolite SCR catalysts obtained from major suppliers were investigated in a lab flow reactor. The performance of catalysts exposed to various aging conditions was evaluated in simulated diesel exhaust gas. This short communication focuses on the correlation between the activity of Cu/zeolite SCR catalysts and the impact of zeolite structure after the combination of hydrothermal aging and urea exposure. The aged catalysts were

* Corresponding author. Tel.: +313 621 4575; fax: +313 594 2963.

E-mail address: ycheng1@ford.com (Y. Cheng).

characterized by ^{27}Al nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction (XRD). Due to the proprietary nature of working with supplier catalyst samples, only NMR and some XRD data can be explicitly presented here. However, other measurements corroborate the conclusions made here and both catalysts studied show similar combined effects of high temperature aging with urea. The results of this study provide valuable information on the durability of SCR catalysts for vehicle applications, most notably demonstrating an important contribution of urea in promoting hydrothermal degradation of these catalysts. This suggests that future investigations of SCR catalysts should consider specifically including this reactant in order to accurately account for catalyst changes under actual operating conditions.

2. Experimental¹

The SCR catalysts used in this study, CatA and CatB, were taken from fully formulated cordierite monoliths with Cu/zeolite washcoats. CatB was a beta zeolite-based SCR catalyst with a Si/Al ratio of 25. The washcoat loading was 2.3 gm/in.³ (15 gm/cm³) and the Cu loading was 200 gm/ft³ (7.4×10^{-3} gm/cm³). For proprietary reasons, details of CatA composition cannot be given in this paper. While the type of zeolite and Cu loading in CatA may well be different than CatB, both catalysts were designed for transient diesel engine applications.

The 1 in. \times 1 in. catalyst monolith core samples were aged and tested using a laboratory flow reactor system. First, the catalysts were aged at the selected temperatures for 30–60 min in three different ways: hydrothermal aging only, hydrothermal aging following wetting of the catalyst core with urea (“wet urea” + hydrothermal), and hydrothermal aging following urea wetting and drying at room temperature overnight (“dry urea” + hydrothermal). A 32.2 wt% aqueous urea solution was used for these aging protocols. For both the “wet urea” and “dry urea” protocols, wetting of catalyst core was accomplished by spraying a mist of the aqueous urea solution into the front face of the core sample. A spray bottle was used and the wetting process was performed at room temperature. The amount of urea solution loaded onto the core samples was the maximum liquid absorption amount of the core catalysts.

The focus of this paper was to investigate if the combination of urea and high temperatures increases the deactivation of Cu/zeolite SCR catalysts that have been considered for diesel vehicle NO_x emission control. While the two catalysts were aged at different temperatures that normally occur on diesel vehicles (CatA was aged at 860 °C and 670 °C, and for CatB a median temperature of 770 °C was selected), these differences do not effect the main conclusions of this short paper.

¹ This paper focuses on a method for characterizing catalyst deactivation and contains a rather less explicit description of the catalysts studied than is typical of papers in *Catalysis Today*. While the Editors would generally insist on the inclusion of adequate information to allow others to reproduce results, we feel in this case that the general applicability of the findings in this paper are independent of the catalysts tested and that they should be made available to the scientific community.

Table 1

Composition of simulated diesel exhaust gas for SCR activity measurement

Component	Concentration
O ₂	14%
H ₂ O	4.5%
CO ₂	5%
NO	350 ppm
NH ₃	350 ppm
N ₂	Balance

After aging, steady-state NO_x performance was measured from 170 °C to 550 °C at 30–50 °C steps in a flow reactor connected to a FTIR instrument from MIDAC Corporation with a heated sample cell system for wet gas analysis. Simulated diesel exhaust gas was flowed through the sample core at space velocities of 30 K h⁻¹, with a composition as shown in Table 1.

The behavior of the zeolite aluminum species during the aging process was characterized by solid-state ^{27}Al NMR spectroscopy. For the NMR experiments, each of the samples after aging treatment were carefully ground, washcoat and substrate together, for a homogeneous and representative sampling of catalyst coated on the monolith support. Then, ~0.3 g of sample was transferred into a gas tight pencil type rotor (7.5 mm OD) and introduced into the NMR spectrometer. Solid-state ^{27}Al NMR spectra were acquired on a Varian/Chemagnetic CMX Infinity 300 MHz instrument, equipped with a Varian/Chemagnetics 7.5 mm HX magic angle spinning (MAS) probe operating at a spectral frequency of 78.2 MHz. All ^{27}Al MAS NMR spectra were externally referenced to aluminum in an aqueous solution of Al(NO₃)₃ defined as 0 ppm chemical shift. All spectra were obtained at a sample spinning rate of 5 kHz and using a 1 s recycle delay.

XRD analysis was carried out on a Philips PW3040/00 X'Pert powder X-ray diffractometer using the Cu K α ¹ radiation ($\lambda = 1.5406 \text{ \AA}$) between $2\theta = 5^\circ$ and 50° , with a step size of $0.02^\circ/\text{s}$. Data analysis was accomplished using JADE (Materials Data, Inc., Livermore, CA) as well as the Powder Diffraction File database (2003 Release, International Center for Diffraction Data, Newtown Square, PA).

3. Results and discussion

The steady-state NO_x conversions of CatA, aged at 860 °C for 30 min using the three aging treatments described above, are shown in Fig. 1. The sample aged with “wet urea” displayed the most severe deactivation. Compared to the NO_x activity of the sample aged without urea, there was up to an 18% and 41% decrease in activity for samples aged with “dry urea” and “wet urea”, respectively. CatA was also aged at 670 °C for 60 min hydrothermally without urea, and with “wet urea” + hydrothermal aging, with the steady-state NO_x conversion for these samples shown in Fig. 2. Unlike the samples aged at 860 °C, the activity of CatA samples aged at 670 °C were very similar regardless of the aging treatment. This result indicates that the urea did not deactivate CatA beyond that caused by thermal deterioration at 670 °C.

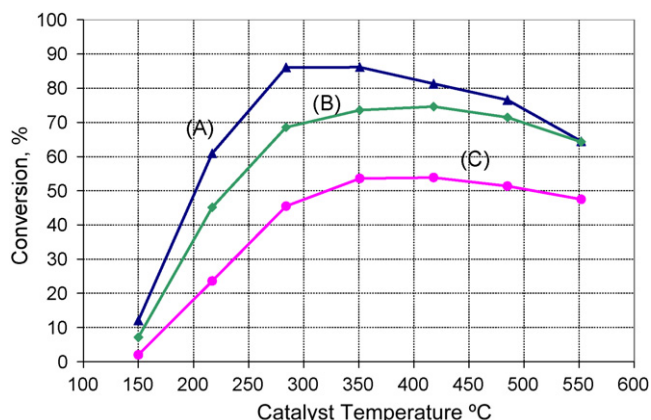


Fig. 1. Steady-state NO_x conversions for CatA after aging at 860°C for 30 min: (A) hydrothermal aging only; (B) “dry urea” + hydrothermal aging; (C) “wet urea” + hydrothermal aging.

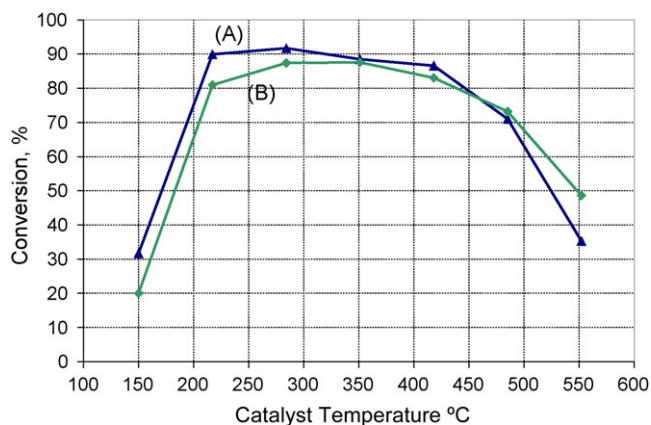


Fig. 2. Steady-state NO_x conversions of CatA after aging at 670°C for 60 min: (A) hydrothermal aging only and (B) “wet urea” + hydrothermal aging.

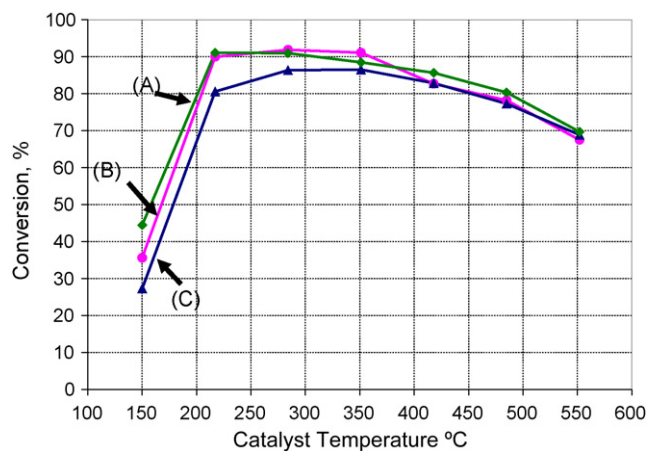


Fig. 3. Steady-state NO_x conversions of CatB after aging at 770°C for 30 min: (A) hydrothermal aging only; (B) “dry urea” + hydrothermal aging; (C) “wet urea” + hydrothermal aging.

The three different aging treatments were also applied to CatB samples at 770°C for 30 min, and the NO_x activities after these aging are shown in Fig. 3. Similar to CatA, the CatB sample aged with “wet urea” deactivated most significantly. However, the decrease of NO_x activity for CatB aged with “wet urea” at 770°C was, at most, 17% compared to the sample hydrothermally aged without urea, and there was no significant difference in NO_x activity between the samples aged hydrothermally without urea and with “dry urea” except at the lowest reaction temperature of 150°C . The smaller decrease in activity for CatB could have been due to the lower aging temperature of at 770°C versus 860°C applied to CatA. The differences may also, at least in part, represent some enhanced stability to these aging protocols for Cat B. In any case, these results demonstrate the impact of un-reacted or partially reacted urea on SCR catalyst durability, and that these effects are a strong function of aging temperature.

Solid-state ^{27}Al NMR is a powerful tool for identifying the chemical nature of aluminum in zeolites [5,6], and has been successfully applied to study zeolite-based urea SCR catalysts [7,8]. It is well known that the aluminum in the zeolite framework has a tetrahedral coordination that gives rise to an ^{27}Al chemical shift of $\sim 50\text{--}60$ ppm relative to Al in $\text{Al}(\text{NO}_3)_3$. But if removed from the zeolite framework (dealuminated), the Al^{3+} cations instead exist primarily in octahedral coordination now with a $\sim 0\text{--}10$ ppm chemical shift in the ^{27}Al NMR spectra.

The ^{27}Al NMR spectra of CatA, obtained after the various aging treatments, are shown in Fig. 4. Fresh CatA had mainly three NMR peaks at peak at 47 ppm, 30 ppm and 5 ppm (small peaks at ~ -30 ppm and 100 ppm are spinning side bands). Based on the spectrum for the cordierite support alone, the 30 ppm and 5 ppm peaks arise from this support material. The 47 ppm peak is due to the aluminum that is tetrahedrally coordinated in the zeolite framework. The small intensity

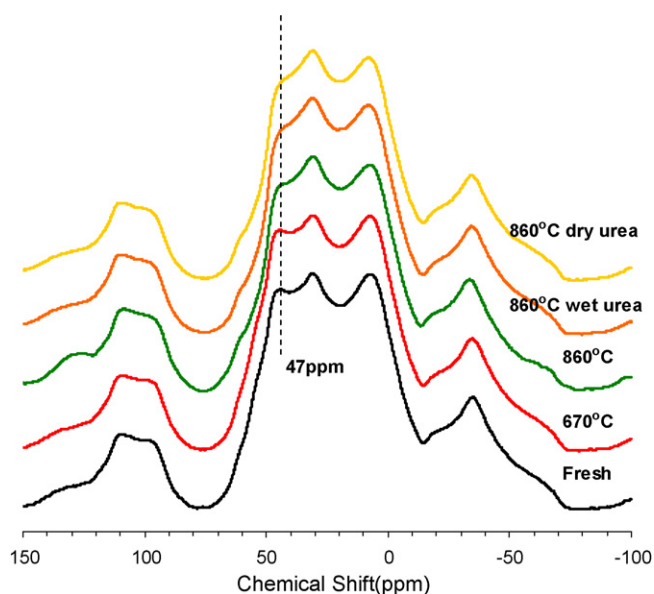


Fig. 4. ^{27}Al NMR of CatA fresh, aged at 670°C under hydrothermally conditions only, and after aging at 860°C for 30 min in the three aging conditions.

changes of this peak with aging thus represent the relative degree of dealumination that occurs during the various aging treatments.

The ^{27}Al NMR spectrum obtained from the CatA sample aged at 670°C was essentially identical to the one from the fresh sample indicating little, if any, dealumination from this treatment. This result is consistent with XRD measurements (not shown in this paper) that indicated no structural change. The steady-state NO_x performance shown in Fig. 2, demonstrated that the urea did not deactivate CatA beyond the thermal deterioration at 670°C . However, the 860°C aged CatA samples all showed significant decreases of the 47 ppm ^{27}Al NMR peak, highlighting significant dealumination from the zeolite framework regardless of aging process. A close inspection of the spectra for the 860°C aged samples reveals that the extent of dealumination is dependent upon the aging treatment used. For more ready comparison of the relative amount of dealumination of CatA with these different aging processes, the fresh catalyst spectrum was subtracted from spectrum of the aged samples (Fig. 5). As shown in the figure, there was no tetrahedral aluminum loss for the sample aged at 670°C . However, for the samples aged 860°C , CatA showed varying levels of tetrahedral aluminum loss. The sample aged hydrothermally had relatively less amount of dealumination. Aging with urea resulted in a significantly larger loss of tetrahedral aluminum, with the “wet urea” treatment leading to the most serious dealumination behavior. These results are consistent with the catalytic activity data shown in Fig. 1. The higher amount of dealumination resulted in lower NO_x conversions, presumably because of the lower amount of active sites associated with these tetrahedral Al^{3+} cations.

The ^{27}Al NMR analysis was also performed on CatB samples as shown in Figs. 6 and 7. The same ^{27}Al NMR features discussed above for CatA are also present in the spectra obtained from CatB. Relatively smaller amounts of the features associated with the cordierite support (peaks at ~ 5 ppm and ~ 30 ppm) are a result of a modified sampling procedure that led

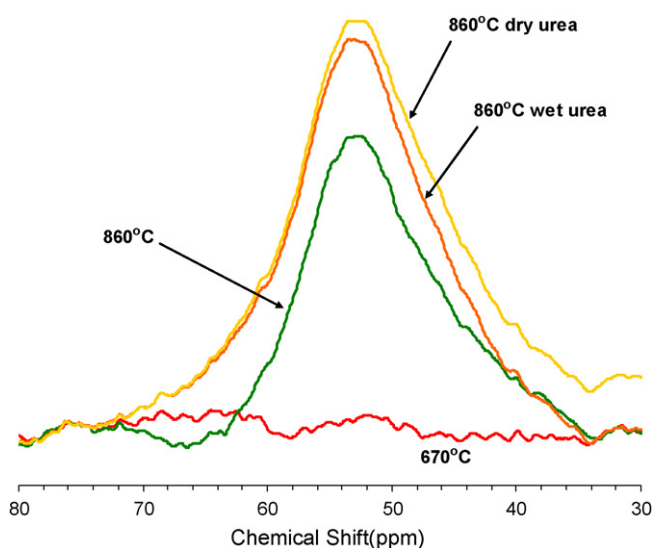


Fig. 5. Relative dealumination of CatA after aging at 670°C hydrothermal only, and after aging at 860°C in the three aging conditions.

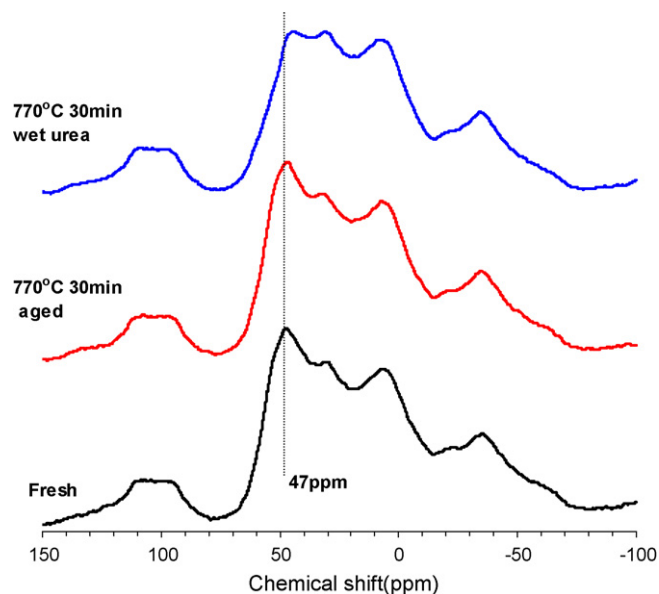


Fig. 6. ^{27}Al NMR of CatB for fresh, and after 770°C 30 min aging with and without urea.

to lower amounts of the support in the CatB samples. CatB samples after hydrothermal aging at 770°C for 30 min had an almost identical spectrum with the fresh catalyst (Fig. 6). Thus, there was little, if any, dealumination during hydrothermal treatment at 770°C for 30 min. However, an aging treatment at 770°C for 30 min with “wet urea” resulted in a significant loss in the peak intensity at 47 ppm, indicating dealumination of tetrahedral aluminum from the zeolite framework. Fig. 7, obtained by subtraction of the spectrum of the fresh sample from those of the two hydrothermally aged CatB samples, highlights these changes in a more clear way. These results were also consistent with the observed loss in catalytic activity shown in Fig. 3, with the “wet urea” aged sample giving a lower level of NO_x conversion than the hydrothermally aged one. Note, however, that the “wet urea” aged sample still had some remaining tetrahedral framework aluminum, thereby at least partially explaining why the activity drop was not as significant as the 860°C aged CatA samples.

XRD was performed to directly follow structural changes of CatB during these aging treatments. Fig. 8 shows the XRD data for CatB for various aging treatments, along with the pattern obtained from a cordierite standard. Additional broad peaks at $2\theta = \sim 8^\circ$ and $\sim 22.5^\circ$ for fresh CatB confirmed the beta zeolite structure. After a thermal aging treatment at 770°C for 30 min, the XRD pattern was not significantly changed. Interestingly, wet urea aged catalysts yielded a very similar XRD pattern to that obtained from the hydrothermally aged catalysts. In both cases, the zeolite structure of CatB was maintained even though a significant amount of dealumination was evident in the ^{27}Al -NMR spectra. This likely explains why this catalyst shows significantly higher activity than CatA after 860°C aging (not shown in this paper). Complete collapse of the zeolite structure was evident for this latter catalyst.

These results clearly demonstrate that dealumination was one of the key processes occurring during deactivation of the aged

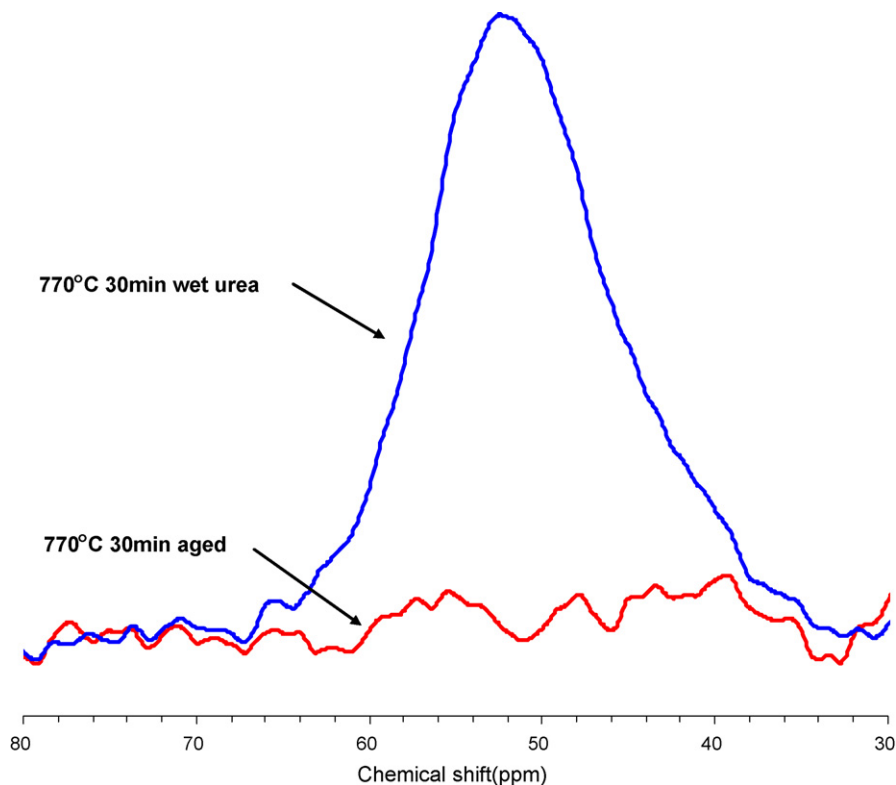


Fig. 7. Relative dealumination of CatB after aging at 770 °C with and without urea.

urea-SCR catalysts used in this study. Such a process likely causes deactivation because zeolytic aluminum is typically the ion exchange sites of catalytically active Cu ions. However, since the characterization of the copper phase has not been performed in this study, we cannot exclude the possibility that the Cu migration (including sintering) might also contribute to the deactivation of aged Cu/zeolite SCR catalysts.

Upon dealumination from the zeolite framework, a small alumina phase forms with a consequent permanent loss of the catalytic active sites. Of special interest, these results document a mode of deactivation specifically due to some process that involves residual un-reacted or partially reacted urea on the SCR catalyst material. We are currently carrying out additional studies to understand the mechanism(s) of this urea-caused deactivation mode. For these kind of dealumination studies, solid-state ^{27}Al NMR is shown to be a powerful tool for characterization of deactivation in urea-SCR catalysts.

4. Conclusions

The combination of urea and high temperature exposure increased the deactivation of Cu/zeolite SCR catalysts beyond that observed by hydrothermal aging alone. Immediate high temperature exposure following wetting of the catalyst core with a urea solution caused the most significant deterioration in performance compared to a sample hydrothermally aged after the core was allowed dry at room temperature overnight following urea exposure. The impact of urea on SCR catalyst durability increased with the aging temperature. NMR analysis suggested that aging with urea results in relatively more dealumination of the zeolite for the Cu/zeolite SCR catalysts in this study.

Acknowledgements

Financial support for studies performed at Pacific Northwest National Laboratory (PNNL) was provided by the U.S. Department of Energy (DOE), Office of FreedomCar and

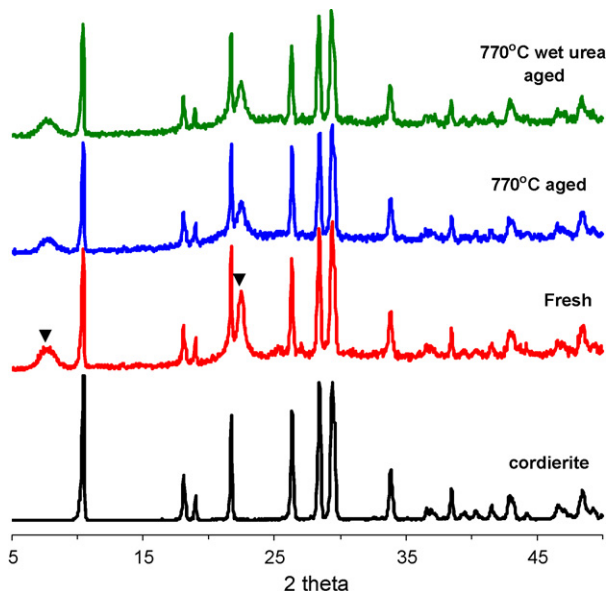


Fig. 8. XRD of CatB for fresh, and after 770 °C 30 min aging with and without urea.

Vehicle Technologies. Portions of the work were performed in the Environmental Molecular Sciences Laboratory (EMSL) at the PNNL. The EMSL is a national scientific user facility and supported by the U.S. DOE Office of Biological and Environmental Research. PNNL is a multi-program national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Reference

- [1] C. Lambert, R. Hammerle, R. McGill, M. Khair, C. Sharp, SAE 2004-01-1292 (2004).
- [2] P. Tennison, C. Lambert, M. Levin, SAE 2004-01-1291 (2004).
- [3] C. Lambert, S. Williams, B. Carberry, E. Koehler, D. Tomazic, “Urea SCR and CDPF System for a Tier 2 Light-Duty Truck”, 15 Aachener Kolloquium Fahrzeug- und Motorentechnik (2006).
- [4] Y. Cheng, L. Xu, J. Hangan, M. Jagner, C. Lambert, SAE 2007-01-1579 (2007).
- [5] E. Bourgeat-Lami, P. Massiani, F. Di Renzo, P. Espiau, F. Fajula, T. Des Courieres, *Appl. Catal.* 72 (1991) 139.
- [6] S.M. Campbell, D.M. Bibby, J.M. Coddington, R.F. Howe, R.H. Meinholdz, *J. Catal.* 161 (1996) 338.
- [7] J.-H. Park, H.J. Park, J.H. Baik, I.-S. Nam, C.-H. Shin, J.-H. Lee, B.K. Cho, S.H. Oh, *J. Catal.* 240 (2006) 47.
- [8] O. Kröcher, M. Devadas, M. Elsener, A. Wokaun, N. Söger, M. Pfeifer, Y. Demel, L. Mussmann, *Appl. Catal. B: Environ.* 66 (2006) 208.