SELECTIVE REDUCTION OF NOX IN OXYGEN RICH ENVIRONMENTS WITH PLASMA-ASSISTED CATALYSIS: CATALYST DEVELOPMENT AND MECHANISTIC STUDIES

Charles H. F. Peden / Pacific Northwest National Laboratory (PNNL)

Stephan E. Barlow / PNNL

John W. Hoard / Ford Motor Company

Ja Hun Kwak / PNNL

Mari Lou Balmer-Millar / PNNL*

Alexander G. Panov / PNNL*

Steven J. Schmieg / GM R&D

János Szanyi / PNNL

Russell G. Tonkyn / PNNL

***Now at Caterpillar, Inc.**

ABSTRACT

The control of NOx (NO and NO_2) emissions from so-called 'lean-burn' vehicle engines remains a challenge. In recent years, there have been a number of reports that show that a plasma device combined with a catalyst can reduce as high as 90% or more of NOx in simulated diesel and other 'lean-burn' exhaust. In the case of propylene containing simulated diesel exhaust, the beneficial role of a plasma treatment is now thought to be due to oxidation of NO to NO_2, and the formation of partially oxidized hydrocarbons that are more active for the catalytic reduction of NO_2 than propylene. *Thus, the overall system can be most usefully described as hydrocarbon selective catalytic reduction (SCR) enhanced by 'reforming' the exhaust with a non-thermal plasma* (NTP) *device.* For plasma-enhanced catalysis, both zeolite- and alumina-based materials have shown high activity, albeit in somewhat different temperature ranges, when preceded by an NTP reactor. This paper will briefly describe our research efforts aimed at optimizing the catalyst materials for NTP-catalysis devices based, in part, on our continuing studies of the NTP- and catalytic-reaction mechanisms. Various alkali- and alkaline earth-cation-exchanged Y zeolites have been prepared, their material properties characterized, and they have been tested as catalytic materials for NOx reduction in laboratory NTP-catalysis reactors. Interestingly, NO_2 formed in the plasma and not subsequently removed over these catalysts, will back-convert to NO, albeit to varying extents depending upon the nature of the cation. Besides this comparative reactivity, we will also discuss selected synthesis strategies for enhancing the performance of these zeolite-based catalyst materials. A particularly important result from our mechanistic studies is the observation that aldehydes, formed during the plasma treatment of simulated diesel exhaust, are the important species for the reduction of NOx to N_2. Indeed, acetaldehyde has been found to be especially effective in the *thermal* reduction of both NO and NO_2 over Ba- and Na-Y zeolite catalysts.

INTRODUCTION

A number of technologies are being developed to deal with one or more of the newly regulated species (NO_x, PM, and SO_x) in the exhaust of diesel-fueled vehicles [1]. In particular, the control of NO_x emissions from these inherently 'lean-burn' engines poses a significant challenge for efficient exhaust emission control [2]. This is because traditional precious-metal based three-way catalysts, remarkably effective for controlling emissions from engines operating at 'stoichiometric' air to fuel ratios, are unable to reduce NO_x under net oxidizing conditions. As such, new technologies that include hydrocarbon selective catalytic reduction (SCR); urea SCR, plasma-enhanced hydrocarbon SCR, and lean-NO_x traps are being considered as strategies for diesel vehicle emission control.

In plasma-enhanced hydrocarbon SCR, a non-thermal plasma reactor is inserted between the engine and a catalyst [3]. Figure 1 is a conceptual schematic of a plasma/catalyst system, and includes a picture of an operating non-thermal plasma (NTP) device designed, constructed, and used by us for engine dynamometer testing [4]. The figure also suggests the role of the various components of the overall device for reducing NOx from the exhaust of a CIDI engine as will be discussed in more detail below. Here, we emphasize that the catalytic process is hydrocarbon SCR, but this process can be significantly enhanced by 'reforming' the exhaust with the NTP device.

In this paper, we briefly summarize results on a program aimed at the development of the plasma-enhanced hydrocarbon

SCR technology for the remediation of NO_x from 'light-duty' diesel engines. In particular, some of our earliest work has shown that an NTP in combination with an appropriate catalyst can provide NO_x emission reduction efficiency of 60-80% or more using a simulated diesel exhaust [5]. Based on these levels of NOx reduction obtained in the lab, a simple model was developed in this program that allows for the estimation of the fuel economy penalty that would be incurred by operating a plasma/catalyst system [6]. Results obtained from this model suggest that a 5% fuel economy penalty is achievable with the then current (2000) state-of-the-art catalyst materials and plasma reactor designs. As will be shown below, more recent significant improvements in the catalyst materials and the device design mean that even lower fuel economy penalties should be realizable.

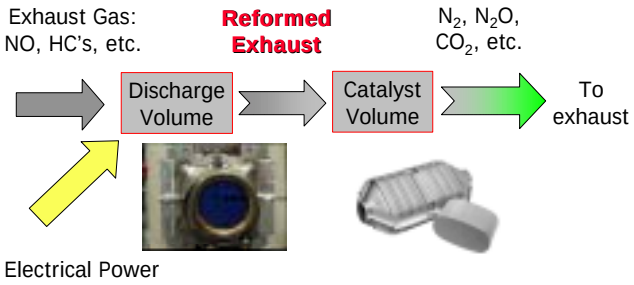

Figure 1: Schematic of Two Step Discharge/ Catalyst Reactor

High NOx reduction efficiencies have been demonstrated in engine dynamometer tests by adding small amounts of diesel fuel up-stream of the plasma-catalyst device [4], although catalyst deactivation, likely due to 'coking' was also observed. Still, the ability of this technology to compete with urea SCR and lean-NOx traps remains to be demonstrated, although it can be noted that the relative development efforts for plasma-enhanced hydrocarbon SCR are orders of magnitude smaller than the other two technologies.

EXPERIMENTAL

Detailed descriptions of the catalyst preparation, and NTP/catalyst testing procedures and equipment are contained elsewhere [5,7,8]. Briefly, the catalysts used in this study were prepared from a sodium Y-type faujasite (NaY) zeolite (Si/Al~2.6), obtained from Zeolyst International Co. (CBV 100), by solution ion exchange. The NaY extrudates (containing approximately 10% alumina binder) were ion exchanged with aqueous solutions containing the desired alkali or alkaline-earth cation. Subsequently, the samples were thoroughly washed with distilled water and then dried at 393K in air. Prior to each catalytic experiment, the samples were calcined at 773K for 4hrs in air. The NO_x reduction activities of the catalysts were measured in a two-stage non-thermal plasma/catalytic reactor system described in detail previously [7]. A simulated exhaust gas mixture of 8% O_2, 2% H_2O, 245ppm NO, and 520ppm C_3H_6 in N_2 balance was used in the catalytic tests. The total flow rate was kept at 2.1L corresponding to a space velocity of approximately 12000h^{-1}. Typically, the reactor was first heated up to 443K in flowing nitrogen without turning on the plasma. Upon reaching the desired reactor temperature, the gas flow was switched to the reactant gas mixture, and as soon as the NO_x levels stabilized, the plasma was turned on at a typical power level of 10 joules/liter (J/l – the protocol for the measurement and adjustment of the plasma power were performed according to Tonkyn, *et al*. [7]). Throughout the catalytic measurements, the NO_x levels ($NO+NO_2$) were monitored with a chemiluminescent NO_x analyzer (Rosemount, Model 955). Periodically the NO levels were measured, allowing us to estimate the quantities of unconverted NO_2. During the catalytic tests, the reaction temperature was raised form 443K to 563K in 30K increments. At each temperature, sufficient time was allowed to reach steady state (or near steady state) to assure that the NOx loss was not due to storage effects.

RESULTS AND DISCUSSION

Role of the plasma: The chemistry inside the plasma reactor is complex, but now fairly well understood [5,9-11]. It is concluded that the two most important processes initiated by the plasma are the practically complete conversion of NO into NO_2, and the partial oxidation of unburned hydrocarbons in the exhaust gas. In fact, modeling of the gas-phase chemistry indicates that these two chemical processes are intimately linked [11]. Thus, the important catalytic chemistry, taking place over the catalyst volume that follows the plasma reactor, involves the reaction of NO_2 with these partially oxidized hydrocarbons.

Both modeling predictions [11] and experimental measurements [5] demonstrate that aldehydes are particularly significant partially oxidized hydrocarbon products from the gas-phase plasma chemistry. In particular, an NTP reactor, operated at ~40 J/l on a simulated diesel exhaust (215ppm NO, 660 ppm propylene (C_3H_6), 8% O_2, 2%H_2O with a balance of N_2 gas), will form 120 ppm of formaldehyde (CH_2O), 160 ppm of acetaldehyde (CH_3CHO), and 145 ppm of CO plus CO_2 [5]. Sending the 'reformed' gas mixture, containing NOx as NO_2 and partially oxidized hydrocarbons in the form of aldehydes, over a NaY catalyst at 200 °C results in almost complete loss of acetaldehyde but little if any reaction of the formaldehyde. In contrast to this, similar studies with alumina-based catalysts, conducted at somewhat higher temperatures, demonstrated that formaldehyde as well as acetaldehyde is a good reductant for NO_2 for these materials useful at the higher exhaust temperatures encountered from 'heavy-duty' diesel engines [12,13]. (In the following section, we discuss the genesis and optimized compositions of catalyst materials for plasma-enhanced hydrocarbon SCR.)

On the basis of the just-described results, we performed experiments to demonstrate that aldehydes are particularly effective reductants for the catalytic conversion of NO_2. In this way, we believe that the specific role of the plasma reactor, in 'reforming' the exhaust to NO_2 and aldehydes, is established. In these experiments, aldehydes were injected into the gas mixture to varying levels, NO or NO_2 was used as the source of NOx (200ppm), and NOx reduction was studied over zeolite-(NaY and BaY) and alumina-based catalysts *without* plasma treatment. These 'thermal' (no plasma) catalysis experiments resulted in NOx conversion levels of 90% or more [5,14].

Catalyst Development: Balmer, *et al*. [15] reviewed early studies aimed at catalyst material selection for plasma-enhanced hydrocarbon SCR. While the beneficial effects of combining a non-thermal plasma device with a catalyst material was recognized early on, it was not clear at that time what catalyst properties were desirable because the role of the plasma reactor had not been established. Many classes of catalysts were investigated including traditional three-way precious metal-based automotive catalysts, and the best 'lean-NOx' catalyst at the time, Cu-ZSM-5. While neither of these two classes of materials proved to be effective, the studies did identify [5, 16] alkali- and alkaline earth-Y zeolites as highly active catalysts for plasma-enhanced hydrocarbon SCR, with optimum activity observed for temperatures around 200 °C. At around this time, alumina-based materials were shown to be effective catalysts at somewhat higher (> 400 °C) temperatures [10]. More recently, the combination of Y zeolite- and alumina-based catalyst materials has been shown to be especially beneficial for broadening the 'temperature window' in which high NOx reduction is observed [5,13], for example as illustrated in Figure 2. Further developments [8,17,18] of both these low- and high-temperature classes of catalysts have been greatly informed by the developing understanding of the plasma chemistry. Here we briefly describe two recent results on the Y zeolite-based catalysts.

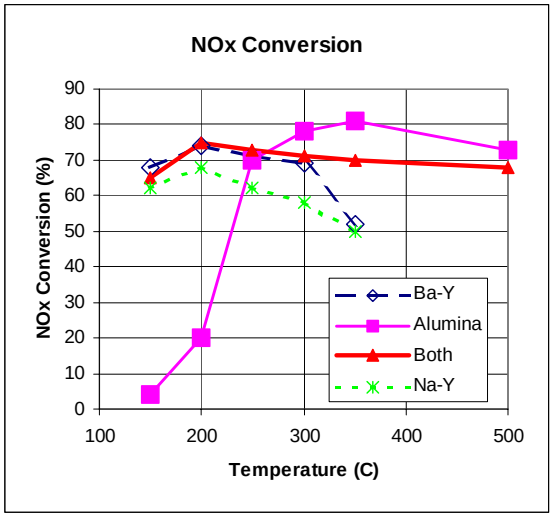

Figure 2: Temperature dependence of NOx conversion over NaY (x), BaY(◊), and γ–alumina (□) for plasma enhanced catalysis of a simulated diesel exhaust.

Recently, we have reported the results of a systematic study on the alkali- and alkaline earth-ion exchanged Y zeolite catalysts [8]. The key question we sought to answer was which cationic forms are the most active catalysts for plasma-assisted NO_x reduction. Figure 3 shows a comparison of NOx conversion levels obtained for plasma-enhanced hydrocarbon SCR as a function of temperature for a series of alkali- (Figure 3a) and alkaline earth-exchanged (Figure 3b) catalysts. NaY in the alkali series, and BaY and SrY in the alkaline earth series show the most promising activity for this reaction. In addition, the alkaline earth-exchanged catalysts show significantly wider 'temperature windows' where good NOx reduction activities are observed. Our results also show that the BaY catalysts are the most active with the widest 'temperature window'. BaY/NaY catalysts, prepared by partial exchange of Na for Ba cations in the zeolite, showed intermediate behavior with a monotonic increase in activity with increasing substitution of Na for Ba [8]. Finally, we observed an approximate correlation between activity and ionic size of the exchanged cation [8], perhaps suggesting that the electronic properties of the zeolite cation play an important role in determining catalyst activity.

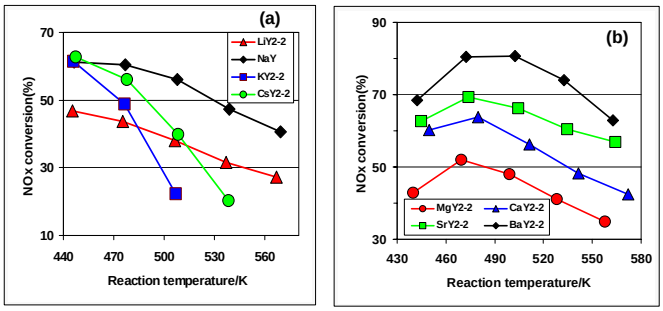

Figure 3: NO_x conversion for (a) Li-, Na-, K-, and Cs-Y zeolites, and (b) Mg-, Ca-, Sr-, and Ba-Y zeolites in the 443-563K temperature range.

In the course of performing these comparative studies, we discovered that specific materials preparation procedures can have a profound effect on activity for these class of catalysts [8,18]. For example, in the limited literature on plasma-enhanced catalysis, significant variations can be seen for apparently similar materials and reaction conditions. To this end we evaluated two NaY zeolites (CBV 100) received from the same manufacturer [8]. Chemical composition, and Al and Si NMR analyses showed no difference between the two materials. However, they behaved significantly differently for the plasma-enhanced hydrocarbon SCR of NO_x with reaction rates that differ by 10% or more. These reactivity differences are similar to those observed in Figure 3 in comparing different alkali- and alkaline earth-exchanged catalysts. Thus, these results serve as a caution to those attempting to quantitatively compare catalytic results obtained from zeolite-based materials that are thought to be very similar. Besides this, we have also recently demonstrated that specific ion exchange/calcinations procedures can lead to significantly improved catalyst performance [18,19].

Figure 4 is a schematic of the two basic catalyst preparation methods compared here. In one method, the starting Na-Y material was ion exchanged one to four times with an aqueous solution containing an excess of the corresponding cation, washed with water and subsequently dried and calcined. These materials are labeled as MY(x-1), where x represents the number of solution ion exchange ($1 \le x \le 4$), and M is the alkali or alkaline earth cation. In the other method, after each solution ion exchange step the catalyst was washed, dried and calcined at 773K for 4hrs in air prior to performing the next ion exchange step. These samples are designated as MY(x-y), where x represents the number of solution ion exchange and y the number of high temperature calcinations ($1 \le x = y \le 4$).

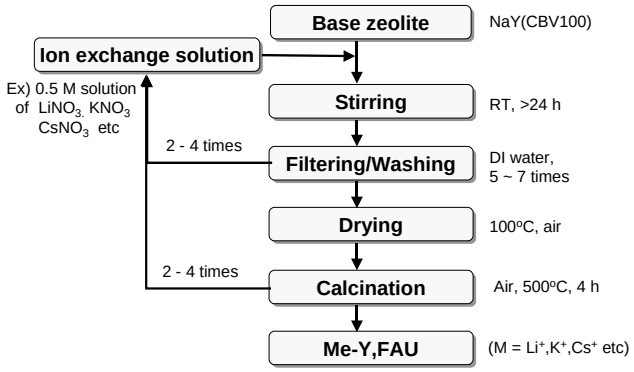

Figure 4: Schematic of the ion-exchange catalyst synthesis procedures.

For Ba-exchanged Y zeolite catalysts, Figure 5 shows NOx reduction activities for the BaY(x-1) series of catalysts prepared by the first method described above. It can be seen that additional ion exchange steps are not useful for enhancing catalyst performance. However, Figure 6, containing data for the MY(x-y) series of catalysts prepared by the second procedure, clearly shows a dramatic enhancement in the catalyst activity when an intermediate calcinations step is performed prior to the second and subsequent solution ion exchange steps. The biggest change occurs between the BaY(1-1) and BaY(2-2) materials with rate enhancements of over 25% at the highest temperatures. Small improvement is still evident through the BaY(4-4) catalysts studied here. On the basis of recent literature [20], we believe that the intermediate high-temperature calcination after a solution ion exchange step results in a redistribution of charge compensating cations in the zeolite framework. This solid-state ion redistribution upon calcination enables more complete ion exchange of Na^+ ions by the alkali- or alkaline earth-cation in solution. Note that we utilized MY(2-2) catalysts for the studies shown in Figure 3 in order to provide a fair comparison of the relative performance of the alkali- and alkaline earth-exchanged catalysts.

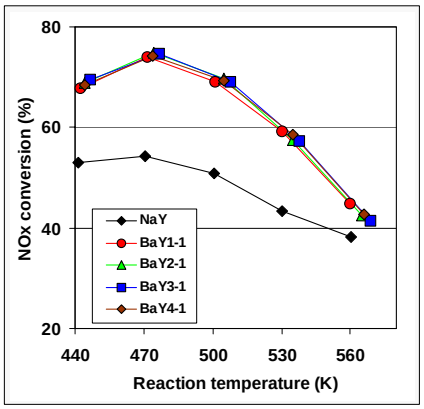

Figure 5: The effect of multiple solution ion exchanges on the catalytic activities of BaY zeolites. The NaY starting material was ion exchanged with $Ba(CH_3COOH)_2$ solution 1-4 times, and then the samples were calcined at 773K for 4hrs.

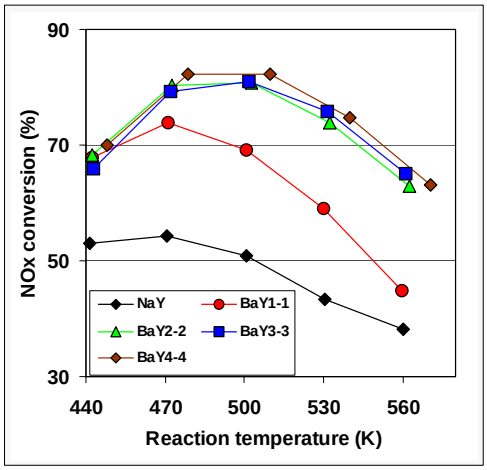

Figure 6: The effect of solution ion exchange/high temperature calcination cycles on the catalytic activities of BaY zeolites. After *each* solution ion exchange step, the catalyst was calcined at 773K for 4hrs.

Studies of the Reaction Mechanism(s): In the last couple of years, we have been performing increasingly detailed studies of the catalytic reaction mechanism(s) over the Y zeolite-based catalysts in order to provide insight into ways in which to improve overall system performance. Recall that the process of plasma-enhanced NOx reduction can be usefully thought of as catalytic hydrocarbon SCR performed on an exhaust stream that has been 'reformed' by the NTP device. As such, we expect these studies to inform the general field of hydrocarbon SCR for 'lean-NOx' reduction. Here, we briefly describe a couple results from our fundamental studies that highlight some specific differences in the behavior between NaY and BaY catalysts.

So far we have discussed the total NO_x conversion levels in comparing the reactivity of alkali- and alkaline earth-exchanged Y zeolite catalysts. As we have discussed above, NO is converted to NO_2 in the plasma and this conversion is essentially 100% under plasma reactor conditions used in our studies. Thus, the zeolites are performing as NO_2 reduction catalysts and it is therefore useful to take a look at the NO_2 conversion levels on these two catalyst series. In prior studies, we have noted the presence of N_2, N_2O, HCN, and NO as the predominant N-containing reaction products exiting the catalyst. The first three products represent reduced products while the simple back conversion to NO does not result in a reduction in NOx levels.

The NO_2 conversion as a function of reaction temperature for the alkali- and alkaline earth-exchanged zeolites is compared in Figures 7 and 8, respectively. For the alkali-exchanged catalysts, the trends observed for NO_2 conversion are strikingly similar to those seen for NO_x conversion in Figure 3. This means that, by and large, the NO_2 that is not converted to the reduced products N_2, N_2O and HCN, leaves the catalyst region unreacted; that is, there is very little back conversion to NO. In contrast, the trends for the alkaline earth-

exchanged catalysts illustrated in Figure 8 show NO_2 conversion levels above 90% over the entire temperature range studied (with the exception of MgY at low temperatures). Thus, the NO_2 that is not reduced to N_2, N_2O and HCN is instead converted back into NO.

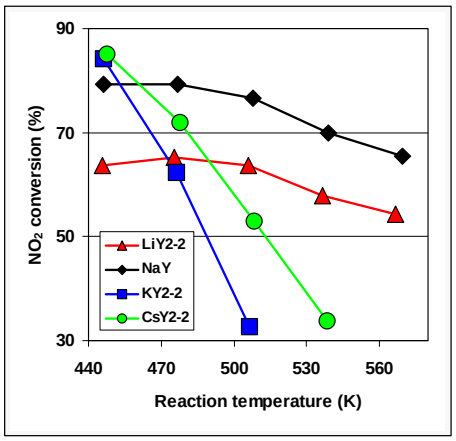

Figure 7: NO_2 conversion for Li-, Na-, K-, and Cs-Y zeolites in the 443-563K reaction temperature range.

It is possible to turn the fact that the *unconverted* NOx is released from the catalyst as NO (especially for the BaY catalysts) into an advantage. We have also noted that a significant fraction of the hydrocarbon survives both the plasma and the catalyst for a system of realistic size. These observations led to a proposal that a second application of plasma followed by a second catalyst bed can significantly improve the overall plasma-catalyst reactor performance [21]. Modeling and experiments have both demonstrated that a "cascade" system composed of two or more series plasma/catalyst regions results in improvements that include both an increase in the maximum NOx conversion obtained, as well as a reduction in the amount of plasma energy required to obtain high NOx conversion.

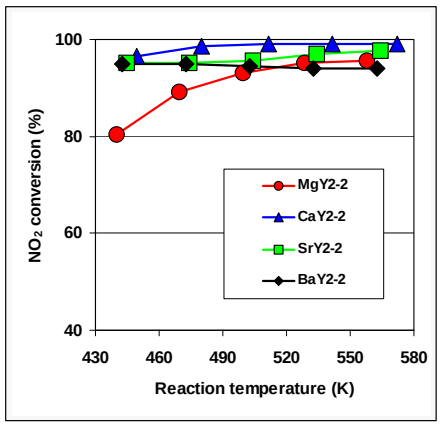

Figure 8: NO_2 conversion for Mg-, Ca-, Sr-, and Ba-Y zeolites in the 443-563K temperature range.

The NO_2 conversion results, shown in Figures 7 and 8, suggest that the interaction between NO_2 and the alkaline earth-exchanged Y zeolites is stronger than it is for the alkali-exchanged catalysts. Recent results from our laboratory [22] provide direct evidence for this. Figures 9 and 10 show the results of comparative temperature-programmed desorption (TPD) and fourier transform infrared (FTIR) spectroscopic studies of room-temperature NO_2 adsorption on NaY and BaY catalysts. The TPD data (Figure 9) show that adsorbed NO_2 desorbs from NaY at much lower temperatures than from BaY. In Figure 10, the top-most spectrum for both NaY and BaY were obtained at room temperature in a background of NO_2 gas. The subsequent spectra shown in this figure were obtained at increasing times after the NO_2 gas was evacuated from the reactor. A detailed discussion of the assignment of the FTIR peaks can be found elsewhere [22,23]. For our purposes here, it is sufficient to note that the spectra for BaY are hardly affected by NO_2 evacuation while the NaY spectra show significant decreases in peak intensities. Thus, both the TPD and FTIR data demonstrate the significantly stronger interaction between NO_2 and BaY relative to NaY.

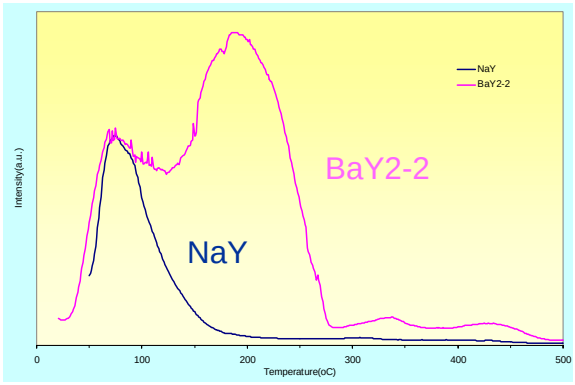

Figure 9: TPD spectra following room-temperature NO_2 adsorption on NaY and BaY.

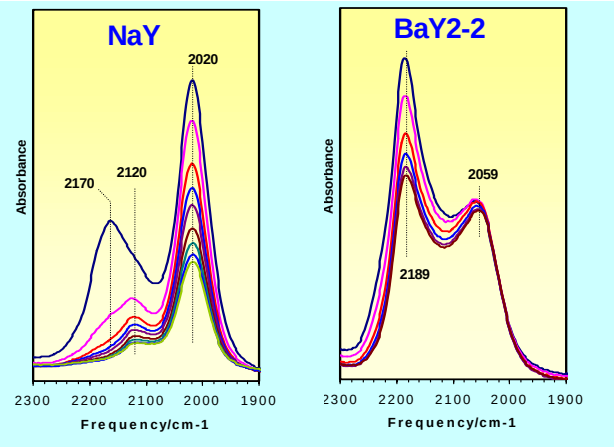

Figure 10: Evacuation at room temperature following NO_2 adsorption on NaY (left) and BaY (right).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the U.S. Department of Energy, Energy Efficiency and Renewable Energy, FreedomCAR and Vehicle Technologies (DOE/OFCVT) for financial support of this program. The work was performed as part of a CRADA with the USCAR Low Emissions Technologies Research and Development Partnership (LEP), Pacific Northwest National Laboratory (PNNL) and DOE/OFCVT. The research described in this paper was performed in the Environmental Molecular Sciences Laboratory (EMSL) at PNNL, at the Ford Scientific Research Laboratory, and at the GM Technical Center. The EMSL is a national scientific user facility and supported by the DOE's Office of Biological and Environmental Research. Pacific Northwest National Laboratory is a multi-program national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

REFERENCES

1. (a) T.V. Johnson, Proceedings of the DEER Workshop, 2003, in press; (b) T.V. Johnson, SAE 2003-01-0039, and references therein.
2. J. Kâspar, P. Fornasiero, and N. Hickey, Catal.Today, **77** (2003) 419.
3. See several recent SAE proceedings books: SP-1395, SP-1483, SP-1566, SP-1639.
4. J.W. Hoard, D.J. Brooks, S. J. Schmieg, C.H.F. Peden, S.E. Barlow, and R.G. Tonkyn, Proceedings of the DEER Workshop, 2003, in press.
5. A.G. Panov, R.G. Tonkyn, M.L. Balmer, C.H.F. Peden, A. Malkin, and J.W. Hoard, SAE 2001-01-3513, and references therein.
6. J. Hoard, P. Laing, M.L. Balmer, and R. Tonkyn, SAE 2000-01-2895.
7. R. Tonkyn, S. Yoon, S.E. Barlow, A. Panov, A. Kolwaite, and M.L. Balmer, SAE 2000-01-2896.
8. J.H. Kwak, J. Szanyi, and C.H.F. Peden, Catalysis Today, in press.
9. C.R. McLarnon, and B.M. Penetrante, SAE 982433.
10. B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin, M.C. Kung, H.H. Kung, C.Z. Wan, and K.E. Voss, SAE 982508.
11. R. Dorai and M.J. Kushner, SAE 1999-01-3683.
12. S.E. Thomas, J.T. Shawcross, R. Gillespie, D. Raybone, and A.R. Martin, SAE 2001-01-3568.
13. K.G. Rappé, J.W. Hoard, C.L. Aardahl, P.W. Park, C.H.F. Peden, D.N. Tran, Catalysis Today, in press.
14. S.J. Schmieg, B.K. Cho, and S.H. Oh, SAE 2001-01-3565.
15. M.L. Balmer, R.G. Tonkyn, S. Yoon, A.C. Kolwaite, S.E. Barlow, G. Maupin, and J.W. Hoard, SAE 1999-01-3640.
16. M.L. Balmer, A.Y. Kim, R.G. Tonkyn, S.E. Barlow, and T.M. Orlando, U.S. Patent Pending (filed October 1, 1998).
17. P.W. Park, J.E. Rockwood, C.L. Boyer, C.S. Ragle, M.L. Balmer-Millar, C.L. Aardahl, C.F. Hageger, K.G. Rappé, and D.N. Tran, SAE 2001-01-3569.
18. J.H. Kwak, J. Szanyi, and C.H.F. Peden, Journal of Catalysis, in press.
19. A.C. Ebeling, A.G. Panov, D. E. McCready, and M.L. Balmer, SAE 2001-01-3571.
20. P. Norby, F.I. Poshni, A.F. Gualtieri, J.C. Hanson, and C.P. Grey, Journal of Physical Chemistry B **102** (1998) 839-856.
21. (a) R.G. Tonkyn and S.E. Barlow, SAE 2001-01-3510; (b) S.E. Barlow, R.G. Tonkyn, J.W. Hoard, and W.C. Follmer, SAE 2001-01-3509; (c) R.G. Tonkyn, S.E. Barlow, and J.W. Hoard, Applied Catalysis B **40** (2003) 207.
22. J. Szanyi, J.H. Kwak, and C.H.F. Peden, in preparation.
23. J. Szanyi, J.H. Kwak, R.A. Moline, and C.H.F. Peden, Physical Chemistry Chemical Physics **5** (2003) 4045.