Catalysis Letters Vol. 109, Nos. 1–2, June 2006 (© 2006)
DOI: 10.1007/s10562-006-0049-3

Non-thermal plasma-assisted NO_x reduction over Na-Y zeolites: *the promotional effect of acid sites*

Ja Hun Kwak, Charles H. F. Peden, and Janos Szanyi*

Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352, USA

Received 29 January 2006; accepted 15 March 2006

The effect of acid sites on the catalytic activities of a series of H^+-modified Na-Y zeolites was investigated in the non-thermal plasma assisted NO_x reduction reaction using a simulated diesel engine exhaust gas mixture. The acid sites were formed by NH_4^+ ion exchange and subsequent heat treatment of a NaY zeolite. The catalytic activities of these H^+-modified NaY zeolites significantly increased with the number of acid sites. This NO_x conversion increase was correlated with the decrease in the amount of unreacted NO_2. The increase in the number of acid sites did not change the NO level, it stayed constant. Temperature programmed desorption following NO_2 adsorption showed the appearance of a high temperature desorption peak at 453 K in addition to the main desorption feature of 343 K observed for the base Na-Y. The results of both the IR and TPD experiments revealed the formation of crotonaldehyde, resulting from condensation reaction of adsorbed acetaldehyde. Strong adsorptions of both NOx and hydrocarbon species are proposed to be responsible for the higher catalytic activity of H^+-modified Na-Y zeolites in comparison to the base NaY material

KEY WORDS: non-thermal plasma-assisted catalytic NO_x reduction; ammonium ion exchange; Na-Y zeolites; FTIR; TPD.

1. Introduction

Increasing fuel efficiency of internal combustion engines and controlling vehicle exhaust emissions are the two major concerns in automotive engine development today. A possible way to enhance fuel efficiency is to operate engines under lean conditions. Currently the only engines that operate under true lean conditions all the time are the diesel engines. Lean engine operation, however, makes NO_x removal from oxygen containing exhaust gas mixtures a very challenging task. Traditional three-way catalysts containing precious metals are unable to remove NO_x under lean conditions.

Alkali- and alkaline-earth-exchanged Y zeolites have shown promising catalytic activities for the removal of NO_x from simulated diesel exhausts when a non-thermal plasma was applied in front of the catalyst bed [1,2]. In the absence of the non-thermal plasma, these materials show no catalytic activity toward the reduction of NO_x. The effect of the plasma on the exhaust gas mixture has been investigated previously [3]. The two most important reactions in the plasma are the complete oxidation of NO to NO_2 and the partial oxidation of hydrocarbons. Over the catalyst bed, NO_2 formed in the plasma undergoes selective catalytic reduction by the partially oxidized hydrocarbons, especially aldehydes. Depending on the catalyst and reaction conditions, the final N-containing compounds are N_2, NO, and N_2O. Recently, we reported the effect of the ion exchange method on the NOx reduction activity of a BaY catalyst [4]. We have shown that Ba-Y catalysts could chemisorb much larger amounts of NO_2 than Na-Y, and that ion exchanged Ba^{2+} held NO_2 stronger than Na^+. These differences in the amount and strength of NO_2 adsorption were proposed to be responsible for the greatly different catalytic activities observed for these two zeolite-based catalysts.

In the present study we investigated the effect of acid sites on the catalytic properties of Na-Y in the plasma assisted NO_x reduction process. NO_2 adsorption, FT-IR and TPD experiments were conducted in order to correlate the observed catalytic activities with the level of H^+ exchange in the Na-Y zeolites.

2. Experimental

The H^+-modified Na-Y catalysts used in this study were prepared from a commercially available NaY zeolite (Si/Al $\sim$ 2.6), obtained from Zeolyst International Co. (CBV-100), by aqueous ion exchange of NH_4^+ and subsequent heat treatment. The NaY extrudates were ion exchanged with an aqueous solution of ammonium nitrate. The ion exchanges were carried out at room temperature for 48 h with solutions of different NH_4^+ concentrations. Following the solution ion exchange, the samples were thoroughly washed with distilled water and then dried at 393 K in air. Prior to each catalytic activity test, the sample was calcined at 673 K for 2 h in air. For the adsorption and TPD

---

*To whom correspondence should be addressed.
E-mail: janos.szanyi@pnl.gov

experiments, the same NH_4^+-loaded Na-Y catalysts (binder-free) were prepared by following the exactly same procedures that we used for the Na-Y extrudates containing the alumina binder.

The catalytic activity measurements were carried out in a two-stage non-thermal plasma/catalytic reactor system described in detail elsewhere [5]. The detailed experimental procedures and conditions are exactly the same as we have discussed in our previous publications [4,6]. We used a simulated diesel exhaust gas mixture of 8% O_2, 2% H_2O, 245 ppm NO, and 520 ppm C_3H_6 in N_2 balance to estimate the NO_x reduction activities of the above described catalysts. Water was introduced into the gas mixture by bubbling the O_2/N_2 mixture through a water bubbler kept at 293 K. The total flow rate was kept at 2.1 L min^{-1}. which corresponds to a space velocity of 12000 h^{-1} in the catalytic reactor. About 10 mL of catalyst was placed in the bottom of the quartz reactor, and the remaining empty volume was filled with glass beads to ensure good heat transfer. In a typical catalytic experiment the reactor was first heated to 443 K in a N_2 flow, and then the simulated exhaust gas mixture was fed into the reactor for about 1 h. After the NO_x levels stabilized, the plasma was turned on at a power level of 10 J L^{-1} (0.35 W). The NO and total NO_x concentrations were measured by a chemiluminiscent NO_x analyzer (Rosemount, Model 955), and the unreacted NO_2 concentration was calculated as the difference between the measured total NO_x and the NO concentrations.

NO_2 TPD experiments were carried out on a RXM-100 catalyst characterization instrument (ASDI). The detailed experimental procedures were described in our previous reports [7]. Briefly, a catalyst sample of ~0.02 g was placed into a quartz container and attached to the instrument. Following room temperature evacuation, the sample was annealed at 673 K for 2 h and then cooled to the adsorption temperature of 293 K. The NO_2 gas used in these TPD experiments was cleaned by a series of freeze/pump/thaw cycles.

Acetaldehyde adsorption and TPD experiments were carried out in a combined *in situ* FT-IR/TPD set-up described in detail elsewhere [7,8]. In short, ~20–50 mg of catalyst sample was pressed onto a fine tungsten mesh and attached to a copper sample holder assembly that, in turn, was connected to a sample holder rod via ceramic feedthroughs. The sample mounted in this way could be heated resistively up to ~1000 K. The sample temperature was monitored by a thermocouple (type K) spot welded onto the top center part of the tungsten grid. The IR cell was a 23/4” stainless steel six-way cube equipped with KBr windows, and connected to both a gas handling manifold system, and a mass spectrometer chamber. This set up allows for the precise control of the amount of gas introduced into the IR cell, and also gas spectrometric analysis of gases evolved during temperature programmed desorption. The IR spectrometer used throughout this study was a Mattson Research Series instrument, equipped with an MCT detector and operated at 4 cm^{-1} resolution. Each spectrum was referenced to a background spectrum recorded with the clean, activated sample, and was the average of 256 scans.

3. Results and discussion

The NO_x conversion as a function of reactor temperature is shown for Na-Y and H^+-modified Na-Y in figure 1(a). The parent Na-Y exhibits fairly high catalytic activity in the entire temperature range studied (430 ~ 560 K). The maximum NO_x conversion of the

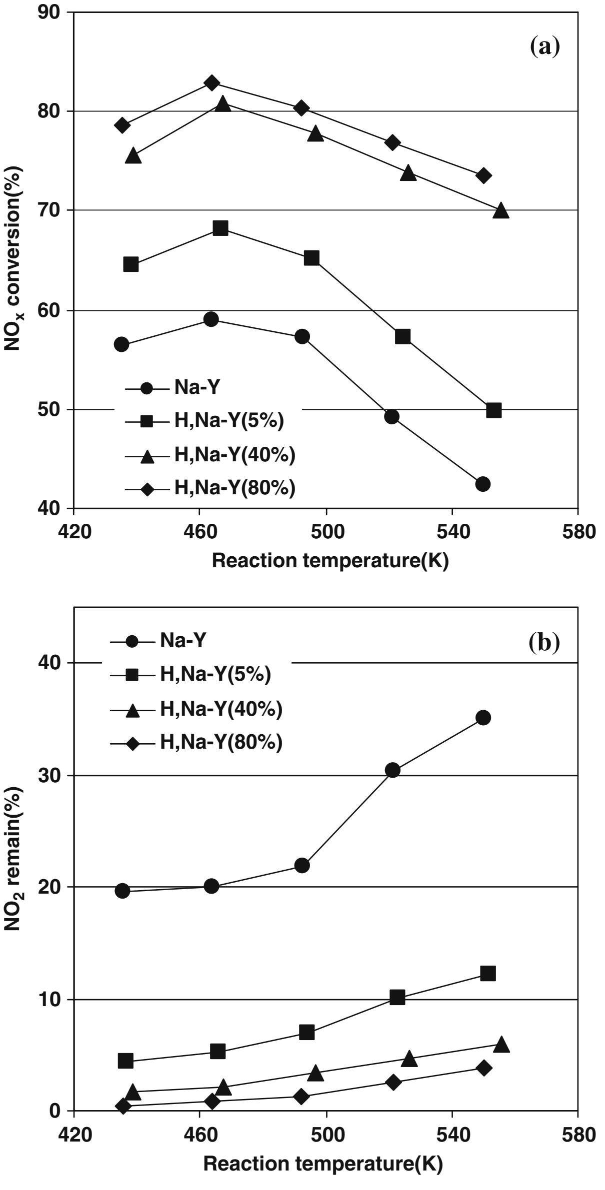

Figure 1. The effect of ion exchange level in H,Na-Y on the NO_x conversion activity ((a) total NO_x conversion, (b) unreacted NO_2). [Percentages in all the figures refer to the concentration of NH_4^+ ions in the aqueous solution used for the ion exchange; e.g. in the 40% solution the number of NH_4^+ ions equals 40% of the Na^+ ions in the parent Na,Y zeolite].

base NaY catalyst is 59% and it is measured at a reaction temperature of 473 K. With increasing temperature above 473 K the activity of Na-Y decreases gradually, and it drops below 40% at 563 K. Substitution of a fraction of the Na^+ ions in the Na-Y catalyst by H^+ brings about a large increase in NO_x reduction activity. Carrying out the ion exchange with a solution contained only 5% of the NH_4^+ ions necessary to obtain 100% ion exchange level resulted in an ~10% increase in NO_x conversion in comparison with the parent Na-Y catalyst. Maximum activity of ~68% was observed at 473 K, while the activity profile as a function of catalyst temperature was very similar to that of Na-Y. The activity profiles with reaction temperature were practically the same for all H,Na-Y samples. Increasing the concentration of NH_4^+ ions in the ion-exchange solution resulted in a continuing increase in the NO_x conversion level. However, above 40% NH_4^+ concentration in the ion-exchange solution, the activity increased only marginally. [The amount of remaining Na^+ in these H,Na-Y catalysts, needed for the unambiguous quantification of the H^+ ion exchange level (in particular when NH_4^+ solutions with concentration of $<40\%$ were used), could not be determined with the required accuracy using ICP analysis due to the small differences in ion exchange levels.]

Figure 1(b) reveals that this increased NO_x conversion is correlated with the higher conversion of NO_2 on H,Na-Y compared to NaY. The amount of unreacted NO_2 was ~20% for Na-Y zeolites at ~473 K, and it increased significantly with reaction temperature. This decrease of catalytic activity corresponds with the decrease in NO_x conversion. But, even the introduction of a small amount of acid sites (5% NH_4^+ solution ion-exchanged sample) results in a significant decrease in the level of unreacted NO_2 at all temperatures. Furthermore, the amount of unreacted NO_2 decreases for samples prepared with increasing concentration of NH_4^+ in the ion exchange solution. The profiles of unreacted NO_2 are opposite to those of NO_x conversion. For comparison, we plot the NO_x conversion, NO_2, and NO yields at the exit of the catalytic reactor at 473 K as a function of NH_4^+ concentrations in the ion exchange solution in figure 2. The strong correlation between NO_x conversion and the level of unreacted NO_2 is evident. In contrast, during this significant increase in NO_x conversion, the NO level exiting the reactor was practically constant. In our previous report [6], we have shown that there was a noticeable difference in the product distribution (selectivity) for alkali and alkaline-earth series of Y,FAU catalysts in the reaction of our interest. Most significant difference between these two series of catalysts is the high NO_2 conversions for alkaline-earth ion exchanged catalysts. We attributed this to the stronger interaction of NO_2 with alkaline earth exchanged catalysts in comparison to alkali exchanged ones. These results are consistent with those observed on the NH_4^+ exchanged catalysts. Specifically, NO_2 on H,Na-Y (as we will discuss it the following sections) shows stronger adsorption than on Na-Y, similarly to alkaline-earth exchanged catalysts. The constant level of NO observed over all the NH_4^+-exchanged catalysts is the consequence of the thermal decomposition of NO_2 in the gas phase, regardless of the nature of the catalyst present.

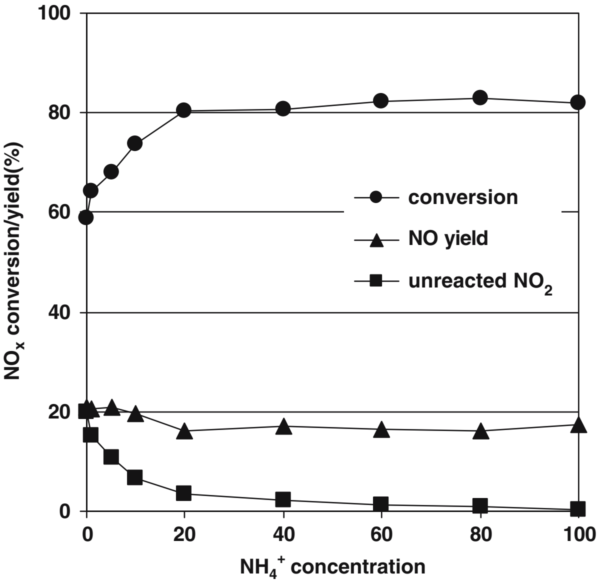

Figure 2. NO_x conversion and NO_2 evolution as a function of H^+ ion exchange level. Activities are compared at a reaction temperature of 473 K.

Figure 3 compares the FT-IR spectra of NO_2 adsorbed on Na-Y and H,Na-Y (prepared using the 40% NH_4^+ solution). NO_2 on NaY shows absorption

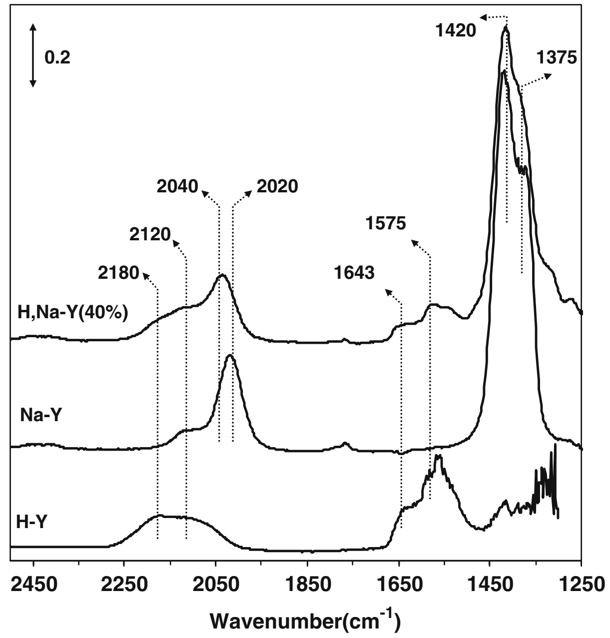

Figure 3. FTIR spectra of NO_2 on Na-Y, H-Y and H,Na-Y (40%) (spectra recorded at 300 K).

bands at 1350 ~ 1450 and 2000 ~ 2200 cm^{-1} regions. Previously we have studied the adsorption of NO_2 on Na-Y in detail [9], and we assigned the features in the 1350 ~ 1450 cm^{-1} region to the split ν_3 vibrations of adsorbed NO_3^- and the 2020 cm^{-1} band to the N–O stretching vibration of adsorbed NO^+ species. In the case of H,Na-Y, new IR features developed at 1550 ~ 1700 cm^{-1} and interestingly, the N–O stretching vibration of NO^+ shifted to 2040 cm^{-1}. We assign these new IR bands in the 1550–1700 cm^{-1} range to nitrate species adsorbed on the acid sites in H,Na-Y. For comparison we also display a spectrum in figure 3 that was obtained after NO_2 adsorption on H-Y faujasite zeolite (Si/Al ~ 2.6, CBV-600 obtained from Zeolyst International Co.) at 300 K. This spectrum clearly shows that the main nitrate features on this material are located at 1575 and 1643 cm^{-1}, and small features, representing nitrate species bound to residual Na^+ ions are seen in the 1350–1450 cm^{-1} spectral region. The position of the IR feature representing adsorbed NO^+ ions is at 2120 cm^{-1}, some 100 cm^{-1} higher than that observed for the NO^+ ions in Na-Y. At higher NO_2 dosages the IR band representing NO^+NO_2 adduct is developing at 2183 cm^{-1}, very similar to the shoulder at high wavenumbers seen on H,Na-Y. The blue shift of the N–O stretching vibration of adsorbed NO^+ suggests a stronger interaction of NO_2 with H-Y than with Na-Y. This is also supported by our findings on Ba-Y [7] in which these vibrations are seen at 2050 cm^{-1} (NO^+) and 2180 cm^{-1} (NO^+NO_2), and the NO_2 was shown to adsorb significantly stronger than on Na-Y.

Figure 4 displays TPD profiles obtained after NO_2 adsorption on Na-Y and H^+-modified Na-Y catalysts, synthesized with the 40% NH_4^+ solution. Na-Y shows a single desorption peak at ~343 K and it is consistent with our previous report [7]. However, in the TPD spectrum of NO_2-saturated H^+-modified Na-Y an additional feature is seen at ~453 K. This high temperature desorption peak is about 70 K lower than that we have reported for Na-Y after coadsorption of NO_2 and H_2O. The appearance of the high temperature desorption feature following the coadsorption of H_2O and NO_2 on NaY was attributed to the strong interaction of NO_2 and H_2O in the zeolite cavities that led to the formation of HNO_x species [7]. Previously, we have reported desorption peaks for the NO_2-saturated Ba-Y zeolite at 353 and 453 K [7], and attributed the high temperature desorption feature to the strong interaction of NO_2 with Ba^{2+} ion. We also proposed that the stronger adsorption of NO_2 on Ba-Y in comparison to Na-Y was the main reason for the higher catalytic activity of the former catalyst in the non-thermal plasma-assisted catalytic NO_x reduction. H^+ modified Na-Y shows similar desorption characteristics as the Ba-Y samples. The results of both the IR and TPD experiments suggest that the substitution of a small fraction of the Na^+ ions by protons brings about a significant stabilization of the adsorbed NO_2 molecules. This increased strength of NO_2 adsorption, in turn, is probably a contributing factor to the significantly enhanced catalytic activities of these H^+-modified Na-Y zeolites.

Figure 5 shows FT-IR spectra in the 1300 ~ 1900 cm^{-1} range obtained after acetaldehyde adsorption on Na-Y and H,Na-Y (prepared with the 40% NH_4^+ solution). As shown in figure 5(a), acetaldehyde adsorbed on Na-Y displays the characteristic C = O stretching vibration at 1726 cm^{-1} and the deformation vibrations of the alkyl group in the 1350–1450 cm^{-1} spectral region [8]. Under the experimental conditions applied, no evidence for the formation of any condensations

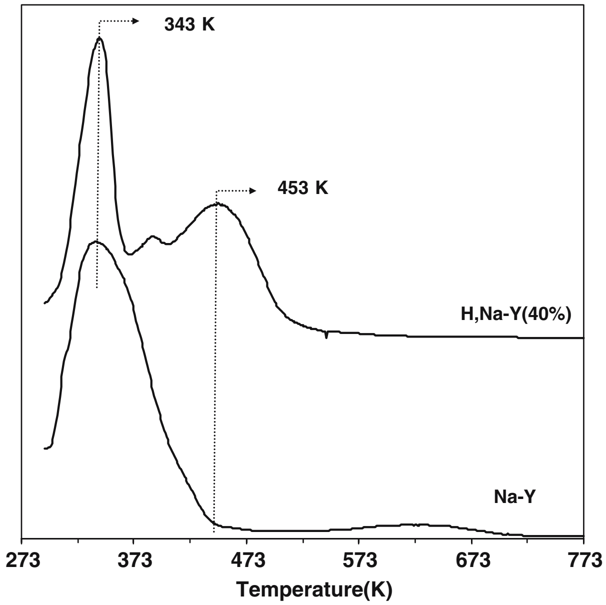

Figure 4. TPD profiles of NO_2 on Na-Y and H,Na-Y (40%).

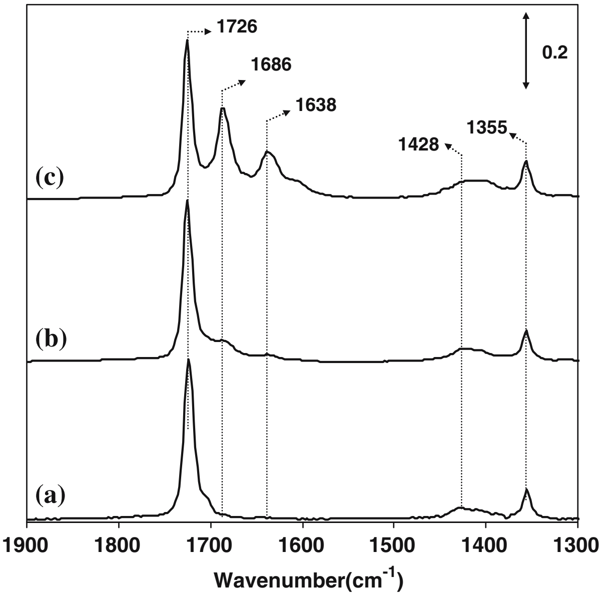

Figure 5. FTIR spectra of CH_3CHO adsorption on (a) Na-Y, (b) H,Na-Y (40%) after 2 min, (c) H,Na-Y (40%) after 60 min at 300 K.

products (in particular crotonaldehyde) was seen. This observation is in agreement with our previously published results [8] where we showed no condensation on Na-Y at 300 K at acetaldehyde partial pressures relevant to the catalytic process of interest. However, at high acetaldehyde partial pressures as well as at elevated temperatures (473 K), formation of crotonaldehyde was observed although to a very limited extent. Spectra (b) and (c) of figure 5 were obtained after adsorption of acetaldehyde on H,Na-Y for 2 and 60 min. New absorption bands appeared at 1686 and 1638 cm^{-1} and significantly increased with time-on-stream. In their IR study, Yeom *et al.* [10] reported the formation of crotonaldehyde on Ba-Y zeolites after adsorption of acetaldehyde. They assigned the 1662 cm^{-1} vibrational feature to the C=O stretching vibration of crotonaldehyde interacting with Ba^{2+} ions, and the 1638 cm^{-1} band to the C=C stretching mode of adsorbed crotonaldehyde. These results support our assignment of the observed two new IR bands at 1686 and 1638 cm^{-1} to crotonaldehyde formed by the condensation reaction of adsorbed acetaldehyde on H,Na-Y. The 1638 cm^{-1} band in figure 5(c), representing the C=C vibration, is at exactly the same position as was observed for adsorbed crotonaldehyde over Ba-Y by Yeom *et al.* [10], while the C=O stretching vibration of crotonaldehyde is seen at 1686 cm^{-1} on H,Na-Y instead of the 1662 cm^{-1} observed on Ba-Y. This 24 cm^{-1} shift in the C=O stretching vibration reflects the change in the adsorption center from Ba^{2+} to H^+. The IR spectrum of acetaldehyde adsorbed on H-Y zeolite at 300 K shows very similar behavior to H,Na-Y (spectrum is not shown). These results clearly show that acid-catalyzed condensation of acetaldehyde to crotonaldehyde is facile on H,Na-Y.

In figure 6, TPD profiles obtained after acetaldehyde adsorption on Na-Y and H,Na-Y (prepared with the 40% NH_4^+ solution) are compared. Acetaldehyde on Na-Y shows only one, symmetric desorption feature centered at ~400 K for both 15 (CH_3) and 28 amu (CO) cracking fragments of acetaldehyde. Previously we reported that acetaldehyde adsorbed molecularly on Na-Y and no evidence for the formation of crotonaldehyde or other condensed products was seen [8]. The desorption profile of the 15 amu fragment following acetaldehyde adsorption on H,Na-Y at 300 K is also symmetric, and is centered at the same desorption temperature as that on Na-Y. However, the 28 amu profile shows a broad, asymmetric feature extending above 500 K. Furthermore, a new desorption feature of 41 amu (that is completely absent in the TPD profile obtained from Na-Y after CH_3CHO adsorption) is also seen, and its position overlaps with the high temperature tail of the 28 amu trace. These results indicate that the crotonaldehyde formed in the condensation reaction of acetaldehyde desorbs molecularly from the H,Na-Y zeolite and produces the cracking fragments of CH_3–CH=CH (41 amu) and CO (28 amu) in the ionization chamber of the mass spectrometer. These findings are in complete agreement with the results of the IR study on the adsorption of acetaldehyde on H,Na-Y, discussed in the previous paragraph.

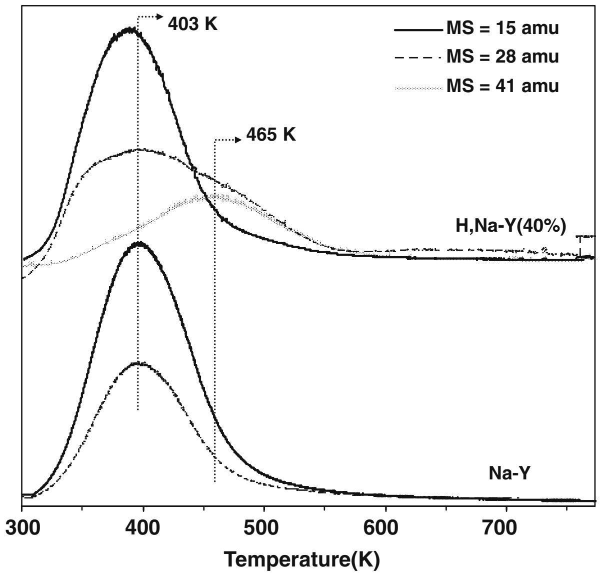

Figure 6. TPD profiles after CH_3CHO adsorption on Na-Y (MS = 15 and 28) and H,Na-Y (40%) (MS = 15, 28 and 41) at 300 K.

These TPD results also show that crotonaldehyde adsorbs stronger to the H,Na-Y zeolite than acetaldehyde does (465 K versus 403 K). We suggest that the formation of crotonaldehyde actually contributes to the observed improvements in NO_x reduction activity of the H,Na-Y catalysts relative to that of Na-Y. We propose that the enhancement in catalytic activity of the H,Na-Y catalysts arises from the increased stabilities of *both* the adsorbed NO_x species *and* the reductant, crotonaldehyde in this particular system. We have to emphasize here, however, that these significant enhancements in NO_x reduction activity are only observed when the H^+ ion exchange level is limited. When highly proton exchanged Y zeolite was tested under true catalytic conditions, deactivation due to extensive condensation of acetaldehyde followed by polymerization and eventual coke formation was observed. Therefore, the delicate balance between the proton exchange level and the extent of the condensation reaction needs to be established in order to develop highly active Na-Y-based catalysts for the non-thermal plasma-assisted NO_x reduction process. At high proton exchange levels, the additional problem of structural instability under practical operation conditions (elevated temperatures and high water concentrations) may arise as well.

4. Conclusion

Significant enhancement in the non-thermal plasma-assisted catalytic NO_x reduction activity of Na-Y zeolites was achieved by the introduction of a limited number of protonic acid sites. Over 20% improvement in NO_x conversion was observed when a Na-Y sample was ion exchanged with an aqueous solution containing NH_4^+ ions in a quantity equal to 40% of the Na^+ ions in the Y zeolite. The results of our FTIR and TPD investigations reveal that both the NO_x and the aldehyde adsorption (in this case crotonaldehyde formed by the condensation of acetaldehyde) are strengthened by the introduction of Brönsted acidic sites into the Na-Y catalyst. The increased stabilities of *both* the reductant *and* the NO_x result in higher concentrations of reactants at the actual reaction temperature, thereby resulting in higher rates of NO_x reduction over H,Na-Y than in Na,Y.

Acknowledgments

The authors gratefully acknowledge the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Freedom CAR and Vehicle Technologies for support of this program. The research described in this paper was performed at the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research and located at PNNL. The Pacific Northwest National Laboratory is operated for the U.S. DOE by Battelle Memorial Institute under Contract No. DE-AC067RLO1831

References

[1] J. Hoard and A. Panov, SAE 2001-01-3512.
[2] R.G. Tonkyn, S. Yoon, S.E. Barlow, A. Panov, A. Kolwaite and M.L. Barmer, SAE 2000-1-2869.
[3] B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitx, G.E. Vogtlin, M.C. Kung, H.H. Kung, C.Z. Wan and K.E. Voss (1998), SAE 982508.
[4] J.H. Kwak, J. Szanyi and C.H.F. Peden, J. Catal. 220 (2003) 291.
[5] S. Yoon, A.G. panov, R.G. Tonkyn, A.C. Ebeling, S.E. Barlow and M.L. Barmer, Catal. Today 72 (2002) 243.
[6] J.H. Kwak, J. Szanyi and C.H.F. Peden, Catal. Today 89 (2004) 135.
[7] J. Szanyi, J.H. Kwak and C.H.F. Peden, J. Phys. Chem. B 108 (2004) 3746.
[8] J. Szanyi, J.H. Kwak, R.A. Moline and C.H.F. Peden, J. Phys. Chem. B 108 (2004) 17050.
[9] J. Szanyi, J.H. Kwak, R.A. Moline and C.H.F. Peden, PCCP 5 (2003) 4045.
[10] Y.H. Yeom, B. Wen, W.M.H. Sachtler and E. Weitz, J. Phys. Chem. B 108 (2004) 5386.