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Journal of Catalysis 220 (2003) 291–298
JOURNAL OF CATALYSIS
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Nonthermal plasma-assisted catalytic NO_x reduction over Ba-Y,FAU: the effect of catalyst preparation

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Received 4 February 2003; revised 23 July 2003; accepted 6 August 2003

Abstract

The effects of catalyst preparation on the NO_x reduction activity of a series of Ba-Y,FAU zeolites were investigated using a simulated exhaust gas mixture. The introduction of Ba^{2+} ions into Na-Y,FAU results in a large increase in their nonthermal plasma-assisted NO_x reduction activity. The NO_x reduction activities of Ba-Y,FAU catalysts were found to increase with increasing Ba^{2+} concentration in the aqueous ion-exchange solutions, which translated into increased Ba^{2+}/Na^+ ratios in the resulting materials. Consecutive ion-exchange procedures at a given Ba^{2+} concentration in the aqueous solution, however, did not improve the NO_x reduction activities of Ba-Y,FAU catalysts; i.e., the activity of the four times ion-exchanged material was the same as that of the one that was ion-exchanged only once. The reaction profiles for all of these Ba-Y,FAU catalysts were the same. In contrast, a significant increase in NO_x reduction activity was observed when a 773 K calcination step was implemented after each solution ion exchange. The reaction profile was also altered as a result of the ion-exchange/calcination cycles. Calcination that followed each ion-exchange step seems to further increase the Ba^{2+}/Na^+ ratio in the zeolite, and in turn increases the NO_x reduction activities of the catalysts prepared this way. Key differences in Na- and Ba-Y,FAU catalysts were found in NO_2 adsorption and TPD experiments. The amount of chemisorbed NO_2 is about twice as high in Ba-Y,FAU than in Na-Y,FAU, and Ba-Y,FAU holds NO_x much stronger than Na-Y,FAU.

Keywords: Plasma-assisted NO_x reduction; Na-Y; Ba-Y; Ion-exchange; Calcination; Cation redistribution; NO_2 adsorption

1. Introduction

Improving the fuel economy of internal combustion engines is the driving force behind changes in engine operation conditions. Improved engine performance can be achieved under lean operation, i.e., in the presence of excess oxygen. Currently the only engines that operate under true lean conditions all the time are the diesel engines. Lean engine operation, however, makes the NO_x removal from an oxygen-containing exhaust gas mixture a very challenging task. Traditional three-way catalysts containing precious metals are unable to remove NO_x under lean conditions. Zeolite-based, primarily transition metal ion-exchanged, catalysts have been extensively studied in the last two decades for the selective catalytic reduction of NO_x [1]. Insufficient activities, narrow operating windows, and the sensitivity of these materials to H_2O and sulfur poisoning have hindered their practical application.

Alkali and alkaline earth ion-exchanged Y,FAU (Y) zeolites have shown promising catalytic activities for the removal of NO_x from simulated diesel exhausts, when a nonthermal plasma was applied in front of the catalyst bed [2,3]. In the absence of the nonthermal plasma these materials show no catalytic activity toward the decomposition of NO_x. The effect of the plasma on the exhaust gas mixture has been investigated previously [4]. The two most important reactions in the plasma are the oxidation of NO to NO_2 and the partial oxidation of hydrocarbons. Over the catalyst bed the NO_2 formed in the plasma undergoes selective catalytic reduction (SCR) by the partially oxidized hydrocarbons. Depending on the catalyst used and reaction conditions the final N-containing compounds are N_2, NO, and N_2O. HCN has also been shown to form in the plasma-assisted NO_x reduction process, but it can be easily removed by a Pt/Al_2O_3 catalysts applied after the NO_x reduction step [3].

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0021-9517/$ – see front matter Published by Elsevier Inc.
doi:10.1016/j.jcat.2003.08.007

The effect of the ion-exchange method on the NO_x reduction activity of a Ba-Y catalyst has been reported previously [5]. The activity of a Ba-Y catalyst prepared by aqueous solution ion exchange was higher than the one that was solid-state ion-exchanged with a chloride salt. The different activities of these two catalysts were explained by the differences in their acidities. The solution ion-exchanged Ba-Y was shown to have higher acidity, making it a better catalyst for hydrocarbon activation. However, this catalyst was prone to deactivation as a result of coke formation on the acidic sites, while no deactivation was observed on the solid-state ion-exchanged Ba-Y.

In our present study we investigated the effect of ion-exchange on the catalytic properties of Ba-Y in the plasma-assisted NO_x reduction process. The effects of Ba^{2+} content in the ion-exchange aqueous solution, the number of consecutive ion exchanges, and calcination following each ion-exchange step were investigated. NO_2 adsorption and TPD experiments were also conducted in order to correlate the observed catalytic activities with the NO_2 adsorption properties of the catalysts studied.

2. Experimental

The catalysts were prepared from a Na-Y zeolite with a Si/Al 2.6 and obtained from Zeolyst International Co. (CBV 100 CY 1.6) as extrudates with an alumina binder. The binder content in the parent zeolite was approximately 10%. All of the Ba-Y catalysts used in this study were prepared by an aqueous ion-exchange method using $Ba(CH_3COO)_2$ solutions. The solution that contained Ba^{2+} ions in a quantity sufficient to achieve a 100% ion-exchange level was denoted as 100% solution. For the study of the effect of Ba^{2+} level on the catalytic activity, the ion-exchange level was controlled by the concentration of Ba^{2+} ions in the ion-exchange solution. Following the solution ion exchange the samples were thoroughly washed with distilled water and then dried at 393 K in air. Prior to the catalytic measurements the samples were calcined at 773 K for 4 h in air. The exact Ba^{2+} ion-exchange levels were determined from elemental analysis using ICP analysis, and are shown in Table 1 for this series of catalysts.

Table 1
Ba^{2+} and Na^+ concentrations in Ba–Na-Y,FAU catalysts prepared from solutions containing Ba^{2+} ions in different concentrations (based on elemental analysis by ICP)

Catalyst	Number of ions per unit cell[a]	
	Na^+	Ba^{2+}
Na-Y	54.0	0.0
Ba-Y(20%)	40.6	6.7
Ba-Y(40%)	30.0	12.0
Ba-Y(60%)	22.3	15.9
Ba-Y(80%)	20.7	16.7
Ba-Y(2-1)	12.9	20.6

[a] Based on ICP analysis.

For the comparison of the ion-exchange methods two series (each consisting of four catalysts) of Ba-Y catalysts were prepared. These Ba-Y catalysts were prepared by carrying out the solution ion exchange with a Ba-acetate solution containing twice the amount of Ba^{2+} needed for complete ion exchange. For the first series of catalysts the parent Na-Y zeolite was ion-exchanged once, twice, three, and four times. Between consecutive ion exchanges the catalysts were washed and dried but not calcined. Calcination at 773 K for 4 h was carried out only after the final ion exchange. These samples are marked as Ba-Y(x-1), where x ($1 \leqslant x \leqslant 4$) refers to the number of ion exchanges, and 1 the calcination after the last ion exchange. In the second series of four samples, the catalysts were prepared by consecutive ion exchanges, but following each ion exchange the catalysts were calcined at 773 K for 4 h. The designation of these samples is Ba-Y(x-y) where x represents the number of ion exchanges and y the number of calcinations. In this series x always equals y. Catalysts that we used in the NO_2 adsorption and TPD experiments were prepared from a powder Na-Y (CBV 100) parent zeolite that contained no binder. For the preparation of these catalysts we followed exactly the same protocol we applied for the preparation of catalysts that were used in the reaction studies.

The catalytic activity measurements were carried out in a two-stage nonthermal plasma/catalytic reactor system described in detail elsewhere [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, which corresponds to a space velocity of 12,000 h^{-1} in the catalytic reactor. Ten milliliters of catalysts was placed to 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 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 (0.35 W). The protocol of the measurement and adjustment of the plasma power were performed according to Tonkyn et al. [2]. The NO and total NO_x concentrations were measured by a chemiluminescent NO_x analyzer (Rosemount, Model 955). The reactor temperature was increased from 443 K to 563 K in 30 K increments. The reaction was run at each temperature until steady state (or near steady state) was reached. The NO and NO_x ($NO + NO_2$) concentrations were continuously recorded throughout the duration of the catalytic experiments, and were used for the calculations of NO_x conversion and unreacted NO_2 concentration at steady state. (NO_x conversion (%) $= \{[NO + NO_2](out)/[NO](in)\} \times 100$ and unreacted NO_2 (%) $= \{[NO_2(out)/[NO](in)\} \times 100$; NO in the plasma reactor was almost completely converted to NO_2; therefore in the calculation of percentage of unreacted NO_2 [NO](into the plasma reactor) = [NO_2](into the catalytic reactor) was assumed.)

The NO_2 adsorption and TPD experiments were carried out on an RXM-100 catalyst characterization instrument (ASDI). A catalyst sample of ~0.02 g was placed into a quartz container and attached to the instrument. Following the room temperature evacuation, the sample was annealed at 773 K for 2 h and then cooled to the temperature of the adsorption, 293 K. The NO_2 gas used in these adsorption/TPD experiments was cleaned by multiple freeze/pump/thaw cycles. After the total amount of NO_2 adsorbed was measured, the sample was evacuated at 293 K for 3 h, and the amount of weakly adsorbed NO_2 was measured in a second adsorption experiment. The amount of strongly adsorbed (chemisorbed) NO_2 was estimated as the difference between the amount of total and weakly adsorbed NO_2. Following the second NO_2 adsorption experiment the sample was evacuated at 293 K and then annealed at 773 K for 2 h. The clean sample was saturated with NO_2 at 293 K (~50 Torr NO_2 for 1 h) and evacuated for 3 h and then a TPD experiment was carried out with a heating rate of 5 K/min from 293 to 773 K.

3. Results and discussion

The effect of the concentration of Ba^{2+} ions in the ion-exchange solution on the catalytic activity is shown in Fig. 1A (catalytic activities of all the materials examined in this study were negligible without the application of the plasma reactor, and are not shown in the figures). The parent Na-Y exhibits fairly high catalytic activity in the entire temperature range of 433–563 K studied. The maximum NO_x conversion of 59% was observed at ~473 K on this material. Above 493 K the catalytic activity gradually dropped with catalyst temperature and reached 39% at 563 K. Carrying out the ion exchange in a solution that contained only 20% Ba^{2+} ions necessary to obtain 100% ion-exchange level resulted in an increase in NO_x conversion in comparison to the parent Na-Y catalyst. The activity trend as a function of catalyst temperature was very similar to that of Na-Y, and in fact it was practically the same for all Ba-Y materials. Increasing the concentration of Ba^{2+} ions in the ion-exchange solution resulted in increases in the NO_x conversion level. The maximum NO_x conversion was observed for the catalyst that was ion-exchanged with a solution containing 100% Ba^{2+} ions for complete ion exchange of Na^+ ions for Ba^{2+}. The activity of this catalyst was the highest in the entire temperature range studied. Fig. 1B reveals that this increased NO_x conversion correlates with the higher conversion of NO_2 on the Ba-Y catalysts than over Na-Y. At the low temperature of 433 K the amount of unreacted NO_2 dropped to <5% on the Ba-Y catalysts, as opposed to the 20% observed for Na-Y. The amount of unreacted NO_2 increases for all catalysts with increasing catalyst temperature; however, with increasing concentration of Ba^{2+} ions in the ion-exchange solution the rate of increase in the amount of unreacted NO_2 decreases. ICP analysis (Table 1) showed that the Ba^{2+}/Na^+ ratio gradually increased with increasing Ba^{2+} concentration in the ion-exchange solution. As Fig. 2 shows the turn over frequency (TOF), defined as the number of NO_x converted/supercage · s, increased linearly with the number of Ba^{2+} ions per unit cell (comparison is made at 473 K reactor temperature). This correlation suggests that the Ba^{2+} ions in the Y,FAU framework have inherently higher catalytic activities in the plasma-assisted NO_x reduction process than Na^+ ions.

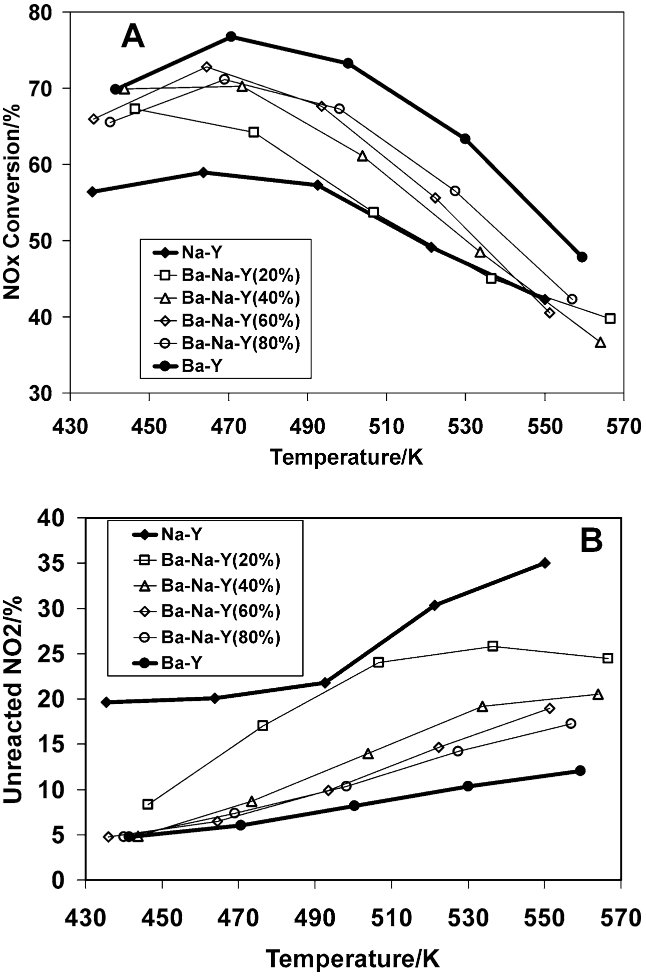

Fig. 1. The effect of Ba^{2+} ion-exchange level on the NO_x conversion (A) and the unreacted NO_2 levels at the exit end of the catalytic reactor (B) over Ba–Na-Y,FAU catalysts. (Percentages refer to the Ba^{2+} ion concentrations in the ion-exchange solutions. For details see text.)

In the next step we carried out consecutive ion exchanges on a Na-Y material with Ba^{2+}-containing solutions. The Ba-Y(1-1) sample is the same as the Ba-Y sample ion-exchanged with 100% solution and discussed in the previous paragraph. Fig. 3 displays the NO_x conversion (A) and the unreacted NO_2 (B) as a function of reactor temperature for these Ba-Y samples. It is evident from these results that there is practically no difference in catalytic activities among samples ion-exchanged with Ba^{2+} solution in a consecutive

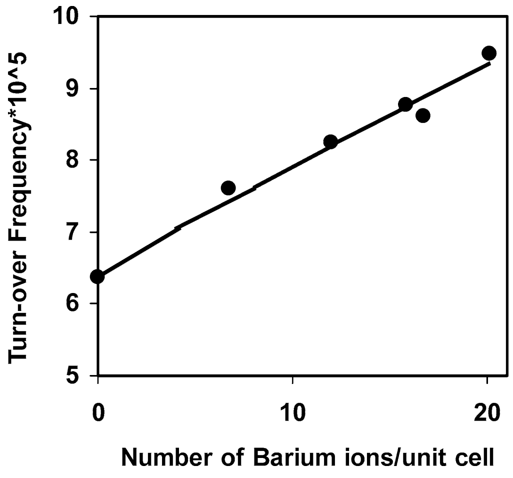

Fig. 2. The dependence of the TOF (as defined in the text) on the number of Ba^{2+} ions/unit cell for Ba–Na-Y,FAU catalysts at 473 K.

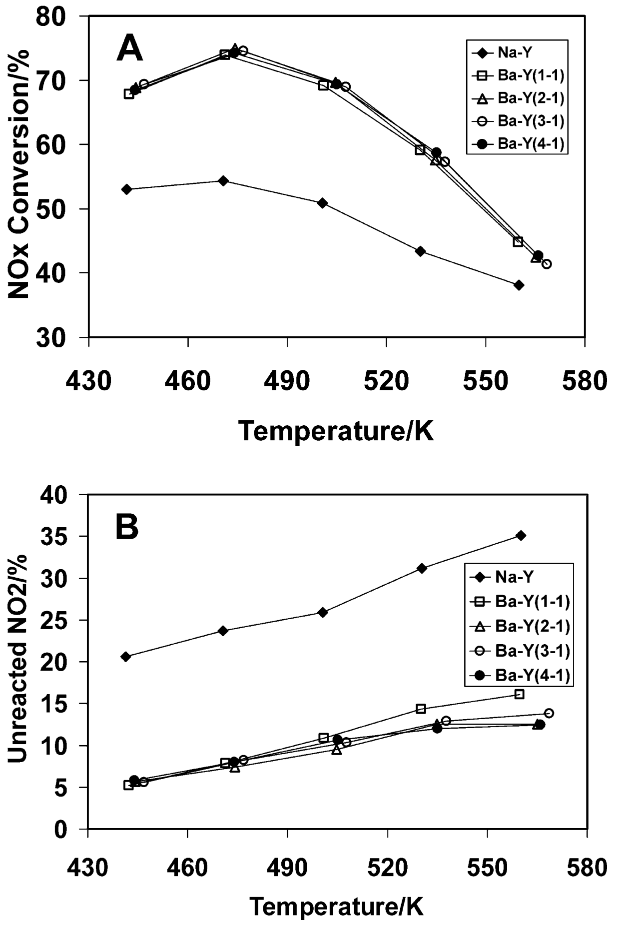

Fig. 3. The effect of multiple solution ion exchange on the NO_x conversion (A) and unreacted NO_2 levels at the exit end of the reactor (B) over Ba(Na)-Y,FAU catalysts.

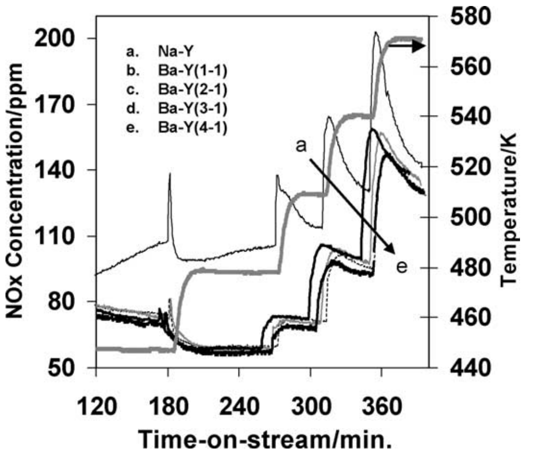

Fig. 4. NO_x levels measured by a chemiluminescent NO_x analyzer at the exit end of the reactor for Ba(Na)-Y,FAU samples prepared by the multiple solution ion-exchange method.

fashion. These results suggest that under the given ion-exchange conditions the Ba^{2+}/Na^{+} ratio does not change upon multiple solution ion exchanges.

The reaction profiles, i.e., NO_x levels at the outlet of the catalyst bed measured by the chemiluminescence NO_x analyzer as a function of time, on these materials are displayed in Fig. 4 and were almost the same at every temperature studied. (The temperature profile for the Na-Y sample is also displayed in Fig. 4, and was very similar for all the other catalysts studied; therefore, it is only shown for this material.) Curve a of Fig. 4 represents the NO_x concentration obtained over our Na-Y starting material. In the first 180 min of time on stream the catalyst was kept at 443 K and the NO_x level was monitored. In most of the cases 180 min was sufficient to reach steady state (or close to steady state). The NO_x conversion was calculated from the NO_x level measured at 180 min time on stream. At 180 min the reactor temperature was raised to 473 K and kept at this temperature until the new steady state was reached. As the reactor temperature was increased from 443 to 473 K, a sharp increase in the NO_x level (NO_x evolution from the catalyst) was observed, and then steady state at the higher temperature was reached in a fairly short time. In the next temperature increase (from 473 to 503 K) this sharp NO_x evolution peak is present only as a shoulder, while a broad NO_x evolution feature develops. As the temperature is further increased, the intensity of this broad feature increases, while the original sharp peak is absent. With increase in the intensity of the broad feature, the NO_x reduction activity of the catalyst decreases. These observations may suggest that with increasing reaction temperature (in the range of this study) the amount of NO_x strongly adsorbed onto the catalyst decreases. As the catalyst contains less and less of this strongly adsorbed NO_x the catalytic activity goes down. The existence of the two types of NO_x evolution features may suggest that there are either two types of adsorbed NO_x species on the catalysts, or there are two different adsorption centers that hold NO_x with different adsorption strengths. The reaction profiles for the Ba-Y catalysts are similar to that of Na-Y; however, there is a major difference between the Na^{+} and the Ba^{2+} form catalysts. At each reaction temperature increase, the intensity of the NO_x evolution feature is much lower for the Ba-Y catalysts than that for the Na-Y sample. For example, at the

443 to 473 K transition the NO_x level jumped about 10 ppm for each Ba-Y catalysts, while there was a 30 ppm jump for the Na-Y sample. Also at the 473 to 503 K transition there was practically no NO_x level increase observed for the Ba-Y samples, while two NO_x evolution features were seen for the Na-Y. With increasing reaction temperature the intensity of the broad NO_x evolution features increases over the Ba-Y catalysts. The implication of these results for understanding the reactivity differences of the various catalysts studied here will be discussed below.

The effect of ion exchange on the activity of Ba-Y was further investigated by modifying the previously discussed preparation procedure. The parent Na-Y sample was consecutively ion-exchanged with Ba^{2+}-containing solutions, but after each ion-exchange step the catalyst was calcined at 773 K for 3 h. The NO_x conversion, unreacted NO_2, and the reaction profile (defined the same way as in the previous paragraph) for these catalysts are shown in Figs. 5A and B and 6, respectively. The catalyst designation Ba-Y(2-2) indicates that this material was prepared by two aqueous ion exchanges, and was calcined in air at 773 K after each ion-exchange step. The NO_x conversion increases in the order of Na-Y < Ba-Y(1-1) < Ba-Y(2-2) ∼ Ba-Y(3-3),(4-4). With increasing number of ion-exchange/calcination cycles the NO_x conversion increases, in particular at higher reaction temperatures. At 563 K the Ba-Y(4-4) catalyst exhibits about 20% higher NO_x conversion than the Ba-Y(1-1) sample. The increase in NO_x conversion after the second ion-exchange/calcination cycle is very small, if any. A high level of NO_x conversion (∼80%) is sustained in a wide temperature range of 463–513 K on catalysts that were ion-exchanged and calcined at least twice. On these catalysts even at 563 K the NO_x conversion stayed above 60%. The unreacted NO_2 exiting the catalytic reactor over all three, multiply ion-exchanged catalysts is very similar, about 5%. Note that the unreacted NO_2 on these catalysts is not affected by the reaction temperature. In contrast, on both Na-Y and Ba-Y(1-1), the amount of unreacted NO_2 increases with increasing reaction temperature.

The reaction profiles are significantly different for the multiply ion-exchanged/calcined samples than those we have previously shown for the multiply ion-exchanged but only once calcined samples. With the number of ion-exchange/calcination cycles the sharp increase in the NO_x level seen for Na-Y and also at lower intensity for the multiply ion-exchanged but only once calcined samples decreases and almost completely disappears for samples Ba-Y(2-2), (3-3), and (4-4) as the temperature is raised from 443 to 473 K. At the next temperature increase step (from 473 to 503 K) practically no NO_x level increase can be seen for these multiply ion-exchanged Ba-Y zeolites. They reach their steady-state activities in a very short period of time. Raising the temperature from 503 to 533 K, and then from 533 to 563 K, steady-state activities are reached without any spike in the NO_x level on these samples. There seems to be a direct correlation between the NO_x level increase upon

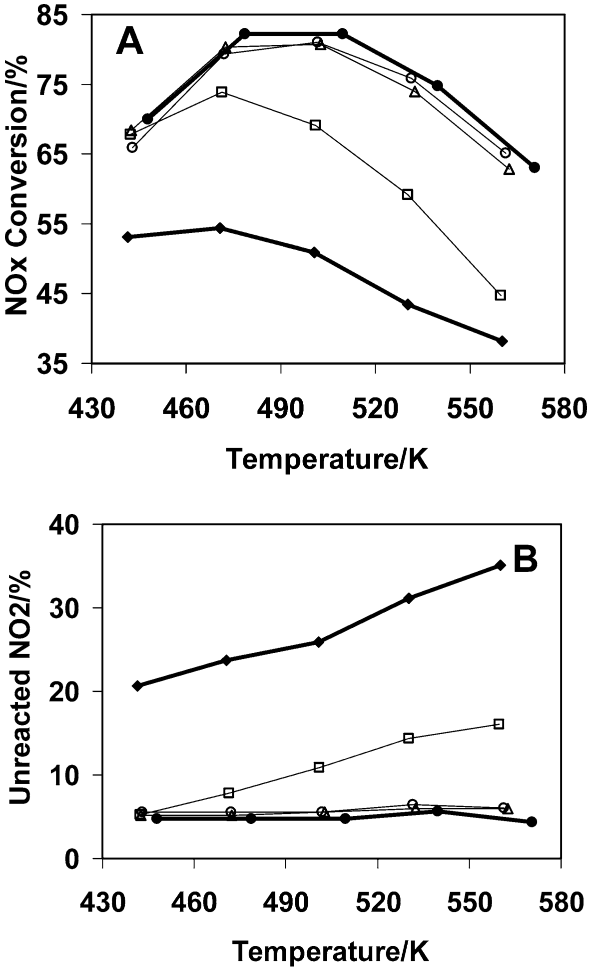

Fig. 5. The effect of multiple ion exchange/calcination on the NO_x conversion (A) and unreacted NO_2 levels at the exit end of the reactor (B) over Ba(Na)-Y,FAU catalysts. [(◆) Na-Y; (□) Ba-Y(1-1); (△) Ba-Y(2-2); (○) Ba-Y(3-3); (●) Ba-Y(4-4)].

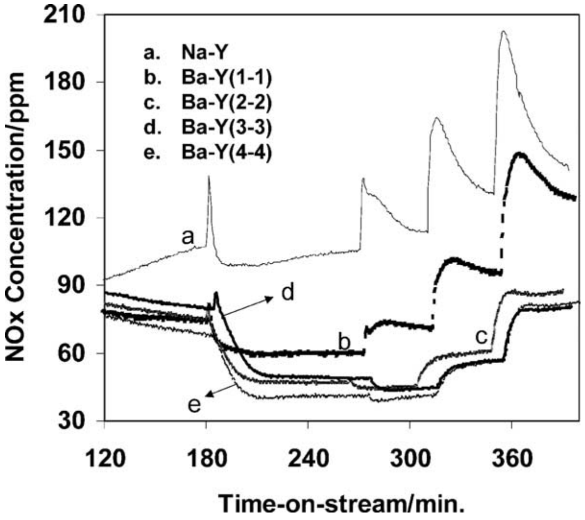

Fig. 6. NO_x levels monitored by the NO_x chemiluminescent analyzer at the exit end of the reactor over Ba(Na)-Y,FAU catalysts prepared by the multiple-ion exchange/calcination procedure.

temperature increase and the NO_x reduction activity of the catalyst. The lower the jump in the NO_x level when going from a lower temperature to a higher one the higher the catalytic activity of that particular catalyst. In other words, catalysts that hold NO_x stronger are more active in the NO_x reduction process.

In comparison of the two sample series discussed above the key issue that needs to be addressed is the main difference between samples that are multiply ion-exchanged but calcined only once, and those that are multiply ion-exchanged and calcined after each ion-exchange step. From the results of Fig. 2, we have concluded that the NO_x reduction activity of Ba^{2+} ion-exchanged Y,FAU catalysts increases with increasing Ba^{2+}/Na^{+} ratio. On the basis of this argument, we can suggest that the Ba^{2+}/Na^{+} ion ratio in the multiply ion-exchanged, but only once calcined, Ba-Y zeolites does not change; i.e., simple multiple solution ion exchange does not measurably increase the Ba^{2+}/Na^{+} ratio after the first ion exchange. This suggests that, under our ion-exchange conditions, most of the readily accessible and, therefore, exchangeable Na^{+} ions are exchanged for Ba^{2+} during the first ion-exchange process. This, however, does not imply that the ion exchange is complete. It simply means that, under the given conditions after the first solution ion exchange, there are no more Na^{+} ions in cationic positions that are accessible for Ba^{2+} ions for exchange. Therefore, again the NO_x reduction activities of these multiply ion-exchanged but only once calcined catalysts are the same because their Ba^{2+}/Na^{+} exchange levels are very similar.

The situation is quite different when multiple ion exchange is carried out in a different fashion, namely, each ion-exchange step is followed by a calcination step at 773 K. Calcining the sample to this high temperature after a solution ion-exchange step results in a redistribution of charge compensating cations in the zeolite framework. Na^{+} ions can move into the supercages of the zeolite framework, while Ba^{2+} ions can move into positions left empty by the Na^{+} ions in the sodalite cages. This ion redistribution upon calcination enables us to remove Na^{+} ions that are now in exchangeable cationic positions, thereby increasing the overall Ba^{2+}/Na^{+} ion ratio in the zeolite framework. The consequence of this increased Ba^{2+}/Na^{+} ion ratio is the increased NO_x reduction activity.

The calcination-induced ion migration in zeolites is not unique for Ba^{2+}/Na^{+} ion pair, or for the Y,FAU framework. For example, migration of Ni^{2+} cations in Y,FAU [7] and a decrease in regularity in Ca^{2+} ion-exchanged chabasite [8] upon dehydration have been demonstrated. More recently, in a detailed in situ powder diffraction and MAS NMR study the migration of cations during dehydration was investigated for a Cs(Na)-Y,FAU [9]. The results unambiguously showed that, upon annealing, Cs^{+} ions lose water from their coordination sphere, and are then able to migrate into cationic positions that are otherwise unavailable to them during ion exchange in aqueous solutions. Upon repeated dehydration/solution ion exchange the Cs^{+}/Na^{+} ratio achieved was significantly higher than that achievable by simple multiple solution ion exchange. The changes in site population upon dehydration were also clearly demonstrated. After the ion exchange with a Cs^{+}-containing aqueous solution, Cs^{+} ions located almost exclusively in SII positions in the supercage in front of a 6-membered rings. The number of Cs^{+} ions in SII cationic sites gradually decreased as the sample was heated at 300, 350, and 500 K, and an increasing number of these cations were seen in SI′, SII′, and SIII sites. The SI′ and SII′ sites are located inside the sodalite cages and are not accessible to hydrated Cs^{+} ions. However, as the annealing temperature is increased the Cs^{+} ions are losing water molecules from their coordination sphere and able to migrate into the sodalite cages. At the same time Na^{+} ions, which were completely absent at SII sites after the Cs^{+} ion exchange, started repopulating these cationic positions. Therefore, by a subsequent Cs^{+} ion exchange these Na^{+} ions could be removed from their SII sites and replaced with Cs^{+} ions, thus ultimately increasing the overall Cs^{+}/Na^{+} ratio in the framework.

Table 2
NO_2 adsorption: total and chemisorbed NO_2 in Na-Y, Ba-Y(1-1), and Ba-Y(2-2) catalysts ($T_{ads.} = 293$ K)

Catalyst	NO_2 adsorption volume (ml/g)	
	Total	Chemisorbed
Na-Y	108.1	13.7
Ba-Y(1-1)	103.1	32.3
Ba-Y(2-2)	112.9	43.4

Now the question that still remains unanswered is what makes Ba-Y a more active catalyst in the plasma-assisted NO_x reduction than Na-Y. Clues may come from NO_2 adsorption and TPD experiments we have carried out on Na-Y, Ba-Y(1-1) and Ba-Y(2-2) samples. The NO_2 adsorption measurements were performed at 293 K. We measured both the total amount of adsorbed NO_2 and the strongly chemisorbed NO_2. The results of these experiments are summarized in Table 2. The total amount of NO_2 adsorbed (physisorbed + chemisorbed) does not change significantly by exchanging Na^{+} ions for Ba^{2+} ions. On the other hand, the number of chemisorbed NO_2/supercage approximately doubles when Ba^{2+} is introduced in Na-Y. This may suggest that catalysts with higher NO_2 chemisorption capacities are better catalysts in the discussed reaction.

TPD experiments that were carried out after the completion of the NO_2 chemisorption measurements reveal another significant difference between Na, and Ba-Y catalysts. Note that these measurements follow evacuation of the sample at room temperature, so desorption products arise only from the strongly adsorbed NO_2 species. In the NO_2 TPD of Na-Y there was only one major desorption feature centered at 353 K. In contrast, we observed two major desorption features for the Ba^{2+} ion-exchanged samples (results are not shown for brevity) centered at around 353 and 463 K. We also noted that the intensity of this second desorption feature increased while that of the lower temperature feature decreased going from Ba-Y(1-1) to Ba-Y(2-2). Thus, the results of the NO_2 adsorption and TPD experiments reveal that Ba-Y adsorbs much more chemisorbed NO_2 than Na-Y, and also it holds the adsorbed NO_2 much stronger than Na-Y does. This may explain the vastly improved catalytic activity of Ba-Y in particular at higher reaction temperatures.

This conclusion is in agreement with the reaction profiles discussed earlier. Notably, as the reaction temperature is increased, Na-Y releases a large amount of NO_x, indicating that at those temperatures it is unable to adsorb large amounts of NO_2 needed for high catalytic activity. The amount of NO_x released upon raising the reaction temperature is significantly lower for Ba-Y(1-1) than for Na-Y. However, at higher temperatures the quantity of NO_x released is still large over this catalyst, almost comparable to Na-Y. This might explain the relatively rapid decrease in NO_x conversion over the Ba-Y(1-1) catalyst at temperatures above about 500 K. Ba-Y samples ion-exchanged and calcined at least twice release only a very small amount of NO_x when the reaction temperature is increased; thus their activity is higher and much more stable in the temperature range of this study. This explanation is also supported by the results shown in Fig. 5B. For Na-Y, even at the low reaction temperature of 443 K the level of unreacted NO_2 exiting the catalytic reactor is $> 20\%$ and gradually increases with increasing reaction temperature, reaching 35% at 563 K. The unreacted NO_2 levels on the Ba-Y(1-1) sample ($\sim 5\%$) at 443 K are significantly lower than on Na-Y, but increases with increasing reaction temperature in the same fashion as we have seen for Na-Y. Again, this is in agreement with the reaction profile that shows significant NO_x evolution from Ba-Y(1-1) at higher reaction temperatures. On the multiply ion-exchanged/calcined Ba-Y samples, however, the unreacted NO_2 levels are constant over the entire temperature range of this study, and there is practically no NO_x evolution in the reaction profiles.

One may propose that the observed improvement in NO_x removal on Ba-Y is associated with NO_x storage rather than NO_x reduction. This might be fueled by the numerous studies on NO_x storage over BaO-containing materials. In our studies, however, this is not the case. The most important proof for this is the sustained catalytic activity of Ba-Y in long-term deactivation studies. All the Na- and Ba-containing Y zeolites we have studied reached their steady-state NO_x reduction activities within short periods of times, and these activities were sustained for the duration of the long-term studies (24 h). If NO_x storage played a significant role on NO_x removal over the Ba-containing catalysts we should have seen a continuous decline in catalytic activity, and eventually a complete saturation of the catalyst with NO_x species. Upon saturation of these catalysts with NO_x the ability of these catalysts to remove NO_x should have disappeared. However, we have never observed any activity loss as a function of time in our experiments (within the 24 h of the duration of the study). Also, these Ba^{2+} ion-exchanged materials are different from materials containing BaO particles which are able to store NO_x. Here the Ba^{2+} ions are located in well-defined cationic positions of the zeolite framework and macroscopic BaO particles that can store NO_x are absent.

We are fully aware that NO_2 adsorption is only one process in the overall reaction mechanism, albeit likely a very important one. The role of hydrocarbons, including partially oxidized ones, and water in determining the catalytic activities of these materials is being currently investigated.

4. Conclusions

Ba^{2+} ion-exchanged Y,FAU zeolites show high catalytic activities in the plasma-assisted selective catalytic reduction of NO_x. The catalytic activity of Ba-Y increases with increasing Ba^{2+}/Na^+ ratio in the zeolite framework. Despite this, multiple solution ion exchange is an ineffective way to improve the catalytic activity of Ba-Y. Rather, the largest improvement in NO_x reduction activity was achieved when multiple solution ion exchange is carried out in a fashion such that each ion exchange was followed by high-temperature calcination. It is believed that during the high-temperature calcination, a redistribution of Ba^{2+} and Na^+ ions take place in the zeolite structure. As a result of this ion migration, additional Na^+ ions can be ion-exchanged for Ba^{2+}, allowing for the preparation of Ba-Y samples with higher Ba^{2+}/Na^+ ratios, than can be achieved by simple multiple solution ion exchanges. The results of NO_2 adsorption and TPD experiments reveal that Ba-Y catalysts can chemisorb much larger amounts of NO_2 than Na-Y. Furthermore, the amount of chemisorbed NO_2 further increased following the multiple ion-exchange/anneal sample preparation method. Y,FAU zeolites ion-exchanged with Ba^{2+} are shown to hold NO_2 stronger than their Na^+ form counterparts. These results suggest that high chemisorption capacity and strong adsorption of NO_2 are prerequisites for high activity in plasma-assisted NO_x reduction.

Acknowledgments

The authors gratefully acknowledge the US 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 DE-AC067RLO1831. The authors thank Mr. T. Hart for the ICP analysis of the zeolite catalysts.

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