

The Catalytic Chemistry of HCN + NO₂ over Na– and Ba–Y,FAU: An in Situ FTIR and TPD/TPR Study

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

Chemical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999,
MSIN K8-93, Richland, Washington 99352

Received: September 23, 2004; In Final Form: November 12, 2004

The adsorption of HCN and the reaction of HCN with NO₂ over Na–, and Ba–Y,FAU zeolite catalysts were investigated using in situ FTIR and TPD/TPR spectroscopies. Both catalysts adsorb HCN molecularly at room temperature, and the strength of adsorption is higher over Ba–Y than Na–Y. Over Na–Y, the reaction between HCN and NO₂ is slow at 473 K. On Ba–Y, HCN reacts readily with NO₂ at 473K, forming N₂, CO, CO₂, HNCO, NO, N₂O, and C₂N₂. The results of this investigation suggest that initial step in the HCN + NO₂ reaction over these catalysts is the hydrogen abstraction from HCN, and the formation of ionic CN[–] and NC[–] species. The formation of N₂ can proceed directly from these ionic species upon their interaction with NO⁺. Alternatively, these cyanide species can be oxidized to isocyanates which then can be further transformed to N₂, N₂O and CO_x in their subsequent reaction with NO_x.

Introduction

The reduction of environmentally harmful NO_x gases produced by internal combustion engines is a challenging task, in particular, when the engines are operating under lean conditions, i.e., in the presence of excess oxygen. Traditional three-way catalysts are unable to reduce NO_x effectively under these conditions due, primarily, to their high activities toward hydrocarbon oxidation. Under lean conditions they readily convert most of the hydrocarbons to CO_x, thus starving the catalyst from an effective reductant. Due to increasingly stringent environmental regulations and the drive to develop more energy efficient engines, the reduction of NO_x from oxygen rich exhaust gases has become the subject of great interest to the catalysis community. A number of possible new technologies have been proposed, but none of them had gained widespread practical use. Among the most promising technologies is the nonthermal plasma assisted lean NO_x reduction. In this process a nonthermal plasma reactor is inserted between the source of the exhaust (engine) and the catalyst bed. Today, the dual role of plasma is well understood—that is, the almost complete conversion of NO into NO₂ and the partial oxidation of some of the hydrocarbons.^{1,2} The resulting “reformed” exhaust gas mixture then passes through a catalyst bed, where the actual NO_x reduction (NO₂ reduction) takes place. In the past few years catalysts with high NO_x reduction activities have been developed in our laboratory.^{3–6} These catalysts are all Y,FAU-based materials, containing alkali or alkaline earth cations in their cationic positions. Among these catalysts, Ba–Y has shown superior catalytic activity at moderate reaction temperatures (440–570 K) when tested in a simulated diesel engine exhaust.

The formation of HCN as an undesired byproduct has been reported in hydrocarbon SCR processes.⁷ On the other hand, Aylor and co-workers⁸ proposed a key role for adsorbed cyanide species as intermediates in the SCR of NO with CH₄ over Co–ZSM5 under lean conditions. The possibility of adsorbed –CN being an intermediate in SCR of NO_x was also raised by Bell

et al. on Cu/ZrO₂⁹ and by Hayes et al. on Cu/ZSM-5.¹⁰ In our FTIR investigations of the acetaldehyde+NO₂ reaction, we also confirmed the formation of both HCN and HNCO over both Na–¹¹ and Ba–Y zeolites.¹²

The key questions that arise from these observations are: How do these compounds form, and what are their reactivities toward other reactants present in the catalytic system? Are these species important components of the overall mechanism or just byproducts of certain side reactions? Here we try to answer the question whether HCN is merely a byproduct or an important intermediate in the overall reaction scheme. To this end we have investigated the adsorption of HCN on both Na– and Ba–Y zeolites and, subsequently, the reactions that take place between HCN and NO₂ on these catalysts, using FTIR and TPD/TPR techniques.

Experimental Section

The experiments described in this work were carried out in an IR cell connected to a gas handling system, a pumping unit and a mass spectrometer. The IR cell itself was a 2³/₄” six-way stainless steel cube equipped with CaF₂ windows. The zeolite samples were pressed onto a fine tungsten mesh, which, in turn, was mounted onto a copper sample holder assembly attached to a ceramic feed through. This arrangement allowed the resistive heating of the sample under the desired atmosphere. The temperature of the sample was monitored through a chromel/ alumel thermocouple spot-welded to the top center of the tungsten mesh. The pressure in the IR cell could be varied between 1 × 10^{–8} and 10³ Torr. The IR cell was connected to a mass spectrometer through two valves; a gate valve was used to ensure good conductance between the IR cell and the mass spectrometer during TPD experiments, while a leak valve enabled us to precisely control the amount of gases leaked into the mass spectrometer compartment from the IR cell.

IR spectra were obtained with a Mattson Research Series FTIT spectrometer operated at 4 cm^{–1} resolution. A background spectrum of the clean zeolite sample was obtained prior to each

* Corresponding author. E-mail: janos.szanyi@pnl.gov.

adsorption/reaction experiment in order to eliminate the contribution of the zeolite framework vibrations to the IR spectra. This way, the only IR bands present in the spectra were the ones that originated from adsorbed species (at the pressure range of this study and due to the short IR beam path length through the IR cell, there was no, or negligible gas-phase contribution to the IR spectra recorded). Each spectrum was the average of 64 scans. This allowed us to collect IR spectra at every 2 min. A UTI 100 mass spectrometer was used throughout this study to analyze gas composition and follow the evolved gases in TPD experiments. The base pressure in the mass spectrometer compartment was $<2 \times 10^{-8}$ Torr. During TPD/TPR experiments, the sample was heated at a constant rate (12 K/min), and masses (up to 10 different ones) were monitored as a function of temperature. In most cases IR spectra were recorded in 20 K intervals. In a parallel set of experiments, we also collected mass spectra at every 20 K, which allowed us to construct contour plots of AMU versus temperature. This method was used to ensure that all the species that were present in the reactor were accounted for.

The materials used in this study were Na– and Ba–Y, FAU zeolites. The Na–Y powder was used as received from Zeolyst International (CBV 100). The Si/Al ratio was about ~ 2.5 , and the sample was free of extraframework alumina as confirmed by ^{27}Al and ^{29}Si NMR. The Ba–Y used here was prepared according to the method described in detail in our previous work.⁵ In short, Na–Y was ion exchanged with an aqueous Ba–acetate solution twice and was calcined at 773 K for 4 h after each ion exchange step. The resulting catalyst showed very high NO_x reduction activity ($>80\%$ NO_x conversion at 470 K) due to its high Ba ion exchange level. For HCN adsorption, a 1% HCN/He gas mixture (Matheson) was used as received with no additional purification. For each adsorption/reaction experiment, 500 Torr of 1% HCN/He gas mixture was expanded into the IR cell, and after 5 min of adsorption time, the cell was evacuated in order to remove He. HCN adsorbed strongly enough on both Na– and, in particular, Ba–Y that this evacuation step did affect the amount of adsorbed HCN on the samples. The NO_2 used throughout this study was cleaned by three cycles of freeze/pump/thaw. Prior to each experiment the catalyst sample was annealed at 823 K for 2 h in order to eliminate the presence of adsorbed water in the zeolite channels.

Results and Discussion

1. Adsorption of HCN. The adsorption of HCN was investigated on dehydrated Na– and Ba–Y catalysts at room temperature, and the IR spectra obtained in these experiments are displayed in Figure 1 (spectrum a for Ba–Y, spectrum c for Na–Y). There are only two IR features observed on both catalysts representing the ν_{CN} (2103–2107 cm^{-1}) and ν_{CH} (~ 3000 – 3300 cm^{-1}) vibrations of molecularly adsorbed HCN. The positions of the IR features indicate that HCN interacts with charge compensating cations (Na^+ and Ba^{2+}) through the lone pair electron on the nitrogen atom. It is interesting to note that although only one ν_{CN} vibrational feature is observed upon HCN adsorption on Na–Y (at 2104 cm^{-1}), there are three ν_{CH} features centered at 3050, 3178, and 3262 cm^{-1} . This might originate from the heterogeneity of the chemical environment around the adsorption centers (Na^+ ions) in Na–Y. Since this phenomenon is not seen for Ba–Y, it may suggest that the chemical environment around the Ba^{2+} adsorption centers are much more uniform than around the Na^+ ions in Na–Y, at least for HCN adsorption. The differences can originate, besides other factors, from the significantly different cation sizes of these two

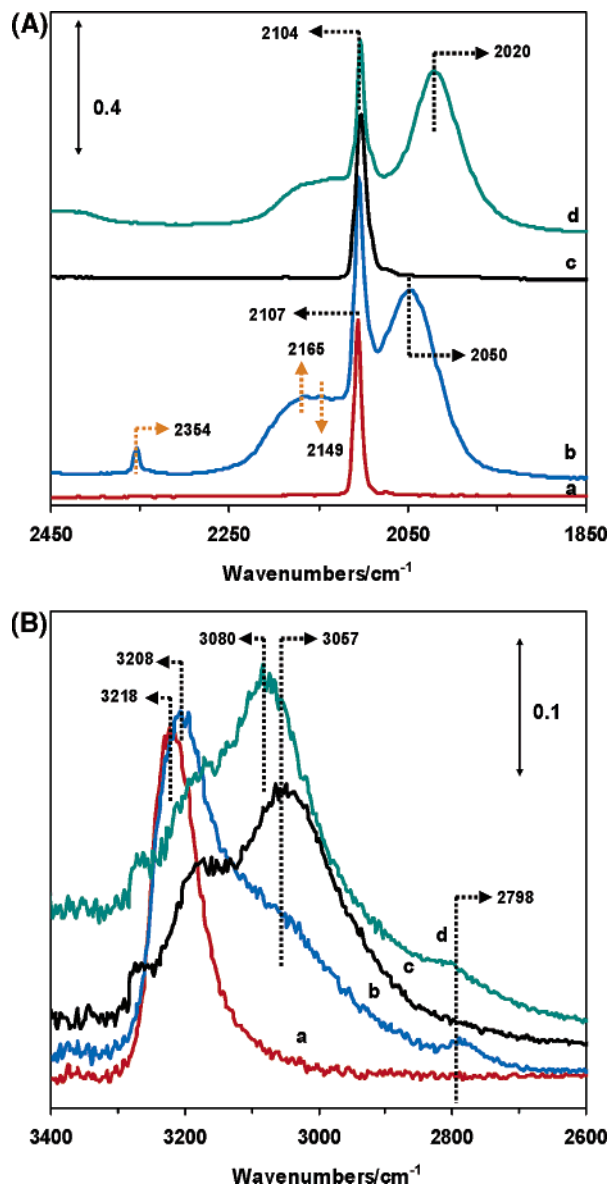


Figure 1. HCN adsorption on Ba–Y (a), Na–Y (c), and HCN + NO_2 coadsorption on Ba– (b) and Na–Y (d) at 300 K.

adsorption centers. The position of the ν_{CN} vibration we observed upon HCN adsorption on Na– and Ba–Y is very close to those reported for HCN adsorbed on oxide surfaces.^{13,14} The adsorption of HCN was studied in detail on silica- and titania-supported Rh catalysts using FTIR spectroscopy by Rasko and co-workers.¹⁵ The characteristic fundamental ν_{CN} vibration of molecularly adsorbed HCN was observed on all the samples studied in the 2080–2105 cm^{-1} spectral region. Over those oxide surfaces, HCN interacts with the surface hydroxyl groups through its lone pair electrons on the N atom. The position of the ν_{CN} vibration of adsorbed HCN (2105 cm^{-1}) is identical to that we report here for the Na– and Ba–Y zeolites. These authors also report on the formation of an aminomethylidene (CNH_2) surface species upon room-temperature adsorption of HCN on both SiO_2 and TiO_2 support materials, similarly to the results seen on Pt(111).¹⁶ On Na– and Ba–Y zeolites, we observed no evidence for the formation of these CNH_2 species under any of the conditions of our study.

Although the positions of the ν_{CN} vibrational features are very close on the two cationic forms of Y,FAU (2103 cm^{-1} for Na–Y and 2107 cm^{-1} for Ba–Y), the thermal stabilities of adsorbed HCN molecules are vastly different over these two

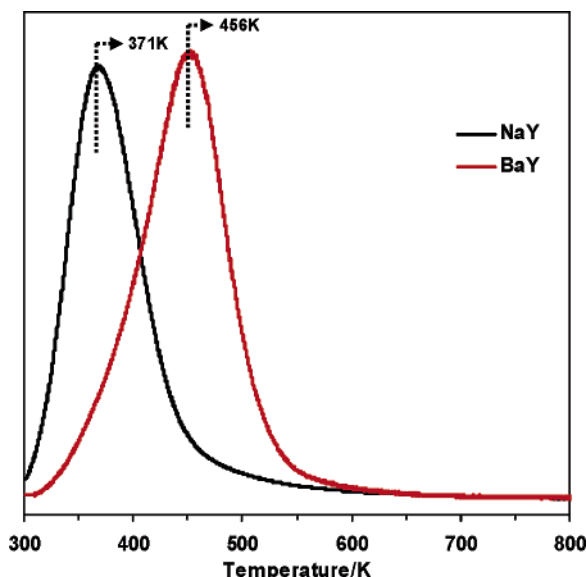


Figure 2. TPD profiles of mass 26 after HCN saturation of Na– and Ba–Y at 300 K [heating rate: 12 K/min].

catalysts. TPD spectra obtained after room-temperature adsorption of HCN on Na– and Ba–Y are shown in Figure 2. The temperature of the maximum desorption rate of HCN on the two catalysts are significantly different. On Na–Y it is observed at 371 K, while on Ba–Y it is at 456 K. This result demonstrates that Ba–Y adsorbs HCN significantly stronger than Na–Y, which, as we will discuss in the following paragraphs, has significant consequences on their reactivities in the HCN + NO₂ reaction. IR spectra collected during TPD (not shown) show no reactions of HCN with the zeolite catalysts, which can be inferred from the fact that no new IR feature is seen during sample heating. Reaction of HCN with SiO₂ and TiO₂ oxide supports was reported at elevated temperatures, resulting in the dissociation of HCN to H_a and CN_a, and the subsequent isomerization of CN_a to NC_a.¹⁵ Under our experimental conditions, these reactions are almost completely absent, as only very low-intensity features can be seen in the spectral region where these adsorbed species of HCN dissociation were suggested to fall after heating the samples in HCN at 473 K for 10 min. From our data we can also conclude that no aminomethylidene (CNH₂) is formed over our catalysts at either 300 or 473 K. This was also substantiated by the results of HCN TPD, which showed that only molecular HCN was desorbed from these catalysts. We have to mention here that upon heating the sample at 473 K for 10 min following HCN adsorption, we observe some very low-intensity IR features on both Na– (2186 and 2280 cm⁻¹) and Ba–Y (2178 and 2206 cm⁻¹), as well as the appearance of the high-frequency zeolitic OH band with very low intensity (3646 cm⁻¹). HCN has been suggested to dissociate to H_a and CN_a over oxide supports¹⁵—as we have mentioned above—at high temperatures, possibly through the reaction with surface OH groups. We attribute the very small extent of reaction observed in our samples to impurities present in our system (trace amount of H₂O present in the zeolite channels even after the high-temperature evacuation, or residual water on the walls of the reactor cell).

2. Coadsorption of HCN and NO₂ at 300 K. In these experiments, first HCN was adsorbed on the catalyst; then NO₂ was introduced into the cell and the changes in the IR spectra were followed as a function of time. IR spectra obtained in these experiments for both Na– and Ba–Y catalysts are displayed in Figure 1. Spectra a and c were recorded from the HCN

exposed Ba– and Na–Y, respectively, prior to NO₂ exposure, while spectra b and d were obtained after 30 min (Ba–Y) and 20 min (Na–Y) exposure to NO₂ at room temperature. The spectral features after HCN exposure have been discussed in the previous paragraphs. After NO₂ introduction onto the (HCN)_{ads}–Na–Y and Ba–Y catalysts, IR absorption features characteristic of NO₂ adsorption over these materials appear. The positions of these IR bands are the same as we have discussed previously for NO₂ adsorption on Na– and Ba–Y.^{17,18} Specifically, the IR signatures of ionically adsorbed NO_x species are observed: NO⁺ at 2020 and 2047 cm⁻¹ for Na– and Ba–Y, respectively, and the NO₃⁻ features in the 1300–1500 cm⁻¹ region. At the same time, we observe no change in the ν_{CN} frequency of adsorbed HCN; it is identical to that seen on the catalysts exposed to HCN only. On the other hand, there are some shifts and broadening of the ν_{CH} absorption features for both catalysts. The most intense IR band assigned to ν_{CH} vibrations of adsorbed HCN in Na–Y (3050 cm⁻¹) blue shifts by about 25 cm⁻¹, while the positions of the other two, lower-intensity ν_{CH} bands remain unchanged. On the other hand, the single ν_{CH} vibrational feature observed for HCN adsorption over the Ba–Y catalyst broadens and a lower frequency shoulder develops at ~3070 cm⁻¹ (~34 cm⁻¹ red shift). At first it seems puzzling that the ν_{CH} bands of adsorbed HCN shift in opposite directions over these two catalysts upon coadsorption with NO₂. However, this observation may be explained by assuming that upon NO₂ introduction the new adsorption sites formed in both catalysts are the same for HCN adsorption. The primary candidate for this center is NO⁺ that forms in the disproportionation of NO₂. Since NO⁺ occupies the same cationic sites in the Y,FAU structure regardless of the nature of the charge compensating cation, HCN adsorbed to these sites shows the same ν_{CH} frequency. It is also interesting to note that the positions of the two higher-frequency ν_{CH} bands of adsorbed HCN in Na–Y did not shift upon NO₂ introduction. This may indicate that in Na–Y adsorption centers exist that are available for HCN adsorption but not for NO₂ adsorption. It is also a possibility that the adsorption of HCN may prevent the adsorption of NO₂ on certain adsorption sites (cationic positions).

At 300 K, no reaction is observed to take place between adsorbed HCN and NO₂ (NO⁺NO₃⁻) over the Na–Y catalyst, which is substantiated by the absence of any new IR features after 20 min time-on-stream. However, on Ba–Y, reaction between these adsorbed species can take place even at 300 K, although with a very low rate. New IR absorption features with very low intensities start developing at 2149 and 2165 cm⁻¹ (assignment will be given in the following paragraphs), the formation of CO₂ can clearly be seen (appearance and development of the 2354 cm⁻¹ band) and the high-frequency zeolitic OH feature appears (3645 cm⁻¹).

3. HCN + NO₂ at 473 K. The reaction between HCN and NO₂ was investigated at 473 K on both Na– and Ba–Y catalysts. First the samples were exposed to HCN; then NO₂ was introduced into the IR cell, and the reaction between HCN and NO₂ was followed at 473 K. A series of IR spectra obtained over Na–Y is shown in Figure 3. Spectrum a was recorded after room-temperature adsorption of HCN (from the 1% HCN/He gas mixture) and subsequent evacuation. Spectrum b was obtained after heating the (HCN)_{ads}–Na–Y sample at 473 K for 10 min and cooling it back to 300 K for 5 min. The intensities of the IR features representing adsorbed HCN on Na–Y decreased significantly (by about 35%) as a result of heating and readsorption. The resulting IR spectrum also shows

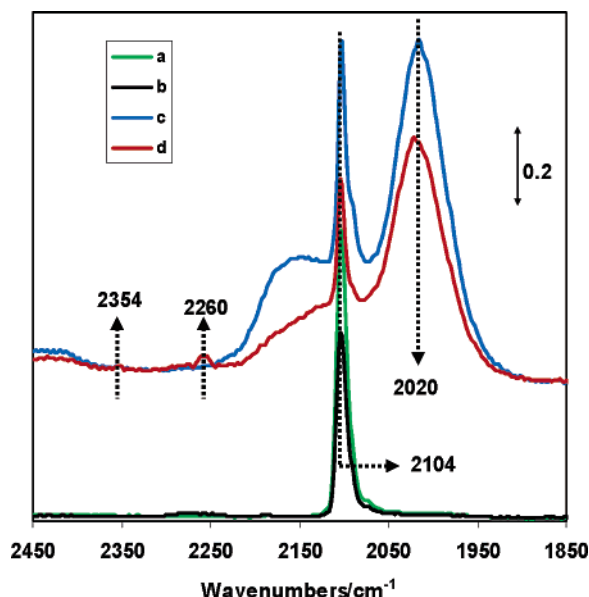


Figure 3. HCN adsorption and evacuation (green), heating at 473 K for 10 min (black), and HCN + NO₂ coadsorption (blue) at 300 K and after HCN + NO₂ reaction at 473 K for 10 min (red) on Na-Y.

that there were no new surface species formed upon heating the HCN saturated Na-Y at 473 K. This was confirmed by TPD following the elevated temperature treatment as well, as only HCN-related fragments were observed. In this experiment all the HCN desorbed from Na-Y upon heating it to 473 K, but its readsorption after cooling was not complete, due, primarily, to the adsorption of HCN on the walls of the IR cell. This is very important to emphasize here, before we discuss the extent of reaction between HCN and NO₂ over this catalyst at 473 K.

As we have discussed above, there is no reaction between adsorbed HCN and NO₂ over Na-Y at room temperature as no new absorption features are seen in the IR spectra following room-temperature coadsorption of HCN and NO₂ (spectrum c of Figure 3). After heating the sample at 473 K for 10 min, the IR features of adsorbed HCN and NO⁺ decrease significantly (spectrum d). The integrated intensity of the ν_{CN} vibrational feature (2104 cm⁻¹) decreased by about 55%, while that of the band representing NO⁺ (2015 cm⁻¹) (+NO⁺NO₂ adduct at 2170 cm⁻¹) decreased by 37%. (The intensity of the nitrate feature decreases as well; however, the extent of its decrease cannot be estimated, due to the saturation of this absorption.) The intensities of the ν_{CH} vibrations of adsorbed HCN decrease as well, in particular the one at 3085 cm⁻¹ (representing adsorbed HCN associated with NO⁺ centers). This demonstrates that some reaction between HCN and NO₂ takes place on Na-Y at 473 K, although not to a great extent. The only new IR bands that we can distinguish after the reaction are the ones at 1270, 2260, 2354 and 3645 cm⁻¹. The intensities of these newly formed IR features are very low. The 1270 cm⁻¹ band represents NO₂⁻, the 2354 cm⁻¹ band adsorbed CO₂, and the 3645 cm⁻¹ band the high-frequency OH vibration of the Y,FAU zeolite.

We have already shown in the previous section that HCN adsorbs significantly stronger on Ba-Y than on Na-Y. Also, we have described elsewhere^{17,18} that the adsorption of ionic NO_x species (NO⁺, NO₃⁻) was much stronger, and the adsorbed amount of NO₂ was about twice as high on Ba-Y as on Na-Y. These differences in the strengths of both NO₂ and HCN adsorption, and the quantity of NO₂ adsorbed may ultimately lead to enhanced activity in the reaction of HCN with NO₂ in Ba-Y. In fact, results obtained in the coadsorption experiments

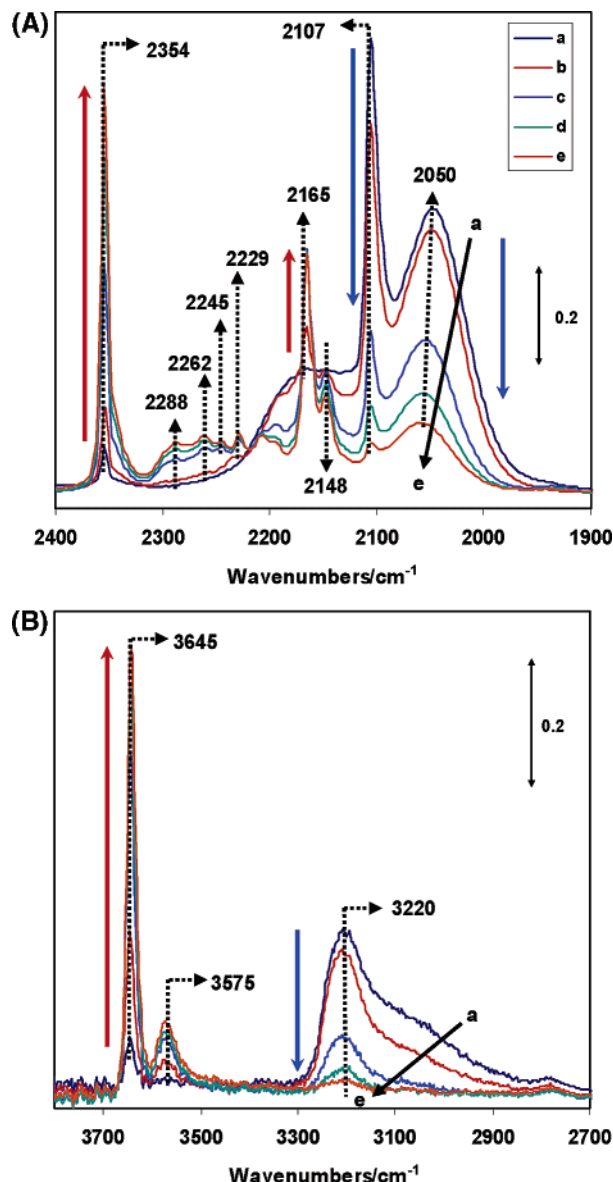


Figure 4. HCN + NO₂ reaction over Ba-Y [295 K (a); 373 K, 16 min (b); 473 K, 1 min (c); 473 K, 6 min (d); 473 K, 16 min (e); HCN/NO₂ = 5/10 (5 and 10 denote pressures in Torr in the gas manifold); blue arrows, bands with decreasing intensities; red arrows, bands with increasing intensities].

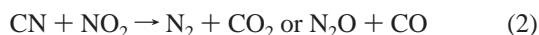
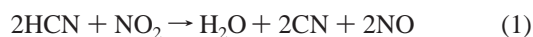
at 300 K already suggested that this might be the case. Here we present the results from the elevated temperature (373 and 473 K) studies on the HCN + NO₂ reaction over Ba-Y.

A series of IR spectra obtained from Ba-Y in the presence of both HCN and NO₂ at 295, 373, and 473 K is displayed in Figure 4. Spectrum a was recorded after 30 min NO₂ exposure of the (HCN)_{ads}-Ba-Y sample at room temperature. (The HCN/NO₂ ratio was 2:1 in this particular experiment.) The main IR features are the ones that represent molecularly adsorbed HCN (2107 and 3000–3200 cm⁻¹) and ionic NO_x species (NO⁺ 2048 cm⁻¹ and NO₃⁻ at 1300–1500 cm⁻¹), as we have discussed it above. Only very weak new IR bands appear as the result of the reactions between HCN and NO₂ at room temperature. Spectrum b was recorded after heating the sample in HCN + NO₂ at 373 K for 16 min. The intensities of the IR bands of adsorbed HCN and NO_x decreased gradually with time the sample was subjected to this elevated temperature. Parallel to these changes, the intensities of the new IR features increased, and bands developed at 1640, 2148, 2166, 2354, 3573, and 3645

cm⁻¹. Also, unresolved features started developing in the 2200–2300 cm⁻¹ range. Heating the sample at 473 K dramatically enhanced the intensities of all these new bands, while the HCN and NO⁺ related features lost most of their intensities. IR spectra c, d, and e were recorded after heating the sample at 473 K for 1, 6, and 16 min, respectively. After a total of 16 min, time-on-stream at 473 K new IR features can be resolved in the 2200–2300 cm⁻¹ region, and they are located at 2207, 2229, 2245, 2262, and 2288 cm⁻¹.

The assignments of some of the IR features observed can be made unambiguously. The 1640 cm⁻¹ band can be assigned to the δ_{HOH} vibration of adsorbed water formed in the reaction between HCN and NO₂. The 2354 and 2245 cm⁻¹ bands represent weakly adsorbed species, as they can be removed completely by a brief (5 min) evacuation at 300 K. As we have shown above, these bands at 2354 and 2245 cm⁻¹ represent weakly held CO₂ and N₂O, respectively. As the reaction proceeds, the intensities of both the high and low-frequency zeolitic OH vibrational features increase.

The observed IR features are consistent with the oxidation of HCN over Na-, and Ba-Y by NO₂:



The H₂O formed in reaction 1 can react with NO₂ to form HNO_x species that in turn can promote the formation of acidic OH groups (3645 cm⁻¹):



where M⁺ is the charge compensating cation in the zeolite (Zeo) structure, e.g., Na⁺.

The remaining IR features represent adsorbed surface species, possibly intermediates, formed in this reaction. Following the changes in the intensities of these bands as a function of HCN/NO₂ ratio, using isotopically labeled NO₂ in the reaction (¹⁸O or ¹⁵N), studying the reaction between HCN with O₂, and investigating the effect of H₂O on the positions of certain IR bands developed during the HCN + NO₂ reaction aided the assignments of most of the IR features observed.

The formation of N₂, N₂O, NO, CO, and CO₂ was substantiated by the results of gas-phase analysis conducted both prior to and following the high-temperature reaction, using a mass spectrometer (MS). To differentiate between N₂ and CO, these experiments were carried out using both ¹⁴NO₂ and ¹⁵NO₂. The results of the MS analysis obtained in the experiments using ¹⁵NO₂ are shown in Figure 5 for Ba-Y zeolite. In these measurements a leak valve, separating the IR cell from the MS, was open so the pressure in the MS chamber was kept at 1 × 10⁻⁷ Torr. After HCN adsorption the observed mass fragments are consistent with the parent HCN molecules (26 and 27 amu) (spectrum not shown). Upon the introduction of ¹⁵NO₂ the primary mass observed at 31 amu originating mainly from the cracking of the ¹⁵NO₂ (mass 47) in the ionizer of the MS. The mass spectrum changes significantly after heating the sample at 473 K for 10 min. Specifically, there is a very large increase in the intensities of the 29 and 44 amu peaks, which indicates the formation of a significant amount of ¹⁵N¹⁴N (29 amu) and CO₂ (44 amu) as a result of the reaction between HCN and ¹⁵NO₂, in accordance with the reaction sequence proposed above. In the presence of NO₂, either prior to or after reaction

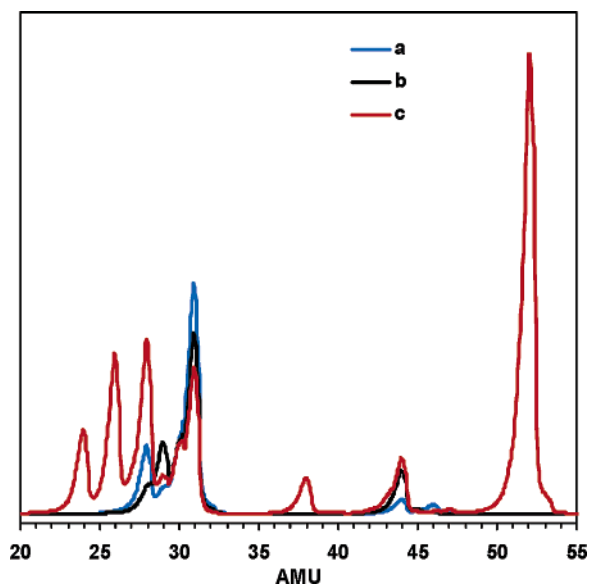


Figure 5. Mass spectrometric gas-phase analysis after HCN + NO₂ coadsorption at 300 K (a), reaction at 473 K for 10 min (b), and after 5 min evacuation at room temperature over the Ba-Y catalyst (c) [spectra a and b were collected by leaking gases into the MS compartment at 1 × 10⁻⁷ Torr pressure; during the collection of spectrum c, the gate valve between the IR cell and the MS compartment was fully open].

at 473 K, we observe no MS signatures of HCN (26 or 27 amu). When the cell is evacuated at room temperature for 5 min after the completion of the high-temperature reaction, new species desorbing from the catalysts can be observed by the MS. In particular, the species representing 52 amu is very interesting. The intensity of the 52 amu peak is the highest after room-temperature evacuation. It suggests the formation of C₂N₂ in the reaction of HCN with NO₂, which can be substantiated by the cracking fragments seen at 24 (C₂), and 38 amu (C₂N). We also need to mention here that no C₂N₂ was observed after heating the BaY catalyst in HCN only at 473K. Following the initial hydrogen abstraction from HCN, CN_a forms and subsequently can dimerize to produce C₂N₂:



It is interesting to note that in the IR spectra we never see any evidence for the formation of this product, most probably due to the very symmetric nature of this molecule which makes it invisible for IR spectroscopy. The extent of reaction over Na-Y (under the same experimental conditions) is much smaller (results are not shown for brevity). We observe only small increases in the intensities of the 29 and 44 amu peaks, and most importantly, we see only a very small feature at 52 amu both after the 473 K reaction, and after room-temperature evacuation.

The advantages of using ¹⁵NO₂ instead of ¹⁴NO₂ in the HCN + NO₂ reaction can clearly be seen from the results of Figure 6. Here we compare the mass spectra obtained from the gas phase after 10 min of HCN + NO₂ reaction at 473 K (panel A) and after room-temperature evacuation for 5 min following the high-temperature reaction (panel B) using either ¹⁴NO₂ (black spectra) or ¹⁵NO₂ (red spectra). Carrying out the reaction with ¹⁴NO₂ gives three main MS peaks at 28, 30, and 44 amu. However, from this spectrum we are unable to show whether N₂ was formed in the reaction or not, since the most intense peak in the mass spectrum for both CO and N₂ is observed at 28 amu. Also, the 44 amu feature can represent both CO₂ and

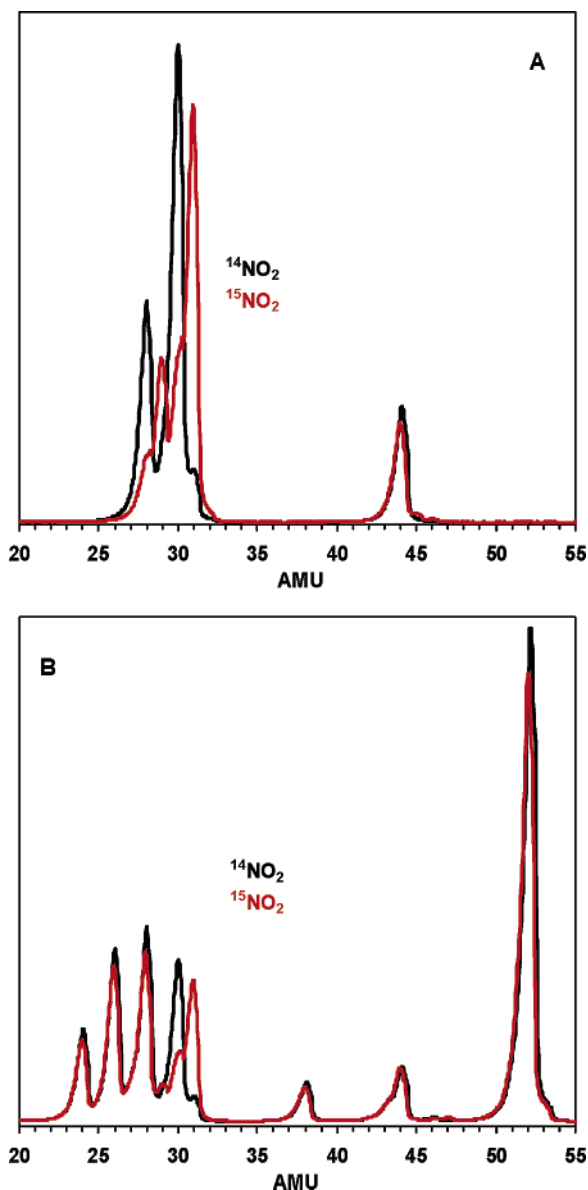


Figure 6. Mass spectral analysis of the gas phase after HCN + NO₂ reaction at 473 K for 10 min (A) and after 5 min evacuation at 300 K (B) [catalyst, Ba–Y; HCN/NO₂ = 5/10].

N₂O, and we have shown in the IR results the formation of a large amount of CO₂ and a small amount of N₂O under these conditions. Switching from ¹⁴NO₂ to ¹⁵NO₂ clearly shows the formation of a significant amount of ¹⁴N¹⁵N (29 amu) and a small amount ¹⁴N¹⁵NO (45 amu). In this case, the intensity of the 28 amu peak is much reduced, while a high-intensity new feature is seen at 29 amu. It is also evident that both N₂ and N₂O are removed by a brief evacuation at room temperature, and the primary species that is still desorbing from the catalyst is C₂N₂. Under the elevated pressure the HCN + NO₂ reaction is studied, C₂N₂ is adsorbed on the Ba–Y zeolite, as no peak at 52 amu is seen in the mass spectra of the gas phase after the reaction. However, it adsorbs weakly on Ba–Y, and it readily desorbs by evacuation at room temperature. Note that all the C₂N₂ formed contain only ¹⁴N atoms, suggesting that there is no isotope scrambling between adsorbed CN and NO_x species.

The results of the gas analysis can help understanding the observations of our IR measurements. As we have mentioned above, the intensities of the IR bands representing adsorbed HCN and NO₂ (NO⁺NO₃[−]) decreased significantly suggesting

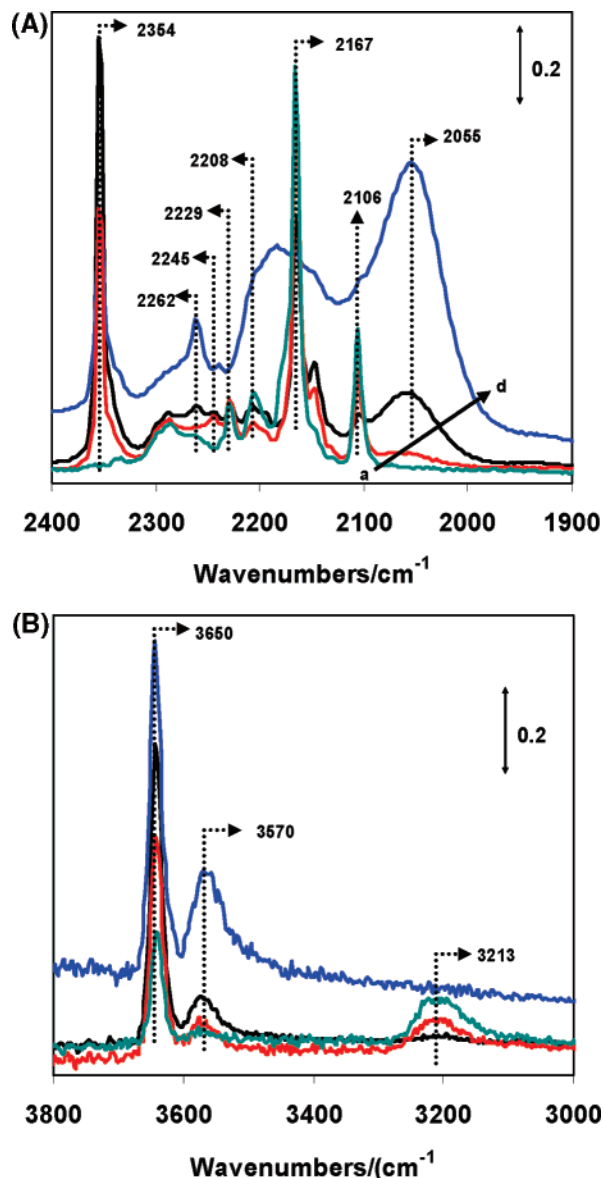


Figure 7. HCN + NO₂ reaction over Ba–Y: the effect of HCN/NO₂ ratio. [HCN/NO₂ = 5/20 (a), 5/10 (b), 5/5 (c), 5/2.5 (d); reaction time = 10 min; *T* = 473 K] (spectra in panel B correspond to the spectra with same colors in panel A.).

appreciable extent of reaction, while new IR bands with only very low intensities appeared. On one hand, this is the consequence of the weak adsorption of some of the species formed (CO₂ and N₂O), while other species do not even adsorb at room temperature on Na–Y (N₂, CO). On the other hand, C₂N₂ that forms and has appreciable strength of adsorption is invisible in our IR measurements. Due to the small changes we observed in both the IR and MS measurements, we did not study this reaction on Na–Y in greater detail, but concentrated on Ba–Y. From here on all the results presented were obtained in the reaction of HCN with NO₂ on Ba–Y.

IR spectra obtained following the HCN + NO₂ reaction (473 K, 16 min) at different HCN/NO₂ ratios are displayed in Figure 7. The amount of HCN adsorbed onto the catalyst prior to its exposure to NO₂ was the same in each experiment, while that of NO₂ was varied such, that the HCN/NO₂ ratios were 2:1 (a), 1:1 (b), 1:2 (c), and 1:4 (d). At the highest HCN/NO₂ ratio (the smallest NO₂ dose), no NO⁺ remained on the catalyst after the reaction, while a significant amount of unreacted, adsorbed HCN is seen (2106 cm^{−1}) (spectrum a). The IR features centered at

2167, 2208, 2229, 2245, and 2288 cm⁻¹ are the most intense at this high HCN/NO₂ ratio. On the other hand, bands located at 2148, 2197, and 2262 cm⁻¹ are the least intense. Also, we can observe a shoulder on the high-frequency side of the 2166 cm⁻¹ band only at this HCN/NO₂ ratio at about 2177 cm⁻¹. Increasing the amount of NO₂ introduced into the IR cell results in the decreases of the 2167, 2208, 2229, and 2245 cm⁻¹ features, while the intensities of the 2148, 2197, and 2262 cm⁻¹ bands increase. These trends may indicate that species responsible for the higher intensity IR features at low NO₂ concentrations are the ones that form initially in the oxidation of HCN with NO₂. Then, as the concentration of the NO₂ present in the cell increases these initially formed species take part in further reactions, resulting either in the development of new IR features or the intensity gains of existing, but low intensity IR bands. These trends can be best seen by following the changes in the intensities of the 2167 and 2262 cm⁻¹ IR features. At low NO₂ pressure (HCN:NO₂ = 2:1), the intensity of the 2167 cm⁻¹ band is the largest among the reactant ratios studied here, while that of the 2262 cm⁻¹ band is the lowest. As the NO₂ concentration increased, the intensity of the 2167 cm⁻¹ band decreases, while that of the 2262 cm⁻¹ feature increases.

The intensity of the IR band representing weakly adsorbed CO₂ (2354 cm⁻¹) increases first with increasing amount of NO₂ present, and then, at the highest NO₂ dose it decreases. This trend is, at least partly, related to the weak adsorption of CO₂ on this catalyst. When a significant portion of the NO₂ introduced is used up in the reaction, a large number of sites open up for CO₂ adsorption, therefore we observe the formation of a large quantity of CO₂. However, at high NO₂ doses most of the adsorption sites are still occupied by NO_x, which binds much more strongly to the Ba²⁺ sites than CO₂ does. Therefore, we observe lower intensity for the CO₂ band, although the HCN conversion is much higher, suggesting the formation of a larger amount of CO₂.

To aid the assignment of the wealth of IR features in the 2100–2400 cm⁻¹ spectral region, we used isotopically labeled NO₂ (¹⁵NO₂ and N¹⁶O_x¹⁸O_{2-x}) in the HCN + NO₂ reaction. (The N¹⁶O_x¹⁸O_{2-x} was prepared by mixing NO and ¹⁸O₂ in ~1/5 molar ratio at room temperature; the mixture was equilibrated overnight, and then the resultant N¹⁶O_x¹⁸O_{2-x} was cleaned by 3 cycles of freeze/pump/thaw.) The IR spectra obtained after 10 min reaction of HCN with NO₂, ¹⁵NO₂, and N¹⁶O_x¹⁸O_{2-x} at 473 K using HCN/NO₂ = 1/2 reactant mixture are displayed in Figure 8. Using ¹⁵N-labeled NO₂ results in an ~8–9 cm⁻¹ red shift in the peak positions of both the 2166 and 2148 cm⁻¹ IR features. The identical shift in the positions of these features suggests that the chemical nature of the adsorbed species these bands represent is similar. Interestingly enough when we substitute one of the oxygen atoms in the NO₂ for ¹⁸O, the positions of these features remain unchanged. These results suggest that these two features (2166 and 2148 cm⁻¹) represent vibrational modes of surface species that do not contain an oxygen atom, most probably a C–N vibration. The observed ~8 cm⁻¹ shift of these features upon substitution of NO₂ for ¹⁵NO₂ is very close to the isotopic shift observed for NCO.¹⁹ However, the lack of any shift in the positions of these features upon ¹⁸O substitution in the NO₂ reactant rules out this possibility. Therefore, we assign these two features to an adsorbed CN species (most probably in the form of CN⁻), formed by the initial oxidation of HCN by NO₂. We also propose that these CN⁻ species are associated with the NO⁺ centers, which may explain the small shift in the ν_{CN} feature as it interacts with ¹⁵NO⁺ instead of ¹⁴NO⁺. The other significant

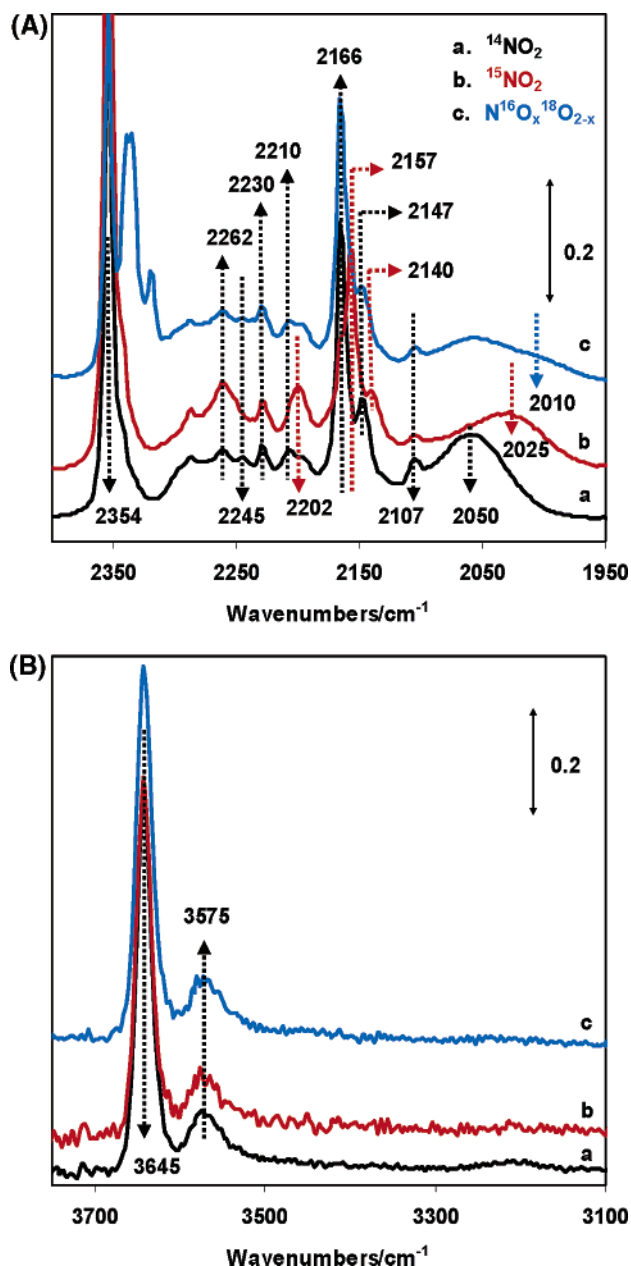
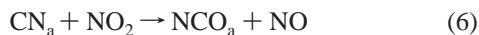


Figure 8. HCN + NO₂ reaction over Ba–Y: the effect of isotopic substitution [NO₂ (a), ¹⁵NO₂ (b), N¹⁶O_x¹⁸O_{2-x} (c); *T* = 473 K; reaction time = 10 min].

change seen in the IR spectra as a result of isotopic substitution is the appearance of four absorption features representing ¹⁸O-labeled CO₂ (2355, 2339, 2335, and 2320 cm⁻¹). The 2245 cm⁻¹ IR peak, which represents weakly adsorbed N₂O (as we have discussed it earlier), shifts to lower wavenumbers upon ¹⁵N substitution in NO₂ (weak shoulder at ~2220 cm⁻¹). When the reaction is carried out with N¹⁶O_x¹⁸O_{2-x}, we observe two features representing N₂O (2245 cm⁻¹) and N₂¹⁸O (2237 cm⁻¹). The absorption feature at 2210 cm⁻¹ is unchanged upon ¹⁸O substitution, while it redshifts by ~8 cm⁻¹ upon ¹⁵N substitution in the NO₂ reactant, similar to the 2166 and 2148 cm⁻¹ features, suggesting that this peak represents NC⁻ species associated with NO⁺ centers. The low-intensity IR feature at 2262 cm⁻¹ does not shift upon ¹⁵N substitution, while it seems to split when ¹⁸O-substituted NO₂ is used (due to the low intensity of this feature in this particular experiment, the mentioned split is not very well seen, but this split can clearly be seen in experiments with different HCN/NO₂ ratios). These observations suggest that

the 2262 cm^{-1} IR band represents adsorbed NCO species, possibly ionic NCO^- . The formation of NCO^- species has been observed on SiO_2 and TiO_2 support materials, when these oxides were heated in HCN atmosphere at 823 K. The oxidation of surface isocyanide species by the hydroxyl groups of these oxides was proposed as a possible reaction route.¹⁵ The asymmetric NCO vibrations of Si-NCO and Ti-NCO were observed at 2314 and $2206\text{--}2213\text{ cm}^{-1}$, respectively. On Na- and Ba-Y we only observe the presence of significant amount of surface NCO species under strongly oxidizing conditions (at low $\text{HCN}:\text{NO}_2$ ratios), when the asymmetric vibrational feature of these surface NCO species is seen at 2262 cm^{-1} on Ba-Y zeolite, which is in the range where the NCO is seen over SiO_2 and TiO_2 . Supporting data for the assignment of the 2262 cm^{-1} feature also obtained from the work of Solymosi and Bansagi²⁰ on the adsorption and reactions of HNCO on H-, Na-, and Cu-ZSM5 zeolites. In the IR spectra of HNCO-exposed H- and Na-ZSM5 zeolites, they observed the $\nu_{\text{a(NCO)}}$ band at 2260 cm^{-1} at room temperature, which they assigned to an Al^{3+} -NCO species. After elevated temperature HNCO exposure they also observed an absorption feature at around 2300 cm^{-1} which they assigned to a Si^{4+} -bound NCO species. The IR feature we observe at $\sim 2290\text{ cm}^{-1}$ on Ba-Y may represent the NCO species that are adsorbed onto Si^{4+} sites of the zeolite. We suggest that NCO is produced by the oxidation of adsorbed cyanide species on these catalysts:



No shift or intensity change is seen for the 2229 cm^{-1} IR feature either upon ^{15}N or ^{18}O substitution in NO_2 . This suggests that this band represent a C-N vibration of cation (possibly Si^{4+})-adsorbed CN^- or NC^- .

Beside the $\text{HCN} + \text{NO}_2$ reaction, we also investigated the oxidation of HCN on Ba-Y, using molecular oxygen. Molecular oxygen is a much weaker oxidizing agent than NO_2 , and the source of nitrogen in the products formed in the $\text{HCN} + \text{O}_2$ reaction is HCN only. A series of IR spectra obtained in the $\text{HCN} + \text{O}_2$ reaction ($\text{HCN}/\text{O}_2 = 5/20$) is shown in Figure 9 (spectra a-c). The spectra demonstrate that no reaction takes place between HCN and O_2 at 300 K (spectrum a), and even at 473 K (b) and 573 K (c), the extent of reaction is very limited. This is expected for a basic zeolite catalyst known for its lack of activity in oxidation reactions with O_2 . The IR features we can observe after 10 min. reaction at 573 K are similar to those we have discussed earlier for the $\text{HCN} + \text{NO}_2$ reaction, though the spectrum is much simpler here. In the $2150\text{--}2300\text{ cm}^{-1}$ spectral region the two most intense features are located at 2174 and 2208 cm^{-1} , and smaller bands can be seen at 2225 and 2260 cm^{-1} . In the $\text{HCN} + \text{NO}_2$ reactions, these are also the main IR features observed, however, the 2174 cm^{-1} band is seen at 2167 cm^{-1} . This observation is another support to our peak assignment of the 2167 cm^{-1} band to a C-N vibration of CN^- that is bound to adsorbed NO^+ . Our proposal that the 2175 and 2165 cm^{-1} band represent very similar CN^- species is further supported by the IR spectrum d of Figure 9, which was obtained 10 min after a small amount of NO_2 was introduced into the system at 300 K, following the $\text{HCN} + \text{O}_2$ reaction at elevated temperatures (spectrum c). Upon NO_2 introduction, the 2174 cm^{-1} feature almost completely lost its intensity, and converted into the 2167 cm^{-1} band. At the same time, the positions and the intensities of all the other IR features remained almost the same as they were after the $\text{HCN} + \text{O}_2$ reaction. Heating the sample at 473 K for 10 min (spectrum e) results in large intensity gains of all the IR features in the $2150\text{--}2400$

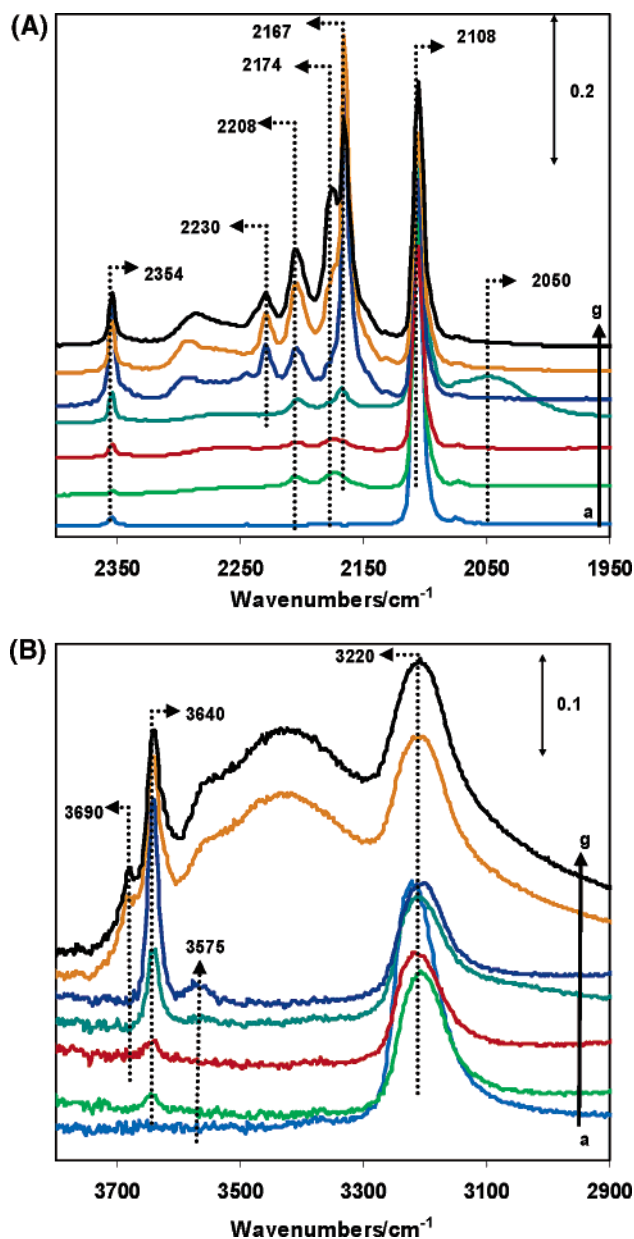


Figure 9. IR spectra after the following: $\text{HCN} + \text{O}_2$ reaction over Ba-Y [300 K (a), 473 K (b), 573 K (c), 10 min at each temperature]; after 573 K (c), a small amount of NO_2 addition at 300 K (d) and reaction at 473 K [10 min] (e); after 473 K (e), H_2O addition at 300 K (f) and reaction at 373 K [5 min] (g).

cm^{-1} spectral region, and a significant intensity drop of 2108 cm^{-1} band of molecularly adsorbed HCN. These assignments are further supported by the results obtained after adding water to the system upon the completion of spectrum e at 300 K (spectrum f). All the IR features are practically unchanged as a result of introduction of H_2O except the 2167 and 2174 cm^{-1} ones. The intensity of the 2167 cm^{-1} band decreased, while the feature at 2174 cm^{-1} began to develop. The introduction of an additional water aliquot onto the sample (twice the amount as in spectrum f) and subsequent heating at 373 K for 5 min result in a large decrease in the intensity of the 2167 cm^{-1} feature, accompanied by a significant intensity gain of the 2174 cm^{-1} band (spectrum g). All of these results strongly suggest that in the presence of NO_2 , but in the absence of H_2O , the C-N vibration of adsorbed CN^- is observed at 2167 cm^{-1} (possibly $\text{CN}^-_a\text{NO}^+_a$), while in the presence of H_2O , this feature is seen at 2175 cm^{-1} (possibly CN^-_aH^+). In the reaction of HCN

+ O₂ water is formed and in the absence of NO₂ only the 2175 cm⁻¹ feature is seen. In the HCN + NO₂ reaction (with no water added) only the 2165 cm⁻¹ band is seen. Addition of H₂O to the HCN + NO₂ system after elevated temperature reaction results in the development of both of these IR features.

4. Relevance to NO_x Reduction. The formation of HCN in NO_x SCR-related studies has been reported for a number of transition metal ion exchanged zeolite materials.^{7,8,26,27} The amount of HCN formed varied substantially depending on the catalyst material used. For example, Cant and co-workers²¹ reported that the amount of HCN produced in the reaction of nitromethane with an NO₂/O₂ gas mixture was significantly higher over Na-ZSM5 than over either H- or Co-ZSM5, while the nitrogen yield was very similar over Na- and Co-ZSM5. Furthermore, the temperature regime where significant amount of HCN formation was seen varied significantly depending on the cationic form of the zeolite.^{22,26} While the maximum amount of HCN over Co-ZSM5 was observed at ~520 K, on the Fe-ZSM5 it was seen at about 620 K, and at 460 K over Cu-ZSM5 when nitromethane was reacted with a NO/O₂ gas mixture. In the nonthermal plasma assisted catalytic NO_x reduction, HCN was also reported on both Na-Y zeolite and Al₂O₃-based catalysts when the tests were carried out in a synthetic exhaust gas mixture containing NO + O₂ + propylene + H₂O.^{23,24} The possibility of HCN or surface adsorbed cyanide being an important intermediate in the NO_x reduction by CH₄ over Co-ZSM-5 has been suggested previously.⁸ These authors have shown that CN species were reactive intermediates, and N₂ and CO₂ were formed in the reaction of CN with NO₂. The possibility of HCN being an important intermediate in the SCR of NO over Cu-ZSM-5 was considered by Cant and Liu.²⁷ They propose two possible reaction paths for the formation of N₂ from HCN. One is the reaction between adsorbed CN and NO₂ to form N₂ and CO₂ (reaction 2 above). They argue that this reaction is feasible due to the presence of NO₂ at the reaction temperature of their study. The second reaction path to N₂ formation is a two-step process, in which HCN is first hydrolyzed to NH₃, which in turn is converted to N₂ by NH₃-SCR. Hydrolysis can proceed on acidic OH groups, or via hydration to formamide followed by a standard acid-catalyzed reaction on Brönsted acidic sites. (These authors also report on the formation of substantial amounts of C₂N₂ both in HCN + NO + O₂ and HCN + O₂ reactions.)

Also, as we have mentioned previously, the reaction between CN and NO₂ was observed to be much faster than that between NCO and NO₂. On the other hand, surface NCO was proposed as the key intermediate in the formation of N₂ over Ag-TiO₂-ZrO₂ catalysts.²⁵ The reaction between -NCO and NO to form N₂ was proposed to be much faster than that between -CN and NO. In our study we find that both -NCO and -CN can react with NO_x and N₂ can form in both reactions; however, the rate of N₂ formation in these two reactions cannot be compared from the results of our study.

The series of reactions (1–6) we propose can explain both the formation of N₂, CO₂, CO, N₂O, and C₂N₂ in the overall reaction, and the observed changes in -CN/-NCO ratio as the HCN/NO₂ ratio is changed. At low NO₂ levels, we see mostly the formation of surface -CN species, while at higher NO₂ concentrations, surface -NCO is formed in the expense of surface -CN, in accordance with reaction 6. The high concentration of surface cyanide species observed throughout this study also explains the relatively high levels of C₂N₂ measured by mass spectrometry. All of these results help us answering our key question that we set out to address: whether

HCN or adsorbed cyanide species can be important intermediates, or whether they are only byproducts of some side reactions. We believe that HCN/CN is an important intermediate in the overall reaction mechanism, and possibly the key intermediate in the formation of N₂. Our results strongly support a mechanism in which N₂ is formed by the direct reaction between CN and NCO species and NO_x. The alternative reaction path that involves the formation of NH₃ by hydrolysis, and the subsequent NH₃-SCR process is not supported by our findings. We did not, under any circumstances, observe the formation of NH₃ or NH₄⁺ that are crucial in the NH₃-SCR reaction (not even in experiments when we added NH₃+NO₂+H₂O onto the BaY catalyst). When we exposed the BaY catalyst to water following HCN + NO₂ reaction, we did not observe the fast hydrolysis of adsorbed NCO species or the appearance of IR features that would support the formation of species containing NH_x (NH₃, NH₄⁺, etc.) entities that is mentioned in some mechanistic studies.¹⁹ There was no increase in the IR signature of CO₂, which would be the other product of the proposed hydrolysis, as well. We only observe a shift in the ν_{CN} frequency of the adsorb CN⁻ species from 2167 to 2174 cm⁻¹ as these species interact with zeolitic OH groups rather than NO⁺ species in the absence of water (Figure 9). The results of these experiments, however, cannot rule out the possibility that under practical catalytic conditions when the concentration of water is much higher than that in this study the formation of NH_x-containing intermediates (e.g., NH₄NO₂) becomes significant. Our experimental set up, however, did not facilitate investigations under these very high water concentrations.

Conclusion

Both Na- and Ba-Y zeolites adsorb HCN molecularly, and the strength of HCN adsorption is much higher on Ba-Y than on Na-Y. Up to 473 K, no reaction between the catalysts and HCN was observed. At 300 K, there is no reaction between HCN and NO₂ on Na-Y, while this reaction proceeds on Ba-Y even at this low temperature. The IR absorption features seen on the two catalyst samples in the HCN + NO₂ reaction at 473 K are very similar, although the intensities of these features are much lower on Na-Y than on Ba-Y, due to the much higher catalytic activity of the latter. In the gas-phase N₂, N₂O, NO, CO, and CO₂ was observed after the reaction at 473 K, while adsorbed cyanide and cyanate species were detected on both catalyst surfaces. Postreaction mass spectrometric analysis also revealed the formation of a significant amount of C₂N₂ formed by the dimerization of adsorbed cyanide species. The results of this investigation strongly suggest that HCN/CN can be an important intermediate in the overall NO_x reduction on these zeolite catalysts. Adsorbed CN⁻ and NCO⁻ ionic species formed in the HCN + NO₂ reaction are believed to be the important surface intermediates. Their reaction with ionic NO_x species (in particular with NO⁺) can lead to the formation of the N-N bond.

Acknowledgment. The authors gratefully acknowledge the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, FreedomCAR, and Vehicle Technologies for 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 at the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE Office of Biological and

Environmental Research and located at the Pacific Northwest National Laboratory (PNNL). PNNL is operated for the U.S. DOE by Battelle Memorial Institute under Contract No. DE-AC0676RLO1831.

References and Notes

- (1) McLarnon, C. R.; Penetrante, B. M. SAE 982433.
- (2) Penetrante, B. M.; Brusasco, R. M.; Merritt, B. T.; Pitz, W. J.; Vogtlin, G. E.; Kung, M. C.; Kung, H. H.; Wan, C. Z.; Voss, K. E. SAE 983508.
- (3) Balmer, M. L.; Tonkyn, R. G.; Yoon, S.; Kolwaite, A.; Barlow, S.; Maupin, G.; Hoard, J. W. SAE 1999-01-3640.
- (4) Panov, A. G.; Tonkyn, R. G.; Balmer, M. L.; Peden, C. H. F.; Malkin, A.; Hoard, J. W. SAE 2001-01-3513.
- (5) Kwak, J. H.; Szanyi, J.; Peden, C. H. F. *J. Catal.* **2003**, *220*, 291.
- (6) Kwak, J. H.; Szanyi, J.; Peden, C. H. F. *Catal. Today* **2004**, *89*, 135.
- (7) Radtke, F.; Köppel, R. A.; Baiker, A. *Catal. Today* **1995**, *26*, 159.
- (8) Aylor, A. W.; Lobree, L. J.; Reimer, J. A.; Bell, A. T. *Stud. Surf. Sci. Catal.* **1996**, *101*, 661.
- (9) Bell, V. A.; Feeley, J. S.; Deeba, M.; Farrauto, R. J. *Catal. Lett.* **1994**, *29*, 15.
- (10) Hayes, N. W.; Grünert, W.; Hutchings, G. J.; Joyner, R. W.; Shpiro, E. S. *J. Chem. Soc. Commun.* **1994**, 531.
- (11) Szanyi, J.; Kwak, J. H.; Moline, R. A.; Peden, C. H. F. *J. Phys. Chem. B* **2004**, *108* (44), 17050.
- (12) Szanyi, J.; Kwak, J. H.; Peden, C. H. F. *in preparation*.
- (13) Low, M. J. D.; Ramasubramanian, N.; Ramamurthy, P.; Deo, A. V. *J. Phys. Chem.* **1968**, *72* (7), 2371.
- (14) Morrow, B. A.; Cody, I. A. *J. Chem. Soc., Faraday Trans. I* **1975**, *71*, 1021.
- (15) Rasko, J.; Bansagi, T.; Solymosi, F. *PCCP* **2002**, *4*, 3509.
- (16) Jentz, D.; Celio, H.; Mills, P. Trenary, M. *Surf. Sci.* **1995**, *341*, 1.
- (17) Szanyi, J.; Kwak, J. H.; Moline, R. A.; Peden, C. H. F. *PCCP* **2003**, *5* (18), 4045.
- (18) Szanyi, J.; Kwak, J. H.; Peden, C. H. F. *J. Phys. Chem. B* **2004**, *108*, 3746.
- (19) Yeom, Y. H.; Wen, B.; Sachtler, W. M. H.; Weitz, E. *J. Phys. Chem. B* **2004**, *108*, 5386.
- (20) Solymosi, F.; Bansagi, T. *J. Catal.* **1995**, *156*, 75.
- (21) Cowan, A. D.; Cant, N. W.; Haynes, B. S.; Nelson, P. F. *J. Catal.* **1998**, *176*, 329.
- (22) Lombardo, E. A.; Sill, G. A.; d'Itri, J. L.; Hall, W. K. *J. Catal.* **1998**, *173*, 440.
- (23) Schmieg, S. J.; Cho, B. K.; Oh, S. E. SAE 2000-01-3565.
- (24) Hoard, J. W.; Panov, A. SAE 2001-01-3512.
- (25) Haneda, M.; Kintaichi, Y.; Inaba, M.; Hamada, H. *Catal. Today* **1998**, *42*, 127.
- (26) Cant, N. W.; Cowan, A. D.; Liu, I. O. Y.; Satsuma, A. *Catal. Today* **1999**, *54*, 473.
- (27) Liu, I. O. Y.; Cant, N. W. *J. Catal.* **2000**, *195*, 352.