

# Catalytic oxidation of HCN over a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst

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## Abstract

The adsorption of HCN on, its catalytic oxidation with 6% O<sub>2</sub> over 0.5% Pt/Al<sub>2</sub>O<sub>3</sub>, and the subsequent oxidation of strongly bound chemisorbed species upon heating were investigated. The observed N-containing products were N<sub>2</sub>O, NO and NO<sub>2</sub>, and some residual adsorbed N-containing species were oxidized to NO and NO<sub>2</sub> during subsequent temperature programmed oxidation. Because N-atom balance could not be obtained after accounting for the quantities of each of these product species, we propose that N<sub>2</sub> was formed. Both the HCN conversion and the selectivity towards different N-containing products depend strongly on the reaction temperature and the composition of the reactant gas mixture. In particular, total HCN conversion reaches 95% above 250 °C. Furthermore, the temperature of maximum HCN conversion to N<sub>2</sub>O is located between 200 and 250 °C, while raising the reaction temperature increases the proportion of NO<sub>x</sub> in the products. The co-feeding of H<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub> had little, if any effect on the total HCN conversion, but C<sub>3</sub>H<sub>6</sub> addition did increase the conversion to NO and decrease the conversion to NO<sub>2</sub>, perhaps due to the competing presence of adsorbed fragments of reductive C<sub>3</sub>H<sub>6</sub>. Evidence is also presented that introduction of NO and NO<sub>2</sub> into the reactant gas mixture resulted in additional reaction pathways between these NO<sub>x</sub> species and HCN that provide for lean-NO<sub>x</sub> reduction coincident with HCN oxidation.

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## 1. Introduction

Hydrogen cyanide (HCN) is observed as an unfortunate byproduct of hydrocarbon selective catalytic reduction (HSCR) of NO<sub>x</sub> over oxide-based catalysts in lean exhaust [1]. For example, we regularly observe HCN exiting a basic zeolite (Na-Y or Ba-Y) catalyst used in a non-thermal plasma/catalytic process studied for application in treating NO<sub>x</sub> emissions from diesel vehicles [2]. C–N bond formation on the catalyst surface, via reactions between adsorbed NO<sub>x</sub> and hydrocarbon species, is considered to be an essential step in the mechanism of HSCR so HCN may well be an unavoidable byproduct of this process. Hydrogen cyanide can also be produced in the process of coal gasification, which constitutes an important consideration for the utilization of the gas [3–5]. In both cases, it is reasonable to propose the use of downstream catalysts for the removal of HCN from these process streams.

Platinum supported on alumina is a very efficient catalyst for hydrocarbon [6–11] and CO oxidation [12–16]. Studies have also shown that NH<sub>3</sub> is readily oxidized on Pt-based catalysts [17–19]. Since the HCN molecule contains both low oxidation state carbon and nitrogen, it is reasonable to expect that Pt/Al<sub>2</sub>O<sub>3</sub> would be active for catalytic HCN oxidation. To our knowledge, there have been only two very brief reports [20,21] in the literature suggesting that HCN can, in fact, be oxidized by O<sub>2</sub> on supported Pt catalysts. Neither of these studies was concerned with identifying the mechanism of this catalytic process.

Catalytic CO and hydrocarbon oxidation reactions over Pt involve the adsorption of oxygen on the metal surface. Similarly, we expect that an important component of any mechanistic HCN oxidation model will include an interaction with chemisorbed oxygen at the active Pt surface sites. Atomic oxygen at the surface of Pt(1 1 1) is the predominant form of adsorbed oxygen upon adsorption of O<sub>2</sub> at temperatures above 150 K [22]. Under UHV conditions, the maximum surface coverage of oxygen was found to be 0.25 oxygen atoms per surface Pt atom [23–25]. However, the coverage increased when either NO<sub>2</sub> [23] or ozone [26] was used as the oxygen

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atom source. Moreover, oxygen adsorption studies at atmospheric pressure show the formation of different platinum oxides [27,28]. The adsorbed O-atom on the platinum surface makes it an efficient oxidation catalyst useful even for the oxidation of soot [29].

Yates and coworkers [30] studied the adsorption of HCN on Pt(1 1 1) and Pt(1 1 2) single crystal surfaces, as well as the reaction of HCN with atomically adsorbed oxygen on these surfaces. HCN dissociation to H(ad) and CN(ad) is shown to be a facile process, leading to recombinative desorption products H<sub>2</sub>, HCN and cyanogen (C<sub>2</sub>N<sub>2</sub>) during TPD. The presence of only these products suggests that no C–N bond breaking occurs under their experimental conditions. In fact, C<sub>2</sub>N<sub>2</sub> desorbs at relatively high temperatures (~680 K) on Pt surfaces again suggesting substantial stability for CN(ad) [30a]. When coadsorbed with atomic oxygen, Yates and coworkers find the additional products H<sub>2</sub>O, CO, CO<sub>2</sub>, and N<sub>2</sub> on both surfaces while the Pt(1 1 2) surface also produces a small amount of NH<sub>3</sub>. The authors propose that HCN is oxidized through an isocyanate (NCO) intermediate as a pre-requisite for C–N bond breaking on the Pt surface.

An important issue for HCN oxidation is the product selectivity. Besides the more desirable products, CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>, N<sub>2</sub>O, NO<sub>x</sub> and C<sub>2</sub>N<sub>2</sub> might also be expected to form. In UHV TPD studies, Yates and coworkers showed that the selectivity towards N<sub>2</sub> over C<sub>2</sub>N<sub>2</sub> increases with oxygen atom coverage [30b]. However, the overwhelming excess of oxygen in diesel exhaust may lead to the regeneration of NO<sub>x</sub> (NO and NO<sub>2</sub>). This latter undesirable reaction pathway should be minimized by choosing the right reaction conditions.

In this paper, we report on the effect of reaction temperature on HCN conversion and selectivity to N-containing products over a supported platinum catalyst. To our knowledge, the present work represents the first detailed mechanistic study to be published concerning HCN oxidation over supported Pt catalysts. We find that at moderate temperatures (200–250 °C), HCN oxidation leads to the formation of primarily the benign N-containing products, N<sub>2</sub> and N<sub>2</sub>O, while still higher temperatures result in the formation of undesirable NO<sub>x</sub> (NO and NO<sub>2</sub>) species. Diesel exhaust, after passing through a non-thermal plasma and zeolite catalyst, is mainly composed of N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O. Small quantities of NO, NO<sub>2</sub>, hydrocarbon and HCN are also present at ppm levels. By co-feeding small concentrations of NO, H<sub>2</sub>O, NO<sub>2</sub>, and propene (C<sub>3</sub>H<sub>6</sub>) with HCN, we studied their effects on the HCN oxidation reaction over Pt under quasi-realistic conditions. Importantly, HCN is shown to be oxidized by NO<sub>x</sub> (NO and NO<sub>2</sub>) leading to the effective removal of both of the undesirable species from an exhaust stream. As background to this study, we measured the adsorption and reaction of these species, but only briefly describe the results for HCN adsorption in this paper.

## 2. Experimental

We used a commercially available platinum catalyst containing 0.5% Pt on Al<sub>2</sub>O<sub>3</sub> (Alfa). The catalyst was pretreated at 450 °C with 6% O<sub>2</sub> (UHP, Air Liquide) for 3 h,

then exposed to a flow of pure N<sub>2</sub> overnight. All experiments were performed at a flow rate of 1 standard liter per minute (slm), with N<sub>2</sub> as the balance gas. Mixtures of NO<sub>2</sub> (0.55%), HCN (0.5%) and NO (0.5%) in N<sub>2</sub> were purchased from Scott Specialty Gases. A mixture of N<sub>2</sub>O (100 ppm) in N<sub>2</sub> was supplied by Matheson, and C<sub>3</sub>H<sub>6</sub> (3.02%) in He was obtained from Air Liquide. Reactions were carried out in a quartz fixed bed reactor with an i.d. of 0.62 in. All experiments utilized 2.1 g of catalyst which had a volume of 2 cm<sup>3</sup> when loaded into the reactor. The catalyst pellets were cylindrical extrudates 0.13 in. in length and 0.13 in. in diameter. The gas hourly space velocity (GHSV), which was determined from the standard flow rate of the gas over by the catalyst bed volume, was 30,300 h<sup>-1</sup>.

The reactor was heated by a cylindrical ceramic fiber heater (WATLOW). Mass flow controllers were used to control and regulate the influent gases (MKS Type 1179 A and Tylan Model FC-260). A variable fraction of the nitrogen flow could be diverted to a water bubbler to adjust the relative humidity of the gas stream. The water concentration was measured by both the FTIR and a humidity transmitter (Vaisala HMP235) in the gas manifold. After the gas constituents were combined and mixed, a three-way valve directed the gas flow either through or around the catalyst reactor and into the FTIR for analysis. The experimental apparatus was very similar to that described by Yoon et al. in an earlier publication [31].

The effluent gas was continuously analyzed by an FTIR spectrometer (Nicolet Magna IR 560, OMNIC QuantPad software) equipped with a heated 2 m multiple path gas cell and a liquid nitrogen cooled MCT detector. For each FTIR spectrum, 25 scans were collected at 0.5 cm<sup>-1</sup> resolution. The concentrations of HCN, NO, N<sub>2</sub>O, NO<sub>2</sub>, H<sub>2</sub>O, CO and CO<sub>2</sub> were quantified by applying a method developed in-house for the OMNIC QuantPad software after taking calibration spectra. Neither N<sub>2</sub> nor C<sub>2</sub>N<sub>2</sub> could be detected in these experiments; N<sub>2</sub> is not IR active and the detection limit for C<sub>2</sub>N<sub>2</sub> is estimated to be ~10 ppm. Thus, their combined concentrations were calculated from N atom balance, assuming all the missing N was converted to one of these two products. In the discussion, however, we will make some arguments about the possible distribution of these two products for a variety of experimental conditions.

A typical experiment proceeded in the following way. The desired gas mixture was fed through the bypass line for a time sufficient to achieve a constant gas composition measurement by FTIR. During this time, the catalyst was maintained at the initial reaction temperature in a static atmospheric pressure of N<sub>2</sub>. After stabilizing, the reactant gas mixture was switched to flow through the reactor and over the catalyst. A small drop in reactant concentration is expected for a short period of time as the reactor volume is flushed with the reactant gas mixture. Additionally, a small temperature rise in the catalyst bed was consistently observed due, in part, to changes in the thermal properties of the gas. Some of this increase may also be the result of the heat of adsorption/reaction but we were unable to separate these effects. For the HCN adsorption experiments, a 30 ppm HCN in N<sub>2</sub> gas mixture was flowed over the catalyst bed, held at 200 °C, for approximately 30 min while

continuously monitoring the effluent by FTIR (we will refer to this period as the “adsorption and reaction phase”). At this point, the gas mixture was again switched to a pure  $N_2$  flow. The catalyst temperature was subsequently increased in a monotonic fashion to  $\sim 400$  °C (referred to here as the “temperature programmed desorption (TPD) phase”) while the formation of additional N- and C-containing products, arising from strongly adsorbed species, were again monitored by FTIR. With the catalyst temperature held at  $\sim 400$  °C, the  $N_2$  flow was switched again to a 6%  $O_2$  in  $N_2$  gas mixture at  $\sim 400$  °C to ensure complete oxidation and removal of residual N- and C-containing species strongly adsorbed on the catalyst. Similar procedures were used for the catalytic HCN oxidation experiments. Notably, after exposure of the catalyst to the reactant gas mixture for 20–30 min (a period we will refer to in this case as the “quasi-steady-state reaction” phase), all reactants other than  $O_2$  were shut off. The 6%  $O_2$  in  $N_2$  mixture continued to flow over the catalyst while the temperature was increased in a monotonic fashion to  $\sim 420$  °C (referred to here as the temperature programmed oxidation or “TPO phase”). The formation of oxidized N- and C-containing products arising from strongly adsorbed species was monitored by FTIR.

### 3. Results and discussion

The results in this section begin with a discussion of HCN adsorption and desorption on 0.5% Pt/ $Al_2O_3$ . Then, we describe the reaction of HCN with oxygen at 210 °C and our subsequent study of the temperature dependence of the product distribution. These sections are followed by our studies of the additional effects of water, propene and  $NO_x$  on the rates and selectivity of HCN oxidation.

#### 3.1. HCN adsorption and desorption on 0.5% Pt/ $Al_2O_3$

Fig. 1 shows the results of a study of HCN adsorption and reaction with a 0.5% Pt/ $Al_2O_3$  catalyst at 200 °C. As shown in

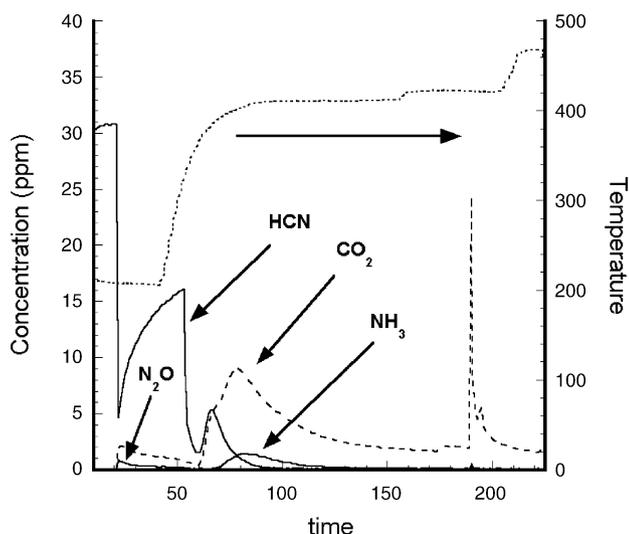


Fig. 1. Adsorption of 30 ppm HCN on 0.5% Pt/ $Al_2O_3$  at 200 °C followed by temperature programmed desorption.

the figure, approximately half of HCN was still adsorbing and/or reacting on the catalyst after  $\sim 30$  min, while only a small amount of  $N_2O$  appeared in the gas phase. We observed a small but significant quantity of  $CO_2$  during the “adsorption and reaction phase”, as well as the desorption of CO and  $CO_2$  during the “TPD phase”. In the absence of  $O_2$  in the feed, these products may form from reactions with residual O(ad) not removed by flowing  $N_2$  overnight over the catalyst at 450 °C. We cannot completely rule out the possibility that our gas feed is contaminated with a very small amount of oxygen, although gas purities are periodically checked with a mass spectrometer, FTIR, and/or the GC. Thus although unlikely we believe, this represents another possible source for residual oxygen.

During the “TPD phase” of the experiments, the observed desorption products included  $CO_2$ , HCN,  $NH_3$ , and CO, as shown in Fig. 1. For all of the HCN experiments, we expected that strongly bound atomic C(ad) and/or N(ad) species were plausible reaction products. As such, subsequent to the “TPD phase” of the experiments we again switched the gas from a pure  $N_2$  flow to 6.1%  $O_2$  in  $N_2$  mixture at 420 °C. This led to a further evolution of NO,  $NO_2$ , and  $CO_2$  via oxidation of the residual N- and C-containing species. The  $CO_2$  evolved at this time was in excess of the evolved  $NO_x$ .

Via integration of the appropriate curves in Fig. 1, we determined that  $\sim 26$   $\mu\text{mol}$  HCN was lost in the 30-min “adsorption and reaction phase” with only a trace of  $N_2O$  out. The only other product in the adsorption stage other than HCN was  $CO_2$ . As the temperature was raised in the “TPD phase”, some HCN and  $NH_3$  desorbed, but over the entire experiment only about 9  $\mu\text{mol}$  of N (approximately 4  $\mu\text{mol}$  of HCN, 2  $\mu\text{mol}$  of  $NH_3$ , 2  $\mu\text{mol}$  of  $NO_x$  (NO and  $NO_2$ ), and 1  $\mu\text{mol}$  of  $N_2O$ ) were recovered. The most likely products that can account for this missing N are  $N_2$ (g) and  $C_2N_2$ , both of which are difficult (impossible for  $N_2$ ) to detect with FTIR. Whether either product forms continuously during the “adsorption and reaction phase” and/or during the “TPD phase” cannot be determined from these experiments. It is possible to distinguish between the two possible products ( $N_2$  and/or  $C_2N_2$ ) that can explain the missing N, by accounting for the carbon that will also come from HCN. To repeat,  $\sim 26$   $\mu\text{mol}$  of HCN were lost during the “adsorption and reaction phase” while only about 4  $\mu\text{mol}$  of HCN were recovered during the “TPD phase”; thus,  $\sim 22$   $\mu\text{mol}$  of carbon need to be accounted for. Some of this missing carbon is recovered as CO and  $CO_2$  at various stages of the experiment and some may be in the reaction product  $C_2N_2$  that we cannot measure. Integrating the CO and  $CO_2$  curves in Fig. 1 over the course of the experiment yields a total of 30  $\mu\text{mol}$ , an amount that actually exceeds the amount of HCN lost. In fact, the error bar on the  $CO_2$  measurement is somewhat higher than other species due to experimental difficulties in calibrating its FTIR spectrum. Despite this, the degree of carbon balance we obtain (again, actually more carbon in products than that lost by HCN removal), and the corresponding significant lack of nitrogen balance argues that there must be at least some  $N_2$  production as the formation of  $C_2N_2$  cannot adequately account for the missing nitrogen.

We ran a similar HCN adsorption/desorption experiment at 40 °C, with very similar results. The only difference was a significant molecular HCN desorption centered at 117 °C (390 K). This is well below the exhaust temperature of even small diesel engines, and hence probably is not an important species under practically relevant conditions. Interestingly, the HCN uptake in 30 min was again 26  $\mu\text{mol}$ . The similarity in the amount of HCN taken up at 40 and 200 °C suggests that we have complete HCN dissociation on Pt in either case.

Under UHV conditions, HCN dissociates on Pt(1 1 1) [30a,30b,32,33], Pt(1 1 0) [34,35], Pt(1 1 2) [30a] and polycrystalline Pt foils [36] to give H(ad) and CN(ad) species that then recombinatively desorb during TPD to yield H<sub>2</sub>(g), HCN(g) and C<sub>2</sub>N<sub>2</sub>(g) without any C–N bond breaking. On Pt(1 1 1), an HCN desorption peak at 264 K was assigned to recombination of CN(ad) and H(ad) [33]. FTIR studies indicate that a C–NH<sub>2</sub> intermediate exists on Pt(1 1 1) between 250 and 400 K [32,33], which decomposes by the sequential loss of hydrogen between 400 and 450 K. This decomposition causes desorption of HNC or HCN. Levoguer and Nix [36] proposed that the intermediate is more likely *trans*-HC:NH at 400 K when HCN was adsorbed on a polycrystalline Pt foil, and the decomposition of this intermediate gives the desorption of HCN at 400–500 K. Thus, the HCN desorption peak around 117 °C observed in our HCN adsorption experiments performed at 40 °C could be from decomposition of CNH<sub>2</sub> or HC–NH intermediates.

Because of the observation of CO<sub>2</sub> and CO during the “adsorption and reaction” and “TPD” phases of the HCN experiments (Fig. 1), we consider the possible roles for residual O(ad) in the mechanism of HCN reactions with Pt. Yates and coworkers [30b], in studies of the oxidation of HCN on Pt(1 1 1) and Pt(1 1 2) by coadsorption with O<sub>2</sub>, observed HCN, C<sub>2</sub>N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> as desorption products in their experiments. An adsorbed isocyanate species, NCO(ad), has been proposed to be an intermediate in the oxidation of CN(ad) groups on Cu(1 1 1) [37], Cu(1 1 0) [38], Rh(1 1 1) [39], Pt(1 1 1) and Pt(1 1 2) [30b]. Gorte et al. [40] found that HNCO was unstable on Pt(1 1 1) above 250 K and desorbed as CO, N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub>. Yates and coworkers [30b] proposed that the isocyanate species formed on both Pt(1 1 1) and Pt(1 1 2) at 200–250 K and quickly decomposed to CO(ad) and N(ad). Although we do not have direct evidence for a similar mechanism on Pt/Al<sub>2</sub>O<sub>3</sub>, an isocyanate adsorbed species seems to be a possible and perhaps likely intermediate in order to explain the production of carbon oxides in our experiments. Notably, the results obtained after switching to an O<sub>2</sub>-containing gas mixture at  $\sim$ 400 °C suggest that C–N bond breaking has occurred to some extent. We observe that after introduction of the 6.1% O<sub>2</sub> in N<sub>2</sub> flow over the catalyst at 420 °C, desorption of CO<sub>2</sub> was much larger than desorption of detectable N-containing species. Thus, either the remaining CN(ad) is oxidized almost exclusively to CO<sub>2</sub> and N<sub>2</sub> or some CN(ad) species had already decomposed to C(ad) + N<sub>2</sub>(g) before the O<sub>2</sub> was introduced.

### 3.2. The reaction of HCN with O<sub>2</sub>

We introduced 30 ppm of HCN and 6% O<sub>2</sub> into the reactor for  $\sim$ 30 min at 210 °C, at which point the HCN was shut off and the reactor temperature increased in a monotonic fashion to 425 °C. The FTIR-measured concentrations of HCN, NO, NO<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> during this entire experiment (both “quasi-steady-state” and “TPO” phases) are shown in Fig. 2. Nearly constant concentrations of all of these species are obtained after  $\sim$ 30 min reaction during the “quasi-steady-state” phase. As such, we will use the species concentrations measured at this point of the reaction to indicate ‘steady-state’ activity. The HCN removal was excellent, with less than 3 ppm escaping the reactor. The observed products at the end of this “quasi-steady-state” phase of the experiment included 0.9 ppm NO, 0.7 ppm NO<sub>2</sub>, 6.7 ppm N<sub>2</sub>O as well as 20 ppm CO<sub>2</sub>.

Even after 30 min we did not obtain complete carbon balance. The sharp rise in the CO<sub>2</sub> signal towards steady state suggests a considerable amount of adsorption occurred. Similarly, a significant fraction of the reacting HCN cannot be accounted for by the measured amounts of nitrogen-containing products NO, NO<sub>2</sub> and N<sub>2</sub>O at the end of the end of the 30 min “quasi-steady-state” phase of the experiment. In particular, while  $\sim$ 27 ppm of HCN were missing at this point, only  $\sim$ 15 ppm (0.9 + 0.7 + [2  $\times$  6.7] ppm) of nitrogen atoms appeared in the observed products. Thus, the ‘steady-state’ amount of ‘missing’ nitrogen atoms after 30 min of reaction was 12 ppm. As noted above, both N<sub>2</sub> and C<sub>2</sub>N<sub>2</sub> are possible nitrogen-containing products that cannot be measured in our experiments.

During the subsequent “TPO” phase of the experiment, additional amounts of NO, NO<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> were formed as

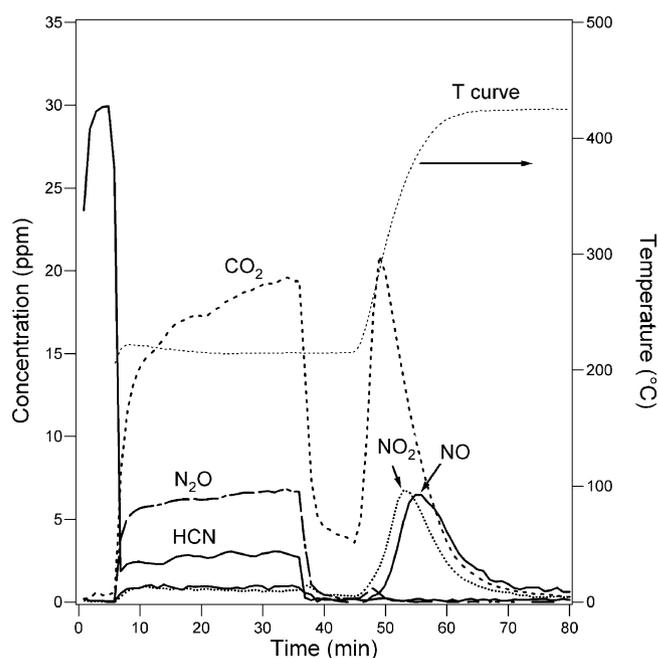
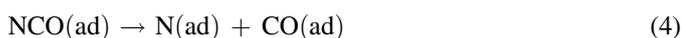
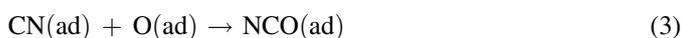


Fig. 2. 30 ppm HCN reaction with 6% O<sub>2</sub> at 212 °C on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub>. The reaction was carried out for 30 min, followed by removal of HCN from the reaction mixture and a subsequent temperature programmed oxidation. Reactant (HCN) and product concentrations, as measured by FTIR, are plotted.

a result of oxidation of residual N- and C-containing species. The desorption peaks for the  $\text{NO}_x$  products, NO,  $\text{NO}_2$  and  $\text{N}_2\text{O}$ , were found at 388, 360, and 257 °C, respectively. In our other experiments (not shown here), we observed that, while  $\text{N}_2\text{O}$  did not adsorb at all at temperatures above 150 °C, the adsorption of NO and  $\text{NO}_2$  on 0.5% Pt/ $\text{Al}_2\text{O}_3$  led to molecular desorption of these species at ~340 and ~300 °C, respectively. These latter temperatures are somewhat to considerably lower than those obtained in the HCN oxidation experiments shown in Fig. 2. Thus, the  $\text{NO}_x$  species observed in the “TPO phase” most likely arise from the oxidation of adsorbed N-containing species produced by HCN dissociation on the Pt/ $\text{Al}_2\text{O}_3$ . As will be discussed below, CN(ad) or NCO(ad) likely accounts for most if not all of the residual nitrogen and carbon species giving rise to products during the “TPO phase”. Over the course of the entire experiment we obtained excellent carbon balance, but a noticeable nitrogen deficit remained. The excellent carbon balance suggests that  $\text{C}_2\text{N}_2$  cannot be a significant gas phase product in our experiments. The noticeable nitrogen deficit most likely indicates  $\text{N}_2$  formation, although we cannot say from our data whether this occurred at 200 °C during “quasi-steady-state” or during the “TPO phase”.

It is reasonable to presume that many of the elementary steps leading to  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation during the “quasi-steady-state” oxidation of HCN studied here would be similar to those proposed for HSCR of  $\text{NO}_x$  over Pt catalysts. In the latter process, adsorbed N-atoms, N(ad), are the most likely reaction intermediate leading to the formation of reduced N-containing products [41]. HCN(g) can be expected to dissociatively adsorb on Pt forming H(ad) and CN(ad); however, direct CN(ad) decomposition to C(ad) and N(ad) is unlikely [30a]. Rather, N(ad) formation has been proposed to arise from decomposition of an intermediate NCO(ad) species, itself formed by reaction of CN(ad) and O(ad) [30b]. Molecular  $\text{N}_2$  formation then arises from recombinative desorption of N(ad), while N(ad) and H(ad) can also be oxidized by O(ad) to NO,  $\text{NO}_2$ , and  $\text{H}_2\text{O}$ . The production of  $\text{N}_2\text{O}$  can then be accounted for by a reaction between NO(ad) and N(ad). Besides N(ad), dissociation of the proposed NCO(ad) intermediate also produces CO(ad). Because  $\text{CO}_2$  is the only gas-phase carbon-containing product observed here, this CO(ad) must all be oxidized to  $\text{CO}_2$  by O(ad). The mechanisms just proposed can be summarized with following elementary reactions:



As noted above, some residual nitrogen and carbon containing specie(s) were present after ‘steady-state’ reaction, and they were oxidized in the “TPO phase” of the experiments to NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CO}_2$ . It is also possible that some additional  $\text{N}_2$  was formed during this period as well. We believe that this residual nitrogen and carbon arises from CN(ad) or NCO(ad). This follows from the fact that CN is strongly adsorbed on Pt and NCO(ad) can migrate to the  $\text{Al}_2\text{O}_3$  surface even though it is not stable on Pt sites [30].

The numerous elementary reactions described in Eqs. (1)–(10) are essentially the same as those previously proposed by Yates and coworkers [30b] from their UHV studies of HCN oxidation on single crystal Pt surfaces. Their rates are all expected to have varying sensitivities to temperature (varying activation energies) thereby affecting the selectivity of HCN oxidation as discussed next.

### 3.3. The rate and selectivity of the HCN + $\text{O}_2$ reaction versus temperature

With experimental procedures identical to those used to obtain the data shown in Fig. 2, HCN +  $\text{O}_2$  reactions were run at a variety of temperatures between 150 and 300 °C. Fig. 3 shows the total HCN conversion and the relative amounts of various N-containing products versus temperature measured at the end of (i.e., ~30 min into) the “quasi-steady-state” phase of the experiments. The latter values are plotted as the percentage of the initial HCN molecules present in the reactant feed converted to the products  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , NO and  $\text{N}_2$ . As above, since CN(ad) and NCO(ad) both lead to an equivalent amount of ‘missing’ carbon and nitrogen atoms,  $\text{N}_2$  is estimated to achieve N-balance by calculating the difference between the ‘missing’ nitrogen and ‘missing’ carbon atoms during the “quasi-steady-state” phase.

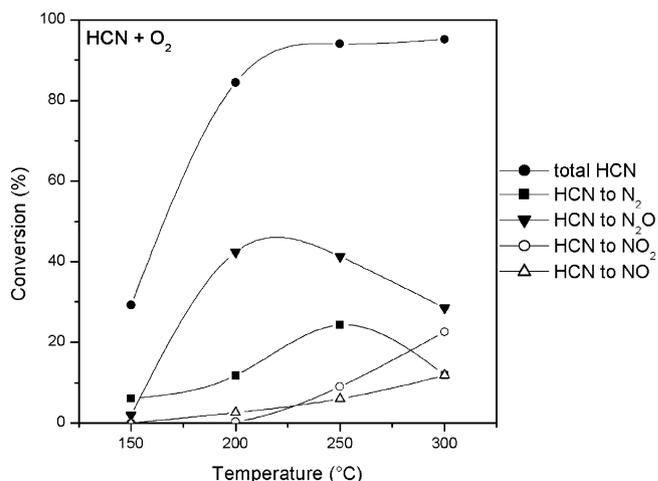
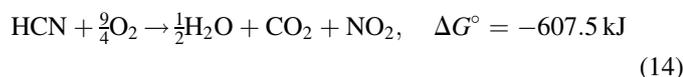
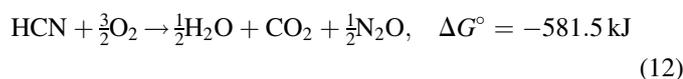
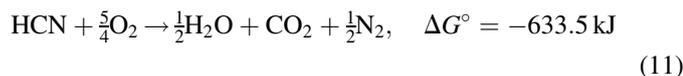


Fig. 3. HCN conversions to different N-containing products vs. reaction temperature when 30 ppm HCN reacts with 6%  $\text{O}_2$  on 0.5% Pt/ $\text{Al}_2\text{O}_3$ .

From the results shown in Fig. 3, the following important observations on the temperature dependence of the product selectivity of the HCN oxidation reaction over 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> can be made. (i) As the temperature was increased the total conversion of HCN markedly increased to more than 95% at or above 250 °C. We suspect the apparent upper limit to HCN conversion is due to a small fraction of the gas that avoids contact with the catalyst and hence remains untreated. (ii) No conversion to N<sub>2</sub>O, NO, and NO<sub>2</sub> was observed at 150 °C implying that selectivity to N<sub>2</sub> was 100% at this temperature. (iii) The selectivity for the most undesirable N-containing species, NO and NO<sub>2</sub>, only became significant at temperatures of 250 °C, and the NO<sub>x</sub> selectivity increased at still higher temperatures. (iv) The selectivity for N<sub>2</sub>O increased dramatically from 150 to 200 °C, reached a maximum at 250 °C, and then decreased at higher temperature. (v) The selectivity for N<sub>2</sub> formation has a similar relationship with temperature as that of N<sub>2</sub>O.

The oxidation of HCN is exothermic, and the various possible overall processes are summarized as follows:



All the above reactions are thermodynamically favorable under our reaction conditions and, indeed, we observe three of the reaction products and infer the fourth. The considerable excess of oxygen in principle favors the NO<sub>x</sub> forming reactions; however, these were not typically dominant. Rather, as alluded to above, the selectivity towards the reduced N-containing products, N<sub>2</sub> and N<sub>2</sub>O, originates from the different kinetic barriers for the elementary surface reactions (Eqs. (1)–(10)) that comprise the overall processes (Eqs. (11)–(14)) that lead to the various products.

The most likely explanation for the specific changes in selectivity towards NO<sub>x</sub> (NO and NO<sub>2</sub>) at higher temperatures is that the results reflect an increasing “steady-state” concentration of O(ad) due to an activated O<sub>2</sub> dissociation reaction that is fairly sluggish at low (<250 °C) temperatures. If the NO + O → NO<sub>2</sub> reaction is faster than N + NO → N<sub>2</sub>O, then an increase in O(ads) would result in increased NO<sub>2</sub> production at the expense of N<sub>2</sub>O. Alternatively the NO(a-d) + O(ad) reaction itself may be the most highly activated of the surface oxidation reactions (i.e., higher than the H(ad) and C(ad) oxidation reactions) and, thus, become more prominent at higher reaction temperatures. In either case, the increase in NO(g) can be explained by an increase in the NO desorption rate relative to the N + NO reaction.

#### 3.4. The effect of H<sub>2</sub>O or C<sub>3</sub>H<sub>6</sub> on the oxidation of HCN

Other oxidants and reductants, in the form of water and residual hydrocarbons, will be present in diesel engine exhaust. In fact, when the HSCR of NO<sub>x</sub> technology is applied, hydrocarbons may have to be added to obtain sufficient levels of NO<sub>x</sub> reduction. We studied the effect of separate addition of water or hydrocarbon on the overall rate and selectivity of the HCN oxidation reaction over the supported Pt catalyst. To simulate exhaust hydrocarbons in diesel engine exhaust, we followed the accepted practice of using propylene (C<sub>3</sub>H<sub>6</sub>).

Again with experimental procedures identical to those used to obtain the data shown in Fig. 2, Fig. 4 shows the HCN conversion to different N-containing products in the presence of 3550 ppm H<sub>2</sub>O. As before, N<sub>2</sub> production is estimated in order to obtain N-atom balance by calculating the difference between the ‘missing’ nitrogen and ‘missing’ carbon atoms at the end of the “quasi-steady-state” phase. A comparison of Figs. 3 and 4 suggests that co-feeding H<sub>2</sub>O has essentially no effect on the HCN conversion or the selectivity to N<sub>2</sub>O, NO, and NO<sub>2</sub> under the reaction conditions studied here. Co-feeding water has a small positive effect on the HCN conversion to N<sub>2</sub>, which lowers the reaction temperature for maximum HCN conversion.

Fig. 5 shows the HCN conversion and the selectivities to different N-containing products for HCN (30 ppm) + O<sub>2</sub> (6%) + C<sub>3</sub>H<sub>6</sub> (250 ppm) reactions run at a variety of temperatures between 150 and 300 °C. The HCN conversion to N<sub>2</sub> is not plotted due to the large carbon source from C<sub>3</sub>H<sub>6</sub>, which caused a problem in calculating the ‘missing’ carbon accurately. As with co-feeding H<sub>2</sub>O, the addition of 250 ppm C<sub>3</sub>H<sub>6</sub> has little, if any, effect on the total conversion of HCN. However, this comparison does show a fairly significant effect of C<sub>3</sub>H<sub>6</sub> addition on the selectivity of the HCN oxidation reaction towards NO production at high temperatures with a corresponding drop in NO<sub>2</sub> production. Within the mechanism proposed above in Eqs. (1)–(10), it is clear that the presence of adsorbed hydrocarbon could have an effect on a number of the

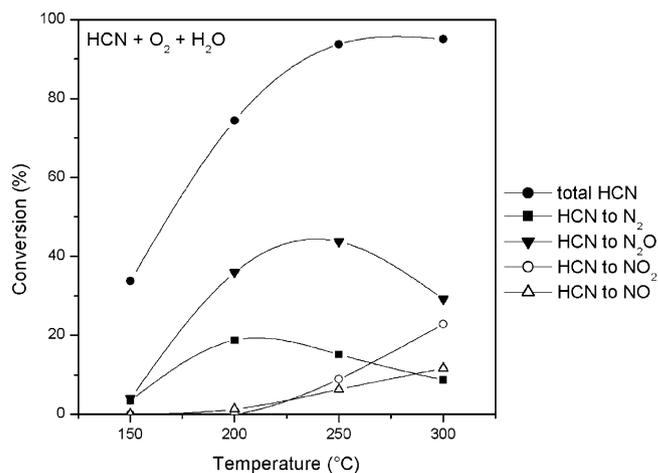


Fig. 4. HCN conversions to different N-containing products vs. reaction temperature when 30 ppm HCN reacts with 6% O<sub>2</sub> on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> in the presence of 3550 ppm H<sub>2</sub>O in the influent.

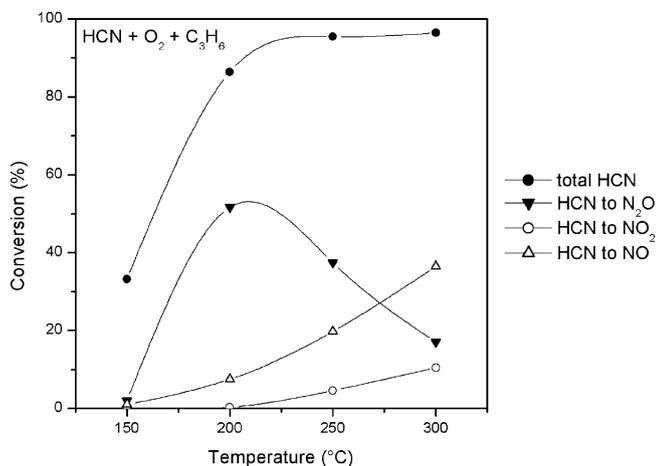


Fig. 5. HCN conversions to different N-containing products vs. reaction temperature when 30 ppm HCN reacts with 6% O<sub>2</sub> on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> in the presence of 250 ppm C<sub>3</sub>H<sub>6</sub> in the influent.

elementary reactions. For example, a relatively simple rationalization of this change in selectivity would be that C<sub>3</sub>H<sub>6</sub> suppresses the oxidation of NO to NO<sub>2</sub> by scavenging O-atoms from the surface.

### 3.5. The effect of NO<sub>x</sub> on the oxidation of HCN

Residual NO<sub>x</sub> (NO and NO<sub>2</sub>) will also be present following upstream lean-NO<sub>x</sub> catalysis. Because Pt is itself a good catalyst for hydrocarbon SCR, it is reasonable to wonder whether the synergistic removal of both HCN and NO<sub>x</sub> is possible with a downstream Pt catalyst. For this reason we studied the effect of separate addition of NO or NO<sub>2</sub> to the HCN oxidation gas mixture. In particular, Fig. 6 shows the total HCN conversion obtained after ~30 min reaction using a 30 ppm of HCN and 6% O<sub>2</sub> in N<sub>2</sub> gas mixture with either an

additional 35 ppm NO or 32 ppm NO<sub>2</sub>. In both cases, HCN conversion is moderately enhanced at a 150 °C reaction temperature, while at higher temperatures neither NO<sub>x</sub> species had an appreciable effect. Another notable difference was a small but significant amount of N<sub>2</sub>O production at the lowest reaction temperature studied here. Thus, the presence of NO<sub>x</sub> enhances the rate of HCN oxidation at 150 °C, implying that NO<sub>x</sub> reduction is also occurring. In our other experiments (not shown), we observed that both NO and NO<sub>2</sub> react with HCN in the absence of oxygen to form N<sub>2</sub>O and N<sub>2</sub>. This can be viewed as the Pt/Al<sub>2</sub>O<sub>3</sub> acting as a lean-NO<sub>x</sub> catalyst by utilizing HCN as the reductant.

Determining HCN conversion to different N-containing products, as was done in Figs. 3–5, is problematic. For example, it is difficult to determine whether an N-atom in any N<sub>2</sub>, N<sub>2</sub>O, NO, or NO<sub>2</sub> exiting the reactor came from the HCN or the reactant NO<sub>x</sub> species. Rather, we again present here raw data plots showing concentrations of all measured reactants and products at a particular reaction temperature as a function of time (similar to Fig. 2). For these, we choose to show the results obtained at a 200 °C reaction temperature because this represents a near-optimum temperature for lean-NO<sub>x</sub> SCR on Pt and is also a practically reasonable exhaust temperature in a light-duty diesel vehicle.

Figs. 7 and 8 show FTIR-measured concentrations of HCN, NO, NO<sub>2</sub>, NO<sub>x</sub> (NO + NO<sub>2</sub>), N<sub>2</sub>O, and CO<sub>2</sub> obtained as a function of time for a 200 °C reaction of 30 ppm of HCN and 6% O<sub>2</sub> in N<sub>2</sub> with an additional amount of either 35 ppm NO or 32 ppm NO<sub>2</sub>, respectively. In both cases, HCN concentrations drop from their initial value of ~30 ppm to less than 5 ppm. The % HCN removed at a 30 min reaction time is what is plotted in Fig. 6. What is also notable in Figs. 7 and 8 is that total NO<sub>x</sub> (NO + NO<sub>2</sub>) levels drop as well, even though we have shown above that NO<sub>x</sub> can be produced by Pt-catalyzed HCN oxidation. NO<sub>x</sub> reduction levels at 200 °C, calculated

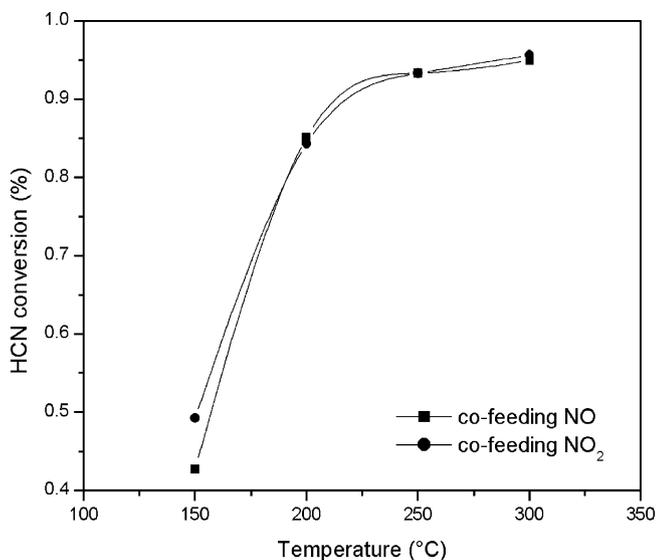


Fig. 6. HCN conversions vs. reaction temperature when 30 ppm HCN reacts with 6% O<sub>2</sub> on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> in the presence of either 35 ppm NO or 32 ppm NO<sub>2</sub> in the influent.

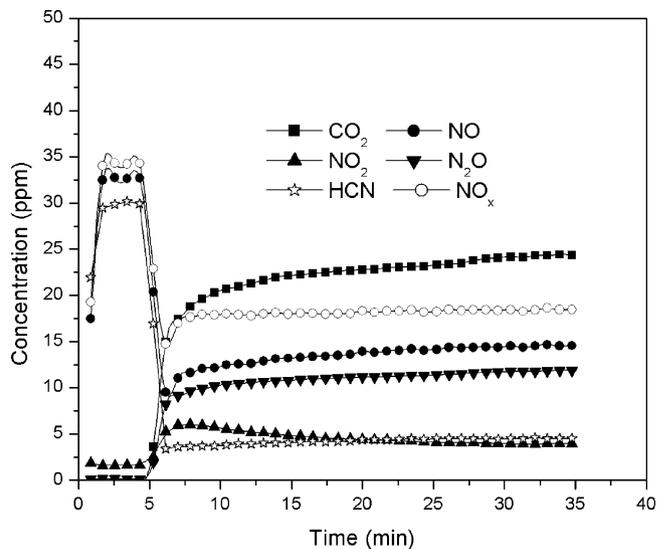


Fig. 7. 30 ppm HCN reaction with 6% O<sub>2</sub> and 35 ppm NO at 200 °C on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub>. Reactant (HCN and NO) and product concentrations, as measured by FTIR, are plotted.

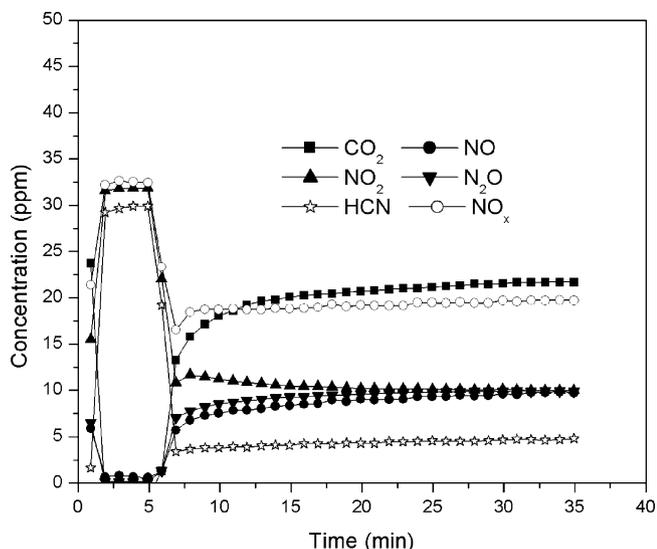


Fig. 8. 30 ppm HCN reaction with 6% O<sub>2</sub> and 32 ppm NO<sub>2</sub> at 200 °C on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub>. Reactant (HCN and NO<sub>2</sub>) and product concentrations, as measured by FTIR, are plotted.

from the data in Figs. 7 and 8, are ~49% and 42% for NO and NO<sub>2</sub> in the reactant gas mixture, respectively. In comparing Figs. 7 and 8 with Fig. 2, it is evident that the absolute amount of N<sub>2</sub>O produced during the reaction in the presence of NO<sub>x</sub> is higher. Similarly, if we again assume that all missing nitrogen (from both HCN and NO<sub>x</sub>) in Figs. 7 and 8 are due to produced N<sub>2</sub>, its absolute quantity has increased relative to HCN oxidation by O<sub>2</sub> alone.

#### 4. Summary

The adsorption of HCN at 200 °C almost certainly led to immediate dissociation into H(ad) and CN(ad). A small molecular HCN desorption peak at 265 °C only accounted for a very small fraction of the HCN adsorbed. Residual strongly bonded O(ad) species promoted the decomposition of CN(ad) in the 270–420 °C temperature range. Reactions between surface species lead to the desorption of CO, CO<sub>2</sub>, HCN and NH<sub>3</sub> in that temperature range. These species indicate the presence of N(ad), H(ad), CO(ad), O(ad), and possibly C(ad). In order to complete the nitrogen balance we assume a modest amount of N<sub>2</sub> was formed.

The oxidation of HCN by O<sub>2</sub> on Pt/Al<sub>2</sub>O<sub>3</sub> produces N<sub>2</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. Other reduced species, such as CO and NH<sub>3</sub>, were not observed in the highly oxidizing conditions used in our studies described here. While we cannot rule out formation of C<sub>2</sub>N<sub>2</sub> due to lack of analytical sensitivity to this species, we argue that it is not a significant reaction product in these experiments because we do, in fact, achieve a good carbon balance. Even in the presence of excess oxygen, the strongly bound reaction intermediate CN(ad) is fully oxidized only above 400 °C. The selectivity to different N-containing products depends significantly on the reaction temperature and on the composition of the reactant gas mixture. For simple HCN + O<sub>2</sub> in N<sub>2</sub> reaction at 150 °C, the only N-containing

product is N<sub>2</sub>, although the total HCN conversion is very low due to the accumulation of CN(ad) and perhaps other strongly bound species. The reaction pathway to N<sub>2</sub>O becomes significant when the catalyst temperature is raised to 200 °C. Raising the reaction temperature further to 250 °C and above leads to the appearance of NO<sub>x</sub> species (NO and NO<sub>2</sub>) as reaction products.

We also investigated the effect that other minor components in diesel exhaust might have on the oxidation of HCN over Pt/Al<sub>2</sub>O<sub>3</sub>. While addition of water or propylene (C<sub>3</sub>H<sub>6</sub>) had no effect on the total HCN conversion over the temperature range (150–300 °C) studied here, adding C<sub>3</sub>H<sub>6</sub> noticeably increased the NO component of the total NO<sub>x</sub>, perhaps due to competition for the available O-atoms on the Pt surface. Adding NO or NO<sub>2</sub> provided a small increase of the overall HCN destruction at very low (<200 °C) temperatures. We also observed moderate NO<sub>x</sub> conversion to N<sub>2</sub> and N<sub>2</sub>O, similar to those observed for catalytic hydrocarbon lean-NO<sub>x</sub> reduction over platinum.

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