them as it was on the supported Pt catalysts included in this study. The differences between the conditions in our steady-state bench-scale experiments and the rapidly varying conditions in automotive exhaust make it impossible to say whether NH_4OCN will be formed to a significant extent when automotive exhaust is converted over Pt or Rh catalysts.

The results reported here enlighten the discussion (*4–12*) of whether OCN groups at the surface of metal catalysts could be important as intermediates in the formation of NH_3. The results show that NO is being converted to NH_4OCN over Pt and Rh catalysts of low surface area, but that hydrolysis of the cyanate over these metallic catalysts is slow near the temperature optimal for NH_4OCN production. They also show that on supported catalysts only a small amount of NH_4OCN is formed. Earlier workers have shown that NCO groups are formed on Pt and other metals (*5*) and may migrate to the oxidic support (*12*). The temperature dependence of the formation of NCO on the surface of Pt catalysts as measured by IR absorption (*9*) is similar (*19*) to the pattern of NH_4OCN formation in Fig. 1 and to the temperature dependence of NH_3 formation [figure 2 in (*25*)]. It therefore seems entirely reasonable to assume that hydrolysis of NCO groups to NH_3 occurs on the Al_2O_3 supports after their formation on the metal surface (*26*). We have also found that on Pt-Rh alloys, hydrolysis of NH_4OCN may be sufficiently fast at low temperatures to account for the formation of NH_3, whereas at higher temperatures hydrogenation of NH_4OCN is an important route to NH_3 (*19*).

For Ru, the variations with temperature of the surface concentration of NCO (*11*), of the formation of NH_4OCN (this work), and of the "CO-assisted" formation of NH_3 (*14*) are also very similar in the low-temperature regime. Since the maximal conversion of NO to NH_4OCN is 10 percent, compared to an NH_3 yield of 50 percent on unsupported Ru at the same temperature, hydrolysis of NCO to NH_3 appears in this case to be fast at the metal surface itself, in accord with the oxidic nature of the Ru surface (*27*).

In summary, we have established that NH_4OCN is a major product of the reduction of NO with CO and H_2, even in the presence of H_2O and O_2, over unsupported Pt and Rh catalysts in the temperature range 300° to 500°C. Almost quantitative conversion of NO to NH_4OCN (~ 95 percent) has been achieved. These results may lead to an alternative process for fixation of nitrogen as urea. They also have implications for the control of NO in automotive exhaust and for the mechanism of the formation of NH_3 in the reduction of NO.

R. J. H. VOORHOEVE
L. E. TRIMBLE
D. J. FREED

Bell Laboratories,
Murray Hill, New Jersey 07974

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Hydrogen Cyanide Production During Reduction of Nitric Oxide over Platinum Catalysts: Transient Effects

Abstract. *The formation of hydrogen cyanide during the catalytic reduction of nitric oxide (NO) with carbon monoxide and hydrogen was studied with a bench-scale flow reactor. The previously reported inhibition by sulfur dioxide of the formation of hydrogen cyanide was found to be counteracted by transient admission of oxygen to the catalyst. These results are discussed in the context of the control of automotive emissions of NO and the prevention of hydrogen cyanide production during such control.*

We recently reported the production of HCN during the reduction of NO with CO and H_2 over Pt catalysts (*1*) and over other noble metal and base metal catalysts (*2*). Since the concentrations of NO, CO, H_2, and H_2O employed (0.3, 5, 0.5, and 3.5 percent, respectively) were similar to those found in automotive exhaust, we stated that "HCN formation over Pt under *reducing* conditions appears possible" in automotive catalytic exhaust systems when there is a low air/fuel ratio (*1*). Subsequent studies in the Environmental Protection Agency (EPA) by Bradow and Stump (*3*) confirmed the production of significant levels of HCN over Pt-Rh and Pt-Pd automotive catalysts. Regulations issued by the EPA require that HCN formation in vehicles must now be monitored for certification purposes (*4*). However, in the automotive tests HCN was formed in the

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presence of 0.03 percent (by weight) of S in the fuel (*3*), while steady-state bench tests had indicated strong inhibition of HCN formation by the corresponding SO_2 levels in the gas mixture entering the catalyst bed (*1, 5*). The work reported here was undertaken to elucidate this apparent discrepancy. It was found that transient injection of O_2 in gas mixtures containing SO_2 leads to significantly higher levels of HCN than are obtained with the same mixtures in the absence of O_2.

The Pt catalyst used was a Pt sponge (Engelhard Industries, Newark, New Jersey) with a specific surface area of 0.12 m²/g. In our earlier measurements, this powder was mixed with α-alumina of low surface area as an "inert" diluent. We observed, however, that the presence of this oxidic material may increase HCN yields by as much as a factor of 2, and no diluent was used in the present measurements. The experimental methods used in the study were described previously (*1, 2, 6*); they included the optoacoustic determination of HCN, NH_3, and H_2O in the effluent and gas chromatographic analysis for NO, N_2, CO, CO_2, and H_2 in the dried effluent. The "standard gas mixture" contained 0.3 percent NO, 0.5 percent H_2, and 5 percent CO in a He diluent.

For each sample of catalyst, the products of the reduction of NO were first analyzed by using the standard gas mixture. The HCN yields ranged from 130 to 210 parts per million (ppm) in the temperature range of interest, 650° to 750° C. Addition of 0.5 percent O_2 to the feed gas mixture decreased the HCN yield to 35 to 100 ppm, corresponding to a relative decrease that ranges from 35 percent to as much as 80 percent, depending on the temperature and the preconditioning of the Pt catalyst.

The effect of O_2 on the inhibition of HCN formation by SO_2 manifests itself in rapid reactivation of a Pt catalyst poisoned by exposure to SO_2 and in partial protection of the catalyst against poisoning by SO_2. Curves A and B in Fig. 1 represent a reactivation experiment. Curve A shows, before time t_1, the yield of HCN from the standard gas mixture at 751°C in the absence of SO_2, but after the Pt catalyst had been poisoned by a 20-minute exposure to 2 to 7 ppm SO_2 in the standard mixture. The level of HCN in the effluent from the catalyst, which was at 125 ppm before exposure to SO_2, recovered only very slowly in the standard mixture (no SO_2). Adding 0.5 percent O_2 at t_1 enhanced the yield of HCN and subsequent removal of O_2 at t_1 left the catalyst nearly fully regenerated, yielding 100 ppm HCN. The formation of NH_3 shows a somewhat different pattern, but the catalyst was also regenerated (curve B). Exposure to air at 750°C for 1 minute had a similar effect.

Simultaneous exposure to SO_2 and O_2 partially protects the Pt catalyst against the sulfur poisoning experienced in the absence of O_2. Curve C in Fig. 1 shows the formation of HCN from a mixture of 0.3 percent NO, 0.5 percent H_2, 5 percent CO, 0.5 percent O_2, and 37 ppm SO_2 in He flowing over the Pt catalyst at 745°C. Exposure to SO_2 and O_2 for nearly 6 hours decreased the concentration of HCN formed from the 206 ppm measured initially in the standard mixture to 5 ppm. Similar experiments in the absence of O_2 showed a decrease of HCN to less than 1 ppm in 1 hour. Removal of O_2 from the feed mixture (at time *t*) while maintaining 37 ppm SO_2 enhanced HCN formation to about 20 ppm. In the presence of 4.5 percent H_2O in the feed gas, similar but somewhat less pronounced effects of O_2 on the SO_2 poisoning were noted.

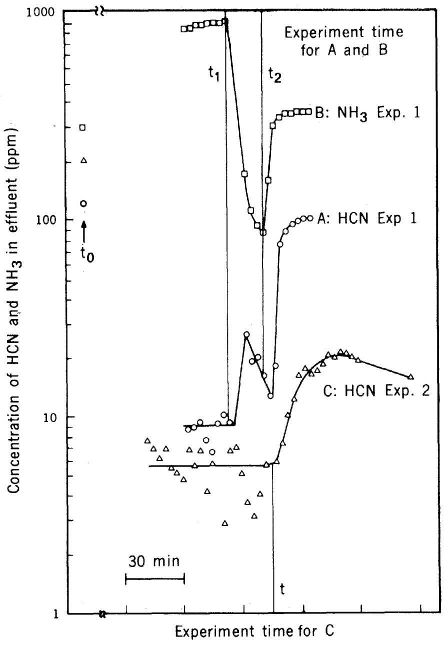

Fig. 1. Yield of HCN over Pt catalyst: effect of O_2 on the poisoning by SO_2. The gas flow was approximately 6 × 10^4 ml/hour per square meter of catalyst surface area. The Pt surface area was 0.12 m²/g; the gas composition is given in the text. Curves A and B represent one experiment (*Exp. 1*) in which a sulfur-poisoned catalyst was regenerated on admission of 1 percent O_2 to the gas flow, between times t_1 and t_2. (Curve A) HCN concentration in the reactor effluent; (curve B) NH_3 concentration in the same experiment at a catalyst temperature of 751°C. The rise and fall in the HCN level between t_1 and t_2 is believed to be due to two effects of O_2, as discussed in the text. Experiment 2 shows protection of the catalyst against the poisoning by SO_2 due to the simultaneous presence of O_2 in the gas. (Curve C) Formation of HCN at 745°C with 37 ppm SO_2 and 0.5 percent O_2 in the gas flow (before time *t*) and after removal of O_2 (at time *t*). Steady-state levels of HCN and NH_3 produced before the exposure to SO_2 and O_2 in the standard gas mixture are indicated at time t_0 for both experiments. For each data point HCN or NH_3 was monitored for ~ 8 seconds. The uncertainty in the HCN measurement is ± 2 ppm or ± 2 percent, whichever is greater.

The results of this study show that oxygen has two effects in the formation of HCN: a short-term effect that is probably due to participation of O_2 in the chemical processes in the absorbed layer, and a long-term effect due to modification of the catalyst. The short-term effect is expected because of the lower redox potential in the presence of O_2 and particularly because of the preferential reaction of H_2 with O_2, which could interfere with the proposed mechanism of formation of HCN by hydrogenation of an OCN^- intermediate (*2*). The long-term effect is suspected to be due to modification of the composition of the surface and subsurface of the catalyst. There is little doubt that SO_2 is reduced to H_2S under the conditions of the standard mixture (*3, 7*), and as a result the Pt surface layers will incorporate S. Regeneration in the presence of O_2 is believed to involve replacing S in the surface layers by O. This explanation is consistent with the Auger analysis data on Pt foils used for reduction of NO in the presence of SO_2 (*8*). Such surface compounds were demonstrated on Pt(110) surfaces by Ducros and Merrill (*9*); in that study they were formed at elevated temperatures (around 800°C).

We conclude from this study that intermittent admission of O_2 over the Pt catalyst may maintain the catalyst in a state where it is able to produce HCN even in the presence of SO_2 in the gas mixture. In automotive exhaust systems, intermittent admission of O_2 occurs during "lean" excursions of the air/fuel ratio [for example, see (*10, 11*)]. Incorporation of base metal oxides as oxygen buffers in automotive catalysts (*12*) may modify the role of O_2 in the formation of HCN, but on the basis of this study it is not possible to make reliable predictions. In any event, the available data (*3*) indicate that HCN formation is observed primarily when one or more of the elements of the exhaust control system is failing, and current regulations (*4*) appear to ensure vigilance in monitoring HCN emissions.

R. J. H. VOORHOEVE
C. K. N. PATEL
L. E. TRIMBLE, R. J. KERL
Bell Laboratories,
Murray Hill, New Jersey 07974

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Carbon: A New View of Its High-Temperature Behavior

Abstract. *An increasing body of research indicates that carbon can exist in a number of polymorphic "carbyne" forms. It is proposed that these forms occur because of a shift to triple bonding in the carbon system as temperature increases above 2600 K. It is also proposed that graphite can dissociate into triple-bonded molecules by a simple mechanism.*

The discovery of new carbon forms in 1968 by El Goresy and Donnay (*1*) and Sladkov and Koudrayatsev (*2*) opened a field of research that is revealing heretofore unsuspected aspects of the behavior of carbon at high temperature. The work of Kasatochkin *et al.* (*3*), the laser Raman results of Nakamizo and Kammereck (*4*), and the work of Fryer (*5*) indicate that these carbon forms contain $-C \equiv C-$ units, probably as chains. Since acetylene is an organic molecule stable at high temperatures, it is reasonable to expect high-temperature carbon forms of this general structure. Also, from a structural point of view, diamond represents the tetrahedral form of carbon and graphite the ring form, and lonsdaleite can be considered a hybrid of these structures. However, before 1968 a polymorph representing triple-bonded carbon was not recognized. Evidently, the new forms fill this gap. The Russian scientists call these new forms "carbynes" (*2*); in this report their nomenclature will be retained.

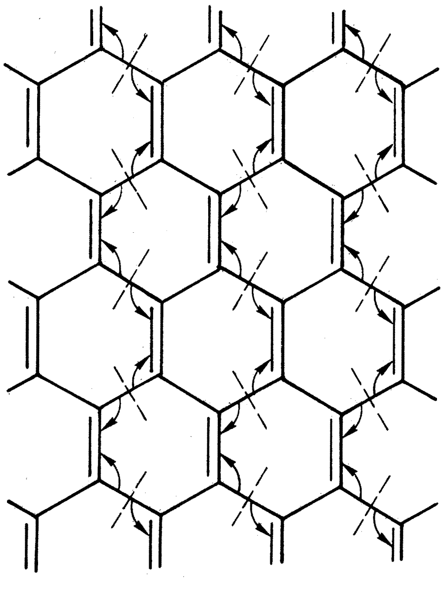

Fig. 1. Mechanism for transformation of a graphite basal plane sheet of atoms into $(-C \equiv C-)_n$ chains.

If the structure of graphite is considered, it is easy to see that it can readily dissociate into $-C \equiv C-$ chains. A mechanism for this is illustrated in Fig. 1, where a portion of a basal plane sheet of atoms from the graphite structure is shown. At high temperatures, a single bond can break and shift an electron into each of the adjacent double bonds. This induces another single bond to break, such that one electron goes to the adjacent "free radical" double bond to form a triple bond and the other goes to the next adjacent double bond. If the process is repeated, as shown in Fig. 1, the entire sheet of atoms separates into $-C \equiv C-$ chains. When it does so, only electrons are shifted to rearrange bonds. Initially, the atoms move only the small distance associated with the change from double to triple bonds. As the new bonds are formed, the bond angles change to produce the linear arrangement of atoms required for $-C \equiv C-$ bonding. This process would be analogous to the well-known high-temperature transformation of benzene to acetylene. The chains can be stacked in a hexagonal array, as proposed by the Russian scientists (*2*), to produce the carbyne forms. Because the chains can be stacked in a number of ways relative to the triple bond positions, one would expect a family of carbyne forms to exist. This indeed appears to be the case. Diffraction data obtained thus far at the Aerospace Corporation indicate that there are eight forms and that there may be more. Kasatochkin *et al.* (*6*) have reported five forms that are in very good agreement with our results. It may be that the carbyne forms are showing what could be called "linear polytypism." Although they appear to be very similar crystallographically, they show a wide range of physical properties. Some forms are very soft, whereas others are superhard—indeed, harder than cubic BN (*7*). This indicates that there must be considerable cross-bonding between chains in some cases. However, the wide range in properties requires a wide variation of the degree of cross-bonding among the various carbyne forms. If cross-bonding between chains is carried to its limit, the result is likely to be the diamond structure. This suggests that these forms may be intermediates in the graphite-diamond transition, and there is a small amount of data in the literature that are consistent with this mechanism (*8*, *9*).

It has been known for several years that the rate of transformation of graphite to a carbyne form (probably chaoite) is very slow compared with that of the reverse transformation. Recently, preliminary rate data have been obtained, and the ratio of the rates was found to be about 500:1, which is consistent with the mechanism proposed in Fig. 1 (*10*). The transformation from the carbyne form to graphite involves a reaction between acetylene-like molecules, which are known to react rapidly and exothermically, whereas the reverse reaction involves the breaking of single bonds as a first step and would be expected to be a much slower process.

The phase diagram in present use must be in error because it does not include the carbyne forms. It has been known for many years that it was difficult to reconcile the high-pressure results with the

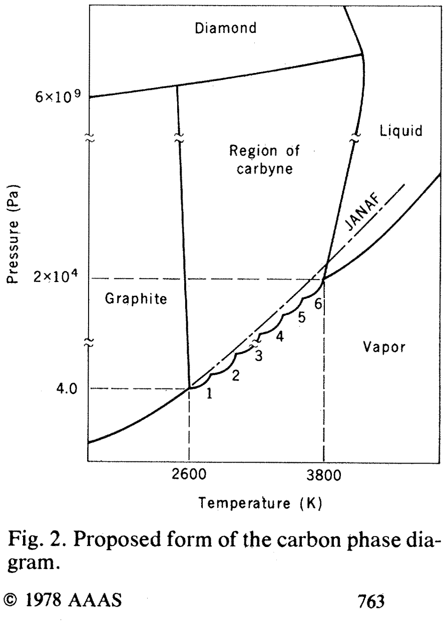

Fig. 2. Proposed form of the carbon phase diagram.

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