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Alternate Pathway to Ammonia Formation in NOx Reduction: Direct Reaction of Acetylene and Nitrogen Atoms on Pt (111)

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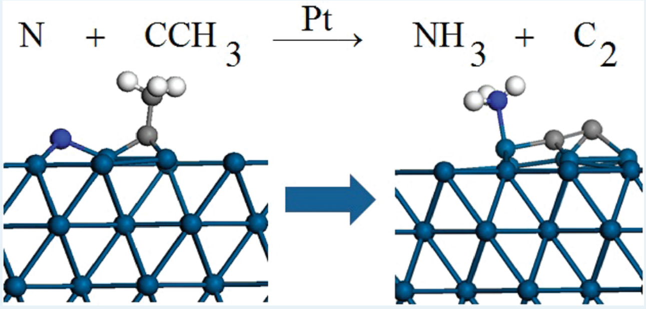
ABSTRACT: The formation of ammonia is detected above 500 K when acetylene is adsorbed on N-covered Pt(111). This temperature is well above the desorption temperature for NH_3 from clean Pt(111), and ammonia cannot be produced from exposure of N atoms to H_2. Therefore, the formation of ammonia must be related to the ability of the hydrocarbon fragment to "store" hydrogen on the metal surface to elevated temperatures that allow for fast formation and desorption of NH_3. This work demonstrates a unique pathway for NOx reduction with hydrocarbons as opposed to hydrogen and could be useful in the development of advanced NOx abatement technologies.



KEYWORDS: ammonia, platinum, NOx reduction, temperature programmed reaction, hydrogen transfer

Improved efficiency in combustion engines can be achieved at higher air-to-fuel ratios, but this leads to an increase in NOx emissions.[1] Pt-based NOx reduction catalysts have received attention because of their activity at relatively low temperature.[2] However, to this point no hydrocarbon based selective catalytic reduction (SCR) system has been shown to be as effective as ammonia/urea based systems. Although ammonia has been used effectively as a reductant for stationary sources, the injection of a urea-water solution (UWS) for deNOx in mobile sources remains problematic because of deposit formation issues at low temperatures and the possibility of ammonia slip.[3] A recent solution to this problem is the use of one catalyst that produces ammonia from NOx, either a lean NOx trap (when rich)[4] or a hydrocarbon SCR (HC-SCR) catalyst (when lean)[5−7] followed by an ammonia-SCR catalyst to maximize N_2 formation These dual catalyst systems offer the distinct advantage of avoiding ammonia and urea handling, while achieving high levels of NOx reduction without significant generation of N_2O or release of ammonia.

Although NH_3 formation has been observed previously in exhaust catalyst studies examining the interaction of combustion products over noble metal catalysts, considerable uncertainty surrounds the reaction mechanism of ammonia production, and therefore it is not clear how to best optimize these systems. In addition, further complications may result from the presence of multiple pathways for ammonia generation. For example, while reactions of NO and NO_2 with hydrogen may be a primary source of NH_3,[8] evidence also points to reactions between hydrocarbons and NOx on Pt[9] and other metals.[10] Recently, the Griffiths group has undertaken a series of surface science studies of the interaction of NO and ethylene on Pt(332).[11−14] Although the presence of the coadsorbed hydrocarbon led to the production of N_2, H_2O, and CO_2, no reaction intermediates were observed and no ammonia was produced. Although NO dissociates on Pt(332), one could surmise that the surface coverage of nitrogen atoms was too low to generate significant amounts of NH_3. To avoid the limitations of NO dissociation on Pt surfaces under UHV conditions,[15] we have studied the interaction of N atoms and C_2H_2 on the Pt(111) surface to determine how ammonia may be formed via a distinctly different reaction than ammonia formation from hydrogenation of NOx. By first creating a well ordered nitrogen layer at a submonolayer coverage, we are able to probe the reaction between acetylene and nitrogen atoms on the Pt(111) surface. We have chosen C_2H_2 as a model hydrocarbon because of its possible appearance as an unburnt hydrocarbon product of combustion.[16] We have observed ammonia formation via temperature programmed reaction, demonstrating that traditional hydrocarbon SCR may lead to ammonia formation via reaction of hydrocarbons with N atoms.

A p-(2×2)-N layer was formed on Pt(111) by exposing 2 L of oxygen and 0.4 L of ammonia to the surface at 90 K and then annealing to 400 K for 60 s following the experimental procedure reported by Herceg et al.[17] After exposure of 0.8 L of perdeutero acetylene (C_2D_2) to the 0.25 ML nitrogen covered Pt(111) surface, ND_3 ($m/z = 20$) desorbs from the surface with a peak at 504 K as shown by the temperature programmed desorption (TPD) results in Figure 1. A comparison of the results of Figure 1 with an ammonia TPD experiment on the clean Pt surface indicates that only about one tenth of the nitrogen has been hydrogenated to ammonia. This is based on comparison of our TPD results for ammonia on clean Pt(111) with those of Fisher[18] where an absolute coverage of 0.25 ML was associated with the maximum amount of ammonia adsorbed in the α state. Most of

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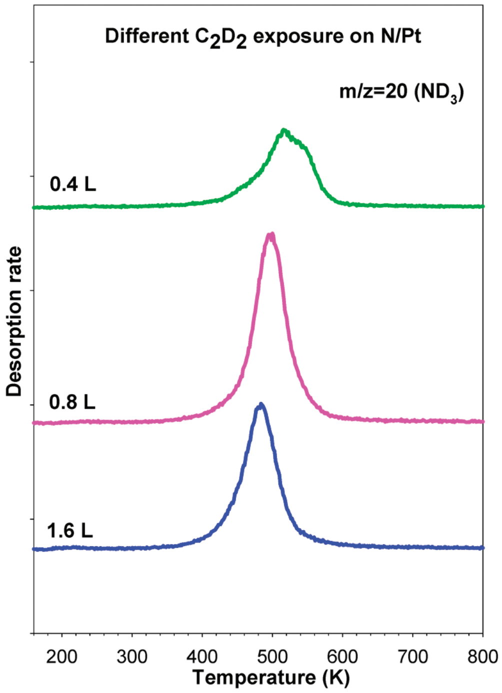

Figure 1. TPD of ND_3 following different exposures of C_2D_2 to p(2 × 2) N/Pt(111).

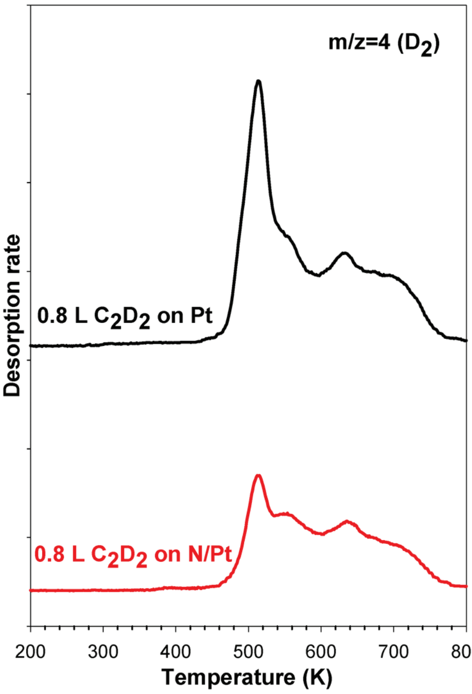

Figure 2. TPD of D_2 following exposure of 0.8 L C_2D_2 to Pt(111) and to p(2 × 2) N/Pt(111).

the remaining unreacted nitrogen atoms (or NH_x species) ultimately recombine (or dehydrogenate before recombination) to form molecular nitrogen, which then desorbs from the surface. A small amount of the nitrogen is also removed as HCN, indicating that carbon−nitrogen occurs to some extent. Our results on the carbon−nitrogen coupling reaction will be published separately. Previous studies have shown that ammonia desorbs from the Pt surface below 400 K[18−22] and, therefore, the ammonia desorbing at 504 K must be a reaction limited product. Furthermore, the presence of acetylene appears to help stabilize nitrogen atoms on the Pt surface and prevents recombination.

Figure 2 depicts the desorption of hydrogen from C_2D_2 on clean and N covered Pt(111). The hydrogen (deuterium) that desorbs from acetylene on the surface can be fit to four peaks at 510 K, 554 K, 626 K, and 702 K, respectively. The ratio of the four integrated peak areas at the different desorption temperatures is approximately 2:1:1:1, suggesting the stepwise dehydrogenation of acetylene on Pt(111). Similarly, hydrogen (deuterium) desorption from acetylene on the nitrogen covered Pt(111) can also be fit to four peaks at the same approximate temperatures. However, on the N covered surface, hydrogen desorption is largely suppressed, with the integrated areas for peaks 1, 2, and 4, only 41%, 65%, and 53% of their values for hydrogen desorption following C_2D_2 adsorption on the clean surface (The peak at 626 K is effectively unchanged). The results suggest that nitrogen is hydrogenated stepwise in an equal manner at these three different desorption temperatures concomitant with the dehydrogenation events of the hydrocarbon. Furthermore, control experiments reveal that molecular desorption of acetylene does not occur from the N-covered surface just as it does not occur from the clean surface. Also, since the acetylene exposure was performed at 90 K, it can be assumed that the initial acetylene coverage was the same for the clean and N-covered surfaces. This leaves ammonia formation and desorption as the only likely channel for hydrogen removal from the surface aside from molecular hydrogen and a very small amount of HCN desorption at higher temperatures. Thus the suppression of hydrogen desorption is further evidence that the hydrogen that comes from acetylene is consumed by hydrogenation of the nitrogen atoms.

Previous studies of C_2H_2 adsorption on Pt(111) have shown that acetylene adsorbed at low temperature converts to ethylidyne (CCH_3) upon warming above room temperature.[23] Experimental results also suggest that vinyl ($CHCH_2$) may be a stable intermediate in the formation of ethylidyne from acetylene on Pt(111). The dehydrogenation is believed to proceed through vinylidene (CCH_2) and CCH. Although many of the mechanistic details remain elusive, as the temperature is raised all of the hydrogen from the acetylene decomposition products desorbs by ∼700 K and by ∼800 K the carbon forms unreactive graphite islands on the surface. There is no reason to suppose that the graphite forming mechanism is substantially altered by the presence of nitrogen atoms on the surface.

Previously it has been observed that exposing hydrogen to a nitrogen covered Pt surface at temperatures as low as 190 K will result in formation of the NH species, which can be readily detected with RAIRS.[24,25] However, the hydrogenation reaction does not proceed beyond NH to form NH_2 or NH_3 under UHV conditions. The NH RAIRS peak intensity was observed to increase as hydrogen exposure increases from 10 to 80 L, but it does not further increase for higher exposures (e.g., 160 L). However, one could argue that a steric effect exists and that the presence of the C_2H_2 fragments on the surface allows for more facile reaction between hydrogen and nitrogen (or more importantly prevents N−H dissociation). To explore this possibility, we performed similar experiments by exposing 10 L of D_2 to a N/Pt(111) surface at 90 K that had already been exposed to C_2H_2 at 350 K and monitored for possible ND_3 desorption as shown in Figure 3. The absence of a m/z = 20 peak agrees with

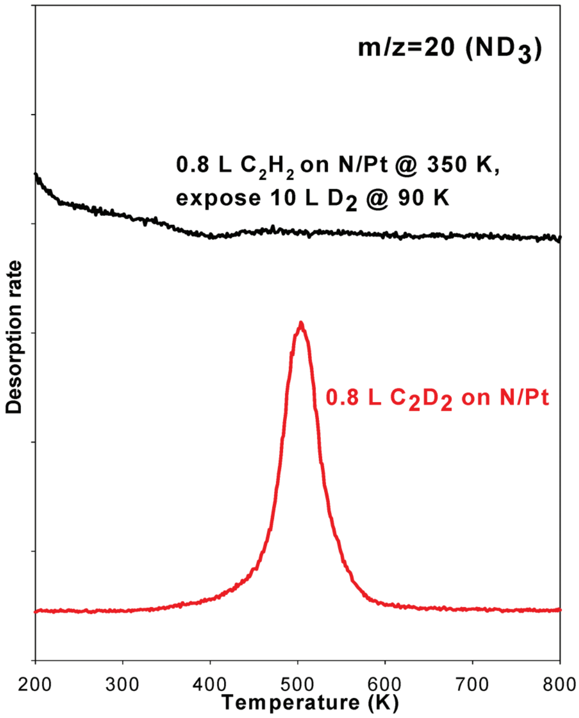

Figure 3. TPD of ND_3 following exposure of 0.8 L C_2H_2 at 350 K followed by exposure to D_2 at 90 K on p(2 × 2) N/Pt(111). Bottom spectrum shows TPD of ND_3 following exposure of 0.8 L C_2D_2 to p(2 × 2) N/Pt(111).

previous studies that assert that direct hydrogenation of the N layer on Pt(111) cannot produce ammonia. The majority of the deuterium desorbs from the surface below 300 K without reacting with the N atoms. Instead, although some of the deuterium likely produced the ND species on the surface, it evidently dissociates before it can be completely hydrogenated.

Our results suggest that the hydrogen source to form ammonia is therefore not surface hydrogen but perhaps is due to direct hydrogenation of N atoms from ethylidyne (CCH_3) or ethynyl (CCH). Previous density functional theory (DFT) results predict that the second hydrogenation step has the highest reaction barrier.[25−27] Therefore, this barrier can only be overcome at temperatures above where hydrogen would ordinarily desorb from the metal surface. When hydrogen is bound to stable hydrocarbon fragments, it is available on the surface at the temperatures needed to complete the hydrogenation of nitrogen to ammonia. The role of the hydrocarbon then is to hold hydrogen on the surface to higher temperatures in the C−H bonds of stable hydrocarbon fragments. This mechanism is distinctly different from NO reduction by hydrogen, which can occur at significantly lower temperatures.[28] In our experiments we cannot identify the precise mechanistic pathway for hydrogenation of N in that we cannot discriminate between direct hydrogen transfer between the adsorbed hydrocarbon and N (analogous to H transfer from methanol to oxygen, as observed, for example, on Ru(0001)[29]) versus a mechanism by which the hydrocarbon decomposition precedes hydrogenation of N. Our experiments have shown a unique pathway for NH_3 formation from a direct reaction between a hydrocarbon and N atoms on a platinum surface, which could play a critical role in advanced NOx reduction technologies.

EXPERIMENTAL SECTION

The experiments were performed in a chamber with a base pressure of ~2 × 10^{-10} Torr. In brief, the system is equipped with a quadrupole mass spectrometer (QMS) (Prisma QMS200 with a measurable mass range of 0−200 amu), low energy electron diffraction (LEED), and an Auger electron spectrometer (AES) system from LK technologies (Series RVL2000). A homemade tin oxide coated glass shield was designed and placed over the ionizer of the mass spectrometer, with a 12 mm wide aperture to ensure that only gases from the sample, not from the background, are detected by the mass spectrometer. The heating rate in the TPD experiment was 2 K/s. The Pt(111) surfaces were cleaned and judged free of impurities by a standard procedure described earlier.[30] Ammonia (99.9992%), and oxygen (99.998%), were purchased from Matheson Trigas and used without further purification. Perdeutero acetylene (C_2D_2, 99%D) was purchased from Cambridge Isotope Laboratories and used without further purification.

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