



Isotopic Temporal Analysis of Products study of anaerobic NO reduction by NH₃ on Pt catalysts

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ABSTRACT

A Temporal Analysis of Products (TAP) study was carried out of the anaerobic NO + NH₃ reaction system on Pt sponge and Pt/Al₂O₃ catalysts. Temperature, pulse timing, and feed composition were varied to quantify the conversion and product selectivities. Isotopically labeled nitric oxide (¹⁵NO) was used to follow reaction pathways to molecular nitrogen and nitrous oxide. A variation in the delay time between sequential pulses of ¹⁵NO and NH₃ had a significant effect on the reaction path to molecular nitrogen. A mixed feed (no delay time) above the light-off temperature resulted in a product mixture nearly balanced between the mixed product ¹⁵NN, and the two single-source products ¹⁵N₂, and N₂. With increased delay time the selectivity of ¹⁵NN decreased significantly in favor of ¹⁵N₂ and N₂. The data suggest at least two major routes to nitrogen formation, one involving direct NO decomposition on reduced Pt sites and the other involving reaction between NH_x species and NO. There is also kinetic evidence for a slower, third minor route involving an unidentified surface complex, possibly HNO_{ad}. The alumina support is shown to suppress this effect of delay time through ammonia adsorption, serving as a source-sink. The trends are interpreted with a mechanistic model constructed from a sequence of elementary steps.

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1. Introduction

The reduction of NO_x has long been the focus of emissions catalysis. One of the stalwarts in the catalytic reaction engineering applied to the environment has been Professor Pio Forzatti. His body of work in the areas of structured catalytic reactors and emission catalysis has provided inspiration to many of us who have followed in his large steps. The authors of this paper are truly privileged to honor Dr. Forzatti's contributions in catalytic reaction engineering and look forward to many more in the coming years.

The three-way catalytic converter (TWC) is the most important application of structured reactors and is arguably the most important environmental technology development of the last century. In the TWC, NO_x is reduced by several exhaust components, including CO, H₂, and hydrocarbons. The NO_x reduction chemistry occurs on all three metals in the TWC (Pt, Pd, and Rh), although Rh is particularly effective because of its activity in breaking the N–O bond. The NO_x reduction occurs primarily during the rich part of the high frequency (~1 Hz) fluctuations in the air/fuel ratio. A byproduct of the catalytic reduction is NH₃. Indeed, the earliest automobile catalytic converter generated too much NH₃. While a fraction of the NH₃

reacts with NO, efforts were undertaken to mitigate NH₃ formation. For example, the addition of ceria helps by supplying oxygen during the rich phase, enabling the oxidation of NH₃.

Increasingly stringent standards for elimination of NO_x from diesel vehicles require the development of robust after treatment catalysts [1]. Lean NO_x reduction can be accomplished with either NO_x storage and reduction (NSR), selective catalytic reduction (SCR), or a combination of both NSR and SCR. NSR involves cyclic operation in which a bifunctional catalyst is exposed to a lean feed, during which NO_x is stored, and then a shorter rich pulse, during which the stored NO_x is reduced to a mixture of N₂, N₂O, and NH₃ [2,3]. Complex spatio-temporal behavior occurs during the ca. 1–2 min long cycles. For example, NH₃ that is produced upstream in the reactor during the regeneration reacts downstream with NO_x released by nitrates and nitrites stored during the previous cycle. In contrast, SCR is an inherently steady-state process involving the reaction of NO_x in the presence of O₂ with ammonia on Fe- and Cu-based zeolite catalysts [4]. That said, Forzatti and coworkers have pointed out similarities between NSR and SCR [5]. A common system design for the SCR involves the controlled feed of an NH₃ precursor such as urea to maintain a high NO_x conversion with minimal slip of unreacted NH₃. More recent research focuses on the combination of NSR and SCR with the NSR converting a fraction of the engine-out NO_x to NH₃ [6]. An ammonia slip catalyst (ASC) must be positioned downstream of the SCR in order to oxidize any unconverted ammonia [7,8]. The ASC contains an ammonia oxidation function, ammonia storage function, and NO_x reduction function.

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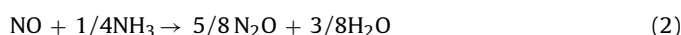
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One approach utilizes a dual-layer catalyst comprising an underlying layer of Pt/Al₂O₃ and a top layer containing a metal-exchanged zeolite resembling the SCR catalyst [9,10]. The Pt catalyzes the oxidation of NH₃ to a mixture of N₂, N₂O, and NO while unreacted NO diffuses into the adjacent zeolite layer where it reacts with NH₃ to form N₂.

Thus, the reaction between NO and NH₃ on Pt is an important contributor to the overall chemistry in the TWC, NSR and ASC environmental catalytic processes. Pt-catalyzed oxidation of NH₃ with NO is also encountered in chemicals manufacturing. For example, the reaction is a side reaction during the oxidation of ammonia to NO, a key step in the manufacture of nitric acid [11]. NO_x-adspecies react with surface NH_x species to form N₂ [11,12]. The overall reactions for producing N₂ and N₂O are:



Understanding the mechanism and kinetics of low temperature reduction of NO by NH₃ is needed to design effective catalysts that maximize the conversion and selectivity to N₂.

A large number of studies have reported various features of the Pt-catalyzed NH₃ + NO reaction. These can be divided into four groups. The first group comprises earlier kinetics and mechanistic studies during the development of the TWC (ca. pre-1990). The second group comprises ammonia oxidation studies which have appeared in the catalysis literature since the discovery of this chemistry by Haber in 1909, and shortly thereafter commercialized by Bosch. The third group comprises studies that focused on complex dynamics of the NH₃ + NO reaction system, predominantly during the ca. 1985–2005 period. The fourth group is the most recent and has involved studies focused on the emergence of the aforementioned lean NO_x trap (LNT) and LNT-SCR systems. Like studies in the first and second groups, here the study of NH₃ + NO was motivated by the occurrence of the reaction as a secondary pathway in a more complex overall reaction system.

We briefly summarize the findings of the key studies from the four groups pertaining to the mechanism and kinetics features of the reaction system. A significant earlier study by Otto et al. [13] utilized ¹⁵NH₃ and NO to follow N₂ and N₂O formation pathways on Pt/Al₂O₃ at lower temperature (200–250 °C). Their data showed the existence of two types of pathways, one involving the direct reaction of adsorbed ¹⁵NH₃ and NO, and the other involving the reduction of NO with H. The former involved the intermediate formation of an unidentified surface complex. Gland and Sexton [14], in a UHV study utilizing EELS, found evidence for a surface species at temperatures below 350 K. The reduction of NO with NH₃ was found to be slower than with H₂. Clayton et al. [15] confirmed this in more recent studies for Pt/BaO/alumina LNT catalysts. Otto et al. [13] found that any reaction between product N₂O and NH₃ was ruled out based on kinetic arguments at temperatures below 250 °C. More recent research by Theis et al. [16] suggests that N₂O reacts with NH₃ over LNT catalyst at temperatures as low as 275 °C. The authors have noted that this would explain the maximum in the N₂O yield with increasing rich purge time. Choi et al. [17] have suggested that the reaction of NH₃ produced upstream during the regeneration reacts with stored NO_x in the downstream section, generating N₂O as one of the products. Thus the net generation of N₂O is clearly impacted by the balance between the rates of generation and consumption.

Pt-catalyzed NO + NH₃ is a fast reaction that has been known to generate interesting and complex spatio-temporal phenomena, including sustained oscillations and traveling waves. Some of the complexity is attributed to the surface reconstruction of Pt(1 0 0) and Pt(1 1 0) planes induced by adsorption. On the other hand, earlier studies by Takoudis and Schmidt [18] and later one by McMillan

et al. [19] indicated that oscillatory behavior occurs on polycrystalline Pt as well even at higher pressures. Nowobilski and Takoudis [20] proposed a reaction sequence built on the concept of a surface intermediate, HNO_{ad}, as well as a precursor NO adsorption sequence. Vantol et al. [21] proposed a mechanistic sequence for the NO + NH₃ reaction system based on the similar NO + H₂ system. They speculated that reconstruction is not necessary to explain the oscillatory behavior, that the competition for vacant sites by the reacting species together with adsorbed NO island formation play important roles.

Kondratenko and Baerns [22] conducted a study of NO reduction by NH₃ on a polycrystalline Pt gauze. Through the use of ¹⁵NO in a TAP reactor, they were able to prove that there are two routes to molecular nitrogen. One route involves the decomposition of NO into N adatoms, which recombine; this was confirmed by the generation of ¹⁵N₂. The other involves the reaction between NO and an ammonia-derived surface species, such as H₂NNO. This second pathway was confirmed by the generation of the mixed product ¹⁵NN. The delay time between the NH₃ and ¹⁵NO pulses was kept fixed (at 0.2 s), so the authors did not explore the relative rates of the two pathways. N₂O was found to be only a minor product in a very narrow temperature window. Similar low selectivity to N₂O has been reported in other studies [21].

Temporal Analysis of Products (TAP) is well-suited to accomplish detailed studies of transient catalysis and kinetics [23,24]. TAP has been used to study a variety of catalytic reactions including those that occur in emission after treatment systems [23,25–29]. The NH₃ + NO reaction is no exception, as demonstrated by Kondratenko and Baerns [12]. As described in detail elsewhere, TAP can track pathways as the catalyst experiences transient feeds, such as a chain of reactant pulses. The TAP reactor is operated at sufficiently low pressure and if the pulse has a sufficiently small number of molecules, the transport approaches that of Knudsen diffusion. This is convenient as this is a well-characterized and quantifiable transport process. Sufficiently small molecular flows (ca. 10^{14–15} molecules per pulse) are used that nonisothermal effects are negligible [24,29]. In addition, isotopic tracers are an affordable method for identifying and following reaction pathways.

In this study we investigate the low to moderate temperature reaction between NO and NH₃, between ca. 100 and 350 °C, conditions encountered in the TWC, LNT, or ASC during cold-start or low-load vehicle operation. Polycrystalline Pt in both unsupported (Pt sponge) and supported (on Al₂O₃) forms are used to assess any effects of the support. To this end, our objective is to identify the major pathways to N-containing products under anaerobic conditions which would likely be encountered during the regeneration of a LNT, for example. We employ isotopically labeled nitric oxide (¹⁵NO) in conjunction with TAP to follow the pathways involving nitrogen leading to desired product N₂ and undesired product N₂O. The effects of temperature, pulse timing, and feed composition are varied to quantify conversion and product selectivities on both unsupported and supported Pt catalysts. The data are interpreted with a phenomenological model constructed from a probable sequence of elementary steps. The experiments provide insight about the key reaction pathways that lead to N₂, as well as data that may be used to estimate rate constants.

2. Experimental

2.1. Catalyst samples

The catalysts used include a porous Pt sponge (powder) and Pt/Al₂O₃ powder. The latter has a Pt loading of ~1.5 wt.% and Pt dispersion of 30%. A comparison of the Pt and Pt/Al₂O₃ catalysts provides insight on the role of the support. The table in Fig. 1 lists

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