



Isocyanate formation and reactivity on a Ba-based LNT catalyst studied by DRIFTS



Yaying Ji^a, Todd J. Toops^b, Mark Crocker^{a,*}

^a Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA

^b Fuels, Engines, and Emissions Research Center, Oak Ridge National Laboratory, Knoxville, TN 37932, USA

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ABSTRACT

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and mass spectrometry (MS), coupled with the use of isotopically-labeled reactants (¹⁵N¹⁸O and ¹³CO), were employed to study the formation of isocyanate species during NO_x reduction with CO, as well as isocyanate reactivity toward typical exhaust gas components. DRIFTS demonstrated that both Ba–NCO and Al–NCO were simultaneously formed during NO_x reduction by CO under dry lean-rich cycling conditions. The Ba–NCO band was more intense than that of Al–NCO, and became comparatively stronger at high temperatures. During rich purging at 300 and 400 °C, a near linear relationship was found between the increase in Ba–NCO band intensity and the decrease in Ba–NO₃ band intensity, suggesting that Ba–NCO is directly derived from the reaction of Ba nitrate with CO. Both temperature-programmed surface reaction (TPSR) and isothermal reaction modes (ISR) were utilized to study the reactivity of isocyanate species under lean conditions. Simultaneous DRIFTS and mass spectrometric measurements during TPSR indicated that isocyanate reaction with H₂O, O₂, NO and NO/O₂ took place almost immediately the temperature was raised above 100 °C, and that all NCO species were removed below 300 °C. The evolution of the NCO IR bands during ISR at 350 °C demonstrated that the kinetics of NCO hydrolysis are fast, although a delay in N₂ formation indicated that N₂ is not the initial product of the reaction. In contrast, immediate N₂ evolution was observed during NCO reaction with O₂ and with NO + O₂. Overall, it can be inferred that under dry cycling conditions with CO as the sole reductant, N₂ is mainly generated via NCO reaction with NO/O₂ after the switch to lean conditions, rather than being evolved during the rich phase. However, in the presence of water, isocyanate undergoes rapid hydrolysis in the rich phase, N₂ generation proceeding via NH₃.

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1. Introduction

Lean NO_x traps (LNTs), also referred to as NO_x storage–reduction (NSR) catalysts, represent a promising technology for the abatement of NO_x emissions from diesel and lean-burn gasoline engines. This technology requires cyclic operation between lean and rich conditions, corresponding to two different reaction phases. Under lean conditions, NO is oxidized to NO₂ and then stored in the form of nitrate (and/or nitrite). Upon periodic short excursions to rich conditions, stored NO_x is released and reduced to N₂. To achieve these dual functions, LNT catalysts are typically composed of precious metals (generally Pt/Pd/Rh) and an alkali or alkaline-earth metal NO_x storage component (most commonly BaO) supported on a high surface area metal oxide such as Al₂O₃ [1–3]. Although LNT technology has been commercialized for lean-burn gasoline and light-duty diesel applications, certain aspects of the mechanism of

NO_x storage and reduction are not fully understood. Relative to the NO_x storage phase, understanding the chemistry of NO_x reduction is particularly challenging. NO_x reduction is generally performed over a very short period (usually 3–5 s), which creates difficulties in analyzing the chemistry of NO_x reduction using standard laboratory techniques. Moreover, the involvement of different reducing agents (H₂, CO and hydrocarbons) in the NO_x reduction process increases the complexity of NO_x reduction chemistry. In an attempt to obtain insights into the NO_x reduction process during rich purging, the NO_x reduction system has been simplified in many studies by the use of H₂ as the sole reductant [4–9]. It has been generally proposed that reduction of stored NO_x occurs via dissociative adsorption of released NO_x and of hydrogen at Pt sites to form Pt–N, Pt–O, and Pt–H species, followed by recombination of surface Pt–N species to give dinitrogen and recombination of surface Pt–N and Pt–H species to give ammonia. Subsequent oxidation of ammonia with stored NO_x and/or oxygen can generate additional N₂ [7–12].

Compared to H₂, CO has been shown to be a less effective reductant, especially at low temperature [13–18], albeit that Cant et al. reported that CO was more effective than H₂ during NO_x

* Corresponding author. Tel.: +1 859 257 0295.

E-mail address: mark.crocker@uky.edu (M. Crocker).

reduction under dry conditions over a Pt-free catalyst [19]. It is generally believed that the poor NO_x reduction behavior obtained with CO is due to Pt poisoning by CO at low temperature [20,21]. In general, the chemistry of NO_x reduction by CO has drawn less attention than NO_x reduction with H₂. Forzatti and co-workers investigated NO_x reduction with CO under dry conditions by means of transient response methods [22–25]. They suggested that stored NO_x was reduced by CO through a Pt-catalyzed surface pathway, in which nitrate was first reduced to nitrites and then surface isocyanate/cyanate species, followed by the reaction of these species with residual nitrates and nitrites to give dinitrogen. These studies also showed that isocyanate (–NCO) can be re-oxidized to surface nitrite and then nitrate upon exposure to oxygen, and that N₂ can be produced during the reduction of stored NO_x by CO under rich purging and also during oxidation of surface NCO species by O₂ and NO/NO₂ during lean operation. However, under wet conditions, almost no NCO species were detected on the catalyst surface during NO_x reduction with CO [22,26], this being ascribed to the hydrolysis of isocyanate to give ammonia [16,22,27,28]. Besides observing the hydrolysis of NCO species, Lesage et al. compared the reactivity of isocyanate with O₂ and with NO [28] and noted a lower reactivity of NCO toward NO compared to O₂. The results of these various studies suggest that isocyanate is an important intermediate during NO_x reduction with CO. Moreover, recent research by DiGiulio et al. has demonstrated that the reactions of NCO with NO and O₂ are metal-catalyzed pathways, while the reaction of NCO with H₂O to produce NH₃ is not. They also emphasized that N₂ production via NCO can be significant [29]. However, a complete picture regarding the reactivity and role of isocyanate species in LNT catalysis is still lacking. Consequently, we undertook the current study in which DRIFTS was employed to monitor the evolution of surface species, while mass spectrometry was used to detect gaseous species formed during the reactions of surface NCO species. To aid in the differentiation of gaseous species in the mass spectrometer, isotopically-labeled reactants (¹⁵N¹⁸O and ¹³CO) were employed.

2. Experimental

2.1. Catalyst preparation

The preparation of Pt/BaO/Al₂O₃ has been described elsewhere [30]. Briefly, γ -alumina (Sasol, surface area of 132 m²/g) was impregnated with aqueous Ba(NO₃)₂, dried and calcined at 500 °C in air. The Ba-loaded Al₂O₃ was subsequently impregnated with aqueous tetraammineplatinum(II) nitrate and further calcined at 500 °C. The Pt and BaO contents of the catalyst were 1 wt% and 20 wt%, respectively (the balance being Al₂O₃). Relative to the bare support, the catalyst shows decreased BET surface area and pore volume (98 m²/g vs. 132 m²/g and 0.32 cm³/g vs. 0.43 cm³/g). This decrease is mainly ascribed to the blocking of some pores during the loading of BaO on the support.

2.2. DRIFTS measurements

DRIFTS measurements were performed in an integrated stainless steel reaction cell, using a MIDAC model M2500 FTIR spectrometer coupled with a Harrick Scientific barrel ellipsoidal mirror DRIFT accessory. This specially designed DRIFTS assembly utilizes a barrel-shaped mirror that encompasses the catalyst sample. With the sample at one focal point of the ellipsoid and the detector at the opposite focal point, the system collects roughly 300° of the reflected IR signal and thus provides high sensitivity and high signal to noise ratios. The system is typically operated at slightly below atmospheric pressure (around 500 Torr) to prevent stagnation in the cell and to maintain the seal between the removable

hemispherical ZnSe dome and the cell body. Mass flow controllers were used to establish the inlet gas concentrations, in conjunction with a sparger system submerged in a recirculating constant temperature bath that controlled the inlet concentration of H₂O. To minimize the initial spectral features associated with carbonates and achieve a good background spectrum, the catalyst was first pretreated under lean-rich cycling conditions at 300 °C overnight, followed by heating to 500 °C in H₂ to completely remove nitrate and carbonate. Clean initial background spectra were recorded every 50 °C in a decreasing sequence from 450 to 100 °C. The cycling gas composition for this initial pretreatment consisted of lean (300 ppm NO and 8% O₂ in Ar) and rich (1% H₂ in Ar) feeds.

Isocyanate formation was investigated in two different types of experiments involving cycling and continuous flowing conditions. For the lean-rich cycling study, the sample was repeatedly exposed to lean and rich phases until a “steady-state” cyclic condition was reached. This state is achieved when the final spectrum recorded at the end of the lean phase is identical to the final lean spectrum of the preceding cycle; additionally, the corresponding final rich phase spectra should also match for each cycle. A new spectrum was recorded every 5 s using an average of 8 scans (scan rate = 2 scans/s). The gas concentrations and times for each phase were: lean – 300 ppm NO, 8% O₂ in Ar for 6.5 min, and rich – 1% CO in Ar for either 2 or 1 min. For the study using continuous flowing gas, NO_x was first stored at 300 °C using feed gas containing 300 ppm NO and 8% O₂ balanced with Ar for different periods of time, after which the sample was purged with Ar and cooled to 250 °C for NO_x reduction by CO with two different concentrations: 1% CO and 0.35% CO. To maximize NCO formation, H₂O was not included in the feed (unless otherwise indicated). To study reactivity of NCO toward H₂O, a sparger system submerged in a recirculating constant temperature bath was used to deliver the desired concentration of water vapor in an Ar flow.

Isocyanate reactivity was tested by two different methods: temperature-programmed surface reaction (TPSR) and isothermal surface reaction (ISR). For the TPSR study, isocyanate species were first generated on the catalyst surface at 350 °C by reaction of NO with CO (500 ppm NO and 1% CO in Ar). Different from the standard approach of generating isocyanate by reduction of stored NO_x with CO, use of the NO + CO reaction can generate significant amounts of isocyanate on the catalyst surface but with very limited formation of nitrate; this avoids excessive interference from nitrate bands during the study of NCO reactivity. This approach has been reported by Bion et al. [31]. In order to differentiate N₂ from CO in the mass spectrometer, labeled ¹⁵N¹⁸O and ¹³CO were used in these experiments. After the surface was saturated by NCO species at 350 °C, followed by cooling to 100 °C in flowing NO + CO, DRIFTS scans were recorded every 10 s using 10 averaged scans at 100 °C, after which the gas was switched to the desired gas for the TPSR experiment. The TPSR study was performed at intervals of 50 °C from 100 °C to 450 °C, using a heating rate of 5 °C/min between each dwell temperature. At each temperature, spectra were recorded using 100 averaged scans. Different from TPSR, ISR experiments were used to investigate the qualitative kinetics of NCO reactions. NCO species were first generated on the catalyst surface by reaction of NO with CO at 350 °C for 5 min, after which the feed gas was switched to one containing the desired reactant. During reaction, spectra were recorded every 10 s using a 10 scan average. The NCO reaction conditions consisted of one of the following: (i) Ar, (ii) 0.6% O₂, (iii) 500 ppm NO, (iv) 500 ppm NO + 0.6% O₂, or (v) 3.5% H₂O. In all cases Ar was used as the balance gas.

2.3. Mass spectrometry

A mass spectrometer (Stanford Research Systems RGA100 with electron multiplier) was used to detect the evolution of gaseous

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