

Quantified NO_x adsorption on Pt/K/gamma-Al₂O₃ and the effects of CO₂ and H₂O

Todd J. Toops^{a,*}, D. Barton Smith^a, William S. Epling^b, Jim E. Parks^b, William P. Partridge^a

^aOak Ridge National Laboratory Fuels, Engines and Emissions Research Center 2360 Cherahala Blvd. Knoxville, TN 37932-1563, USA

^bEmeraChem 2375 Cherahala Blvd. Knoxville, TN 37932-1564, USA

Received 29 April 2004; received in revised form 20 July 2004; accepted 29 October 2004

Available online 18 December 2004

Abstract

A multi-component NO_x-trap catalyst consisting of Pt and K supported on γ -Al₂O₃ was studied at 250 °C to determine the roles of the individual catalyst components, to identify the adsorbing species during the lean capture cycle, and to assess the effects of H₂O and CO₂ on NO_x storage. The Al₂O₃ support was shown to have NO_x trapping capability with and without Pt present (at 250 °C Pt/Al₂O₃ adsorbs 2.3 μ mol NO_x/m²). NO_x is primarily trapped on Al₂O₃ in the form of nitrates with monodentate, chelating and bridged forms apparent in Diffuse Reflectance mid-Infrared Fourier Transform Spectroscopy (DRIFTS) analysis. The addition of K to the catalyst increases the adsorption capacity to 6.2 μ mol NO_x/m², and the primary storage form on K is a free nitrate ion. Quantitative DRIFTS analysis shows that 12% of the nitrates on a Pt/K/Al₂O₃ catalyst are coordinated on the Al₂O₃ support at saturation.

When 5% CO₂ was included in a feed stream with 300 ppm NO and 12% O₂, the amount of K-based nitrate storage decreased by 45% after 1 h on stream due to the competition of adsorbed free nitrates with carboxylates for adsorption sites. When 5% H₂O was included in a feed stream with 300 ppm NO and 12% O₂, the amount of K-based nitrate storage decreased by only 16% after 1 h, but the Al₂O₃-based nitrates decreased by 92%. Interestingly, with both 5% CO₂ and 5% H₂O in the feed, the total storage only decreased by 11%, as the hydroxyl groups generated on Al₂O₃ destabilized the K–CO₂ bond; specifically, H₂O mitigates the NO_x storage capacity losses associated with carboxylate competition.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Lean NO_x traps; DRIFTS; Chemisorption; Potassium; Pt; γ -Al₂O₃

1. Introduction

Multi-component NO_x adsorber catalysts are a leading solution for the impending stricter diesel emissions regulations [1]. They are based on the ability of alkali, alkaline, and alkaline earth elements to trap NO_x under lean conditions in the form nitrates [2–4]. The stored nitrates are then released and reduced by H₂, CO, or hydrocarbons in a brief rich interval to obtain benign N₂. These catalysts require an oxidation component, typically a noble metal like Pt, a storage component, commonly Ba, and a high surface

area support such as γ -Al₂O₃. Potassium is another element that has shown potential as a storage component [5–6], especially in conjunction with Ba [7–8]. Numerous studies have shown that K has a strong interaction with Al₂O₃ supports [9–12], but there is scarce information on the specific contributions of K to NO_x storage, especially in the presence of CO₂ and H₂O.

This study was primarily focused on understanding the NO_x adsorption step of a catalyst consisting of Pt and K phases on an Al₂O₃ support. Additionally, the contributions of each catalyst component were explored by studying the following model catalysts: Pt on Al₂O₃, K on Al₂O₃, and Al₂O₃ only. Diffuse Reflectance mid-Infrared Fourier Transform Spectroscopy (DRIFTS) was the primary analytical tool used to determine the form of stored NO_x.

doi of the original article: 10.1016/j.apcatb.2004.10.021

* Corresponding author. Tel.: +1 865 946 1207; fax: +1 865 946 1354.

E-mail address: toopstj@ornl.gov (T.J. Toops).

Table 1
Formulation and characterization of studied catalysts

Catalyst	Pt (wt%)	K ₂ CO ₃ (wt%)	Al ₂ O ₃ (wt%)	Dispersion (Pt _s /Pt _T)	Surface area (m ² /g)
γ-Al ₂ O ₃	–	–	100	–	146
Pt/Al ₂ O ₃	1.0	–	99	37%	151
K/Al ₂ O ₃	–	8.0	92	–	146
Pt/K/Al ₂ O ₃	1.0	8.0	91	18%	149

A method for quantifying DRIFT absorbance spectra, described in an earlier publication [13], was used to analyze some portions of the NO_x adsorption.

In addition to the component contribution study, the individual and combined effects of CO₂ and H₂O were also studied. Often during evaluations of preliminary catalysts the effects of common exhaust components are ignored, however, it has been shown that these ubiquitous components can have considerable, and at times detrimental effects, on the functionality of lean-NO_x reducing catalysts [14–20].

2. Experimental

The model catalysts were γ-Al₂O₃, 1 wt% Pt on γ-Al₂O₃ (Pt/Al₂O₃), 8.0% K₂CO₃ on γ-Al₂O₃ (K/Al₂O₃), and the complete NO_x adsorber catalyst, 8% K₂CO₃ on 1% Pt/Al₂O₃ (Pt/K/Al₂O₃).¹ An 8% loading of K₂CO₃ corresponds to 64% of a monolayer. The catalyst formulations are summarized in Table 1 along with results from H₂ chemisorption and N₂ physisorption measurements. Before experimentation, all catalysts underwent a pretreatment with 50 cm³ (STP)/min (sccm) of 1% H₂ in N₂ (99.999% pure) at 450 °C; the length of this pretreatment depended on the catalyst formulation. The pretreatment established a consistent starting point for each experiment.

The DRIFTS system was detailed in an earlier paper [13,21]. It consists of a MIDAC model M2500 FTIR spectrometer coupled to a Harrick Scientific barrel ellipsoidal mirror DRIFT accessory with an integrated stainless-steel reaction cell. The catalyst samples were reacted under carefully controlled temperature and gas-flow conditions. The system can be heated to 525 °C, is configured to allow up to 10% H₂O in the feed, and is typically operated at slightly below atmospheric pressure, typically 500 Torr, to prevent stagnation in the cell and to sustain the seal between the removable hemispherical ZnSe dome and the cell body. Tylan General mass flow controllers establish the inlet gas concentrations, in conjunction with a dual sparger system submerged in a NESLAB RTE-110 recirculating constant temperature bath that controls the inlet concentration of H₂O. A General Eastern DewPro humidity sensor is used to verify the water concentration. The reactant gases used in the measurements had the following purities: CO₂ (99.999%), 1% H₂ in N₂ (99.999%),

1000 ppm NO in N₂ (99.0%), 1000 ppm NO₂ in N₂ (99.0%), and N₂ (99.999%).

Before exposure to the NO_x gas mixtures, each catalyst sample was pretreated in the cell by heating it to 450 °C and reacting it with a 50 sccm flow of 1% H₂/N₂. The pretreatment continued until the carbonate absorbance features in the FTIR spectra were diminished and stabilized at their minimum intensities. The pretreatment was typically accomplished in 1 h; pretreatment for longer periods produced no measurable reduction in carbonate peak intensities. Following pretreatment, the 1% H₂/N₂ flow was continued while the sample was cooled to 250 °C. At 250 °C, the cell was sealed, and reactant gas mixture was routed through the bypass loop for a period of 5 min to stabilize the gas mixture concentrations. A background DRIFT spectrum was acquired just before introducing the reactant mixture. All NO_x adsorption experiments discussed in this paper were performed at 250 °C, and the majority of the DRIFT spectra were obtained in situ at 250 °C.

3. Results

Experiments were performed with two specific goals. The first goal was to determine the contributions of the various catalyst phases and identify the functional groups associated with specific DRIFTS features. The second goal was to quantify the effects of H₂O and CO₂ on the NO_x adsorption capacity of the Pt/K/Al₂O₃ catalyst.

Al₂O₃ without Pt was the first material evaluated, at 250 °C with 10 sccm of 500 ppm NO in N₂. Fig. 1a shows the DRIFT spectra after 1, 10, 20, and 60 min of NO exposure. The observed absorbance peaks correspond closely to the surface nitrogen species observed in previous work on NO and Al₂O₃. Table 2 lists the assignment of functional groups to the absorbance [22–29]. In general, nitrate formation was slow on Al₂O₃. Linear nitrite, at 1460 cm⁻¹, and chelating nitrate, at 1590 cm⁻¹, form in the first minute of NO exposure; no additional formation of these surface species occurs with continued NO exposure. Further uptake was nominal until 25 min when a peak associated with unidentate nitrate appears at 1550 cm⁻¹. This peak represents the primary surface species formed for NO exposures beyond 25 min. The unidentate nitrate, at 1550 cm⁻¹, apparently does not displace the linear nitrite, 1460 cm⁻¹, or the chelating nitrate, 1590 cm⁻¹, based on their stability over long NO exposures. The DRIFT spectrum obtained after adding 5% O₂ to the base 500 ppm NO flow

¹ EmeraChem provided all catalysts for this study.

Download English Version:

<https://daneshyari.com/en/article/9609893>

Download Persian Version:

<https://daneshyari.com/article/9609893>

[Daneshyari.com](https://daneshyari.com)