Quantification of the in situ DRIFT spectra of Pt/K/γ-A1$_2$O$_3$ NO$_x$ adsorber catalysts

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Abstract

A method to quantify DRIFT spectral features associated with the in situ adsorption of gases on a NO$_x$ adsorber catalyst, Pt/K/Al$_2$O$_3$, is described. To implement this method, the multicomponent catalyst is analysed with DRIFT and chemisorption to determine that under operating conditions the surface comprised a Pt phase, a pure γ-Al$_2$O$_3$ phase with associated hydroxyl groups at the surface, and an alkalized-Al$_2$O$_3$ phase where the surface –OH groups are replaced by –OK groups. Both DRIFTS and chemisorption experiments show that 93–97% of the potassium exists in this form. The phases have a fractional surface area of 1.1% for the 1.7 nm-sized Pt, 34% for pure Al$_2$O$_3$ and 65% for the alkalized-Al$_2$O$_3$. NO$_2$ and CO$_2$ chemisorption at 250 °C is implemented to determine the saturation uptake value, which is observed with DRIFTS at 250 °C. Pt/Al$_2$O$_3$ adsorbs 0.087 μmol CO$_2$/m^2 and 2.0 μmol NO$_2$/m^2, and Pt/K/Al$_2$O$_3$ adsorbs 2.0 μmol CO$_2$/m^2 and 6.4 μmol NO$_2$/m^2. This method can be implemented to quantitatively monitor the formation of carboxylates and nitrates on Pt/K/Al$_2$O$_3$ during both lean and rich periods of the NO$_x$ adsorber catalyst cycle.
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1. Introduction

A solution to the stricter EPA NO$_x$ emission's regulations has not been fully realized and research efforts are continuing. A leading solution is a multicomponent catalyst that utilizes the ability of alkali and alkaline elements to trap NO$_x$ under lean conditions, in the form of a nitrate [1]. The stored nitrate is then reduced by H$_2$, CO, or hydrocarbons in a brief rich-burn interval to obtain the benign products N$_2$ and H$_2$O. To work effectively these catalysts require an oxidation component, typically a noble metal like Pt, a storage component, commonly Ba, and a high surface area support like γ-Al$_2$O$_3$. Potassium is another element that has shown potential as a storage component [2–3], especially in conjunction with Ba [4–5]; however, despite the numerous studies showing a strong interaction of potassium with Al$_2$O$_3$ supports [6–9], reports on the specific contributions of potassium are scarce.

This study discusses the state of potassium in a Pt/K/Al$_2$O$_3$ NO$_x$ adsorber catalyst and the application of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for quantitative analysis of adsorbate. This technique could be a valuable tool for screening catalyst components and determining the optimal loadings of these components. The DRIFT system used in this work is capable of analysing catalyst surface species in realistic exhaust conditions during measurement intervals as short as 5 s, and when combined with a volumetric chemisorption system, the system provides quantitative adsorbate analysis. Although the primary focus of this quantitative study is on the carboxylate and ionic nitrate that form on the potassium phase of the catalyst, the contribution of the support is fully investigated to allow correct and full catalyst system analysis. A complimentary DRIFTS study discussing NO$_x$ adsorption with this catalyst in a synthetic exhaust stream is discussed elsewhere [10].

Nomenclature

Al_s	aluminum surface atoms
$\overline{A}_{total}$	specific surface area of Pt/K/Al$_2$O$_3$ (m^2/g)
B_R	systematic standard deviation (%)
K_P	equilibrium constant
$M_{K_2CO_3}$	mass fraction of K$_2$CO$_3$ (g K$_2$CO$_3$/g Pt/K/Al$_2$O$_3$)
P_{NO_2}	partial pressure of NO$_2$ (Torr)
$P_{N_2O_4}$	partial pressure of N$_2$O$_4$ (Torr)
P_{std}	standard pressure (Torr)
P_T	total pressure (Torr)
Pt_S	platinum surface atoms
Pt_T	total platinum atoms
RF_i	response factor of species i ((μmol/m^2)/(absorbance cm^{-1}))
SA_i	specific surface area of species (m^2/g$_i$)
$S_{\overline{X},R}$	experimental standard deviation (%)
U_{AlOK}	NO$_2$ on AlOK surface of Pt/K/Al$_2$O$_3$ (μmol NO$_2$/(m^2)Pt/K/Al2O3)
$U_{Al_2O_3}$	NO$_2$ on Al$_2$O$_3$ surface of Pt/K/Al$_2$O$_3$ (μmol NO$_2$/(m^2)Pt/K/Al2O3)
U_{ISO}	ISO total uncertainty (%)
U_{Pt/Al_2O_3}	NO$_2$ on total surface of Pt/Al$_2$O$_3$ (μmol NO$_2$/(m^2)Pt/Al2O3)
$U_{Pt/K/Al_2O_3}$	NO$_2$ on total surface of Pt/K/Al$_2$O$_3$ (μmol NO$_2$/(m^2)Pt/K/Al2O3)
σ_K	surface number density of K (K atom/length^2)

2. Experimental

The base catalyst was 1 wt.% Pt on γ-Al$_2$O$_3$, and the NO$_x$ adsorber catalyst, Pt/K/Al$_2$O$_3$, contained 8.01 wt.% K$_2$CO$_3$, added by the incipient wetness technique.[i] Before experimentation, all catalysts underwent a pretreatment with 50 cm$^3_{STP}$/min (sccm) of 1% H$_2$/N$_2$ (99.999% pure) at 450 °C; the length of this pretreatment depended on the system used, and is discussed in detail below. The goal of this pretreatment was to establish a consistent starting point for each experiment.

The DRIFTS system used in this work was specially designed for in situ analysis of a sample surface in a temperature-controlled flowing gas cell. This DRIFTS system has been previously described elsewhere [11]. It consists of a Harrick Scientific ellipsoidal mirror DRIFT accessory coupled to a MIDAC model M2500 FTIR spectrometer, as depicted schematically in Fig. 1. In the system, a collimated beam of infrared light emitted by the FTIR spectrometer is focused by a parabolic mirror onto the surface of a sample, positioned at one focus of the barrel ellipsoid. A mercury–cadmium–telluride (MCT) detector obtained from *Infra Red Associates* is positioned at the

opposing focus of the ellipsoid. The ellipsoidal mirror geometry enables maximum detection of light diffusely scattered at all azimuthal angles from the sample surface, while the parabolic focusing mirror blocks detection of light specularly reflected from the sample surface. Since nearly 360° of the diffusely reflected radiation is received by the detector in this barrel ellipsoid attachment compared to only about 75° in the Praying Mantis^{TM}, designed by Harrick, the signal to noise ratio is about five times greater. A customized version of the GRAMS/32 spectrum acquisition and analysis software is used to operate the DRIFTS system. One hundred scans were used for each recorded spectra, which were converted to absorbance units using Eq. (1):

$$\text{Absorbance} = -\log_{10}\left[\frac{\text{sample file}}{\text{background file}}\right] \tag{1}$$

The background file varied depending on the experiment, and it is identified for each spectrum in Section 3. Kubelka–Munk (KM) units, defined as:

$$\frac{1 - [\text{sample file/background file}]^2}{2[\text{sample file/background file}]} \tag{2}$$

are not used due to the possibility of a peak having a negative response. There are residual carbonates that are difficult to completely remove under the standard pretreatment. KM units treat all differences between the sample and the background as positive responses.

The catalyst samples reacted under carefully controlled temperature and gas-flow conditions. The reaction cell consisted of a stainless-steel vacuum fixture with a heated sample holder. The IR light is transmitted to and from the sample surface through a removable hemispherical dome of spectral-grade zinc selenide (ZnSe) that was sealed to the cell using a fluoroelastomer o-ring gasket. The sample was heated by a 100 W Chromalox cartridge heater welded into the base of the fixture. A type K thermocouple was embedded in the cartridge, which was temperature controlled via an Omega PID temperature controller. Samples were prepared for the cell by loosely packing the catalyst powders into 0.32 cm diameter, 0.26 cm deep stainless-steel rings. The sample surface was levelled with the ring edge to facilitate alignment of the sample at the coincident focus of the parabolic and ellipsoidal mirrors. The samples were placed directly on the sample holder, and a type K thermocouple probe was placed in thermal contact with the ring to allow measurements of the sample temperature. The sample temperature differed by less than 2 °C from that of the cartridge. The cross-sectional area of the exposed catalyst was 0.08 cm^2, and approximately 0.03 cm^2 of this surface was illuminated by the focused IR beam from the FTIR spectrometer. A manifold of Tylan General FC-280S mass flow controllers provided the gas mixture feed to the cell. Gases were withdrawn from the cell

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