

**QUANTIFICATION OF THE *IN-SITU* DRIFT SPECTRA OF Pt/K/GAMMA-
Al₂O₃ NO_x ADSORBER CATALYSTS**

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Submitted to:

Applied Catalysis B
April 2004

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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/Al₂O₃, is described. To implement this method the multicomponent catalyst is analyzed with DRIFT and chemisorption to determine that at operating conditions the surface is comprised of a Pt phase, a pure γ -Al₂O₃ phase with associated hydroxyl groups at the surface, and an alkalinized-Al₂O₃ 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 Al₂O₃ and 65% for the alkalinized-Al₂O₃. NO₂ and CO₂ chemisorption at 250°C is implemented to determine the saturation uptake value that is observed with DRIFTS at 250°C. Pt/Al₂O₃ adsorbs 0.087 $\mu\text{mols CO}_2/\text{m}^2$ and 2.0 $\mu\text{mols NO}_2/\text{m}^2$ and Pt/K/Al₂O₃ adsorbs 2.0 $\mu\text{mols CO}_2/\text{m}^2$ and 6.4 $\mu\text{mols NO}_2/\text{m}^2$. This method can be implemented to quantitatively monitor the formation of carboxylates and nitrates on Pt/K/Al₂O₃ during both lean and rich periods of the NO_x adsorber catalyst cycle.

Keywords: NO_x adsorber catalysts, Lean NO_x Traps, Quantified DRIFTS, Chemisorption, Potassium, Pt, γ -Al₂O₃, Pt/K/Al₂O₃.

Introduction

A solution to the stricter EPA NO_x emissions 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 H₂, CO, or hydrocarbons in a brief rich burn interval to obtain the benign products N₂ and H₂O. 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 -Al₂O₃. 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 Al₂O₃ supports [6-9], reports on the specific contributions of potassium are scarce.

This study discusses the state of potassium in a Pt/K/Al₂O₃ NO_x adsorber catalyst and the application of *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for quantitative analysis of adsorbates. 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 analyzing catalyst surface species in realistic exhaust conditions during measurement intervals as short as 5 seconds, 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].

Experimental

The base catalyst was 1 wt% Pt on γ -Al₂O₃, and the NO_x adsorber catalyst, Pt/K/Al₂O₃, contained 8.01 wt% K₂CO₃ added by the insipient wetness technique¹. Before experimentation, all catalysts underwent a pretreatment with 50 cm³_{STP}/min (sccm) of 1% H₂/N₂ (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 *InfraRed 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

¹ *EmeraChem* (2375 Cherahala Blvd., Knoxville, TN 37932) provided all catalysts for this study.

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™ design 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 Equation 1:

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

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

$$\text{KM} = \frac{1 - \left[\frac{\text{sample file}}{\text{background file}} \right]^2}{2 \cdot \left[\frac{\text{sample file}}{\text{background file}} \right]} \quad (2)$$

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 were 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 leveled 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 cm² and approximately 0.03 cm² 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 with a Gast model MDA-P109-AA oil-less vacuum pump. A needle valve in the connection between the cell and pump was adjusted to maintain the cell pressure at a value slightly below atmospheric pressure, typically 500 torr, to prevent stagnation in the cell and to sustain the tightness of the seal between the ZnSe dome and the vacuum fixture. The leak rate of ambient air into the cell due to the subambient pressure was less than 2×10^{-4} sccm. 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%). The measurements were completed within the purity certification period certified by the vendor, and standard precautions for preventing cross-contamination of the gas mixtures were followed.

Each catalyst sample was pretreated in the cell before exposing it to the NO_x gas mixtures by heating the sample to 450°C in 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 one hour; pretreatment for longer periods produced no measurable differences in carbonate peak intensities. Following pretreatment, the 1% H₂/N₂ flow was continued while the sample temperature was decreased to 250°C. At 250°C, the cell was sealed, and reactant gas mixture was routed through the bypass loop for a period of five minutes. A background DRIFT spectrum was acquired just before introducing the reactant mixture.

The chemisorption and physisorption analyzer used for surface area determinations, measuring active metal dispersions, and quantifying adsorbates is a conventional volumetric system that was developed in-house. The analyzer consists of a glassware gas-mixing manifold for introducing H₂, CO₂ and N₂ gases, a U-shaped quartz sample cell, and an oil-less high vacuum system that provides base pressures in the low 10⁻⁷ torr range when evacuating the manifold and removing adsorbates from the samples. The system was configured to allow gas flow through the sample cell using an MKS Type 247 control unit with MKS 179A11CS1AM mass flow controllers, and all o-rings in the Pyrex/stainless steel system were constructed of perfluoroelastomers to withstand the use of NO₂. The sample cell was heated with a 700W OMEGALUX vertical furnace in conjunction with a PID temperature controller. The dead volume between the sample cell and furnace wall was filled with a copper insert to increase thermal stability in the

sample cell. Isotherm pressure readings were obtained using a Mensor 6100 DPT pressure transducer with 0.01% full-scale accuracy. Fresh samples were dried for 1 h at 150°C in He flowing at 50 sccm to remove adsorbed H₂O; the samples were then weighed and reloaded in the sample cell. The dried catalysts were pretreated in 50 sccm of 1% H₂/N₂ at 450°C overnight, evacuated to the base pressure, and then cooled to the appropriate temperature under vacuum. Once thermal stability was achieved in the sample cell, the probe gas was introduced. The data points for total uptake were recorded after the average rate of uptake was less than 0.01 torr/min with a minimum time allotment of 1 hour for the first measurement; the 3-5 subsequent points were typically recorded after equilibrating for 10 minutes. Where applicable, the reversible uptake was measured by evacuating to the base pressure for 1 hour and repeating the procedure.

H₂ chemisorption was used to calculate the Pt dispersion, i.e. percentage of Pt surface atoms (Pt_S) compared to total Pt atoms in the sample (Pt_T), based on the irreversibly adsorbed hydrogen uptake and an H:Pt_S ratio of one. The chemisorption apparatus was also used to determine a quantitative standard for calibration of the DRIFT-measured concentration of catalyst surface species in terms of μmols/m². The calibration value for carbon-based adsorbates was obtained with CO₂ chemisorption and the value for the nitrate features was obtained with NO₂ chemisorption, both at 250°C.

Accurate chemisorption measurements of NO₂ required an additional consideration due to the dimerization of NO₂ to form N₂O₄ in the gas phase, according to the equilibrium reaction:

where K_p is the equilibrium constant. The equilibrium constant at temperature T (Kelvin) can be expressed in terms of the partial pressures in the gas mixture:

$$K_p(T) = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \cdot \frac{1}{P_{\text{std}}}, \quad (3)$$

where P_{NO_2} and $P_{\text{N}_2\text{O}_4}$ are the partial pressures of NO_2 and N_2O_4 and P_{std} is the pressure at one standard atmosphere. Since the chemisorption system is based on pressure measurements that are converted to moles of gas, and NO_2 chemisorption is based on the adsorption of NO_2 , it is vital to be able to measure NO_2 “units”, or monomers, in the system. Using Bodenstein’s empirical formula for $K_p(T)$ [12]:

$$\text{Log}_{10} K_p(T) = -\frac{2692}{T} + 1.75 \log_{10} T + 4.83 \times 10^{-3} \cdot T - 7.14 \times 10^{-6} \cdot T^2 + 3.06 \quad (4)$$

and the relationship between the total pressure P_T and the sum of the partial pressures:

$$P_T = P_{\text{NO}_2}^2 + P_{\text{N}_2\text{O}_4} \quad (5)$$

it is possible to calculate P_{NO_2} and $P_{\text{N}_2\text{O}_4}$ at any T and P_T . In the implementation of this calculation, obtaining equilibrium before and after introduction of the gas to the cell is essential.

Results

N_2 physisorption at -196°C indicated the surface area of $\text{Pt/K/Al}_2\text{O}_3$ and $\text{Pt/Al}_2\text{O}_3$ to be 150 and 151 m^2/g , respectively. H_2 chemisorption at 25°C revealed the Pt dispersion to be 59% on $\text{Pt/K/Al}_2\text{O}_3$ and 55% on $\text{Pt/Al}_2\text{O}_3$. Room temperature absorbance spectra of the two untreated catalysts are compared to the pretreated catalysts

in Figure 2. Spectral assignments are listed in Table 1 for Pt/Al₂O₃ and Table 2 for Pt/K/Al₂O₃. These assignments are primarily based on previous work with NO_x on Al₂O₃ [13-20] and CO₂ on K/Al₂O₃ [7,9,13,18,21-22]; details are discussed elsewhere [10]. For the purposes of this paper, the pretreated spectra in Figures 2b and 2d will be referred to as the initial state of the catalyst, where the near elimination of the absorbance peaks associated with carbonate formation is evident.

NO₂ adsorption on Pt/Al₂O₃ at 250°C in the DRIFTS reactor with a feed gas concentration of 300 ppm NO₂ in N₂ resulted in the appearance of two groups of peaks centered near 1570 cm⁻¹ and 1270 cm⁻¹ as shown in Figure 3. Both groups consist of contributions from several nitrate species formed on alumina and are assigned according to Table 1. NO₂ adsorption continued, with storage dominated by the nitrate features until the catalyst surface was saturated, i.e. until no temporal change was observed in the spectra. NO₂ adsorption on Pt/K/Al₂O₃ at 250°C in the DRIFTS reactor with a feed gas concentration of 300 ppm NO₂ in N₂ resulted in the appearance of one dominant peak at 1380 cm⁻¹ and four lesser peaks at 1750 cm⁻¹, 1525 cm⁻¹, 1315 cm⁻¹ and 1260 cm⁻¹. The dominant peak was assigned to the NO₃⁻ free nitrate, or ionic nitrate, group adsorbing on the potassium phase of the catalyst, the peak at 1750 cm⁻¹ was assigned to a combination band associated with the free nitrate [18], and the remaining peaks are attributed to free nitrites and Al₂O₃-based nitrates; the details of these assignments are discussed elsewhere [10].

Flowing 5% CO₂ over Pt/K/Al₂O₃ at 250°C resulted in the immediate appearance of spectral features at 1600 and 1310 cm⁻¹, features associated with carboxylate ions;

conversely, Pt/Al₂O₃ did not adsorb CO₂ in appreciable amounts. The resulting spectra at carboxylate saturation are shown in Figure 4 for both catalysts.

The absorbance peaks associated with the primary nitrate and carbonate species appear in the 1900 to 1150 cm⁻¹ region of the DRIFT spectra, as indicated by the spectral assignments for the functional groups listed in Tables 1 and 2. This region of interest was analyzed in each spectrum by using the GRAMS/32 least-squares curve fitting routine to resolve the positions and intensities of overlapping peaks and compute the areas of the fitted curves. The fitting procedure for each spectrum began with a determination of the number of nitrate or carbonate species peaks present in the spectrum. Only peaks that could be correlated to the functional groups listed in Tables 1 and 2 were selected for inclusion in the curve fit analysis. A linear baseline and a mixture of Lorentzian and Gaussian shape functions was used to fit each peak. The fitting procedure was constrained to find the spectral position of each peak within 5 cm⁻¹ of the value assigned in the tables. The iterative fitting procedure varied the peak width, peak height, and weighting factors for the shape functions to obtain a convergence of the fit (minimization of the residuals in the least-squares approximation). For some spectra, the reduced chi-squared optimization value indicated that the fit was not optimized. This was a consequence of the limitation placed on the selection of the number of peaks. No attempt was made to improve the analysis by adding peaks for unidentified species.

The repeatability of the results in this procedure was established by performing a series of five NO₂ adsorption measurements at 250°C on the same Pt/K/Al₂O₃ sample. The sample was reduced in H₂ at 450°C prior to each of the adsorption measurements.

The analysis of the five independent NO_x adsorption experiments to full capacity yielded an experimental standard deviation, $S_{\bar{x},R}$, of 1.2% for the calibration area (i.e., area of the feature associated with the free nitrate ion) with no evidence of degraded capacity under the thermal cycling. Seven independent scans of one of the fully loaded samples indicated a 0.5% systematic standard deviation, B_R . Using the ISO uncertainty model with 95% confidence interval:

$$U_{ISO} = \pm t_{95} \left[\left(\frac{B_R}{2} \right)^2 + (S_{\bar{x},R})^2 \right]^{1/2} \quad (6)$$

these experimental and systematic errors translate to a total uncertainty, U_{ISO} , of 3.5% [23].

Chemisorption measurements were performed on Pt/K/Al₂O₃ and Pt/Al₂O₃ under conditions similar to those in the DRIFTS reactor to establish quantitative standards for the carboxylate and nitrate features observed at 250°C in the DRIFTS spectra. The samples were pretreated (reduced) at 450°C in a 50 sccm flow of 1% H₂/N₂ before the measurement of adsorption isotherms. To establish the carboxylate standards, measurements of the total and irreversible uptakes of CO₂ were performed over the range of CO₂ partial pressures available in the chemisorption/physisorption analyzer. Figure 5 shows the isotherms of the total and reversible uptakes. The partial pressure of CO₂ in the DRIFTS experiments was 25 torr (5% CO₂ concentration in 500 torr total pressure). An extrapolation of the isotherms to this partial pressure shows that Pt/K/Al₂O₃ adsorbed a total of 2.0 μmole/m² with 1.0 μmole/m² irreversibly adsorbed. For the same conditions, Pt/Al₂O₃ only had a total adsorption of 0.087 μmole/m², with no irreversible

uptake—a result that was consistent with the DRIFTS measurements. The total nitrate adsorption was established for both Pt/K/Al₂O₃ and Pt/Al₂O₃ based on NO₂ chemisorption at 250°C. Figure 6 shows the isotherms of the total and irreversible uptakes. Unlike CO₂, NO₂ readily adsorbs on both Pt/Al₂O₃ and Pt/K/Al₂O₃; this is illustrated by the magnitude of the nitrate absorbances in Figure 3 and the total uptake isotherms. The partial pressure of NO₂ in the DRIFTS experiments was 0.15 torr (300 ppm concentration of NO₂ in 500 torr total pressure). An extrapolation of the isotherm to this partial pressure shows that Pt/Al₂O₃ adsorbs 2.0 μmole/m² and Pt/K/Al₂O₃ adsorbs 6.4 μmole/m². N₂ physisorption at -196°C was measured before and after chemisorption experiments, and BET calculations revealed no change in the specific surface area of 151 m²/g for Pt/Al₂O₃ or 150 m²/g for Pt/K/Al₂O₃.

Similar to the DRIFTS work, it was of interest to determine the total error associated with the chemisorption apparatus and technique, especially since the equilibrium issues associated with the dimerization of NO₂ could lead to significant errors. Three independent NO_x adsorption experiments at 250°C to full capacity indicated an experimental standard deviation, $S_{\bar{x},R}$, of 3.1% for the total NO₂ uptake; three repeated measurements of one sample indicated a 1.0% systematic standard deviation, B_R . Using the ISO uncertainty model with 95% confidence interval, this translates to a total uncertainty, U_{ISO} , of 13% [23].

Discussion

DRIFTS lends itself to the study of NO_x adsorbers quite well due to its ability to detect small concentrations of surface species on catalysts. In most catalyst studies, DRIFTS is used simply as a qualitative tool to detect surface species that are involved in reactions on catalyst surface. Its diagnostic utility would be greatly enhanced by improving its ability to quantify the concentrations of surface species, especially in a time resolved study. Quantification is not trivial and is not typically performed, but with the aide of a quantitative volumetric chemisorption system, it is possible as discussed below.

The quantitative analysis of DRIFT spectra is based on an application of Beer's Law, which relates the intensity of an absorbance peak to the concentration of a species on the surface. The absorbance is assumed to be linearly proportional to the concentration of the absorbing species when the absorbance peak has a magnitude below 2.0 [24], which was the case for this study where absorbances were generally below 1.0 in the region of interest. As stated in the Experimental section, the DRIFTS spectra were calculated and presented in diffuse absorbance units rather than the Kubelka-Munk units that are often used in quantitative DRIFTS analysis. The Kubelka-Munk function compensates for differences between samples with identical adsorbate concentrations but variations in particle size distributions, particle shape distributions, and packing densities that affect the scattering of light within the samples. In this study, absorbance spectra were measured on a given sample at constant temperature and pressure, and there was no variability in the scattering within the sample. In applying Beer's Law, two calibration points are necessary to define the linear relationship, and if it is assumed that there is no

absorbance at zero concentration only one standardized measurement is necessary for the calibration. Absorbance is based on the area of the specific feature, 1380 cm^{-1} for the K-based nitrate and 1599 cm^{-1} for the K-based carboxylate, and concentration is based on $\mu\text{mol}/\text{m}^2$ adsorbate determined by chemisorption and BET measurements. The calibrations yield DRIFT response factors, RF_i , for species i such that:

$$\text{RF}_i = \frac{\text{Uptake of species } i [\mu\text{mol}/\text{m}^2]}{\text{Peak Area of Species } i [\text{absorbance} \cdot \text{cm}^{-1}]} \quad (7)$$

As noted earlier this response factor is specific to the adsorbate as well as the temperature and pressure. The response factors are applied multiplicatively to DRIFT measured features of specific catalyst surfaces species to quantify the amount adsorbed.

If the catalyst had a single phase and the adsorption occurred in a single form, the quantification of this form would be a straightforward calculation. Since NO_x storage can occur on pure Al_2O_3 as well as the potassium phase of the $\text{Pt}/\text{K}/\text{Al}_2\text{O}_3$, it is necessary to account for NO_2 adsorption on both phases. This can be accomplished if the surface area fractions of each phase are known, i.e. surface area of Pt, Al_2O_3 , and potassium, as well as the adsorptive behavior of these phases, but before doing this the nature of the $\text{Pt}/\text{K}/\text{Al}_2\text{O}_3$ surface should be discussed in detail. Although potassium was added to Al_2O_3 with K_2CO_3 , the carbonate begins decomposing at 200°C as shown in Figure 7 and noted in numerous reports [6-9,21-22,24]. This is well below the documented thermal decomposition temperature of K_2CO_3 of 891°C [25]; however, the decomposition is initiated by the hydroxyl groups on the surface of $\gamma\text{-Al}_2\text{O}_3$, which are known to react with potassium carbonate to form OK groups following the reaction [8]:



The decomposition can also be noted in the reduced –OH stretching region, 2500-3700 cm^{-1} , in Figure 7. The studies of Stork et al. [6], Krupay et al. [7], Kantschewa et al. [9], and Iordan et al. [21] were focused on determining the nature of the K-phase during this decomposition. All three studies were unable to find evidence of a distinct K_2O phase using high-temperature XRD, XPS, and phosphorescence spectroscopy, and each study independently concluded that the formation of a highly dispersed Al-OK group on the surface of Al_2O_3 is the predominant K-phase. Therefore, if decomposition is complete, an effective K-dispersion of 100% is possible via formation of Al-OK groups since there is no evidence of diffusion of K into bulk $\gamma\text{-Al}_2\text{O}_3$ [6-7]. This is not surprising due to the large discrepancy in ionic radii of the cations—1.3 Å for K^+ versus 0.5 Å for Al^{3+} [26]. Based on the K_2CO_3 studies [6-7,9,21], it is apparent that the surface of Pt/K/ Al_2O_3 consists of a Pt fraction (SA_{Pt}), an alkalinized alumina fraction (SA_{AlOK}), and a non-alkalinized, or clean, Al_2O_3 fraction ($\text{SA}_{\text{Al}_2\text{O}_3}$), such that:

$$\text{SA}_{\text{Pt}} + \text{SA}_{\text{AlOK}} + \text{SA}_{\text{Al}_2\text{O}_3} = 100\% \quad (9)$$

Through this relationship, the partitioning of the total adsorbed species among the component catalyst surfaces can be quantified to provide a more detailed understanding of the catalyst chemistry.

Figures 2 and 7 suggest that the K_2CO_3 phase is nearly completely decomposed. A comparison of the spectra recorded at 25°C before and after the thermal treatment in Figure 7 shows a 97% decrease in carbonate peak area at 1545 cm^{-1} . If complete decomposition of K_2CO_3 is assumed, as suggested by both experimentation in this work

and previous detailed studies [6-7,9,21], each K is associated with a single surface aluminum atom, Al_s . It is then possible to calculate SA_{AlOK} based on the mass fraction of K_2CO_3 , $M_{K_2CO_3}$, according to the following relationship:

$$SA_{AlOK} = \frac{M_{K_2CO_3}}{MW_{K_2CO_3}} \cdot \frac{2 \text{ mol K}}{1 \text{ mol } K_2CO_3} \cdot \frac{N_A \cdot (1/\sigma_K)}{\bar{A}_{Total}} \quad (10)$$

where $MW_{K_2CO_3}$ is the molecular weight of K_2CO_3 , N_A is Avogadro's number, \bar{A}_{Total} is the specific surface area, and σ_K is the surface number density of potassium with units of K atom/length². Each of these quantities is readily obtained except for σ_K , which must be calculated based on the crystal structure of $\gamma-Al_2O_3$. A defect spinel with a vacancy in one out of every eight cation positions is the most common unit cell describing $\gamma-Al_2O_3$ [27-28]; moreover, the surface is known to consist of (110) and (100) planes [29]. The (110) plane in a spinel unit cell consists of 7.5 cations and the (100) plane consists of 5. When combined with the cubic unit cell dimension of 7.9 Å, σ_{Al} is determined to be between 7.0 and 7.5 Al_s/nm^2 . At K_2CO_3 loadings less than a monolayer, every potassium atom is associated with one Al_s , although every Al_s is not associated with a potassium atom (12.4wt% represents a monolayer using a Al:K ratio of unity); hence, the surface number densities are equivalent for both Al_s and K in terms of surface atom/ nm^2 . For this study, the average of the (110) and (100) plane surface number densities is used, 7.2 K atoms/ nm^2 , which indicates SA_{AlOK} is 64.5%.

The calculation of SA_{Pt} is a significantly easier operation and is based on Pt dispersion, D_{Pt} . The dispersion indicates the percentage of the platinum available to the gas-phase, and the particle size, d_{Pt} , can be estimated using the simple relationship [30]:

$$d_{\text{Pt}} \text{ (nm)} = 1/D_{\text{Pt}} \quad (11)$$

This is based on an average metal surface number density and a cubic or spherical geometry. As noted in the Results section, H₂ chemisorption at 25°C revealed the Pt dispersion was 59% on Pt/K/Al₂O₃ and 55% on Pt/Al₂O₃. Therefore, the Pt particle sizes, d_{Pt} , were 1.7 nm and 1.8 nm, respectively, and the 1 wt% Pt loading occupies a small fraction of the surface with a SA_{Pt} 1.1%. The area fractions, SA_{Pt} , SA_{AlOx} , and $SA_{\text{Al}_2\text{O}_3}$, are 1.1 %, 65%, and 34%.

The partitioning of the total adsorbed NO₂ between the individual component surfaces of the Pt/K/Al₂O₃ catalyst can be quantified using the calculated area fractions. Specifically, the NO_x adsorbed on the clean and alkalized Al₂O₃ surface can be determined. The uptake of NO₂ adsorbed on Pt/Al₂O₃, $U_{\text{Pt/Al}_2\text{O}_3}$ (moles NO₂ adsorbed on Pt/Al₂O₃/m² Pt/Al₂O₃), was determined from the chemisorption measurements in Figure 6. This is used to determine the fraction of NO₂ that is chemisorbed on the Al₂O₃ component of Pt/K/Al₂O₃, $U_{\text{Al}_2\text{O}_3}$ (moles NO₂ adsorbed on Al₂O₃/m² Pt/K/Al₂O₃), via:

$$U_{\text{Al}_2\text{O}_3} = U_{\text{Pt/Al}_2\text{O}_3} \cdot SA_{\text{Pt/Al}_2\text{O}_3} \quad (12)$$

where $SA_{\text{Pt/Al}_2\text{O}_3}$ is the sum of SA_{Pt} and $SA_{\text{Al}_2\text{O}_3}$. For simplicity, this approach assumes the uptake of NO₂ on the surface of Pt is negligible compared to the dominant oxide surfaces. It follows that the uptake on the alkalized Al₂O₃ component, U_{AlOx} , is determined via:

$$U_{\text{AlOx}} = U_{\text{Pt/K/Al}_2\text{O}_3} - U_{\text{Al}_2\text{O}_3} \quad (13)$$

A similar approach follows for the CO₂ uptake where the minor adsorption on clean Pt/Al₂O₃ is ignored due to negligible chemisorbed CO₂ and the lack of a corresponding DRIFT spectral feature.

This approach offers a method for determining the amount of NO₂ chemisorbed on each phase of the catalyst, which in turn allows the calculation of adsorbed nitrates on Pt/K/Al₂O₃. The complete decomposition of the K₂CO₃ phase was the most significant assumption that was made in the execution of this method, so further experimental substantiation of this step was sought. To verify that potassium is highly dispersed as noted in earlier publications [6-9], NO₂ chemisorption was performed at 25°C following the pretreatment. At room temperature and at an equivalent NO₂ pressure of 0.15 torr, Pt/Al₂O₃ has a total NO₂ uptake of 5.3 μmol/m² and Pt/K/Al₂O₃ chemisorbs 8.9 μmol/m², as shown in Figure 8. Using equations 12 and 13, U_{AlOK} is determined to be 7.2 μmol/m². Assuming each chemisorbed NO₂ represents one surface potassium atom, AlOK:NO₂ = 1, this U_{AlOK} value predicts a K-dispersion of 93%. While this experiment suggests that 100% decomposition may not be achieved, it is within the 13% uncertainty of the measurements noted earlier for NO₂ chemisorption, and offers strong evidence of a highly dispersed potassium phase that has a surface density similar to that of Al in the γ-Al₂O₃ lattice.

Having experimental corroboration for the state of potassium and the fractional surface coverage calibration values, the DRIFTS spectra can be used to quantify the detailed temporal chemistry. The resulting total uptakes at 250°C are listed in Table 3 for the relevant adsorbates and surfaces along with the corresponding peak areas and RF

values. Due to the multiple nitrate adsorbates on alumina and the inability to resolve each of these features the calculated RF_{Pt/Al_2O_3} value is a best estimate due to the lumping of multiple peaks into one. This does not affect the values obtained for the alkalized phase since the alumina peak area is not used in any of the other calculations. The results of Table 3 indicate that 88% and 98% of the total NO_2 and CO_2 capacity (i.e. $U_{AlOK}/U_{Pt/K/Al_2O_3}$), respectively, is due to the AlOK component although it comprises only 65% of the catalyst surface area.

Summary

A technique for quantifying DRIFTS features in terms of the concentration, $\mu\text{mol}/\text{m}^2$, of the corresponding adsorbate has been detailed for the Pt/K/ Al_2O_3 NO_x adsorber catalyst system. The technique resolves the detailed partitioning of the total adsorbed species between the alkalized phase of the catalyst as well as the support at 250°C. Such chemistry detail is critical to the study of mixed adsorber catalyst systems and is used extensively in a complimentary study [10]. The calibration factors developed through this technique are temperature specific; however, the technique can be applied to studies involving temperature and material variations by developing more extensive calibration curves covering the appropriate parameter range. The response factors determined here are used in a follow-up study that investigates NO_x adsorption behavior under Sulfur-free synthetic exhaust streams.

Acknowledgment

This research was sponsored by the U.S. Department of Energy, Office of Transportation Technologies with Gurpreet Singh as the Program Manager. The authors thank Dr. Louis Powell of the Oak Ridge Y-12 National Security Complex for use of the MIDAC FTIR spectrometer. The contribution of Todd J. Toops was supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute for Science and Education and the Oak Ridge National Laboratory. Oak Ridge National Laboratory operates under DOE contract number DE-AC05-00OR22725 and is managed by UT-Battelle. EmeraChem LLC of Knoxville, TN is a catalyst and surface chemistry company with commercial experience in NO_x adsorber catalysis.

List of Symbols

P_{tS}	Platinum surface atoms
P_{tT}	Total Platinum atoms
K_P	Equilibrium constant, dimensionless
P_{NO_2}	Partial pressure of NO ₂ , Torr
$P_{N_2O_4}$	Partial pressure of N ₂ O ₄ , Torr
P_T	Total pressure, Torr
P_{std}	Standard Pressure, Torr
$S_{\bar{x},R}$	experimental standard deviation, %
U_{ISO}	ISO total uncertainty, %
B_R	Systematic standard deviation, %

RF_i	Response factor of species I , $(\mu\text{mol}/\text{m}^2)/(\text{absorbance}\cdot\text{cm}^{-1})$
SA_i	Specific surface area of species, m^2/g_i
$M_{\text{K}_2\text{CO}_3}$	Mass fraction of K_2CO_3 , $\text{g K}_2\text{CO}_3/\text{g Pt/K/Al}_2\text{O}_3$
Al_s	Aluminum surface atoms
\bar{A}_{Total}	specific surface area of Pt/K/Al ₂ O ₃ , m^2/g
σ_{K}	surface number density of K, K atom/length ²
$U_{\text{Pt/Al}_2\text{O}_3}$	NO ₂ on total surface of Pt/Al ₂ O ₃ , $\mu\text{mols NO}_2/(\text{m}^2)_{\text{Pt/Al}_2\text{O}_3}$
$U_{\text{Pt/K/Al}_2\text{O}_3}$	NO ₂ on total surface of Pt/K/Al ₂ O ₃ , $\mu\text{mols NO}_2/(\text{m}^2)_{\text{Pt/K/Al}_2\text{O}_3}$
$U_{\text{Al}_2\text{O}_3}$	NO ₂ on Al ₂ O ₃ surface of Pt/K/Al ₂ O ₃ , $\mu\text{mols NO}_2/(\text{m}^2)_{\text{Pt/K/Al}_2\text{O}_3}$
U_{AlOK}	NO ₂ on AlOK surface of Pt/K/Al ₂ O ₃ , $\mu\text{mols NO}_2/(\text{m}^2)_{\text{Pt/K/Al}_2\text{O}_3}$

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Table 1. Assigned frequencies (cm^{-1}) for Pt/ Al_2O_3 [10,13-20].

Peak Position	Infrared Vibration	Structure
<i>bridging bidentate nitrate</i>		
1610	N=O stretch	Al — O — N = O
1210	NO_2 asymmetric stretch	Al — O — N = O
<i>chelating bidentate nitrate</i>		
1590	N=O stretch	Al — O — N = O
1297	NO_2 asymmetric stretch	Al — O — N = O
<i>unidentate nitrate</i>		
1550	NO_2 asymmetric stretch	Al — O — N — O
1257	NO_2 symmetric stretch	Al — O — N — O
<i>linear nitrite</i>		
1460	N=O stretch	Al — O — N = O
<i>bridging bidentate nitrite</i>		
1302	NO_2 asymmetric stretch	Al — O — N
1230	NO_2 symmetric stretch	Al — O — N

Table 2. Assigned frequencies (cm^{-1}) for Pt/K/ Al_2O_3 .

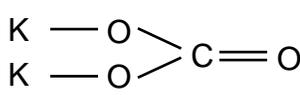
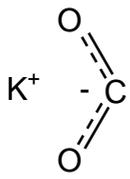
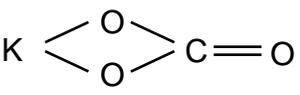
Peak Position	Infrared Vibration	Structure
<u>Nitrogen-based adsorbates [10,13-20]</u>		
<i>Alumina-based nitrates</i>		
1525	Combinations of nitrates noted in Table 1.	
1315		
1260		
<i>free nitrite ion</i>		
1250	asymmetric stretch	NO_2^-
<i>free nitrate ion</i>		
1380	asymmetric stretch	NO_3^-
1750	combination band	
<u>Carbon-based adsorbates [7,9,13,18,21-22]</u>		
<i>bicarbonate (associated with clean Al_2O_3 phase)</i>		
1641	C=O stretch	HCO_3^-
1456	CO_2 asymmetric stretch	
1260	CO_2 symmetric stretch	
<i>bridged bidentate carbonate</i>		
1648	C=O stretch	
1256	CO_2 asymmetric stretch	
990	CO_2 symmetric stretch	
<i>carboxylate ion, CO_2^-</i>		
1599	CO_2 asymmetric stretch	
1310	CO_2 symmetric stretch	
<i>chelating bidentate carbonate</i>		
1545	C=O stretch	
1363	CO_2 asymmetric stretch	
<i>carbonate ion</i>		
1408	asymmetric stretch	CO_3^-
1091	symmetric stretch	

Table 3. Total equilibrium uptakes of NO₂ (at 0.15 Torr) and CO₂ (at 25 Torr) for the specific surfaces of Pt/K/Al₂O₃ at 250°C, and the corresponding response factors for the quantification of DRIFT spectroscopic features.

Surface	Total Uptake ($\mu\text{mol}/\text{m}_{\text{total}}^2$)	Peak Position (cm^{-1})	Peak Area ($\text{abs}\cdot\text{cm}^{-1}$)	Response Factor ($\mu\text{mol}/\text{m}_{\text{total}}^2$)/($\text{abs}\cdot\text{cm}^{-1}$)
NO₂ Adsorption				
Al ₂ O ₃	0.67	1525	19	0.035
AlOK	4.8	1383	58	0.083
CO₂ Adsorption				
Al ₂ O ₃	0.039	n/a	n/a	n/a
AlOK	2.3	1599	94	0.022

Figure Captions

Figure 1. Schematic of DRIFTS reactor system.

Figure 2 IR spectra of the catalysts untreated (—) and following 1 h of pretreatment (.....) at 450°C in 50 sccm of 1% H₂/N₂ for Pt/Al₂O₃ (a and b) and Pt/K/Al₂O₃ (c and d). All spectra were taken at 25°C and referenced to a brushed Al plate; spectra are offset for clarity.

Figure 3 DRIFT spectra (—) at 250°C after saturation with NO₂ on (a) Pt/Al₂O₃ and (b) Pt/K/Al₂O₃. Also shown for Pt/K/Al₂O₃ is the fitted curve for the clean alumina nitrates (.....) and the free nitrate ion (—). Spectra referenced to catalyst at t = 0 and offset for clarity. Reactor conditions – 300 ppm NO₂ in N₂, 50 sccm, 500 Torr.

Figure 4 DRIFT spectra (—) at 250°C after saturation with CO₂ on (a) Pt/Al₂O₃ and (b) Pt/K/Al₂O₃. Also shown for Pt/K/Al₂O₃ is the fitted curve for the carboxylate ion asymmetric stretch (.....). Spectra referenced to catalyst at t = 0 and offset for clarity. Reactor conditions – 5% CO₂ in N₂, 50 sccm, 500 Torr.

Figure 5 CO₂ chemisorption on (◆,■) Pt/K/Al₂O₃ and (◇,■) Pt/Al₂O₃ at 250°C.

Figure 6 NO₂ chemisorption on (◆) Pt/K/Al₂O₃ and (◆) Pt/Al₂O₃ at 250°C.

Figure 7 DRIFT spectra of K₂CO₃ decomposition during heating to 450°C in N₂, and after cooling to 25°C. All spectra were referenced to brushed Al plate whose spectra was recorded at the given temperature; spectra are offset for clarity.

Figure 8 Total NO₂ chemisorption on (◆) Pt/K/Al₂O₃ and (◆) Pt/Al₂O₃ at 25°C.

FIGURE 1

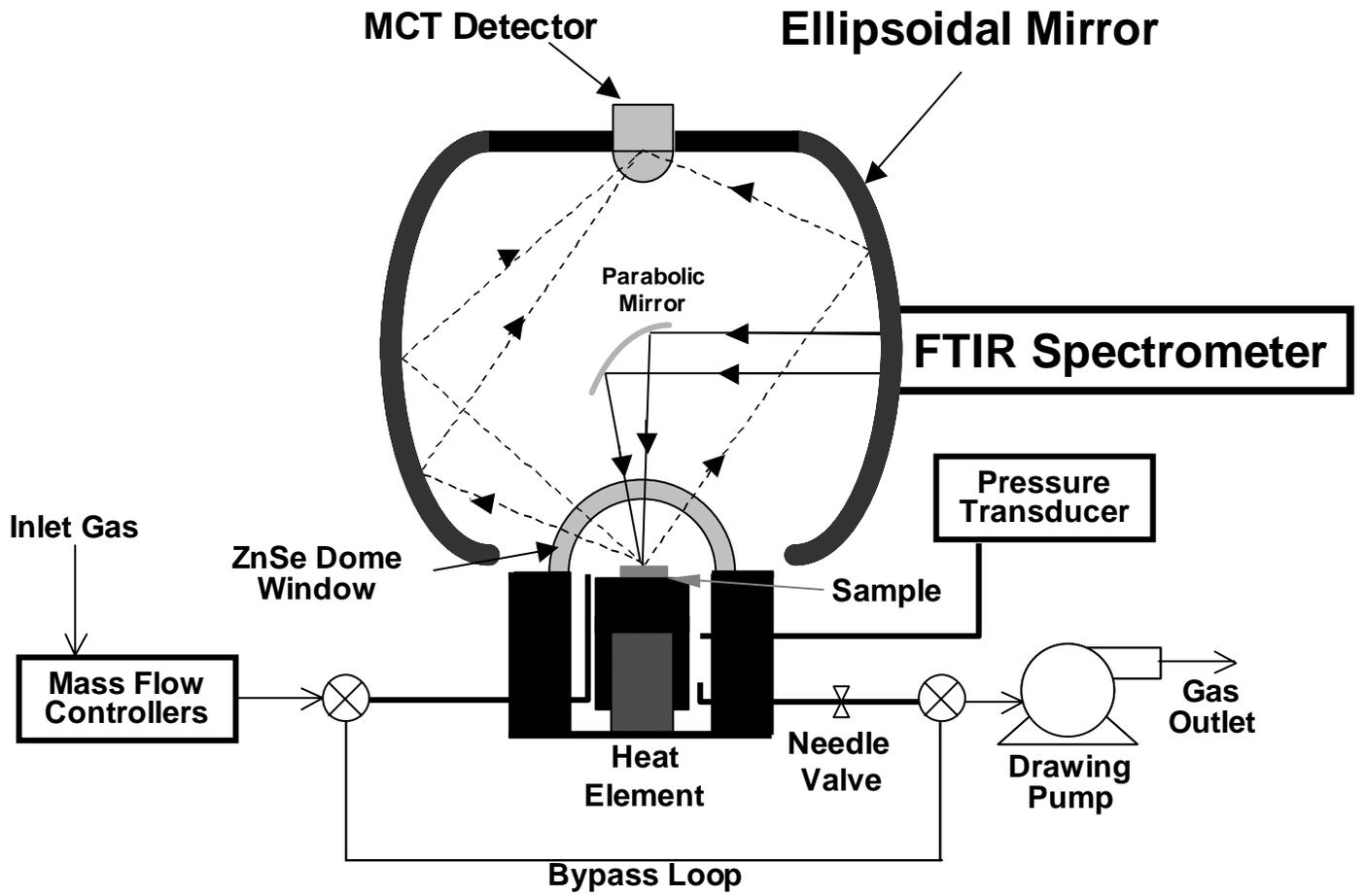


FIGURE 2

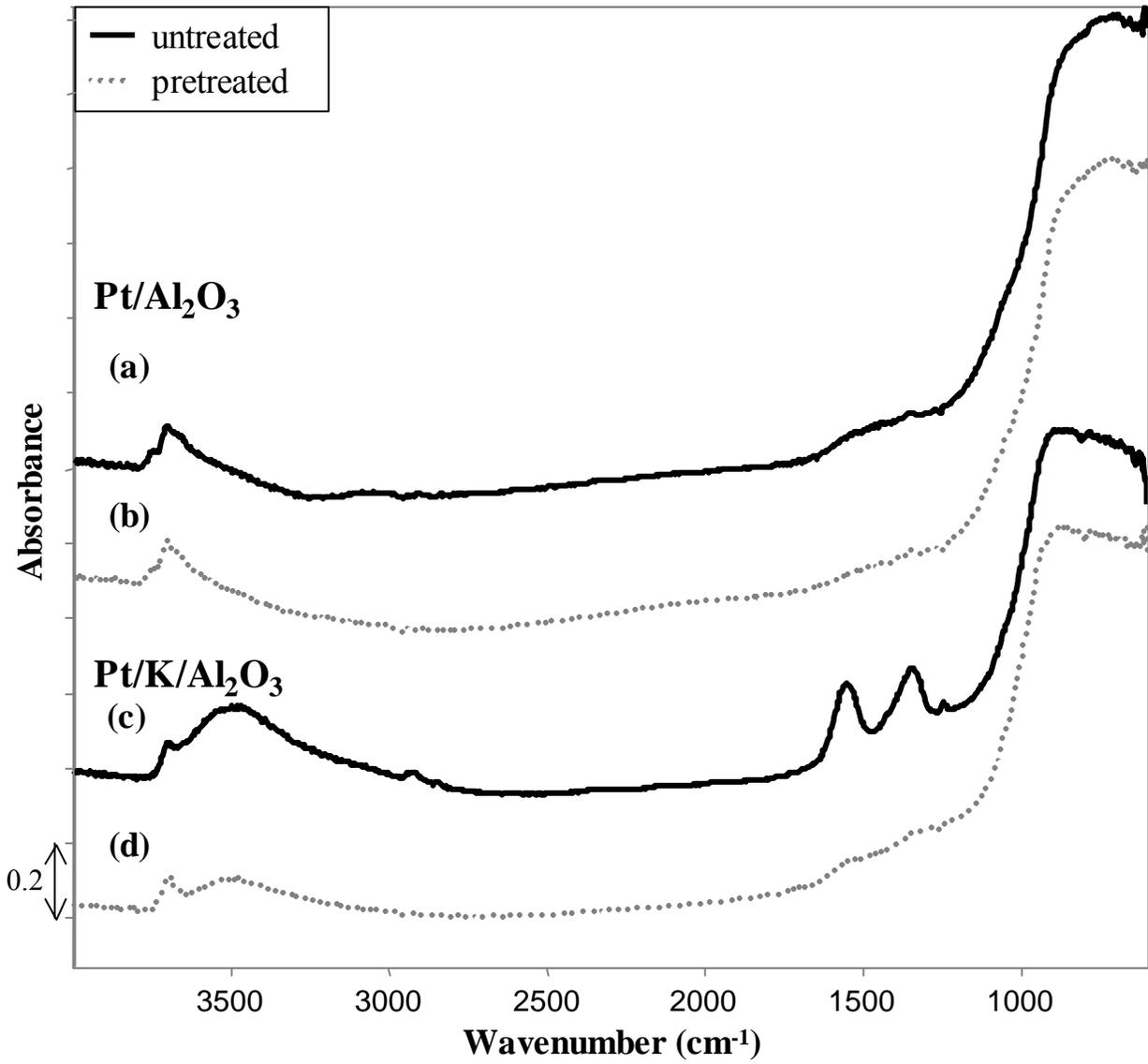


FIGURE 3

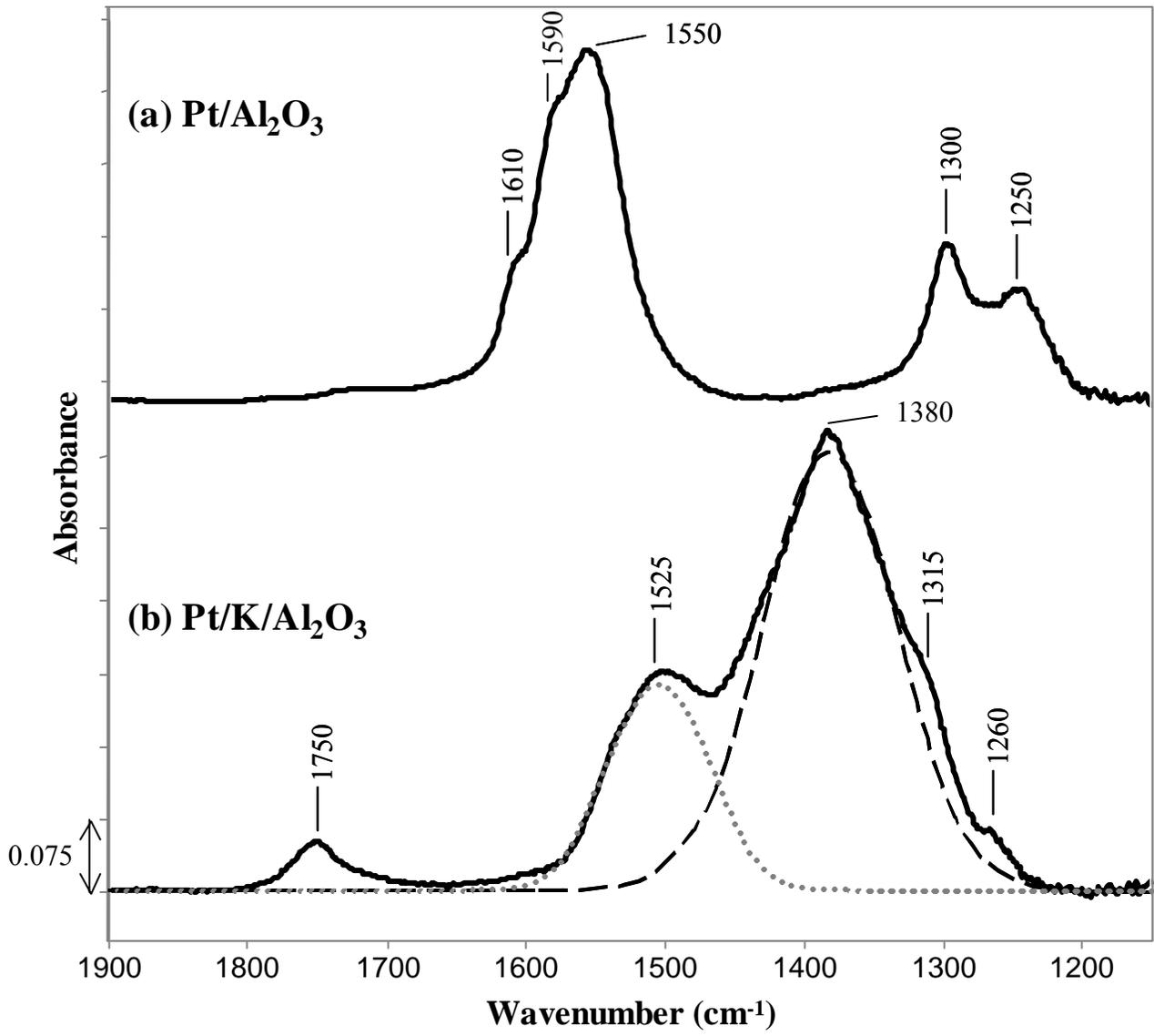


FIGURE 4

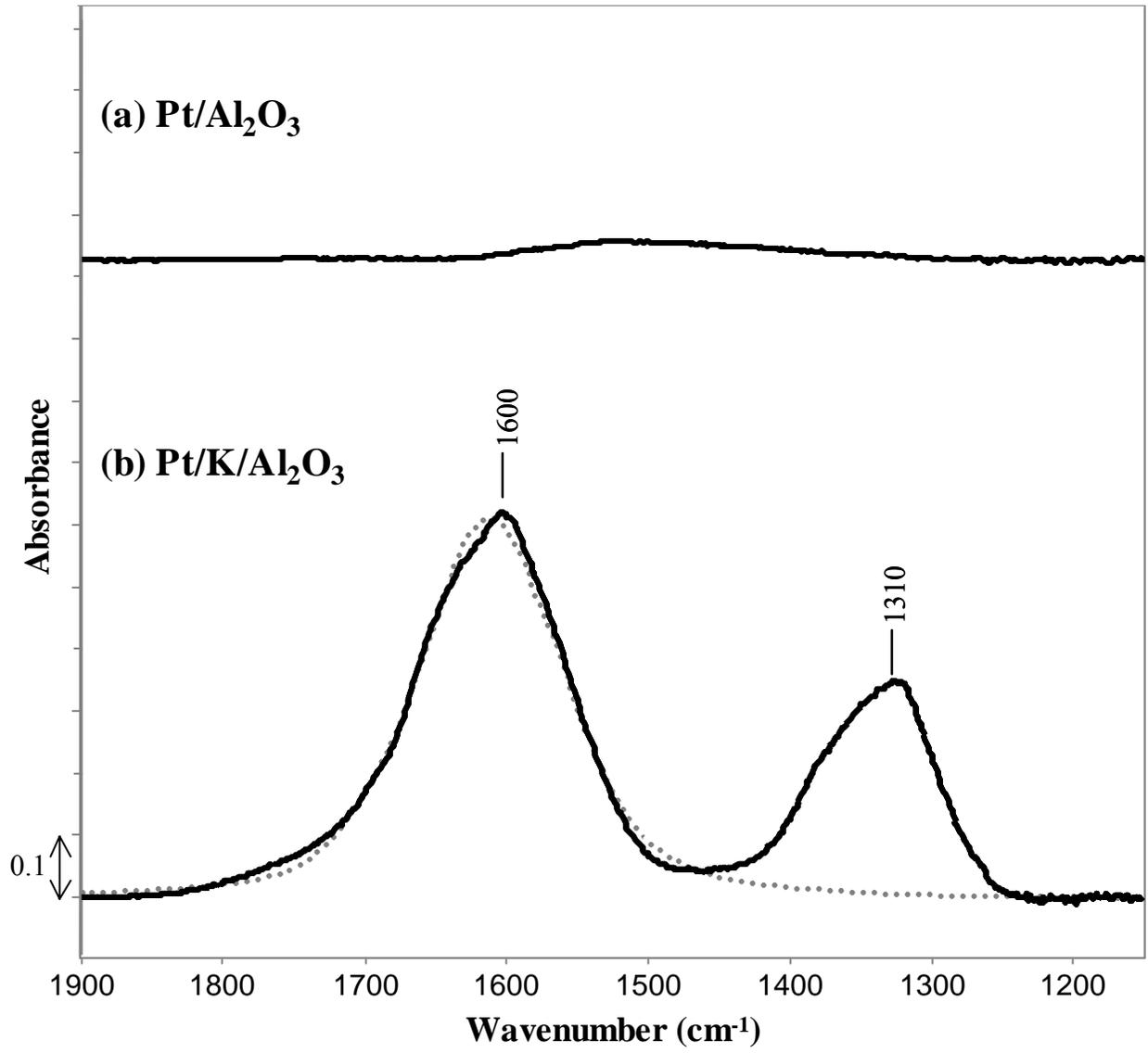


FIGURE 5

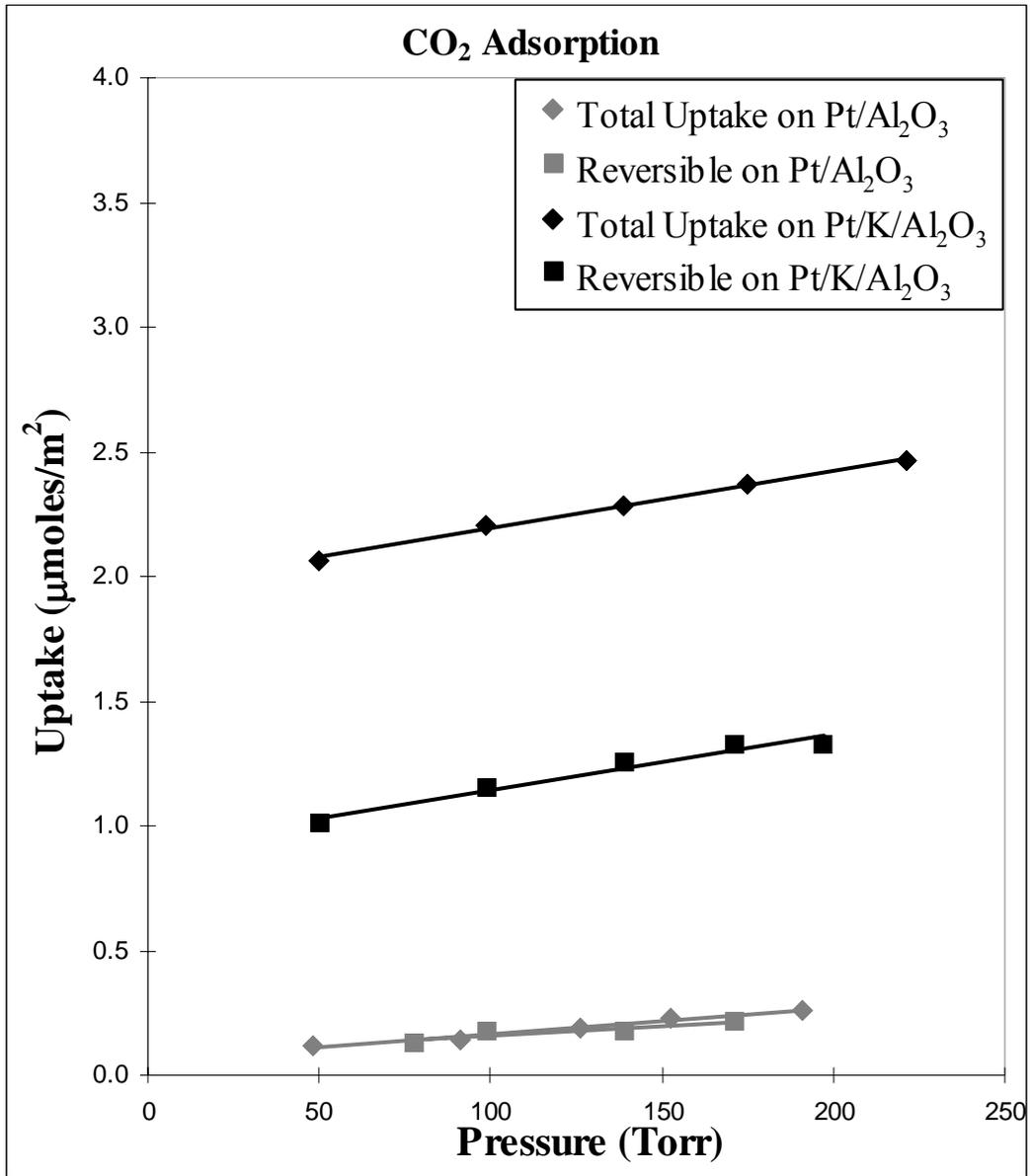


FIGURE 6

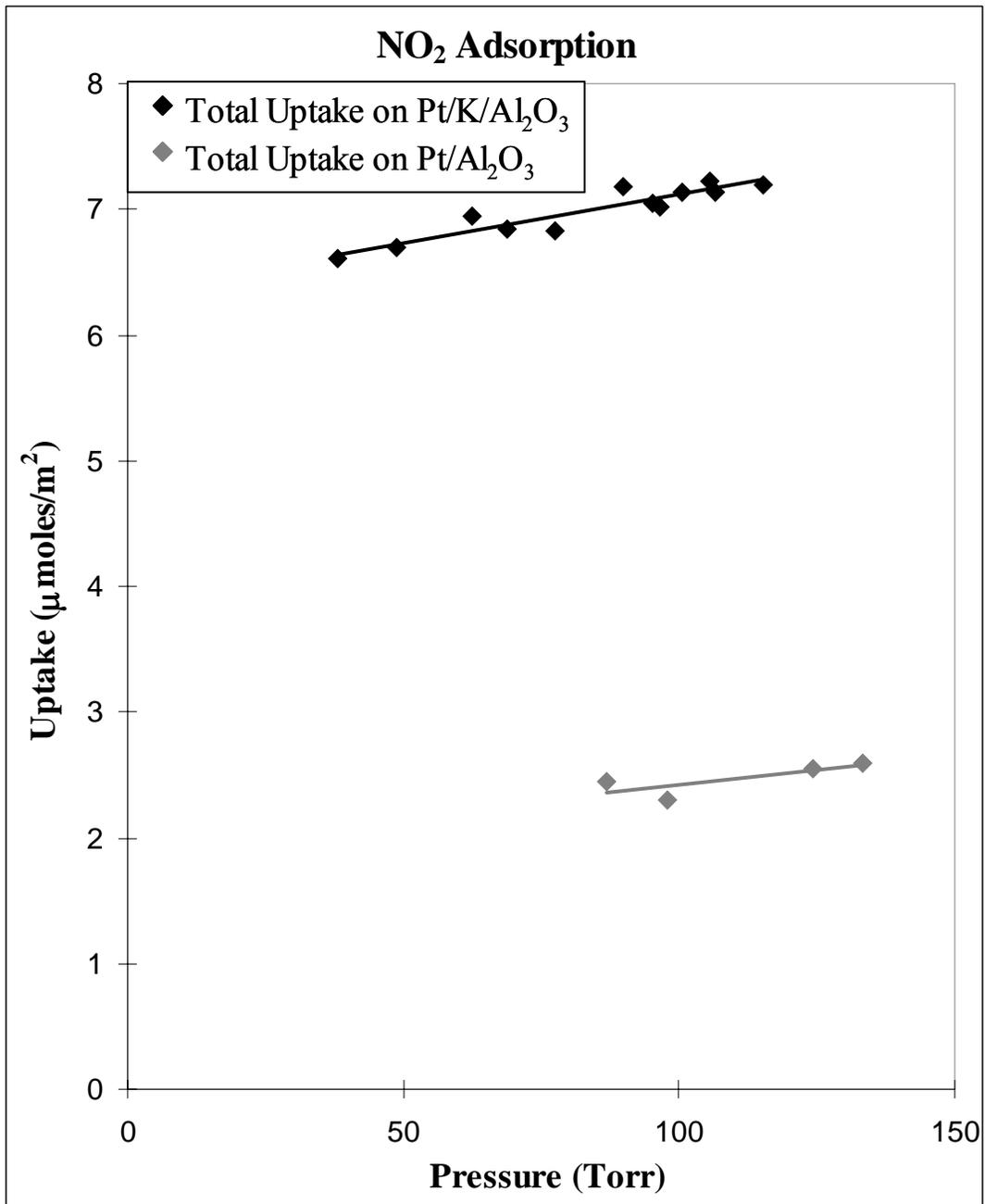


FIGURE 7

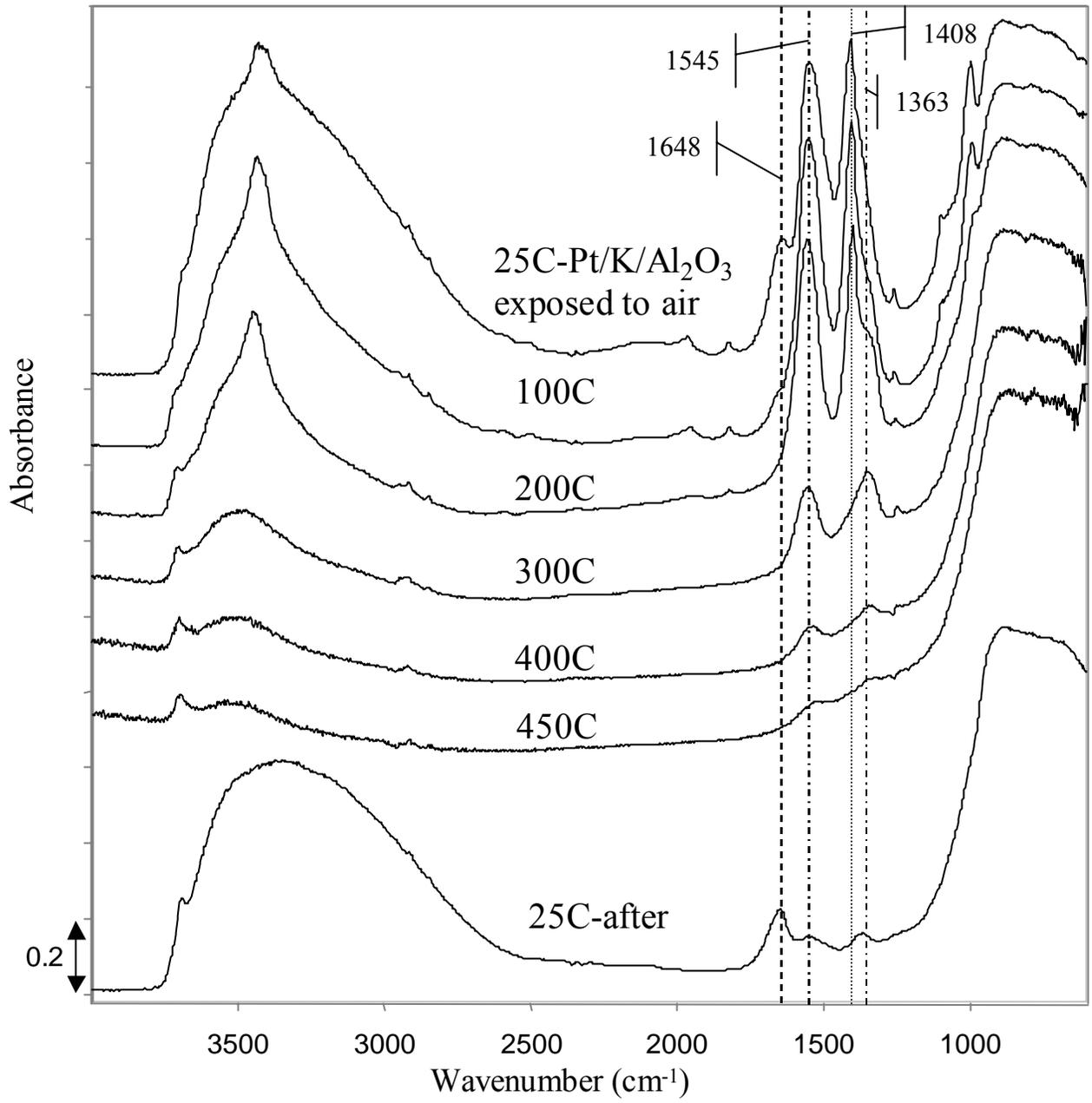


FIGURE 8

