NO_X Adsorption on Pt/K/γ-$A1_2O_3$ and the Quantitative Effects of H_2O and CO_2

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Abstract
The NO_x trap catalyst, with alkaline and/or alkali materials, is a potential candidate for meeting future combustion related emissions standards. A Pt/K/γ-Al_2O_3 NO_x-trap catalyst was studied with DRIFTS at 250˚C. The Al_2O_3 support was shown to adsorbs 2.0 μmols NO_x/m^2 in the form of covalently bound nitrates. Pt is instrumental in the oxidation of NO to NO_2, and the addition of K to the catalyst increases the adsorption capacity to 5.5 μmols NO_x/m^2 with the primary storage form on K being a free nitrate ion. Individually, the addition of 5% CO_2 reduces stored nitrates by 45%, and 5% H_2O causes a 16% decrease. Interestingly, with both 5% CO_2 and H_2O the total storage is only decreased by 11%.

Introduction

Multi component NO_x adsorber catalysts are a leading solution to the soon to be implemented stricter emissions regulations. They are based on 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 or hydrocarbons in a brief rich interval to obtain N_2 and H_2O. 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_2O_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 indicating a strong interaction of potassium with Al_2O_3 supports [6-9], reports on the specific contributions of potassium are scarce especially in the presence of CO_2 and H_2O.

Specific Objectives

To advance the understanding of this relatively new catalyst system it is necessary to determine what makes a component beneficial, so that this characteristic can be optimized. This study is primarily focused on the NO_x adsorption step of a catalyst consisting of Pt and K phases on an Al_2O_3 support; additionally, the contributions of each component are explored by studying Pt on Al_2O_3, K on Al_2O_3, and Al_2O_3 only. Diffuse Reflectance mid-Infrared Fourier Transform Spectroscopy (DRIFTS) is the primary analytical tool used to determine the form of stored NO_x. Based on a routine described elsewhere [10], some portions of the DRIFTS analysis are quantitative.

In addition to the component contribution study, the effects of CO_2 and H_2O are also studied. Often during tests of preliminary catalysts the effects of common exhaust components are ignored; however, it has been shown that these components can have considerable and, at times, detrimental effects on catalyst functionality. The catalysts in this study are evaluated based on common diesel exhaust concentrations of 5% H_2O and 5% CO_2.

Experimental

EmeraChem LLC provided all catalysts for this study. The model catalysts were γ-Al_2O_3, 1 wt% Pt on γ-Al_2O_3 (Pt/Al_2O_3), 8.0% K_2CO_3 on γ-Al_2O_3 (K/Al_2O_3), and the complete NO_x adsorber catalyst, 8% K_2CO_3 on 1% Pt/Al_2O_3 (Pt/K/Al_2O_3). 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 catalyst used, but its purpose was to establish a consistent initial condition for each experiment.

The DRIFTS system was detailed elsewhere [10-11], but is essentially a MIDAC model M2500 FTIR spectrometer with a Harrick Scientific ellipsoidal mirror DRIFT attachment and a heated reaction cell. The system can be heated up to 525˚C, is configured to allow up to 10% H_2O in the feed, and is typically operated at a slight vacuum, typically 500 torr, to prevent stagnation in the cell and to sustain the ZnSe dome seal. Tylan mass flow controllers are used to establish the inlet gas concentrations, in conjunction with a dual sparger system submerged in a NESLAB RTE-110 recirculating constant

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temperature bath to control the H_2O concentration. A General Eastern DewPro humidity sensor is used to verify water concentration. The reactant gases had the following specifications: CO_2 (99.999%), 1% H_2 in N_2 (99.999%), 1000 ppm NO in N_2 (99.0%), 1000 ppm NO_2 in N_2 (99.0%), and N_2 (99.999%).

Each catalyst sample was pretreated *in situ* before exposure it to the NO_x gas mixtures by heating the sample to 450°C in a 50 sccm flow of 1% H_2/N_2. The pretreatment continued until the carbonate spectral features 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% H_2/N_2 flow was maitained while the sample temperature was decreased to 250°C. At 250°C, the cell was sealed, and the reactant gas mixture was routed through a bypass loop for a period of five minutes to allow concentration stabilization. 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.

Results and Discussion

$Pt/K/Al_2O_3$ is the primary catalyst of interest for this study, and before delving into its behavior in the presence of NO_x it is necessary to discuss the state of the catalyst surface with regards to its three components. Gamma alumina is a commonly used catalyst support that is attractive because of its high specific surface area and low cost; however, it often does not behave as an ideal support as it is known to interact with both the catalyst and the reactants primarily via surface hydroxyl. As was shown elsewhere [10], Al_2O_3 constitutes 34-44% of the $Pt/K/Al_2O_3$ catalyst surface area, so its behavior in the presence of NO_x should be significant. The role of Pt in the adsorption step is to oxidize NO to NO_2 so that it is more effectively trapped as a nitrate. Following the pretreatment, H_2 chemisorption measurements indicated a Pt dispersion (surface-to-total Pt ratio, or fraction of Pt available for surface reaction) of 37%, which corresponds to clusters of ca. 2.7 nm in diameter and a surface area fraction of only 1%. The potassium phase is loaded with K_2CO_3 which decomposes above 200˚C decomposes through a reaction with the hydroxyls of Al_2O_3, to produce –OK surface groups [6-9]. NO_2 chemisorption shows that 85-100% of the K atoms are available at the surface which means that 55-65% of the surface is covered by the alkalized phase [10]. The three catalysts are pictorially represented in Figure 1.

DRIFTS analysis of Pt-free Al_2O_3 was shown to form nitrates at 250˚C with 10 sccm of 500 ppm NO in N_2. The spectral features were in agreement with previous work on NO and Al_2O_3, are assigned as indicated in Table

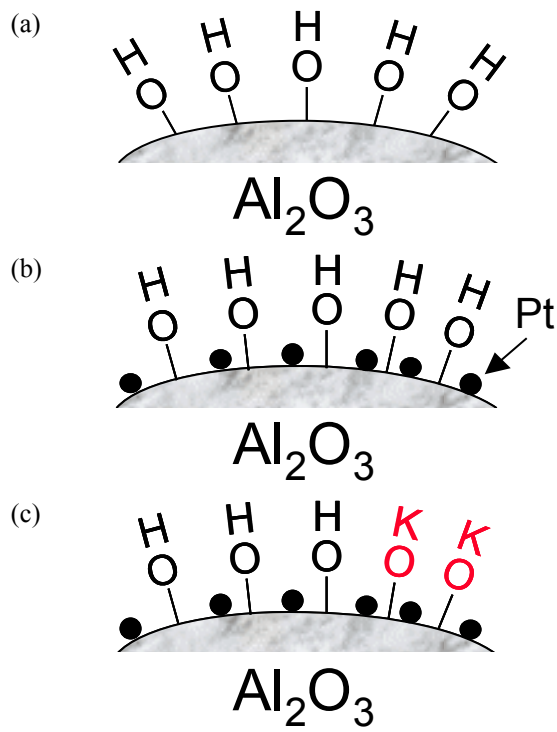
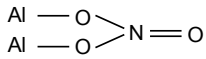
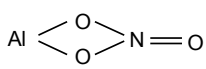
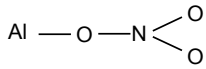
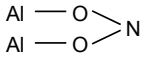


Figure 1. Pictorial Representation of the (a) γ-Al_2O_3, (b) Pt/Al_2O_3, and (c) $Pt/K/Al_2O_3$.

1 [12-20]. In general, nitrates formed slowly on Al_2O_3. Formation of the linear nitrite at 1460 cm^{-1} and a chelating nitrate at 1590 cm^{-1} and 1297 cm^{-1} was observed in the first minute of exposure. Further uptake was nominal until at 25 minutes a feature at 1550 cm^{-1} appears in the spectra. This feature, associated with unidentate nitrate, dominates the spectral feature after 30 minutes of adsorption, although the initial peaks at 1460 and 1590 cm^{-1} do not diminish in intensity. When flowing 5% O_2 with the 500 ppm NO the nitrite feature was not observed at all and the unidentate nitrate at 1550 cm^{-1} was observed in the first minute of adsorption along with a smaller chelating nitrate feature at 1590 cm^{-1}. When O_2 was included in the feed stream the expected result, an increase in NO oxidation and therefore an increase in the NO_x storage rate, was not observed; instead, total NO_x uptake was surprisingly less when O_2. This observation is not fully understood, but probably relates to non-dissociated O_2 blocking adsorption sites on Al_2O_3. If 500 ppm NO_2 is fed to the DRIFTS reactor at 10 sccm the total nitrate absorbance increases by a factor of ca. 4 compared to the $NO+O_2$ adsorption experiment. The spectral features are similar, both unidentate and chelating nitrates are apparent in the first minute with no sign of nitrites, although there is a third spectral feature apparent at 1610 cm^{-1} where bridged nitrates are expected. This is clear evidence that the adsorption of NO_x on Al_2O_3 is limited by the oxidation of NO to NO_2. A characteristic

Table 1. Assigned frequencies (cm^{-1}) for Al_2O_3 and Pt/Al_2O_3 [12-20].

Peak	Infrared Vibration	Structure
bridging bidentate nitrate		
1610	N=O stretch	
1210	NO_2 asymmetric stretch	
chelating bidentate nitrate		
1590	N=O stretch	
1297	NO_2 asymmetric stretch	
unidentate nitrate		
1550	NO_2 asymmetric stretch	
1257	NO_2 symmetric stretch	
linear nitrite		
1460	N=O stretch	
bridging bidentate nitrite		
1302	NO_2 asymmetric stretch	
1230	NO_2 symmetric stretch	

DRIFT spectrum of $NO+O_2$ adsorption on Al_2O_3 is shown in Figure 2.

When an oxidation catalyst, e.g. Pt, is added to Al_2O_3 the adsorption behavior with either NO or $NO+O_2$ in the feed is markedly different; in fact, it is nearly identical to NO_2 adsorption on non-platinated Al_2O_3. This is evidence of the excellent oxidative properties of Pt, since it was able to oxidize NO to NO_2 effectively on Pt/Al_2O_3 even without O_2 in the feed (surface hydroxyls were the oxidation source). NO_2 chemisorption on Pt/Al_2O_3 at 250˚C shows that the platinated support adsorbs a total of 2.0 μmols NO_2/m^2. A characteristic DRIFT spectrum of $NO+O_2$ adsorption on Pt/Al_2O_3 is shown in Figure 3.

Another study was carried out on K/Al_2O_3 with similar results. Flowing either NO or $NO+O_2$ produced very slow nitrate formations, much slower than Al_2O_3, as shown in Figure 4 for $NO+O_2$ where the last spectrum displayed is taken after 17.5 hours on stream. However, when NO_2 was in the feed stream the uptake was expeditious, and the rates were on par with the other catalysts. The spectral features of the K/Al_2O_3 system were markedly different from those of Al_2O_3, but agreed with previous studies of potassium- and alumina-based materials as listed in Table 2 [7,9,12-22]. Unlike NO_x adsorption on Al_2O_3, the surface species observed on K/Al_2O_3 were the same regardless of the form of NO_x in the feed, although the rate of formation was greatly affected. Due to trace amounts of CO_2 either in the feed or in the cell, a carboxylate feature immediately formed at

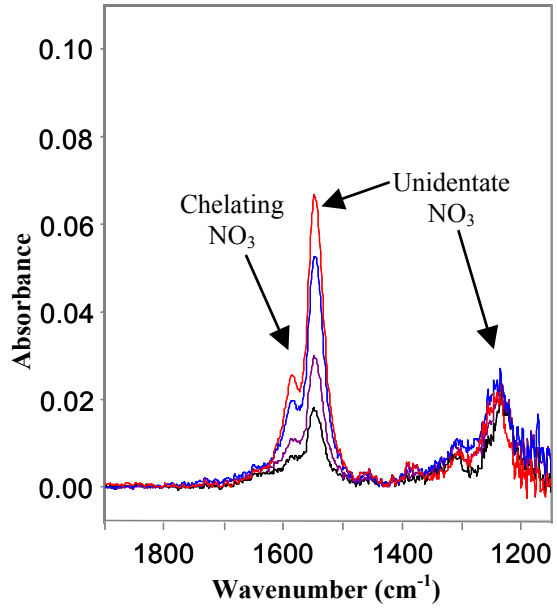


Figure 2. DRIFT spectra of Al_2O_3 at 250˚C after (—) 1 minute, (—) 40 minutes, and (—) 1 hour. Spectra taken at 250˚C and referenced to t = 0. Feed: 500 ppm NO and 5% O_2 in N_2 at 10 sccm.

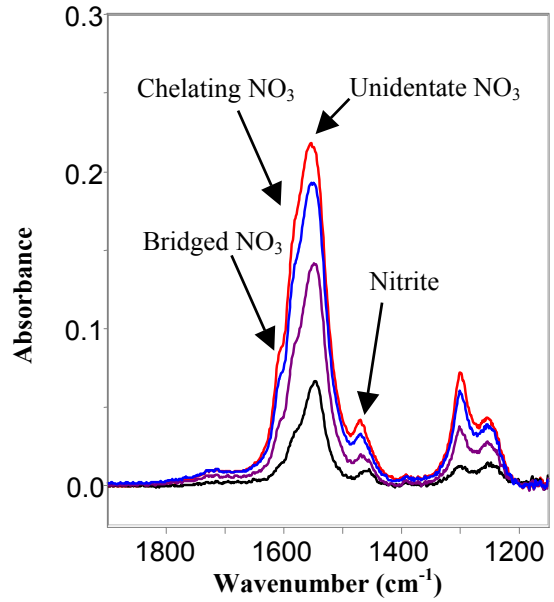
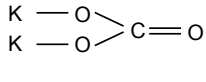
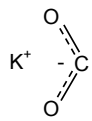
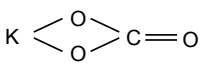


Figure 3. DRIFT spectra of Pt/Al_2O_3 at 250˚C after (—) 1 minute, (—) 20 minutes, (—) 40 minutes, and (—) 1 hour. Spectra taken at 250˚C and referenced to t = 0. Feed: 500 ppm NO and 5% O_2 in N_2 at 10 sccm.

1600 cm^{-1} with its associated symmetric peak at 1310 cm^{-1}, but did not continue to adsorb after the first minute, as shown in Figure 4. Also adsorbing in the first minute is a small feature near 1255 cm^{-1} that corresponds to a nitrite ion, NO_2^-. The dominant nitrogen-based adsorbate was a free ionic nitrate, NO_3^-, at 1380 cm^{-1} that is associated with K. As previously mentioned the non-alkalized Al_2O_3 phase can also adsorb NO_x, and as the ionic sites become saturated, a spectral feature is observed on the front shoulder of the 1380 cm^{-1} feature centered near 1510 cm^{-1}. Due to its position on the shoulder it is difficult to assess which nitrates this feature corresponds to, and it is conceivable that it is a lumped feature of the three dominant nitrates observed in the Al_2O_3 study. If only one nitrate is adsorbing, the unidentate or chelating forms are the most likely candidates due to their location near 1510 [12].

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

Peak	Infrared Vibration	Structure
Nitrogen-based adsorbates [12-20]		
Alumina-based nitrates		
1525	n/a	n/a
1320	n/a	n/a
free nitrite ion		
1255	asymmetric stretch	NO_2^-
free nitrate ion		
1380	asymmetric stretch	NO_3^-
1750	combination band	
Carbon-based adsorbates [7,9,12-13,20-22]		
bicarbonate (associated with clean γ-Al_2O_3 phase)		
1641	C=O stretch	
1456	CO_2 asymmetric stretch	HCO_3^-
1260	CO_2 symmetric stretch	
bridged bidentate carbonate		
1648	C=O stretch	
1256	CO_2 asymmetric stretch	
990	CO_2 symmetric stretch	
carboxylate ion, CO_2^-		
1599	CO_2 asymmetric stretch	
1310	CO_2 symmetric stretch	
chelating bidentate carbonate		
1545	C=O stretch	
1363	CO_2 asymmetric stretch	
carbonate ion		
1408	asymmetric stretch	$CO_3^=$
1091	symmetric stretch	

The $Pt/K/Al_2O_3$ catalyst shows the same spectral features that were observed on K/Al_2O_3, but the rate of adsorption is considerably faster. Furthermore, $NO+O_2$ and NO_2 adsorb at about the same rate with NO-only adsorption just slightly slower. Also, the carboxylate that is formed initially desorbs, such that after one hour on stream the feature is no longer detectable. Al_2O_3-based nitrates are also observed after ca. 20 minutes on stream. These DRIFTS features are illustrated in Figure 5 for the feed stream with 500 ppm NO and 5% O_2. Quantitative analysis of the spectra reveal that 12% of the 5.5 µmols NO_x/m^2 adsorbed on a saturated $Pt/K/Al_2O_3$ catalyst is stored on the Al_2O_3 phase.

The work discussed to this point was instrumental in detailing the state of the catalyst and its adsorption behavior in several "neat" gas environments. Using this information as a base, the chemistry of NO_x adsorption on $Pt/K/Al_2O_3$ was further analyzed with typical post-combustion components, CO_2 and H_2O. The temporal adsorption behavior is shown in Figure 6a for the "neat" adsorption of 300 ppm NO and 12% O_2 (balance N_2) flowing at 50 sccm. Figure 6b shows that when 5% CO_2 was included in a feed stream with 300 ppm NO and 12% O_2 the amount of NO_3^- storage is decreased by 45% after one hour on stream; this degradation is due to competition

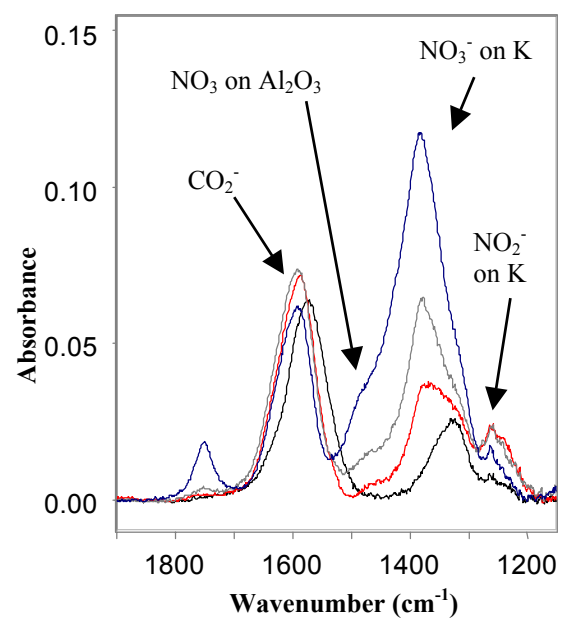


Figure 4. DRIFT spectra of K/Al_2O_3 at 250˚C after (—) 1 minute, (—) 1 hour, (—) 2.5 hours, and (—) 17.5 hours. Spectra taken at 250˚C and referenced to t = 0. Feed: 500 ppm NO and, 5% O_2 in N_2 at 10 sccm.

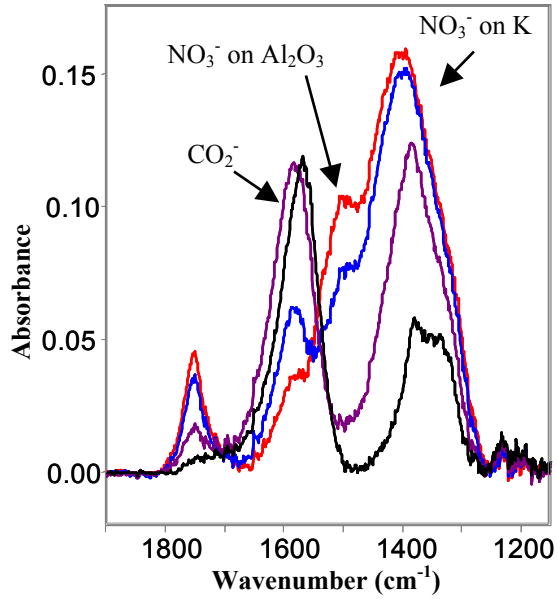


Figure 5. DRIFT spectra of $Pt/K/Al_2O_3$ at 250˚C after (—) 1 minute, (—) 20 minutes, (—) 40 minutes, and (—) 1 hour. Spectra taken at 250˚C and referenced to t = 0. Feed: 500 ppm NO and, 5% O_2 in N_2 at 10sccm.

between the adsorbed free nitrates and carboxylates for adsorption sites. Figure 6c shows that when 5% H_2O was included in a feed stream with 300 ppm NO and 12% O_2 the amount of K-based nitrate storage decreases by 16% after one hour, but the Al_2O_3-based nitrates decreased by 92%. This result shows the strong interaction that H_2O has with the Al_2O_3 surface. The presence of H_2O saturates the Al_2O_3 surface with hydroxyl groups, which leads to few vacant sites for NO_x to adsorb. Figure 6d interestingly shows with both 5% CO_2 and 5% H_2O in the feed the total storage only decreased by 11% compared to that of $NO+O_2$ after one hour. This is driven by the large quantitiy of hydroxyl groups generated from H_2O on Al_2O_3, which destabilizes the K-CO_2 bond in a similar interaction that leads to the decomposition of K_2CO_3 at 200˚C [6-9], or ca. 700˚C below its normal thermal decomposition value [23].

Conclusions

A multicomponent NO_x-trap catalyst consisting of Pt and K supported on γ-Al_2O_3 was studied to determine the contributions of the individual catalyst components, the adsorbing species during the lean capture cycle, and the quantitative effects of H_2O and CO_2. The Al_2O_3 support was shown to have NO_x trapping capability with or without Pt present; NO_x is primarily trapped in the form

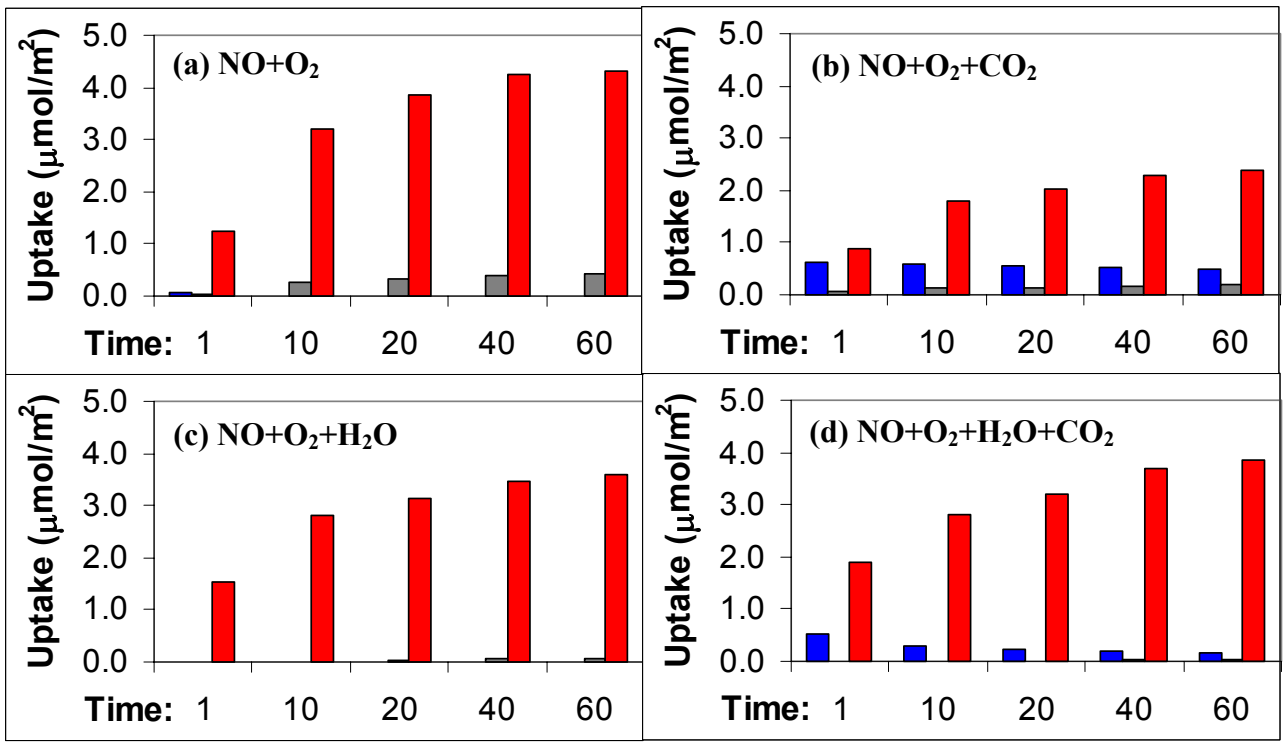


Figure 6. Temporal NO_x uptake on $Pt/K/Al_2O_3$ at 250˚C with (a) 300 ppm NO and 12% O_2, (b) 300 ppm NO, 12% O_2, and 5% CO_2, (c) 300 ppm NO, 12% O_2, and 5% H_2O, and (d) 300 ppm NO, 12% O_2, 5% CO_2, and 5% H_2O. (■) K-based free nitrate, (■) K-based carboxylate, and (■) Alumina-based nitrates. Flow rate was 50 sccm with N_2 as the balance.

of nitrates on the Al_2O_3 surface with unidentate, chelating and bridged forms apparent in DRIFTS analysis. Pt is instrumental in the oxidation of NO to NO_2, which is essential for a fast adsorption step. The addition of K to the Pt/Al_2O_3 catalyst increases the adsorption capacity, and the primary storage form on K is free nitrate ions. When CO_2 was included in a feed stream with NO and O_2 the amount of K-based nitrate storage decreases. However, H_2O significantly remedies the detrimental effect of carboxylate formation on NO_x storage capacity.

Much of the current research on NO_x adsorber catalysts ignores the effects of both the support and common exhaust components like CO_2 and H_2O. This study strongly suggests that the results from such studies could be very misleading, especially if these results are used in modeling.

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