An FTIR/TPD study on the adsorption of NO_2 and CO on Pt-BaO/Al_2O_3 NSR catalysts: the effect of Ba-loading

Tamás Szailer and János Szanyi*, Ja Hun Kwak, and Charles H.F. Peden
Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352 USA
*janos.szanyi@pnl.gov

Introduction

Among the different methods for removing NO_x from exhaust gases presented so far, the "NO_x storage-reduction" (NSR) catalyst technology promises good solutions. These catalysts can be used with engines that operate under lean conditions. In the NOx uptake cycle, NO_x in the exhaust gases is adsorbed onto the catalyst, then in a brief rich cycle, the stored NO_x is converted to nitrogen by excess hydrocarbons. NSR catalysts are constituted usually by a NO_x storage component (typically an alkaline or earth-alkaline metal oxide) and by a noble metal (Pt, Pd, Rh) which is responsible for both the conversion of NO to NO_2, the reduction of the stored NO_x [1,2]

Several mechanisms have been proposed [1-3] for NO_x storage; however, further investigation is required in order to better understand the fundamentals of NO_x uptake/release and the role of the noble metal in these processes. In this presentation we will report the results of a combined FTIR/TPD study on the adsorption of NO_2 on 2%Pt-BaO (8 and 20wt%)/Al_2O_3 catalysts. In particular, we focused on the effect of the amount of NO_2 added to the Pt-BaO/Al_2O_3 catalysts. We have also studied the effect of BaO loading on the adsorption of CO on the Pt particles.

Materials and Methods

The catalysts were prepared by incipient wetness impregnation of a γ-alumina support (Condea, 200 m^2/g) with aqueous solutions of dinitrodiammine platinum (Aldrich) to yield 2wt% loading and barium-nitrate (Aldrich) to obtain 8 or 20 wt% BaO loadings. The powders were dried in air at 393 K and activated at 773 K. The samples were characterized by XRD and BET. The catalyst sample was pressed onto a fine tungsten mesh, and placed into the infrared cell. The cell was connected to a gas handling/pumping station, and through both a leak and a gate valve to a mass spectrometer. This set up allowed us to conduct TPD experiments (open gate valve), and to analyze the gas composition in the IR cell (through the leak valve).

Results and Discussion

Two NSR catalysts were investigated: one with 8 wt% BaO loading (A) and another with 20 wt% BaO (B). Both catalysts contained 2% of Pt as precious metal. Prior to NO_2 adsorption, the catalysts were annealed at 973 K for 1hr in vacuum in order to ensure the complete removal of nitrates and carbonates.

The availability of Pt sites was checked with CO adsorption at 300K. On 2%Pt-8wt%BaO/Al_2O_3, three intense bands were observed. The absorption feature at 2085 cm^{-1} is associated with linearly adsorbed CO on Pt^0. The other two bands indicate the formation of carbonates upon CO exposure, mainly of bidentate type (bands at 1650-1550, 1350-1250 cm^{-1}). There is another low intensity peak at 2220 cm^{-1} which can be associated with CO chemisorbed on Al^{3+} Lewis acid sites [2,3]. This features indicated that part of the Al_2O_3 surface is available for CO adsorption. On 2%Pt-20wt%-BaO/Al_2O_3, linear CO was also observed on Pt at 2079 cm^{-1}. The intensity of this CO band is similar on the two catalysts, indicating that the accessibility of Pt particles is not hindered at the higher BaO loading of 20wt%. On the other hand, the carbonate formation was enhanced on catalyst B which might originate from the higher Ba-content. After CO adsorption, TPD experiments were conducted. As the IR spectra of Fig 1. indicate, CO is very stable on these catalysts and higher Ba content seems to lower the strength of Pt-CO binding, although the surface accessibility of Pt remains the same. NO_2 exposure of the $CO_{ads.}$-Pt-BaAl samples results in the disappearance of the CO absorption features at much lower temperatures (~400K), due, at least in part, to the Pt-catalyzed reaction between CO and NO_x.

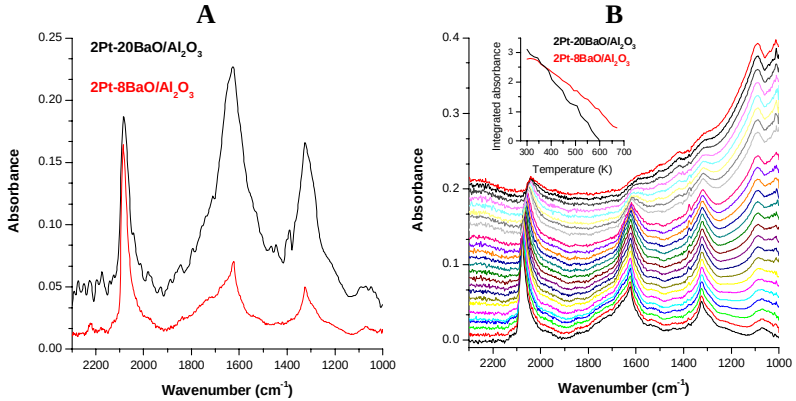

Figure 1. IR spectra after CO adsorption on 2%Pt-8wt%-BaO/Al_2O_3 and 2%Pt-20wt%-BaO/Al_2O_3 catalysts at 300K (A). A series of IR spectra collected during TPD after CO adsorption on 2%Pt-8wt%-BaO/Al_2O_3 (B). The insert on (B) shows the integrated intensities of the CO band as a function of catalyst temperature for both materials.

NO_2 adsorption was carried out at different NO_2 exposures (1, 5, and 10 Torr). Two different types of nitrates were found: surface (bidentate) and bulk (ionic) nitrates. Using spectral deconvolution, changes in the individual absorption features as a function of NO_2 exposure were obtained for both catalysts. Increasing the amount of adsorbed NO_2 the ratio between these two NO_x species changed. Monitoring the gas phase composition during the adsorption, NO, N_2O and N_2 were detected, while no traces of ammonia was found. FTIR spectra collected during TPD showed that surface nitrates were transformed to bulk nitrates as the temperature was increased.

Significance

Better understanding the NO_2 adsorption mechanism on NSR catalysts enables us to design catalysts with improved NO_x storage capacity.

References

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