

Infrared Study of NO Reduction and Decomposition over Pd-based Catalysts under Simulated Lean-burn Conditions

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Introduction

Hydrogen has been shown to exhibit promising reactivity for reducing NO to N₂ on Pd-based catalysts under lean burn condition where more than 1% of O₂ is present in the automobile and diesel exhaust. (1, 2) Design of a highly active, selective, and durable catalyst for the effective use of H₂ as a reductant requires a better understanding of the reaction pathways of hydrogen and all other key reactants including NO, O₂, and CO in the exhaust stream. The objective of this study is to investigate the mechanism of NO reduction and decomposition on Pd/Al₂O₃ and Ag-Pd/Al₂O₃ under simulated lean-burn condition. In situ infrared (IR) study coupled with mass spectrometry (MS) was used for this study to determine the dynamic behavior of adsorbed species and to elucidate the reaction mechanism.

Materials and Methods

The 5 wt% Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts were prepared by incipient wetness impregnation of γ -Al₂O₃ support with PdCl₂ solution. Approximately 150 mg of Pd and Pd-Ag catalyst was loaded into the DRIFTS (Diffuse Reflectance Infrared Fourier Transfer Spectroscopy) reactor and reduced in situ at 773 K for 30 minutes. (3) Dynamic behaviors of adsorbed species on both catalysts were studied by temperature-programmed reaction (TPR) and step switching of the reactant flow from NO/CO/O₂/He to NO/CO/O₂/H₂/He to the DRIFTS system. The steady state and transient IR spectra were collected by a Varian FTS 4000 FT-IR. The effluent gases of the DRIFTS reactor were monitored by a Pfeiffer Omnistar™ Mass Spectrometer

Results and Discussion

Fig. 1 (a) shows the infrared spectra of adsorbed species during temperature-programmed reaction of NO/CO/O₂/H₂ on Pd/Al₂O₃. At 298 K, NO reacted with O₂ to produce NO₂ at 1633 cm⁻¹ which further adsorbed on the catalyst surface as nitrates at 1500-1330 cm⁻¹. Raising the reaction temperature shifted the reaction from NO oxidation to the reaction of NO with H₂ to produce a dominant NH₃ band at 3321 and 3200 cm⁻¹ at 398 K as shown by the IR intensity profile in Fig. 1 (b). The decrease in NH₃ IR intensity to a minimum at 450 K, corresponding to the maximum for N₂ formation, suggesting adsorbed NH₃ plays a significant role in reducing NO to N₂ in the presence of O₂. Continuing increase in temperature led to increase in the direct oxidation of H₂ to H₂O as evidenced by the maximum of the H₂O intensity profile at 540 K in Fig. 1 (b).

The IR intensity of NH₃ decreased and N₂ MS intensity increased as the reaction temperature increases beyond 600 K. At this temperature, only gaseous CO₂, H₂O, and a low intensity of adsorbed NH₃ were observed. The absence of other IR-observable intermediates indicates the rates of their formation are slower than the rate of their consumption.

Step switch of the reactant flow from NO/CO/O₂/H₂ to NO/CO/O₂/He at 473 K resulted in a rapid decrease in adsorbed H₂O, but little variation in the IR intensity of adsorbed NH₃, indicating that NH₃, which is responsible for the reduction of NO to N₂ is strongly adsorbed on the catalyst surface. This paper will present the results of in situ IR study of NO/CO/O₂/H₂ and discuss the reaction pathway and the nature of active site for NO under both fuel rich and lean-burn conditions on Pd/Al₂O₃ and Ag-Pd/Al₂O₃.

Significance

- Pd/Al₂O₃ catalyst exhibited activity for the reduction of NO to N₂ in the two temperature ranges: 440 – 480 K and temperatures above 600 K. Strongly adsorbed NH₃, produced from the reaction NO with H₂, plays a key role in reduction of NO to N₂ in 440 - 480 K.
- IR observation of adsorbed species during the reaction allows elucidation of the reaction pathways.

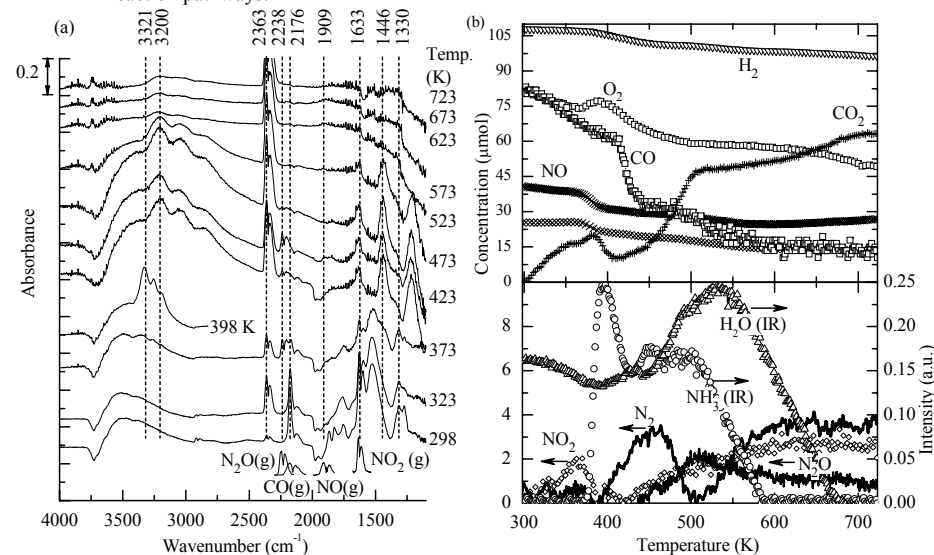


Figure 1. (a) Transient FTIR spectra during the NO/CO/O₂/H₂/He (1.4/2.8/2.8/8.5/84.5 vol%) TPR (10 K/min) at a total flow rate 70.7 cm³/min; (b) Concentration profile NO/O₂/CO₂/N₂.

References

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