

ESTIMATION OF EFFECTIVE DIFFUSIVITY OF STORED NO_x IN THE BARIUM PHASE OF Pt/BaO/Al₂O₃ CATALYST USING TAP

Ashok Kumar, Michael P. Harold* and Vemuri Balakotaiah*
Department of Chemical & Biomolecular Engineering
University of Houston, Houston, TX

Summary

A systematic study over Pt/BaO/Al₂O₃ powder catalyst is carried out using Temporal Analysis of Products (TAP) to estimate the effective diffusivity of stored NO_x in the barium phase. The pre-nitration of Pt/BaO/Al₂O₃ using sequential pulses of NO followed by reduction results into the evolution of N₂ and NH₃. The reduction is carried out in the transport limited regime where diffusion of the stored NO_x from BaO storage phase to Pt/BaO interface was rate controlling process. The effluent profiles of N containing species were used to estimate stored NO_x diffusivity and diffusion activation energy.

Keywords

NO_x, NSR, TAP, Diffusivity

Introduction

NO_x Storage and Reduction (NSR) is an emerging technology for NO_x emission abatement in lean burn gasoline and diesel engines. The NO_x removal process involves storage of NO_x on an alkaline earth component (Ba, Ca) mediated by precious metals (Pt, Rh), and followed by injection of a rich pulse for a shorter duration to reduce the stored NO_x. The reduction of stored NO_x involves transfer of stored NO_x from barium phase to Pt/BaO interface followed by reaction of NO_x with H₂ at Pt or Pt/BaO interface to form N₂, NH₃ and N₂O. Another possible mechanism reported in literature is transfer of activation H from Pt to BaO followed by NO_x reduction in barium phase to produce N containing effluent.

In this study, we employ Temporal Analysis of Products (TAP) to estimate the effective diffusivity of stored NO_x in barium phase. The diffusivity data at various temperatures is used to compute stored NO_x diffusion activation energy in the barium phase of the catalyst. TAP experiments are carried out isothermally over the powder catalyst, thereby avoiding thermal and mass transport complications typical of atmospheric pressure reactors.

Experimental

The Pt/BaO/Al₂O₃ catalyst powder used in this study was provided by BASF Catalyst LLC, Iselin, NJ. It has a Pt dispersion of 3.2%, and contained 2.48 wt% Pt and 13.0 wt% BaO. About 41.4 mg of catalyst was sandwiched

between two inert quartz bead zones. The estimated number of exposed Pt sites in the catalyst sample was 1.0×10^{17} .

In a typical experiment, catalyst was first reduced by flowing H₂ for 2 hr at 400 °C, and was then brought down to reaction temperature (250 °C – 400 °C). The feed (NO or H₂) was injected in the reactor using fast pulsing valve. The spacing between two successive pulses was kept 40 ms. Effluent species including N₂, NO, N₂O, NH₃ were monitored with calibrated UTI 100C quadrupole mass spectrometer.

Results and discussion

NO pulse experiments were carried out at 250 – 400 °C range on pre-reduced catalyst. The amount of NO_x stored was fixed at 4.4×10^{18} molecules for storage at different temperatures. It means, storage at lower temperature was performed using large amount of NO fed per pulse and/or longer storage times while high temperature storage was performed with smaller NO pulse sizes and/or shorter storage times.

The storage is followed by reduction of pre-nitrated catalyst with H₂. Several reduction trials were performed using different spacing times between consecutive H₂ pulses. The spacing times greater than 0.1 s results into H₂ feed limited regime during initial part of the reduction. It

* To whom all correspondence should be addressed

means, if H₂ pulse size is increased, it results in increased effluent flux of N containing species (N₂ and NH₃). On the other hand, the reduction with H₂ pulse spacing times smaller than 0.1 s results in an identical effluent N profile for reduction with varied H₂ pulse sizes. Moreover, H₂ pulse sizes were chosen sufficiently high so that the reduction process is not limited by the supply of H₂. The reduction is not controlled by NO_x and H₂ chemistry on Pt during the temperature range¹. Based on above results spacing time between consecutive H₂ pulses was chosen (40 ms) such that reduction is controlled by transport of stored NO_x in barium phase. The typical effluent profile for N₂, NH₃ at is plotted in Fig. 1.

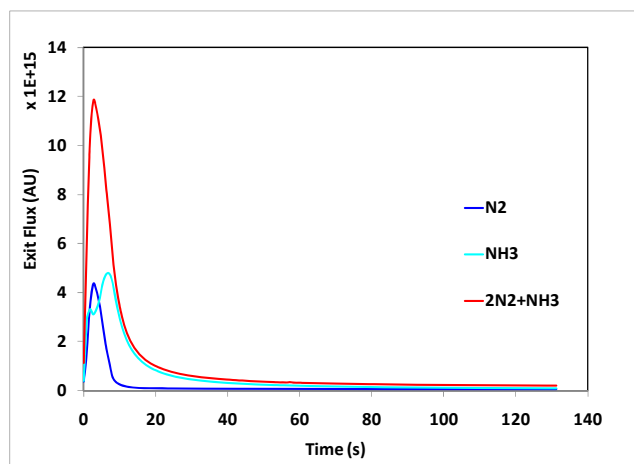


Fig. 1. Effluent profiles of N₂ and NH₃ during stored NO_x reduction at 350 °C

The NO_x is assumed to be uniformly stored in proximity of Pt. The radius of NO_x reduced during reduction, r_o, was calculated². Using the moment of stored NO_x in barium phase wrt Pt/BaO interface, the effective radius of stored NO_x is calculated as

$$r_e = r_1 + \frac{1}{3} \left(\frac{2r_o^3 - 3r_1 r_o^2 + r_1^3}{r_o^2 - r_1^2} \right)$$

where, r₁ is the radius of Pt crystallite. The reduction of pre-nitrated catalyst results in the formation of N₂ and NH₃. The mean time of evolution of N containing species during the reduction is estimated as

$$t_e = \frac{\int_0^{\infty} t J(t) dt}{\int_0^{\infty} J(t) dt}$$

where, J(t) is the flux of effluent N containing species during reduction. Based on effective radius and mean time, the effective diffusivity of stored NO_x is estimated as

$$D_e = \frac{(r_e - r_1)^2}{t_e}$$

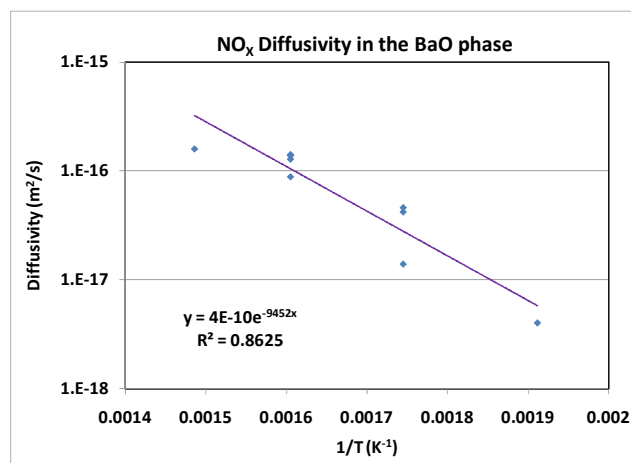


Fig. 2. Effective diffusivity of stored NO_x in barium phase

The diffusivity is plotted against 1/T and activation energy of NO_x diffusion is estimated to be 78.6 kJ/mol. A more detailed modeling in progress and will be presented.

References

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