

Promotion of Oxygen Desorption To Enhance Direct NO Decomposition over Tb–Pt/Al₂O₃ Catalyst

Steven S. C. Chuang* and Cher-Dip Tan

Department of Chemical Engineering, University of Akron, Akron, Ohio 44325-3906

Received: December 19, 1996[®]

Promotion of oxygen desorption at low temperatures holds the key to the development of an effective NO decomposition catalyst. Addition of Tb oxide to Pt/Al₂O₃ allows oxygen from dissociated NO to desorb at 593 K, which is significantly lower than the reported oxygen desorption temperatures for Pt catalysts. Combined temperature-programmed desorption/reaction with *in situ* infrared study reveals that desorbed oxygen is produced from decomposition of chelating bidentate nitrato, which may result from the reaction of adsorbed oxygen on Pt and adsorbed NO on Tb oxide. The Tb-promoted Pt/Al₂O₃ catalyst which possesses oxygen desorption capability at low temperatures shows the activity for decomposition of NO to N₂, N₂O, NO₂, and O₂ under pulse and steady-state reaction conditions at 773–923 K.

Introduction

The direct decomposition of nitric oxide to harmless nitrogen and oxygen is an attractive approach for the control of NO emission because of its chemical simplicity.¹ The direct NO decomposition, 2NO → N₂ + O₂, is thermodynamically favorable at temperatures below 2000 K. Development of an effective catalyst for the direct NO decomposition will eliminate the use of reducing reactants, such as H₂, CO, NH₃, and hydrocarbons, significantly simplifying the NO removal process and dramatically decreasing the cost of NO control for the exhausts of various combustion processes. Extensive catalyst searching and screening studies for the past two decades have led to the discovery of Cu–ZSM-5 catalysts, which exhibit the highest activity for the direct NO decomposition among various catalysts tested.² However, the narrow temperature window of operation for Cu–ZSM-5, its susceptibility to SO₂ poisoning, and rapid deactivation by H₂O severely limit its potential for practical use.^{2,3} Development of a durable catalyst for the direct NO decomposition remains a major challenge in the area of environmental catalysis.^{4–6}

Knowledge of elementary processes governing the NO decomposition may help guide the development of practical catalysts. Examination of the proposed elementary steps for NO decomposition has revealed that the low NO decomposition activity of a catalyst is due to its inability to desorb oxygen produced from NO dissociation.¹ Oxygen from dissociated NO is strongly bonded to the catalyst surface, poisoning NO dissociation sites and preventing further NO dissociation. The conventional approach to remove adsorbed oxygen from the catalyst surface includes (i) the utilization of high temperature to desorb adsorbed oxygen and (ii) the employment of gaseous reductant to react with adsorbed oxygen. The former is a high-temperature process that requires use of extensive energy; the latter involves a reductant that eliminates the unique advantage of the direct NO decomposition.

A novel approach to improve the activity of a NO decomposition catalyst is to enhance either the desorption of adsorbed oxygen or spillover of adsorbed oxygen from the NO dissociation site.^{7,8} Promotion of oxygen desorption should create free sites needed for further NO dissociation. A literature search in

the area of oxygen spillover revealed that nonstoichiometric rare earth oxides such as Tb and Pr oxides may uptake and release adsorbed oxygen and exhibit self-decomposition activity, releasing oxygen at 773 and 613 K, respectively.^{9–11} We have, therefore, postulated that the nonstoichiometric rare earth oxides may act as a promoter either to facilitate the spillover of adsorbed oxygen or to promote the desorption of adsorbed oxygen from the NO dissociation site, resulting in enhancing the NO decomposition activity. This paper reports the result of an investigation of the effect of Tb oxide on the nature (i.e., reactivity and structure) of adsorbates for NO dissociation and for oxygen desorption by a combined *in situ* infrared spectroscopy and temperature-programmed desorption/reaction technique as well as steady-state reaction study.

Experimental Section

The catalyst used for this study is a 1 wt % Tb–Pt/Al₂O₃ (Tb:Pt = 10:1), which was prepared by coimpregnating a solution of Tb(NO₃)₃·5H₂O (Alfa Products) and H₂PtCl₆·6H₂O (Alfa Products) onto a large surface area γ-Al₂O₃ support (Alfa Products, 100 m²/g of surface area, 0.01–0.02 μm pore size). The low loading of Pt is used to emulate the loading of precious metal in the automotive catalysts. The ratio of the volume of solution to the weight of alumina support used in the impregnation step was 1 cm³ to 2 g. The catalyst was dried overnight in air at 303 K after impregnation and then reduced in flowing hydrogen at 673 K for 8 h. The Tb–Pt/Al₂O₃ catalyst prepared was characterized by X-ray diffraction (XRD). The XRD pattern reveals the presence of Tb₂O₃ crystallite and a possible Tb₃Al₂Al₃O₁₂ species on the Al₂O₃ surface. The absence of the XRD pattern of Pt crystallite indicates that Pt is highly dispersed on the catalyst with the crystallite size smaller than 30 Å.

The details of *in situ* infrared (IR) reactor cell, experimental apparatus, and procedures have been reported elsewhere.¹² The catalyst powder which has been exposed to air was pressed into three self-supporting disks (40 mg each); one of the disks was placed in the IR cell, and the other two disks were broken down into flakes and placed at the exit line in the immediate vicinity of the infrared beam path. The additional catalyst disks were used to increase the amount of desorbing species and conversion to obtain a strong signal in the mass spectrometer.

Following the pretreatment of the catalyst in the IR cell with helium flow at 773 K for 1 h, the catalyst was exposed to 10

* To whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, March 15, 1997.

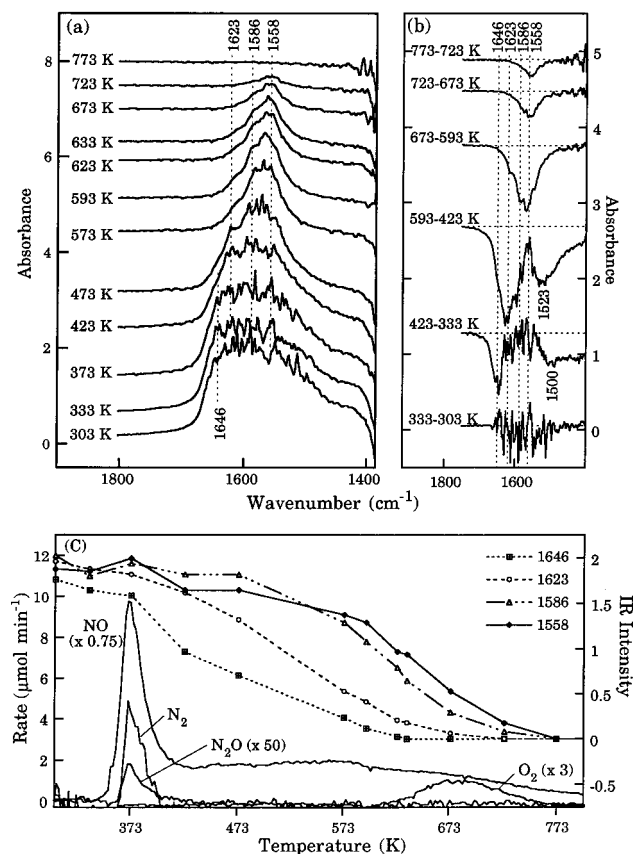


Figure 1. (a) Infrared spectra during NO TPD/R on 1 wt % Tb–Pt/Al₂O₃ at a heating rate of 20 K min^{−1} from 303 to 773 K. (b) Spectral differences; the 423–333 K spectrum is a result of the subtraction of IR absorbance at 333 K from that at 423 K. (c) Rate of elution for gaseous species from the IR cell and variation of IR intensities with temperature.

cm³ min^{−1} of NO for 10 min at 303 K. Temperature-programmed desorption/reaction (TPD/R) studies were carried out from 303 to 773 K at a heating rate of 20 K min^{−1} with a 40 cm³ min^{−1} of He flow. TPD/R is referred to both desorption and reaction of adsorbed NO taking place simultaneously as adsorbates are subject to temperature-programmed heating. Changes in concentration of adsorbates and products during TPD/R and pulse reaction studies were determined simultaneously by infrared spectroscopy and mass spectrometer, respectively. Catalyst activity and selectivity were tested by two modes: pulsing either 500 μL or 1 cm³ of NO into 40 cm³ min^{−1} He flow over catalyst in an *in situ* IR cell at 673 and 723 K and steady-state flow reaction study over the catalyst in a stainless steel tubular reactor from 723 and 923 K. Concentration of product effluent from stainless steel tubular flow reactor is monitored by mass spectrometry, GC/MS (gas chromatography/mass spectrometry), and infrared spectroscopy with a gaseous IR cell.

Results and Discussion

Figure 1a shows the IR spectra of adsorbates during the TPD/R in 40 cm³ min^{−1} He flow following the NO adsorption at 303 K. IR bands below 1400 cm^{−1} were not observed due to the large noise-to-signal ratio and the cutoff of the IR transmission below 1250 cm^{−1} by Al₂O₃ support. The initial spectrum, a result of exposure of the catalyst to the NO flow at 303 K, shows the Pt–NO[−] band at 1646 cm^{−1} and nitrate bands in the 1630–1400 cm^{−1} region. The assignment of infrared spectra of adsorbed nitrate species has not been well established. Comparison of the infrared spectra of adsorbed nitrate (NO₃[−])

with those of nitrate complexes suggests that the 1623 cm^{−1} band may be assigned to the bridged bidentate,



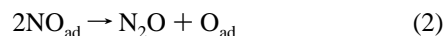
the 1558 cm^{−1} band and the shoulder band at 1550 cm^{−1} to the chelating bidentate,



where M is a metal atom.¹³

Temperature-programmed desorption/reaction (TPD/R) caused variation in both infrared spectra of adsorbed NO species and eluted rate of gaseous species. In order to clearly discern the change in the concentration of various adsorbates due to TPD/R, spectral differences were taken in Figure 1b and compared with the eluted rate of gaseous products in Figure 1c to reveal the contribution of the specific adsorbates to the formation of gaseous products. The elution rate of each species was obtained by multiplying its MS intensity with a calibration factor that is determined by injecting a known amount of the species into the MS and measuring the area under the response curve.

Figure 1a shows that the intensities of Pt–NO[−] at 1646 cm^{−1}, and bidentate nitrates in the 1545–1500 cm^{−1} region began to decrease at temperatures above 333 K. The decrease in the intensity of these bands is highlighted in Figure 1b by the negative difference spectrum for 423–323 K where NO, N₂, and N₂O evolved, giving the peak temperature at 373 K in Figure 1c. The amount of NO, N₂, and N₂O desorbed under the 373 K peak corresponds to 30.6, 20.7, and 1.0 μmol, respectively. Formation of N₂ and N₂O suggests the occurrence of



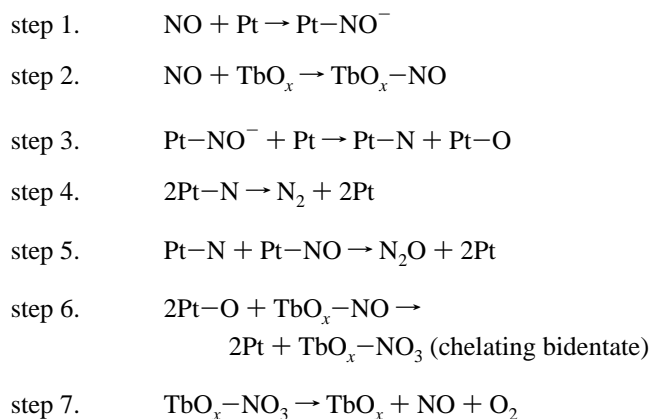
Stoichiometry of reactions 1 and 2 suggests that the formation of these N₂ and N₂O at 373 K peak should leave 42.4 μmol of adsorbed oxygen on the catalyst surface. Adsorbed oxygen on the surface of metal and metal oxide cannot be observed from this study because its vibrational frequency in 200–450 cm^{−1} region¹⁴ is below the IR transmission range of CaF₂ and Al₂O₃ support used in this study. Adsorbed oxygen did not desorb as gaseous oxygen molecule until temperature reaching 593 K. In the temperature range between 423 and 593 K, the main TPD-IR feature is the constant NO elution rate (Figure 1c) with a substantial decrease in the bidentate bands at 1623 and 1523 cm^{−1}. A marked decrease in IR intensity of these bidentate bands has also been observed with NO elution in the same temperature range during TPD/R of adsorbed NO on Al₂O₃. The similarity in the negative difference spectra for these two catalysts suggests a part of the bidentate nitrates at 1623 and 1523 cm^{−1} is a result of direct adsorption of NO on the Al₂O₃ surface.

At temperatures above 593 K, adsorbed oxygen began to desorb and exhibited the peak at 683 K while difference IR spectra showed a significant decrease in the intensity of the 1558 cm^{−1} band. The amount of desorbed oxygen (4.7 μmol) is less than that of oxygen produced during the formation of N₂ and N₂O at 373 K.

Since a practical catalyst for NO decomposition must work in an oxidizing environment, the catalyst was further treated with air at 773 K for 1 h and then cooled to 303 K in helium for NO adsorption and TPD/R studies to determine the activity

of the oxidized Tb–Pt/Al₂O₃ for the NO decomposition. Figure 2a shows the IR spectra during the NO TPD/R on the oxidized Tb–Pt/Al₂O₃. Comparison of results in Figures 1 and 2 reveals the effect of air treatment at 773 K on the reactivity of adsorbates and the catalyst surface state. The air treatment led to the following changes in IR spectra and TPD/R product profiles: (i) Air treatment decreased the intensity of Pt–NO[−] band at 1646 cm^{−1} by 50%. (ii) Air treatment decreased the amount of N₂ formation and completely suppressed N₂O formation. (iii) Air treatment increased the amount of O₂ and NO desorbed at 683 K. These changes brought about by the air treatment suggest that (1) formation of N₂O requires a large fraction of reduced Pt surface and (2) Pt–NO[−] may be the precursor for the NO dissociation. One common feature between the reduced and air-treated catalysts is that oxygen desorption at 683 K is closely related to a significant decrease in IR intensity of chelating bidentate at 1558 cm^{−1}. A subtle difference in the formation of chelating bidentate on these two catalysts was noted. The majority of chelating bidentate was formed during NO adsorption on Tb–Pt/Al₂O₃ at room temperature while some of chelating bidentate was generated during TPD/R on air-treated Tb–Pt/Al₂O₃ at 333–473 K.

The above observations led to postulation of the following pathway for the decomposition of NO to N₂, N₂O, and O₂ on the Tb–Pt/Al₂O₃:



It should be noted that the whole Pt–NO[−] entity should be considered neutral. The proposed pathway for the formation of gaseous oxygen molecules from TPD/R involves (i) the dissociation of adsorbed NO on the Pt surface, step 3, at temperatures below 473 K, (ii) the reaction of adsorbed oxygen with adsorbed NO on the Tb oxide surface to form a chelating bidentate species, step 6, and (iii) the decomposition of the chelating bidentate to produce NO and O₂, step 7, at temperatures above 593 K.

To compare the oxygen desorption profile of Pt/Al₂O₃ and Tb–Pt/Al₂O₃, TPD/R of adsorbed NO was also carried out on Pt/Al₂O₃. O₂ was not found in the temperature range 303–873 K during TPD/R of adsorbed NO on Pt/Al₂O₃. Due to the operating temperature limit of the IR cell, TPD/R was not able to conduct at temperatures above 873 K. Oxygen from dissociated NO has been found to desorb at 1000 K for Pt(111) surface which does not exhibit NO decomposition activity in the 673–973 K.¹⁵ Lowering the oxygen desorption temperature on the Tb–Pt/Al₂O₃ should facilitate desorption of adsorbed oxygen and regenerate sites needed for NO dissociation to complete the catalytic site for NO decomposition.

Since the oxygen desorption peak temperature was observed near 673 K on Tb–Pt/Al₂O₃, the activity of the catalyst was first tested at 673 K by pulsing 500 μL of NO into helium carrier gas over the catalyst. Pulse reaction studies allow accurate

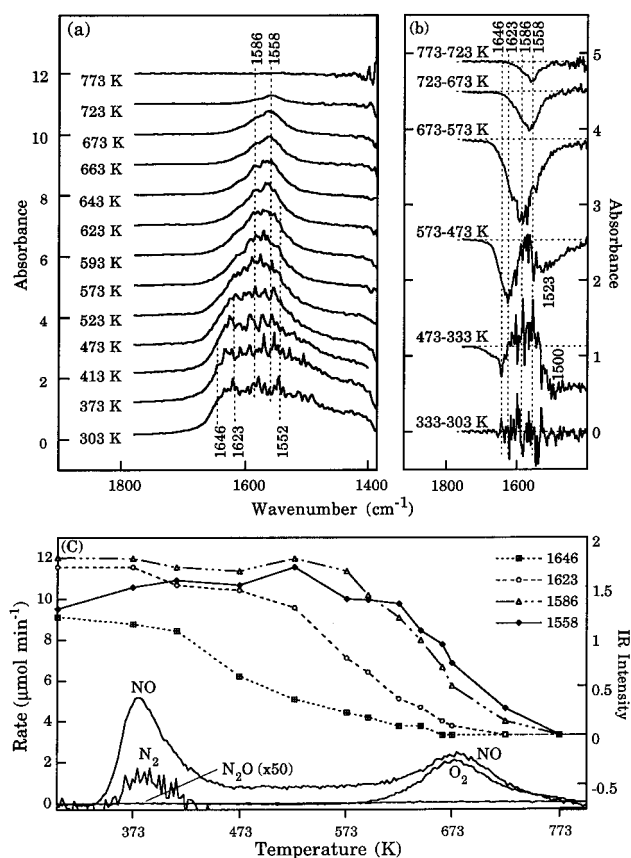


Figure 2. (a) Infrared spectra during NO TPD/R on oxidized 1 wt % Tb–Pt/Al₂O₃ at a heating rate of 20 K min^{−1} from 303 to 773 K. (b) Spectral differences. (c) Rate of elution for gaseous species from the IR cell and variation of IR intensities with temperature.

determination of mass balance which provides information on the moles of gaseous reactant entering the reactor and those of gaseous products leaving the reactor. Figure 3a shows the response of the IR reactor effluent composition. The number near each peak of the response indicates the amount (micromoles) of the species determined by the area under each peak multiplied by its calibration factor. The 500 μL (20.1 μmol) NO pulses produced N₂ and N₂O at 673 K. Lack of oxygen formation indicates that the catalytic cycle for the decomposition of NO to N₂ and O₂ was not complete; formation of gaseous N₂ and N₂O leaves oxygen from dissociated NO on the catalyst. The 500 μL NO pulses were continued at 723 K in an attempt to facilitate oxygen desorption. The initial four 500 μL and one 1 mL NO pulses produced only N₂ as a product, and infrared spectra remain unchanged as the NO pulsed through the catalyst disk. The absence of variation of IR spectra indicates that (i) the residence time and concentration of adsorbates resulting from NO pulses are too low for adsorbates to be detected by infrared spectroscopy or (ii) the adsorbates produced from the NO pulse are not in the IR-active form.

Figure 3a shows that N₂O and O₂ began to be produced at pulse VI. Further NO pulses led to increase in O₂ production and decrease in N₂O and N₂ formation. Increase in NO at the effluent of the reactor indicates decrease in NO conversion. Time scale and MS intensity for the pulses VI, VII, and VIII are expanded in Figure 3b to examine the lead/lag relationship in product formation. Elution of NO lagged behind the formation of N₂, N₂O, and O₂. This behavior is in contrast to transient responses of N₂, N₂O, and O₂ formation on Cu–ZSM-5 which shows that O₂ formation lagged behind that of N₂ and N₂O.¹⁶

NO₂ was not observed by mass spectroscopy during TPD/R and pulse reaction studies due to its small calibration factor.

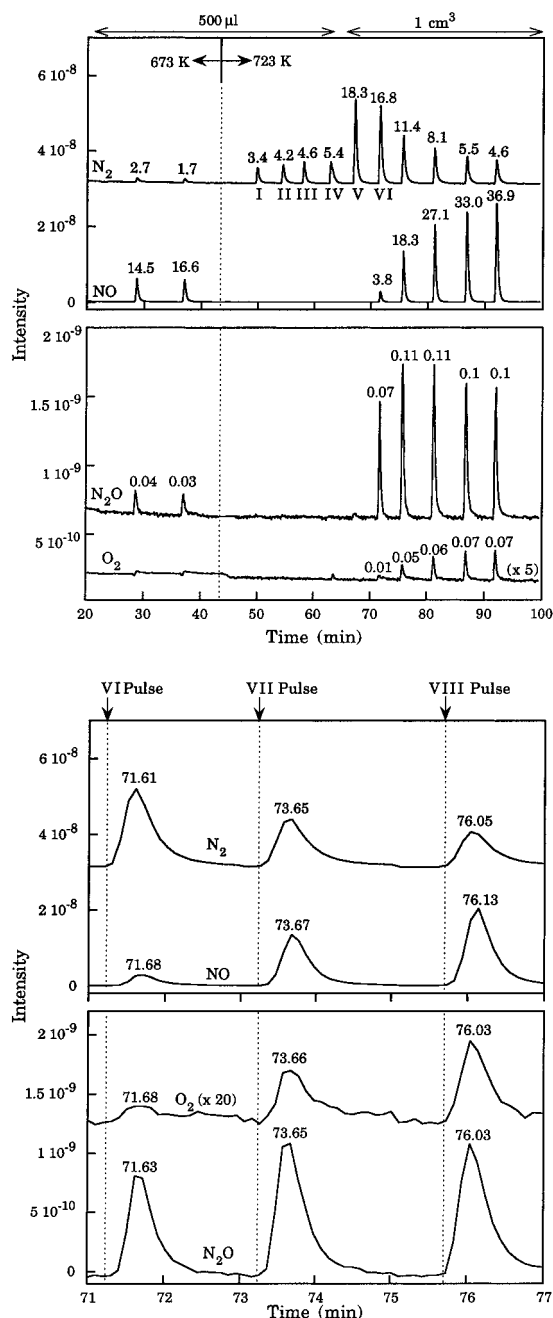


Figure 3. (a, top) MS response of the IR reactor effluent composition during the pulse NO reaction on 1 wt % Tb–Pt/Al₂O₃ at 673 and 723 K. The number near each peak of the response indicates the amount (μmol) of the species. (b, bottom) Pulses VI, VII, and VIII in (a) at 723 K.

The low NO₂ calibration factor does not allow detection of low concentration of NO₂ in the effluent of the IR cell. Inability to accurate quantification of NO₂ formation of gas chromatography and mass spectroscopy has presented serious problems in determining catalyst selectivity and mass balance between reactants and products in the literature.

In order to quantify NO₂ formation and determine the steady-state catalyst activity and selectivity, the steady-state NO decomposition was carried out over the catalyst in a tubular reactor by step switch of the inlet flow from steady-state He flow to NO/Ar flow. Ar is added to NO stream to determine the flow pattern of reactant flow during the step switch. The reactor effluent is monitored by mass spectrometer, GC/MS, and infrared spectroscopy with a gaseous IR cell. The MS intensity profiles of the reactor effluent monitored by mass

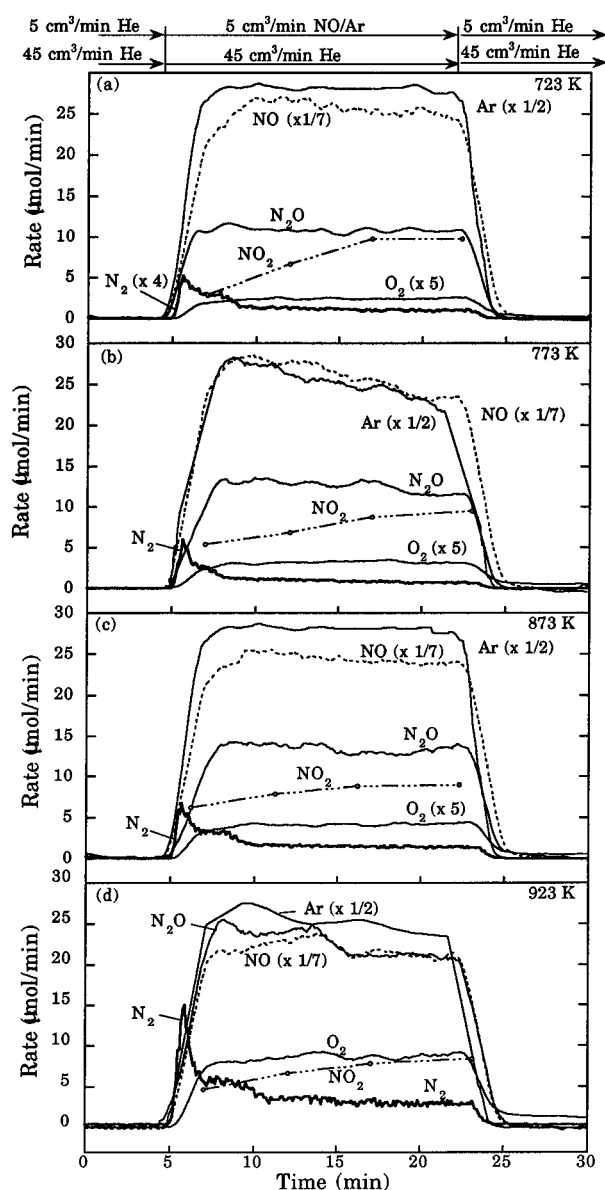


Figure 4. Steady-state NO decomposition on 1 wt % Tb–Pt/Al₂O₃ catalyst in stainless steel tubular reactor at (a) 723, (b) 773, (c) 873, and (d) 923 K. The catalyst was reduced with H₂ at 773 K for 30 min prior to reaction studies at each temperature. Reaction mixture consists of 5 cm³ min⁻¹ NO (with 2% Ar) and 45 cm³ min⁻¹ He with a total flow rate of 50 cm³ min⁻¹.

spectroscopy were adjusted to the elution rate profiles by quantitative measurement of N₂O, N₂, O₂, and NO by GC/MS and that of NO, N₂O, and NO₂ by infrared spectroscopy. In order to ensure reproducibility, the catalyst was reduced by hydrogen flow at 773 K prior to step switch reaction studies at each temperature.

Figure 4 shows that N₂ formation gave an overshoot response while N₂O and O₂ formation increased gradually to steady state between 723 and 923 K following the step switch of flow from He to NO/Ar. The overshoot of N₂ indicates the high initial activity of NO decomposition due to the reduced state of Pt. NO₂ was determined by a large gaseous IR cell with a long IR beam path which does not allow determination of transient formation of NO₂. A separate calibration run shows that NO₂ was produced from reaction of O₂ with NO.¹⁶ The results are consistent with those reported by Li and Hall, who has demonstrated that O₂ produced from NO decomposition reacts with NO to produce NO₂.³ Product yields in Table 1 shows the selectivity to NO₂ decreased with increasing temperature.

TABLE 1: NO Conversion (%) and Yields (%) versus Temperature for the NO Decomposition

temp (K)	NO conversion	yields ^a (%)			
		N ₂	N ₂ O	O ₂	NO ₂
673	11.88	0.00	32.35	1.72	35.29
723	16.05	0.77	34.10	1.57	30.26
773	16.99	2.01	34.18	1.79	27.62
873	18.60	3.67	34.39	2.24	23.88
923	27.75	4.56	37.97	15.58	14.94

^a Yield = (number of moles produced)/(number of moles of NO reacted) × 100%.

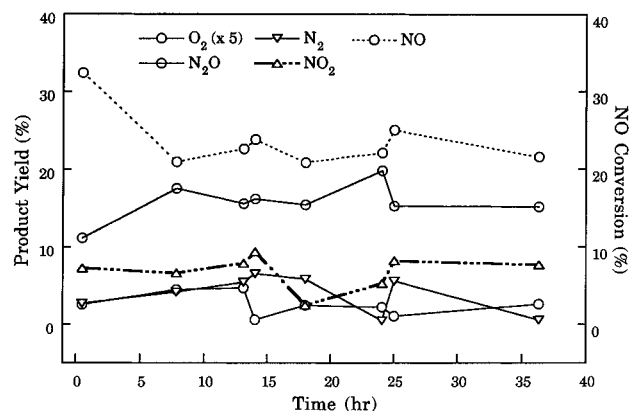


Figure 5. NO conversion and product yield versus reaction time at 873 K. Reaction mixture consists of 5 cm³ min⁻¹ NO (with 2% Ar) and 45 cm³ min⁻¹ He with a total flow rate of 50 cm³ min⁻¹.

Long-term catalyst deactivation study at 873 K in Figure 5 demonstrates that the catalyst exhibits the stable activity and selectivity after initial 8 h of reaction.

Conclusions

Combined TPD/R with *in situ* IR study reveals that both Tb–Pt/Al₂O₃ and air-treated Tb–Pt/Al₂O₃ catalysts exhibit O₂ desorption profile centered at 693 K. The O₂ desorption is resulted from decomposition of chelating bidentate nitrate which is produced from the direct exposure of the catalysts to gaseous

NO. The Tb–Pt/Al₂O₃ catalysts which exhibit low-temperature O₂ desorption show the activity for NO decomposition at temperatures above 723 K under the pulse reaction and steady-state condition. The catalyst exhibits steady-state activity and selectivity for 37 h at 873 K. Further study is underway to determine the effect of air, H₂O, and SO₂ on the NO decomposition under steady-state flow condition.

Acknowledgment. The authors gratefully acknowledge financial support for this research from the U.S. Department of Energy Grant DE-FG22-95PC95224.

References and Notes

- (1) Hightower, J. W.; Van Leirsburg, D. A. In *The Catalytic Chemistry of Nitrogen Oxides*; Klimisch, R. L., Larson, J. G., Eds.; Plenum Press: New York, 1975; p 63.
- (2) Iwamoto, M. In *Studies in Surface Science and Catalysis*; Misono, M., Moro-oka, Y., Kimura, S., Eds.; Elsevier: Amsterdam, 1990; Vol. 54, p 121.
- (3) Li, Y.; Hall, W. K. *J. Phys. Chem.* **1990**, *94*, 6140.
- (4) Li, Y.; Armor, J. N. *Appl. Catal.* **1991**, *76*, L1.
- (5) Kung, M. C. *Catal. Lett.* **1993**, *18*, 111.
- (6) Aylor, A. W.; Larsen, S. C.; Reimer, J. A.; Bell, A. T. *J. Catal.* **1995**, *157*, 592.
- (7) Tan, C.-D.; Krishnamurthy, R.; Chuang, S. S. C. Abstract of 33rd Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Pittsburgh, PA, May 10–11, 1995.
- (8) Chuang, S. S. C.; Krishnamurthy, R.; Tan, C.-D.; Brundage, M. Abstract of 7th Japan–China–USA Symposium on Catalysis, Tokyo, Japan, July 26–28, 1995; p O-29.
- (9) Kyomasu, A.; Okuhara, T.; Misono, M. *Nippon Kagaku Kaishi* **1991**, *5*, 651.
- (10) Takasu, Y.; Yoko-o, T.; Matsui, M.; Matsuda, Y.; Toyoshima, I. *J. Catal.* **1982**, *77*, 485.
- (11) Takasu, Y.; Matsui, M.; Tamura, H.; Kawamura, S.; Matsuda, Y.; Toyoshima, I. *J. Catal.* **1981**, *69*, 51.
- (12) Chuang, S. S. C.; Brundage, M. A.; Balakos, M. W.; Srinivas, G. *Appl. Spectrosc.* **1995**, *49* (8), 1151.
- (13) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.
- (14) Fisher, G. B.; DiMaggio, C. L.; Beck, D. D. In *New Frontiers in Catalysis*; Proceedings of the 10th International Congress on Catalysis, 1992; Guzzi, L., Solymosi, F., Tetenyi, P., Eds.; Akademiai Kiado: Budapest, Hungary, 1993; Part A, p 383.
- (15) Gland, J. L.; Sexton, B. A.; Fisher, G. B. *Surf. Sci.* **1980**, *95*, 587.
- (16) Konduru, U. V. M.S. Thesis Preliminary Study, The University of Akron, 1996.