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IN SITU INFRARED STUDY OF CATALYTIC DECOMPOSITION OF NO

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In Situ Infrared Study of Catalytic Decomposition of NO

Abstract

During the second semi-annual period, promotion of oxygen desorption to enhance direct NO decomposition over Tb-Pt/Al$_2$O$_3$ catalyst has been studied. 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/Al$_2$O$_3$ 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 be resulted from the reaction of adsorbed oxygen on Pt and adsorbed NO on Tb-oxide. The Tb-promoted Pt/Al$_2$O$_3$ catalyst which possesses oxygen desorption capability at low temperatures shows the activity for decomposition of NO to N$_2$, N$_2$O, and O$_2$ at 723 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, $2NO \rightarrow N_2 + O_2$, 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 H$_2$, CO, NH$_3$, 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 last 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 SO$_2$ poisoning, and rapid deactivation by H$_2$O 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 which requires use of extensive energy; the latter involves a reductant which 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. 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 to either 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 letter 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.

Experimental

The catalyst used for this study is a 1 wt.% Tb-Pt/Al_2O_3 (Tb:Pt=10:1), which was prepared by coimpregnating a solution of $Tb(NO_3)_3 \cdot 5H_2O$ (Alfa Products) and $H_2PtCl_6 \cdot 6H_2O$

(Alfa Products) onto a large surface area γ-Al_2O_3 support (Alfa Products, 100 m^2/g of surface area, 0.01-0.02 Micron of 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 cm^3 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/Al_2O_3 catalyst prepared was characterized by X-ray diffraction (XRD). XRD pattern reveals the presence of Tb_2O_3 crystallite and a possible $Tb_3Al_2Al_3O_{12}$ species on the Al_2O_3 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 hr, the catalyst was exposed to 10 cm^3 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 cm^3 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. Catalyst activity was tested by pulsing either 500 µl or 1 cm^3 of NO into 40 cm^3 min^{-1} He at 673 and 723 K. Changes in concentration of adsorbates and products during TPD/R and pulse reaction studies were determined simultaneously by infrared spectroscopy and mass spectrometer, respectively.

Results and Discussion

Figure 1(a) shows the IR spectra of adsorbates during the TPD/R in 40 cm^3 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 CaF$_2$ windows and Al$_2$O$_3$ 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 (NO$_3^-$) with those of nitrato 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.[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 1(b) and compared with the eluted rate of gaseous products in Figure 1(c) 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 which is determined by injecting a known amount of the species into the MS and measuring the area under the response curve.

Figure 1(a) 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 1(b) by the negative difference spectrum for 423-323 K where NO, N$_2$ and N$_2$O evolved, giving the peak temperature at 373 K in Figure 1(c). The amount of NO, N$_2$, and N$_2$O desorbed under the 373 K peak corresponds to 30.6, 20.7, and 1.0 µmol, respectively. Formation of N$_2$ and N$_2$O suggests the occurrence of

$$2NO_{ad} \rightarrow N_2 + 2O_{ad} \tag{1}$$

$$2NO_{ad} \rightarrow N_2O + O_{ad} \tag{2}$$
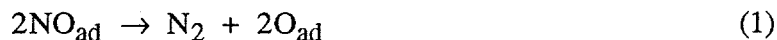
Stoichiometry of reactions 1 and 2 suggests that the formation of these N$_2$ and N$_2$O at 373 K peak should leave 42.4 µmol of adsorbed oxygen on the catalyst surface. Adsorbed oxygen on the surface of metal and metal oxide can not be observed from this study because its vibrational frequency in 200–450 cm^{-1} region[14] is below the IR transmission range of CaF$_2$ and Al$_2$O$_3$

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 (Fig. 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 Al_2O_3. The similarity in the negative difference spectra for these two catalysts suggests the bidentate nitrates at 1623 and 1523 cm^{-1} is a result of direct adsorption of NO on the Al_2O_3 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 N_2 and N_2O 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 hr and then cooled down to 303 K in helium for NO adsorption and TPD/R studies to determine the activity of the oxidized Tb-Pt/Al_2O_3 for the NO decomposition. Figure 2(a) shows the IR spectra during the NO TPD/R on the oxidized Tb-Pt/Al_2O_3. 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:
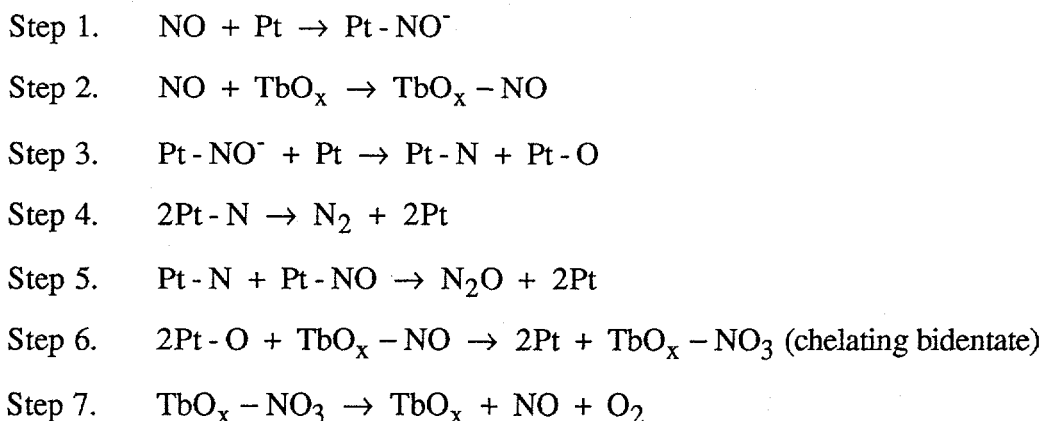
- Air-treatment decreased the intensity of Pt-NO$^-$ band at 1646 cm^{-1} by 50%.

- Air-treatment decreased the amount of N_2 formation and completely suppressed N_2O formation.

- Air-treatment increased the amount of O_2 and NO desorbed at 683 K.

These changes brought about by the air-treatment suggest that (i) formation of N_2O requires a large fraction of reduced Pt surface; and (ii) 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/Al$_2$O$_3$ at room temperature while some of chelating bidentate was generated on air-treated Tb-Pt/Al$_2$O$_3$ at 333–473 K.

The above observations led to postulation of the following pathway for the decomposition of NO to N$_2$, N$_2$O and O$_2$ on the Tb-Pt/Al$_2$O$_3$:

Step 1. $NO + Pt \rightarrow Pt\text{-}NO^-$

Step 2. $NO + TbO_x \rightarrow TbO_x\text{-}NO$

Step 3. $Pt\text{-}NO^- + Pt \rightarrow Pt\text{-}N + Pt\text{-}O$

Step 4. $2Pt\text{-}N \rightarrow N_2 + 2Pt$

Step 5. $Pt\text{-}N + Pt\text{-}NO \rightarrow N_2O + 2Pt$

Step 6. $2Pt\text{-}O + TbO_x\text{-}NO \rightarrow 2Pt + TbO_x\text{-}NO_3$ (chelating bidentate)

Step 7. $TbO_x\text{-}NO_3 \rightarrow TbO_x + NO + O_2$

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 1, 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 O$_2$, step 7, at temperatures above 593 K.

To compare the oxygen desorption profile of Pt/Al$_2$O$_3$ and Tb-Pt/Al$_2$O$_3$, TPD/R of adsorbed NO was also carried out on Pt/Al$_2$O$_3$. O$_2$ was not found in the temperature range of 303–873 K during TPD/R of adsorbed NO on Pt/Al$_2$O$_3$. 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/Al$_2$O$_3$ 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/Al$_2$O$_3$, 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 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 3 shows the response of the IR reactor effluent composition. The number near each peak of the response indicates the amount (μmol) of the species determined by the area under each peak multiplied by its calibration factor. The 500 μl (20.1 μmol) NO pulses produced N_2 and N_2O at 673 K. Lack of oxygen formation indicates that the catalytic cycle for the decomposition of NO to N_2 and O_2 was not complete; formation of gaseous N_2 and N_2O 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 N_2 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. Further NO pulses produced N_2, N_2O and O_2. Although the formation of O_2 indicates completion of the catalytic cycle for NO decomposition to N_2 and O_2, the amount of O_2 produced remains significantly less that of N_2 and N_2O, indicating the accumulation of oxygen on the catalyst. In the 10 NO pulses at 723 K, 0.26 μmol of gaseous oxygen was desorbed. The accumulated oxygen was further released after a series of NO/air pulses.

Conclusions

Combined TPD/R with *in situ* IR study reveals that both Tb-Pt/Al$_2$O$_3$ and air-treated Tb-Pt/Al$_2$O$_3$ catalysts exhibit O_2 desorption profile centered at 693 K. The O_2 desorption is resulted from decomposition of chelating bidentate nitrato which is produced from the direct exposure of the catalysts to gaseous NO. The Tb-Pt/Al$_2$O$_3$ catalysts which exhibit low-temperature O_2 desorption show the activity for NO decomposition at temperatures above 723 K under the pulse reaction condition. Further study is underway to determine the effect of air, H_2O, and SO_2 on the NO decomposition under steady-state flow condition.

Acknowledgment

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Figure Captions

Figure 1. (a) Infrared spectra during NO TPD/R on 1 wt.% Tb-Pt/Al$_2$O$_3$ 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.

Figure 2. (a) Infrared spectra during NO TPD/R on oxidized 1 wt.% Tb-Pt/Al$_2$O$_3$ 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.

Figure 3. MS response of the IR reactor effluent composition during the pulse NO reaction on 1 wt.% Tb-Pt/Al$_2$O$_3$ at 673 and 723 K. The number near each peak of the response indicates the amount (μmol) of the species.
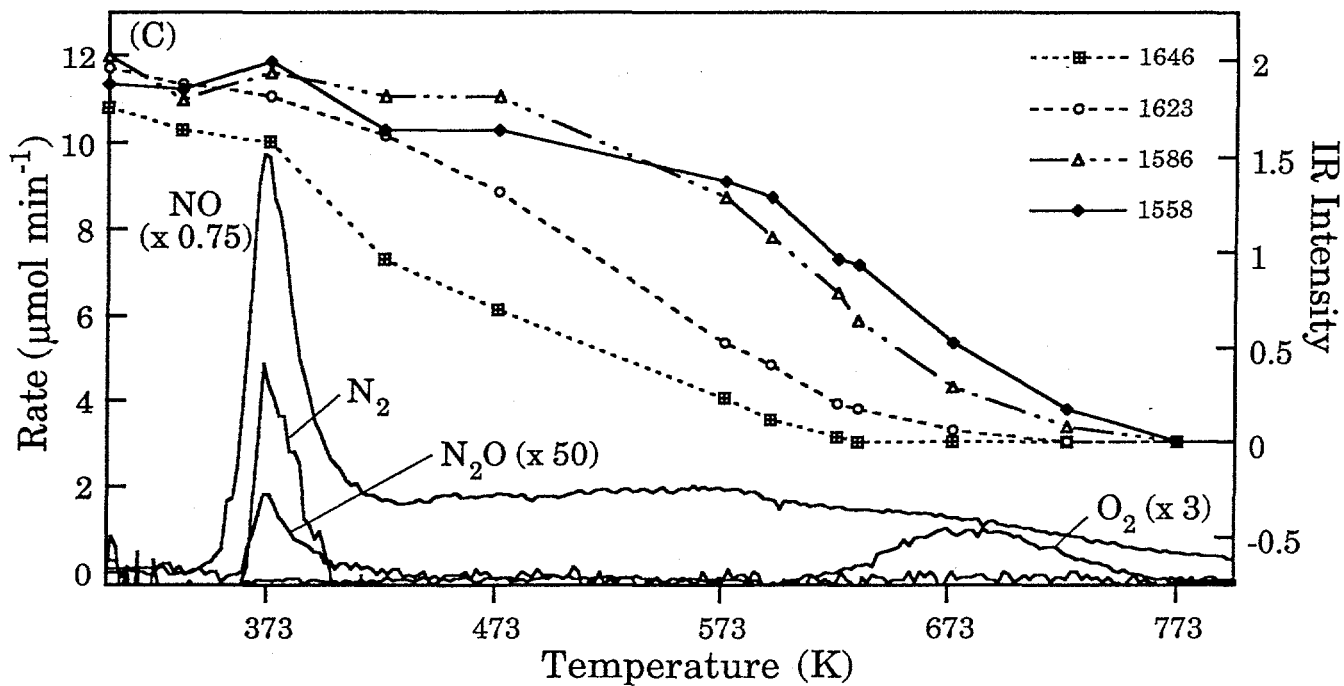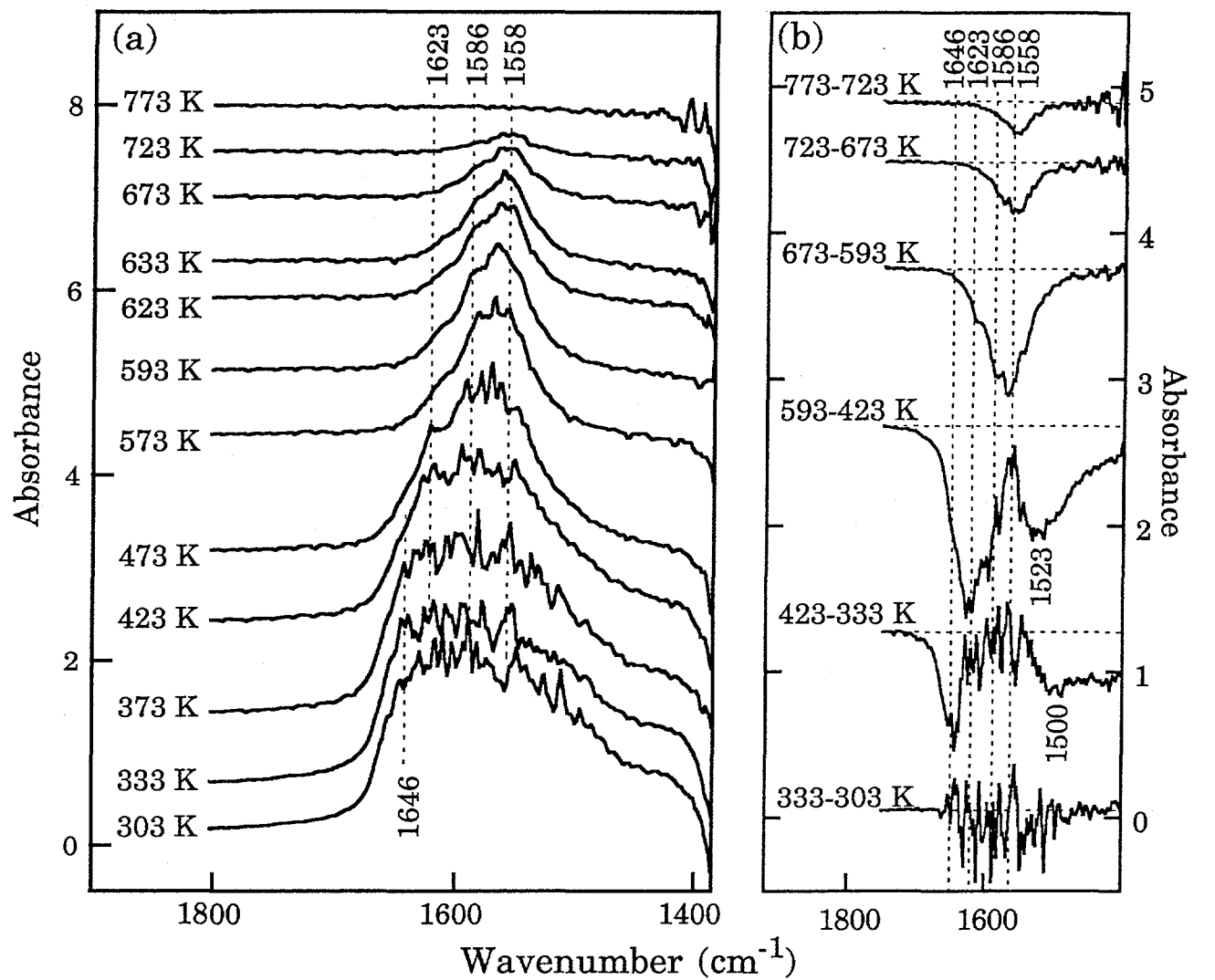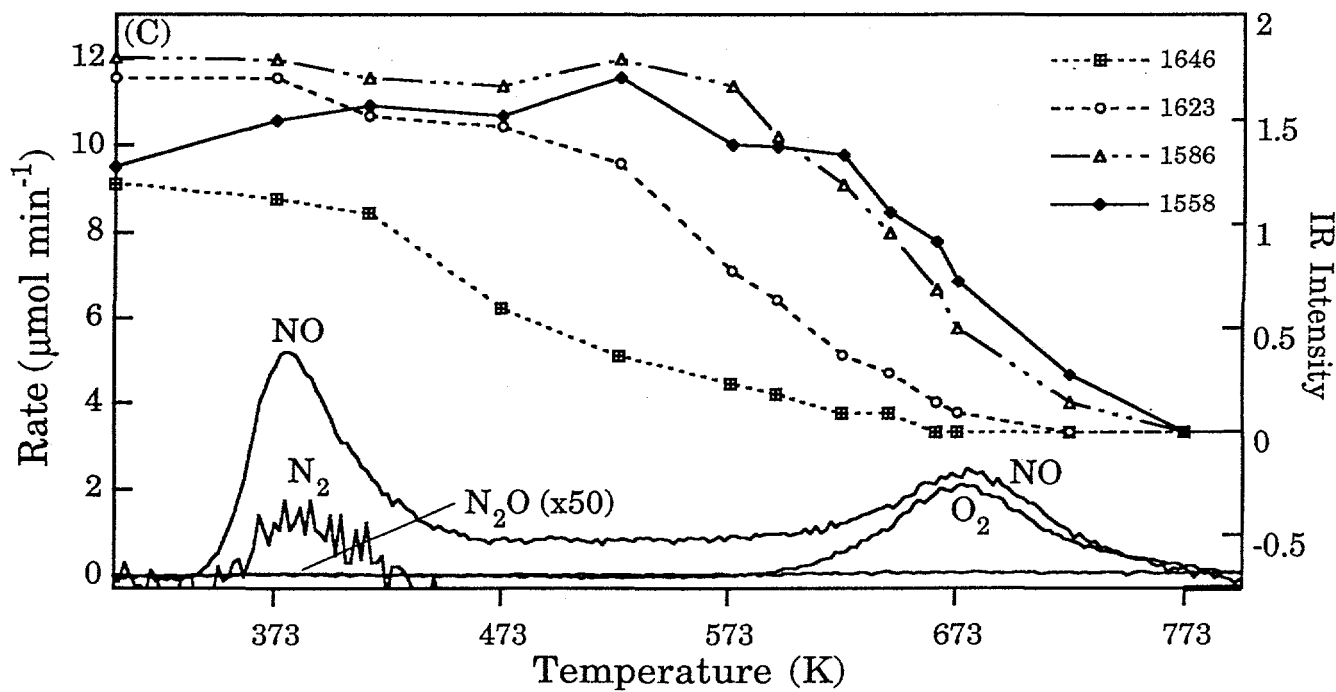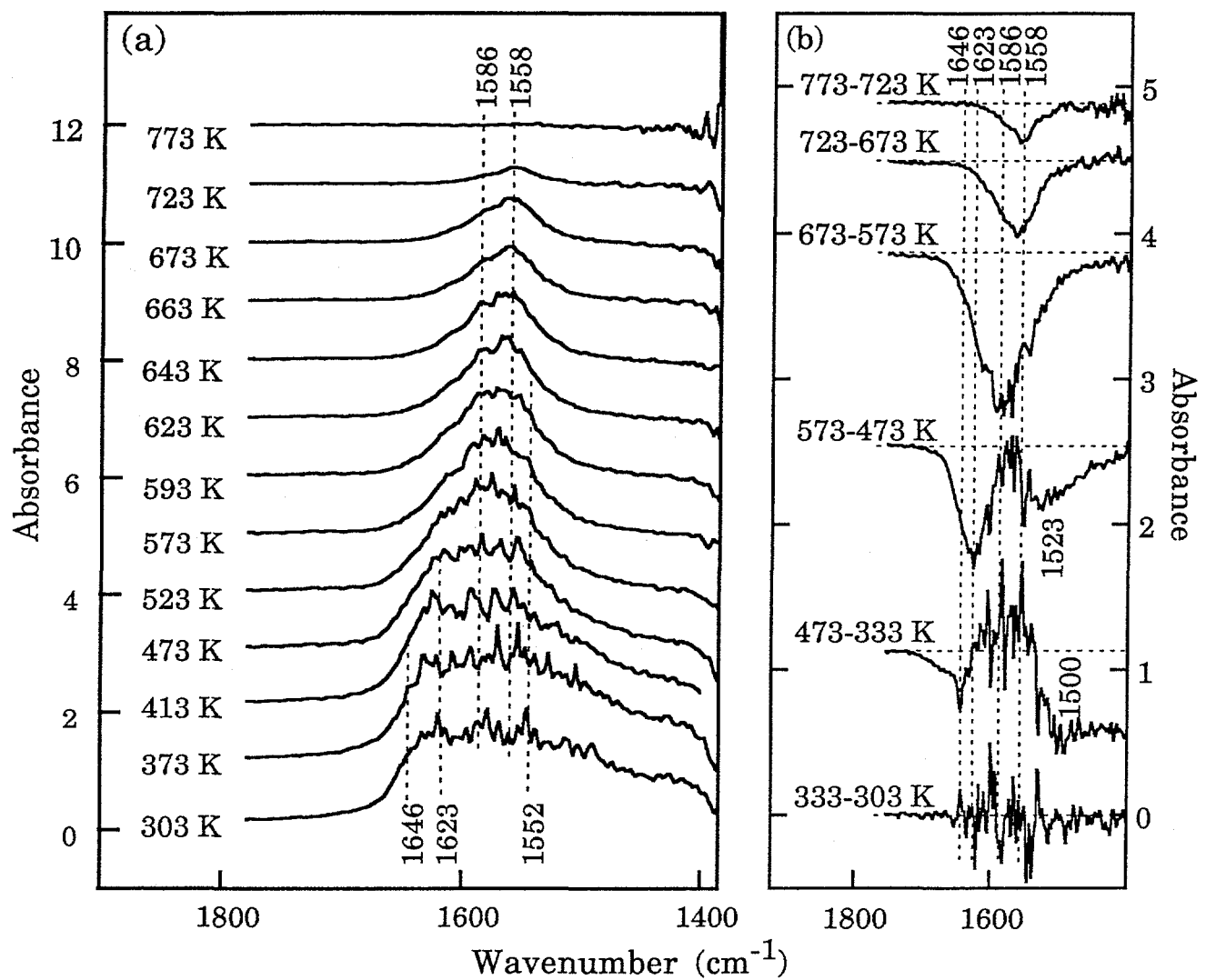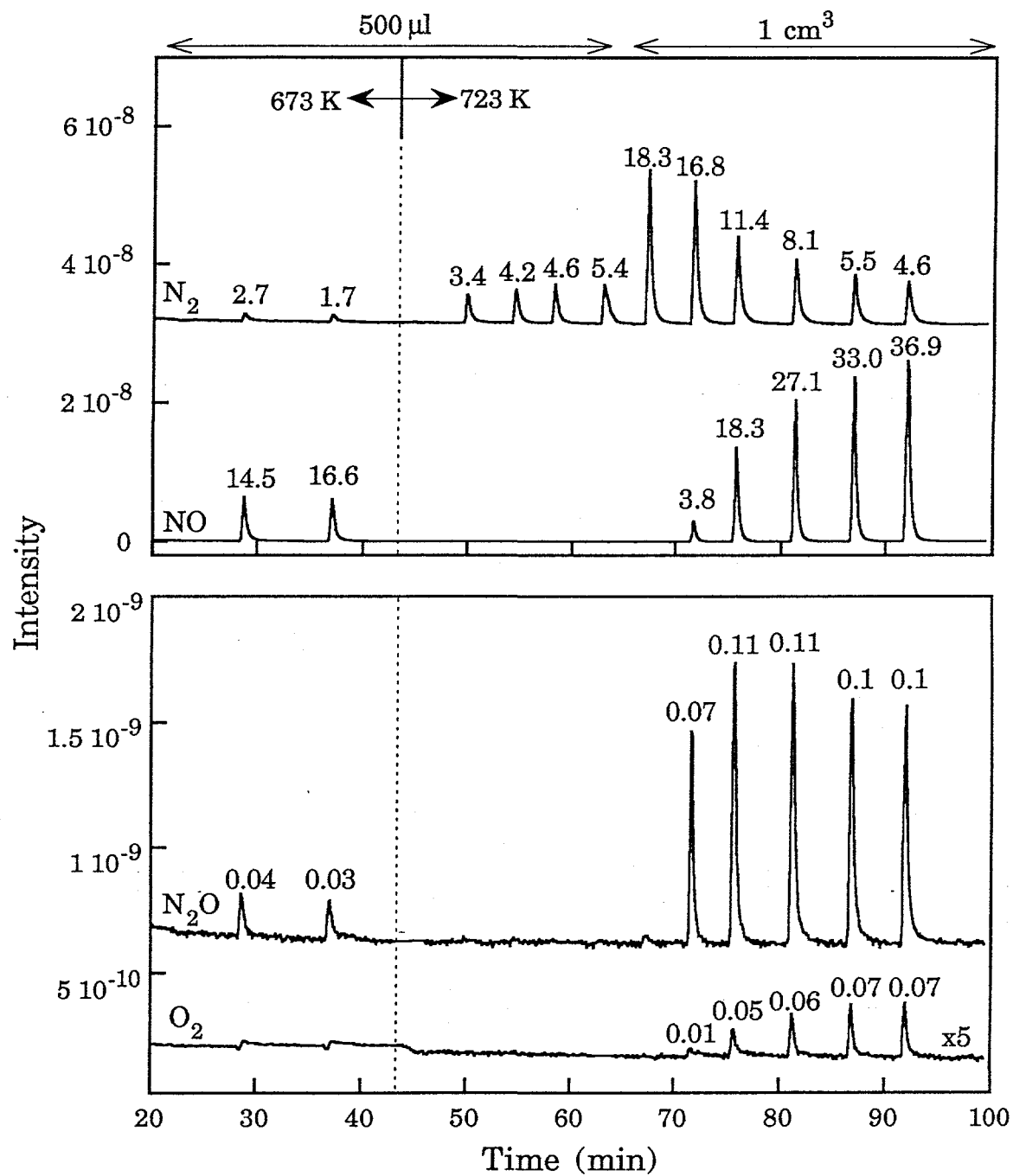
Fig 1
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Fig 2
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Fig 3
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