Applied Surface Science 414 (2017) 153–162

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

N_2 emission in steady-state $N_2O + CO$ and $NO + CO$ reactions on Ir(110) by means of angle-resolved desorption

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ARTICLE INFO

Article history:
Received 10 December 2016
Received in revised form 25 February 2017
Accepted 29 March 2017
Available online 12 April 2017

Keywords:
N_2 emission
NO reduction
N_2O intermediate
Angular distribution
Iridium

ABSTRACT

This paper confirms the intermediate $N_2O(a)$ pathway to N_2 in the NO reduction on iridium surfaces. The spatial distributions of desorbing product N_2 have been compared with each other in steady-state $N_2O + CO$ and $NO + CO$ reactions on Ir(110) by means of angle-resolved desorption. In the former reaction, the N_2 emission is fairly concentrated on the normally directed plane in the [001] direction and split into two-directional ways, being collimated at 46–58° off normal. In the latter reaction, the N_2 desorption consists of a normally directed component and two-directional components. The former component shows remarkable anisotropy; i.e., the distribution is sharp on the normally directed plane in the [001] direction and broad on the plane perpendicular to it. This component originates from the association of adsorbed nitrogen atoms. The other components are collimated at around 54° off normal towards the [001] and $[00\bar{1}]$ directions and they come from the decomposition of intermediate $N_2O(a)$. The off-normal components significantly share the total N_2 emission below approximately 550 K. At higher temperatures, these become minor and mostly invisible above 650 K. The desorption of counter-product CO_2 is normally directed and shows anisotropy in both reactions.

1. Introduction

N_2 emission in the catalyzed NO reduction on the best metal catalysts (palladium and rhodium) takes place through either $N_2O(a)$ intermediate decomposing to $N_2(g) + O(a)$ or nitrogen association as $N(a) + N(a) \rightarrow N_2(g)$ [1–4]. On iridium surfaces, however, the lack of contribution of the $N_2O(a)$ pathway to N_2 has been widely accepted since iridium-based deNOx catalysts show high selectivity toward N_2 [5–10] and negligibly small amounts of N_2O are found in the thermal desorption of NO-covered iridium surfaces [11–15]. The present paper delivers the first angle-resolved desorption (ARD) analysis of steady-state $N_2O + CO$ and $NO + CO$ reactions on Ir(110), confirming considerable contributions of the N_2O pathway to N_2 at low temperatures.

NO reduction on late-transition metals has received much attention because of the main process over after-treatment catalysts for diesel and lean-burn gasoline engines [16–18]. The selectivity to the undesirable byproduct N_2O has been frequently examined in the presence of CO because this harmful species is more or less found in deNOx treatments of metal catalysts [16–21]. Furthermore, this byproduct has remarkable effects toward greenhouse activity [22] and stratospheric ozone depletion [23]. However, mechanistic studies regarding the branching of N_2O/N_2 formation are rare on iridium-based catalysts probably because neither highest deNOx performance [11–15] nor experimental method can provide ample evidence of intermediate $N_2O(a)$ to N_2 in the course of catalyzed NO reduction, except for our ARD analysis [1–3]. This difficulty is due to immeasurable amounts of intermediate $N_2O(a)$. The surface residence time of this intermediate is too short to be detected by surface vibrational spectroscopy in the course of catalyzed NO reduction above 450 K because of the small adsorption heat and fast decomposition [2,14,24–26]. Only ARD analysis can evaluate the contribution of intermediate $N_2O(a)$ decomposition to N_2 through the peculiar spatial distribution of the product N_2 [1,3].

$N_2O(a)$ on Ir(111) is desorbed at 100–110 K without decomposition [27]. In contrast, on Ir(110) its desorption and decomposition are affected even below 100 K by preadsorbed oxygen [28]. The AR-temperature-programmed desorption (TPD) of N_2O-covered Ir(110) was reported, showing the off-normal N_2 emission on the plane in the [001] direction at 90–180 K without three-dimensional (3D) analysis [29]. The present paper is first to report 3D distributions on Ir(110) at fixed temperatures. First, the $N_2O + CO$ reaction is examined as a reference. The N_2 emission is fairly concentrated

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http://dx.doi.org/10.1016/j.apsusc.2017.03.304
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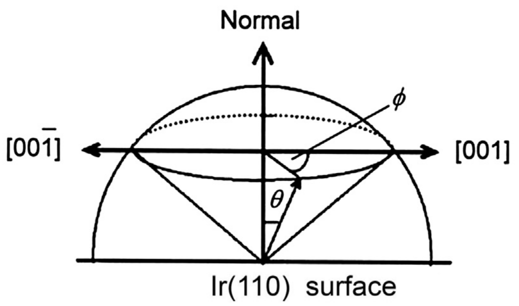

Fig. 1. Definition of the desorption (θ) and azimuth (ϕ) angles.

on the normally directed plane in the [001] direction and split into two-directional ways over a wide temperature range up to above 850 K. Each component is collimated at ±(46–58)° off-normal. On the other hand, in the NO + CO reaction, N_2 desorption consists of a normally directed component and two-directional components. The former is predominant except for low temperatures and shows remarkable anisotropy, similar to that of $N(a) + N(a) \rightarrow N_2(g)$ on Pd(110) [4]. The other components are collimated at around ±54° off normal on the plane in the [001] direction, showing the decomposition of intermediate $N_2O(a)$. These off-normal components largely share the total N_2 emission below approximately 550 K. At higher temperatures, these become minor and mostly invisible above 650 K. The desorption of counter-product CO_2 is normally directed and shows some anisotropy.

2. Experimental

The apparatus consists of three ultra-high vacuum chambers connected through small slits [1,30]. Briefly, these chambers are separately evacuated with high pumping rates. The reaction chamber has low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy optics, an Ar ion gun, and a mass spectrometer for angle-integrated (AI) signals. The analyzer has another mass spectrometer for angle-resolved (AR) measurements. Steady-state reaction conditions are established in the reaction chamber and not disturbed by ARD measurements. The N_2 or CO_2 flux is measured with the AR mass spectrometer without sensitivity corrections due to different velocities as a function of the desorption angle (θ; polar angle) because no serious shift is caused when constructing the angular distribution [31]. The desorption angle is scanned in the normally directed plane along the azimuth between the [001] and the $[1\bar{1}0]$ directions. The azimuth angle (ϕ) is defined as a deviation from the [001] direction (see Fig. 1).

An iridium crystal (from Surface Preparation Laboratory, Netherlands) in a disk-shaped slice is mounted on top of a manipulator. The LEED pattern shows a streaky (1 × 2) form after repeated cleaning procedures by Ar^+ ion bombardments, heating in oxygen, and flashing to 1100 K [32–35]. The resultant surface is still covered by an approximately 0.5 monolayer of oxygen because this annealing temperature is far below 1600 K for the complete desorption [33,36]. Then, the surface is further treated into either a (1 × 1) or a (1 × 2)-rich form before being measured; i.e., it is heated in 1.3×10^{-5} Pa of O_2 for 30 min at 850 K and cooled to room temperature in O_2. At this stage, the surface shows the Ir(110)(1 × 1)-c(2 × 2)-O lattice [33–35,37]. It is heated to 580 K after sufficient CO exposure for saturation to remove surface oxygen. After this removal of oxygen, the surface shows a (1 × 1) LEED pattern without superstructure spots. This surface is denoted as (1 × 1). The surface is further kept at 960 K for 30 min in a vacuum for the work designated as (1 × 2)-rich, in which the surface is partly converted into the reconstructed form as judged from streaky half-order spots in the [001] direction. The resultant surface likely consists of small domains with mostly (1 × 1), (1 × 2), and (1 × 3) structures [32,34,35].

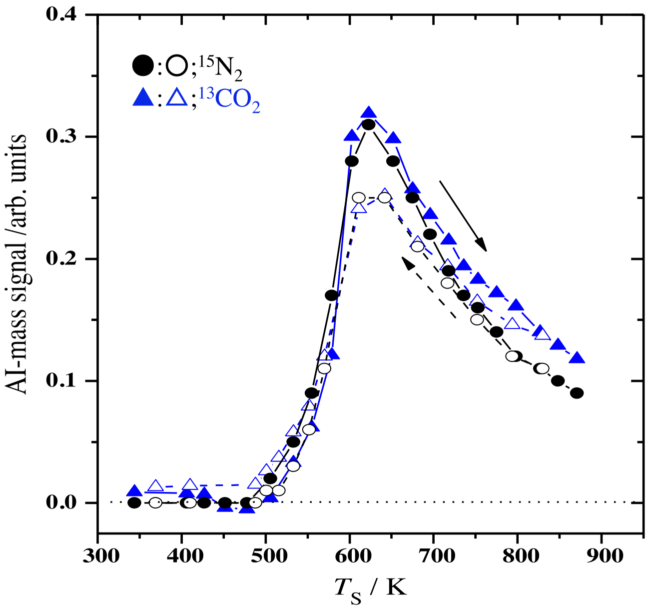

Fig. 2. Surface temperature (T_S) dependence of the AI-signals of products $^{15}N_2$ and $^{13}CO_2$ in a steady-state $^{15}N_2O + ^{13}CO$ reaction at $P_{N2O} = 1.8 \times 10^{-5}$ Pa and $P_{CO} = 1.2 \times 10^{-5}$ Pa. The temperature is increased stepwise to 880 K and then decreased in a similar way. The mass signals observed in the direction of increasing surface temperature are indicated by filled symbols and those in the downward direction by open symbols. ●, ○: $^{15}N_2$ and ▲, △: $^{13}CO_2$. The surface was pretreated into the (1 × 2)-rich form in advance.

The reaction was performed in a flow mode by dosing $^{15}N_2O$ or ^{15}NO and ^{13}CO at constant partial pressures. Without further purification, commercial $^{15}N_2O$ (isotope purity: 99%) or ^{15}NO (99%) and ^{13}CO (purity: 99%) are backfilled through separate variable leak valves. Hereafter, isotopes ^{15}N and ^{13}C are simply designated as N and C in the text. The AI or AR signals from the products are determined as the signal difference between a desired surface temperature and room temperature. Pressure readings with a Bayard-Alpert ionization gauge were corrected by the relative sensitivities for CO, CO_2, N_2O and NO toward that of N_2, 1.03, 1.4, 1.6, and 1.17, respectively [38,39].

3. Results

3.1. Temperature dependence of N_2O reduction

The steady-state $N_2O + CO$ reaction noticeably proceeds above T_S (surface temperature) = 500 K and shows a broad peak of N_2 or CO_2 formation at around 620 K, following slow decreases at higher temperatures (Fig. 2). The surface is pretreated into the (1 × 2)-rich form before introducing reactants. The surface temperature is increased stepwise to 880 K and then decreased in a similar way. The ratio of the AI-CO_2 signal to that of AI-N_2 is close to unity over a wide temperature range, consistent with the reaction of $N_2O + CO \rightarrow N_2 + CO_2$. The AI-signal of N_2 involves significant ambiguity of approximately ±8% at around the peak temperature because of the relatively large background that represents about 85% of the total observed signal.

The quality of the AI-CO_2 signal is much better; i.e., the maximum net value reaches about 90% of the total signal. The AI signals of both N_2 and CO_2 are somewhat reduced with decreasing surface temperature. Such decreases in activity are more or less observed during a set of measurements. It takes approximately 2 h to complete a set of angle- or temperature-dependence measurements.