Available online at www.sciencedirect.com

SCIENCE DIRECT®

Surface Science 586 (2005) 1–14

SURFACE SCIENCE

www.elsevier.com/locate/susc

Model car-exhaust catalyst studied by TPD and TP-RAIRS: Surface reactions of NO on clean and O-covered Ir{1 0 0}

Sabyasachi Khatua, Georg Held, David A. King *

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Received 26 January 2005; accepted for publication 23 April 2005

Abstract

The adsorption of NO on Ir{1 0 0} has been studied as a function of NO coverage and temperature using temperature programmed reflection absorption infrared spectroscopy (TP-RAIRS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). After saturating the clean (1 × 5)-reconstructed surface with NO at 95 K, two N_2 desorption peaks are observed upon heating. The first N_2 peak at 346 K results from the decomposition of bridge-bonded NO, and the second at 475 K from the decomposition of atop-bonded NO molecules. NO decomposition is proposed to be the rate limiting step for both N_2 desorption states. For high NO coverages on the (1 × 5) surface, the narrow width of the first N_2 desorption peak is indicative of an autocatalytic process for which the parallel formation of N_2O appears to be the crucial step. When NO is adsorbed on the metastable unreconstructed (1 × 1) phase of clean Ir{1 0 0} N_2 desorption starts at lower temperatures, indicating that this surface modification is more reactive. When a high coverage of oxygen, near 0.5 ML, is pre-adsorbed on the surface, the decomposition of NO is inhibited and mainly desorption of intact NO is observed.

Keywords: Iridium; Single crystal surfaces; Nitrogen oxide; Oxygen; Nitrogen; Surface chemical reaction; Thermal desorption spectroscopy; Infrared absorption spectroscopy

---

1. Introduction

The catalytic conversion of NO_x species to N_2 and O_2 in car exhaust gases has recently received growing interest in connection with the challenge posed by lean-burn engines [1,2]. These engines operate with a higher oxygen content in the

---

[*] Corresponding author. Tel.: +44 1223 336449; fax: +44 1223 762829.

E-mail address: dak10@cam.ac.uk (D.A. King).

doi:10.1016/j.susc.2005.04.045

combustion mixture than conventional engines. As a consequence, there is excess oxygen in the exhaust gas which makes the reduction of NO_x species thermodynamically less favourable and tends to poison most platinum-metal catalysts. Iridium-based catalysts were found to be among those able to selectively perform this reaction under oxygen-rich conditions when small quantities of hydrocarbons are present in the reaction gas mixture [3–6]. Many fundamental questions concerning this process are, however, still unsolved, for instance the origin of the catalyst poisoning by excess oxygen or the exact nature of the elementary surface reaction steps. These questions were addressed recently in a detailed theoretical study by Liu et al. [6] for NO oxidation/reduction on the Ir{1 1 1} and {2 1 1} surfaces, identifying oxidation of the Ir substrate and a lower activation barrier towards NO_2 formation as the key limiting factors for NO reduction under oxygen-rich conditions. There is, however, a need for further experimental evidence to support these findings.

The adsorption of NO on metal surfaces has been the subject of a large number of surface science experiments in recent years because of its profound importance in many fields of science and technology [7]. Due to its relatively low dissociation energy of 630 kJ/mol, NO is more susceptible to dissociation than CO, which has a dissociation energy of 1076 kJ/mol [8]. Both molecular and dissociative adsorptions of NO are observed on many transition metal single crystals. This topic has been reviewed recently by Brown and King [7]. As a consequence of the dissociative adsorption, a variety of surface species such as NO_2, N_2O, $(NO)_2$ and N and O adatoms have been found on transition metal surfaces under different reaction conditions. Apart from the competition between molecular and dissociative adsorption, the situation becomes even more complex when the surface topology changes during adsorption, as for Ir{1 0 0}. The most stable structure of the clean surface is the (1×5) quasi-hexagonal reconstruction, which can be lifted by the adsorption of CO or NO at relatively low temperatures [9,10]. An earlier study of NO adsorption on Ir{1 0 0} by Gardner et al. using high resolution electron energy loss spectroscopy (HREELS), reflexion absorption IR spectroscopy (RAIRS), temperature programmed desorption (TPD), and low energy electron diffraction (LEED), has shown that there is a close correlation between the substrate structure and the decomposition of NO [11]. The present study concentrates on the reaction mechanisms and kinetics of the different decomposition steps occurring on this surface. A detailed discussion of adsorption energies and the assignment of bands in the RAIR spectra on the basis of density functional theory (DFT) calculations will be published separately [12].

2. Experimental procedures

The experiments were performed in an UHV chamber at a base pressure of about 2×10^{-10} mbar. Details of sample preparation and experimental conditions are described elsewhere [9,10,12–15]. In brief, the sample was cleaned by Ar ion sputtering at 900 K, annealing at 1400 K, oxygen treatment at 1160 K and finally flashing to 1400 K. This procedure produces a sharp (1×5) LEED pattern with low background intensity, indicating a well ordered surface. In order to prepare the metastable (1×1) phase, the surface was first exposed to 20 L of oxygen at 475 K and then annealed to 750 K, which lifts the reconstruction completely. Oxygen was then titrated off by dosing 30 L of CO at room temperature. The remaining CO was removed by heating the sample again to 750 K, which produces a sharp (1×1) LEED pattern.

Temperature programmed reflection absorption infrared spectroscopy (TP-RAIRS) [16] was used as the principal technique of investigation supplemented by LEED and TPD. All TP-RAIR spectra were recorded continuously through a computer programme at $4\,cm^{-1}$ resolution and presented as a ratio against clean surface spectra, also obtained during temperature ramping. In all TPD and TP-RAIRS experiments, the temperature was ramped linearly at $2\,K\,s^{-1}$; the spectra are presented as raw data unless otherwise stated. TPD and TP-RAIR spectra were recorded simultaneously on two separate computers. Each RAIR spectrum takes 15 s to record plus 1 s to reinitialise