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ScienceDirect

Surface Science 601 (2007) 1285–1295

SURFACE SCIENCE

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Phase mixing and phase separation accompanying the catalytic oxidation of CO on Ir{1 0 0}

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Received 25 August 2006; accepted for publication 18 December 2006
Available online 29 December 2006

Abstract

The co-adsorption of CO and O on the unreconstructed (1 × 1) phase of Ir{1 0 0} was examined by low energy electron diffraction (LEED) and temperature programmed desorption (TPD). When CO is adsorbed at 188 K onto the Ir{1 0 0} surface precovered with 0.5 ML O, a mixed c(4 × 2)-(2O + CO) overlayer is formed. All CO is oxidised upon heating and desorbs as CO_2 in three distinct stages at 230 K, 330 K and 430 K in a 2:1:2 ratio. The excess oxygen left on the surface after all CO has reacted forms an overlayer with a LEED pattern with p(2 × 10) periodicity. This overlayer consists of stripes with a local p(2 × 1)-O arrangement of oxygen atoms separated by stripes of uncovered Ir. When CO is adsorbed at 300 K onto the surface precovered with 0.5 ML O an apparent (2 × 2) LEED pattern is observed. LEED IV analysis reveals that this pattern is a superposition of diffraction patterns from islands of c(2 × 2)-CO and p(2 × 1)-O structures on the surface. Heating this co-adsorbed overlayer leads to the desorption of CO_2 in two stages at 330 K and 430 K; the excess CO (0.1 ML) desorbs at 590 K.

LEED IV structural analysis of the mixed c(4 × 2) O and CO overlayer shows that both the CO molecules and the O atoms occupy bridge sites. The O atoms show significant lateral displacements of 0.14 Å away from the CO molecules; the C–O bond is slightly expanded with respect to the gas phase (1.19 Å); the modifications of the Ir substrate with respect to the bulk-terminated surface are very small.

Keywords: Low energy electron diffraction (LEED); Thermal desorption spectroscopy; Chemisorption; Catalysis; Iridium; Carbon monoxide; Oxygen

1. Introduction

Iridium, together with platinum, palladium and rhodium, falls in the group of transition metals that exhibit high efficiency towards the catalytic oxidation of CO to CO_2 [1,2]. This reaction is important in several respects in the context of automotive exhaust catalysis: the conversion of CO from the incomplete combustion of fuel, the removal of atomic O from the decomposition of NO, and, under learn-burn conditions, the removal of the excess oxygen from the catalyst surface. The latter is especially important as O was found to inhibit NO reduction on Ir{1 0 0} [4,3]. In this paper, we continue to investigate the properties of Ir{1 0 0}, this time focusing on the oxidation reaction of CO to CO_2. Heterogeneously catalysed reactions on metal surfaces are assumed to proceed via the Langmuir–Hishelwood mechanism [1,2]. Therefore, co-adsorption structures and the subsequent reaction of CO and O on single metal surfaces have been extensively studied in order to give an insight into the kinetics and dynamics of CO oxidation [5,7,6,8]. Generally the co-adsorption of O and CO on the surface destabilises both species compared to pure chemisorbed layers. The reason

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0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.12.067

being that both O and CO compete for the same electron charge density available from the substrate surface [7].

The oxidation of CO was found to be structure sensitive on fcc{1 0 0} surfaces [6]. In particular, the structure of pre-adsorbed O was found to greatly affect the reaction rate: the higher the O coverage, the easier the reaction proceeded, i.e., CO_2 desorption was observed at lower temperatures. On both Rh{1 0 0} and Pd{1 0 0}, chemisorbed oxygen forms p(2 × 2) overlayers at 0.25 ML with O adsorbed on the fourfold hollow sites [9–11]. CO oxidation was found to be similar on these two surfaces, proceeding through three different channels that have been associated with the reaction of CO within oxygen islands (at low temperatures) and CO at the boundaries of oxygen island (at high temperatures) [6,8]. On Pt{1 0 0}, the CO oxidation reaction was found to be oscillatory at higher pressures [12]. In the non-oscillatory low-pressure regime, temperature programmed desorption (TPD) and low energy electron diffraction (LEED) indicate that CO forms c(2 × 2) islands surrounded by a matrix of O atoms [13]. No ordered mixed O + CO structures or compressed structures due to the subsequent adsorption of the second species were observed. Similarly, no ordered mixed O + CO co-adsorption overlayers were reported on Rh{1 0 0} [6], Pd{1 0 0} [8] nor on any other fcc{1 0 0} surface, even though for Rh{1 0 0}, the authors postulated that two of the CO oxidation channels observed were from the reaction of CO within p(2 × 2)-O and c(2 × 2)-O islands.

Structural studies of O and CO co-adsorption systems have mostly been carried out on hexagonal close-packed surfaces such as fcc{1 1 1} and hcp{0 0 0 1}, where adsorption of CO onto the p(2 × 2)-O surface typically results in the formation of mixed O + CO phases [7]. An exception being Pd{1 1 1}, where CO and O form phase separated islands of high density rather than establishing a mixed O + CO overlayer [14,15]. At a coverage of 0.5 ML O normally forms p(2 × 1) overlayers on these surfaces occupying threefold hollow sites. This densely packed overlayer structure cannot accommodate substantial amounts of CO on steric grounds, but on Ru{0001} [16] and Rh{1 1 1} [17,18], adsorption of CO onto the p(2 × 1)-O covered surfaces results in the displacement of half the O atoms to other threefold hollow sites (fcc sites on Ru, hcp sites on Rh), this way allowing CO to chemisorb on atop sites. Depending on the substrate and the oxygen coverage, the co-adsorption of O and CO on these hexagonal surfaces can, thus, lead to a variety of different effects (see the review by Over [7] for more detail).

In contrast to other fcc{1 0 0} surfaces, on Ir{1 0 0} oxygen adsorbs on bridge sites instead of fourfold hollow sites. The p(2 × 1) overlayer of pure oxygen was analysed by a combination of LEED IV and density functional theory (DFT) ab initio model calculations [19]. The O atoms were found to adsorb on bridge sites such that no two O atoms share a nearest neighbour Ir atom. This unusual adsorption site for O was found to be stabilised by row pairing of the top most Ir atoms. The study also indicated that even at O coverages below saturation ($\theta_O < 0.5$ ML), O atoms would still form small p(2 × 1) islands instead of forming a p(2 × 2) superstructure as observed on other fcc{1 0 0} surfaces [20]. It is interesting from this perspective, to find out how this difference in adsorption sites and configuration of O atoms on the surface affects the CO oxidation reaction.

A recent structural analysis of the pure Ir{1 0 0}-c(2 × 2)-CO overlayer using LEED and DFT found that the CO molecules occupy atop sites [21] in agreement with reflection absorption infrared spectroscopy (RAIRS) [22] and high-resolution electron energy loss spectroscopy (HREELS) [23] studies. Both LEED and DFT agreed on the key structural parameter: a significant buckling of the first Ir layer, a short Ir–C bondlength and a slight lengthening of the CO bond. Further DFT analysis of a hypothetical Ir{1 0 0}-p(2 × 2)-CO phase, which has never been seen experimentally, found this structure to display on identical local bonding geometry to the c(2 × 2)-CO phase but a slightly lower binding energy, indicative of an attractive nearest neighbour interaction. On Ir{1 1 1} [24] and Ir{1 1 0} [25] CO was found to block oxygen adsorption, while on the O-precovered surfaces CO adsorption is possible. The effect of pre-adsorbed CO on Ir{1 0 0} was not investigated in the present study. For all O + CO co-adsorption experiments described here the saturated p(2 × 1)-O overlayer was used as starting template. The present article concentrates on the characterisation of CO + O co-adsorption and reaction by LEED IV and TPD.

2. Experimental

The ultra-high vacuum (UHV) chamber, described in detail elsewhere [26], is equipped with a four-grid Omicron reverse-view LEED optics, and attains a base pressure of 5×10^{-11} mbar. The Ir{1 0 0} sample was cleaned by cycles of argon ion bombardment at 300 K, annealing to 1400 K, exposure to 5 L O_2 ($1 \text{ L} = 1 \times 10^{-6}$ Torr s) at 1060 K and flash annealing to 1400 K. Reproducible oxygen temperature programmed desorption (TPD) [27] and a sharp (1 × 5) diffraction pattern with low background intensity provided evidence for cleanliness. The (1 × 1) phase (unreconstructed Ir{1 0 0} surface) was produced by background exposure to 20 L oxygen at 750 K, followed by 30 L CO at room temperature then flashing the crystal to 750 K. In all TPD experiments, the temperature is ramped linearly at 3 K s^{-1}.

The O and CO co-adsorption system was prepared by first exposing the (1 × 1) phase to 10 L O_2 at 700 K, this produces a p(2 × 1) diffraction pattern with low background intensity and sharp spots [19]; thereafter, the sample was cooled to room temperature or 200 K to adsorb CO. The initial coverage of O atoms on the surface corresponds to saturation coverage, 0.5 ML.

LEED measurements were carried out at a sample temperature of 200 K to reduce thermal vibrations. The diffraction patterns were recorded at normal incidence using