Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 583 (2005) 36–45
SURFACE SCIENCE
www.elsevier.com/locate/susc

Analysis of the kinetics of N_2O–CO reaction on Pd(1 1 0)

Vladimir P. Zhdanov [a,b,*], Yunsheng Ma [a], Tatsuo Matsushima [a]

[a] *Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan*
[b] *Boreskov Institute of Catalysis, Russian Academy of Sciences, Novosibirsk 630090, Russia*

Received 17 December 2004; accepted for publication 14 March 2005

Abstract

Experimental studies indicate that the N_2O–CO reaction occurring on Pd(1 1 0) under UHV conditions exhibits a first-order kinetic phase transition in the steady-state case and also transient kinetics strongly dependent on the initial state of the system. We construct a mean-field kinetic model describing these phenomena. With a minimal number of the fitting parameters, the model reasonably reproduces the special features of the reaction kinetics.

Keywords: Computer simulations; Reaction kinetics; Kinetic phase transitions; Low index single crystal surfaces; Pd(1 1 0); N_2O; CO; N_2; Oxygen

1. Introduction

During or after adsorption of N_2O on Pt-group metals, one can observe N_2O decomposition accompanied by formation of adsorbed oxygen and N_2 desorption. The decomposition process is rather rapid. Under temperature-programmed conditions, it typically occurs below 200 K [1–5]. To run N_2O decomposition under steady-state conditions, one can remove adsorbed oxygen by CO. CO oxidation on Pt-group metals is well known to be also rapid. In particular, the steady-state kinetics of the CO–O_2 reaction is often controlled by reactant adsorption and/or blocking of adsorption sites by CO and accordingly exhibits a first-order kinetic phase transition (see, e.g., the review by Razon and Schmitz [6] and more recent experimental data for Pt(1 1 1) [7], Pt(1 1 0) [8], Ir(1 1 1) [9], and supported Pd [10]; for general theory of kinetic phase transitions, see Refs. [11,12]). In analogy with CO oxidation, this phenomenon is possible in the N_2O–CO reaction as well. In particular, it was observed by Sadnankar et al. [14] on alumina-supported Pt at atmospheric pressure. Recent experimental studies performed in our group [15] indicate that the N_2O–CO reaction exhibits a

---

[*] Corresponding author. Tel.: +7 3832 329513; fax: +7 3832 344687.
E-mail address: zhdanov@catalysis.nsk.su (V.P. Zhdanov).

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.03.020

first-order kinetic phase transition also on Pd(1 1 0) under UHV conditions in the steady-state case. In addition, the transient kinetics are found to be strongly dependent on the initial state of the system. In this paper, we present a mean-field kinetic model of these phenomena. The results obtained are of interest from the point of view of theory of the kinetics of rapid catalytic reactions and also from the view-point of applied environmental chemistry [13], because N_2O is one of the harmful ingredients of motor vehicle gas.

The paper is organized as follows. First, we outline the key experimentally observed features of the reaction kinetics under consideration (Section 2). Our kinetic model is described in Section 3. The model parameters are validated in Section 4. The results of the calculations are shown and discussed in Section 5. Section 6 contains a brief summary.

2. Experimental data

The kinetics of the N_2O–CO reaction was studied on Pd(1 1 0) under UHV conditions by using the technique [1–5] allowing measurement of the angular-resolved distribution of desorbing species. The results focused on the temperature dependence of the reaction rate have already been published in a brief report [16]. More complete data including the pressure dependence of the reaction rate will be presented in detail elsewhere [15]. Here, we show typical steady-state and transient kinetics which are essential for our analysis and discussions below.

The specifics of the reaction under consideration is that the yield is small and accordingly we can hardly get an accurate angular-integrated signal. Fortunately, the angular-resolved signal is enhanced at around the collimation angle (43° off normal into the [0 0 1] direction) because of the sharp distribution, and can be used to follow the reaction. In particular, Fig. 1 exhibits the N_2-desorption rate measured under steady-state conditions at fixed N_2O pressure as a function of CO pressure at surface temperatures of 450, 470, 500 and 520 K. At $T_s \geqslant 500$ K, with increasing CO pressure, the rate of N_2 desorption first monotonously increases (in this region, the reaction rate is proportional to CO pressure), then reaches a maximum, and afterwards monotonously decreases. At lower temperatures, the N_2-desorption rate exhibits a stepwise behaviour classified as a first-order kinetic phase transitions. Such kinetic phase transitions are often associated with a hysteresis if pressure is changed back and forth (see e.g. experiments [7,9,10] and theory [11,12]). The width of a hysteresis may however be narrow or it can even be reduced to a single line corresponding to the equistability criterion [12]. The latter seems to happen in the reaction under consideration, because a hysteresis has not been observed in this case.

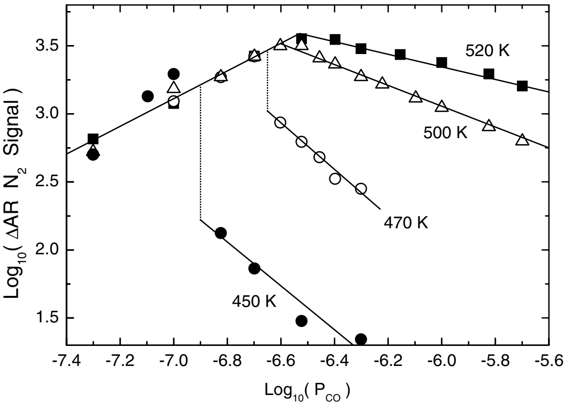

Fig. 1. N_2-desorption signal (arb. un.) as a function of CO pressure, P_{CO} (Torr), during N_2O–CO reaction on Pd(1 1 0) under steady-state conditions for $P_{N_2O} = 3.3 \times 10^{-6}$ Torr and surface temperatures of 450, 470, 500 and 520 K. The N_2-desorption rate was measured at 43° off normal into the [0 0 1] direction (at this angle, the rate is maximum). ΔAR means "angular resolved" (Δ indicates that the background N_2 signal has been subtracted).

Fig. 2 shows the transient kinetics in the situation when first the reaction is run at steady state and then, at $t = 0$, the CO pressure is switched off. If under steady-state conditions the CO pressure is lower than that corresponding to the reaction-rate maximum (Fig. 2(a)), the N_2- and CO_2-desorption rates drop at $t > 0$ relatively slowly and almost instantaneously, respectively. If initially the CO pressure is higher than that associated with the reaction-rate maximum (Fig. 2(b)), the transient kinetics observed at $t > 0$ are somewhat more complex. Specifically, the N_2- and CO_2-desorption rates first increase and than after