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Simulation of thermal desorption spectra of N_2 observed during N_2O decomposition on Rh(1 1 0)

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Abstract

Under temperature-programmed conditions, N_2O decomposition occurs on Rh(1 1 0) between 60 and 190 K and results in N_2 desorption. Experimental studies of the angular distribution of the flux of the reaction products indicate that N_2 molecules leave the surface both during and after N_2O dissociation events. The N_2 TPD spectra observed are complex. In particular, there are four peaks, registered between 60 and 150 K and related to N_2 desorption accompanying N_2O-dissociation acts, and a peak recorded at 160 K and attributed to desorption of adsorbed N_2 molecules. We present Monte Carlo simulations of these spectra. Our model takes into account both channels of N_2 desorption and also N_2O–O lateral interactions stabilizing N_2O adsorption. With these relatively simple ingredients, the model reproduces the main features of the measured TPD kinetics, including the positions and intensities of all the peaks.

Keywords: Computer simulations; Thermal desorption; Lateral interactions; Low index single crystal surfaces; Rh(1 1 0); N_2O; N_2; Oxygen

1. Introduction

Temperature-programmed desorption (TPD) spectroscopy is widely used to study kinetic processes occurring in adsorbed overlayers [1,2]. The advantage of this technique is that it makes it possible to clarify various factors complicating the desorption and/or reaction kinetics. In particular, the shape of the TPD spectra is fairly sensitive to surface heterogeneity, adsorbate–adsorbate lateral interactions, spontaneous and adsorbate-induced changes in a surface, and/or limited mobility of adsorbed species. Due to the abundance of factors which influence or may influence the desorption kinetics, interpretation of the TPD spectra is often

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far from straightforward especially in the situations when complementary data on the adsorbed species are lacking.

The available simulations of the TPD kinetics are focused primarily on the cases when desorption is a single rate process in the adsorbed overlayer. For example, we may mention recent studies of O_2 desorption from Pt(1 1 1) [3] and Ru(0 0 0 1) [4], N_2 desorption from Cu(1 1 0) [5], CO desorption from Rh(0 0 1) [6] (many references to earlier works can be found in [1,7]). There are also a few treatments of the TPD spectra observed in chemically reactive systems (see, e.g., recent simulations of various aspects of NO decomposition on Rh(1 1 1), Rh(1 0 0) and Pt(1 0 0) [8–10], CO oxidation on Pt(1 1 1) [11], and references in [7]).

In this paper, we present Monte Carlo (MC) simulations of the N_2 TPD spectra observed during N_2O decomposition on Rh(1 1 0) [12–14]. Interpretation of these spectra is of considerable intrinsic interest from the point of view of general theory of thermal desorption and also is important from the view-point of applied chemistry. In particular, the system under consideration provides an instructive example of thermal desorption occurring under reactive conditions. The corresponding TPD spectra are complex (there are five TPD peaks) and before our project it was far from obvious that one could interpret all the peaks in detail, because the results might be complicated by a multitude of various adsorbate–adsorbate interactions and the availability of different sites for adsorption of different species. Scrutinizing the system, we argue below that its behaviour is crucially dependent first of all on N_2O–O lateral interactions stabilizing N_2O adsorption. Following this idea, we have constructed a relatively simple model reproducing the main features of the measured TPD kinetics.

Concerning applications, it is appropriate to note that the understanding of the behaviour of N_2O on Rh(1 1 0) is of interest from the point of view of applied environmental chemistry, because N_2O is one of the harmful ingredients of motor vehicle gas.

The paper is organized as follows. First, we briefly recall the specifics of the N_2 TPD spectra measured after N_2O adsorption on Rh(1 1 0) (Section 2). Empirical kinetic equations describing some of the features of these spectra are outlined in Section 3. A lattice-gas model and general equations forming a basis of our MC simulations are presented in Section 4. The algorithm of the simulations is formulated in Section 5. The results of the simulations are shown and discussed in Section 6. Section 7 contains a brief summary.

2. Experimental TPD data

Temperature-programmed decomposition of N_2O on the (1×1) Rh(1 1 0) surface has been studied [12–14] at 50–200 K by analysing the angular-resolved and -integrated distributions of desorbing species (for a general review of angular-resolved measurements, see Ref. [15]). The main attention was paid to the behaviour of the first adsorbed N_2O overlayer. At these conditions, below saturation, the dominant desorbing product was found to be N_2. N_2O desorption,

$$(N_2O)_{ad} \rightarrow (N_2O)_{gas}, \tag{1}$$

was observed as well. At relatively low initial N_2O coverages, $\theta_{N_2O} \leqslant 0.5$ ($\theta_{N_2O} = 1$ corresponds to saturation), the integral intensity of the N_2O signal was however nearly negligible (lower that 10%) compared to that of the N_2 signal. With increasing initial N_2O coverage, the role of N_2O desorption increased so that near saturation the integral N_2O signal was about two times lower than the N_2 signal.

Scrutinizing the angular-resolved and -integrated N_2 TPD spectra [14] made it possible to distinguish five peaks, $\beta_1 - \beta_5$ (Fig. 1), located at temperatures between 60 and 180 K, or more specifically at ≃75 (β_5), 95 (β_4), 120 (β_3), 140 (β_2), and 160 K (β_1). The relative intensities of the peaks are strongly dependent on the initial N_2O coverage.

If the initial N_2O coverage is low (below 0.2), N_2 desorption occurs primarily at relatively high temperatures. In particular, the β_1 peak located at $T \simeq 160$ K completely dominates. In addition, one can observe the tiny β_4 and β_5 peaks (in the angular-resolved spectra, these two peaks are resolved better than in Fig. 1). The other peaks (β_3 and β_4) are nearly not visible.