Catalysis Letters 37 (1996) 163–165

Simulation of kinetics of nitrogen desorption from Rh(111)

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Received 6 September 1995; accepted 10 October 1995

Associative desorption of N atoms from the Rh(111) surface is simulated in the framework of the lattice–gas model. The Arrhenius parameters and nearest-neighbour lateral interaction employed to describe the measured thermal desorption spectra are as follows: $\nu = 10^{13}\ \mathrm{s}^{-1}$, $E_d = 40$ kcal/mol, and $\epsilon_1 = 1.7$ kcal/mol. The results obtained are used to clarify the role of nitrogen desorption in the NO + CO reaction on Rh(111) at $T = 400$–700 K and $P_{NO} \approx P_{CO} \approx 0.01$ atm.

Keywords: nitrogen; Rh(111); thermal desorption; Arrhenius parameters; lateral interactions; NO decomposition

Reduction of nitrogen oxide to nitrogen in current automotive catalytic converters occurs on Rh catalysts [1,2]. The elementary steps involved in this process seem to be well established. The understanding of the overall kinetics of NO reduction is, however, still lacking because quantitative data on the elementary steps are limited. Even for the Rh(111) surface, the available studies are not complete. The goal of our letter is to present the parameters for describing the kinetics of nitrogen desorption from Rh(111). This step is expected to play an important role in the process of NO reduction.

Recombination of nitrogen atoms on Rh is usually studied by employing the temperature programmed desorption (TPD) technique (see a recent paper by Borg et al. [3] and references therein). In such experiments, nitrogen is produced via NO adsorption and decomposition. If NO decomposition occurs thermally in the course of TPD, it is accompanied by NO desorption. In the framework of this scheme, one cannot obtain nitrogen coverages above 0.25 ML (1 ML corresponds to 1.6×10^{15} atoms/cm^2). In addition, the kinetics of N_2 desorption is affected by the presence of oxygen on the surface. To overcome these shortcomings, one needs to employ non-standard ways of nitrogen adsorption. Experiments of the latter type have recently been done by Bugyi and Solymosi [4] and Belton et al. [5]. To form the nitrogen overlayer, the former group used atomic nitrogen generated in the high-frequency discharge tube. The latter one employed electron beam dissociation of adsorbed NO (oxygen was cleaned off via the O + CO reaction). The agreement between the results reported in refs. [4,5] is reasonable.

The TPD spectra measured in refs. [4,5] do not correspond to simple second-order kinetics (see fig. 1) and their interpretation is not unique. Really, Bugyi and Solymosi [4] did not try to analyze the desorption kinetics in detail. Belton et al. [5] have formally simulated the TPD spectra by assuming that the observed desorption rate is composed of desorption rates from three discrete states (the relative population of different states was considered to depend on the initial coverage). Such an interpretation does not appear to be reasonable from the physical point of view.

In our simulations of the TPD spectra for the N/Rh(111) system, we assume that nitrogen adsorption occurs on one of the two different types of the threefold hollow sites (below which there is another substrate atom or vacancy, respectively). Thus, the adsorption sites are considered to form a triangular lattice. In the framework of the lattice–gas approximation, the

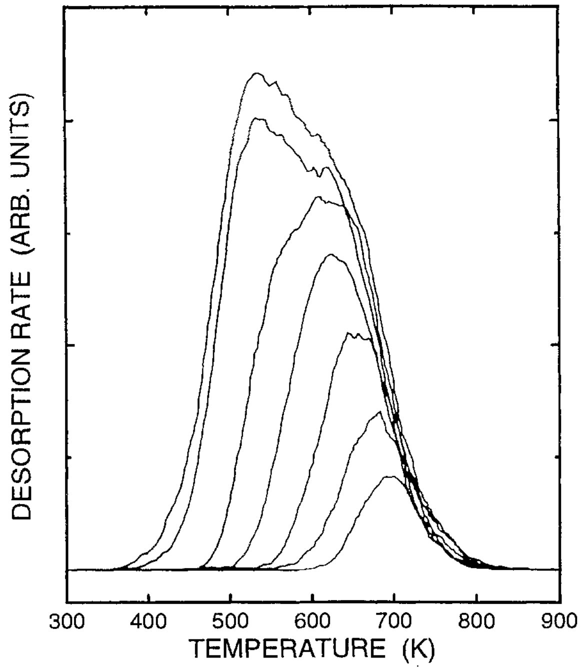

Fig. 1. N_2 TPD spectra for the N/Rh(111) system [5]. The initial nitrogen coverages are 0.04, 0.08, 0.13, 0.20, 0.31, 0.44, and 0.49 ML. The heating rate is 10 K/s.

kinetics of associative desorption is then described as [6] (we use $k_B = 1$)

$$d\theta/dt = -\nu \sum_i \mathcal{P}_{AA,i} \exp[-(E_d + \Delta\epsilon_i)/T], \qquad (1)$$

where ν and E_d are the Arrhenius parameters at low coverages, $\mathcal{P}_{AA,i}$ is the probability that two adjacent sites are occupied by pair AA (A refers to the adsorbate) and that this pair has the environment marked by index i, and $\Delta\epsilon_i = \epsilon_i^* - \epsilon_i$ is the difference of the lateral adsorbate–adsorbate interactions in the activated and ground states (ϵ_i^* and ϵ_i, respectively) for a given configuration. Usually the former interaction is minor compared to the latter one. Neglecting ϵ_i^*, we can represent eq. (1) in the following form convenient in applications (cf. eqs. (4.9) and (4.10) in ref. [7])

$$d\theta/dt = -\nu \exp[(2\mu - E_d)/T]\mathcal{P}_{OO}, \qquad (2)$$

where $\mathcal{P}_{OO}$ is the probability that two nearest-neighbour sites are empty, and μ is the chemical potential of adsorbed particles defined so that $\mu = T\ln(\theta)$ at low coverages. To calculate $\mathcal{P}_{OO}$ and μ, we take into account only the nearest-neighbour interaction, ϵ_1, and use the Bethe–Peierls approximation as described in detail in ref. [8] (note that table 1 in ref. [8] contains a misprint: Y^4Z^4 in line 12 should be replaced by Y^4Z^2).

To fit the measured TPD spectra, we have three free parameters, ν, E_d and ϵ_1. The preexponential factor for N_2 desorption can in principle be in the range from 10^{13} to 10^{19} s^{-1} [6,9]. Taking into account that N_2 adsorption is activated, we may expect that the activation complex for adsorption and accordingly for desorption has only vibrational degrees of freedom. In this case, the preexponential factor for desorption is expected to be low, and we may employ $\nu = 10^{13}$ s^{-1}. $E_d = 40$ kcal/mol has been obtained from the position of TPD peaks at low coverages. The last parameter, $\epsilon_1 = 1.7$ kcal/mol, has been used to reproduce a shape of the TPD spectra. The results of calculations with these parameters are in good agreement with the experimental data (cf. figs. 1 and 2).

Employing the parameters obtained, it is of interest to compare the N_2 desorption rate calculated at different coverages with that measured during NO decomposition on Rh(111) at steady-state conditions (fig. 3). At temperatures and pressures interesting from the practical point of view (e.g., at $T = 400$–700 K and $P_{NO} = P_{CO} = 8$ Torr), the measured rate (ref. [10]) is of the same order of magnitude as the calculated one if the coverage of nitrogen atoms is 0.45.

The data shown in fig. 3 can be used in order to evaluate the applicability of kinetic models proposed by Oh et al. [11] and Cho [12] to describe *quantitatively* the kinetics of NO decomposition on Rh(111) at $T = 400$–700 K and $P_{NO} \approx P_{CO} \approx 10$ Torr. The former calculations indicate that the surface is almost completely covered by nitrogen (e.g., $\theta_N = 0.96$ and 0.99 at $T = 500$ and 675 K, respectively). Our results (fig. 3) rule out such regimes of NO decomposition at the reaction conditions under consideration because the nitrogen coverage cannot be so high (otherwise, the N_2 desorption rate would be much larger than the measured one). The failure of the model [11] is connected with poor description of nitrogen desorption. The kinetic parameters employed in ref. [11] for describing this process correspond to relatively low coverages. At high coverages, the nitrogen desorption rate calculated with these parameters is too low (fig. 4).

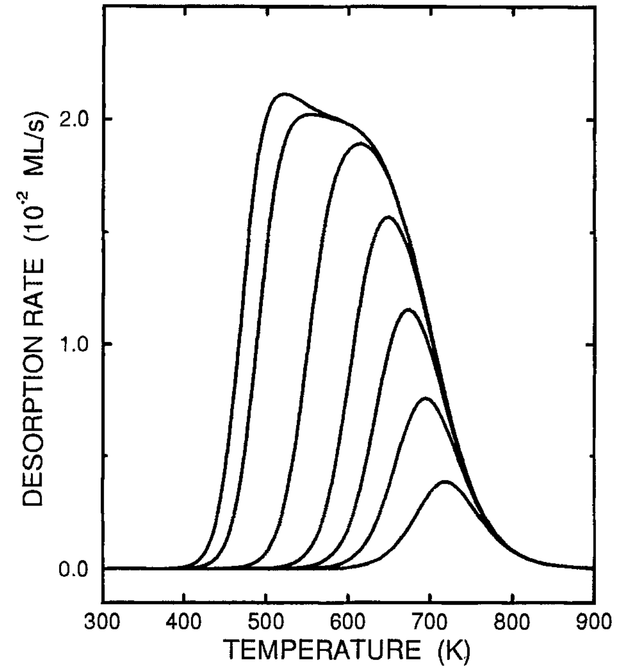

Fig. 2. N_2 TPD spectra calculated for the N/Rh(111) system in the framework of the lattice-gas model with the parameters presented in the text. The initial coverages and heating rate are the same as in fig. 1.

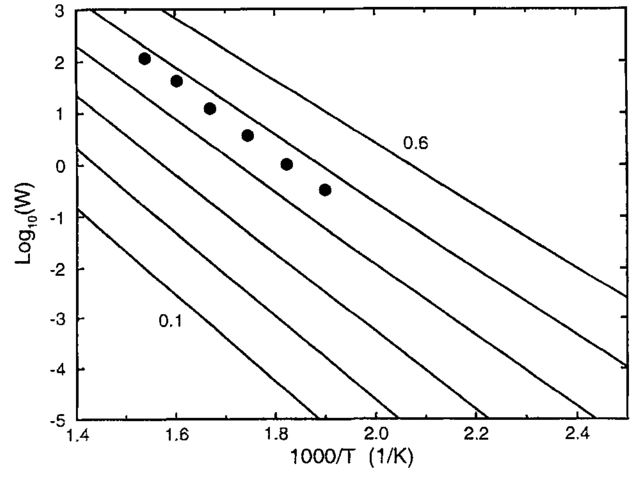

Fig. 3. N_2 desorption rate (in ML/s) as a function of temperature: solid lines, the model calculations for nitrogen coverages 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 ML; filled circles, the steady-state rate measured at $T = 400$–700 K and $P_{NO} = P_{CO} = 8$ Torr [10].

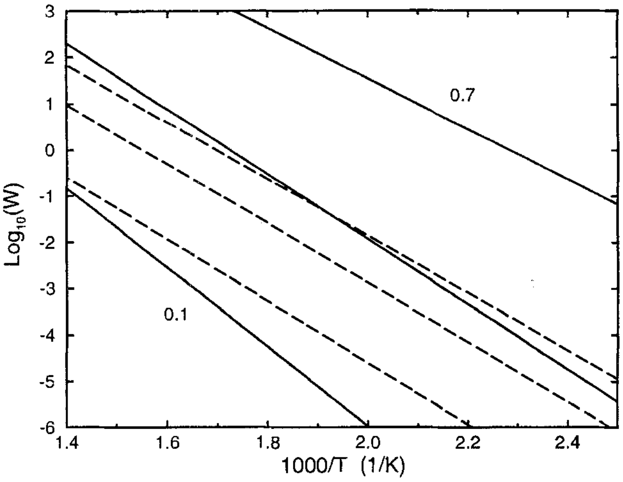

Fig. 4. N_2 desorption rate (in ML/s) as a function of temperature for nitrogen coverages 0.1, 0.4 and 0.7 ML: solid lines, our results; dashed lines, according to ref. [11] (in the latter case, the desorption rate is given by $W = 6 \times 10^{10} \exp[-(31 - 4\theta)/T]\theta^2$ ML/s).

The analysis presented by Cho [12] is explicitly based on the assumption that the N_2 desorption rate is negligible compared to the rate of N_2 formation via other steps (the dominant adsorbed species are expected to be CO and N with $\theta_{CO} = 0.38$ and $\theta_N = 0.34$ at 583 K). According to our calculations, this assumption does not appear to be correct because at these coverages the contribution of N_2 desorption to the total rate of the N_2 formation should be considerable (fig. 3).

In summary, we may conclude that the available kinetic models of NO decomposition on Rh(111) need revision and modifications.

Acknowledgement

The author thanks Professor B. Kasemo for useful discussions. The financial support of the Swedish Research Council for Engineering Sciences is also appreciated.

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