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# Coupled diffusion on the NO + $H_2$ reaction on Pt(1 0 0): chemical wave pattern formation by defects

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#### Abstract

The catalytic reduction of nitric oxide by  $H_2$  over the Pt(1 0 0) surface is studied as a function of partial pressures and diffusion of the reactants. Within the mathematical mean field model, originally proposed by Makeev and Nieuwenhuys [A.G. Makeev, B.E. Niewenhuys, Mathematical modeling of the NO + H<sub>2</sub>/Pt(1 0 0) reaction: "surface explosion", kinetic oscillations, and chaos, J. Chem. Phys. 108 (1998) 3740–3749], we incorporate the diffusion of adsorbed NO and H and the inhibitory site-blocking effect of adsorbed species N, O, NH, NH<sub>3</sub>. By considering the influence of non-uniformities or defects, resulting in blocking or enhancing adsorption sites on the catalyst surface, the results show anisotropic front propagation with ellipsoidal shape in agreement with experimental results. The influence of the inert sites on global coupling as they are increased continuously is also studied.

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## 1. Introduction

The catalytic reduction of NO is important because the contaminant effects of NO in air [1]. The major reactions of NO conversion to nitrogen in the automotive catalytic converter are (Taylor [1]; Egelhoff [2]):

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

 $2NO + 2CO \rightarrow N_2 + 2CO_2$ 

however this last step is too slow to provide a major path for NO reduction [2] and NO can also react to produce NH<sub>3</sub> :

$$NO + \frac{5}{2}H_2 \rightarrow NH_3 + H_2O$$

The selectivity of this reaction is governed by the temperature and the feed composition. These reactions were originally studied in polycrystalline systems but recently they have been studied on monocrystal of  $Pt(1\ 0\ 0)$  at low pressure because in this case the reactions can be considered isothermic. The extend of fundamental studies of NO reduction on single crystal surfaces has increased greatly in the last few years. The knowledge produced can provide a basis for proposing practical NO reduction catalysts.

Surface chemical reactions have a central role in the processes of heterogeneous catalysts, which are extensively used in chemical industry and environmental technology. In a catalytic process, the molecules of reactants are adsorbed from the gas phase onto a metal surface, diffuse on it, and react to form a product that goes back to the gas phase. Under certain circumstances these reactions can exhibit complex oscillations. Oscillations will not occur if the deviations from equilibrium are small and in this case the system can be described by linear relations. The oscillations occur due to feedback, either chemical (such as autocatalysis) or due to temperature (as in a non-isothermal reaction). Heterogeneous catalytic reactions satisfy the necessary requirements for the appearance of auto-oscillations because the continuous mass flow of reactants and heat exchange with the surroundings. The

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### Nomenclature

- $D_i$  diffusion coefficient of chemisorbed species without influence of other coadsorbed species  $(m^2 s^{-1});$
- $D_{ij}$  diffusion coefficient of specie *i* influence by coverage of specie *j*;
- $I_{\alpha}$  lateral interactions;
- $k_i$  reaction rates;
- *L* characteristic length of catalyst;

 $p_{\rm NO}$  NO partial pressure (bar);

- $p_{\rm H_2}$  H<sub>2</sub> partial pressure (bar);
- $R_d = D_v/D_x$  diffusivity relationship
- $R_i$  rates of elementary reaction steps;
- $S_i$  sticking probabilities (i = NO, H<sub>2</sub>);
- *T* catalyst temperature (K);
- t time (s)

#### Greek letters

$\epsilon_{ap}$	parameters of lateral interactions;
$\theta_{i}$	fractional coverage of chemisorbed species, (i
	= NO, H, N, O, NH, NH <sub>3</sub> );
$\theta_*$	fraction of free adsorption sites;
$\alpha, \beta, \delta$	effective phenomenological parameters for in-
	hibated adsorption

flux of energy and matter through the open system maintain it far from equilibrium and temporal and spatial organization become possible.

The occurrence of kinetic oscillations during the catalytic reduction of NO with either CO or H<sub>2</sub> [3–9], have been observed and found to occur for gas reactant pressures in the range  $10^{-6}$  to  $10^{-5}$  mbar in the range of temperatures from 430 to 500 K. These reactions show complex dynamical behavior as pattern formation and chaotic behavior. The review by Imbihl [10], Imbihl and Ertl [11] and Slinko and Jaeger [12] on a large number of catalytic reactions are very instructive.

To describe the occurrence of kinetic oscillations, Cobden et al. [6] have proposed a "vacancy" mechanism to explain the kinetic oscillations. In this "vacancy model" the oscillations are due to autocatalytic surface reaction, which increase the number of vacant sites for NO dissociation. Later, Makeev and Niewenhuys [13] have developed a mathematical model to prove that autocatalysis of NO decomposition by vacant sites is one of the main properties that keeps the system oscillating. A very important ingredient of this model is the coverage dependency of the activation energies for NO and CO desorption. So, in this model the system presents oscillatory behavior without involvement of the surface structural transformation,  $hex \rightarrow 1 \times 1$ , which takes place on Pt surfaces due to the presence of adsorbates and has been showed to be important for other chemical oscillations such as in NO + CO [3]. So, it can be considered that oscillations for the NO +  $H_2/Pt(1\ 0\ 0)$  reaction take place on a surface that is completely in the 1 × 1 structure.

The interplay and synchronization between reaction kinetics and diffusion can produce a rich variety of spatial patterns in surfaces, especially due to the anisotropy of diffusion in surfaces. Furthermore, diffusion of adspecies can vary in several orders of magnitude. The traditional approach for considering diffusion is adding terms which obey Fick's second law with constant diffusion coefficients to the equations describing the kinetics. In a reaction-diffusion system, the concentrations  $C_i$  of the chemical species are described by the following partial differential equation (PDE)

$$\frac{\partial C_i}{\partial t} = f(\dots C_j, \dots) + D_i^0 \bigtriangledown^2 C_i$$

where  $D_i^0$  is the diffusion coefficient for the ith substance and  $f_i$  specifies the reaction mechanism. In a recent paper we have taken such approach for the NO + H<sub>2</sub> reaction on Pt(1 0 0) [14] on a two dimensional lattice and showed that differences in the diffusivity in the *x* and *y* directions change the oscillation periods. But this approach ignores the influence of coadsorbed species in diffusion and front propagation is not observed.

Steps and other mesoscopic surface defects have also a considerable influence on the course of the reactions. Steps and kinks are also called line defects, to distinguish them from atomic vacancies, or adatoms, which are called point defects. These point defects are present in most surfaces and are important participants of atom transport along the surface (surface diffusion), although their equilibrium concentrations are much less than 1% of a monolayer. Defects will make synchronization more difficult which causes a breakdown of global coupling, leading from spatially uniform oscillations to the formation of wave patterns.

Interest in the effect that site blocking has on catalytic reactions stems from its occurrence in real systems. For example in catalytic converters inert species, such as sulphur, deposit on the catalyst surface during the exhaust of the combustion gases. These inert species cause the active sites to be non-reactive and also block potential adsorption sites on the catalyst surface. This lead to inefficiencies in the system. Crystal defects produced on the catalyst surface also result in non-binding or blocked sites.

In this paper we make an study of the NO +  $H_2/Pt(1 \ 0)$ O) reaction, incorporating a realistic description of diffusion by considering site blocking effects for NO and hydrogen diffusion by the coadsorbed species. We also consider the influence of defects, considered here as blocking inert sites for the NO adsorption. Our investigation began by studying the effect that a single inert defect has on the local environment and we made the center point of the lattice a defective site. Then we study the scenario which develops in a medium as the influence of defects is continuously increased. For the elementary reaction steps we use the model proposed by MaDownload English Version:

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