Modeling of the Reactivity of Vibrationally Excited Molecules in a Corona Plasma for Catalytic Reactions

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Abstract

A model is developed to describe the transfer of vibrational energy from excited gas molecules to a heterogeneous surface or to heating of the gas. Diffusion of excited species is included in the model. The model is used to compute the maximum possible energy efficiency of a plasma-induced catalytic reaction, which is driven by vibrationally excited molecules. The computational results of the model are correlated to experimental data on quenching rates and the relevant parameters of the self-sustained discharge. It is concluded that the mechanism of plasma-induced catalysis with vibrationally excited molecules is highly unlikely.

1 Introduction

In this work we will focus on the energy efficiency of a catalytically chemical synthesis reaction which is induced by vibrationally excited molecules from a self-sustained discharge. The temperature of the catalyst and the excitation of the reactant can be uncoupled by the excitation in a non-equilibrium discharge. In principle new, low T catalytic reaction routes are possible. Vibrations are the lowest non-equilibrium excited state of a molecule that can enhance the dissociative adsorption rate to a catalyst (see the theory of Polanyi [1] and Wolken [2], the quantum mechanical calculations of Hansen [3], and molecular beam experiments [4–8]). Since the reaction rate is proportional to $\exp(-E_a)$, a large enhancement of the reaction rates can be obtained for vibrational excitation near the dissociation threshold. The use of higher excitations of molecules such as electronical excitation, dissociation, and ionization, is usually too energy intensive for chemical synthesis of bulk chemicals.

The model, presented in this work, describes the de-excitation of vibrationally excited molecules on a catalytic surface and in the gas phase. The first de-excitation route is assumed to induce the desired reaction on the heterogeneous catalyst, whereas the second leads to heating of the gas. Diffusion is included because gradients are expected near the surface. In this model, the efficiency of vibrationally excited molecules for heterogeneous catalytic reactions is defined by the ratio of vibrational energy transferred to the catalyst and to gas heating, *E_wall/E_gas*.

The expectation is that the larger the catalyst surface area in the plasma reactor is, the higher will be the efficiency of vibrational excited molecules. However, a constraint is that the voids in the bed of catalyst particles must be large enough to allow the existence of the self-sustained discharge. The value of the minimum gap spacing, d_{min}, which is required for a self-sustained discharge in neon, scales with the pressure p according to the following relation [9]:

$$p.d_{min} \approx 2 \qquad [\mathrm{m.Pa}] \tag{1}$$

The value of the product $p.d_{min}$ depends slightly on the gas mixture, and will be >2 for air. Equation (1) gives the *lower limit* of the void size in the bed. The characteristic size of the voids in the packed bed is 0.6 times the diameter of the catalyst particles.

2 Modeling

The physical situation in the experimental reactor is a pulsed corona discharge that proceeds through the complex shaped channels (voids) in the bed of supported catalyst particles. The discharge cannot penetrate into the micro-pores of the support since the minimum gas spacing for a self-sustained discharge d_{min} is of the order $20 \cdot 10^{-6}$ m at p = 1 bar. In order to perform model calculations, the following simplifications and assumption are made in the model:

- The shape of the channel in the catalyst bed is cylindrically.
- Vibrationally excited molecules are produced by the discharge instantaneously and homogeneously in the channel.
- A collision of a vibrationally excited molecule to the channel wall is assumed to be 100% effective for the catalytic reaction.
- The ideal gas approximation is used for the reactant gases.

It is realized that none of these assumptions is rigorously valid in reality. The surface area of a cylindrical channel is smaller than that of the complex shaped real channel in the bed, which is enlarged by its turtuosity by a factor >1. However, a 100% effective layer of active catalytic material on the surface seldom exists. Furhter, the quenching of a vibrationally excited molecule on the catalyst has only a small probability for dissociative adsorption [3–8]. In conclusion, these assumptions will give the upper limit of the efficiency for the use of vibrational energy to induce catalytic reactions on a heterogeneous catalyst.

Three types of vibrational energy transfer are considered in the model: 1. *homogeneous* quenching in the gas phase, 2. *heterogeneous* quenching on a surface, and 3. *diffusion* of excited molecules. Convection does not play a role in voids of a packed bed since the Reynolds number are small. The equations of the model are given below. Vibrationally excited molecules are abbreviated by '$M(\nu)$' in the rest of this section.

a.) Homogeneous quenching:

Homogeneous quenching is energy transfer from the highly vibrational excited states to the low, non–reactive vibrational levels, translations and rotations, i.e. heating of the neutral gas. The homogeneous quenching is modeled by an exponential decay with a relaxation time τ_q:

$$\left.\frac{\mathrm{d}\,[M(\nu)]_t}{\mathrm{d}t}\right|_{\text{homo}} = -\frac{1}{\tau_q}.\,[M(\nu)]_t \qquad (2)$$

The relaxation time of quenching, τ_q, can be related to the quenching rate constant k_q and the pressure p by $k_q.p = 1/\tau_q$

b.) Heterogeneous quenching:

The heterogeneous quenching is energy transfer from vibrations to the surface. This energy transfer is related to the chemical reaction of vibrationally excited molecules on the catalyst. The rate of heterogeneous quenching is a function of the collisional frequency to the wall, $f_c^{\perp}$, and the concentration of $M(\nu)$:

$$\left.\frac{\mathrm{d}\,[M(\nu)]_t}{\mathrm{d}t}\right|_{\text{hetero}} = -f_c^{\perp}.\frac{A}{V}.\frac{[M(\nu)]_t}{[M]} \qquad (3)$$

where A is the surface area of the channel and $V = A.\Delta r$ is the volume fraction in which the heterogeneous quenching is important. The ratio $[M(\nu)]_t/[M]$ is the fraction of vibrationally excited molecules. The $f_c^{\perp}$ follows from the pressure equation $p = f_c^{\perp}.2m\bar{u}_z$ where m is the mass of the molecule, and $\bar{u}_z = 1/4\,(8k_bT/\pi m)^{1/2}$ the mean speed perpendicular to the wall.

c.) Diffusion:

Near the surface of the channel, there is an extra contribution of the surface to the quenching of the $M(\nu)$. Transport of $M(\nu)$ is only possible by means of diffusion, since the flow is laminar in small channels. The flux of $M(\nu)$ in the channel, $J_{M(\nu)}$, is defined by the law of Fick:

$$J_{M(\nu)}\Big|_{\mathrm{diff}} = \mathcal{D}.\frac{\mathrm{d}\,[M(\nu)]_r}{\mathrm{d}r} \tag{4}$$

where r is the radius coordinate of the channel in the catalyst bed. The diffusion coefficient $\mathcal{D}$ of an ideal gas is defined in the gas kinetics theory as $\mathcal{D} = \frac{1}{3}\,\bar{v}\bar{\lambda}$ where $\bar{v} = (8kT/\pi m)^{1/2}$ is the mean speed of the molecules, and $\bar{\lambda} = 1/n\pi d^2$ the mean free path between collisions [10]. The collisional diameter of the gas molecules is d, and the density of gas molecules n, expressed in the number of molecules per unit volume.

This set of continuous equations for homogeneous, heterogeneous quenching and diffusion cannot be solved exactly anymore. A computer program has been developed to compute the concentration profiles of vibrationally excited molecules numerically. The channel in the catalyst bed is modeled as a cylinder with radius R, and divided in N concentric shells because of symmetry. The homogeneous quenching is computed in each shell, and the heterogeneous quenching only in the outer shell near the wall surface. The numerical integration is continued until >99% of the vibrational energy is transferred.

3 Results and Discussion

The ratio of energy transfer from the vibrationally excited molecules to the channel wall, *E_wall*, and the gas phase, *E_gas*, is computed for different quenching rates and channel radii. The computations are performed for 1% vibrationally excited molecules in helium at p = 1 bar and T = 500 K. The vibrational relaxation time τ_q is varied between 10^{-4} and 10^{-7} s. These quenching rates cover the experimentally found values, see [11–15]. The channel radius was varied between 1 and $1000 \cdot 10^{-6}$ m. The range of bed particle sizes used in our experiments fall within this range.

The chemical efficiency of vibrational excited molecules, expressed by the ratio *E_wall/E_gas*, as a function of the vibrational relaxation time τ_q is plotted in figure 1. Vibrationally excited molecules are only efficient for catalytic reactions

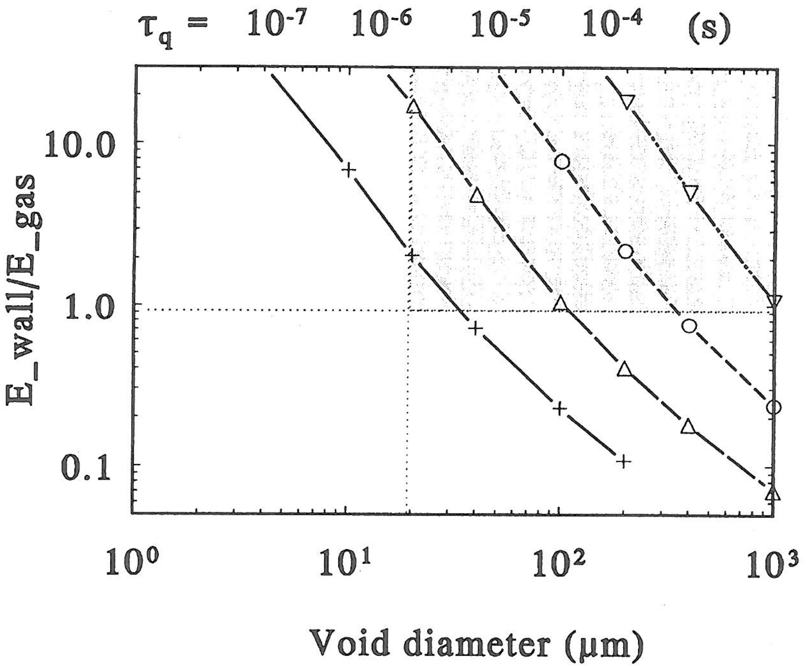

Figure 1: *The ratio of energy transfer to the wall and gas phase as a function of the relaxation time τ_q at p = 1 bar and T = 500 K. The $[M(\nu)]_0$ is 1% in the bulk gas helium. The gray area is the window of the existence of a self-sustained discharge* and *an efficient transfer of vibrational energy to the channel wall.*

when the ratio $\{E\_wall/E\_gas\} \gg 1$. The *maximum* channel diameters as a function of the vibrational relaxation rate can be derived from figure 1. The *minimum* channel diameter, determined by the existence of the self-sustained discharge is estimated to be about $20 \cdot 10^{-6}$ m (from equation (1)). The relaxation time must be $> 10^{-6}$ s to realize an efficient utilization of vibrational energy. This order of relaxation times is experimentally observed only in some exceptional cases. Especially protonated molecules such as CH_4, NH_3, and H_2O are rapidly de-excited, and are very efficient quencher molecules for other vibrationally excited molecules. Relaxation times of $> 10^{-6}$ s at p = 1 bar are exceptional [11–15].. Therefore, the mechanism of plasma-induced catalysis with vibrationally excited molecules is unlikely.

The conclusions following from the model calculations are independent of the pressure. The relaxation time τ_q, the minimum void diameter d_{min}, and the diffusion constant $\mathcal{D}$ scale proportionally to the inverse of the pressure p^{-1}. Hence, figure 1 remains exactly the same for a given quenching rate constant k_q at different pressures except for a proportional scaling of the x-axis and the relation times.

Finally, it must be realized that the chemical efficiency of the plasma-induced process is probably some orders of magnitude lower than the ratio of energy transfer $\{E\_wall/E\_gas\}$. Firstly, the surface coverage of the catalyst on the inert support particle is usually only a few percent, especially for the noble metal catalysts. Secondly, the reaction probability of vibrationally excited molecules upon a collision with the active catalyst exceeds the 10% only at translational/vibrational energies near the dissociation threshold energy. [3–8]. It are just these highly vibrational excited states which are de-excited most efficiently [7,14].

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