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Can plasma be formed in catalyst pores? A modeling investigation

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ABSTRACT

We investigate microdischarge formation inside catalyst pores by a two-dimensional fluid model for various pore sizes in the μm-range and for various applied voltages. Indeed, this is a poorly understood phenomenon in plasma catalysis. The calculations are performed for a dielectric barrier discharge in helium, at atmospheric pressure. The electron and ion densities, electron temperature, electric field and potential, as well as the electron impact ionization and excitation rate and the densities of excited plasma species, are examined for a better understanding of the characteristics of the plasma inside a pore. The results indicate that the pore size and the applied voltage are critical parameters for the formation of a microdischarge inside a pore. At an applied voltage of 20 kV, our calculations reveal that the ionization mainly takes place inside the pore, and the electron density shows a significant increase near and in the pore for pore sizes larger than 200 μm, whereas the effect of the pore on the total ion density is evident even for 10 μm pores. When the pore size is fixed at 30 μm, the presence of the pore has no significant influence on the plasma properties at an applied voltage of 2 kV. Upon increasing the voltage, the ionization process is enhanced due to the strong electric field and high electron temperature, and the ion density shows a remarkable increase near and in the pore for voltages above 10 kV. These results indicate that the plasma species can be formed inside pores of structured catalysts (in the μm range), and they may interact with the catalyst surface, and affect the plasma catalytic process.

1. Introduction

In recent years, there is growing interest for plasma catalysis as an effective technology for environmental protection, like gaseous pollutant removal, hydrocarbon reforming and CO_2 conversion into value-added chemicals [1–6]. Plasma catalysis builds on the integration of a plasma and a catalyst, for an improved performance, i.e., a higher energy efficiency and a better product selectivity [7–16]. This is called the synergistic effect in plasma catalysis. The catalyst can either be placed in the plasma zone, so-called single-stage plasma catalysis, or the plasma and catalyst can be physically separated, so-called two-stage plasma catalysis. In single-stage systems, the plasma interacts directly with the catalyst, and this interaction in turn directly influences the properties of both the plasma and the catalyst. This mutual interaction is causing the possible synergistic effects.

Clearly, the synergistic effect in plasma catalysis is rather complicated. On one hand, the existence of abundant short-lived active species (i.e., ions, radicals, and excited species) in the plasma affects the catalyst properties, such as its morphology or its work function [17–22]. On the other hand, by including a catalyst in the plasma zone, the discharge characteristics will be modified [23–27]. For instance, the presence of a catalyst might significantly enhance the electric field, and the adsorption of pollutants on the catalyst surface may lead to a longer residence time and thus a higher pollutant destruction efficiency. Moreover, some researchers reported the formation of microdischarges inside catalyst pores as another important effect in plasma catalysis, which has a significant influence on the plasma properties [28–33]. Indeed, the strong electric field inside pores leads to different electron energy distributions. This, in turn, gives rise to modified electron impact reaction rates and changes in the plasma chemistry and in the plasma performance for environmental applications.

The existence of short-lived oxidants in the interior of porous catalysts has been experimentally revealed by Holzer et al., for typical pore sizes in the order of 10 nm [28,29]. They concluded that

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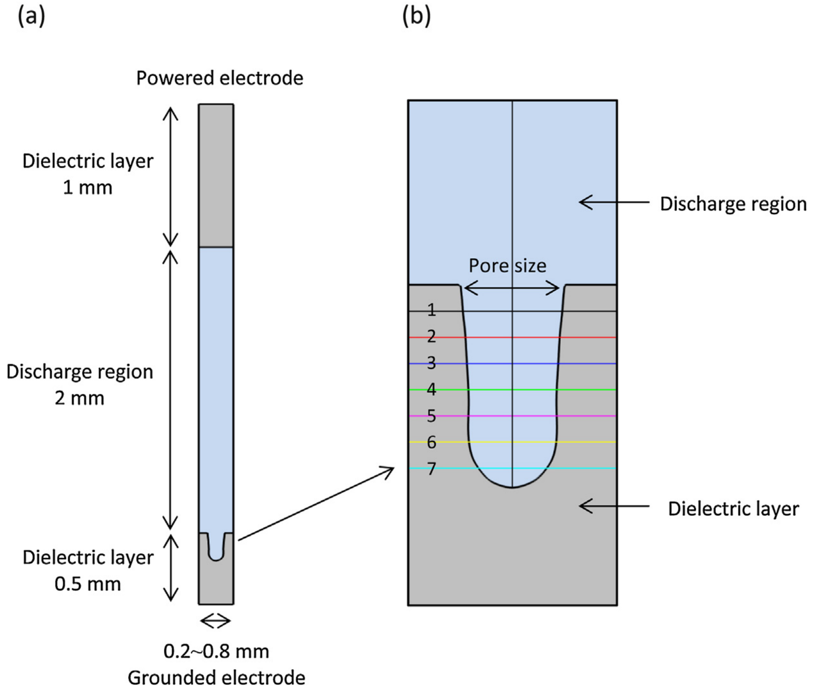

Fig. 1. Geometry used in the model (a), and magnification of the pore structure (b).

these short-lived species might be formed inside the pores, if the electric field there was much stronger than in the bulk plasma. In addition, the stabilization of short-lived species by adsorption on the surface during their diffusion from the plasma into pores might be another explanation, as it significantly increases their lifetime and gives rise to the availability of these species for subsequent surface reactions. Furthermore, the same authors investigated the influence of ferroelectric materials on the performance of non-thermal plasmas for the removal of air pollutants [30]. The results indicated that for a constant applied voltage, the energy input in a reactor filled with ferroelectric pellets was 6–10 times higher than in an empty reactor. This was attributed to the formation of strong microdischarges inside intra- and inter-particle pores (with particle size in the range of 1000–5000 μm) upon introducing ferroelectric pellets into the plasma zone.

In order to obtain a better insight in the microdischarge properties inside pores, Hensel et al. [31] focused on porous ceramic materials in a direct current (DC) hybrid plasma-catalyst system, in the context of pollutant abatement from car exhaust. They demonstrated that for a pore size of 0.8 μm, the discharge only developed on the dielectric surface (so-called surface discharge). However, for a pore size of 15 μm, a transition in discharge mode was observed above the threshold voltage (i.e., 8.6 kV), and microdischarges inside the ceramic were observed. Subsequently, by using an alternating current (AC) high voltage source, they studied the physical properties of microdischarges for various pore sizes, discharge powers, and gas mixtures [32]. The onset voltage of microdischarge formation was found to decrease with increasing pore size, and a different behavior was seen in oxygen and in nitrogen. Indeed, in oxygen gas, the microdischarge channels mostly concentrated around the outer circumference of the ceramic, while a homogeneous distribution was observed in nitrogen. In a follow-up study, the pore size and the amplitude of the applied voltage were identified as the critical parameters for microdischarge formation [33]. When a porous dielectric layer was present at the electrode, charged species generated by the discharge accumulated on the surface. If the voltage drop across the layer exceeded a critical value, the discharge may leak into the porous ceramic.

The generation of a stable plasma inside catalyst pores is a very important factor for plasma catalysis, as it determines the active surface of the catalyst that is available for the reaction. Therefore, it is of uttermost importance to understand the plasma properties and the mechanisms of microdischarge formation inside pores. However, although some effort has already been put in studying microdischarges inside pores, all of the studies mentioned above are performed experimentally, and the inherent mechanisms behind the formation of microdischarges, as well as their influence on the plasma phase, remain poorly understood. In the present work, we therefore investigate microdischarge formation as a function of pore size and applied voltage, by using a two-dimensional fluid model. The calculations are performed for a helium dielectric barrier discharge (DBD) sustained by an AC source, with the applied voltage varying from 2 kV to 100 kV, which are typical values in DBDs [34,35]. Although catalyst pore sizes are typically in the microporous (<2 nm) and mesoporous (2–50 nm) range, the inter-particle meso-macro (μm) pores in structured catalysts are also of crucial importance in catalysis, e.g., for the pressure drop, and mass and heat transfer of catalysts [30,36–39]. Besides, for typical DBD plasma conditions (i.e., electron density (n_e) of 10^{17} m^{-3} and electron temperature (T_e) of 3 eV), the Debye length is about 40 μm, which suggests that microdischarges cannot be formed in sub-μm pores. Therefore, pores with sizes in the range of 10–400 μm are considered in this work, for investigating the effect of the pore size on the microdischarge formation.

2. Description of the model

A two-dimensional fluid model is developed within the COMSOL simulation software [40]. In the model, the continuity equations for the electron density and mean electron energy are solved

$$\frac{\partial}{\partial t}(n_e)+\nabla\cdot[-n_e(\mu_e\cdot\boldsymbol{E})-D_e\cdot\nabla n_e]=R_e,$$

$$\frac{\partial}{\partial t}(n_\varepsilon)+\nabla\cdot[-n_\varepsilon(\mu_\varepsilon\cdot\boldsymbol{E})-D_\varepsilon\cdot\nabla n_\varepsilon]+\boldsymbol{E}\cdot[-n_e(\mu_e\cdot\boldsymbol{E})-D_e\cdot\nabla n_e]=R_\varepsilon.$$