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A multidisciplinary approach to understand the interactions of nonthermal plasma and catalyst: A review

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ABSTRACT

Low temperature catalytic reactions induced by nonthermal plasma (NTP) have been of great interest in plasma chemistry for application to pollution control and energy-related issues. Current progress in the experimental observations and the understanding of interactions between NTP and catalyst are reviewed herein. Considering the diffusion length and lifetime of reactive species, we introduced a dimensionless parameter Λ that describes the criteria for a direct interaction between NTP and catalysts. Several lines of experimental evidences on the interaction were introduced: discharge mode, formation of metal cluster ions, and plasma-induced fluorescence from the catalyst. For faujasite zeolites, the Si/Al ratio was found to be an important parameter that determines the propagation of surface streamers and catalytic performance. The oxidation status of metals is closely correlated with the Si/Al ratio, which is related to substantial changes in electrical resistivity.

1. Introduction

Electrical discharges can produce nonthermal plasma (NTP) under moderate conditions (i.e. room temperature and atmospheric pressure) favorable for the removal of various pollutants (e.g., NOx, odors, and volatile organic compounds (VOCs)). Extensive studies in the 1990s shed light on the merits and demerits of using NTP processes for environmental applications [1–3]. The demerits include high energy consumption and the formation of unwanted byproducts [4,5]. Plasma-catalysis can overcome the disadvantages observed when plasma or the catalyst is used alone. Most of the work published after 2000 focused on the combination of NTP and catalysts to find solutions to these problems [6–11]. This combination is attracting greater attention for a number of specific applications, including methane reforming [12–14], hydrogen production [15], VOC removal [16], and NOx removal [17–19]. Irradiation of the catalyst with an electron-beam can also induce similar plasma-catalysis phenomena at ambient temperature and pressure [20–23].

The main purpose of the combination of NTP and catalyst is to achieve removal efficiency, selectivity toward CO_2, and carbon balance [24–27]. There is considerable literature on experimental observations that showed increase in both the removal efficiency and CO_2 selectivity, and higher carbon balance by combining the catalyst with NTP. However, the difficulty of studying interactions between NTP and the catalyst has led to a new set of academic challenges. The collection of experimental and theoretical data on the interactions between NTP and the catalyst occupies an important place in understanding the mechanism and in the extended use of plasma-catalysis in new fields. There are many unresolved questions on the nature of the interactions. In this review, the current status of experimental observations and understanding of the interactions of plasma–catalyst systems is presented.

2. Interactions in plasma-catalysis

2.1. Experimental observations (literature survey)

The combined effects of NTP and the catalyst have been studied experimentally over the last 15 years. The most widely accepted observations relate to the following aspects.

- Increase in the removal efficiency of VOCs.
- Increase in the CO_2 selectivity.
- Good carbon balance (carbon recovery close to 100%).

Many research groups have reported increased VOC removal efficiency for VOCs and catalyst systems such as benzene–MnO_2 [28], toluene–Pt/Al_2O_3 [29], benzene–Pt/TiO_2 or V_2O_5/TiO_2 [30], and benzene–Ag/TiO_2 [31]. Two ideal final products in the VOC

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removal process are CO_2 and H_2O. However, improper conditions may lead to the formation of harmful or odorous intermediates such as aldehydes [32,33], organic acids [34,35] and carbon monoxide (CO) [36,37].

There is some discrepancy on the role of water vapor in the removal processes. For example, some papers report the negative effect of water vapor on the VOC removal of toluene–TiO_2 [38], toluene–TiO_2 or MnOx [39]. At the same time, positive effect has also been reported for formaldehyde (HCHO) removal over alumina [40]. Carbon balance is also an important parameter that must be carefully considered in plasma-catalysis. In the gas-phase plasma processing of VOCs, the formation of aerosols or the deposition of solid product on the reactor wall has been confirmed as a reason for low carbon balance [31,41,42]. In addition to gas-to-particle conversion, VOC adsorption onto the catalyst is another important reason for the loss of carbon balance. It is therefore evident that plasma-catalysis should simultaneously satisfy three parameters: efficient removal efficiency, no undesirable byproducts, and carbon balance. If one of these three parameters is not satisfied, a process may lose its potential for industrial use.

A substantial increase in both the removal efficiency of VOC and the selectivity of CO_2 can be achieved with a plasma-catalysis reactor as the oxygen content increases, even at a fixed input energy. This is a highly O_2 content-dependent behavior that does not appear in processes using the catalyst or NTP alone [43]. Materials such as $BaTiO_3$, glass beads, non-porous ZrO_2, and non-porous Al_2O_3, all of which have very low surface areas (<ca. 2 $m^2\,g^{-1}$), did not exhibit positive O_2-content dependence. For most of the catalytic materials tested in our laboratory, the higher the O_2-content, the higher the removal efficiency of VOC and the greater the selectivity for CO_2. This unique behavior provided the basis for cycled system [44] consisting of two steps—adsorption and subsequent decomposition of adsorbed VOC—using O_2 plasma. Many recent studies confirmed the advantage of the cycled system for the removal of benzene [45,46], toluene [47,48], and HCHO [49] using a variety of adsorbent/catalyst combinations. Adsorption followed by treatment with air plasma can also enhance the energy efficiency of VOC removal [50,51]. However, attention must be given to the formation of nitrogen oxides (N_xO_y) from air, particularly when the reactor is operated at a relatively high input power [52,53].

Fig. 1 depicts the layouts of plasma-catalysis reactor according to the position and number of catalyst bed. The single-stage (henceforth called "1-stage") configuration, where catalysts are located inside the plasma zone, is also referred to as plasma-driven catalysis (PDC) [54,55] or in-plasma catalysis (IPC) [56]. In 1-stage reactor with dielectric barrier, the gap distance d is

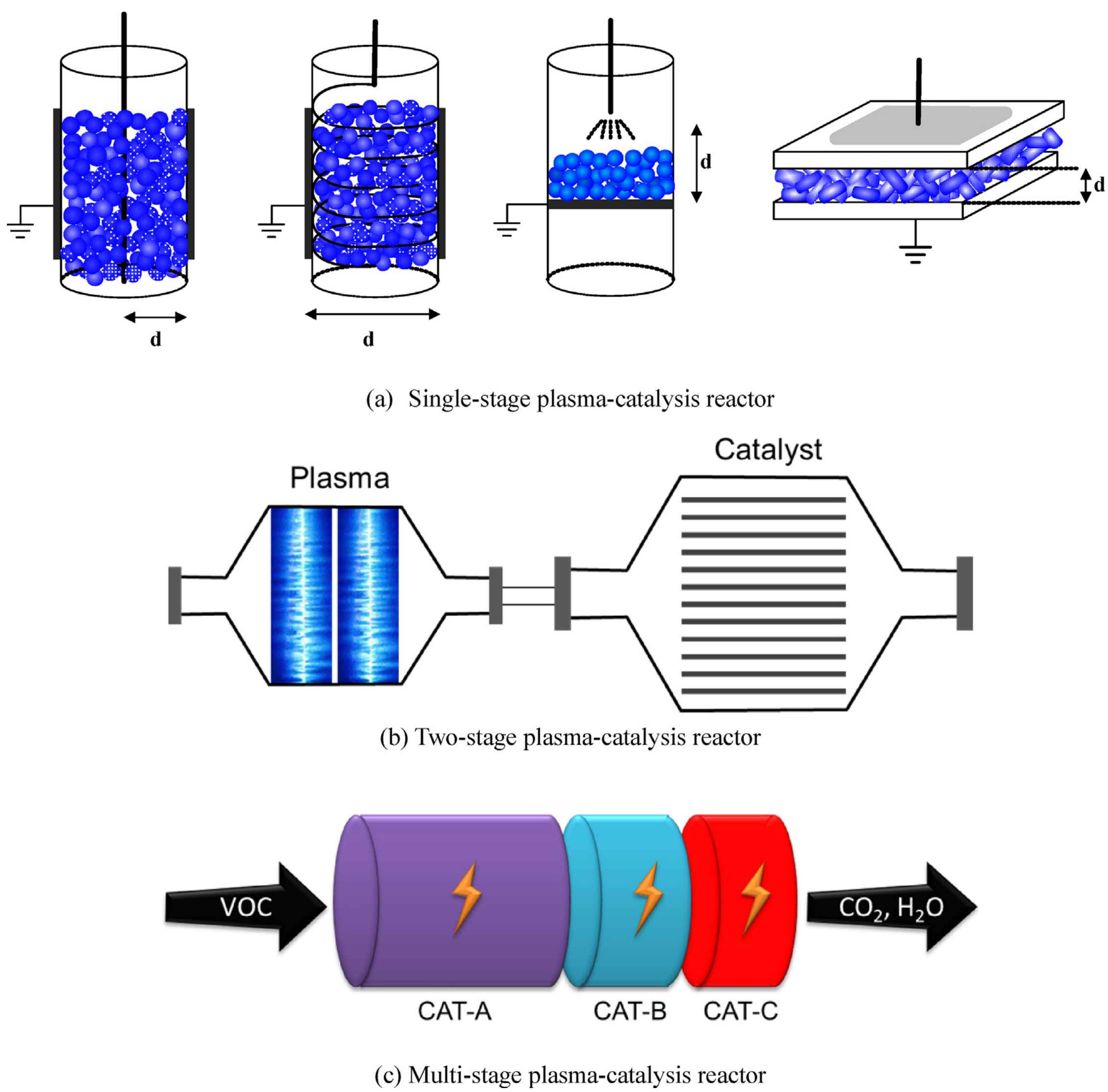

Fig. 1. Layout of plasma-catalysis reactor with a multilayered catalyst bed.