Plasma-catalytic hybrid reactor: Application to methane removal

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ABSTRACT

Methane oxidation was investigated in a pulsed dielectric barrier discharge at atmospheric pressure coupled with Pd/Al$_2$O$_3$ catalysts. Comparison between plasma, catalytic, and plasma-catalysis (both in-plasma and post-plasma catalysis) systems were performed in the temperature range of 25–500 °C and specific input energy up to 148 J/L. For plasma-alone experiments, CH$_4$ conversion reached a maximum of 67% and the main products obtained were CO, CO$_2$, O$_3$, and HNO$_3$. The plasma catalytic treatment leads to an increase of the CH$_4$ oxidation even at low temperature. It is evidenced that, compared to plasma alone, both Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalysts coupled plasma discharge increase the CH$_4$ conversion. Moreover, for all plasma-catalytic systems, the CH$_4$ conversion plots were shifted toward lower temperature as the specific input energy increases. Although the difference is low, the in-plasma catalysis configuration seems to be more efficient compared to post-plasma catalysis. In all cases, CH$_4$ oxidation in presence of Pd/Al$_2$O$_3$ catalyst becomes more selective in CO$_2$ formation than the reaction in plasma alone.

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1. Introduction

The emission of volatile organic compounds (VOCs) and nitrogen oxides (NO$_x$) by various industrial processes and human activities is a serious source of air pollution, therefore, a problem for human health and the environment in general. Among VOCs, methane (CH$_4$) as a potent greenhouse gas, is the most abundant reactive trace gas in the atmosphere and arises from both natural and anthropogenic sources. Although the CH$_4$ lifetime in the atmosphere is much shorter than that of CO$_2$, CH$_4$ is more efficient at trapping radiation than CO$_2$. The comparative impact of CH$_4$ on climate change is over 20 times higher than CO$_2$ at equivalent emission rates. For these reasons, and according the current and future worldwide regulations, CH$_4$ emissions must be necessarily reduced.

Catalytic combustion of CH$_4$ has been widely explored in the last few decades for both pollutant abatement and power generation. This environmentally friendly technology offers the possibility to produce heat and energy at much lower temperatures than the conventional thermal combustion. Currently, catalysts such as supported noble and transition metals are being extensively used [1–3]. The most active catalysts for oxidation of saturated hydrocarbons, including CH$_4$, are platinum and palladium, the latter is

considered as superior due to its high activity, thermal stability, low cost compared to the Pt-based catalysts [4]. It is often suggested that the active form of Pd in CH$_4$ oxidation at low temperature is crystalline PdO, but it is reported that at high temperature metallic Pd may also be active [5].

While presenting interesting performances for the abatement of different type of molecules (aromatic, oxygenated or paraffinic of medium molecular weight), the conventional VOC treatment technologies are not appropriate and not cost-effective in the case of moderate gas flow rates containing low amounts of pollutant [6]. On the other hand, the severe emission tolerances are often difficult to handle using these conventional technologies [7]. Thus, it is necessary to develop new methods for CH$_4$ conversion. As an alternative to the catalytic oxidation, non-thermal plasma (NTP) such as dielectric barrier discharges (DBD) and corona discharges have been extensively investigated for VOCs abatements [8–11]. In NTP, background gaseous species are excited and/or dissociated directly by electronic impact while the gas temperature remains relatively low, and thus the product distributions far from the chemical equilibrium may be obtained. In that case, the deposited energy controls the production of active species, which lead to the chemical conversion of VOCs.

Plasmas processes offer a unique way to induce gas phase reactions by electron collisions, but they produce large amounts of by-products and are often less selective than the catalytic processes. As emphasized by different groups, a more effective use of NTP is possible by exploiting its inherent synergistic potential

through coupling with a heterogeneous catalyst. NTP has been extensively used for several chemical and catalytic processes and only a few studies were related to the total oxidation of CH_4. Examples are the treatment of diesel exhaust gases [12–16], abatement of volatile organic compounds [17–21], hydrocarbons reforming processes [22,23], partial oxidation [24,25], and total CH_4 oxidation in natural gas combined heat power [26–28].

In this paper, NTP-DBD reactor coupled with Pd/Al_2O_3 catalysts are used to investigate the oxidation of CH_4 at atmospheric pressure. In order to understand the synergistic effect of NTP–catalyst coupling, CH_4 oxidation has been performed using (i) thermal catalysis; (ii) NTP without catalyst; and (iii) NTP–catalyst coupling in both in-plasma catalysis (IPC) and post-plasma catalysis (PPC) configurations. Results will be presented as a function of the gas temperature and the plasma specific input energy (SIE).

2. Experimental

2.1. Plasma-catalytic system

The experimental set-up comprises the mass flow controllers, a high voltage power supply, a plasma-catalytic reactor installed in a tubular furnace, and a Fourier Transform Infrared Spectrometer. The system was described in detail previously [20] and is briefly described here for clarity.

The plasma reactor is a dielectric-barrier discharge (DBD) reactor in a cylindrical configuration. It consists of 0.9 mm-diameter tungsten wire used as main electrode. The tungsten wire was placed in the center of, 300 mm long Pyrex®, tube using two ceramic rings. The outer surface of the tube was wrapped with copper grid and used as a ground electrode. The discharge length was fixed as 100 mm and the corresponding discharge volume is 18 cm^3.

The plasma reactor gives a possibility to combine catalyst in two ways: the catalyst in the discharge zone (in-plasma catalysis, IPC) or the catalyst downstream the discharge zone (post-plasma catalysis, PPC) as shown in Fig. 1. In IPC arrangement, the catalyst is directly in contact with the discharge and the active species are generally close vicinity of the catalyst surface (e.g., excited-state atoms and molecules, reactive radicals, photons, and electrons). In addition, in IPC configuration plasma modifies the catalyst surface. In contrast, in the PPC arrangement, the catalyst is exposed only to long-lived species that exit from the plasma zone (ozone). For IPC configuration the catalyst, 2.2 or 3.1 g, was placed in the middle of the discharge zone. It leads to the catalyst volume of 2.8 and 4.1 ml. In case of PPC, the catalyst was placed just after the plasma

Fig. 1. Schematic overview of the plasma-catalytic reactor: (a) in-plasma catalysis (IPC) and (b) post-plasma catalysis (PPC).

discharge zone. For the two arrangements, the catalyst in the form of beads (1.0 or 1.8 mm diameter) was placed in between quartz wool.

The plasma-catalyst reactor temperature was increased from 22 to 500 °C, at the rate of 5 °C min^{-1}, using tubular furnace. The reactor temperature was measured by a K-type thermocouple placed on the reactor surface and the temperature uncertainty is ±3 °C. The experiments are steady state experiments; we have waited at least 30 min for stabilization.

The DBD reactor is driven by a homemade pulsed HV generator (20 kV, 200 Hz). Electrical characterization of the plasma was performed by current and voltage measurements using a Tektronix P6015A HV probe and a Pearson 4001 current probe, respectively. The output signals were transmitted to a Tektronix DPO 3054 oscilloscope and the energy consumption was evaluated through the specific input energy (SIE) calculated from Eq. (1) where E_p, f, and Q denote the pulse energy, pulse frequency, and gas flow rate, respectively.

$$\text{SIE} \left(\frac{J}{L} \right) = \frac{E_P(J) \cdot f(\text{Hz})}{Q(L/s)} \qquad (1)$$

End-products detection and quantification were carried out using a FTIR (Nicolet 6700, Thermo-Scientific) equipped with a MCT detector and 10 m gas path cell.

Steady-state activity, CH_4 conversion, was measured in the presence and in the absence of catalyst at temperatures ranged from 22 to 500 °C. The uncertainty was determined by repeating each experiment four times. After reproducibility, we can conclude that the experimental relative uncertainty error is less than 5%.

2.2. Catalysts preparation

Palladium supported catalysts were prepared by impregnating alumina beads (diameters: 1.0 and 1.8 mm) (Sasol Germany GmbH), using a palladium tetramine nitrate solution ($Pd(NH_3)_4(NO_3)_2$; STREM Chemicals Inc.) as the metal precursor. The concentration of the precursor was calculated from the desired metal loading of the final catalyst (0.5 and 1 wt.%). The suspension was stirred for 3 h at 50 °C and at atmospheric pressure. After a complete evaporation of water under reduced pressure, the impregnated samples were dried at 120 °C for 24 h. Finally, the dried samples were calcined at 500 °C for 4 h at the heating rate of 3 °C min^{-1}, under air flow to obtain the final form of supported catalysts.

2.3. Catalysts characterization

2.3.1. Chemical analysis

The Pd metal loading was determined by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) using an ACTIVA spectrometer from Horiba Jobin Yvon. Samples (ca. 0.5 g) were treated in H_2SO_4:HNO_3:HCl solutions.

2.3.2. Specific surface area and porosity

Specific surface area/porosity measurements were conducted using a Micromeritics ASAP 2010 apparatus with N_2 as the sorbate at −196 °C. Prior to surface area measurement, all the samples were outgassed at 300 °C and under 5×10^{-3} Torr pressure for 3 h. The total specific surface area was determined by the multi-point BET method, and the mesoporosity was evaluated using the Barrett–Joyner–Halenda (BJH) method.

2.3.3. X-ray diffraction (XRD)

XRD analyses were conducted with a Bruker D5005 powder diffractometer scanning using Cu-Kα radiation. Samples were scanned (0.02°/step) in the 2θ range of 4–80° (scan time = 2 s/step). Diffraction patte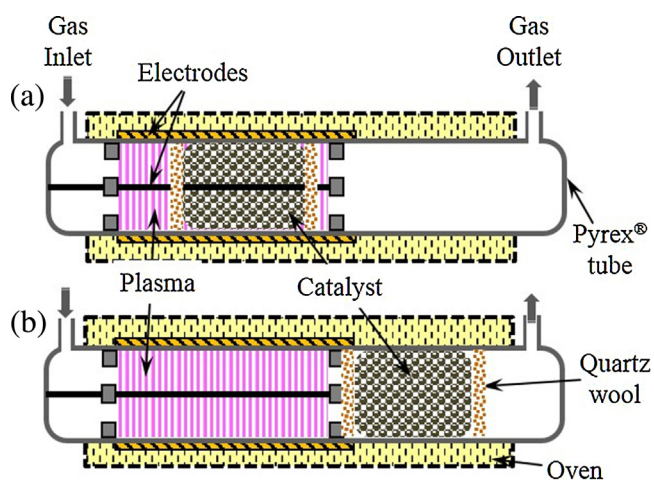rns were assigned using Joint Committee on