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Simultaneous laser induced breakdown spectroscopy and Pd-assisted methane decomposition at different pressures

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ABSTRACT

Methane decomposition is investigated during Pd-assisted laser induced plasma in the controlled chamber at various pressures using Q-switched Nd:YAG laser. Real time LIBS monitoring is applied to reveal the involved mechanisms during methane decomposition by inspecting the plasma parameters at mano-metric pressures of 1 to 10 mbar. The dependence of electron density and plasma temperature with pressure is also studied. It is shown that the plasma recreates higher hydrocarbons during the decomposition of methane. In addition, Fourier transform infrared spectroscopy, gas chromatography, scanning electron microscopy and transmission electron microscopy are applied to support the findings.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a spectra-chemical technique to be successfully applied as a straightforward in situ method for the determination of the elemental composition of solids, liquids and gases [1,2]. Nowadays, there is an increasing demand for LIBS in the multi-disciplinary applied research. The ability to obtain rapid, multi-elemental, in-situ analysis represents a unique advantage of LIBS with respect to the competitive analytical techniques [3,4]. Moreover, extensive studies in the recent decades exhibit that LIBS could be an effective technique for understanding the kinetics of reactions within the plasma leading to the determination of the elemental compositions [5,6]. Efforts have been focused on the solid targets in air [7], CO_2 [7,8], and Ar [9] as well as SF_6 [10–12] in order to investigate LIBS at various atmospheres. Laser induced breakdown spectroscopy of Pd during nanoparticle generation was also investigated using the nanosecond laser at 1064 nm [13].

Methane conversion to higher hydrocarbons is considered a crucial issue. The conventional methods, e.g. oxidation and Fischer–Tropsch, for the conversion of methane to the other products need high pressure and high temperature conditions. Recently, several methods have been carried out such as thermo-catalytic [14], arc discharge induced plasma [15] and direct photo-dissociation by femto-second laser [16–19]. Those could potentially lead to the development of simultaneous CO_2-free C_2^+ and hydrogen production process with high selectivity and help to solve the global issues such as air pollution and greenhouse effects offering the next generation of energy sources [20–22].

Suzuki et al. [23] reported the formation of formaldehyde from photo-oxidation of methane over a molybdena-silica catalyst, at 463–493 K, under UV radiation. Hill et al. [24] suggested photo-induced reactions of methane on the surface of molybdena-silica using UV exposure. They noted that methane was adsorbed on the catalyst surface. Subsequently, when the catalyst is heated up from 293 to 473 K, desorption processes have produced a considerable amount of ethylene, ethane, hydrogen and smaller amounts of C_3 and C_4 alkenes and alkanes.

Wang et al. [16] investigated that dissociation of methane proceeds via a stepwise mechanism by gradually increasing the intensity of Ti:sapphire laser at 800 nm. Sharifi et al. [17] also studied high-power laser ionization–dissociation of CH_4 at various femtosecond laser intensities ranging from 10^{14} to 10^{15} W/cm^2 having 48 fs pulse duration.

Here, the nanosecond laser at 1064 nm was employed for methane decomposition based on the metal assisted induced plasma. To our knowledge, this work offers the first investigation of real time LIBS monitoring of species using Q-switched Nd:YAG laser with focal point just close to the Pd target. It reveals the kinetics of CO_2-free methane conversion processes toward higher hydrocarbons such as C_2^+ and C_3^+ alkenes and alkanes effective production with high selectivity. The same laser was utilized to induce the process and to permit simultaneous diagnostics. Furthermore, gas chromatographs (GC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied accompanying LIBS for analyzing of synthesized elements in the plasma.

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2. Experimental

The experimental set-up consists of an irradiation chamber, high vacuum systems, conducting and focusing optics, laser pulse diagnostics and LIBS instrument as shown in Fig. 1. The home-made cross type chamber, as a couple of hollow cross cylinders, was made up of stainless steel with a ~200 cm^3 volume and an inner diameter of 7.5 cm. A BK_7 window with 5 cm dia was employed to traverse laser beam into the chamber. A Pd target was inserted inside, which is in front of the AR-coated BK_7 window. Moreover, A couple of broadband (9–11 μm) AR-coated ZnSe windows were situated perpendicular to the axis along the BK_7 window, in order to monitor the dominant characteristic absorption peaks using FTIR. Moreover, a couple of AR-coated CaF_2 windows, perpendicular to both of the mentioned axes, were situated to transmit the plasma emissions towards the spectrometer. A Balzer vacuum valve was connected to the chamber in order to maintain high vacuum and block the atmospheric pressure. A gas dosing Balzer needle valve was utilized for methane gas injection at various mano-metric pressures [25]. The micro-plasma was generated by focusing a pulsed Q-switched Nd:YAG laser (50 mJ/pulse, 10 ns duration, 5 Hz repetition rate, 1064 nm) through a BK_7 lens (f = 15 cm) in the middle of the chamber, normal to the Pd target. The Pd surface was manually well polished after each experiment and before the next laser exposure. Then, the gas in the chamber was evacuated using a rotary pump to the background pressure of ~10^{-3} mbar. Afterwards, CH_4 (99.999%) flow was tuned by the needle valve and fed into the chamber. The chamber was kept at pressures of 1, 2, 5 and 10 mbar, respectively in order to study methane dissociation during the laser exposure. Subsequent higher hydrocarbon formation takes place using the Pd-assisted induced plasma. A single laser was employed simultaneously to induce the chemical reactions and to ignite plasma for the LIBS investigation. The spectral emissions of the plasma were acquired by means of the AvaSpec-2048 fiber optic spectrometer coupled to a CCD (0.4 nm resolution and 300 lines/mm). The emitted plasma radiation was then collected by the fiber located perpendicular to the laser beam direction. The fiber (NA = 0.22) position was chosen to achieve the strongest plasma emission. Furthermore, the laser irradiation condition was kept constant to evaluate the plasma parameters during the LIBS experiments. Finally, the spectra were recorded and processed using a PC equipped with AvaSoft-7.6-USB2 software. The time gating and delay were set to be 1.1 ms and 2 μs for the data acquisition in the spectral range of 200–1100 nm. Each spectrum was obtained from the statistical accumulation of the signals averaging over 50 successive laser shots.

Several preparation prerequisites methods were taken after laser exposure and before microanalysis. After laser irradiation, the generated higher hydrocarbons were identified exploring a Fourier transform IR spectrometer (Bruker-Vertex 70, Germany) ranging from 400 to 4000 cm^{-1} via ZnSe windows. The irradiation chamber was also used as the sampling cell for FTIR analysis.

The stable products such as ethane, ethylene, and propane have been characterized using a YoungLin-M600D (column: 30 ft of Hayesep D) gas chromatographic system equipped with the flame ionization detector (FID) and a capillary column in a temperature-programmed oven.

A gas sample from the irradiation chamber after laser exposure was injected into the GC instrument via a needle valve. SEM (XL30, Philips) and TEM (XL, Philips) were also exploited to inspect the morphology and microstructure of the deposited carbon on the windows, accordingly. In addition, the selected area electron diffraction (SAED) pattern was used to determine the crystalline structures of the samples. For TEM analysis, the deposited carbon on the windows was gathered and dispersed into an ethanol solution. Then, it was sonicated by an ultrasonic bath and one drop of the suspension was deposited on a carbon-coated copper grid. The deposited powder carbon on the windows was utilized for SEM analysis too.

3. Results and discussion

The micro plasma takes place when an Nd:YAG laser with sufficient power density (≥10^8 W/cm^2) is focused on Pd target. Fig. 2

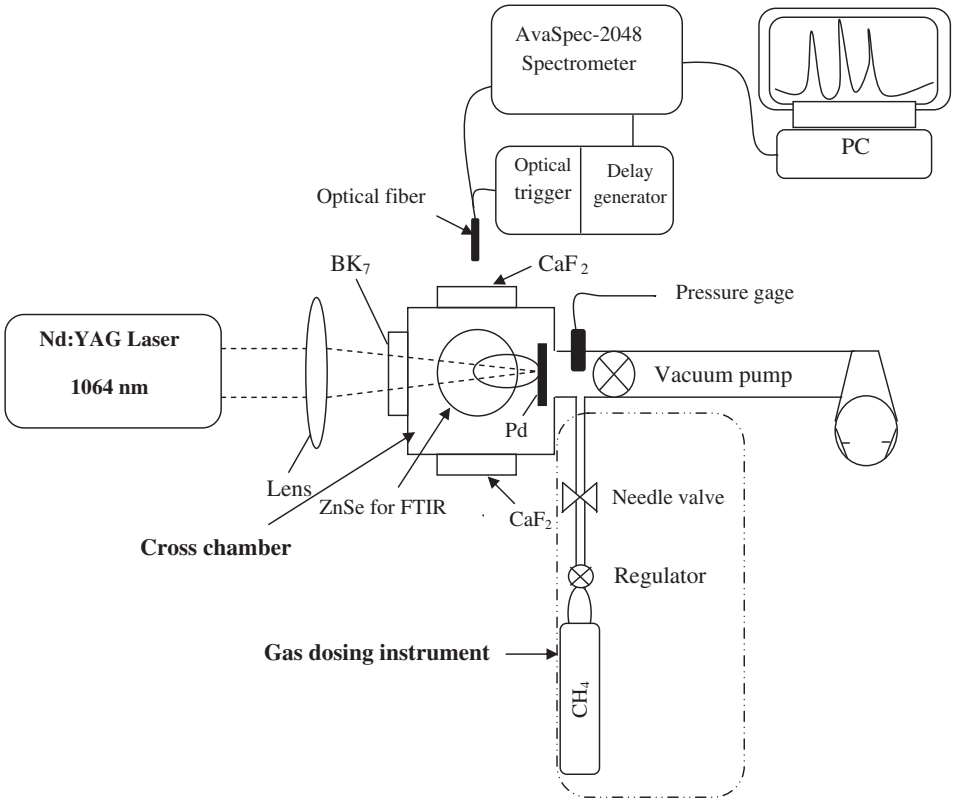

Fig. 1. Schematic of experimental set-up for the Pd-assisted methane decomposition due to induced plasma by Nd:YAG laser in the controlled chamber.