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Ionic liquids as novel catalysts for methane conversion under a DC discharge plasma

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ABSTRACT

Nine imidazolium-based ionic liquids were investigated as novel catalysts for methane conversion in a direct current (DC) discharge plasma reactor. The conversion of methane increased from 21.2% to 43.6% in the plasma system when the $C_6MIMHSO_4$ IL was used as a catalyst, C_6MIMBF_4 successfully achieved 91.0% selectivity for C_2 hydrocarbons. The results of the optical emission spectroscopy indicate that the intensity of the C_2, CH, H, C^+, and C active species from methane decomposition increased when $C_6MIMHSO_4$, C_6MIMCF_3COO, and C_6MIMBF_4 were introduced into the plasma system. FTIR analysis indicates that C_6MIMBF_4 is steady in the DC discharge plasma.

1. Introduction

At present, the sources of petroleum are gradually becoming depleted. However, the storage of natural gas is comparatively abundant, and will play an increasingly important role in chemical supplies in the future. Methane, the main component of natural gas, is one of the most inert organic compounds, and its direct conversion to useful products is a difficult process done via conventional heating [1,2]. In recent years, the novel idea of manufacturing valuable chemicals via cold plasma catalytic methane conversion has become available [3–7]. Cold plasma is an effective technology of converting methane to more valuable products, such as acetylene (C_2H_2) and ethylene (C_2H_4). However, this radical process has a lower selectivity for C_2 hydrocarbons. Many researchers have used solid catalysts, such as metals and metal oxides, to enhance the selectivity of products and reduce coke deposition [8–10]. Jan et al. [11] found that the conversion of methane with CO_2 can be effectively conducted in a hybrid plasma–catalytic system using a dielectric barrier discharge (DBD) reactor operated at 1.2 bar over the 120–290 °C temperature range. With the Pd/Al_2O_3 catalyst, the overall methane conversion was 30–50% and the methane conversion to C_2–C_4 hydrocarbons reached 22%. Moreover, the solid deposit formation radically slowed down. Dai et al. [12] discussed the hydrogenation coupling of methane using pulsed corona plasma and its synergism with a catalyst (Ni/γ-Al_2O_3). The participation of Ni/γ-Al_2O_3 improved the distribution of the C_2 hydrocarbons. Młotek et al. [13] demonstrated that the hybrid plasma–catalytic system joining the gliding discharge and mobile bed of the catalyst exhibits high efficiency in non-oxidative methane coupling at medium temperatures. Aside from H_2, C_2 hydrocarbons are the basic products of methane conversion. In the presence of Pt and Pd catalysts, soot formation is strongly reduced, and C_2H_4 and ethane (C_2H_6) become the main gaseous products, replacing a major portion of the C_2H_2.

In recent years, ionic liquids (ILs) have attracted increasing interest and have been successfully used in different kinds of catalytic reactions as green reaction media. They are widely used as organic solvents and catalysts in chemical reactions because of their composition, which consists of only positive and negative ions, as well as their extremely low vapor pressure, high heat capacity and chemical stability, and nonflammability [14–16]. Xu et al. [17] investigated the synthesis of tributyl citrate using an acid-functionalized IL as catalyst. The results indicated that acidic ILs exhibit good catalytic and reusable performance. Under optimum conditions, the conversion of citric acid using 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulphate as the catalyst was 97%. After easy separation from the products, the ionic liquid could be reused 13 times without disposal, and the conversion of citric acid was not less than 93%. Buriol et al. [18] described an efficient method of synthesizing pyrazole that combines the use of an IL and microwave irradiation. The corresponding system exhibited a synergistic promoting effect, resulting in shorter reaction times and better yields compared with the classical method. Li et al. [19] reported a green chemical process for methane oxidation using gold nanoparticles as the catalyst and ILs as solvents. The results showed

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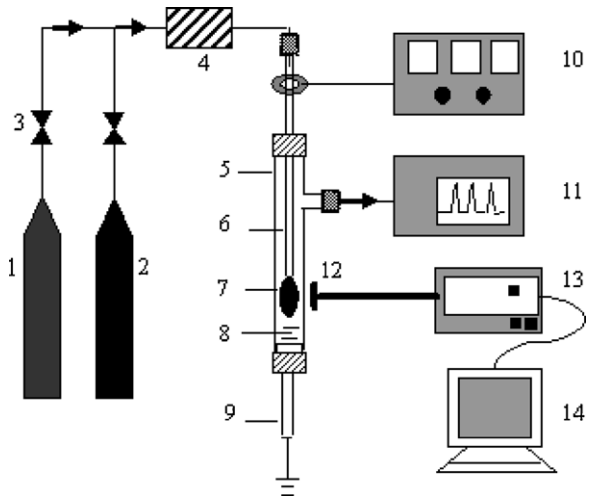

Fig. 1. Schematic diagram of the plasma apparatus. (1) methane, (2) hydrogen, (3) mass flow controller, (4) mixture, (5) quartz tube, (6) plasma powered electrode, (7) plasma zone, (8) ionic liquids, (9) grounded electrode, (10) DC plasma generator, (11) gas chromatography equipment, (12) optical fiber, (13) OES, (14) computer.

that the IL acted as a dissolution medium for the nano-Au/SiO_2, while playing a key role in promoting the reactivity of gold and rendering a reaction with high selectivity. The nano-Au/SiO_2 and IL system can be recycled, and the conversion of methane in the recycled system still remained at a high level. Wei and Liu [20] achieved a clean synthesis of gold nanoparticles using the sub-atmospheric dielectric barrier discharge plasma reduction in the C_4MIMBF_4 IL. Kaneko et al. [21] prepared nanocomposite materials using discharge plasmas in contact with ILs at lower gas pressures.

In the present paper, nine imidazolium-based ILs were developed as novel catalysts for methane conversion under a DC discharge plasma at atmospheric pressure. The effects of ILs on methane conversion, C_2 hydrocarbon selectivity, and C_2 hydrocarbon yield were also investigated. Optical emission spectroscopy (OES), which can be performed without any physical contact with the plasma, was conducted to investigate the stability of ILs in the DC discharge plasma and their effects on methane dissociation. FTIR spectroscopy was used to confirm the stability of the C_6MIMBF_4 IL in the discharge plasma. To the best of our knowledge, methane conversion in a DC discharge plasma system using ILs as catalysts has not been previously reported.

2. Experimental

The schematic diagram of the DC discharge plasma setup equipped with the OES diagnostic system is shown in Fig. 1. A high-voltage DC generator supplied power to the reactor. The value of its peak voltage could be adjusted in the range 10–28 kV. The total power consumed in the generator and reactor was measured with a wattmeter. The quartz tube 20 mm in inner diameter and 90 mm in length contained two electrodes. The powered electrode (made of a stainless steel pipe) was located in the gas phase region, while the grounded electrode (made of a copper plate) was immersed in the ILs at a depth of 2 mm, approximately. The gap between the powered electrode and the IL surface was 6 mm. As controlled experiments, the gap between the powered electrode and the grounded electrode was also 6 mm when the ILs was not introduced on the grounded electrode. The feed gas flow was adjusted and controlled with a mass flowmeter. The effluent gas composition was analyzed by on-line GC chromatography with a Shimadzu GC-14A equipped with a flame ionization detector and a GDX-502 column. In this column, it is possible to separate CH_4, C_2H_6, C_2H_4, and C_2H_2.

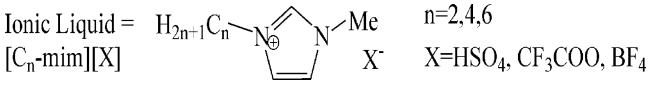

Fig. 2. Structure of the ionic liquid used for methane conversion under a DC discharge plasma.

In the present experiment, methane conversion, C_2 hydrocarbon selectivity, and C_2 hydrocarbon yield were calculated as follows:

$$\%\text{conversion of } CH_4 = \frac{\text{moles of } CH_4 \text{ consumed}}{\text{moles of } CH_4 \text{ introduced}} \times 100$$

$$\%\text{selectivity of } C_2 \text{ hydrocarbon} = \frac{2 \times (\text{moles of } C_2H_6 + \text{moles of } C_2H_4 + \text{moles of } C_2H_2)}{\text{moles of } CH_4 \text{ reacted}} \times 100$$

$$\%\text{yield of } C_2 \text{ hydrocarbon} = \%CH_4 \text{ conversion} \times C_2 \text{ selectivity}$$

The OES spectra were obtained using an AvaSpec-2048 (Avantes) fiber optic spectrometer which was based on an Avabench-75 symmetrical Czerny-turner design with a 2048 pixel charge-coupled device detector array. The 200–1100 nm scanning range provided a resolution of 0.2 nm. The optical fiber was collimated and vertically placed along the plasma flame, and the distance from the optical fiber to the quartz tube was fixed at 6 mm.

A series of imidazolium ILs (Fig. 2) with different alkyl chain lengths (C_2, C_4, and C_6) was investigated as novel catalysts for the conversion of methane under plasma. The ILs used in the current work were synthesized by the Center of Green Chemistry in Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China. The viscosity of the ILs was determined using a Stabinger viscometer (SVM 3000/GR). The conductivity measurement was performed with a Mettler-Toledo SevenMulti meter. The temperature for the determination of the viscosity and conductivity was maintained at $25 \pm 0.1\,^{\circ}C$ using an external temperature controller. The C_6MIMBF_4 IL used before and after the reaction in the plasma was monitored on a Spectrum one-B FTIR (PerkinElmer).

3. Results and discussion

3.1. IL properties

The names, conductivity, and viscosity of the ILs are summarized in Table 1. All nine imidazolium-based ILs have high conductivities and viscosities. ILs with the same cations have different viscosities and conductivities for different anions. The conductivity follows the order $BF_4^- \approx CF_3COO^- > HSO_4^-$. However, the viscosity follows the order $HSO_4^- > CF_3COO^- \approx BF_4^-$. In the same way, ILs with the same anion showed a decrease in conductivity and an increase in viscosity with the increment of the length of the alkyl chain. In our experiments, the conductivity of the ionic liquids affect the DC discharge plasma and suitable conductivity of the ionic liquids contribute to the plasma discharge. The viscosity of the ionic liquids affect the stability of gas–liquid interfacial plasma, high viscosities enable the generation of a stable gas–liquid interfacial plasma. Thus, the conductivity and viscosity of the ionic liquids are important factors for methane conversion under a DC discharge plasma. The Brönsted acidity of ILs depends on the acidity of the ILs anion. ILs with Brönsted acidity can dissolve radicals and, due to the fact that methane conversion under a DC discharge plasma is a radical process, can promote methane conversion and improve product selectivity. In addition, due to the unique properties of ionic liquids such as their high conductivity, ionic liquids can be regarded as a liquid electrode for discharge plasma in our experiments.