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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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