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Review

Hydrogen production from alcohols and ethers via cold plasma: A review

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ABSTRACT

Hydrogen is one of the most promising energy and the fuel for fuel-cell-powered automobiles. Liquid fuels have been considered as the most suitable source for onboard hydrogen production, and cold plasma is proved to be a potential way to convert them. In this review, the conversion of methanol, ethanol and dimethyl ether (DME) using different types of cold plasma has been summarized. Hydrogen is the main product with different by-products depending on reaction conditions. The conversion of liquid fuels for hydrogen production via cold plasma has good prospects, and reaction conditions optimization and reactor design are very important for its future application onboard.

Introduction

Hydrogen has attracted increased attention as one of the most promising energy source, due to the limited storage of fossil fuels and serious environmental problems [1]. The combustion of hydrogen release more heat than other fuels do, and water is the only product. This makes hydrogen a clean energy with high calorific value. In addition, hydrogen is the fuel for fuel-cell-powered automobiles [2,3]. But it is difficult to store hydrogen gas due to its low bulk density. So hydrogen production onboard is necessary. At present, thermal conversion (such as reforming and partial oxidation) of hydrocarbons and alcohols is the main approach to produce hydrogen or hydrogen-rich gas onboard [4].

Usually, the thermal conversion processes require energy input and catalysts. But catalysts often suffer from deactivation inevitably, and most of them need long warm-up time. Additionally, some of these catalysts could be very expensive. These shortcomings restrict the applications of catalytic conversion for onboard hydrogen production. In this case, cold plasma can be used to avoid the use of catalysts and shorten the warm-up time.

Plasma is seen as the four state of matter, and it mainly consists of electrons, ions and heavy particles. Plasma is generated by supplying energy to working gas (usually neutral

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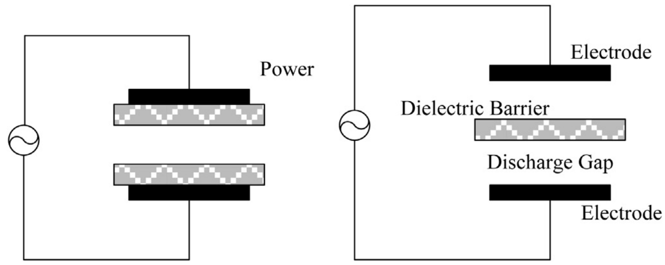

Fig. 1 – Basic configurations of DBD plasma.

gas) causing the ionization of gas. Plasma can be divided into thermal plasma and non-thermal plasma (also called cold plasma) according to the temperature of electrons [5–11]. When the temperature of electrons is lower than that of gas, the plasma is in non-thermal equilibrium and becomes cold plasma. Cold plasma has low gas temperature, but it contains a lot of highly energetic electrons. Through the collision between electrons and reactants, cold plasma can activate reactants and enhance gas phase chemistry without the need for elevated gas temperature. Thus, cold plasma can be used to convert raw materials into hydrogen for fuel cell [12].

The raw materials mostly used for onboard hydrogen production via cold plasma include methane [13–15], gasoline [16,17], heavy hydrocarbons [18,19], diesel [20,21], alcohols [22–24], ethers [25], and so on. However, methane is a gas and not easy to liquefy, so the storage of methane onboard will be a problem. Liquid fuels are more suitable here when it comes to storage issue. But gasoline, hydrocarbons and diesel all come from fossil fuels, while alcohols and ethers can be produced from biomass. Thus alcohols and ethers turn out to be the most suitable raw materials for onboard hydrogen production.

There are various ways to generate cold plasma, such as dielectric-barrier discharge, corona discharge and spark discharge [5–11]. In this review, reports relating to the conversion of methanol, ethanol and dimethyl ether (DME) for hydrogen production using cold plasma are summarized and categorized according generating ways of cold plasma.

Conversion of methanol into hydrogen via cold plasma

Methanol has high hydrogen to carbon ratio, high energy density, consistently high quality (sulfur content <5 ppm), and it is easy to handle [26]. Methanol is easy to store and ship, and can be manufactured from methane, which is abundant [27]. In addition, the conversion of methanol to hydrogen can take place at milder conditions than petroleum-based hydrocarbons. So methanol has been regarded as an attractive fuel for on-board hydrogen production [28].

Conversion of methanol using DBD plasma

The dielectric barrier discharge (DBD), also called silent discharge, is a typical way to generate non-thermal plasma at atmospheric pressure [5]. This type of plasma is generated between two electrodes with a dielectric barrier in between, and the gap between these two electrodes is small, only a few millimeters usually. DBD requires a voltage of 1–100 kV with frequencies of 50 Hz–1 MHz to maintain the discharge, while the current is depended on the dielectric material used. Three basic configurations of DBD [29] are shown in Fig. 1.

Sato et al. [30] have studied the decomposition of methanol in a non-thermal plasma flow generated by DBD with a voltage of 16–20 kV, and air was the working gas. The plasma generator they used is shown in Fig. 2. In their experiments, methanol can be 100% converted by plasma under right discharge conditions. Then the experimental data was numerically analyzed using a reaction mechanism model which consists of 108 elementary reactions and 41 chemical species. Analytical results demonstrate that OH is the most important radical to decompose methanol, and the plausible reaction pathways for methanol decomposition in air were brought up. Even thought high decomposition efficiency was achieved, they did not report the composition of the product. The hydrogen concentration and yield in their experiments is unclear.

Tanabe et al. [31] used DBD plasma generated by a low voltage of 2–6 kV to decompose methanol in Ar. The main product of methanol decomposition was hydrogen. CO or CO_2 was other major product, respectively, in the absence or presence of water in the feedstock. A maximum methanol conversion of 80% was achieved, and the hydrogen yield increased with increasing input power in the absence of water. A hydrogen yield more than 100% was achieved in the

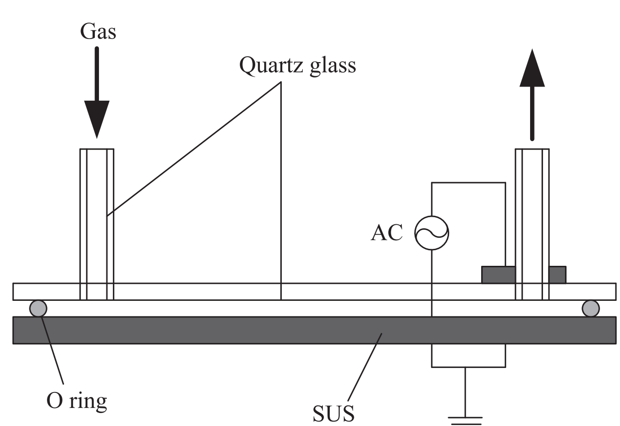

Fig. 2 – Detail configuration of DBD reactor of Sato et al. [30].