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Short Communication

A novel catalyst-free process for producing hydrogen and carboxylate from biomass-derived alcohols



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ABSTRACT

In this study, we presented an unexpected environmentally benign and easy-to-implement reaction for producing highly pure hydrogen (99.8%) and value-added carboxylate from primary alcohols under basic conditions. No catalyst was required, and no environmentally harmful gas, such as CO and CO₂, was produced. The reaction conditions, different reactants and the water tolerance of the reaction were examined. It was found that as long as the temperature is higher than 500 K, no matter what the pressure is, hydrogen and carboxylate can be produced from primary alcohols. Strong alkalinity and high solubility of the base is necessary for the reaction. It was confirmed that ethanol-water mixtures, which could be produced from biomass fermentation, can be used as feedstock in this process, making it more meaningful in terms of sustainability. The mechanism of the reaction was also investigated in detail.

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Introduction

Decreasing reserves of the fossil fuels, together with the pollution caused by the continuously increasing energy demands, has accelerated the urgency to explore clean and renewable sources of energy [1–4]. Among the alternative and advanced fuels, hydrogen shows excellence in many respects:

light weight, high energy density, zero carbon-emission and so on. Currently, hydrogen is mainly achieved from non-renewable petroleum and natural gas [5–8]. To achieve a sustainable route, great attention has been paid to the production of hydrogen from bioethanol because it can be derived readily from renewable sources [9–11]. Methods for hydrogen production from ethanol are generally as follows: steam reforming, partial oxidation, oxidative steam reforming and

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autothermal reforming [12–17]. However, high temperatures and noble metal catalysts were employed to obtain hydrogen with high purity, and the process cost would be simultaneously increased. Furthermore, these methods usually inevitably generate CO, CO₂ and some other greenhouse gases. Trace amount of CO may result in poisoning the platinum anodes in the fuel cells or the metal-based catalysts in chemical processes. Reichman et al. [18] had developed a process for producing pure hydrogen from hydrocarbon compounds with a base, while water and/or a catalyst were needed in the system, and the dehydrogenation product was carbonate. Beller and co-workers [19] reported the high efficient dehydrogenation of ethanol under unprecedented low temperatures in the presence of ruthenium complexes and pincer-type ligands, and the dehydrogenation product of ethanol was acetaldehyde. In this study, we report an unexpected reaction that alcohols can react with base at elevated temperature without any catalyst to produce pure hydrogen and carboxylate. The critical reaction conditions including temperature and pressure were investigated. Different alcohols and bases were examined. Because to our best knowledge, this reaction has never been reported previously, the reaction mechanism was investigated in detail.

Experimental

Experimental procedure

The typical experiment was carried out generally as follows: certain amount of alcohol (methanol, ethanol, n-butanol, n-octanol, n-hexadecanol, isopropanol or tertiary butanol) and alkali (NaOH, KOH, LiOH, Ca(OH)₂ or Mg(OH)₂), 30 g : 3 g for alcohol excess and 3 g : 30 g for base excess reaction, were loaded into a 110 mL Zr alloy autoclave (or in a glass liner which was embedded in a Parr autoclave), and stirred at a rate of 500 rpm under 0.1 MPa N₂ atmospheres (to eliminate the influence of O₂). The mixtures were heated to the target temperature in 30 min and reacted for 2 h, then cooled down in water bath after the reaction. Although the reactions may start at lower temperature, the reaction time was recorded when the preset temperature was reached. The temperature and pressure were recorded at different time during the reaction and after reaction. The gas generation rate and yield were calculated by Clapeyron equation [20] from the data of pressure deducting the saturated vapor pressure of ethanol under the corresponding temperature. The details can be seen in the [Supporting Information](#), Section 2.1. After reaction, the pressure was also recorded at room temperature and then the gas, liquid and solid products were collected for further analysis.

Gas analysis

An SP-6890 (Lunanruihong, China) gas chromatography with a thermal conductivity detector (TCD) and a 60–80 mesh packed molecular sieve TDX-01 column (2 m × 2 mm) was used to analysis the gas product. Argon (99.999%) was used as the carrier gas. Hydrocarbons from C₂ to C₄ were analyzed by a Fuli 9750 (Fuli Instrument, China) gas chromatography with

flame ionization detector (FID). The column was packed with 80–100 mesh Hayesep.

For analysis conditions of H₂, HD and D₂, the Al₂O₃ coated with MnCl₂ was packed into a chromatographic column for use as a separating column. High-purity helium was used as the carrier gas. The column temperature was hold at –196 °C. Varian GC-450 was equipped with a TCD detector.

Liquid analysis

The organic components of the liquid were analyzed by GC/MS (Agilent 5975C), using a 30 m × 0.25 mm × 0.25 μm HP-5MS fused silica capillary column. The injector temperature was held at 180 °C in split mode. Helium (99.999%) was used as carrier gas with a constant velocity. The oven temperature was held at 40 °C for 4.0 min and then heated to 280 °C at the rate of 10 °C/min, and held for 5.0 min at 280 °C. The mass spectrometer was operated in EI mode. Based on the National Institute of Standards and Technology (NIST) MS library, confident identification of chromatographic peaks can be achieved.

Solid analysis

Fourier transform infrared absorption (FT-IR) spectrum of the solid residues was measured at 25 °C by a Bruker EQUINOX55 FT-IR spectrometer using the KBr pellet method (Supporting Information, Section 2.5.1).

Results and discussion

This interesting reaction was found almost completely by chance when we were attempting to decompose lignocellulosic biomass in the presence of sodium hydroxide using ethanol as solvent. While the autoclave was heated, the system pressure started to increase drastically. Dramatically, analyses showed that biomass was not decomposed, but highly pure H₂ was yielded, and the main component of the solid product was determined as sodium acetate (Supporting Information, Section 2.5.1). In order to confirm that the hydrogen was formed from ethanol, another experiment, in which the reactants were merely ethanol and sodium hydroxide, was conducted and received the same result. To eliminate the catalytic effect of the impurities or even the autoclave, the experiments were performed in a glass liner which was embedded in different deeply cleaned autoclaves, and similar results were obtained. The control experiment without NaOH was also performed in the same equipment, and no gas was produced. This indicated that NaOH or OH[–] was a key factor for the H₂ production. Onwudili and co-workers [21] had reported the production of hydrogen from carbohydrate in alkaline hydrothermal media at 723 K, with a highest hydrogen yield of 76%. Meanwhile, lots of CO, CO₂ and CH₄ were generated. However, to the best of our knowledge, the dehydrogenation of alcohol in the presence of strong base without using any catalyst but just elevated temperature to produce pure hydrogen and carboxylate has never been reported to date in consulted literature.

The effect of temperature and pressure on the reaction was investigated. Moreover, to understand the stoichiometric of

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