



Low temperature catalytic reverse water gas shift reaction assisted by an electric field



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ABSTRACT

Catalytic reverse water gas shift reaction was conducted in an electric field (denoted as E-RWGS) over various catalysts at low temperature as 423 K. A platinum catalyst supported on lanthanum doped zirconia (Pt/La-ZrO₂) showed the highest yield (ca. 40%) for the E-RWGS reaction even at such low temperature condition. In contrast to a bare oxide catalyst, metal loading catalysts showed higher activities and efficiencies for the reaction. Roles of the impregnated platinum and doped lanthanum on the catalytic activity were investigated, and we found that loaded platinum worked as an active site for the E-RWGS reaction, and La doping stabilized the structure of ZrO₂. The effect of the electric field was discussed based on thermodynamic evaluation and experimental results.

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1. Introduction

Reducing carbon dioxide emission is an important issue for sustainability of the earth. Therefore, it is desired that emitted carbon dioxide is captured and reused, so called CCS (carbon dioxide captured and storage) process. For examples, utilization as a solvent for polymer synthesis, methanol synthesis [1,2], and other methods are proposed. However, each process requires high concentration of carbon dioxide. The concentration of carbon dioxide captured with chemical recovery is not so high, and further condensation such as cryogenic separation requires more energy. Therefore we focused on the utilization of carbon dioxide as a feedstock for catalytic reaction, which does not require high concentration of carbon dioxide. The catalytic immobilization of carbon dioxide as chemical products contributes to construct the carbon neutral cycle, which does not depend on plants or climate.

Our proposed carbon neutral cycle is as shown in Fig. 1. Carbon monoxide, which is a feedstock of C1 chemicals, can be produced from carbon dioxide emitted at chemical plants and electrical power generators, and hydrogen produced from renewable energies such as water electrolysis. Carbon monoxide can be converted to methanol [3–5], methane [6,7] or FT oil [8–10] with hydrogen, and these are important products and feedstock for chemical processes. However, reverse water gas shift reaction (RWGS; Eq. (1))

[11–15], which is the most important reaction in this carbon neutral cycle, requires high temperature due to thermodynamics as shown in Fig. 2.

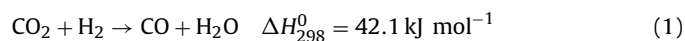


Fig. 2 shows equilibrium conversions for the RWGS reaction at atmospheric pressure. At a stoichiometric composition of the feed gas, the RWGS requires over 1000 K in order to achieve 50% of the conversion. And this carbon neutral cycle requires a water removal process after the RWGS reaction in order to prevent the deactivation for methanol synthesis. It causes a difficulty of cascade utilization of high temperature heat. Then we aimed to lower the reaction temperature with a utilization of electrical power as an external force.

We have investigated some non-conventional catalytic processes combining catalyst and electrical assist [16–22]. We have conducted methane steam reforming and methane oxidative coupling with carbon dioxide, with a utilization of an electric field, and accomplished lowering reaction temperature. In these cases, molar amount of reactants activated from an electron is more than a stoichiometric reaction. Therefore, this combined catalytic reaction is a non-Faradaic reaction like as the NEMCA (Non-Faradaic electrochemical modification on catalytic activity) [23], and has high energy efficiency. From our previous research [22], we found that lanthanum doped zirconia (La-ZrO₂) showed high catalytic activity for carbon dioxide activation in the electric field. It has been reported that the intermediate of the RWGS reaction is carbon-ate species on the catalyst surface [13–15]. And Stagg-Williams

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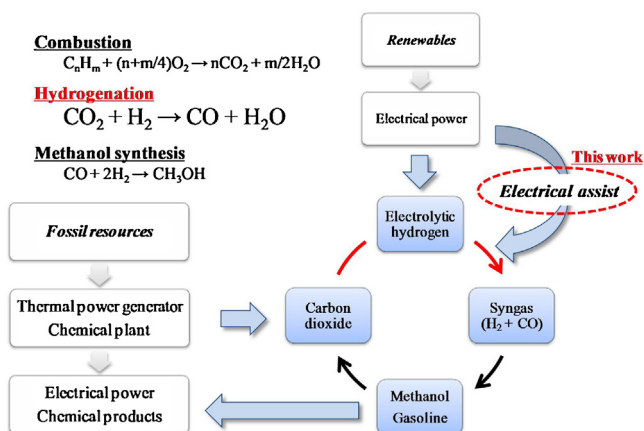


Fig. 1. Carbon neutral cycle using carbon dioxide as an energy carrier.

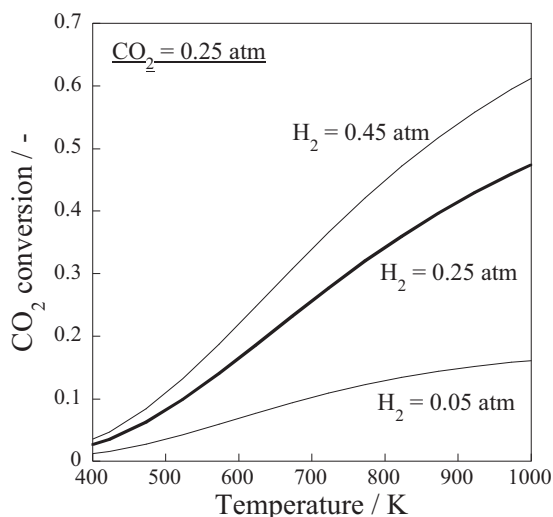


Fig. 2. Equilibrium conversion of reverse water gas shift reaction at atmospheric pressure.

et al. reported that La-ZrO₂ was an effective catalyst-support for methane dry reforming, because La promoted CO₂ dissociation [24,25]. Then, in this study, we conducted the reaction in the electric field (denoted as E-RWGS) over various catalysts supported on La-ZrO₂, and screened an effective catalyst for the E-RWGS reaction. In addition, we evaluated the energy efficiency of the system in order to propose this system as a carbon neutral cycle.

2. Experimental

2.1. Catalyst preparation

As a catalyst support, x mol%La-ZrO₂ ($x=5, 10$ or 15) and 10 mol%Y-ZrO₂ were prepared with a complex polymerized method. Precursor of each element was La(NO₃)₃·6H₂O, ZrO(NO₃)₂·2H₂O and Y(NO₃)₃·6H₂O, respectively. Each element was dissolved into distilled water with subsequent addition of citric acid and ethylene glycol. After condensation in a water bath at 353 K, the gel was stirred and heated to remove the water completely. Pre-calcination was conducted at 673 K for 2 h, and calcination was conducted at 1123 K for 10 h in air flow condition.

Pt, Pd, Ni, Fe or Cu was loaded on the catalyst support as an active metal by an impregnation method. Precursor of each element was Pt(NH₃)₄(NO₃)₂, Pd(CH₃COO)₂, Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O or Cu(NO₃)₂·3H₂O respectively. Calcination was conducted at 973 K

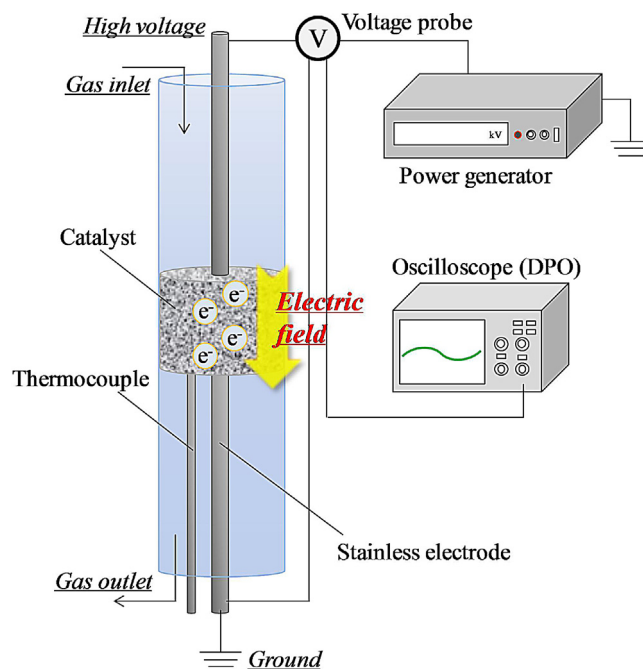


Fig. 3. Experimental setup for the reaction in an electric field.

for 3 h. The amount of the loaded metal was 1 wt% except the Section 3.2.

2.2. Activity test

The experimental setup for catalytic activity tests in an electric field is shown in Fig. 3. Two SUS304 rods (2 mm o.d.) were inserted from each end of the catalyst bed as electrodes, and a thermocouple was inserted to the catalyst bed to measure the reaction temperature in the catalyst bed. The composition of feed gas was CO₂:H₂:Ar = 25%:25%:50%, total flow rate: 100 mL min⁻¹, and the W/F was 1.6 g-cat h⁻¹ mol⁻¹ in CO₂-based. In order to remove impurities on the catalyst surface, pre-treatment was conducted before the application of the electric field at 723 K for 30 min in Ar atmosphere. A DC high voltage power supply was used to generate the electric field. The electric field was controlled with the value of input current, and the values were 3.0, 5.0 and 7.0 mA in this study. The imposed voltage waveform was monitored with a digital phosphor oscilloscope (TDS 2001C with a voltage probe P6015A; Tektronix). The imposed voltage was determined by the nature of the catalyst, the electrode gap and the atmosphere, and the value was from 1.0 to 2.0 kV in all experiments (shown in Table). The reactor was heated at 423 K to prevent the condensation of produced water. Products after passing a cold trap were analyzed with a GC-FID (GC-2014; SHIMADZU Corp.) with a Porapak N packed column after methanation by Ru/Al₂O₃ catalyst (for analyses of CH₄, CO, CO₂) and a GC-TCD with a molecular sieve 5A packed column (for analysis of H₂). In all experiments, conversion, selectivity and yield were calculated by CO₂-based.

2.3. Characterizations

As characterizations of these catalyst supports, X-ray diffraction pattern, BET specific surface area and surface atomic concentration were measured. Crystalline structure of these catalyst supports was characterized by XRD (RINT-2000; Rigaku Corp.) operating at 40 kV and 20 mA using Cu-K α radiation filtered by nickel. All catalyst supports showed a single cubic ZrO₂ structure (Space group No. 225). Specific surface area was measured using N₂ adsorption

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