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# Aqueous phase reforming of ethylene glycol over bimetallic platinum-cobalt on ceria–zirconia mixed oxide

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## ABSTRACT

The roles of cobalt promoter on the bimetallic platinum-cobalt supported on the CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide were investigated for aqueous phase reforming reaction of ethylene glycol (EG) to verify the effects of cobalt to an enhanced activity and stability of PtCo/CeO<sub>2</sub>-ZrO<sub>2</sub>, where the CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide was prepared by sol–gel method at a fixed Ce/(Ce + Zr) molar ratio of 0.4. The enhanced catalytic activity for an aqueous-phase reforming (APR) as well as water gas shift (WGS) reaction of EG was observed on the PtCo/CeO<sub>2</sub>-ZrO<sub>2</sub> at a Co/Pt molar ratio of 0.5. The higher activity and stability on the PtCo/CeO<sub>2</sub>-ZrO<sub>2</sub> at an optimal Co/Pt ratio were mainly attributed to an enhanced WGS activity and less aggregation of active metals due to a high dispersion of platinum nanoparticles with a proper interaction between platinum and oxophilic cobalt nanoparticles. A facile reduction behavior of the supported bimetallic platinum-cobalt nanoparticles through an enhanced hydrogen spill-over on the platinum nanoparticles also increased C–C cleavage reaction of EG with the suppressed deposition of inactive coke precursors on the partially reduced active nanoparticles. These synergy effects of platinum-cobalt nanoparticles with a close interaction and a less aggregation of active metals were responsible for an enhanced APR and WGS activity on the PtCo/CeO<sub>2</sub>-ZrO<sub>2</sub> at an optimal Ce/(Ce + Zr) ratio as well.

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## Introduction

Efficient catalytic systems for transforming an alternative and renewable feedstock such as biomass-derived intermediates to the value-added chemicals or environmentally-benign clean energy sources have been largely investigated due to

the limited reservoirs of fossil fuels from coal, crude oil and natural gas [1]. In addition, the biomass-derived chemicals have been known as one of the feasible and sustainable alternative feedstocks through a neutral carbon recycle without any significant emission of green-house gases such as CO<sub>2</sub> and CH<sub>4</sub> [1]. Since the biomass derivatives generally

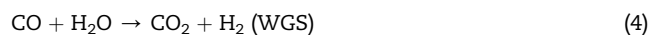
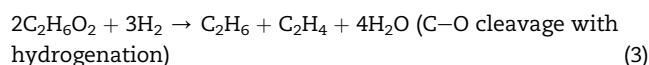
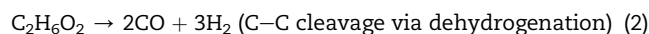
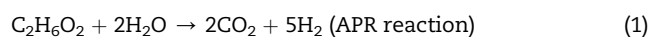
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contain a larger amount of oxygen and nitrogen atoms in the backbone structures with a high O/C ratio compare to fossil fuels, the promising catalytic systems for an efficient conversion of biomass derivatives are still under investigation largely around the world. To reduce high O/C content, aqueous phase reforming (APR) reaction of the biomass-derived intermediates to hydrogen has been reported as an efficient catalytic system working at a lower reaction temperature with a high production rate of hydrogen compare with other conventional steam reforming reactions of hydrocarbon sources. APR reaction has been generally conducted at a temperature range of 200–250 °C and a pressure of 2.5–4.5 MPa, which are much mild reaction conditions compare with the methane steam reforming reaction [2–4]. Among some transition metals, Pt, Ru, Pd, Ni and Rh metals have been reported to have a high catalytic activity for APR reaction [5], and APR reaction is composed with various reactions such as C–C or C–O bond cleavage by (de)hydrogenation and water gas shift (WGS) reaction as summarized in Eqs. (1)–(4) using a biomass-derived model substrate of ethylene glycol (EG, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>).



Aqueous-phase hydrodeoxygenation (HDO) reaction for C–O bond cleavage in the biomass-derived intermediates has been known to be more favorable under hydrogen-rich condition to light hydrocarbons (Eq. (3)). During APR reaction, C–C bond cleavage (Eq. (2)) with a subsequent WGS reaction (Eq. (4)) as well as HDO reaction (Eq. (3)) can also proceed simultaneously as side reactions [6–10]. For APR reaction of ethylene glycol (EG) (Eq. (1)), the dehydrogenation generally occurs over the supported active metallic sites by forming the hydrogenated ethylene glycol intermediates [6–8], and dehydrogenated intermediates can be converted into hydrogen or final products via C–O bond cleavage through a facile hydrogenation reaction. The C–O and C–C bond cleavages of EG have been reported as competitive reactions, which lead to form the deoxygenated functional organic products such as alcohols, ketones, aldehyde, carboxylic acid and so on through many side reactions. The competitive C–C and C–O bond cleavages were strongly affected by the exposed amount of active metals and their metal-support interactions as well [10].

In our earlier report [9], we have observed that Pt-loaded CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide at a molar ratio of Ce/(Ce + Zr) = 0.4 showed a superior activity wherein the amount of defect sites of CeO<sub>2</sub>-ZrO<sub>2</sub> support altered the dispersion of active platinum metal by forming the strong interaction between platinum

nanoparticles and CeO<sub>2</sub>-ZrO<sub>2</sub> support [9,11]. A variation of these defect sites known as F-Center also changed the dispersion of active metals over the support largely [12–16]. Compared to single metal supported catalysts, some bimetallic catalysts have many advantages such as a resistance of coke formation by enhancing catalysts life time and a high selectivity toward desired final products as well [17]. For Pt–M bimetallic catalysts, efficient promoters of second metals (M) namely Pd, Ni, Co, Fe, Mo and Re have been reported in the literatures [2,17–21]. Even though the Pt-Co bimetallic catalysts for many hydrocarbon reforming reactions have been largely investigated, there are only few reports for APR reaction using a model component of EG over Pt-Co/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst for optimizing the amount of cobalt promoter as far as we know. In the present investigation, the platinum-cobalt supported on the CeO<sub>2</sub>-ZrO<sub>2</sub> mixed metal oxides was investigated for APR as well as WGS reaction to verify the roles of cobalt promoter of the bimetallic Pt-Co/CeO<sub>2</sub>-ZrO<sub>2</sub> for the enhanced activity and stability.

## Experimental section

### Catalyst preparation and activity test

The CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide with a Ce/(Ce + Zr) molar ratio of 0.4 was prepared through sol–gel method as precisely reported in our previous work [9]. In more detail, a desired amount of each metal precursors of cerium (III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Sigma–Aldrich) and zirconium (IV) oxychloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, Kanto chemical) was separately dissolved in deionized water. With a through mixing of metal precursors, a citric acid was dissolved in EG, and they were vigorously stirred at 60 °C till making a clear solution at a molar ratio of metal precursor/citric acid/ethylene glycol = 1/5/5. All mixed solutions were thoroughly agitated at 110 °C for 6 h, and as-prepared gel was calcined under air flow at 600 °C for 4 h. The synthesized CeO<sub>2</sub>-ZrO<sub>2</sub> supporting material having a Ce/(Ce + Zr) molar ratio of 0.4 was denoted as CZ. For further preparing platinum-cobalt mixed metal supported on the CZ, two metal precursors of tetraammineplatinum(II) nitrate (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, Alfa Aesar) and cobalt(II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Samchun) were co-impregnated on the CZ support. A amount of active platinum metal was fixed at 3 wt% based on the weight of CZ support, and cobalt metal promoter was simultaneously impregnated at a different molar ratio of Co/Pt from 0 to 2. As-prepared bimetallic Co-Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> after the calcination under air environment at 350 °C for 2 h was finally denoted as the PtCo(x)/CZ, where x represents the molar ratio of Co/Pt metal.

APR reaction of EG was carried out in a fixed-bed tubular reactor at the reaction conditions of T = 250 °C, P = 4.5 MPa and space velocity (SV) = 2.0 h<sup>-1</sup> for 20 h on stream. 0.3 g of PtCo/CZ was loaded in the reactor followed by reducing at 350 °C for 2 h using 5 vol% H<sub>2</sub> balanced with N<sub>2</sub>. EG reactant was selected as a model component from the biomass-derived chemical intermediates to simply elucidate the roles of the supported bimetals on the CeO<sub>2</sub>-ZrO<sub>2</sub> due to its well-known dissociation mechanisms and simple chemical structure. A

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