Co-CeO2 Catalyzed Water-Gas Shift Reaction

Subjects: Others

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$Co\text{-}CeO_2$ catalysts were synthesized by the different methods to derive the optimal synthetic method and to investigate the effect of the preparation method on the physicochemical characteristics of $Co\text{-}CeO_2$ catalysts in the high-temperature water-gas shift (HTS) reaction. $Co\text{-}CeO_2$ catalyst synthesized by a sol-gel method features the strong metal to support interaction and the largest amount of oxygen vacancies compared to other catalysts, which affects the catalytic activity. As a result, $Co\text{-}CeO_2$ catalyst synthesized by the sol-gel method exhibited the highest WGS activity among the prepared catalysts, even in the severe conditions (high CO concentration: ~38% in dry basis and high gas hourly space velocity: 143,000 h^{-1}).

waste-derived synthesis gas
high-temperature water-gas shift
Co-CeO2 catalyst
preparation method
oxygen vacancy

1. Introduction

Economic development and population growth have increased the amount of globally generated waste, which is expected to rise from 2.0 billion tons per year in 2016 to 3.4 billion tons per year in 2050 [1][2]. Consequently, much attention has been directed at the development of waste to energy technologies such as waste gasification to reduce the extent of landfill depletion, environmental pollution, and waste treatment costs [3][4][5]. Notably, waste gasification can reduce waste mass (by ~80%) and volume (by ~90%), save landfill space, and decrease the emission of pollutants such as NO_x and SO_x [3].

Waste gasification typically affords synthesis gas (H_2 and CO), which can be used to generate value-added products such as synthetic crude oil, methanol, and dimethyl ether, and can also be employed as a substitute of reformed natural gas for pure H_2 production through the water-gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) [4][6][7][8][9].

The growing importance of fuel-cell-based vehicles and related devices has increased the demand for H_2, used as a fuel in fuel cells [10][11][12][13]. However, more than 96% of H_2 is generated from natural gas- and petroleum-derived sources (i.e., from fossil fuels), which highlights the need for practical alternative sources such as waste. In particular, combustible waste with minimum calorific value (4000–5000 kcal kg^{-1}) can be gasified to afford synthesis gas containing CO (~38%) and H_2 (~28%), along with relatively small amounts of CH_4, CO_2, N_2, and other impurities [14].

The WGS reaction is exothermic and is thus favored by low temperatures. Therefore, according to thermodynamic limitations and kinetic aspects, the WGS reaction can be conducted in two distinct temperature ranges, namely at 350–550 °C (high-temperature shift, HTS) over Fe_2O_3–Cr_2O_3 and at 190–250 °C (low-temperature shift, LTS) over CuO–ZnO–Al_2O_3 [15][16]. Due to the high outlet temperature of the waste gasification process (>500 °C), HTS is better suited for H_2 production through waste gasification than LTS [17][18]. However, commercial Fe_2O_3–Cr_2O_3 catalysts are not suitable for the HTS reaction of waste-derived synthesis gas, as the high CO levels of this feedstock (~38% CO, cf. ~9% CO of natural gas-derived synthesis gas) may lead to rapid catalyst deactivation [19]. Hence, customized catalysts for waste-derived synthesis gas processing are highly sought after. Furthermore, upon operation, Cr^{3+} present in fresh Fe_2O_3–Cr_2O_3 catalysts is oxidized to Cr^{6+}, which may leach out from spent catalysts to cause environmental and health problems [8][20]. For this reason, the replacement of Cr for other metals in commercial HTS catalysts is also required [21].

2. Result

Previously, we have developed a Co-based catalyst for H_2 production from waste-derived synthesis gas via the HTS reaction, showing that this catalyst exhibits high activity in a wide temperature range and at high gas hourly space velocity (GHSV) to demonstrate the feasibility of using Cr-free catalysts [22][23][24][25]. Compared to the unsupported Co_3O_4 catalyst, CeO_2-supported Co catalysts featured enhanced stability and redox activity [22][23]. This behavior was attributed to the strong interaction between Co and the CeO_2 support, which prevented the sintering of the Co^0 active phase [17][25]. In addition, the large amount of oxygen defects in the Co–CeO_2 catalyst resulted in high CO conversion [24].

In general, CeO_2 is known as an active substance that drives water dissociation in the WGS reaction. Additionally, it shows unique redox properties and promotes the formation of oxygen vacancies. The formation of oxygen vacancies can be interpreted as the generation of mobile oxygen on the CeO_2 surface, improving the catalytic activity in the WGS reaction [22]. In addition, CeO_2 features the improved oxidative strength and photoelectronic activity due to unique solid-state reactivity of Ce [26]. Arena et al. developed the nanocomposite $MnCeO_x$ catalyst, and proved that Ce promotes the dispersion of the active metals and the exposure of the active sites at the surface of the catalyst [27][28][29][30][31]. As has been widely reported, the use of CeO_2, which has unique properties in a variety of catalytic chemical reactions including the WGS reaction, is prevalent. Accordingly, changes in redox properties and oxygen storage capacity (OSC) of catalysts by applying the Ce have been investigated in various literatures. The Co_3O_4 catalyst for total oxidation of propene enhanced the mobility of lattice oxygen by applying the CeO_2 support, and the mobile oxygen reacts with the propene, showing high catalytic activity [32]. Au/CeO_2–ZnO/Al_2O_3 catalyst showed excellent performance in the WGS reaction because of the enhanced oxygen storage capacity and reducibility [33]. The Au/Co_x/CeO_2–Al_2O_3 catalyst showed outstanding activity in the CO oxidation reaction due to the superior redox properties and oxygen storage/release properties of CeO_2 [34].

Many attempts have been made to enhance catalyst performance through the optimization of preparation methods [35][36][37][38][39][40][41][42]. Wang et al. prepared MgAl catalysts for dehydroxylation by a sol-gel technique, showing that the generation of oxygen defects is influenced by the choice of synthesis method [35]. Kakihana et al. observed that the sol-gel method affords catalysts with higher homogeneity/purity in the form of powders with submicron particle size [36]. In addition, the sol-gel method has also been reported to be highly economical because of the reduced catalyst preparation time and cost [37]. Avgouropoulos et al. ascribed the improved catalytic performance of hydrothermally prepared CuO–CeO_2 catalysts for the selective CO oxidation to the high dispersion of CuO and its strong interaction with the CeO_2 support [38]. The enhanced CO oxidation activity of the co-precipitation-prepared catalyst was attributed to the increased surface area of CeO_2 and the enhanced redox properties due to Ce–Fe–O solid solution formation [39]. Megarajan et al. claimed that the high diesel soot oxidation activity of a Co_3O_4–CeO_2 catalyst prepared by incipient wetness impregnation was due to the high dispersion of Co_3O_4 nanoparticles on the CeO_2 support [40]. Although the preparation method strongly affects catalyst performance, no related research has been conducted in the case of Co-based catalysts for the HTS reaction using waste-derived synthesis gas.

In the present study (https://doi.org/10.3390/catal10040420), we probed the effects of the preparation method (sol-gel, co-precipitation, incipient wetness impregnation, and hydrothermal) on the physicochemical characteristics of Co-CeO_2 catalysts and established an optimal preparation method by comparing their activities for the HTS reaction using waste-derived synthesis gas.

Co-CeO_2 catalysts prepared by various synthetic methods were used to promote the HTS reaction of waste-derived synthesis gas, with the best performance observed for Co-CeO_2 catalyst prepared by sol-gel (SG), even under harsh conditions (GHSV = 143,000 h^{-1}, CO level = 38.2%). The high performance of Co-CeO_2 (SG) catalyst was explained as follows. First, oxygen vacancy concentration affects the HTS reaction. Raman spectroscopy, XPS, and H_2-O_2 pulse reaction results showed that Co-CeO_2 (SG) catalyst had the highest concentration of oxygen vacancies among the prepared catalysts. As the WGS reaction primarily proceeds through a redox mechanism, it is strongly influenced by the concentration of oxygen vacancies. Second, the SMSI effect is important for catalytic reactions. According to TPR results, the CoO reduction temperature was highest for Co-CeO_2 (SG) catalyst, which was ascribed to the SMSI of this catalyst. As a result, the Co-CeO_2 (SG) catalyst showed the outstanding catalytic activity in the HTS reaction despite the extremely high GHSV and CO concentration.

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