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Effect of Re addition on the activities of Co/CeO_2 catalysts for water gas shift reaction

Kingkaew Chayakul, Tipaporn Srithanratana, Sunantha Hengrasmee*

Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

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ABSTRACT

The catalytic activities of Re–Co/CeO_2 bimetallic catalysts for the water gas shift (WGS) reaction were investigated and compared with activities of Co/CeO_2. It was found that the rate of WGS reaction over Re–Co/CeO_2 bimetallic catalysts was higher than that of a single catalyst of Co on ceria. It seems that Re influences the catalysts and the catalyst performance in several ways. XRD and Raman spectroscopy results indicate that metal oxides were dispersed on ceria surface and H_2-chemisorption indicated better dispersion of Co on the ceria surface upon addition of Re. X-ray absorption near edge structure (XANES) spectra of Re–Co/CeO_2 indicate that Re promotes the reduction of surface ceria to Ce_2O_3 and provides oxygen vacancies that facilitate the redox process at the surface. XANES also indicated that electron densities were withdrawn from Co d-state to Re, leading to weaker Co-adsorbate bonds. All of these effects contribute to an increase in the WGS reaction rate.

1. Introduction

The water gas shift (WGS) reaction is an important step in reducing the amount of CO from H_2 feed gas that will be used in fuel cells. H_2 feed gas is obtained as the major product of a reforming reaction together with a small amount of by-products such as CH_4, H_2O, and CO. Among these impurities, CO is poisonous to the Pt electrode in a PEM fuel cell and decreases Pt activity. Removal of CO from the feed gas is necessary, and the water gas shift reaction which can reduce the amount of CO to less than 0.5–1% is a candidate for this step.

In the WGS reaction, carbon monoxide is converted to carbon dioxide by water vapor. The WGS reaction is described by the following reaction,

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -41.2\,\text{kJ/mol}$$

This reaction is exothermic and the rate equilibrium conversion is lower with increasing temperature. In order to keep good conversion rates at low temperature, catalysts must be employed.

The catalysts that are widely used are metal–ceria based catalysts [1–6]. Ceria (CeO_2) is a suitable support due to its high oxygen storage capacity, high reducibility and high oxygen mobility [7–11]. Many precious metals such as Pt, Pd, Rh, Ru and Au have been reported to show high WGS reaction rate when they are doped on ceria supports [12–21]. Among these metals, Pt and Au which are rare and expensive are the most promising promoters because of their better catalytic activity at low temperature. Many research groups are trying to develop new types of catalysts from metals that are less expensive and more abundant. Many studies have shown that a combination of two metals can provide rather good WGS activities. Many bimetallic systems have been studied for many reactions, for example Pt–V/CeO_2, Pt–Re/CeO_2–ZrO_2 and Au–M on iron(III) oxide (M = Ag, Bi, Co, Cu, Mn, Ni, Pb, Ru, Sn and Tl) have been found to increase the rates of WGS reactions [22–26], while Pt–Sn/Nb_2O_5 is also active for selective CO-oxidation [27,28]. Among the second metals that have been used to form bimetallic catalysts, Re is the most widely studied. Apart from increasing the WGS rate, Pt–Re/carbon has also been reported to be active for many other reactions such as hydrocarbon reforming [29] and conversion of glycerol to synthesis gas [30]. Our initial investigation found that Re also increased the rate of WGS reaction when it was doped on Co/CeO_2.

The manner in which Re improves the catalytic performance varies. For the WGS reaction, Choung et al. [23] indicated that the effect was partly due to better dispersion of Pt on the support, but the actual role was more complex. Iida and Igarashi [25], in comparing the rate of WGS reaction of Pt–Re/TiO_2 (rutile) and Pt–Re/ZrO_2, indicated that the effect of Re on Pt dispersion and catalytic activity was largely affected by the state of the Re. In a recent paper on conversion of glycerol by Pt–Re catalysts [30], Re was reported to participate in weakening the binding energy of CO to the neighboring Pt sites. X-ray absorption spectroscopy was employed to study the oxidation state of Re and Pt. Hilbrig et al. [31] demonstrated that X-ray absorption near edge structure (XANES) can be used to determine the degree of reduction/interaction of bimetallic catalysts and

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* Corresponding author. Tel.: +66 43202222x12243; fax: +66 43202373.
E-mail address: sunhen@kku.ac.th (S. Hengrasmee).

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reported XANES-TPR studies of Pt–Re/Al_2O_3 and silica-supported Pt/Ni catalysts [31,32]. Apart from identifying the binding energies and oxidation state, XANES can also indicate changes in electron density of the metal d-band. Study of Pd L_3 near-edge absorption in Ag-promoted Pd catalyst indicated increases in the Pd d-band electron densities upon addition of Ag [33]. Pereira et al. [34] used XANES to study bonding of CO on Pt-based bimetallic catalysts and found increases of Pt 5d-band vacancies for Pt–M/C bimetallic catalysts, which indicated a lowering of electron back-donation to the CO molecules. In studying the activity of Re–Co/alumina in the Fischer–Tropsch reaction, Re was reported to be a reduction promoter that facilitated the rate of reduction of cobalt species interacting with the support and generated more available active cobalt metal sites to participate in the reaction [35].

In WGS reaction, the oxidation–reduction process is one of the rate limiting steps that control the reaction rate. Many studies reported that the reducible support (CeO_2, ZrO_2, TiO_2, etc.) is usually used due to its participation in enhancing the WGS reaction. CeO_2 can store and release oxygen to undergo oxidation–reduction cycles and promote catalytic activity for this reaction. Several studies have reported that metal-modified ceria has a higher oxygen storage capacity and reducibility than pure ceria [36–38]. Sanchez and Gazquez [39] proposed that oxygen vacancies in the fluorite structure of the supported catalysts alter the morphology and dispersion of the supported metal. In an attempt to dope Pt/CeO_2 catalysts with many metal cations, Panagiotopoulou and co-worker [40] reported that the WGS activities of Pt/Ce–Me–O catalysts (Me = metal cations) depended on the nature of the dopants employed and the promotions affected the reducibility and oxygen ion mobility of the CeO_2 support. Creation of oxygen vacancies lead to an improvement of oxygen mobility from the support to the adsorbed species on the catalyst surface.

In this paper, we report the enhancement of WGS reaction rate when Re is doped to Co/ceria catalysts. The catalysts were prepared by the incipient-wetness impregnation method and characterized by X-ray diffraction (XRD), N_2-adsorption, H_2-chemisorption, Raman spectroscopy and H_2-temperature programmed reduction (H_2-TPR). XANES of the catalysts was employed to investigate the movement of metal d-electrons in the catalysts.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation of support

CeO_2 support was prepared by the urea gelation method which was similar to the process described by Kundakovic and Flytzani-Stephanopoulos [5] and Bickford et al. [41]. An appropriate amount of cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99%, Aldrich) and 12 g of urea (H_2NCONH_2, 98%, Aldrich) were dissolved in 100 mL of deionized water. The mixture was stirred and heated at 100–120 °C until the salts were dissolved. While the mixture was heated, 2 mL of ammonium hydroxide (NH_4OH, Aldrich) was added dropwise to obtain a yellow precipitate. The suspension was heated and stirred for 4 h to remove excess ammonia and to age the support. After aging, the precipitate was filtered and washed with boiling deionized water. The filtered support was dried overnight at 110 °C in a furnace and calcined at 450 °C for 4 h.

2.1.2. Preparation of catalysts

The incipient wetness impregnation method with a minimum amount of solvent was used to prepare the catalysts. The desired amounts of ammonium perrhenate (NH_4ReO_4, 99%, Aldrich) and cobalt(II)nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 98%, Carlo Erba) were dissolved in a minimal amount of deionized water. The solution was added dropwise to the prepared CeO_2 support. The impregnated supports were dried at 110 °C overnight and calcined at 650 °C for 8 h.

2.2. Catalyst characterization

2.2.1. Standard characterization

XRD patterns of ceria based catalysts and all doped metal–ceria based catalysts were obtained from Bruker XRD D8 Advance GX 280 with Cu K_α radiation of wavelength 1.5406 Å. The diffractograms were recorded in the range of $2\theta = 20{-}80^\circ$ with a scan speed of 0.5 s per step. The crystalline sizes of the samples, d_{hkl}, were estimated from Scherrer's equation

$$d_{\mathrm{hkl}} = \frac{0.9\lambda}{\mathrm{FWHM}\ \cos\theta} \tag{1}$$

where λ is the X-ray wavelength of Cu K_α radiation (1.5406 Å), FWHM is the broadening (in radians) at half-maximum of the (1 1 1) crystallographic plane which is the most intense peak and θ is the diffraction angle corresponding to the (1 1 1) plane. Lattice parameter (a) is calculated by Bragg's equation with the same crystallographic plane.

The specific surface areas of the catalysts were obtained from the N_2 adsorption isotherm at 77 K using the Brunauer Emmett Teller (BET) method by Quantachrome Autosorb 1-C instrument. The catalysts were degassed at 300 °C for 3 h prior to an adsorption experiment. The specific surface area was calculated by the multipoint-BET method and the average pore volume and diameter were determined at relative pressure $P/P_0 \sim 0.99$.

H_2-chemisorption of all catalysts was studied by Quantachrome Autosorb 1-C instrument. The catalysts were first pretreated by Helium at 120 °C (rate 20 °C/min) for 30 min, then H_2 (99.999%, Thai Industrial Gas) was flowed over the sample while the temperature was raised at the rate of 20 °C/min to reach 350 °C and was held at this temperature for 120 min. After sample preparation, the sample was cooled down under vacuum to room temperature (40 °C). The adsorbing gas (H_2) was sequentially added to the sample. An adsorbed volume (V) vs. Equilibrium pressure (P/P_0) isotherm was generated. The H_2 chemisorbed and the percentage of metal dispersion can be deduced from this chemisorbed isotherm. The method used to obtain the volume of monolayer uptake (V_{m}) is an extrapolation method. The monolayer of hydrogen uptake (N_{m}) is expressed in μmol of hydrogen per gram of sample, that is

$$N_{\mathrm{m}} = 44.61 V_{\mathrm{m}} \tag{2}$$

where V_{m} (cc/g) is determined by extrapolating the isotherm to zero pressure. The percent metal dispersion (D) can be estimated from the equation

$$D = \frac{N_{\mathrm{m}} S M}{100 L} \tag{3}$$

where S is the adsorption stoichiometry of H_2 which is equal to 2, M and L are the molecular weight of loading metal and percent loading of the supported metal, respectively.

2.2.2. Raman spectroscopy

The Raman spectra of all catalysts were recorded by Jobin Yvon T 64000 Raman spectrometer equipped with BX51 Olympus optical microscope. The Raman spectrometer was used to observe the vibrational mode of prepared catalyst powder and the vibrational signal was detected by Charge Coupled Device (CCD) detector. The samples were irradiated by Ar ion laser with an output power 30 mW and wavelength of 514.532 nm. The Raman spectra were collected in the range of 200–2000 cm^{-1}.