



Pre-reduction and K loading effects on noble metal free Co-system catalyst for water gas shift reaction



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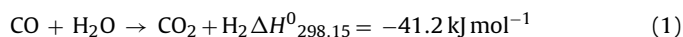
ABSTRACT

Water gas shift (WGS) reaction over a noble metal free Co-system catalyst was investigated. Although K/Co₃O₄ showed no WGS activity with no pre-treatment, it showed high and stable activity after reduction by CO + H₂ (syngas). Moreover, the high activity was retained even after post-treatment in water vapor. Characterization of the catalyst was conducted using XRD, XPS, and XAFS, which revealed that conducting pre-reduction, especially using CO + H₂ caused the formation of Co₂C, which is a potential candidate as an active site, and that K donated electrons during reduction to form stable Co₂C, suppressing the formation of metallic Co. The catalyst has high competence in activity with noble metal WGS catalysts and conventional LTS catalyst, which can be a promising candidate for a WGS reaction catalyst.

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1. Introduction

The water gas shift (WGS) reaction for carbon monoxide removal has been investigated over the years, along with the development of the steam reforming reaction. WGS is an important reaction for hydrogen production for polymer electrolyte fuel cell (PEFC) or other hydrogen production processes. Furthermore, considering carbon capture and sequestration (CCS) in hydrocarbon utilization, WGS is an important reaction for this purpose. The reaction equation is shown below.



Most industrial hydrogen production processes include two WGS stages for removing CO at a high rate. In the first step, high-temperature shift (HTS) proceeds at 590–730 K, accompanied by Fe–Cr catalyst. The next step, low-temperature shift (LTS) proceeds at 320–573 K, accompanied by Cu/Zn catalyst [1]. For HTS, the reaction is regulated by thermodynamic equilibrium because the WGS reaction is exothermic. For LTS, the required amount of catalyst is extensive for achieving low CO concentration [2] because the reaction order for CO is close to 1. It is necessary to develop a WGS process that proceeds in a one-step reaction, and to develop a catalyst that is stable at rather low temperatures, with high tolerance to an oxidative condition in steam or air.

Many works for WGS catalysts have been reported in the past three decades. Noble metals reportedly enhance the activity of metal-based catalysts [3–6], but their scarcity raises the price of metals, creating concerns when applying the catalyst in an industrial setting. Furthermore, several combinations of metals have been reported as candidates for use as LTS catalysts [7–11]. Co catalysts are known to be highly active for WGS at high temperatures [12–14]. We have proposed a Co-system catalyst: Pd/K/Co₃O₄ [15] and have reported that it shows highly stable WGS activity. The catalyst, however, includes palladium, a noble metal described above. Therefore, we investigated noble metal free K/Co₃O₄ catalyst with various pretreatments. Although it shows no activity with no pre-reduction, CO + H₂ pre-reduction enabled the catalyst to show high activity, even without noble metals. Potassium loading and the pre-reduction mode are necessary for the catalyst to show high activity. Therefore, the active structure and the effect of K loading along with CO + H₂ pre-reduction over the catalyst were investigated. Moreover, the conventional LTS catalyst (Cu/Zn system described above) is known to degrade after repeated oxidation and reduction. Particularly, the effects of steam in air are unavoidable when catalysts are used in industrial systems. Therefore, we also compared the robustness of K/Co₃O₄ catalyst with Cu/Zn catalyst.

2. Experimental

2.1. Catalyst preparation method

Each Co-system catalyst was prepared using impregnation with Co₃O₄ (Kanto Chemical Co. Inc.) as a support. K was loaded using an

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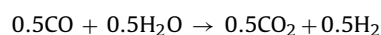
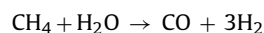
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aqueous solution of K_2CO_3 as a precursor. Details of the preparation methods applied are described elsewhere [15]. The loading amount of potassium was changed in the range of 0.20–5.89 wt%.

To compare the activity of our catalyst with that of conventional LTS catalyst, we prepared a model Cu/Zn catalyst using a co-precipitation method [16–19]. An aqueous solution containing copper and zinc nitrates ($Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$; molar ratio is 1.0) and an aqueous solution of sodium carbonate was added simultaneously to water with constant stirring. The precipitation temperature was maintained at 338 K. The obtained precipitate was filtrated and washed with distilled water. Then, dried at 393 K for 12 h, and calcined in air at 623 K for 2 h.

2.2. Catalytic activity tests

Activity tests were conducted using a fixed bed flow reactor. In a standard condition, 40 mg of catalyst were packed in a glass tube (8 mm diameter) with quartz wool and set in a furnace. Catalytic activities for all catalysts were evaluated in a pseudo-kinetic condition (i.e., not high conversion, not close to thermodynamic equilibrium of WGS). The furnace was heated to 573 K at a heating rate of $10 K min^{-1}$. Inert gas was Ar/He. The composition of pseudo-WGS gas was $CO:H_2O:H_2:Ar:He = 10:50:70:33:147$. The composition of the reaction gas was determined considering an ideal gas composition of methane steam reforming and consecutive partly shift (50%) by WGS.



The total flow rate was 310 SCCM. The reaction tube was connected to a Q-Mass (Model QGA; Hiden Analytical Ltd.) while the exit gas was measured. The pre-reduction conditions were the following: 3.3% CO + 23% H_2 or 23% H_2 with a flow rate of $300 mL min^{-1}$ for 200 min. The reproducibility of activity data was confirmed by the same experiments for many times, and the accuracy was within ± 2 points.

2.3. Characterization of catalysts

BET measurements were conducted using a nitrogen physisorption apparatus (Gemini VII; Micrometrics Inc.). Each sample was pretreated at 523 K in N_2 flow for 2 h before measurements. The specific surface area was measured at 77 K with liquid nitrogen. It was calculated using the BET method.

Powder XRD patterns of each catalyst (after pre-reduction using CO, H_2 , and CO + H_2) were recorded using SmartLAB (Rigaku Corp.) equipped with Fe- $K\alpha$ radiation over the range of 10–120°, 40 kV at 20 mA. The scan rate was 40°/min.

XPS analyses were conducted (PHI-5000 VersaProbe II; Ulvac-Phi Inc.), with 25 W Al $K\alpha$ emission as the X-ray source. Each catalyst was treated with 3.3% CO + 23% H_2 (200 min), or other reducing agents and cooled to room temperature during inert flow before analysis. Binding energies were calibrated with a C 1s peak at 284.8 eV.

To observe the fine structure of Co, X-ray absorption fine structures (XAFS) were observed at the BL14B2 station at SPring-8 (Hyogo, Japan) using a transmission method. The catalyst was pressed into a pellet (7 mm ϕ). Each sample was diluted with BN, and was reduced using CO + H_2 using the same conditions as those for pre-reduction for activity tests, and was cooled to room temperature in He purge. Then the pellet was packed into a gas-barrier bag in N_2 atmosphere, and measurement was conducted as it was. The XAFS data were analyzed using Athena software. The Fourier

transformation of each k^3 -weighted EXAFS spectrum was obtained in the k -range of 0.3–1.2 nm^{-1} .

3. Results and discussion

3.1. Activity test

3.1.1. Effect of pre-reduction over Co-system catalysts

First, it is noteworthy that K/ Co_3O_4 shows no WGS activity if it is not pre-reduced. Reduction of the support (Co_3O_4) was necessary for the catalyst to show WGS activity. We examined activity tests with various pre-reduction conditions using K/ Co_3O_4 . Additionally, we prepared Cu/ZnO as a model for industrially used LTS catalyst. We compared the activities of 0.78 wt%K/ Co_3O_4 , Co_3O_4 , and Cu/ZnO; pre-reduction was conducted using H_2 or CO + H_2 . Results are presented in Fig. 1. The K/ Co_3O_4 catalyst pre-reduced with syngas (CO + H_2) showed high and stable WGS activity. However, K/ Co_3O_4 pre-reduced by H_2 showed no high WGS activity at the initial stage of the reaction. The catalytic activity on the catalyst pre-reduced by H_2 still increased during the test for three hours, on the other hand, the catalyst pre-reduced by CO + H_2 showed very high activity from the initial stage of the reaction. This shows an advantage of the reduction by CO + H_2 . Bare Co_3O_4 catalyst showed less or no WGS activity at all pretreatment conditions. TG results (Supporting data Fig. S1) showed that reducing Co_3O_4 using CO + H_2 brought the catalyst into metallic Co. Our previous research revealed that Co metal shows no WGS activity [15]. K/ Co_3O_4 pre-reduced by syngas (CO + H_2) also showed high selectivity to CO_2 and H_2 more than 99% (not shown), and carbon deposition was under the detection limit of a temperature programmed oxidation apparatus. In the same pre-reduction condition, Cu/ZnO showed lower activity. Carbon balances were in 99.5%–100.5% for all experiments. Selectivity to methane formation was negligible small (<0.1%) for K-loaded Co-catalysts.

Hydrogen has high reducing ability. Co_3O_4 was reduced to metallic Co, as described later in 3.2.1. Furthermore, reduced metallic-Co seems to have less or no WGS catalytic activity from these results. Potassium loading seems to suppress excess reduction of the Co. Potassium has the effect of stabilizing the activity and the structure of the catalyst. K/ Co_3O_4 pre-reduced only by CO also showed high activity, as shown in Supporting data Fig. S2. However, considering an industrial use of the catalyst, pre-reduction by only CO is not feasible. CO + H_2 is popularly used as syngas. Ultimately, we can obtain syngas from the exit side of the steam reforming reaction. Therefore, it is more convenient to use CO + H_2 than CO as

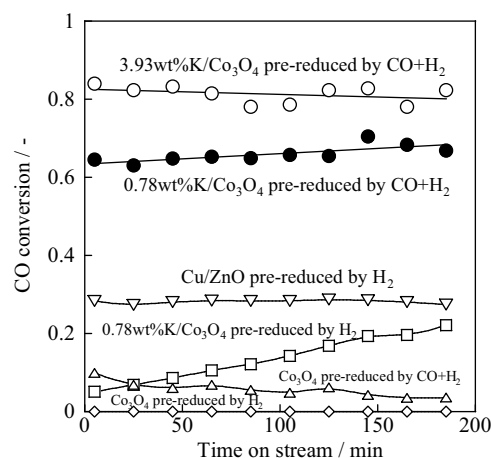


Fig. 1. Activity tests over K/ Co_3O_4 and Cu/ZnO, 40 mg of catalyst were charged in the reactor.

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