



Promoting effect of small amount of Fe addition onto Co catalyst supported on α -Al₂O₃ for steam reforming of ethanol

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ARTICLE INFO

Article history:

Received 27 January 2010

Received in revised form 20 May 2010

Accepted 20 May 2010

Available online 27 May 2010

Keywords:

Steam reforming of ethanol

Promotion effect of iron

Cobalt catalyst

ABSTRACT

We examined the promotion effect of loading small amounts of Fe onto various Co catalysts for steam reforming of ethanol. Among these catalysts, catalysts supported on SrTiO₃ and α -Al₂O₃ showed remarkable effects of iron loading onto cobalt catalyst. The Fe-loaded Co/ α -Al₂O₃ showed higher yield of hydrogen, low coke deposition on the catalysts, and high activity for steam reforming of acetaldehyde, which was an intermediate of the steam reforming of ethanol. Characterization of the catalyst revealed that Fe and Co metal coexisted on the catalyst support. Synergetic effects of these two metals were observed.

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1. Introduction

Recently, biomass has attracted much attention as a renewable energy resource [1,2]. Among many utilizations of biomass, utilization of biomass-derived-ethanol has been conducted actively [3,4]. Ethanol obtained through fermentation of saccharide (sugar) includes much water, so the water must be removed completely before the utilization as a gasoline-substitute. Large amounts of energy are required for rectification of ethanol. A useful process is therefore steam reforming of ethanol [5,6], which is applicable to hydrogen production directly with no rectification; the reaction is endothermic without loss of calorific value. The resultant hydrogen is available for various applications such as fuel cells and hydrogen combustion. For those reasons, the obtained biomass-derived hydrogen can be regarded as a high-efficiency, clean energy resource [7–9].

To date, various transition metal catalysts such as Rh, Ni, and Co have been investigated for steam reforming of ethanol. Some reports show that noble metals such as Rh exhibit high activity and high stability [10,11]. Nevertheless, it is undesirable to use noble metals because of their high cost. On the other hand, many reports have described that base metals such as Ni [12–15] and Co [15–25] exhibit high activity for steam reforming of ethanol. The Ni-based catalysts show high ethanol conversion at low temperatures [14], but Ni-based catalysts generate more byproduct CH₄ than Co-based catalysts [15]. Therefore, Ni-based catalysts are

deemed unsuitable for aspiring to a high H₂ yield. The Co-based catalysts, with lower generation of undesired byproduct CH₄ [16], have been researched actively among various transition metal catalysts, but their deactivation by sintering of the catalyst or carbon deposition on Co-based catalysts presents a serious obstacle to their wider use [17,18]. Some investigations have revealed that application of a basic oxide such as MgO [13,18], CeO₂ [26], ZnO [19] or perovskite-type oxide [27] is a promising method for suppressing carbon deposition on the catalyst. We have reported that Co-based catalysts supported on perovskite-type oxides (SrTiO₃) show high activity [20]. Regarding the second metal addition on Co-based catalysts, carbon deposition on catalysts was depressed by sodium addition [22], and Ru addition on Co/ γ -Al₂O₃ was effective among some noble metals (Pt, Pd, Ru, and Ir) [23]. The Fe supplementation of a Co-based catalyst, Co₃O₄ [24] and Co/ZnO [25] has been investigated by other researchers; we also have found that addition of small amounts of Fe to Co/SrTiO₃ promotes its catalytic activity [21]. Therefore, we investigated the effects of Fe addition on Co-based catalyst with various supports by controlling many factors and parameters such as reaction temperature and contact time (=W/F), etc. In addition, the physical structure of Fe-loaded Co catalyst was characterized to investigate the interaction of Co and Fe. Moreover, a comparison of the catalytic nature between Fe/Co/ α -Al₂O₃ and physically mixed catalyst (Fe/ α -Al₂O₃ and Co/ α -Al₂O₃) was conducted.

2. Experimental

As catalyst supports, SiO₂ (JRC-SIO-5), MgO (Ube 1000A), SrTiO₃ (synthesis method explained in Ref. [21]) of perovskite oxide and α -

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Al₂O₃ (JRC-ALO-1; calcined at 1573 K for 3 h) were used. In addition, 5 wt% of Co and/or 0.22 wt% of Fe as an active metal was supported by an impregnation method. As precursors of these supported metals, Co(NO₃)₂·6H₂O and Fe(C₅H₇O₂)₃ were used. Distilled water was used as a solvent to support Co; acetone was used for Fe. First, a mixture of catalyst-support and liquid solution of the precursor was heated on the stirrer and evaporated to dryness. The resultant powder was dried in an oven at 393 K for 20 h in air. Then, it was calcined in a muffle furnace at 823 K for 3 h. Then Fe addition onto Co-based catalysts was conducted using a sequential impregnation method, and 0.22 wt% Fe was supported using the above-referenced method.

Activity tests were conducted in a continuous flow reactor with a fixed bed of catalyst under atmospheric pressure. A quartz tube (8 mm inner diameter) was used as a reactor. The catalyst powder was pressed at 60 kN for 15 min, crushed, and sieved to obtain a particle size of 250–500 μm. Then the sieved catalyst was charged in the catalyst bed with dilution of SiC to 10-mm height. The temperature inside the reactor was controlled using a heater with a thermocouple in the catalyst bed. The reactor was heated with 10 K min⁻¹ up to the reduction temperature (873 K) in H₂ flow (50 mL min⁻¹). Then it was held for 1 h. After the reactor was cooled to the reaction temperature with purging by N₂, an aqueous solution of ethanol (steam to carbon ratio: S/C=5.0) was fed to the reactor using a syringe pump through a vaporizer. The flow rate of ethanol was 7.7 × 10⁻⁴ mol min⁻¹, and W/F was changed between 0.08 and 5.2 g-cat h mol⁻¹ by changing the catalyst amount. As an internal standard gas, N₂ (20 mL min⁻¹) was fed simultaneously, and 80 mL min⁻¹ of Ar was fed simultaneously to the reactor as a carrier gas. Qualitative and quantitative analyses of gas components were conducted using a gas chromatograph (GC). Then H₂ and N₂ were analyzed using a thermal conductivity detector (TCD)-GC (GC-8A; Shimadzu Corp.). Subsequently, CO, CO₂ and CH₄ were analyzed using a flame ionization detector (FID)-GC (GC-8A; Shimadzu Corp.) with a methanizer (Ru/Al₂O₃). In addition, hydrocarbon compounds (CH₄, C₂ and C₃), liquid products (such as CH₃CHO) and the unreacted ethanol were analyzed using a FID-GC (GC-14B; Shimadzu Corp.) with a six-way valve.

Ethanol conversion and H₂ yield were calculated according to Eqs. (1) and (2). The H₂ yield would be maximum (200%) from Eq. (2) if all the ethanol was reformed to CO₂ and H₂ with a water gas shift reaction.

$$\text{ethanol conversion (\%)} = \frac{F_{\text{carbon mole of all product}}^{\text{out}}}{F_{\text{carbon mole of C}_2\text{H}_5\text{OH}}^{\text{in}}} \quad (1)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{F_{\text{H}_2}^{\text{out}} \times 100}{F_{\text{C}_2\text{H}_5\text{OH}}^{\text{in}} \times 3} \quad (2)$$

The amount of deposited carbon on the catalyst was analyzed using temperature-programmed oxidation (TPO). The catalyst was heated 10 K min⁻¹ up to 1173 K with 10% O₂/N₂ gas flow, and the quantities of generated CO and CO₂ were measured using an infrared gas analyzer (Shimadzu CGT-7000). Finally, the amount of carbon was calculated using these values. The Co particle size was measured using transmission electron microscopy (TEM, JEM-1011; JEOL). The average diameter of Co particles was measured using TEM and then calculated. The physical structures of Co and Fe on Fe/Co/α-Al₂O₃ were observed using scanning transmission electron microscopy (STEM, HF-2210; Hitachi Ltd.) and energy dispersive X-ray spectrometry (EDX, Genesis4000; EDAX Inc.).

3. Results and discussion

3.1. Catalytic activities of various Fe-loaded catalysts

We previously reported that catalytic activity over Co/SrTiO₃ catalyst was promoted by Fe addition [21]. First, we investigated effects of support among Fe/Co-based catalysts. The ethanol conversion, H₂ yield and amount of carbon were compared on Fe/Co-based catalysts with various supports, SiO₂, MgO, SrTiO₃, α-Al₂O₃. Table 1 presents results of catalytic activity tests and amount of carbon after 185 min of reaction. Here, the optimized amount of Fe loading (=0.22 wt%) was chosen from the previous result over Fe/Co/SrTiO₃ catalyst [21].

From Table 1, improvement of H₂ yield and suppression of carbon deposition were not observed by Fe addition for catalysts of Co/SiO₂ and Co/MgO. On the other hand, the promoting effects of Fe on ethanol conversion and H₂ yield, and the suppression of carbon deposition were observed for catalysts of Co/SrTiO₃ and Co/α-Al₂O₃. Although the Co/α-Al₂O₃ catalyst showed less ethanol conversion and H₂ yield than Co/SrTiO₃ catalyst, Fe-loaded Co/α-Al₂O₃ catalyst showed higher activity and stability than Fe/Co/SrTiO₃ catalyst. From this result, we concluded that Fe addition on Co/α-Al₂O₃ was effective for steam reforming of ethanol.

Therefore, effects of Fe addition on Co/α-Al₂O₃ catalyst were considered by changing amounts of Fe loading and the calcination time. Table 2 presents results of activity tests. As shown in Table 2, all Fe-loaded Co/α-Al₂O₃ catalysts showed higher activity and less selectivity to CH₃CHO than that of Co/α-Al₂O₃ catalyst. Some reports have described that steam reforming of ethanol proceeds via CH₃CHO as an intermediate [5,21]. Therefore, it was considered that steam reforming of CH₃CHO was promoted by Fe addition from results of Table 2 and that the H₂ yield was improved. Based on these results, we chose 0.22 wt% Fe/5 wt% Co/α-Al₂O₃ (calcined for 3 h after Fe loading) as the best catalyst for additional investigations.

3.2. Selectivity to products over Fe-loaded catalyst

To investigate the effective temperature window on these catalysts, we examined the effect of reaction temperature over catalysts of Co/α-Al₂O₃ and Fe/Co/α-Al₂O₃. Activity tests were conducted at each reaction temperature (753, 783, 823, and 873 K). Fig. 1a presents ethanol conversion and Fig. 1b shows the H₂ yield at each reaction temperature. Based on the results portrayed in Fig. 1a and b, ethanol conversion and H₂ yield were promoted by Fe addition at each temperature. Furthermore, the improvement of activity by Fe addition was observed dominantly at 783 and 823 K. The apparent activation energy was calculated from Fig. 1a. The value for Co/α-Al₂O₃ catalyst was 67.3 kJ mol⁻¹; that for Fe/Co/α-Al₂O₃ catalyst was 53.9 kJ mol⁻¹. From these values, it was confirmed that the apparent activation energy was reduced by Fe addition.

Subsequently, catalytic activity over catalysts of Co/α-Al₂O₃ and Fe/Co/α-Al₂O₃ was compared by changing the contact time (=W/F) to examine the reaction passage over these catalysts. Fig. 2 shows carbon-based yields of products on each W/F after 185 min of reaction. Results confirmed that Fe/Co/α-Al₂O₃ catalyst promoted steam reforming and that larger amounts of CO, CO₂—of course including hydrogen—were obtained than with Co/α-Al₂O₃ catalyst, as shown in Fig. 2. Furthermore, Fe/Co/α-Al₂O₃ catalyst showed a lower yield of the reaction intermediate, CH₃CHO, than with Co/α-Al₂O₃ catalyst by comparison between high W/F. These results also demonstrated that Fe addition promoted the steam reforming activity of CH₃CHO. In addition, the yield of byproducts such as CH₄ and carbon over Fe/Co/α-Al₂O₃ catalyst was lower

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