

Short communication

Hydrogen production by auto-thermal reforming of ethanol over Ni/ γ -Al₂O₃ catalysts: Effect of second metal addition

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Abstract

Ni/ γ -Al₂O₃ catalysts containing a second metal (Ce, Co, Cu, Mg and Zn) are prepared by a co-impregnation method to investigate the effect of second metal addition on the catalytic performance in the auto-thermal reforming of ethanol. Among the second metals tested, Cu is found to be the most efficient promoter for the production of hydrogen. It is revealed that Cu species are active in the water-gas shift reaction to produce hydrogen from CO and H₂O, and furthermore, Cu species serve as a barrier for preventing the growth of Ni particles. In particular, the addition of Cu decreases the interaction between Ni-species and γ -Al₂O₃, leading to the facile reduction of Ni-Cu/ γ -Al₂O₃ catalyst. Among Ni-Cu/ γ -Al₂O₃ catalysts with different Cu content, a 5 wt.% Cu-containing Ni-Cu/ γ -Al₂O₃ catalyst, which retains an intermediate state of Cu species between copper aluminate and copper oxide, shows the best catalytic performance in terms of hydrogen production and CO composition in the outlet stream. By contrast, a 7 wt.% Cu-containing Ni-Cu/ γ -Al₂O₃ catalyst exhibits rather a low catalytic performance in the production of hydrogen because of the suppressed gasification activity over large Cu particles in the catalyst.

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1. Introduction

Hydrogen has attracted much attention as an alternative energy carrier due to its non-polluting nature [1]. In particular, technological advances in hydrogen utilization such as the fuel cell make hydrogen more important as a new fuel. For the practical use of hydrogen, therefore, it is necessary to establish feasible production methods because hydrogen does not occur freely but has to be produced from water or organic compounds [2,3].

There are many routes for the production of hydrogen, including electrical or photochemical splitting of water, closed thermo-chemical cycles, and reforming of organic fuels such as alcohols, gasoline and methane. Among these methods, hydrogen production via the steam reforming of light alcohols such

as methanol and ethanol has been recognized as a promising method because these liquid fuels can be easily handled and are widely distributed throughout the world. Although methanol has been commonly used as a hydrogen source, ethanol can also serve as an alternative for the production of hydrogen because of its low toxicity, high volumetric energy density and ready availability [4–8].

Several catalytic systems, including noble metal-based and base metal-based catalysts, have been developed for the production of hydrogen by the steam reforming [9–20] and the auto-thermal reforming of ethanol [21–26]. Although a high yield of hydrogen has been achieved by auto-thermal reforming of ethanol at low temperature over noble metal-based catalysts such as Rh/Al₂O₃, the high cost of noble metals is the main drawback for the successful application of this technology [22–24]. It has been reported, however, that non-noble metal-based catalysts also exhibit relatively high catalytic performance in the auto-thermal reforming of ethanol [25,26]. In particular, Ni-based catalysts have been highlighted as promising materials

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due to their high intrinsic activity [25]. Therefore, rational design of Ni-based catalysts is of great importance for the efficient production of hydrogen via this route.

In this work, Ni/ γ -Al₂O₃ catalysts containing a second metal (Ce, Co, Cu, Mg and Zn) are prepared by a co-impregnation method and are applied to the auto-thermal reforming of ethanol for the production of hydrogen. The prepared catalysts are characterized by X-ray diffraction (XRD) and temperature-programmed reduction (TPR) measurements to elucidate the catalytic performance. The effect of second metal addition on the catalytic performance of Ni/ γ -Al₂O₃ catalysts is investigated. In particular, the role and effect of Cu addition on the performance of Ni/ γ -Al₂O₃ catalysts is extensively studied.

2. Experimental

2.1. Preparation of Ni/ γ -Al₂O₃ catalyst containing a second metal

Ni/ γ -Al₂O₃ catalysts containing a second metal were prepared by co-impregnating appropriate amounts of nickel precursor (Ni(NO₃)₂·6H₂O, Aldrich) and metal precursor onto γ -Al₂O₃ (Degussa). Cerium nitrate (Ce(NO₃)₂·6H₂O, Aldrich), cobalt nitrate (Co(NO₃)₂·6H₂O, Aldrich), copper nitrate (Cu(NO₃)₂·6H₂O, Fluka), magnesium nitrate (Mg(NO₃)₂·6H₂O, Aldrich) and zinc nitrate (Zn(NO₃)₂·6H₂O, Aldrich) were used as second metal precursors. In all cases, the Ni loadings on γ -Al₂O₃ were fixed at 20 wt.%. The co-impregnated catalyst samples were dried at 120 °C and then calcined at 900 °C for 8 h. The prepared Ni/ γ -Al₂O₃ catalysts containing a second metal were denoted as 20Ni_xM ($x=0, 3, 5$ and 7 ; M=Ce, Co, Cu, Mg and Zn). For example, a 20Ni₃Cu catalyst means that 20 wt.% Ni and 3 wt.% Cu were loaded on γ -Al₂O₃.

2.2. Characterization

Crystalline phases of calcined and reduced catalysts were identified by XRD (MAC Science, M18XHF-SRA) measurements using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 50 kV and 100 mA. In order to check the reducibility of catalysts, temperature-programmed reduction (TPR) measurements were carried out in a conventional flow system with a moisture trap connected to a thermal conductivity detector (TCD) at temperatures ranging from room temperature to 1000 °C with a ramping rate of 5 °C min⁻¹. For the TPR measurements, a mixed stream of H₂ (2 ml min⁻¹) and N₂ (20 ml min⁻¹) was used for 0.1 g of catalyst sample

2.3. Auto-thermal reforming of ethanol

Auto-thermal reforming of ethanol was carried out in a continuous flow fixed-bed reactor at atmospheric pressure. Each calcined catalyst (50 mg) was charged into a tubular quartz reactor and then was reduced with a mixed stream of H₂ (30 ml min⁻¹) and N₂ (30 ml min⁻¹) at 700 °C for 3 h. Ethanol and water supplied by means of syringe pumps were sufficiently

vaporized by passing a pre-heating zone and fed into the reactor continuously together with N₂ carrier (30 ml min⁻¹). Feed ratios of H₂O:EtOH and O₂:EtOH were fixed at 2.0 and 0.8, respectively. The reaction temperature was maintained at 550 °C and the contact time was fixed at 175 g-catalyst min per EtOH-mole. The reaction products were periodically sampled and analyzed using an on-line gas chromatograph (Younglin, ACME 6000) equipped with two TCDs.

3. Results and discussion

3.1. Effect of second metal addition

Several second metals (Ce, Co, Cu, Mg and Zn) were tested as a potential promoters for a Ni/ γ -Al₂O₃ catalyst in the auto-thermal reforming of ethanol. The catalytic performances of 20Ni and 20Ni₃M (M=Ce, Co, Cu, Mg and Zn) are shown in Fig. 1. All the catalysts tested exhibit 100% ethanol conversion at 550 °C, but the product distributions are different according to the identity of the second metal. Among the second metals tested, it is found that only Cu and Co serve as efficient promoters for a Ni/ γ -Al₂O₃ catalyst in hydrogen production. Although both the 20Ni₃Cu and 20Ni₃Co catalysts show enhanced hydrogen production compared with the 20Ni catalyst, the product distributions over these two catalysts are quite different. It is found that the 20Ni₃Co catalyst has higher ethylene selectivity than the 20Ni₃Cu catalyst (although these are not shown here), which indicates enhanced dehydration activity with the 20Ni₃Co catalyst. This result is well consistent with those of other workers who have reported [13–15] that a Co catalyst supported on γ -Al₂O₃ is highly active for the dehydration of ethanol to ethylene. On the other hand, the 20Ni₃Cu catalyst gives an enhanced yield of hydrogen and a suppressed yield of CO compared with the 20Ni catalyst. This is because the 20Ni₃Cu catalyst easily converts CO and H₂O into hydrogen via the water-gas shift reaction (CO + H₂O → CO₂ + H₂). This result is well supported by the fact that Cu is highly active in the water-gas shift reaction (WGSR) [16,17]. Although Zn is also known to be very

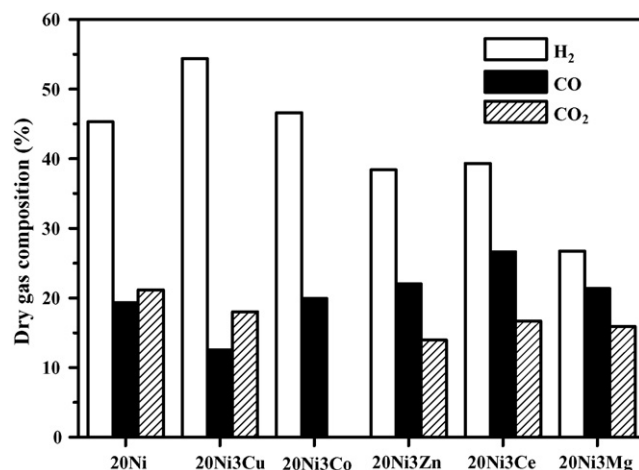


Fig. 1. Catalytic performance of 20Ni and 20Ni₃M (M=Ce, Co, Cu, Mg and Zn) in the auto-thermal reforming of ethanol.

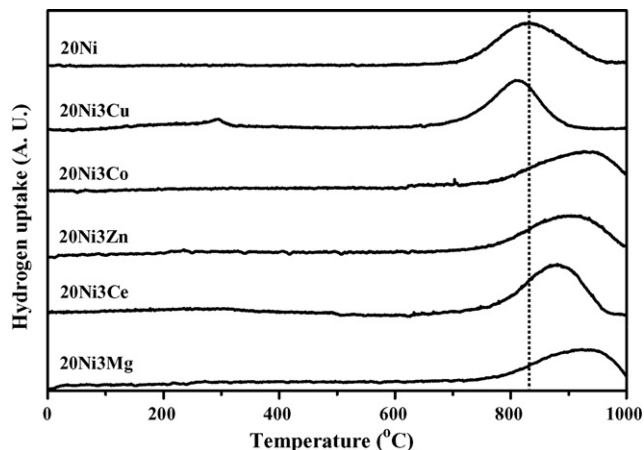


Fig. 2. TPR patterns of 20Ni and 20Ni3M (M = Ce, Co, Cu, Mg and Zn).

active in the WGS [14,15], a poor hydrogen yield is observed over the 20Ni3Zn catalyst, which is contrary to our expectation. The difference in catalytic performance between 20Ni3Cu and 20Ni3Zn may be explained in terms of their different reducibility, as described below.

The TPR patterns of 20Ni and 20Ni3M (M = Ce, Co, Cu, Mg and Zn) are shown in Fig. 2. The monometallic Ni20 catalyst gives a broad reduction band at 700–900 °C, which is attributed to the reduction of nickel aluminate-like species [27]. Upon the addition of a second metal, the supported bimetallic catalysts showed different reduction patterns depending on the identity of second metal. The reduction band of the 20Ni3Cu catalyst appears at a lower temperature than that of the Ni20 catalyst (the reduction behaviour of 20Ni_xCu catalysts will be discussed in the next section). The other supported bimetallic catalysts are reduced at higher temperatures than the 20Ni catalyst, which indicates that these bimetallic catalysts have lower reducibility than the 20Ni catalyst. The active sites for both WGS and auto-thermal reforming of ethanol are the reduced metallic phases on the support. Therefore, it is believed that the poor catalytic performance of 20Ni3Zn, compared with 20Ni3Cu, is due to the low reducibility of the 20Ni3Zn catalyst. Among the second metals examined, Cu is found to be the best promoter for the Ni/ γ -Al₂O₃ catalyst used in hydrogen production by the auto-thermal reforming of ethanol. Therefore, the remainder of this work focuses on the role and effect of Cu addition on the catalytic performance of 20Ni_xCu catalysts in the auto-thermal reforming of ethanol.

3.2. Effect of Cu addition

The XRD patterns of γ -Al₂O₃ and 20Ni_xCu ($x=0, 3, 5$ and 7) calcined at 900 °C are presented in Fig. 3. No peaks representing nickel oxide and copper oxide are observed in the case of 20Ni_xCu catalysts. It is interesting to note that the peak for alumina (440) shifts to a lower angle on addition of Cu. It is known that a strong interaction between γ -Al₂O₃ and divalent metal species results in the formation of a metal aluminate phase (for example, nickel aluminate and copper aluminate in this system) on heat treatment at high temperature [28,29]. Although XRD

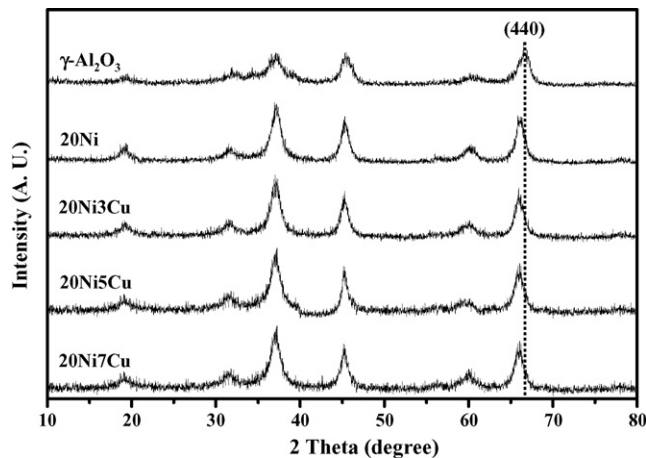


Fig. 3. XRD patterns of γ -Al₂O₃ and 20Ni_xCu ($x=0, 3, 5$ and 7) calcined at 900 °C.

peaks representing metal aluminates cannot be clearly resolved, the formation of metal aluminates can be confirmed by the shift in the XRD peak. This is also confirmed by TPR measurements (Fig. 5), as will be discussed later.

The XRD patterns of 20Ni_xCu ($x=0, 3, 5$ and 7) reduced at 700 °C is given in Fig. 4. The reduced 20Ni catalyst displays characteristic XRD peaks for metallic Ni. It is interesting, however, that these XRD peaks for metallic Ni disappear with increasing Cu content. This result demonstrates that the size of Ni particles in the 20Ni_xCu catalyst decreases with increasing Cu content. It is considered that the highly dispersed Cu species serve as a barrier for preventing the growth of Ni particles during both the calcination and the reduction steps.

The interaction between the metal and the support increases with decreasing size of the metallic species and the resulting enhanced interaction leads to the poor reducibility of the supported metal catalyst. As evidenced by XRD analyses, the size of the metallic Ni species in 20Ni3Cu is decreased by the role of Cu species compared with that in 20Ni. In order to investigate the reducibility of 20Ni_xCu catalysts, therefore, TPR measurements were carried out as shown in Fig. 5. The TPR patterns of the 20Ni_xCu ($x=3, 5$ and 7) catalysts are somewhat

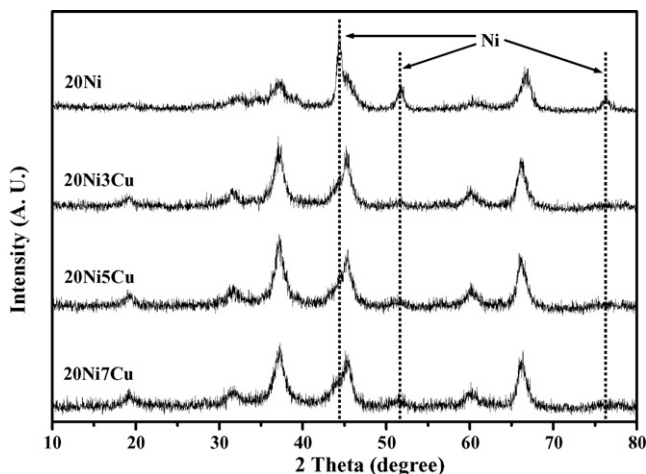


Fig. 4. XRD patterns of 20Ni_xCu ($x=0, 3, 5$ and 7) reduced at 700 °C.

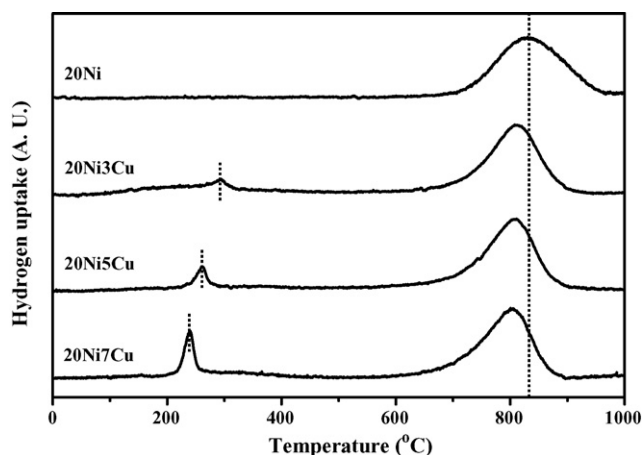


Fig. 5. TPR patterns of 20Ni x Cu ($x=0, 3, 5$ and 7).

different to those of the 20Ni catalyst. That is, two reduction bands are observed with the 20Ni x Cu ($x=3, 5$ and 7) catalysts. The weak band appearing at 200–300 °C is attributed to the reduction of the Cu species, while the strong band at around 800 °C is due to the reduction of the Ni species. Compared with the Ni species of 20Ni, the Ni species in 20Ni x Cu ($x=3, 5$ and 7) catalysts are reduced at low temperature, which demonstrates the enhanced reducibility of 20Ni x Cu ($x=3, 5$ and 7) catalysts. These findings show that the interaction between Ni species and γ -Al₂O₃ is decreased by the effect of Cu addition, despite the fact that the size of the Ni particles in 20Ni x Cu is decreased. It is well known that Cu species, like Ni species, strongly interact with γ -Al₂O₃ to form a hydrotalcite-like precursor and a copper aluminate species [30]. In other words, the added Cu species in the present catalyst system can occupy reactive sites on the γ -Al₂O₃ by forming a hydrotalcite-like precursor or aluminate species, which results in decreased interaction between the Ni species and γ -Al₂O₃. As also shown in Fig. 5, the reduction band for the Cu species in 20Ni x Cu ($x=3, 5$ and 7) shifts to a lower temperature with increasing Cu content. The reduction band of 20Ni₃Cu appearing at around 300 °C is attributed to the reduction of copper aluminate, while that of 20Ni₇Cu appearing at 240 °C is due to the reduction of copper oxide. From the reduction band of 20Ni₅Cu at 260 °C, therefore, it is inferred that the 20Ni₅Cu catalyst retains an intermediate state of Cu species between copper aluminate and copper oxide [31–33]. This result implies that Cu species are segregated from copper aluminate to copper oxide with increasing Cu content.

The catalytic performance of 20Ni x Cu ($x=0, 3, 5$ and 7) in the auto-thermal reforming of ethanol is demonstrated in Fig. 6. All the catalysts exhibit 100% ethanol conversion. The 20Ni x Cu ($x=3$ and 5) catalysts produce much more hydrogen than the 20Ni catalyst. Among the catalysts tested, the 20Ni₅Cu catalyst that retains an intermediate state of Cu species between copper aluminate and copper oxide gives the best catalytic performance in terms of hydrogen production and CO composition in the outlet stream. It is interesting to compare the yields for CH₃CHO over 20Ni x Cu catalysts. The yields for CH₃CHO are 2.95 and 6.12% over 20Ni₅Cu and 20Ni₇Cu, respectively (although these are not shown here). As mentioned previously, the Cu species

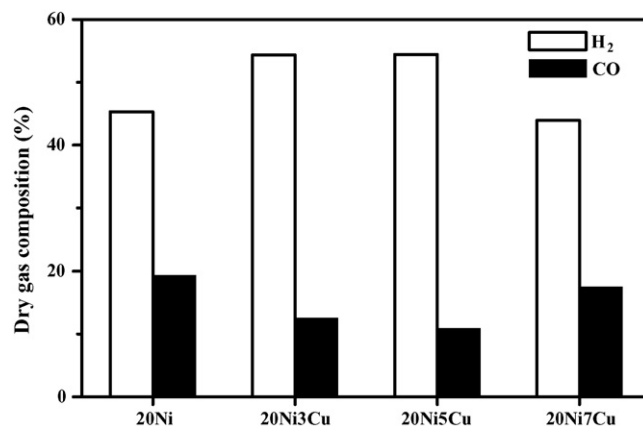


Fig. 6. Catalytic performance of 20Ni x Cu ($x=0, 3, 5$ and 7) in auto-thermal reforming of ethanol.

in 20Ni x Cu catalysts exists as copper oxide at high Cu content (20Ni₇Cu). This indicates that the size of the Cu species in 20Ni x Cu was increases with increasing Cu content. Although Cu is highly active in the WGS, it is likely that its gasification activity is suppressed over the 20Ni₇Cu catalyst with large Cu particles and thereby results in a low yield of hydrogen. This conclusion is well supported by previous work [26] that reports that the gasification of CH₃CHO is suppressed over a catalyst with large Cu particles.

4. Conclusions

Supported Ni-based bimetallic catalysts have been prepared to investigate the effect of second metal (Ce, Co, Cu, Mg and Zn) addition on their performance in the auto-thermal reforming of ethanol. Among the second metals tested, Cu serves as the most efficient promoter for the production of hydrogen. It is found that Cu species are active in the water-gas shift reaction and, at the same time, serve as a barrier for preventing the growth of Ni particles. In particular, the addition of Cu decreases the interaction between Ni-species and γ -Al₂O₃ and this leads to the facile reduction of the Ni-Cu/ γ -Al₂O₃ catalyst. Among the 20Ni x Cu catalysts, the 20Ni₅Cu catalyst that retains an intermediate state of Cu species between copper aluminate and copper oxide shows the best performance in the auto-thermal reforming of ethanol. By contrast, the 20Ni₇Cu catalyst exhibits a rather low catalytic performance in the production of hydrogen because of suppressed gasification activity over the large Cu particles in the catalyst.

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