Hydrogen Production by Steam Reforming of Ethanol Using Cobalt and Nickel Catalysts Supported on Strontium Titanate

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The steam reforming of ethanol over Co and Ni catalysts supported on $SrTiO_3$ was carried out at 823 K and atmospheric pressure. It was found that $Co/SrTiO_3$ showed a high catalytic activity and long-term stability and remarkably inhibited carbon deposition.

In recent years, ethanol produced from renewable biomass resources has attracted considerable attention as an energy source alternative to fossil fuels.[1,2] Since the concentration of ethanol in biomass-derived aqueous solution is 12–15 wt %, energy intensive and rather expensive distillation processes has been used for recovering highly concentrated ethanol. Instead, hydrogen manufacture by the steam reforming of ethanol has been proposed to be an effective way for the utilization of the biomass-derived ethanol without distillation.

The number of publications on the catalytic steam reforming of ethanol has substantially been increasing.[3–11] Although Rh seems to be most catalytically active for the steam reforming of ethanol,[5–7] the use of a noble metal is considered to be disadvantageous mostly due to an economical reason. On the other hand, sintering of Ni and Co and coke formation often cause deactivation of supported Ni and Co catalysts.[8–11]

One of the approaches to improve the stabilities of the Co and Ni catalysts is the selection and modification of catalyst support.[9–11] We previously reported that $Ni/SrTiO_3$ shows a high catalytic activity and durability under the conditions of the steam reforming of methane at 1073 K because the lattice oxygen in $SrTiO_3$ possibly promotes the oxidation of CHx fragments and hinders the production of inactive carbonaceous species.[12] Ni catalysts supported on some perovskite type-oxides such as $SrTiO_3$ have been reported for partial oxidation of methane[13,14] and dry reforming of methane.[15]

Based on these results, in this study, we investigated the catalytic activities and stabilities of Co and Ni catalysts supported on $SrTiO_3$ for the steam reforming of ethanol and compared with those of Co and Ni catalysts supported on MgO or γ-Al_2O_3, which have been studied by several researchers.[3,4,6–9,11]

MgO (Kanto Chemical Co., Inc, BET = 46.4 m^2 g-cat^{-1}), γ-Al_2O_3 (JRC-ALO-2, the Catalysis Society of Japan, BET = 280 m^2 g-cat^{-1}) and $SrTiO_3$ were used as the support. $SrTiO_3$ was prepared by physically mixing TiO_2 (anatase) and $SrCO_3$ and then calcining the resultant mixture at 1423 K for 10 h. The BET specific surface area was 7.7 m^2 g-cat^{-1}. Co and Ni catalysts were prepared by an impregnation method using these supports and an aqueous solution of $Co(NO_3)_2$ and $Ni(NO_3)_2$, respectively. The amount of Co or Ni loaded was 5 wt % as metal.

Catalytic activities were tested in a continuous flow reactor with a fixed bed of catalyst at 823 K and atmospheric pressure. Before the activity test, the catalyst was reduced for 1 h at 873 K in a hydrogen stream. After the reduction with hydrogen, a mixture of ethanol, steam and argon was fed into the reactor at 823 K. The flow rate of ethanol, steam and argon were 4.5, 45, and 50 cm^3 min^{-1} (STP), respectively. The products were analyzed by means of a gas chromatograph (Shimadzu GC-14B. The hydrogen yield was defined as

$$\text{Hydrogen yield} = F_{H_2}{}^{out} \times 100/(3 \times F_{C_2H_5OH}{}^{in} + F_{H_2O}{}^{in})$$

where $F_{H_2}{}^{out}$ is the formation rate of hydrogen, $F_{C_2H_5OH}{}^{in}$ is the feed rate of ethanol, and $F_{H_2O}{}^{in}$ is the feed rate of water. The maximum hydrogen yield calculated is 46% when both the levels of ethanol conversion and the selectivity to carbon dioxide reach 100% ($C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$).

We tested the activities of Co and Ni catalysts supported on $SrTiO_3$, MgO and γ-Al_2O_3. Figure 1 and Table 1 show the levels of ethanol conversion as a function of time on stream and the yields of products, respectively. The catalytic activities signifi-

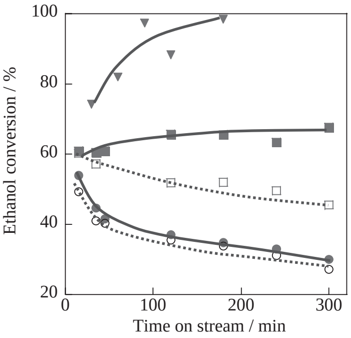

Figure 1. Steam reforming activities of supported Ni and Co catalysts. Catalyst: ●, Co/MgO; ○, Ni/MgO; ■, $Co/SrTiO_3$; □, $Ni/SrTiO_3$; ▼, Co/γ-Al_2O_3.

Table 1. Carbon-containing product yield for steam reforming ethanol over supported Ni and Co catalysts

Catalyst	[a]TOS /min	Yield/%			
		CO	CO_2	CH_4	C_2H_4
Co/MgO	55	13.9	21.5	4.3	0
Co/MgO	300	11.1	15.7	3.2	0
Ni/MgO	55	10.7	21.5	6.0	0
Ni/MgO	300	8.6	14.5	4.1	0
Co/γ-Al_2O_3	60	6.3	4.4	2.2	69.1
Co/γ-Al_2O_3	180	6.1	3.8	2.0	86.5
$Co/SrTiO_3$	55	22.4	28.9	7.8	0
$Co/SrTiO_3$	300	21.0	38.2	8.5	0
$Ni/SrTiO_3$	55	19.1	27.2	9.8	0
$Ni/SrTiO_3$	300	16.4	23.0	6.2	0

[a] Time on stream

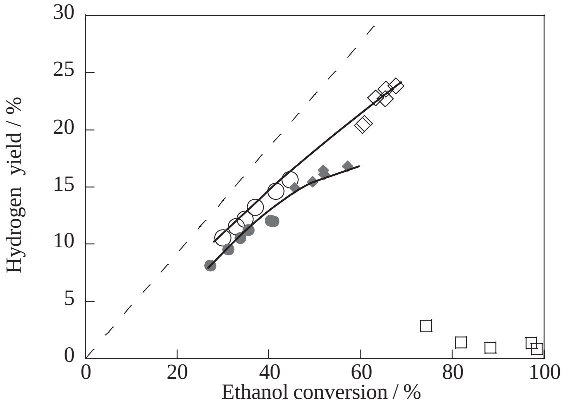

Figure 2. Hydrogen yield as functions of ethanol conversions of over supported Co and Ni catalysts. Catalyst: ○, Co/MgO; ●, Ni/MgO; ◇, Co/$SrTiO_3$; ◆, Ni/$SrTiO_3$; □, Co/γ-Al_2O_3. Maximum hydrogen yield at a given ethanol conversion was shown as the dotted line.

cantly depended on the kind of catalyst support. Although Co/γ-Al_2O_3 gave the highest levels of conversion of ethanol among the catalysts tested, the yield of ethylene was extremely high as shown in Table 1, resulting in small amounts of hydrogen formed. It is known that dehydration of ethanol on an acidic γ-Al_2O_3 support let to the selective formation of ethylene.[3,4,9–11] On the other hand, the products over other catalysts tested were composed of hydrogen, carbon dioxide, carbon monoxide and methane. Other products such as oxygenated compounds or ethylene were not detected.

Co/MgO and Ni/MgO featured similar levels of conversion. While the levels of ethanol conversion over Co/MgO and Ni/MgO after 15 min on stream were 54 and 49%, respectively, both catalysts deactivated rapidly in the first hour of reaction. After the reaction for 300 min, the levels of ethanol conversion over Co/MgO and Ni/MgO decreased to 30 and 27%, respectively.

We found that $SrTiO_3$ is suitable as a support of Co and Ni, compared with conventional γ-Al_2O_3 and MgO. Although the conversion level over Ni/$SrTiO_3$ decayed from 60.3% after 15 min to 45.6% after 300 min, the rate of deactivation was reduced in comparison with Ni/MgO. It should be noted that the catalytic activity of Co/$SrTiO_3$ gradually increased with time on stream: the level of ethanol conversion increased from 60% after 15 min to 68% after 60 min and level off.

Figure 2 shows the hydrogen yield as a function of ethanol conversion. The maximum hydrogen yield at a given ethanol conversion is calculated when the selectivity to carbon dioxide reaches 100%. All the catalysts used show a similar trend except for Co/γ-Al_2O_3 producing ethylene as the main product. The hydrogen yields over Co catalysts are slightly higher than that over Ni catalysts at a given level of ethanol conversion. The selectivities to methane over Co/$SrTiO_3$ and Co/MgO were ca. 12 or 10%, respectively, while Ni/$SrTiO_3$ and Ni/MgO gave slightly higher selectivities to methane of ca. 14 and 15%, respectively. The lower selectivities to methane over Co catalysts caused higher yield of hydrogen.

As described above, the catalytic activities of Co/MgO and Ni/MgO decreased rapidly although these catalysts showed high catalytic activities in the early stage of reaction. On the other hand, Co and Ni catalysts supported on $SrTiO_3$ showed much longer-term stability. One of the crucial reasons for the deactivation of catalysts in the steam reforming of ethanol is the coverage of active sites with deposited carbon. The amounts of carbon deposited during the reaction were quantified by the combustion of carbon in a stream containing 30% O_2. Figure 3 shows the amounts of carbon deposited after the activity test for 2 and 5 h. Carbon was deposited on the catalysts mostly up to 2 h on stream. We, thus, consider that the decrease in the activities of Co/MgO, Ni/MgO, and Ni/$SrTiO_3$ in the early stage of reaction is mainly due to coking on catalysts and the blockage of the active sites.

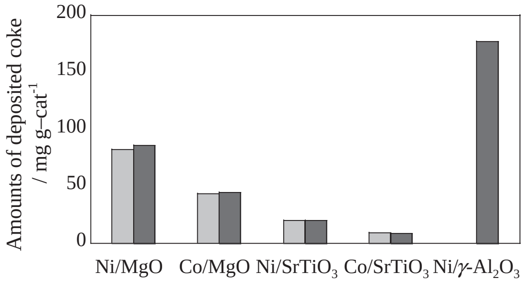

Figure 3. Amounts of coke deposited on Co and Ni catalysts after time course experiments of (▨) 2 h and (■) 5 h.

The amounts of carbon deposited on Co/$SrTiO_3$ and Ni/$SrTiO_3$ were much smaller than those on Ni/MgO, Co/MgO, and Co/γ-Al_2O_3. In particular, the amounts of carbon deposited on Co/$SrTiO_3$ after the activity test for 5 h were extremely small, 9 mg g-cat^{-1}. As described above, we have reported that in the case of the steam reforming of methane over supported Ni catalysts at 1073 K, Ni catalysts using perovskites as support suppress the formation of inactive carbonaceous species. In the present study, we presume that $SrTiO_3$ similarly acts to inhibit coke formation at a lower temperature employed for the steam reforming of ethanol.

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