

## Research Letter

# Hydrogen Production via Steam Reforming of Ethyl Alcohol over Palladium/Indium Oxide Catalyst

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We report the synergetic effect between palladium and indium oxide on hydrogen production in the steam reforming reaction of ethyl alcohol. The palladium/indium oxide catalyst shows higher hydrogen production rate than indium oxide and palladium. Palladium/indium oxide affords ketonization of ethyl alcohol with negligible by-product carbon monoxide, while indium oxide mainly affords dehydration of ethyl alcohol, and palladium affords decomposition of ethyl alcohol with large amount of by-product carbon monoxide. The catalytic feature of palladium/indium oxide can be ascribed to the formation of palladium-indium intermetallic component during the reaction as confirmed by X-ray diffraction and X-ray photoelectron spectroscopic measurements.

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## 1. Introduction

Hydrogen is a globally accepted clean fuel. Current methods for hydrogen production are mainly based on nonrenewable fossil fuels [1]. Renewable resources such as solar and biomass have attracted much attention as hydrogen resources to achieve the full environmental benefit for generating power with hydrogen fuel cells [2, 3]. Ethyl alcohol is preferable as the hydrogen resources for the fuel cells compared with other resources since it can be easily produced from biomass by fermentation [4]. The most effective process for hydrogen production from ethyl alcohol is the steam reforming reaction,  $C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$ . For this reaction, Cobalt-[5, 6], Nickel-[7], or Rhodium-[8] based catalysts exhibited high activities. In the previous literature, catalysts capable of converting ethyl alcohol to carbon dioxide and hydrogen without carbon monoxide formation have been reported but they need high temperatures (> 623 K) or show low-hydrogen production rates. Carbon monoxide is a by-product, which should be removed to prevent from the poisoning of electrode catalysts of fuel cells. On the other hand, we have reported that simple indium oxides exhibit high activities for hydrogen production from ethyl alcohol via the following reaction,  $2C_2H_5OH + H_2O \rightarrow$

$4H_2 + CO_2 + CH_3COCH_3$  at 623 K [9]. Over the indium oxide catalysts, hydrogen is generated without detectable carbon monoxide contamination, while hydrogen production rate is low below 623 K. Otherwise, it has been reported that decomposition of ethyl alcohol to hydrogen accompanied by the formation of carbon monoxide and methane mainly occurs over supported palladium catalyst, while the supports greatly affect the product distribution over palladium catalysts [10, 11]. The effects of support oxides on product selectivity over palladium catalysts have been reported in reactions such as dehydrogenation of ethyl alcohol [12] and steam reforming of methyl alcohol [13]. The specific interaction of palladium with a certain metal oxides leads to high activity for hydrogen production from ethyl alcohol.

Herein, we present the results of the synergetic effect between palladium and indium oxide on hydrogen production in the steam reforming reaction of ethyl alcohol.

## 2. Experimental

**2.1. Catalyst Preparation.** The Pd/In<sub>2</sub>O<sub>3</sub> catalysts with Pd contents of 0.2–10.0 wt.% were prepared by impregnation method using 0.1 M aqueous solution of Pd(NO<sub>3</sub>)<sub>2</sub> · nH<sub>2</sub>O

TABLE 1: Conversion and product distribution for the reaction of ethyl alcohol and steam over various catalysts.<sup>a</sup>

Catalyst	Conversion (%)	Composition (%) <sup>b</sup>							
		H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CHO	CH <sub>3</sub> COCH <sub>3</sub>
Pd	95.4	34.9	33.3	—	31.2	—	—	0.7	—
In <sub>2</sub> O <sub>3</sub>	79.2	21.7	—	4.1	—	59.1	0.6	6.2	8.3
Pd/In <sub>2</sub> O <sub>3</sub> <sup>c</sup>	97.8	62.1	—	12.3	—	0.9	—	2.9	21.8

<sup>a</sup>Reaction conditions: C<sub>2</sub>H<sub>5</sub>OH : H<sub>2</sub>O : N<sub>2</sub> = 0.5 : 2.0 : 97.5 (molar ratio), N<sub>2</sub> flow rate = 50 mL min<sup>-1</sup>, reaction time = 10 h, reaction temperature = 573 K.

<sup>b</sup>Molar percentage of products (water not included).

<sup>c</sup>Pd loading of Pd/In<sub>2</sub>O<sub>3</sub> = 5.0 wt.%

(Kishida Chem. Co.) and commercial In<sub>2</sub>O<sub>3</sub> (Mitsuwa Chem. Co.). The commercial In<sub>2</sub>O<sub>3</sub> was immersed in the aqueous Pd(NO<sub>3</sub>)<sub>2</sub> solution and was dried with a rotating evaporator at 343 K. The sample was calcined in air at 623 K for 3 h. The specific surface area of In<sub>2</sub>O<sub>3</sub> catalyst is 7 m<sup>2</sup> g<sup>-1</sup>, and the specific surface area of 5.0 wt.% Pd/In<sub>2</sub>O<sub>3</sub> catalyst is 10 m<sup>2</sup> g<sup>-1</sup>. Unsupported Pd catalyst was prepared by thermal decomposition of Pd(NO<sub>3</sub>)<sub>2</sub> · nH<sub>2</sub>O in air at 623 K for 3 h. All the catalysts have been used without reduction pretreatment before the reaction.

**2.2. Characterization of Catalysts.** Powder XRD measurements were performed on a RINT2200 diffractometer (Rigaku) equipped with a Cu K $\alpha$  X-ray tube operating at 40 kV and 40 mA. X-ray photoelectron spectra (XPS) were acquired with an ESCA-3400 spectrometer (Shimadzu) equipped with an Mg K $\alpha$  X-ray exciting source (1253.6 eV) operating at 10 kV and 10 mA. The binding energies (BE) were referred to the C 1 s peak at 285.0 eV.

**2.3. Evaluation of Catalytic Performance.** The catalysts (65 mg) held in L-shaped quartz tubes were loaded in a fixed-bed flow reactor (TPR-5D, Bell Japan Inc.). The premixed solution of water and ethyl alcohol was fed by a syringe pump (KD Science) to a vaporizer heated at 403 K, through which an N<sub>2</sub> stream was passed. A flow of 0.5% C<sub>2</sub>H<sub>5</sub>OH/2.0% H<sub>2</sub>O in N<sub>2</sub> stream (molar ratio) was introduced into the reactor with a rate of 50 mL min<sup>-1</sup> at 573 K. Effluent gas was analyzed by two online microgas chromatographs, GC3000A and M-200H (Agilent), equipped with TC detectors. GC3000A is equipped with Porapak Q using He as the carrier gas for separating CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, CH<sub>3</sub>CHO, and C<sub>2</sub>H<sub>5</sub>OH and Molecular Sieve 5 A using Ar as the carrier gas for separating H<sub>2</sub>, CO, and CH<sub>4</sub>. M-200H is equipped with Porapak Q using He as the carrier gas for separating C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, and CH<sub>3</sub>COCH<sub>3</sub> and Molecular Sieve 5 A using He as the carrier gas for separating CO and CH<sub>4</sub>. The detection limit of CO is < 50 ppm.

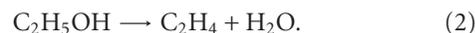
### 3. Results and Discussion

Table 1 shows the conversion and product distribution over Pd, In<sub>2</sub>O<sub>3</sub>, and Pd/In<sub>2</sub>O<sub>3</sub>, catalysts at 573 K in the condition for steam reforming of ethyl alcohol. The table lists the conversion of ethyl alcohol and the molar composition of

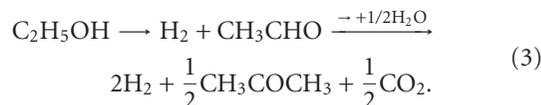
the products. All the catalysts show conversions of ethyl alcohol higher than 77%, while the composition of hydrogen depends on the catalyst. The Pd catalyst gives rise to the formation of hydrogen, carbon monoxide, and methane as the main products, indicating that Pd is highly active for decomposition of ethyl alcohol through the dehydrogenation step to acetaldehyde as follows [11]



In<sub>2</sub>O<sub>3</sub> catalyst shows the lowest composition of hydrogen with ethene as the main product, indicating that In<sub>2</sub>O<sub>3</sub> is highly active for dehydration of ethyl alcohol as follows:

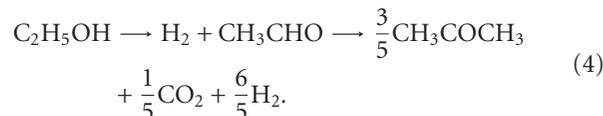


This reaction is known to proceed over acidic catalysts [14]. By combining Pd on In<sub>2</sub>O<sub>3</sub>, we observed a significant increase in hydrogen yield. As 2-propanone and carbon dioxide are also produced in this reaction, the Pd/In<sub>2</sub>O<sub>3</sub> catalyst is highly selective for ketonization of ethyl alcohol with acetaldehyde as the reaction intermediate as follows [9]:



According to (3), the steam reforming of ethyl alcohol gives the products with the molar ratio of H : C : O = 7.2 : 2.0 : 1.5.

Another route to the formation of 2-propanone is as follows;



No steam is consumed in this reaction, which gives the products with the molar ratio of H : C : O = 6.0 : 2.0 : 1.0.

The observed molar ratio of H : C : O over the 5.0 wt.% Pd/In<sub>2</sub>O<sub>3</sub> catalyst is 6.5 : 2.0 : 1.2 (Table 1), suggesting that 0.20 mol of H<sub>2</sub>O per converted ethyl alcohol is consumed. Moreover, no CO impurity was detected within the detection limit (< 50 ppm) over the catalyst, and no deactivation was observed for the catalyst during the reaction for 10 h.

Figure 1 depicts XRD profiles of the Pd/In<sub>2</sub>O<sub>3</sub> catalysts with 0.2, 1.0, and 5.0 wt.% Pd before and after the reaction.

TABLE 2: Effect of Pd loading on conversion and product distribution for the reaction of ethyl alcohol and steam over Pd/In<sub>2</sub>O<sub>3</sub>.<sup>a</sup>

Pd (wt.%)	Conversion (%)	Composition (%) <sup>b</sup>							
		H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CHO	CH <sub>3</sub> COCH <sub>3</sub>
0	79.2	21.7	—	4.1	—	59.1	0.6	6.2	8.3
0.2	77.8	53.0	—	5.3	—	10.8	—	21.1	9.8
1.0	93.7	59.9	—	12.1	—	2.3	—	5.1	20.6
5.0	97.8	62.1	—	12.3	—	0.9	—	2.9	21.8
10.0	99.9	60.1	—	14.2	—	—	0.1	1.9	23.7

<sup>a</sup>Reaction conditions: C<sub>2</sub>H<sub>5</sub>OH : H<sub>2</sub>O : N<sub>2</sub> = 0.5 : 2 : 97.5 (molar ratio), N<sub>2</sub> flow rate = 50 mL min<sup>-1</sup>, reaction time = 10 h, reaction temperature = 573 K.

<sup>b</sup>Molar percentage of products (water not included).

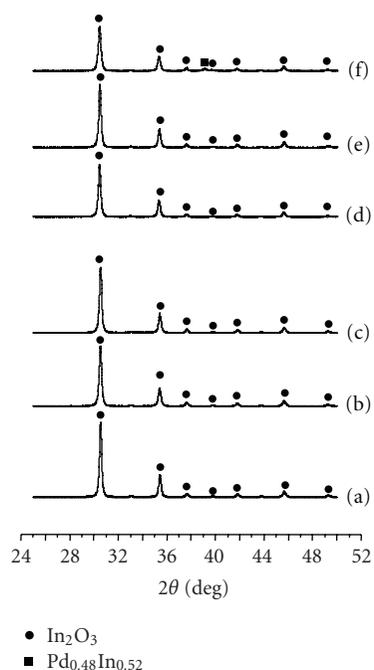


FIGURE 1: Powder X-ray diffraction patterns for the Pd/In<sub>2</sub>O<sub>3</sub> catalysts before reaction with (a) 0.2 wt.%, (b) 1.0 wt.%, and (c) 5.0 wt.% Pd and after reaction at 573 K with (d) 0.2 wt.%, (e) 1.0 wt.%, and (f) 5.0 wt.% Pd.

Only the peaks ascribed to In<sub>2</sub>O<sub>3</sub> phases appear at  $2\theta = 30.5, 35.4, 37.7, 39.8, 45.7,$  and  $49.3$  (JCPDS: 6-0416) in the profile for all the catalysts before reaction. A new small peak appears at  $2\theta = 39.1^\circ$  for the Pd/In<sub>2</sub>O<sub>3</sub> catalyst with 5.0 wt.% Pd after reaction, which can be ascribed to Pd<sub>0.48</sub>In<sub>0.52</sub> (JCPDS: 46-1011) [15, 16]. The result indicates that Pd<sub>0.48</sub>In<sub>0.52</sub> intermetallic species is formed in the Pd/In<sub>2</sub>O<sub>3</sub> catalyst during the reaction of ethyl alcohol, which might be the active phase for ketonization of ethyl alcohol.

Figure 2 represents the XPS spectra in Pd 3d region (left) in the Pd/In<sub>2</sub>O<sub>3</sub> catalysts before and after the reaction. The peak intensities of Pd 3d spectra for the Pd/In<sub>2</sub>O<sub>3</sub> catalysts with 0.2, 1.0, and 5.0 wt.% Pd before reaction increase with increase in Pd loading. All the spectra of the catalyst before reaction exhibit a Pd 3d<sub>5/2</sub> band at 336.9 eV, which can be associated with oxidized surface Pd species [16]. The intensity of Pd 3d lines for 0.2 and 1.0 wt.% Pd/In<sub>2</sub>O<sub>3</sub> catalyst

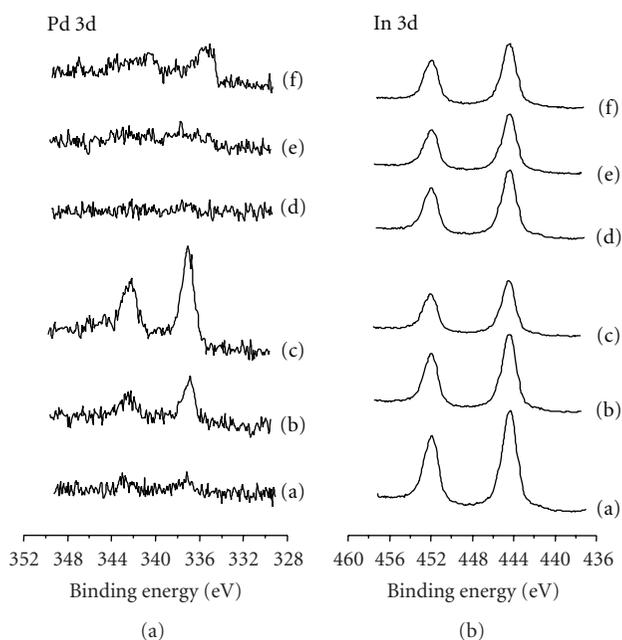


FIGURE 2: X-ray photoelectron spectra in the Pd 3d (left) and the In 3d (right) region for the Pd/In<sub>2</sub>O<sub>3</sub> catalysts before reaction with (a) 0.2 wt.%, (b) 1.0 wt.%, and (c) 5.0 wt.% Pd and after reaction at 573 K with (d) 0.2 wt.%, (e) 1.0 wt.%, and (f) 5.0 wt.% Pd.

after reaction is too small to identify the peaks of Pd 3d spectra, whereas the spectrum of the 5.0 wt.% Pd/In<sub>2</sub>O<sub>3</sub> catalyst exhibits a Pd 3d<sub>5/2</sub> band at 335.4 eV. This peak is slightly shifted from the peak position associated with metallic Pd (335.0 eV) [15, 16], suggesting the formation of Pd-In intermetallic species during the reaction of ethyl alcohol and steam [15, 16]. All the XPS spectra in In 3d region in the Pd/In<sub>2</sub>O<sub>3</sub> catalysts before and after the reaction exhibit In 3d<sub>5/2</sub> bands at 444.4–444.5 eV (Figure 1, right). The bands can be associated with oxidized surface In<sup>3+</sup> species [17]. A small In<sup>0</sup> peak (443.7 eV [15]) for the Pd-In intermetallic species observed in the XRD measurement may be overlapped by the broad In<sup>3+</sup> peak at around 444.5 eV.

As shown in Table 1, in the case of Pd catalyst without In<sub>2</sub>O<sub>3</sub> support, the decomposition of the acetaldehyde intermediate rapidly decarbonylated to carbon monoxide and methane (1), whereas for the Pd/In<sub>2</sub>O<sub>3</sub> catalyst the

acetaldehyde intermediate, which may be stabilized by the  $\text{Pd}_{0.48}\text{In}_{0.52}$  species [12], gives 2-propanone and carbon dioxide with hydrogen product via ketonization (3).

Table 2 shows the effect of Pd loading on the activity of Pd/In<sub>2</sub>O<sub>3</sub> catalyst for the reaction of ethyl alcohol and steam. All the catalysts show conversions of ethyl alcohol at the same levels, while the composition of hydrogen depends on the Pd loading. In<sub>2</sub>O<sub>3</sub> mainly affords the dehydrate product, C<sub>2</sub>H<sub>4</sub>, (2) with production of small amount of hydrogen. With increasing the loading from 0 to 0.2 wt.%, the composition is significantly increased. The dehydrate product, C<sub>2</sub>H<sub>4</sub>, is drastically decreased from 59.1% to 9.8%, while acetaldehyde is increased from 6.2% to 21.1% ((3), first step). Further increase of Pd loading from 0.2 to 1.0–10.0 wt.% gives rise to the increase of 2-propanone, carbon dioxide, and hydrogen ((3), second step) as the compensation of acetaldehyde.

#### 4. Conclusions

We have investigated the synergetic effect between palladium and indium oxide on hydrogen production in the steam reforming reaction of ethyl alcohol. Palladium/indium oxide catalyst is highly active for ketonization of ethyl alcohol with high composition of hydrogen and negligible by-product carbon monoxide, while indium oxide is highly active for dehydration of ethyl alcohol with low composition of hydrogen, and palladium is highly active for decomposition of ethyl alcohol with large amount of by-product carbon monoxide. No deactivation was observed for the palladium/indium oxide catalyst during the reaction for 10 h. The results of XRD and XPS measurement suggest that palladium-indium intermetallic species is formed during the reaction as the active phase for the reaction. The intermetallic species stabilizes acetaldehyde intermediate and promotes ketonization of the intermediate to hydrogen, 2-propanone, and carbon dioxide.

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