

Liquid Phase Ethanol Reforming with Water over Alumina Supported Ir and Pt Catalysts

Shuichi Naito*, Takehiko Sakamoto, Sachio Takemoto, and Akihiro Yoshida
 Department of Material and Life Chemistry, Kanagawa University,
 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan.

Introduction

The production of hydrogen by reforming of hydrocarbons or alcohols has attracted great attention for fuel cell applications. Among the liquid feedstocks proposed for producing hydrogen, ethanol is one of the most promising candidates because of its relatively high hydrogen content, possibility to form from renewable origin (bio-ethanol), non-toxicity, and storage and handling. Accordingly, the steam reforming of ethanol has received significant attention and various catalysts have been reported, which can effectively break the C-C bond in ethanol to produce H_2 and CO_2 . The reaction is highly endothermic and takes place at above 650K, and undesirable by-products are formed in significant amount at lower temperatures. The formation of intermediates such as C_2H_4 (by dehydration) and CH_3CHO (by dehydrogenation) may reduce the productivity of H_2 and causes the deactivation of catalysts.

On the other hand, very few studies have been reported on the liquid phase reforming of alcohols with water probably due to the difficulty of experimental setup and product analyses. Recently we have investigated liquid phase reforming of methanol at 373K and found that Pt-Mo/ Al_2O_3 or Ir-Re/ TiO_2 catalysts are very active and selective for hydrogen production [1,2]. In the present work, we have extended our study to the liquid phase reforming of ethanol with water, from which we can expect the improvement of the selectivity and durability of the catalysts at lower temperatures.

Materials and Methods

Al_2O_3 supported Ir and Pt catalysts (5 wt%) were prepared by a conventional impregnation method employing H_2IrCl_6 and H_2PtCl_6 as precursors. The reaction was carried out in a stainless steel autoclave (volume: 400 ml) with a reflux condenser connected to an online TCD and FID gas chromatographs for gas phase and liquid phase product analysis, respectively. After the reduction of the catalyst (0.5g) with H_2 at 623 K, 80 cm^3 of degassed ethanol solution ($EtOH:H_2O = 1:1$) was introduced into the reactor under nitrogen atmosphere and the reaction was started at 473 K under 2.5 to 3.0 MPa. During the reaction, the liquid phase content of the autoclave was stirred vigorously by a magnetic stirrer. The catalysts were characterized by means of TEM, XPS and XRD techniques as well as H_2 adsorption at room temperature for the estimation of metal dispersion (D_{H_2}).

Results and Discussion

Figure 1 shows the times courses of the liquid phase $EtOH-H_2O$ reaction over 5wt% Ir/ Al_2O_3 and Pt/ Al_2O_3 catalysts at 473K. The amounts of H_2 , CH_4 and CO_2 increased linearly

Table 1. Dispersion, conversion of EtOH and selectivity(%) of the products(after 10 hrs)

Catalysts	Disp.	Conv.	H_2	CH_4	CO_2	AcH	AcOH	AcOEt
Ir/ Al_2O_3	38%	3.8%	62	5	18	4	5	7
Pt/ Al_2O_3	37%	4.8%	62	12	11	2	7	6

with time suggesting the formation of these gases as final products at 473K. On the contrary, the amount of liquid phase products (AcH, AcOH and AcOEt) stayed rather constant during the reaction, suggesting the successive formation of gas phase products from liquid phase ones.

Fig 2 represents the plausible reaction scheme for the liquid phase $EtOH-H_2O$ reaction.

Acetaldehyde and acetic acid may be formed by the successive dehydrogenation of ethanol releasing H_2 , whereas equimolar amount of CH_4 and CO_2 may be formed by the decomposition of CH_3COOH (Path (1)). In the case of Pt/ Al_2O_3 , almost the same amount of CH_4 and CO_2 was formed as shown in Table 1, indicating that hydrogen is formed only from the dehydrogenation process of ethanol. On the contrary over Ir/ Al_2O_3 , more than three times of CO_2 were formed, indicating the occurrence of reforming of acetaldehyde with water forming H_2 and CO_2 (Path(2)). To investigate the mechanistic difference of H_2 formation over Ir/ Al_2O_3 and Pt/ Al_2O_3 catalysts more clearly, FT-IR spectra were compared during gas phase $EtOH-H_2O$ reaction over both catalysts at elevated temperatures. At around 473K, two characteristic bands were observed at around 1575 and 1465 cm^{-1} , which can be assigned to adsorbed acetate species on the metal surfaces. Over Pt/ Al_2O_3 acetate bands disappeared at 573K, whereas over Ir/ Al_2O_3 , these bands were stable even above 673K.

Consequently, it is reasonable to suppose that stabilization of acetate species on Ir/ Al_2O_3 may be important to give a chance for reforming acetate with water forming H_2 and CO_2 .

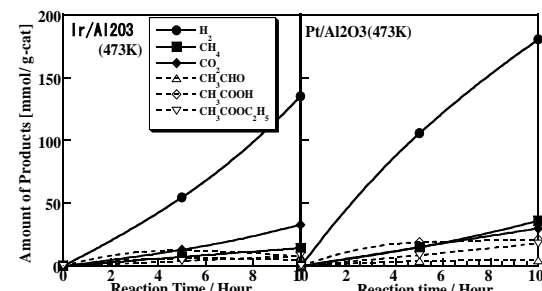


Fig. 1 Time courses of liquid phase $EtOH-H_2O$ reaction

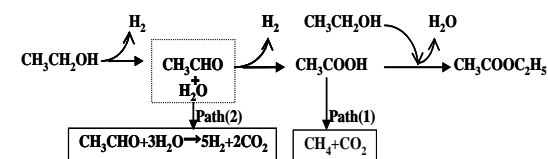


Fig.2 Reaction scheme of ethanol reforming

Significance

Liquid phase reforming of ethanol with water was investigated over Ir/ Al_2O_3 and Pt/ Al_2O_3 catalysts for the first time. Gas phase products were formed by the successive reaction of CH_3CHO and CH_3COOH in the liquid phase. Over Ir catalysts, surface acetate species may be active for the reforming with water to form H_2 and CO_2 even at lower temperatures as 473K.

References

1. T. Miyao and S. Naito et al., Catal. Commun., 6, 113-117 (2005).
2. T. Miyao and S. Naito et al., Appl. Catal., A:General, 299, 285-291 (2006).