Methanolysis of ammonia borane over supported AuPd alloy catalyst

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Abstract: Highly dispersed AuPd alloy nanoparticles (NPs) with various Pd/Au molar ratio on active carbon (AuPd/AC) were synthesized and the catalytic activity for methanolysis of ammonia borane ($H_3NBH_3+4CH_3OH \rightarrow NH_4B(OCH_3)_4+3H_2$) was examined. The activity of Pd/AC catalyst was significantly enhanced by alloying with Au atoms and TOF value was increased with decreasing Pd/Au ratio. The structural characterization combined with kinetic analysis elucidated the formation of electron-deficient and isolated single Pd atoms in random AuPd alloy NPs with a low Pd/Au ratio, which can accelerate the coordination of methanol to boron species to form H_2.

Keywords: Dehydrogenation, ammonia borane, AuPd alloy nanoparticle

1. Introduction

Hydrogen is considered to be alternative energy carriers to oil because it is high gravimetric energy density and environmental friendly. On the other hand, hydrogen is low volumetric energy density and flammable. Therefore, an important issue is how to store and transport hydrogen effectively and safety. Recently, development of a new forms of energy carrier has been carried out by many researchers in order to realize hydrogen energy-based society. Ammonia borane (NH_3-BH_3:AB) has attracted attention as a promising hydrogen carriers due to its high hydrogen content (19.6 %) and H_2 release at ambient conditions.[1] In this study, the correlation between the catalytic activity toward methanolysis of AB and the state of supported AuPd alloy NPs was investigated.

2. Experimental

Supported AuPd alloy NPs were prepared by sol-immobilization method. A Pd and Au aqueous solution was prepared by dissolving $PdCl_2$, $HAuCl_4$ and polyvinylalcohol (PVA), then $NaBH_4$ aqueous solution was added to form the colloidal solution. Active carbon (AC, Ketjen Black carbon ECP) was added to the colloidal solution, followed by filtered, washed and dried at 353 K. The obtained catalysts were denoted xAuyPd/AC, where x and y denote the molar ratio of Au to Pd. The total loading amount of metals was fixed at 5 wt%. Methanolysis of AB was carried out in 30 mL two-necked round bottom flask with a reflux condenser and equipped with gas burette under N_2 atmosphere. The volume of generated gas was measured by recording the displacement of water level and analyzed by GC. The supported AuPd alloy catalysts were characterized by XRD, TEM, XAFS, and CO adsorption.

3. Results and discussion

Figure 1 shows catalytic activity and H_2 production rate for methanolysis of AB over AuPd alloy catalysts with various molar ratio. xAuyPd/AC showed higher H_2 production rate than Pd/AC, whereas Au/AC showed no activity, implying that Pd is active species. The H_2 production rate depended on Pd/Au ratio. Among xAuyPd/AC tested, 1Au1Pd/AC exhibited the highest activity per unit weight of catalyst. CO can adsorb on AuPd/AC and Pd/AC, but no adsorption was observed on Au/AC. The TOF value normalized amount of adsorbed CO was improved with decreasing Pd/Au ratio and 10Au1Pd/AC showed the highest TOF. TEM images of xAuyPd/AC mentioned the size of AuPd alloy NPs were estimated to about 2~3 nm regardless of Au/Pd molar ratio, indicating the enhancement of catalytic activity was not attributed to the change in particle size. The white line intensity of Au L_3 edge XANES spectra increased with decreasing Pd/Au ratio, indicating the charge transfer from Pd to Au atoms. Curve-fitting analysis of EXAFS at Pd K-edge and Au L_3-edge showed the coordination numbers of Pd-Au and Au-Pd gradually increased and the coordination numbers of Pd-Pd decreased with an increase in the Au/Pd ratio. These results indicate the formation of random AuPd alloy NPs (Fig. 2). Based on the model, it seems that electron-deficient and isolated single Pd atoms surrounded by Au atoms were formed on the catalysts with a low Pd/Au ratio (cf. Pd/Au ratio=0.1 and 0.2).

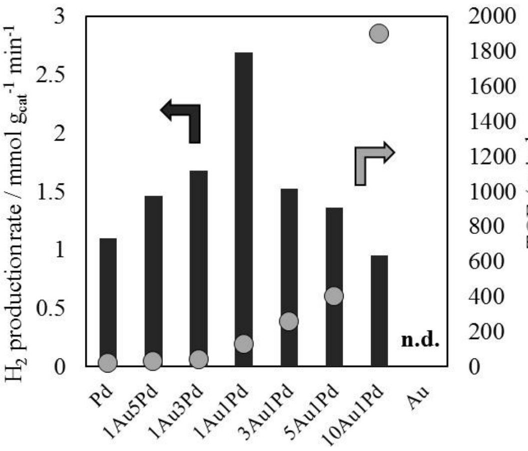

Fig 1. Catalytic activity over AuPd/AC at 298 K catalyst 30 mg, AB 30 mg, MeOH 5 mL

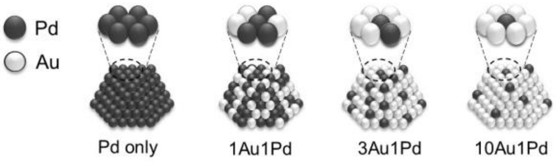

Figure. 2. Formation of isolated Pd site in random AuPd alloy nanoparticle

Table 1. Effect of substrate and catalyst
$r = k\,[AB]^{\alpha}\,[CH_3OH]^{\beta}\,[Catalyst]^{\gamma}$

Catalyst	α	β	γ	KIE
Pd/AC	-0.25	0.30	1.54	2.9
10Au1Pd/AC	-0.28	0.57	1.76	4.7

To investigate the reaction mechanism, dependency of H_2 production rate against concentration of substrate and catalyst was investigated (Table 1). The order of [AB] was negative and [MeOH] was positive in spite of the presence or absence of Au. Furthermore, the kinetic isotope effect using CH_3OD were examined, revealing rate-determining step was including the activation step of methanol (Table 1). Methanolysis of trimethylamine borane (TMAB) and dimethylamine borane (DMAB) were carried out over Pd/AC and 10Au1Pd/AC to examine the effect of property of amine group on H_2 production rate. Methanolysis of DMAB was faster than methanolysis of AB, but TMAB was slower. Because methyl group works as electron-donating, Lewis basicity of amine borane was affected by replacing H atom of amine group to methyl group. Moreover, the effect of steric hindrance of amine group, which is increased with increasing number of substituted methyl group, causes the negative effect of adsorption of amine borane and methanol. Considering reaction results, it seems that the strength of Lewis basicity and steric effect of amine borane have considerable effect on H_2 production rate. The change in white line intensity of Au L_3 XANES spectra indicate that the electron density of Au was decreased with decreasing Pd/Au ratio, suggesting that Lewis acid strength of Au in random AuPd alloy NPs was increased with decreasing Pd/Au ratio. The increasing in Lewis acid strength of Au may promote adsorption of amine borane on Au atoms through amine site, resulting in acceleration of coordination of methanol to boron species to form H_2.

4. Conclusions

In conclusion, we found that supported AuPd alloy catalysts showed a high activity for methanolysis of AB. Catalytic activity of AuPd alloy NPs depended on Pd/Au ratio and TOF value was significantly improved with decreasing Pd/Au ratio. XAFS spectra and TEM images elucidated the charge transfer from Pd to Au, and the formation of random AuPd alloy nanoparticles with a size of 2~ 3 nm. Moreover, isolated single Pd atom surrounded by Au atoms was mainly formed when Pd/Au ratio was low (cf. 0.1 and 0.2). Kinetic analysis indicated that the rate-determining step is the activation step of methanol. The results of methanolysis of amine borane suggested that the rate of methanolysis is influenced by both Lewis basicity and steric effects of amine borane.

References

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