Selective Decomposition of Formic Acid on Pd-Au Bimetallic Surfaces

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Abstract: The catalytic decomposition of formic acid (HCOOH) at Pd-Au bimetallic surfaces was studied using temperature-programmed desorption (TPD) and reactive molecular beam scattering (RMBS) techniques. Using H_2-TPD, Pd-Au interface sites and Pd(111)-like sites (lack neighboring Au atoms) are characterized qualitatively and quasi-quantitatively at the Pd-Au model surface. HCOOH-RMBS experiments indicate that surface Pd atoms facilitate the activation of HCOOH *via* dehydrogenation at Pd-Au interface sites, whereas *via* dehydration at Pd(111)-like sites. These findings suggest that the HCOOH dehydrogenation at Pd-Au surfaces could be optimized by controlling the arrangement of surface Pd and Au atoms.

Keywords: Pd-Au alloy, formic acid, H_2 production.

1. Introduction

Hydrogen is a promising energy carrier for electricity generation in a fuel cell; however, hydrogen storage and distribution remain challenging issues. Formic acid (HCOOH) has been proposed as a potential liquid organic hydrogen carrier (LOHC) to circumvent these issues. For practical applications, suitable catalysts are essential to facilitate HCOOH decomposition *via* dehydrogenation as opposed to dehydration to supply H_2 at ambient temperatures. Pd-Au catalysts have shown exceptional performance for H_2 production from HCOOH decomposition.[1, 2] The high yield toward H_2 production has been attributed to (i) a higher resistance to CO poisoning due to alloying of Pd with Au;[1] and (ii) the possible charge transfer between Au and Pd (*i.e.*, a ligand effect).[2] In this contribution, the surface chemistry of HCOOH on Pd-Au bimetallic model surfaces was investigated[3] using a surface science approach in an attempt to enhance the fundamental understanding to the catalytic properties of Pd–Au bimetallic surfaces for HCOOH decomposition.

2. Experimental

All experiments[3] were conducted in an ultrahigh vacuum (UHV) chamber equipped with an Auger electron spectrometer (AES), a quadrupole mass spectrometer (QMS), and Fourier transform infrared spectrometer (FT-IR). Pd-Au bimetallic surfaces were generated by depositing 1-4 monolayer (ML) of Pd atoms onto the Au(111) surface at 77 K followed by annealing to 500 K for 10 min. The surface structures of annealed Pd-Au surfaces were characterized by AES, FT-IR using CO as a probe molecule, and H_2-TPD. H_2-TPD is used to provide the qualitative and quasi-quantitative information regarding the Pd-Au interface sites and Pd(111)-like sites at the surface. The reactivity of HCOOH at Pd-Au surfaces was evaluated by HCOOH-RMBS and HCOOH-TPD. The activity for HCOOH decomposition and selectivity for H_2 production at Pd-Au surfaces was estimated from the QMS signals of HCOOH, H_2, CO_2, CO, and H_2O during HCOOH impingement at a surface temperature of 500 K.

3. Results and discussion

The H_2-TPD results of Pd-Au surfaces are depicted in **Figure 1**.[3] The peaks centered at ~208 K and ~300 K are assigned as the desorption of H_2 from Pd-Au interface sites and Pd(111)-like sites, respectively. The integral of the peak area under each H_2-TPD trace is proportional to the amount of Pd atoms at each surface. The relative number of surface Pd atoms increased from 0.32 to 1 (relative to that of the annealed 4

ML Pd/Au(111) surface) for the Pd-Au surface with the initial Pd coverage from 1 to 4 ML (**Table 1**).[3] The fraction of Pd-Au interface site is estimated as unity for the annealed 1 ML Pd/Au(111) surface and reduces to ~0.6 for surfaces with higher initial Pd coverages, *i.e.*, 2–4 ML. The reactivity of HCOOH on Pd-Au surfaces was evaluated by HCOOH-RMBS (**Table 1**).[3] The HCOOH decomposition rate increased as the relative number of surface Pd atoms increased, suggesting that the presence of Pd adatoms on the Pd–Au surface can facilitate HCOOH decomposition (no HCOOH decomposition was detected on the Au(111) surface under the same conditions). A sharp increase in the HCOOH decomposition rate was observed with the emergence of Pd(111)-like sites. The specific activity for H_2 production is expressed in terms of turnover frequency (TOF_{H2}). With the increase of the relative number of surface Pd atoms, the TOF_{H2} first increased to 0.012 H_2 Pd_S^{-1} s^{-1}, and then slightly decreased to 0.009 H_2 Pd_S^{-1} s^{-1}. These results suggest that the side reaction, *i.e.*, dehydration (or decarbonylation), occurs. The dehydrogenation selectivity is expressed by the relative H_2/CO QMS area ratios (**Figure 2**). It is found that hydrogen selectivity correlates well with the fraction of Pd atoms that exist as Pd–Au interface sites, suggesting that HCOOH dehydrogenation occurs at Pd–Au interface sites on the surface.

Table 1. Summary of relative number of surface Pd atoms, fraction of Pd-Au interface sites, HCOOH decomposition rate, turnover frequency for H_2 production, relative H_2/CO QMS ratio on the annealed Pd/Au(111) surfaces.[3]

Initial Pd coverage (ML)	Relative number of surface Pd atoms (-)	Fraction of Pd-Au interface sites (-)	HCOOH decomposition rate (HCOOH cm^{-2} s^{-1})	Turnover frequency for H_2 production (H_2 Pd_S^{-1} s^{-1})	Relative H_2/CO QMS ratio (-)
1	0.32	1	3.5×10^{12}	0.006	2.08
2	0.63	0.66	1.4×10^{13}	0.012	1.19
3	0.84	0.62	3.3×10^{13}	0.011	1.05
4	1	0.60	4.4×10^{13}	0.009	1

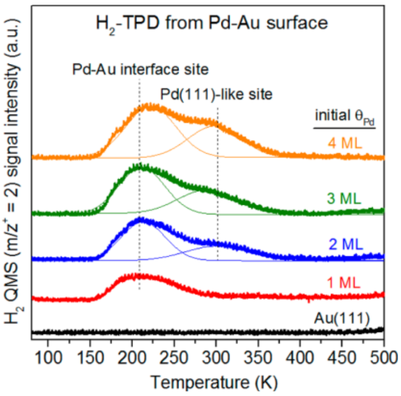

Figure 1. H_2-TPD spectra from Pd–Au surfaces with initial Pd coverages ranging from 0 to 4 ML.[3]

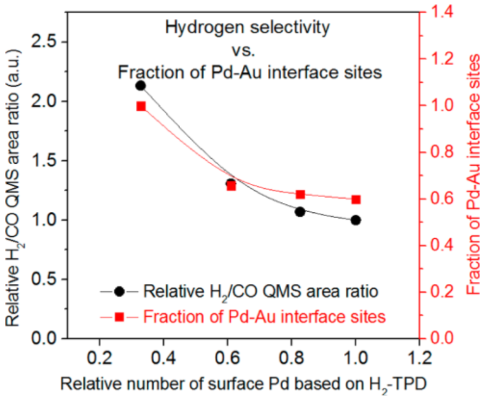

Figure 2. Relative H_2/CO QMS area ratios from HCOOH decomposition vs. the fraction of Pd–Au interface sites on Pd–Au surfaces.[3]

4. Conclusions

We have conducted a model catalyst study showing that Pd atoms which lack adjacent Au atoms favor dehydration of HCOOH, whereas Pd atoms that possess Au atoms as nearest neighbors favor dehydrogenation of HCOOH, which is desirable for efficient production of hydrogen. We believe these findings will be informative for the design of Pd–Au bimetallic catalysts that selectively decompose HCOOH to produce hydrogen.

References

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