

Discovery of *in situ* generated Pd–Au–C_x from Pd–Au during the acetoxylation of ethylene

Vinyl acetate monomer (VAM) is an important chemical intermediary in industry for the manufacture of paints, adhesives, fibers, and surface coatings. A well-known commercial technique for the manufacture of VAM is the catalytic acetoxylation of ethylene ($\text{CH}_3\text{COOH} + \text{C}_2\text{H}_4 + 1/2\text{O}_2 \rightarrow \text{VAM} + \text{H}_2\text{O}$) over silica-supported Pd–Au bimetallic catalysts (Pd–Au/SiO₂) with potassium acetate (KOAc). In this reaction, the addition of Au to Pd boosts the VAM formation rate while also increasing the VAM selectivity moderately. Additionally, the KOAc addition further boosts the catalytic activity and selectivity. Although this process has been used commercially for decades, no literature that offers thorough insights into the functions of Au and KOAc for Pd in the commercial catalyst has been reported [1].

The major technical challenge of the Pd–Au system is the preparation of homogeneously distributed Pd–Au alloy nanoparticles with high-phase purity. Employing nonuniform Pd–Au alloy nanoparticles induces undesired changes in alloy phases, which has complicated this system and hampered the elucidation of the roles of Au and KOAc additives in the commercial catalyst (Fig. 1(a)). In detail, researchers have overlooked the *in situ* formation of Pd–Au–C_{lattice} during the reaction. In this study, we developed the synthetic method to obtain uniform Pd–Au alloy nanoparticles on SiO₂ and thoroughly characterized the structural changes of

the Pd–Au alloys before and after the VAM synthesis using X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) (Fig. 1(b)). As a result, we found that there was no change in the Pd/Au ratio in uniform Pd–Au alloys after reaction, while the carbon atoms were spontaneously doped into the lattice of Pd–Au to form Pd–Au–C_{lattice}. During the process, the KOAc addition dramatically raised the amount of incorporated carbide atoms. Guided by this discovery, we performed in-depth experimental and theoretical analyses, revealing that the alloying Pd with Au and doping carbon atoms *in situ* to the interstitial voids are the keys to enhance the catalytic activity and selectivity of VAM synthesis.

A series of Pd_{1-x}Au_x/SiO₂ was synthesized by pore-filling co-impregnation with freeze-drying. The as-prepared Pd_{1-x}Au_x/SiO₂ was further annealed at 500°C for 1 h under a H₂ atmosphere, then the KOAc additive was loaded by pore-filling co-impregnation with freeze-drying. It should be noted that the successful synthesis of homogeneously distributed Pd_{1-x}Au_x alloy nanoparticles on SiO₂ with desired alloy compositions without pristine Pd and Au was confirmed by the powder XRD and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements.

XAFS measurements were performed at SPing-8 BL01B1 and BL14B2 beamlines. The Fourier transforms of the extended XAFS spectra (FT-EXAFS)

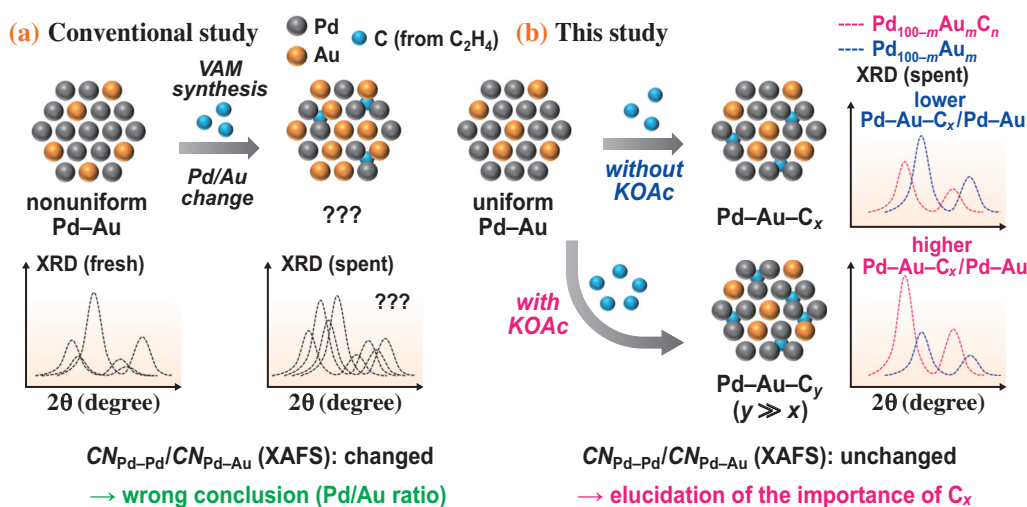


Fig. 1. Schematic illustrations of the different between the (a) conventional study and (b) this study for the acetoxylation of ethylene over nanoparticulate Pd–Au alloy. This study excluded the change in alloy compositions during the VAM synthesis, thereby, we found that carbon atoms spontaneously dope into the Pd–Au alloy lattice and function as a “Trojan horse” dopant to enhance catalytic performance.

of Pd_{1-x}Au_x/SiO₂ catalysts ($x = 0, 0.2, \text{ and } 0.5$) are shown in Fig. 2(a). After alloying, the peak intensity at 2.45 Å due to Pd–Pd scattering was reduced, and a new peak at 2.80 Å assignable to Pd–Au scattering appeared. Then, we performed curve fitting analysis for Pd *K*-edge k^3 -weighted EXAFS spectra. Pd_{0.8}Au_{0.2}/SiO₂ showed Pd–Pd and Pd–Au scatterings at 2.76 Å ($CN_{\text{Pd–Pd}} = 7.3$) and 2.77 Å ($CN_{\text{Pd–Au}} = 2.3$), respectively. Additionally, Pd_{0.5}Au_{0.5}/SiO₂ showed Pd–Pd and Pd–Au scatterings at 2.76 Å ($CN_{\text{Pd–Pd}} = 5.0$) and 2.79 Å ($CN_{\text{Pd–Au}} = 4.6$), respectively. Importantly, the ratios of $CN_{\text{Pd–Au}}/CN_{\text{Pd–Pd}}$ in Pd_{0.8}Au_{0.2}/SiO₂ and Pd_{0.5}Au_{0.5}/SiO₂ were 0.31 and 0.93, which matched with the ideal ratios of 0.25 and 1.0, respectively. Therefore, we successfully synthesized the Pd_{1-x}Au_x/SiO₂ catalysts with high-phase purities.

Then, we carried out the acetoxylation of ethylene in the presence of O₂ at 160°C using Pd_{1-x}Au_x/SiO₂ catalysts with and without KOAc as a promoter, then characterized the structural changes after reaction. The XRD patterns of the spent catalysts showed the appearance of new peaks at lower diffraction angles, which suggests that the alloy compositions changed and/or that a light element like hydrogen or carbon have been incorporated into the lattice of the alloy. Importantly, the expansion of crystal lattice was also observed for the spent Pd/SiO₂ catalyst, as previously reported in the monometallic Pd systems (PdC_y) [2], which supports the presence of dopants in the lattice. The XANES spectrum of the spent KOAc/Pd_{0.8}Au_{0.2}/SiO₂

catalyst is shown in Fig. 2(b). The spectral feature around 24375 eV was widened, indicating carbide formation rather than hydride formation [3]. We then performed curve fitting analysis for Pd *K*-edge k^3 -weighted EXAFS spectrum revealed that the alloy composition and *CN* did not change from those of the fresh catalyst (Figs. 2(c) and 2(d)). These results demonstrates that, during the reaction, carbon atoms were spontaneously incorporated into the lattice voids of Pd or Pd–Au alloys, resulting in the formation of carbides while retaining the alloy compositions. Furthermore, we quantitatively evaluated the Pd–Au–C_{lattice} species, finding that the KOAc addition dramatically increased the amount of incorporated carbon atoms.

Based on the discovery of Pd–Au–C_{lattice}, we performed in-depth kinetic studies and theoretical calculations to separately understand the roles of Au and interstitial carbon atoms (KOAc). The coupling of acetate and ethylene, which is the rate-determining step, is effectively promoted by the synergistic contributions of Au (electronic/geometric effects) and interstitial carbon (electronic effect). In addition, this synergy inhibited ethylene dehydrogenation, which ultimately slowed the formation of CO₂. The contentious debates about the roles of Au and KOAc in the acetoxylation of ethylene have been resolved owing to the experimental and theoretical insights into the roles of Pd–Au formation, Au/Pd ratio, and interstitial carbon atoms.

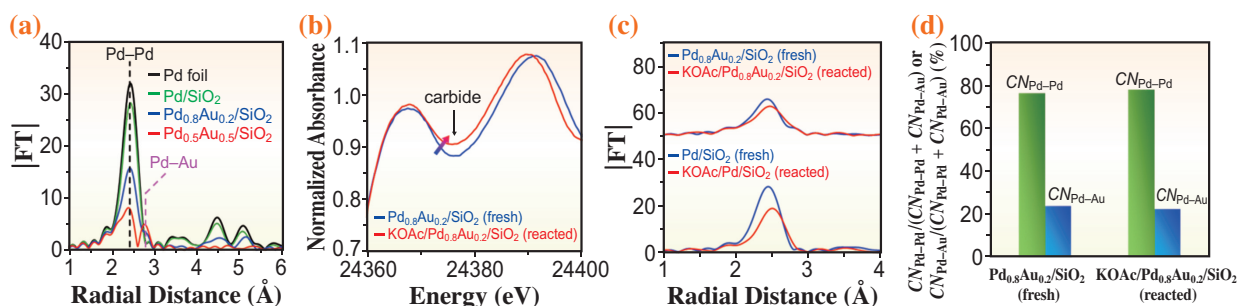


Fig. 2. (a) Pd *K*-edge k^3 -weighted FT-EXAFS spectra of the fresh Pd_{1-x}Au_x/SiO₂ catalysts ($x = 0, 0.2, 0.3, \text{ and } 0.5$). (b) Pd *K*-edge XANES spectra of fresh Pd_{0.8}Au_{0.2}/SiO₂ and reacted KOAc/Pd_{0.8}Au_{0.2}/SiO₂. (c) Pd *K*-edge k^3 -weighted Fourier transform EXAFS spectra. (d) Alloy compositions in the fresh Pd_{0.8}Au_{0.2}/SiO₂ and reacted KOAc/Pd_{0.8}Au_{0.2}/SiO₂ catalysts using $CN_{\text{Pd–Pd}}$ and $CN_{\text{Pd–Au}}$ values.

Yuki Nakaya and Shinya Furukawa*

Graduate School of Engineering, Osaka University

*Email: furukawa@chem.eng.osaka-u.ac.jp

References

- [1] Y. Nakaya, S. Furukawa: Chem. Rev. **123** (2023) 5859.
- [2] Y. Han *et al.*: J. Catal. **230** (2005) 353.
- [3] W. Jones *et al.*: ChemCatChem **11** (2019) 4334.
- [4] Y. Nakaya, E. Hayashida, R. Shi, K. Shimizu, S. Furukawa: J. Am. Chem. Soc. **145** (2023) 2985.