Direct observation of H_2 dissociation and spillover process on Pd/Cu single atom alloy catalyst surface by spectroscopic method

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The dissociation of hydrogen molecules on the catalyst surface is an important elementary reaction in various industrial processes. For example, Cu-based catalysts in methanol synthesis reactions show low H_2 dissociation activity, and thus a high temperature is required. However, it is unfavorable for exothermic methanol generation from CO_2 and H_2. More active catalysts for H_2 dissociation are indispensable for efficient hydrogenation reactions. For this purpose, Pd/Cu single atom alloy catalyst (SAAC) is one of the attractive solution, in which a few percent of Cu surface atoms are replaced with Pd atoms. It has been reported that H_2 is dissociated on the Pd/Cu SAAC surface even at low temperatures, and that H atoms spillover onto the Cu host surface[1]. In this study, the processes of hydrogen dissociation and spillover on Pd/Cu SAAC surface was investigated using high-resolution X-ray photoelectron spectroscopy (XPS) and infrared reflection absorption spectroscopy (IRAS).

For XPS experiments, the Pd/Cu(977) SAAC was prepared in which the coverage of Pd(θ_{Pd}) was 0.07 ML. The peak of $Pd3d_{5/2}$ was observed at 335.3 eV on the clean SAAC surface. As a function of exposure to H_2 at 80 K, the $Pd3d_{5/2}$ peak was shifted to 335.6 eV and 336.5 eV in two steps(Fig. 1 (a)).

For IRAS experiments, the ML Pd/Cu(111) SAAC was prepared(θ_{Pd} = 0.01 ML). Time-resolved IRAS measurements were performed during H_2 exposure at 83 K. The H-Cu vibrational peak appeared at 1143 cm^{-1} about 300 s after starting H_2 exposure[2], and it developed with elapsed time (Fig. 1 (b)).

These results directly indicated the processes of hydrogen dissociaion, adsorption and spillover on the Pd/Cu SAAC surface. The Pd atoms act as a site for H_2 dissociation and initial H adsorption, and the spillover to Cu sites occurs only after Pd sites are saturated with H atoms.

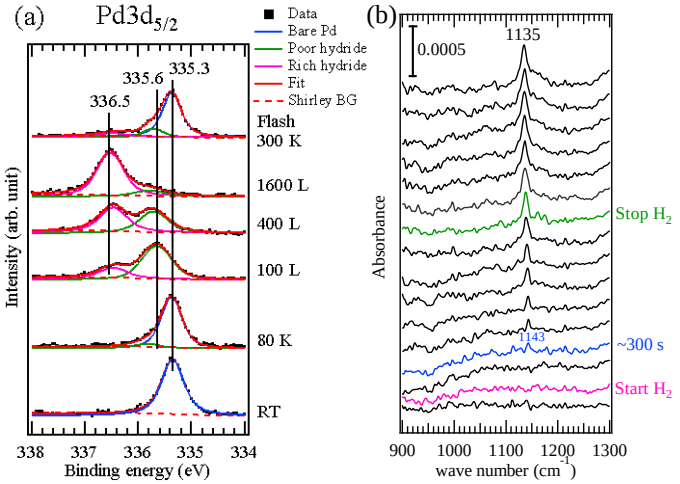

Fig. 1 Results of (a) XPS, *hv* = 680 eV. (b) IRAS, 4 cm^{-1} of resolution, 500 scans.

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