

## Supporting Information; Computing a rate constant of the first oxidation process of PdZn nanoparticles

Figure S1 (a) shows DXAFS spectra before ( $t=0$  s) and after ( $t=48.8$  s) the first oxidation process of PdZn nanoparticles at 673 K under oxygen atmosphere ( $P_{O_2} = 22$  kPa). Absorbance at 24356 eV which indicates the oxidation state of Pd didn't change between 0 s and 48.8 s. This supports the idea that Pd atoms were not oxidized during the first 50 s. The coordination number of Zn decreased during the first 50 s as shown in Table 1. PdZn nanoparticles segregated to Pd nanoparticles and ZnO during the period. Absorbance at 24398 eV is shown in Figure S1 (b) and (c) ((b) was obtained by QXAFS and (c) was by DXAFS). In Figure S1 (b), the absorbance changed very quickly during the first 50 s, which should correspond to segregation of PdZn nanoparticles. Absorbance change at 24398 eV during the first 50 s is shown in Figure S1 (c). Variation of the absorbance was fitted with a single exponential function and a rate constant for the first oxidation process was estimated as  $0.14 \text{ s}^{-1}$ .

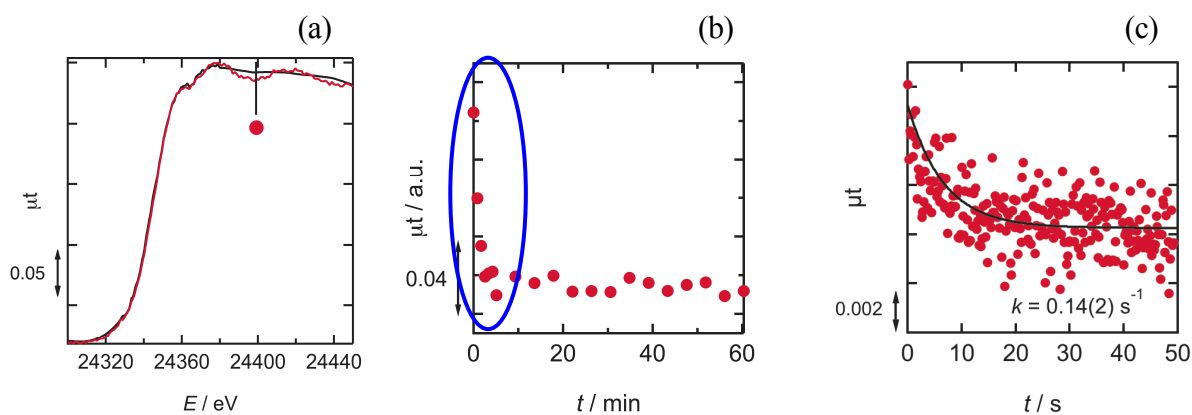


Figure S1 The first oxidation process of Pd/ZnO at 673 K under the oxygen atmosphere ( $P_{O_2} = 22$  kPa); (a) XANES spectra of Pd K edge measured before (black line) and after (red line; 48.8 s), the first oxidation step, (b) variation of X-ray absorbance at 24398 eV measured by QXAFS, (c) that at 24398 eV measured by DXAFS.