

Supporting information for

Investigation on the enhanced catalytic activity of Ni-promoted Pd/C catalyst for formic acid dehydrogenation: Effects of preparation methods and Ni/Pd ratios

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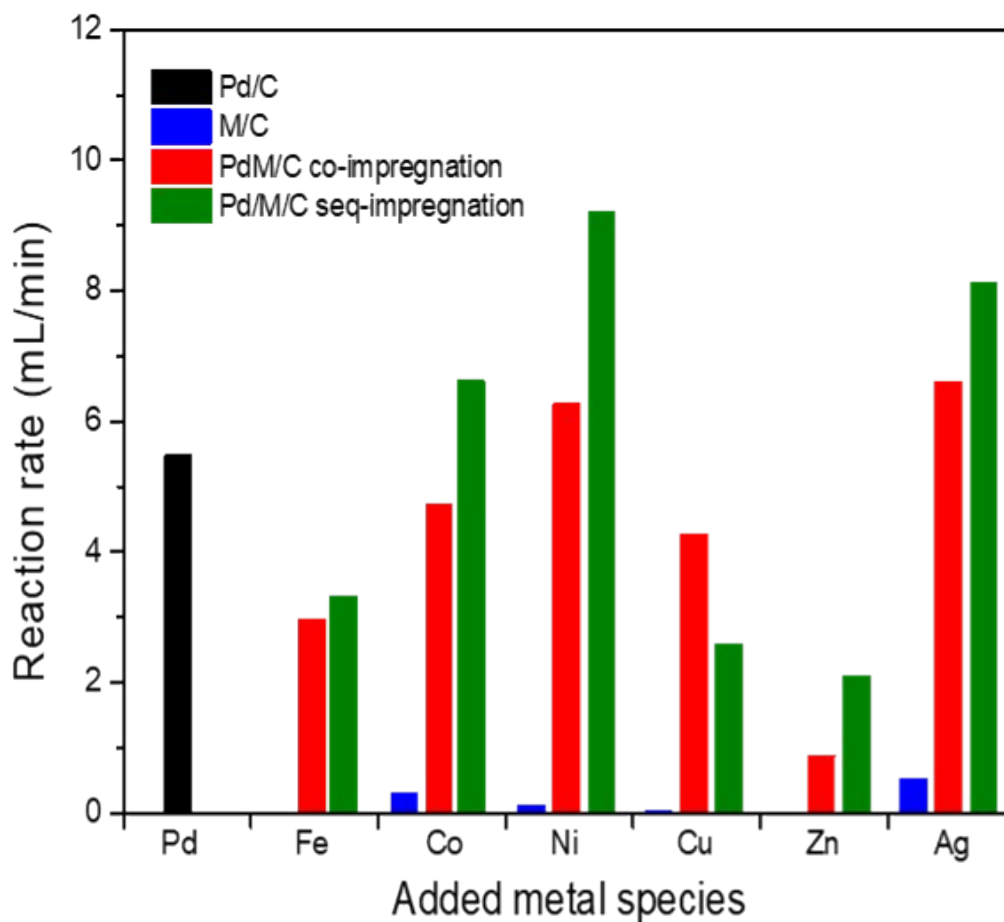


Figure S1. Initial rates at first 30 min during the reaction of 10 mL formic acid (1 M) at 60 °C over the various catalysts (0.05 g) prepared by two preparation methods with nominally 10 wt% Pd and 5 wt% metal.

Several metals were chosen to screen promoting metal, and they were impregnated with Pd on carbon by applying two different impregnation methods; co-impregnation and sequential impregnation. As nickel represented the best promoting effect, Ni-promoted catalysts were investigated in our research.

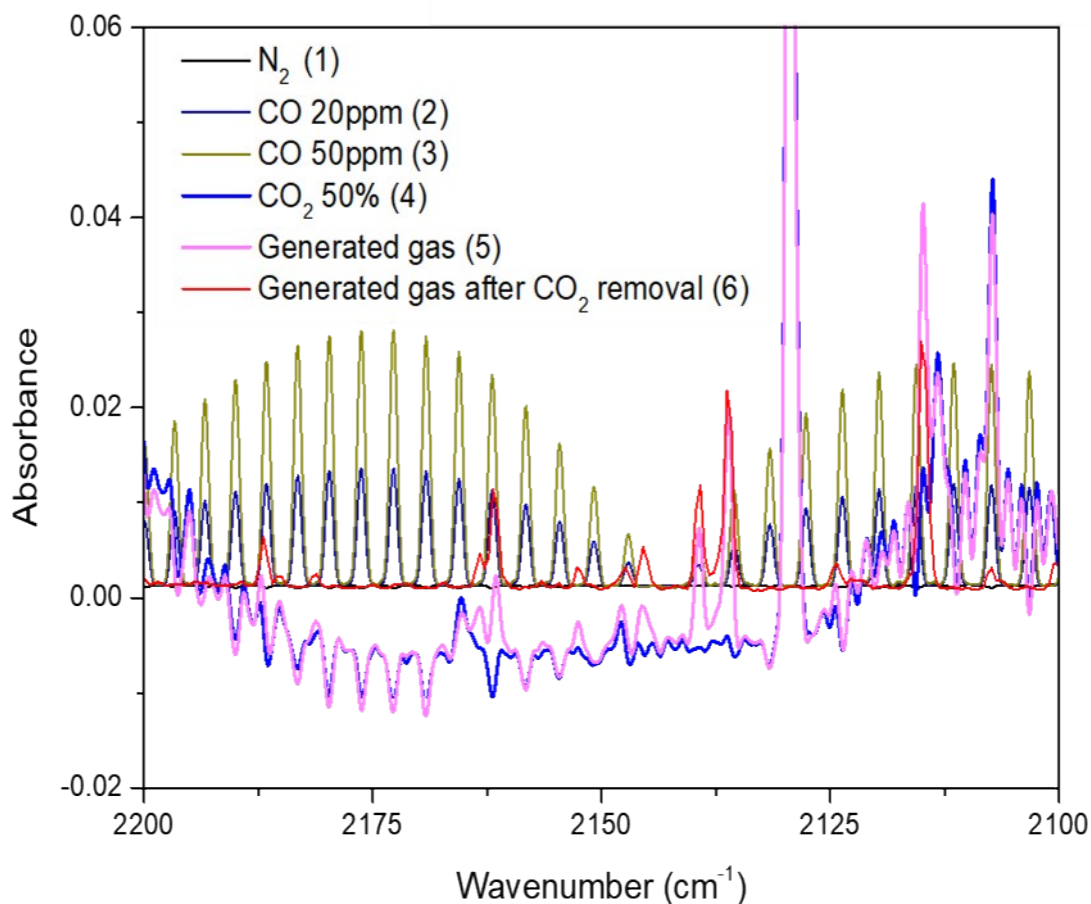


Figure S2. FT-IR spectra of N₂ gas, reference CO gas (20 ppm and 50 ppm CO balanced with N₂), reference CO₂ gas (50 vol% balanced with N₂) and generated gas (with or without removal of CO₂ by NaOH treatment) from formic acid decomposition reaction over Pd₁/NiO_{1.3}/C (seq) catalyst.

The generated gas without NaOH treatment was analyzed, and the result is shown in Figure S2 as pink line (5). Though the base line of IR was deviated from zero intensity due to the high sensitivity of FT-IR analyzer to such a high content of CO₂ (~50%), the difference between reference gas of 50% CO₂ (blue line (4)) and the generated gas (pink line (5)) is hardly seen in the range of 20 ppm CO (navy line (2)). Hence it can be concluded that there is none of CO (much less than 20 ppm) in the generated gas. The additional analysis was performed for the generated gas after the NaOH treatment to show the result more clearly with a flat baseline. The result of NaOH treated gas also confirms that there is no dehydration reaction to produce CO during the formic acid decomposition reaction.

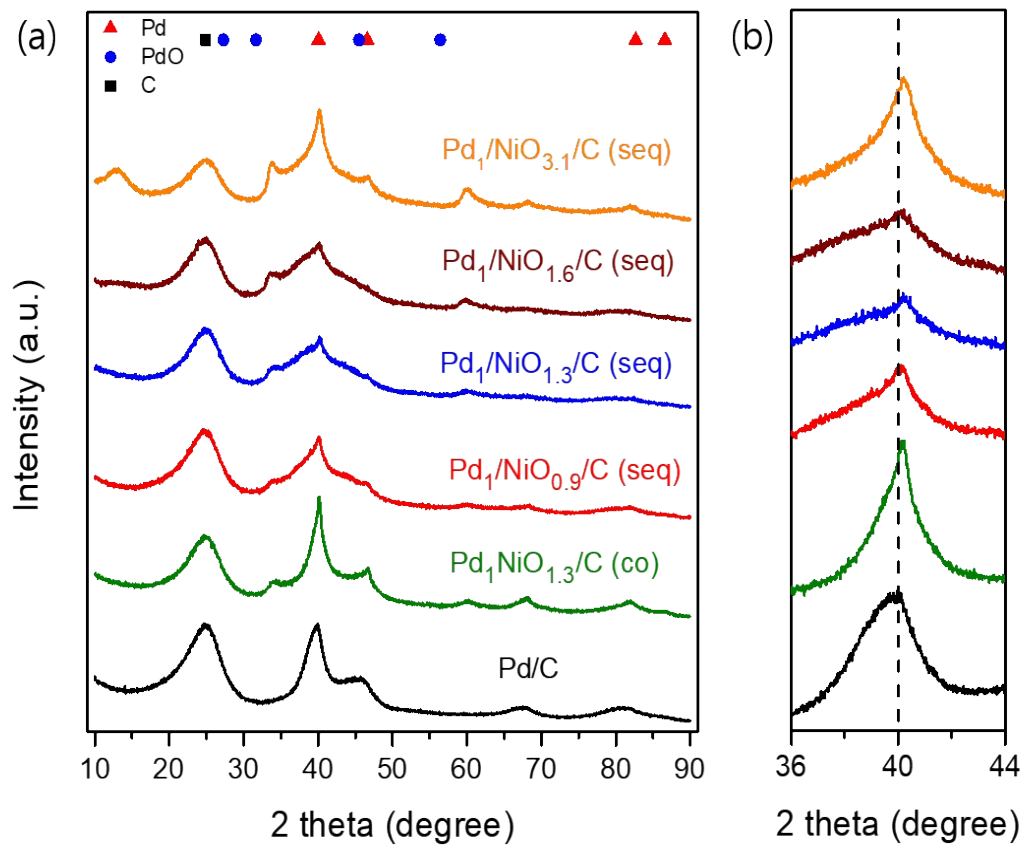


Figure S3. (a) X-ray diffraction patterns and (b) zoomed-in patterns at around 40 ° of various Pd-NiO/C catalysts.

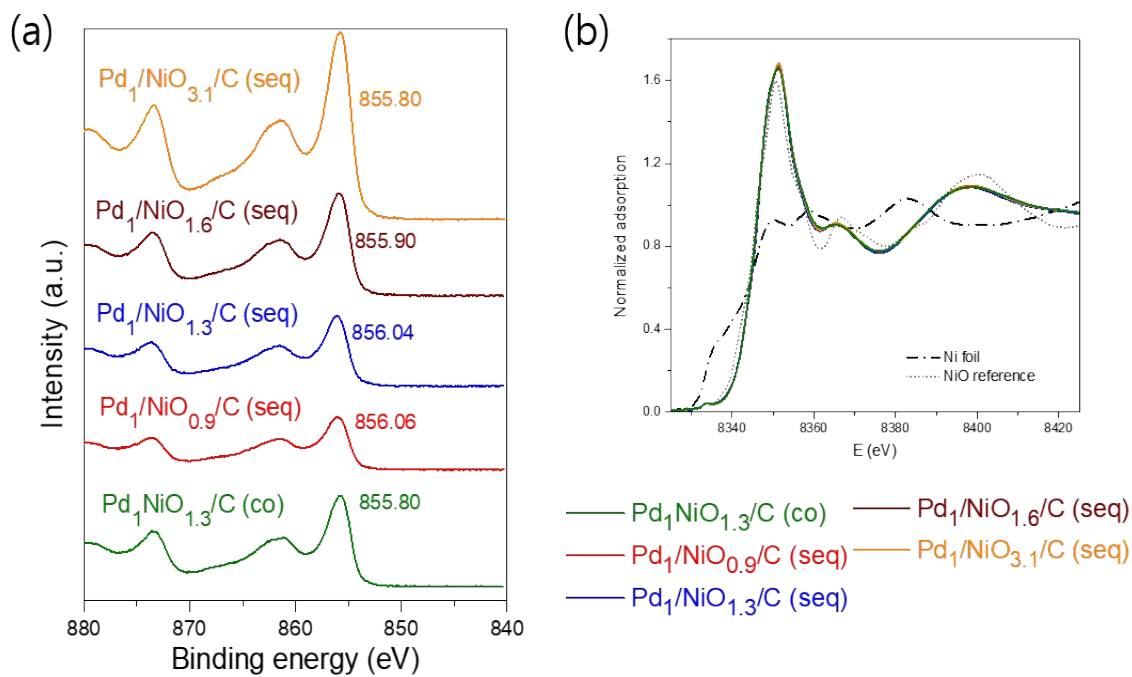


Figure S4. (a) XP spectra in Ni 2p region of Pd-NiO/C catalysts and (b) Normalized XANES spectra for Ni K-edges of Pd-NiO/C catalysts with references (i.e. Ni foil and NiO reference)

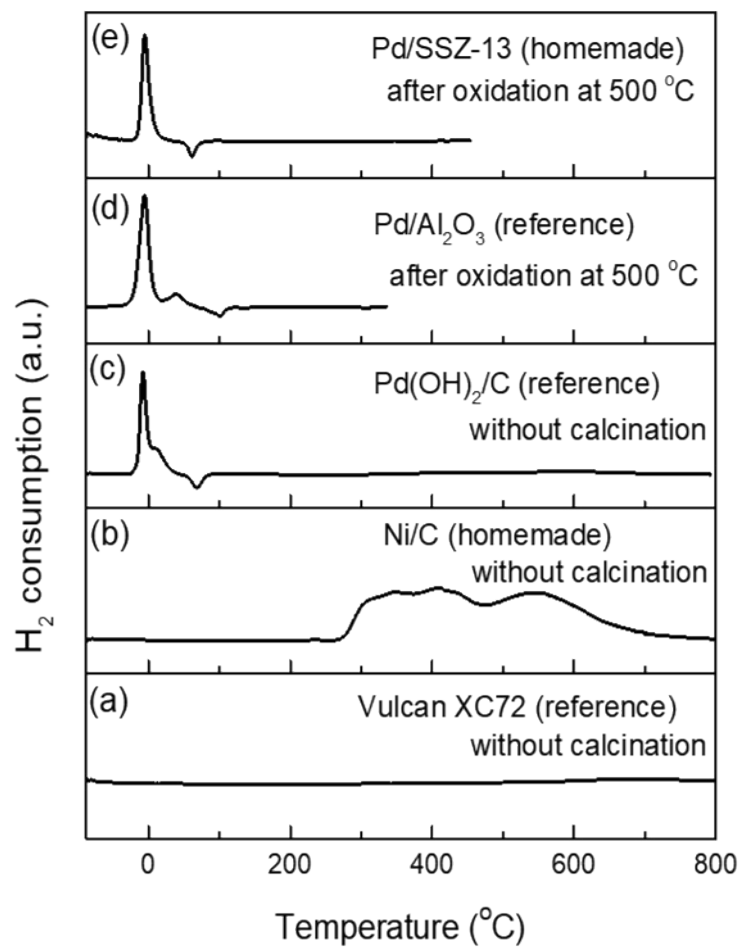
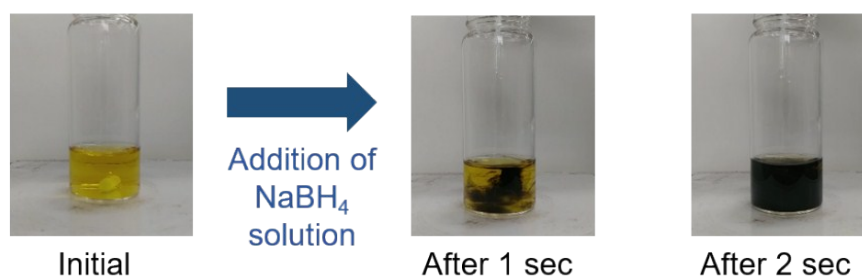


Figure S5. Cryogenic H₂-TPR spectra of (a) Vulcan XC72 (reference), (b) Ni/C (homemade) and (c) Pd(OH)₂/C (reference) without calcination, and (d) Pd/Al₂O₃ (reference) and (e) Pd/SSZ-13 (homemade) after calcination under oxidative condition at 500 °C for 2 h.

(a) Reduction of Pd^{2+} by NaBH_4



(b) Reduction of 10 wt% of NiO on Al_2O_3 by NaBH_4

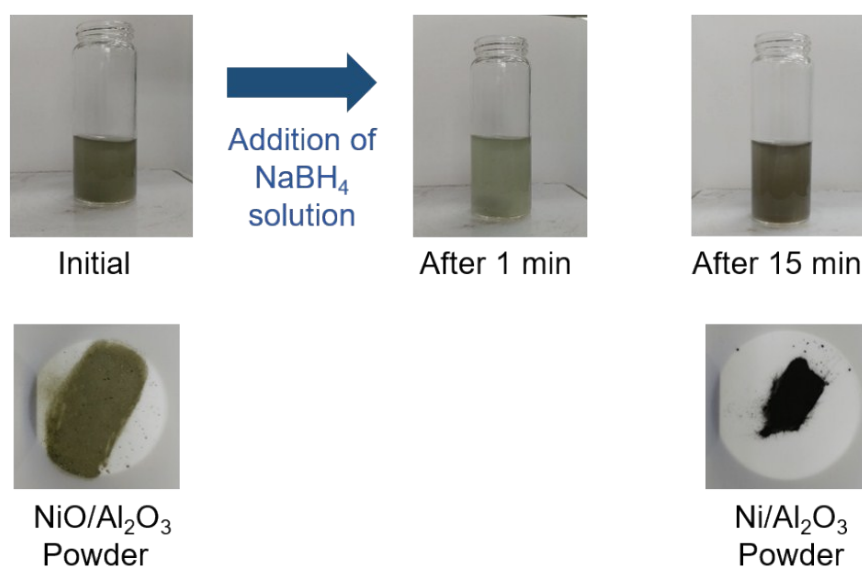


Figure S6. Time-dependent changes in color of (a) Pd^{2+} and (b) $\text{NiO}/\text{Al}_2\text{O}_3$ after addition of NaBH_4 solution

Although both Pd^{2+} and NiO can be reduced by NaBH_4 , the reduction of Pd^{2+} occurs much faster than reduction of NiO . In order to indirectly compare the reduction rate by observing changes in the color of solution, Pd^{2+} solution and NiO on alumina (10 wt% of Ni) solution were prepared, and then reduced by NaBH_4 solution. The reduction of Pd^{2+} was completed within a couple of seconds as represented in Figure S7(a). In contrast, the reduction of NiO on alumina took more than 1 min as shown in Figure S7(b). Therefore, when preparing $\text{Pd}_1/\text{NiO}_x/\text{C}$ (seq) catalyst, Pd^{2+} might be rapidly reduced by NaBH_4 before the reduction of NiO .

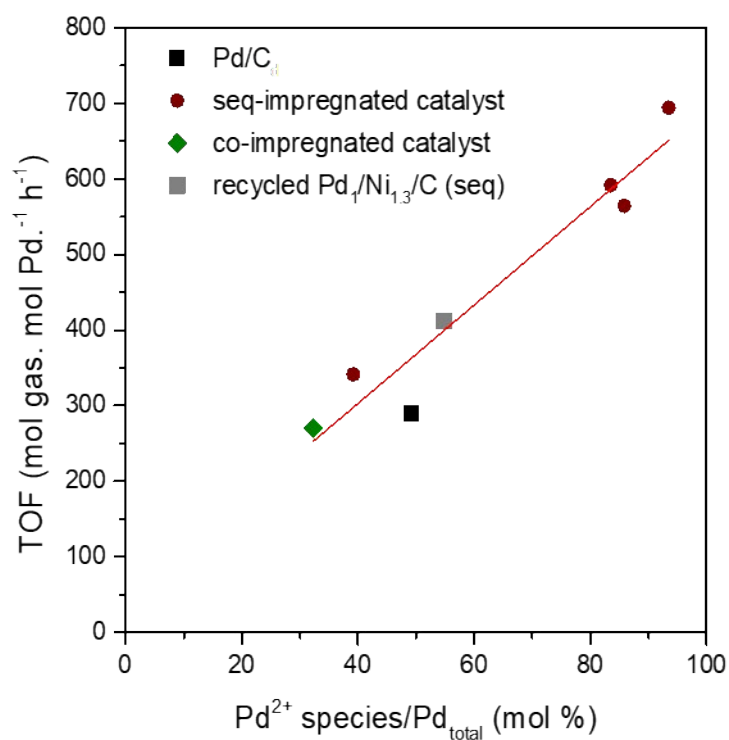


Figure S7. The correlation between Pd²⁺ species/Pd_{total} (mol %) and the TOF (mol gas · mol Pd⁻¹ · h⁻¹) of the catalysts same as Figure 7 in manuscript with the point of recycled Pd₁/NiO_{1.3}/C (seq) catalyst (gray square).