Supplementary Information (SI) for Energy & Environmental Science.

Supplementary Materials for

Industrially viable formate production with 50% lower CO_2 emissions

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Supplementary Text

Synthesis of electrocatalysts

The synthesis of $Pt_x@Ni(OH)_2$ (x = 1.05, 3.00, and 4.91) catalysts involves depositing Pt nanoparticles onto commercially available $Ni(OH)_2$.[1] Initially, 200 mg of $Ni(OH)_2$ and 150, 200, or 250 mg of $PtCl_4$ are dissolved in 40 ml of hexanol in a flask. The mixture is stirred at 500 rpm and heated to 60 ℃ for 10 minutes to ensure the uniform dispersion of $Ni(OH)_2$. Subsequently, the solution is heat-treated at 120℃ for an hour, resulting in a black precipitate. The final $Pt_x@Ni(OH)_2$ product is obtained by washing the mixture with ethanol and deionized water five times and then centrifuging it at 8000 rpm for 40 minutes. For the Pt nano catalyst, 200 mg carbon black (Vulcan 72) is used instead of $Ni(OH)_2$.

Material Characterizations. The Bruker D8 Advance X-ray diffraction machine equipped with Cu−Kα radiation (λ = 1.5418 Å) is used to analyze the crystal structures of $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91) and Pt nano. High-resolution transmission electron microscopy (HRTEM) on a JEOL 2100F transition electron microscope with 200 kV accelerating voltage is utilized to examine the morphological information of $Pt_x@Ni(OH)_2$ and Pt nano (Figure S1,2). XPS measurements are performed using a PHI-5400 machine with a position-sensitive detector (PSD) and Al Kα beam source (250 W). The angle resolution is 45°, the binding energy resolution is 0.8 eV, and the detection limit is 80 K CPS. The Ar ion sputtering speed is 0.28 nm/s over an area of $300 \times 300\ \mu m^2$. The base pressure of the measurement chamber is 3.0×10^{-7} Pa. The obtained results are calibrated using the adventitious carbon peak of the C 1s spectra (EB = 284.8 eV). The Lorentz-Gaussian fitting method is used to deconvolute the Ni, Pt, and O XPS spectra.[2-5]

Electrochemical Tests. Electrochemical tests are performed using a three-electrode method in an H-cell, with a decorated 0.196 cm^2 glassy carbon, $1\times2\ cm^2$ Pt plate, and Hg/HgO (1 M KOH) as the working, counter, and reference electrodes, respectively. An FAB-PK-130 anion exchange membrane separates the anode and cathode compartments. The working electrode is prepared using an ink-cast method, where 20.0 mg catalyst and 5 mg carbon black are dispersed in a mixture of 4.0 mL ethanol and 100 μL of Nafion perfluorinated resin. The mixture is sonicated for 60 minutes to achieve a homogeneous dispersion. Subsequently, 10 μL of the ink is deposited onto a glassy carbon electrode, resulting in a mass loading of 249 $\mu g_{cat}\ cm^{-2}$.

All electrochemical potentials mentioned in this study are referenced against RHE. To convert potentials from versus Hg/HgO to versus RHE, the following equations are used[6]:

$$E\ (\text{vs RHE}) = E\ (\text{vs Hg/HgO}) + E_{Hg/HgO}\ (\text{vs SHE}) + 0.059 \times pH$$

$$E_{Hg/HgO}\ (\text{vs SHE}) = 0.098\ V \text{ at } 25\ °C$$

The performance of the catalysts in methanol e-refinery is evaluated using CV between 0.05 and 1.1 V vs RHE at a scan rate of 20 mV s^{-1} in 1 M KOH + 1 M CH_3OH, in comparison with 1 M KOH alone. CA tests are carried out at 0.8 V vs RHE for a duration of 2 hours.

Product Analysis. ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra are recorded using a Bruker AV 400 MHz NMR spectrometer. To prepare the NMR sample, 500 microliters electrolyte and 56 microliters D_2O are mixed. Pre-configured Dionex ICS-1000 integrated system is utilized to perform IC tests with the conductivity detection method at an eluent (0.038 M KOH) flow rate of 1.2 mL/min and a column temperature of 35 °C.

After obtaining the concentration of $HCOO^-$, the $HCOO^-$ production rate and Faradic Efficiency are calculated by the following equations:

R=C×V/(t×S×l)

R: $HCOO^-$ production rate (mmol h^{-1} $mg_{cat}{}^{-1}$); C: $HCOO^-$ concentration (mmol L^{-1}); V: volume of anolyte (L); t: reaction time of CA test (h). S: area of working electrode immersed into anolyte (cm^2); l: loading of catalyst (mg cm^{-2}).

FE=(C/1000×V×4×F)/Int×100%

FE: Faradaic efficiency of $HCOO^-$ (%); C: $HCOO^-$ concentration (mmol L^{-1}); V: volume of anolyte (L); F: Faradaic constant (C mol^{-1}). Int: integral of CA curves (C).

Theoretical calculations.

DFT calculations are performed using the Vienna ab initio simulation package (VASP), employing the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[7-9] A plane wave basis set with an energy cutoff of 500 eV is employed to expand the electronic wavefunction. Brillouin zone integration utilizes a Monkhorst–Pack k-point mesh of 3×3×1. Convergence criteria for geometry calculations are defined as 10^{-6} eV for energy and 0.02 eV/Å for forces.

The Gibbs free energy of each elemental step (ΔG) is calculated following the works of Nørskov *et al.*[10, 11]

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH}$$

where ΔE is the changed energy, ΔE_{ZPE} is the zero-point energy difference between the adsorbed intermediates, ΔS is the entropy difference between the adsorbed intermediates, T is the temperature (T = 298.15 K), ΔG_U is defined as $-eU$ (with e representing the charge of an electron and U denoting the applied potential), and ΔG_{pH} is determined as 0.059 × pH. In this work, the applied potential and pH are assumed to be zero. The energy of a proton and electron pair (H^+ + e^-) is calculated as the energy of 1/2 H_2.

Global warming effect calculation of methanol electrochemical refinery under optimistic assumptions

The LCA is conducted in accordance with the ISO 14040 and 14044 frameworks [12, 13]. During the calculations, the geographical scope of this LCA is defined as global to ensure universal representativeness. Data for the methanol e-refinery MEA cell are derived from the experimental results of this study. To simplify the analysis process, the electrolyte is assumed to be 1 M methanol in pure water. Data for conventional formic acid production are obtained from existing production data for the methanol and carbon monoxide combination route in the database. Inventory analysis is performed using the Ecoinvent 3 database within SimaPro 9.0 software, and the impact assessment is carried out using the ReCiPe 2016 (H) V 1.03 method.

Economic calculation of methanol electrochemical refinery under optimistic assumptions

The cumulative net profit of the methanol electrochemical refinery (methanol e-refinery) + hydrogen evolution reaction (HER) membrane electrode assembly (MEA) at a current density of 50 mA cm_{geo}^{-2} is calculated here. Based on the MEA results, the Faradaic efficiency of formate is set as 51.4% and the voltage is 0.674 V. To simplify the calculation process, the electrolyte is assumed to be 1 M methanol in pure water.

Basic production information:

Assuming a comparable formic acid production rate to that of Sinochem [14], approximately 1,100,000 kg/day, the necessary partial current is:

$$Partial\ current\ =\ 1100000 \times \frac{kg}{day} \times \frac{day}{86400\ s} \times \frac{1000\ g}{kg} \times \frac{mol}{46.03\ g} \times 4e^{-} \times 96480 \frac{C}{mol}$$

$$=\ 1.0674 \times 10^{8}\ A$$

The total current equals the formic acid partial current divided by the Faradaic efficiency:

$$Total\ current\ =\ \frac{1.0674 \times 10^{8}}{51.4\%}\ =\ 2.0770 \times 10^{8}\ A$$

The electrolyzer area is the total current divided by the current density:

$$Total\ electrolyzer\ area\ =\ \frac{2.0770 \times 10^{8}}{0.05\,\frac{A}{cm^{2}}} * \frac{m^{2}}{10^{4}\ cm^{2}}\ =\ 4.154 \times 10^{5}\ m^{2}$$

The power needed is:

$$Power\ =\ 0.6742\ V\ \times\ 2.0770 \times 10^{8}\ A\ \times \frac{W}{10^{6}\ MW}\ =\ 140.0316\ MW$$

Then, CH_3OH consumption rate is:

$$Methanol\ consume\ rate\ = \frac{1.0674 \times 10^8\ A}{96480 \frac{C}{mol} \times 4e^-} \times \frac{0.03204\ kg}{mol} /mol \times \frac{86400\ s}{day}$$

$$= 7.6567 \times 10^5\ kg/day$$

In neutral conditions, methanol and water are consumed with a 1/1 molar ratio at the anode:

$$H_2O\ consume\ rate_{anode}\ = \frac{1.0674 \times 10^8\ A}{96480 \frac{C}{mol} \times 4e^-} \times \frac{0.01802\ kg}{mol} \times \frac{86400\ s}{day} \times \frac{0.2642\ gal}{kg}$$

$$= 1.1377 \times 10^5\ \ gal/day$$

HCOOH flow rate is:

$$Formic\ acid\ flow\ rate\ = \frac{1100000\ kg}{day} \div \frac{1220\ kg}{m^3} \times \frac{1000\ L}{m^3} \div \frac{24 \times 60\ min}{day}\ = 626.1384 \frac{L}{min}$$

Assume formic-acid-rich electrolyte is recycled until a volume concentration of 10% is reached before distillation. Then the electrolyte flow rate for distillation is:

$$Distill\ flow\ rate\ = \frac{626.1384\ L}{min} \div 10\%\ = 6.2614 \times 10^3 \frac{L}{min}$$

The water consumption rate at the cathode side (HER) is:

$$H_2O\ consume\ rate_{cathode}\ = 2.0770 \times 10^8\ A\ \times \frac{86400\ s}{day} \div \frac{96480\ C}{mol} \div 2 \times \frac{0.018\ kg}{mol} \times \frac{0.2642\ gal}{kg}$$

$$= 4.4227 \times 10^5\ A \frac{gal}{day}$$

H_2 flow rate is:

$$H_2\ flow\ rate\ = 2.0770 \times 10^8\ A\ \times \frac{86400\ s}{day} \div \frac{96480\ C}{mol} \div 2 \times \frac{0.002\ kg}{mol}\ = 1.8600 \times 10^5 \frac{kg}{day}$$

Capital investment costs:

The DOE Current Central H2A base case for an alkaline electrolyzer is used as a reference for the capital investment and operating costs of the electrolyzer [15, 16]. The reference case is derived from a Norsk Hydro HPE Atmospheric Type No. 5040 alkaline electrolyzer and the operating conditions are 175 $mA\ cm^{-2}$ and 1.75 V. Under those conditions, the capital investment for the stack component is \$250.25 kW^{-1}. To make the case suitable for the calculation in this work, the stack capital investment is normalized to operation areas: (A factor of 1.2 is applied to counteract the possible underestimation of the investment)

$$Ref.\ stack\ investment\ = \frac{250.25\ USD}{kW} \times \frac{0.175\ A}{cm^2} \times 1.75\ V \times \frac{10^4\ cm^2}{m^2} \times \frac{kW}{1000\ W} \times 1.2$$

$$= 920 \frac{USD}{m^2}$$

Furthermore, the catalysts and electrolytes need replenishment from time to time and the equipment needs maintenance as well, so a factor of 2.5% of the capital investment is assumed to be the maintenance cost of the electrolyzer per year.

The balance of plant (BoP) investment is assumed to be 35% of the stack investment of the electrolyzer system. These values are also derived from the H2A model [15, 16].

Correspondingly, the stack and plant investments in this work are:

$$Stack\ investment\ = 4.154 \times 10^5\, m^2 \times \frac{920\ USD}{m^2} = 3.820 \times 10^8\ USD$$

$$Plant\ investment\ = 3.820 \times 10^8\ USD \times \frac{35\%}{65\%} = 2.0572 \times 10^8\ USD$$

After electrolysis, HCOOH requires a separation process to be purified. This process is calculated following Feng Jiao et al. [16, 17], in which they have modeled and analyzed the HCOOH separation process by the Aspen Plus software RadFrac block and the Aspen Plus Economic Analyzer. The model contains one single column and assumes the product would leave near the azeotropic concentration. The electrolyte flow rate is set as 1000 L/min and the product concentration is assumed to be 10% in water. The capital investment costs are scaled with a capacity factor of 0.7, while the utility costs are scaled linearly [16].

As a result, the distillation equipment investment is:

$$Distillation\ investment\ = 4162240\ USD \times \left(\frac{6.2614 \times 10^3\, \frac{L}{min}}{1000\, \frac{L}{min}} \right)^{0.7} = 1.5031 \times 10^7\ USD$$

Operating cost and yearly profit:

The electricity cost is obtained through the multiplication of the power and the US electricity price [18]:

$$Electricity\ cost\ = 140.0316\ MW \times \frac{1000\ kW}{MW} \times \frac{24\ hour}{day} \times \frac{0.03\ USD}{kW\ h} = 1.0082 \times 10^5 \frac{USD}{day}$$

The maintenance cost per year is assumed to be 2.5% of the stack investment and the working day per year is set as 350:

$$Maintenance\ cost\ = \frac{3.820 \times 10^8\ USD \times \frac{0.025}{year}}{350 \frac{day}{year}} = 2.729 \times 10^4 \frac{USD}{day}$$

The distillation operating cost is:

$$Distillation\ operating\ cost\ =\ 9895\frac{USD}{day}\times\frac{6.2614\times10^{3}\,\frac{L}{min}}{1000\,\frac{L}{min}}\ =\ 6.1956\times10^{4}\frac{USD}{day}$$

The price of methanol is 0.4 [19] $USD\ kg^{-1}$. Thus, the cost of methanol is:

$$Methanol\ cost\ =\ \frac{7.6567\times10^{5}\ kg}{day}\times\frac{0.4\ USD}{kg}\ =\ 3.0627\times10^{5}\,\frac{USD}{day}$$

The price of water is 0.0054 [16] $USD\ gal^{-1}$. As a result, the cost of water is:

$$Water\ cost\ =\ \left(\frac{4.4227\times10^{5}\ gal}{day}+\frac{1.1377\times10^{5}\ gal}{day}\right)\times\frac{0.0054\ USD}{gal}\ =\ 3.0026\times10^{3}\frac{USD}{day}$$

The total operating cost is:

$$Total\ operating\ cost\ =\ 1.0082\times10^{5}\frac{USD}{day}+2.729\times10^{4}\frac{USD}{day}+6.1956\times10^{4}\frac{USD}{day}$$

$$+\,3.0026\times10^{3}\,\frac{USD}{day}+3.0627\times10^{5}\frac{USD}{day}\ =\ 4.9934\times10^{5}\frac{USD}{day}$$

Then, the yearly profit is the product income minus the total operating cost (the price of formic acid is set as 0.74 [20] $USD\ kg^{-1}$):

$$Yearly\ profit\ =\ \left(\frac{1100000\ kg}{day}\times\frac{0.74\ USD}{kg}+1.8600\times10^{5}\,\frac{kg}{day}\times\frac{1.26\ USD}{kg}-4.9934\times10^{5}\frac{USD}{day}\right)$$

$$\times\,\frac{350\ day}{year}$$

$$=\ 1.9216\times10^{8}\frac{USD}{year}$$

Cumulative net profit:

The total income tax is assumed to be 21%. In year zero, because the facility is built, the cumulative net profit would be a negative value:

$$Year\ 0\ cumulative\ profit\ =\ -\,(3.820\times10^{8}\ USD+2.0572\times10^{8}\ USD+1.5031\times10^{7}\ USD)$$

$$=\ -\,6.028\times10^{8}\ USD$$

In year one, the earnings are:

$$Year\ 1\ earnings\ =\ 2.1333\times10^{8}\frac{USD}{year}\times(1-0.21)\times1\ year\ =\ 1.518\times10^{8}\ USD$$

So, year 1 cumulative net profit is:

$$Year\ 1\ cumulative\ profit\ =\ -\,6.028\times10^{8}\ USD+1.518\times10^{8}\ USD\ =\ -\,4.510\times10^{8}\ USD$$

The calculations are repeated for the following years.

Supplementary figures

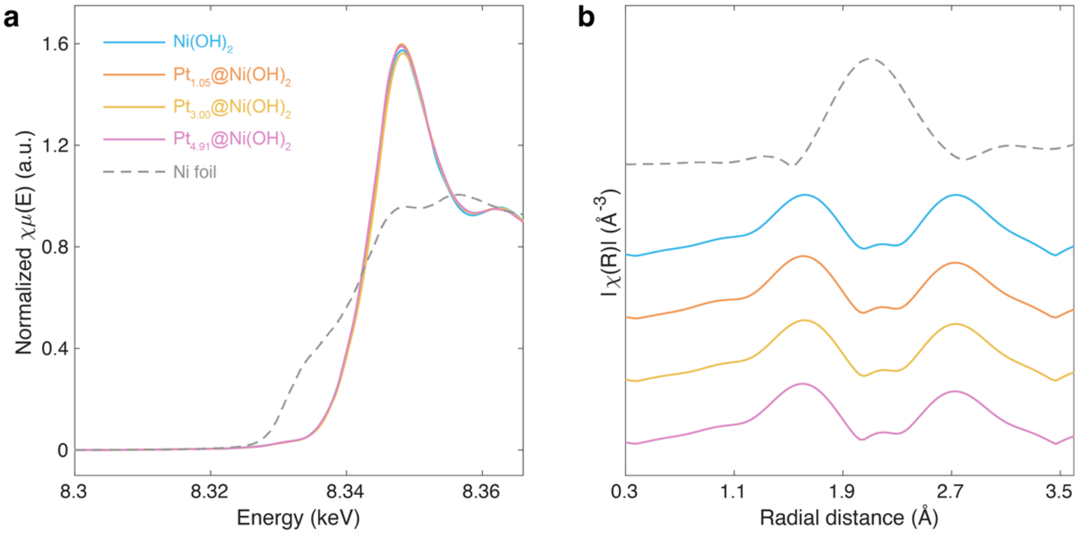

Figure S1. (a), Nickel X-ray absorption near-edge structure (XANES) and (b), extended X-ray absorption fine structure (EXAFS) of $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91).

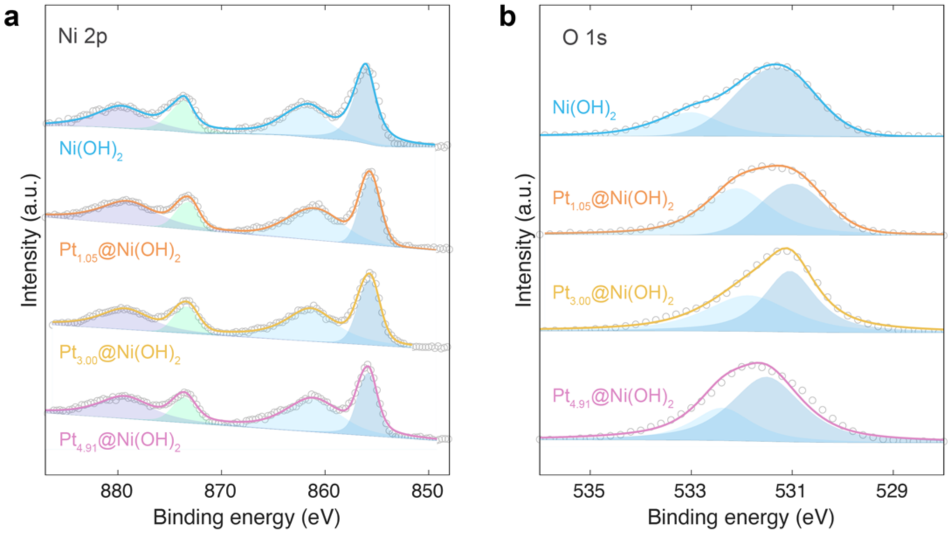

Figure S2. (a), Ni 2p and (b), O 1s X-ray photoelectron spectroscopy (XPS) spectra for $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91).

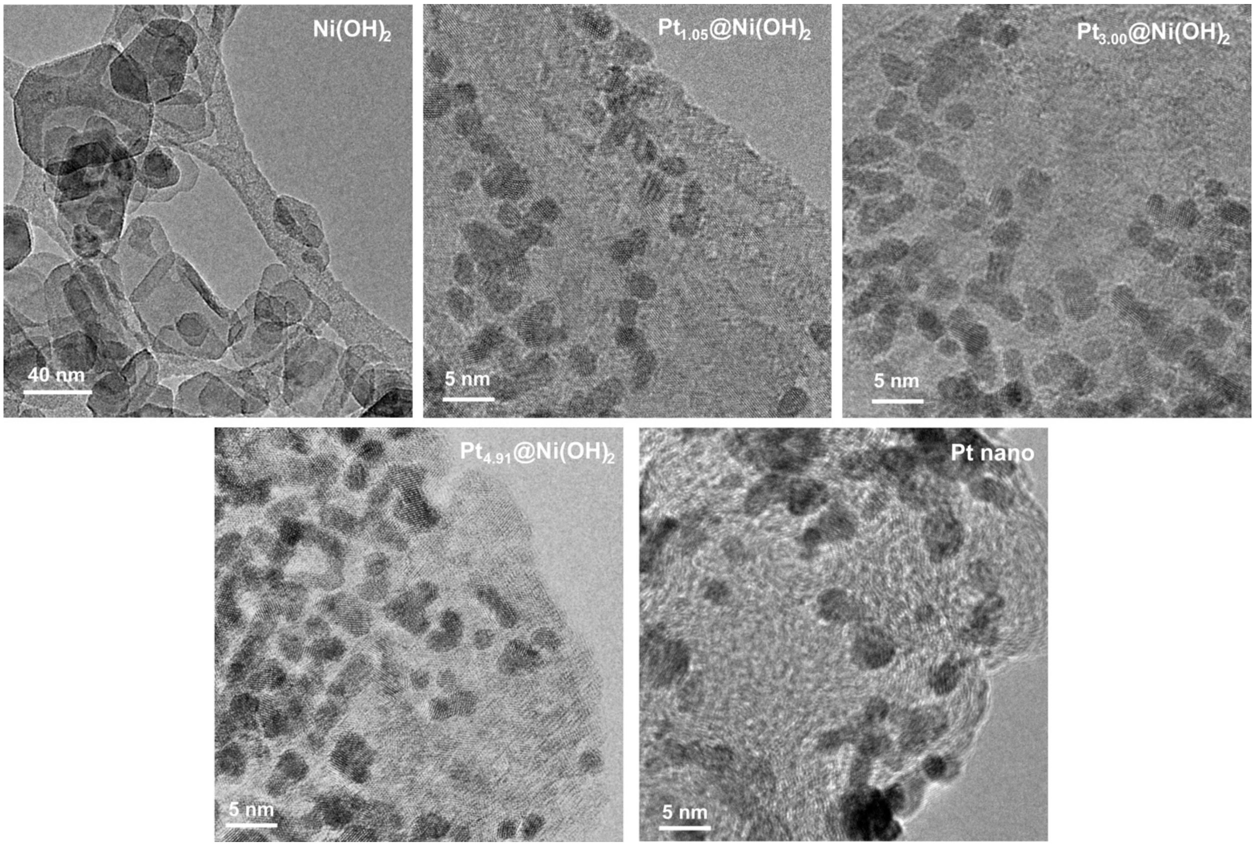

Figure S3. Transmission electron microscopy (TEM) images of $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91) and Pt nano.

Figure S4. High-resolution transmission electron microscopy (HRTEM) images of $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91), and Pt nano.

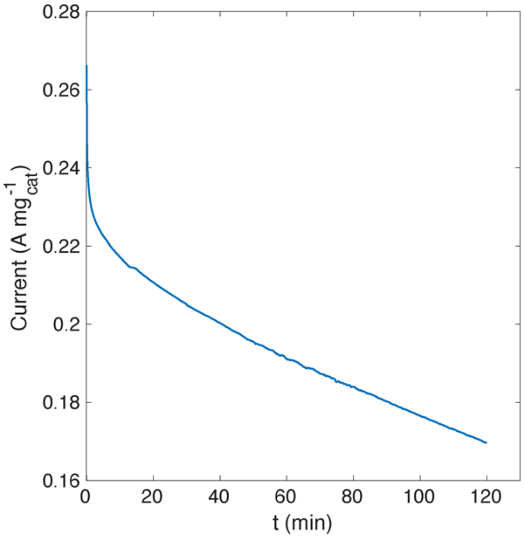

Figure S5. A representative CA profile for $Pt_{1.05}@Ni(OH)_2$.

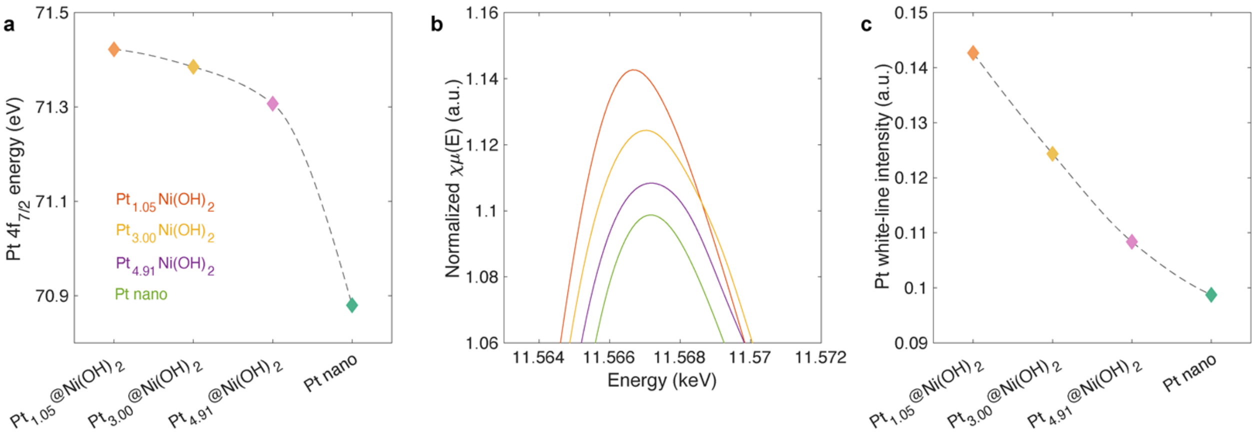

Figure S6. (a) Correlation between the Pt $4f_{7/2}$ binding energy and the formate Faradaic efficiency of $Pt_x@Ni(OH)_2$ (x = 1.05, 3.00, and 4.91) and Pt nanoparticles. (b) A magnified view of the XANES spectrum presented in Figure 1b. (c) White-line intensity in the XANES spectra for the investigated Pt-based catalysts.

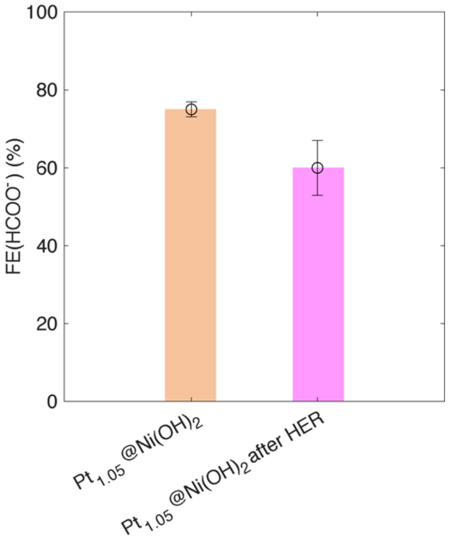

Figure S7. Formate Faradaic efficiency of a 2-hour methanol e-refinery reaction in comparison with that of methanol e-refinery after HER on $Pt_{1.05}@Ni(OH)_2$. For methanol e-refinery after HER, a 5-minute methanol e-refinery reaction at 0.8 V versus RHE is conducted following a 5-minute HER in 1 M KOH at -0.1 V versus RHE. The process is repeated 24 times, resulting in a total methanol e-refinery time of 2 hours.

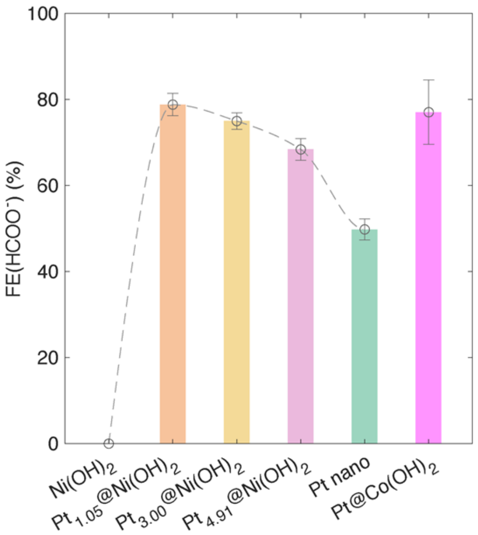

Figure S8. Formate Faradaic efficiency of $Pt@Co(OH)_2$ in comparison with that of $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91) and Pt nano.

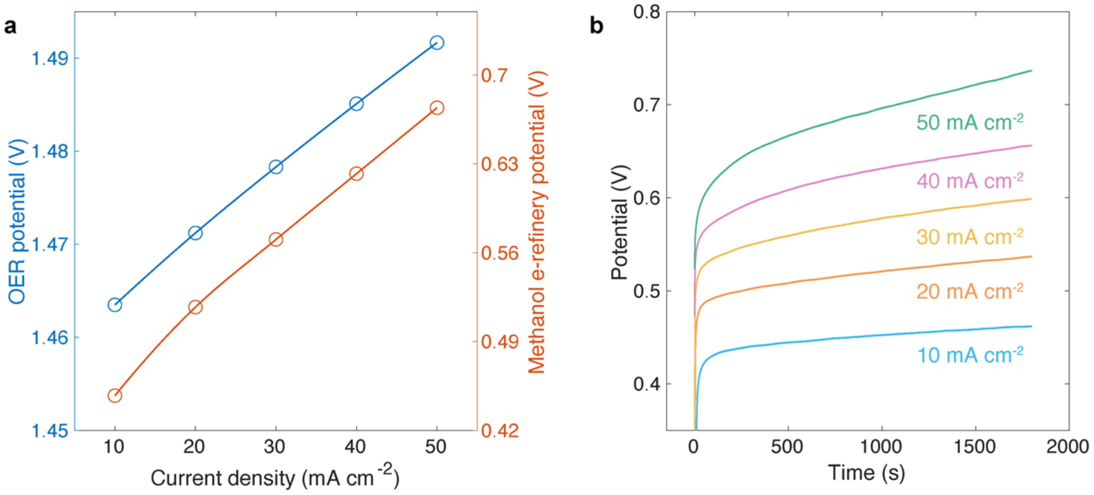

Figure S9. MEA results. (a) Polarization results of $Pt_{1.05}@Ni(OH)_2$ in 1 M KOH + 1 M CH_3OH in comparison with 1 M KOH at 10, 20, 30, 40, and 50 mA cm^{-2}. (b) The CP profiles of $Pt_{1.05}@Ni(OH)_2$ in 1 M KOH + 1 M CH_3OH recorded over a 30-minute duration at current densities of 10, 20, 30, 40, and 50 mA cm^{-2}.

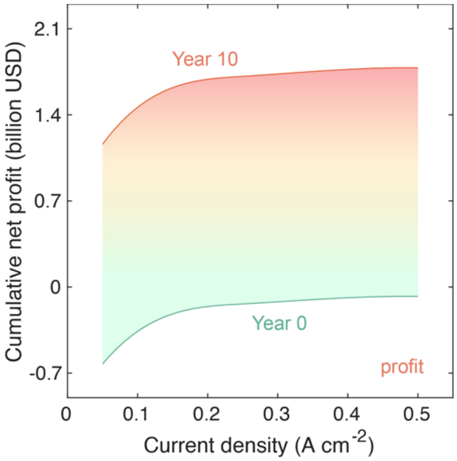

Figure S10. Predictive cumulative net profit for the methanol e-refinery MEA cell plant. The potential is assumed to be the one at 50 mA cm^{-2} and the current is varying from 50 to 500 mA cm^{-2}.

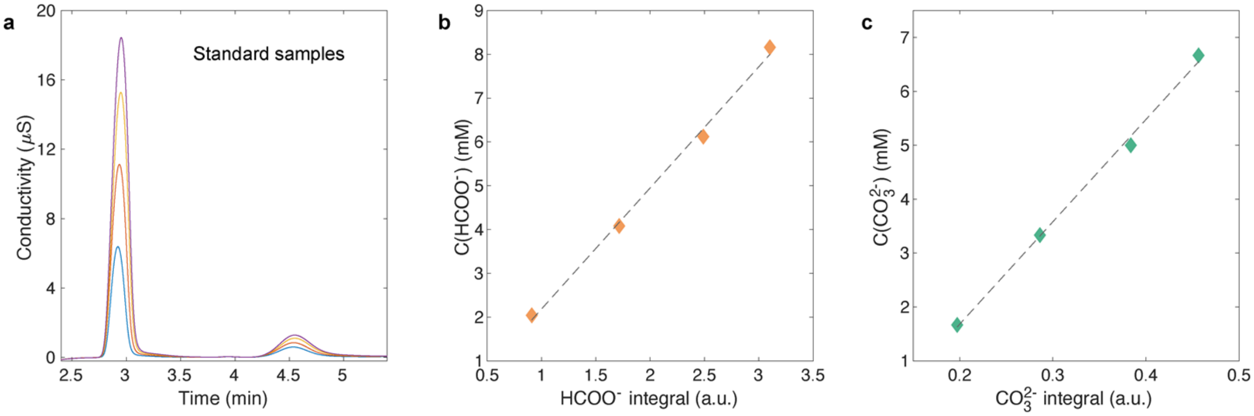

Figure S11. IC calibration results. (a) The IC curves for standard samples. The calibration data for (b) formate and (c) carbonate ions.

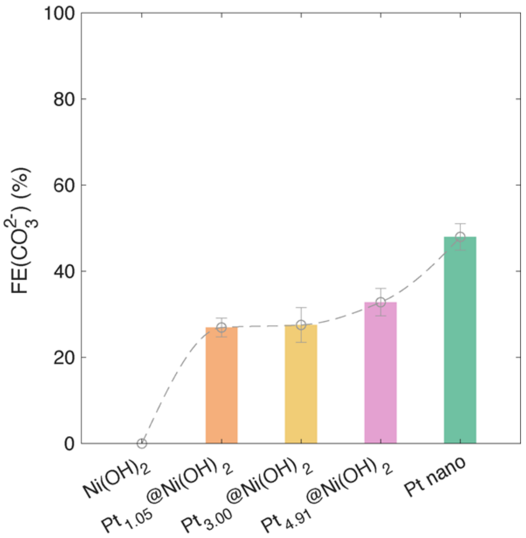

Figure S12. Carbonate Faradaic efficiencies of $Pt_x@Ni(OH)_2$ (x = 0.00, 1.05, 3.00, and 4.91) and Pt nano.

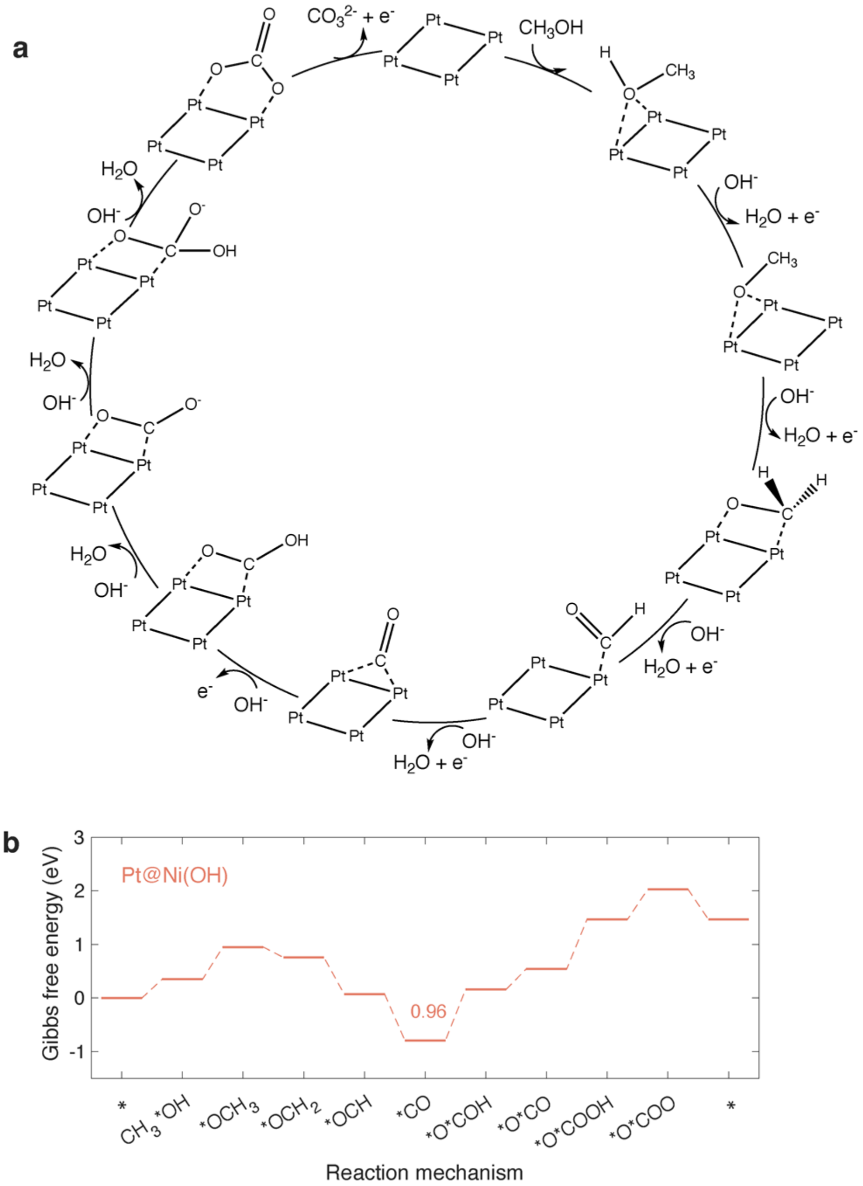

Figure S13. (a) Reaction diagram and (b) energy variation of methanol to carbonate on Pt@Ni$(OH)_2$.

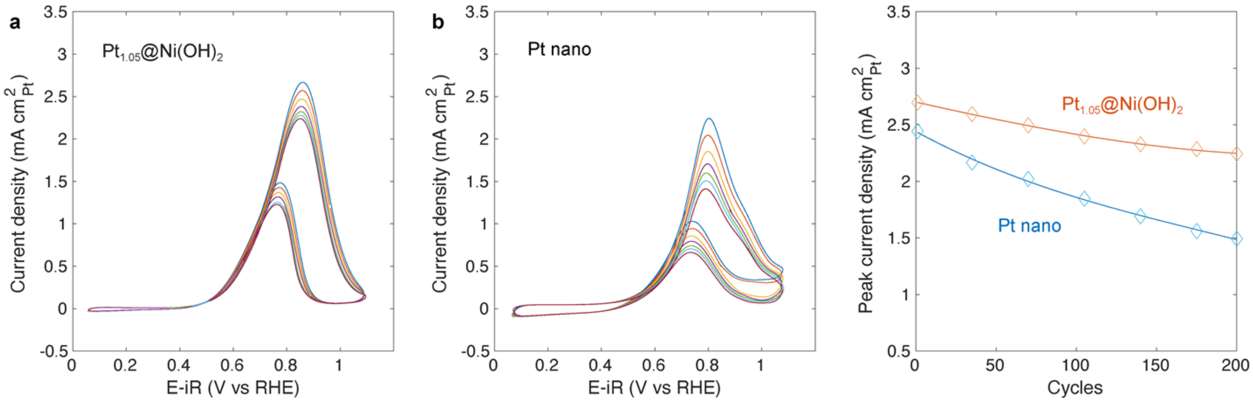

Figure S14. The representative cycling performance of (a) $Pt_{1.05}$@$Ni(OH)_2$ and (b) Pt nano in 1 M KOH + 1 M CH_3OH at a scan rate of 100 mV s^{-1}. (c) The evolution of the CV peak current density during the forward scan over 1 to 200 cycles for both $Pt_{1.05}$@$Ni(OH)_2$ and Pt nano.

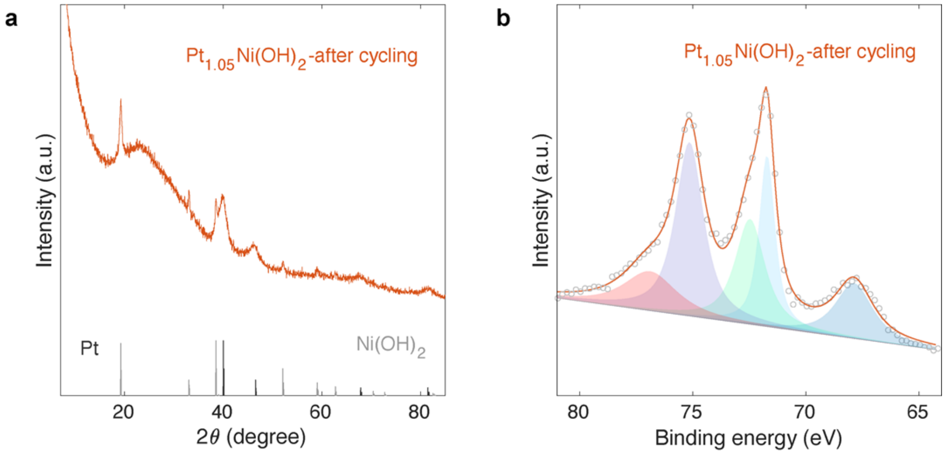

Figure S15. The (a) XRD and (b) XPS curves of $Pt_{1.05}$@$Ni(OH)_2$ after cycling.

Supplementary Tables

Table S1. Inductively coupled plasma mass spectrometry results of $Pt_x@Ni(OH)_2$ (x = 1.05, 3.00, and 4.91).

	Pt (ppb)	Ni (ppb)	Pt/Ni ratio (mol/mol)
$Pt_{1.05}@Ni(OH)_2$	201	58.8	1.05
$Pt_{3.00}@Ni(OH)_2$	280	28.7	3.00
$Pt_{4.91}@Ni(OH)_2$	404	25.3	4.91

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