Electronic supplementary information

Isolated $Ni(OH)_2$ Sites for Selective Electrooxidation of Ethanol to Acetate

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EXPERIMENTAL SECTION

1. Materials

Ketjenblack (ECP600JD, Lion Specialty Chemicals Co., Ltd.), nickel(II) nitrate hexahydrate (Kanto Chemical Co., Inc.), ethanol (Kanto Chemical Co., Inc.), acetic acid (Kanto Chemical Co., Inc.), acetaldehyde (approx. 2% in *N*,*N*-dimethylformamide, Tokyo Chemical Industry Co., Ltd.), acetaldehyde (Sigma-Aldrich), sodium hydroxide (FUJIFILM Wako Pure Chemical Corp.), 1 M sodium hydroxide aqueous solution (FUJIFILM Wako Pure Chemical Corp.), 5, 10, and 20% Nafion dispersion (FUJIFILM Wako Pure Chemical Corp.), 0.5 M sulfuric acid aqueous solution (FUJIFILM Wako Pure Chemical Corp.), distilled water (FUJIFILM Wako Pure Chemical Corp.), deuterium oxide (FUJIFILM Wako Pure Chemical Corp.), and Isotopically labeled water ($H_2{}^{18}O$, ≥98%) (Rotem Industries Ltd.) were used as received.

2. Preparation of $Ni(OH)_2$/C-modified electrode

A catalyst ink was prepared by dispersing 4 mg of Ketjenblack (KB), 50 μL of 40 mM $Ni(NO_3)_2{\cdot}6H_2O$, and 40 μL of 10% Nafion dispersion in ethanol to a total volume of 510 μL. The mixture was ultrasonicated for 10 min to obtain uniform dispersion. Then, 5 μL of the ink was drop-cast onto a mirror-polished glassy carbon (GC) electrode (geometric area: 0.196 cm^2) and dried at room temperature to evaporate ethanol, resulting in the immobilization of $Ni(NO_3)_2{\cdot}6H_2O$ and KB on the electrode surface (denoted as $Ni(NO_3)_2{\cdot}6H_2O$/C). The $Ni(OH)_2$/C catalyst was subsequently obtained by immersing this precursor electrode in an alkaline ethanol–water solution, as shown in Section 3. The resulting $Ni(OH)_2$/C-modified GC electrode contained 40 μg of total catalyst (Ni + KB).

To vary the catalyst loading, the composition ratio of KB, Ni precursor, and Nafion in the catalyst ink was kept constant, while the total amounts were adjusted so that 5 μL of ink resulted in 10, 20, 30, or 40 μg of Ni and KB deposited on the GC electrode.

3. Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed using a potentiostat/galvanostat (Vertex. One EIS, Ivium Technologies). A three-electrode single-compartment cell was employed, using the $Ni(OH)_2$/C-modified GC electrode (prepared as described in Section 2) as the working electrode, a Hg/HgO electrode filled with 1 M NaOH as the reference electrode, and a graphite rod as the counter electrode. CVs were recorded in 1 M NaOH aqueous solution with and without 0.2 M ethanol (0.056–1.056 V vs. Hg/HgO at a scan rate of 20 mV s^{-1}; Fig. 2a).

The electrochemically active Ni amount was quantified from CVs measured in 0.1 M NaOH (0–0.715 V vs. Hg/HgO, 20 mV s^{-1}) over 50 cycles (Fig. 1a). The amount of electrochemically active Ni^{2+} (N / mol) was calculated from the charge (Q / C) obtained by integrating the reduction current observed between 0.315 and 0.515 V vs. Hg/HgO, after subtracting the capacitive current associated with double-layer charging. The value of N was determined using Eq. (S1), where F is the Faraday constant (C mol^{-1}) and n is the number of electrons transferred (n = 1 in this case):

$$N = Q/nF \qquad \text{(S1)}$$

To evaluate ethanol electrooxidation on $Ni(OH)_2$/C, CV was performed in 1 M NaOH and in 1 M NaOH containing 0.2 M ethanol. The potential was scanned from −0.944 to 1.056 V vs. Hg/HgO at a

scan rate of 20 mV s^{-1} for a single cycle. The potentials were converted from Hg/HgO to RHE using Eq. (S2):

$$E \text{ (vs. RHE)} = E \text{ (vs. Hg/HgO)} + 0.118 + 0.059 \text{ pH} \qquad \text{(S2)}$$

4. Electrochemical ethanol oxidation reaction (EOR)

EOR was carried out in a three-electrode, two-compartment cell. The electrolyte consisted of 30 mL of 1 M NaOH aqueous solution containing 0.05–1 M ethanol. The working electrode was the $Ni(OH)_2$/C-modified GC electrode, the reference electrode was a Hg/HgO electrode, and a graphite rod was used as the counter electrode. Only the anode compartment was stirred with a magnetic stirrer, and the anode and cathode compartments were separated by a membrane filter (PTFE, diameter 25 mm, pore size 1 μm, ADVANTEC®, H100A025A). Potentiostatic electrolysis was performed using a potentiostat/galvanostat (Vertex. One EIS, Ivium Technologies) at 0.356–0.756 V vs. Hg/HgO for 2 h.

Product analysis was conducted by high-performance liquid chromatography (HPLC). The HPLC system consisted of a Shimadzu LC-20AD pump and a Shimadzu CTO-20AC column oven. A 5 mM H_2SO_4 aqueous solution was used as the mobile phase, and a HyperREZ XP Carbohydrate H+ column (300 × 7.7 mm) was employed. The analysis was performed at 60 °C with a flow rate of 0.6 mL min^{-1}. Acetaldehyde and acetic acid were detected using a refractive index detector (Shimadzu RID-20AD) and a UV detector (Shimadzu SPD-20A), respectively. Calibration curves used in this study is shown in Fig. S1.

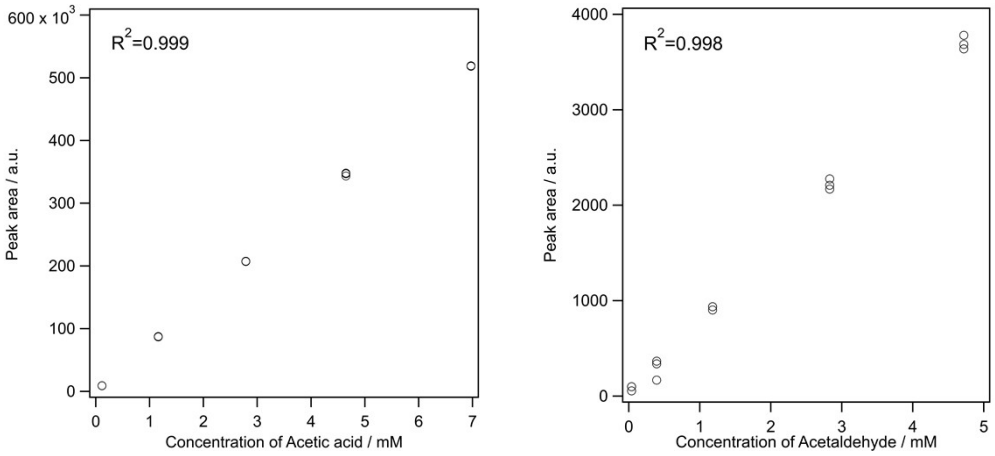


Fig. S1 Calibration curves for acetic acid and acetaldehyde.

Faradaic efficiency (FE) was calculated from the total charge passed during electrolysis and the number of electrons required for the formation of each product, as expressed in Eq. (S3):

$$FE(\%) = (\text{charge to form products}) / (\text{total charge passed}) \times 100 \quad (S3)$$

The isotope-labeling experiment using $H_2{}^{18}O$ was carried out in a two-electrode, single-compartment cell containing 660 μL of 1 M $NaOH/H_2{}^{18}O$ solution with 1 M ethanol. EOR was performed at 1.8 V for 2 h. $Ni(OH)_2$/C on a GC electrode was used as the working electrode, and a Pt wire served as the counter electrode. After electrolysis, the reaction solution was neutralized to approximately pH 4 by adding 0.5 M H_2SO_4. The product analysis was conducted using gas chromatography–mass spectrometry (GC–MS, SCION SQ, Bruker) equipped with a ULBON HR-1 column (Shinwa Chemical Industries Ltd.).

5. Characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using an aberration-corrected transmission electron microscope (JEM-ARM 200CF, JEOL) operated at 200 kV. A catalyst ink with the same composition of $Ni(NO_3)_2{\cdot}6H_2O$/KB/Nafion as described in Section 2 was prepared, but diluted more than tenfold with ethanol to reduce the catalyst loading on the grid. A 0.5 μL of the ink was droped onto an Au microgrid, dried at room temperature, and then vacuum-dried overnight to obtain $Ni(NO_3)_2{\cdot}6H_2O$/C on the grid. For the preparation of $Ni(OH)_2$/C, the grid coated with the catalyst ink was dried at room temperature, immersed in 1 M NaOH aqueous solution, and then vacuum-dried overnight.

X-ray diffraction (XRD) measurements were performed using a Bruker D2 Phaser diffractometer with Cu Kα radiation as the X-ray source. Ni K-edge X-ray absorption fine structure (XAFS) measurements were conducted at the BL11S2 beamline of the Aichi Synchrotron Radiation Center (Aichi, Japan) using the transmission mode with a Si(111) monochromator. The extended X-ray absorption fine structure (EXAFS) spectra were weighted by k^3 and Fourier-transformed over the k range of 3–12.8 $Å^{-1}$. The samples for XRD and EXAFS measurements were prepared as follows. 100 mg of KB, 1.25 mL of 40 mM $Ni(NO_3)_2{\cdot}6H_2O$ solution, and 500 μL of 20 wt% Nafion dispersion were added to 10 mL of ethanol, followed by ultrasonication for 10 min to obtain a catalyst ink. The ethanol was then removed using a rotary evaporator to yield the $Ni(NO_3)_2{\cdot}6H_2O$/C sample. For XAFS measurements, the sample was pressed into a pellet.

The Brunauer–Emmett–Teller (BET) specific surface area was determined from nitrogen adsorption measurements conducted at 77 K using a BELSORP-mini instrument (MicrotracBEL Corp.).

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an AVANCE 300 spectrometer (Bruker) operating at 300 MHz using D_2O as the solvent. Chemical shifts were reported in parts per million (ppm) and referenced to the residual proton signal of H_2O at 4.7 ppm.

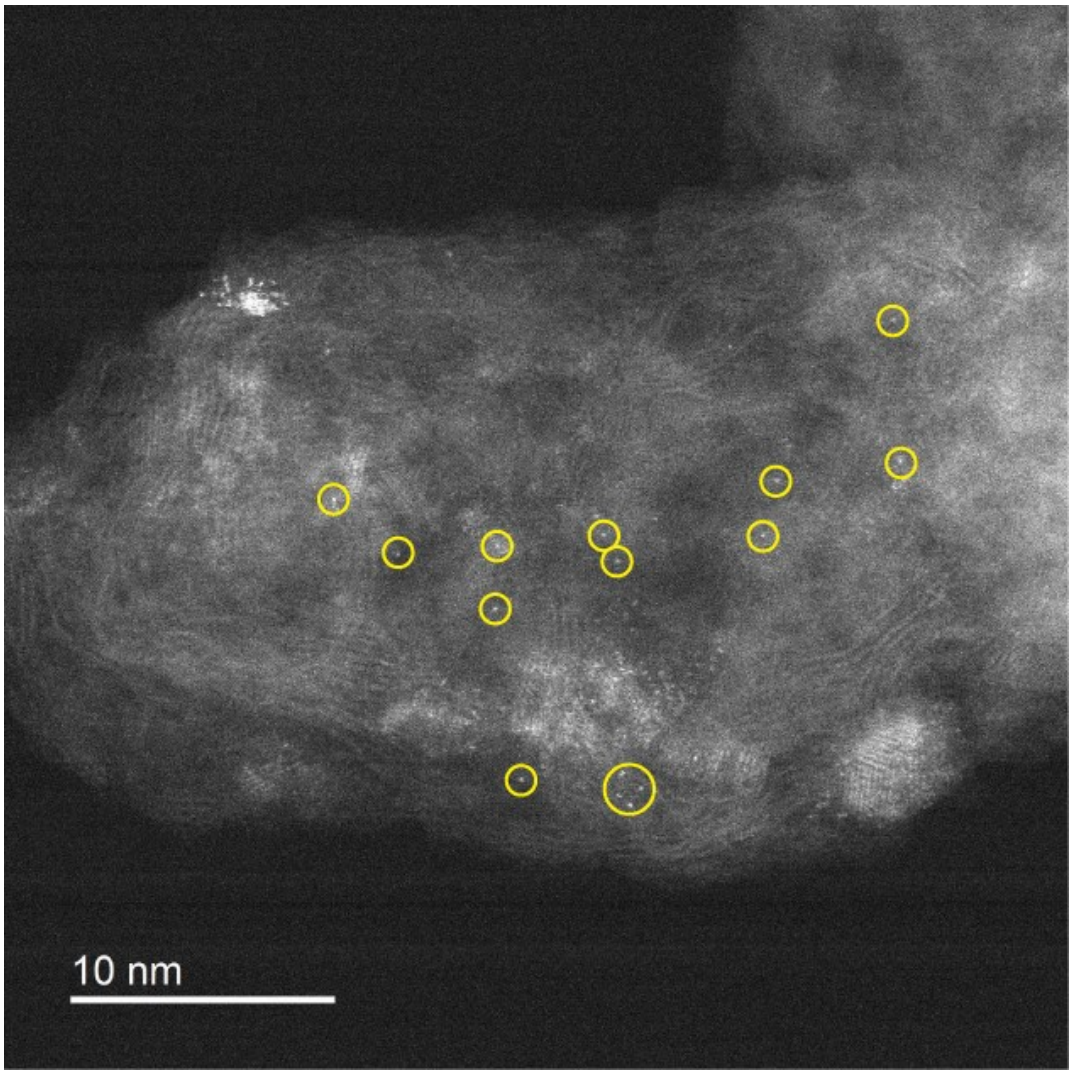


Fig. S2 HAADF-STEM image of $Ni(OH)_2$/C.

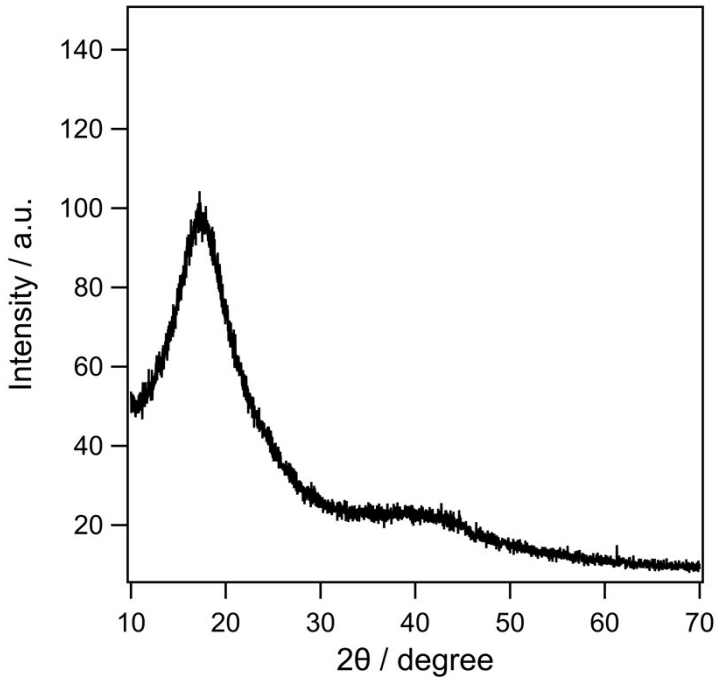
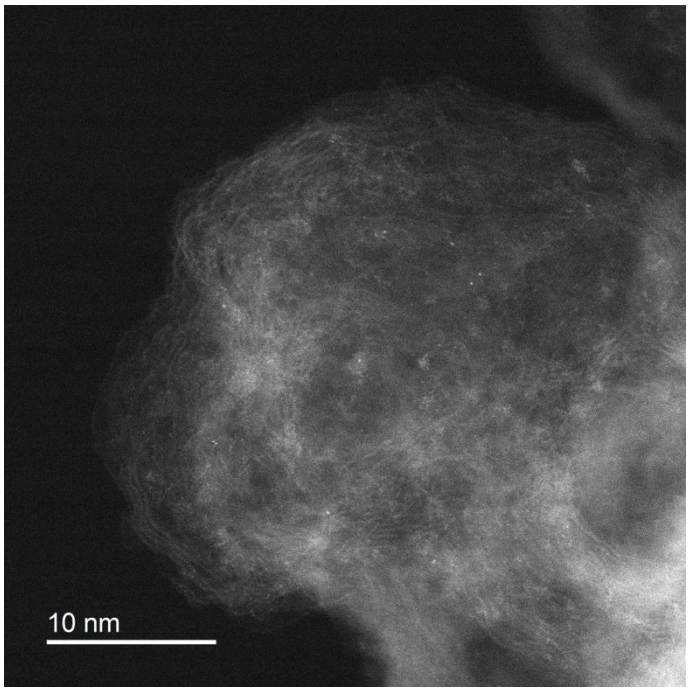
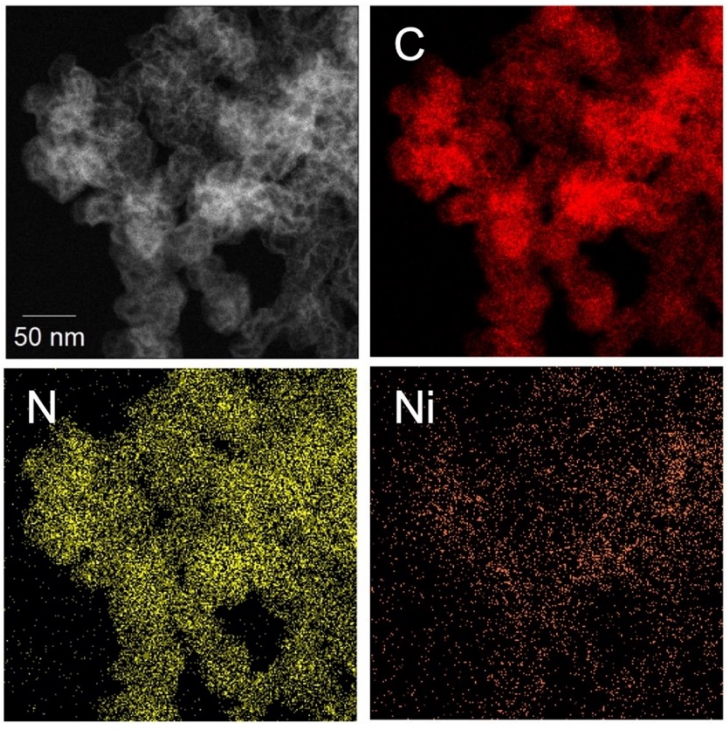


Fig. S3 XRD pattern of $Ni(NO_3)_2 \cdot 6H_2O$/C.



(a)



(b)

Fig. S4 (a) HAADF-STEM and (b) EDS mapping images of $Ni(NO_3)_2 \cdot 6H_2O$/C.

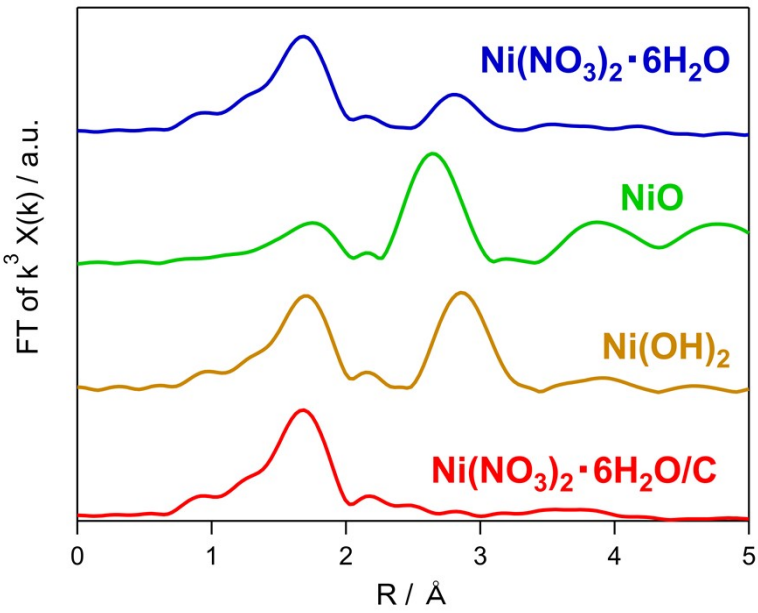


Fig. S5 Ni K-edge Fourier transforms (FT) of k^3-weighted EXAFS oscillations of $Ni(NO_3)_2 \cdot 6H_2O/C$.

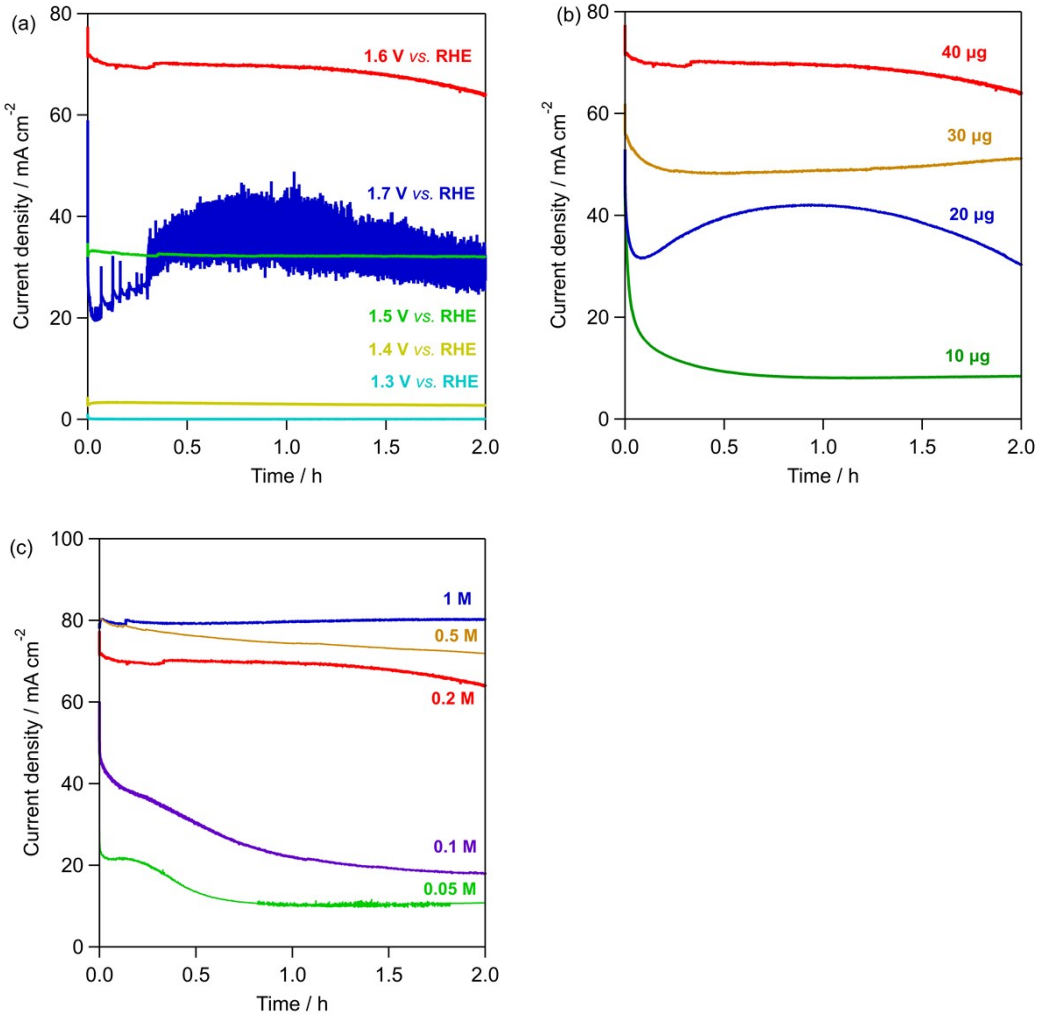


Fig. S6 Effects of applied potential, catalyst loading, and ethanol concentration on current density during EOR.

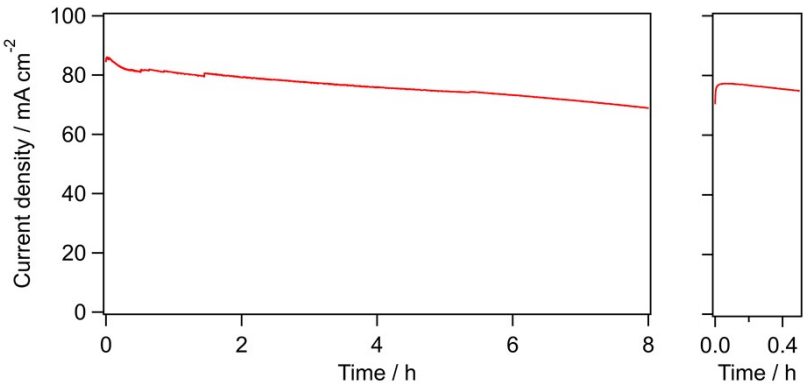


Fig. S7 Stability test of EOR on $Ni(OH)_2$/C at 1.6 V vs. RHE in 1 M ethanol with a catalyst loading of 40 μg.

The left panel shows continuous electrolysis for 8 h, while the right panel shows electrolysis using the same electrode after replacing the electrolyte with fresh solution.

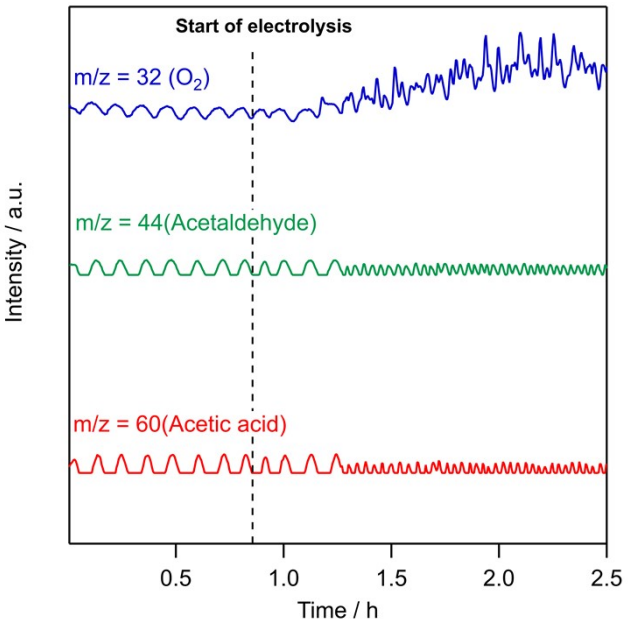


Fig. S8 Mass spectrometric analysis recorded during EOR in 0.2 M ethanol and 1 M NaOH aqueous solution at 1.7 V vs. RHE with a catalyst loading of 40 μg for 2 h. The headspace of the electrolysis cell was continuously purged with He at a flow rate of 5 mL min^{-1}, and the outlet gas was analyzed by mass spectrometry (Pfeiffer Vacuum, GSD-350 OmniStar)

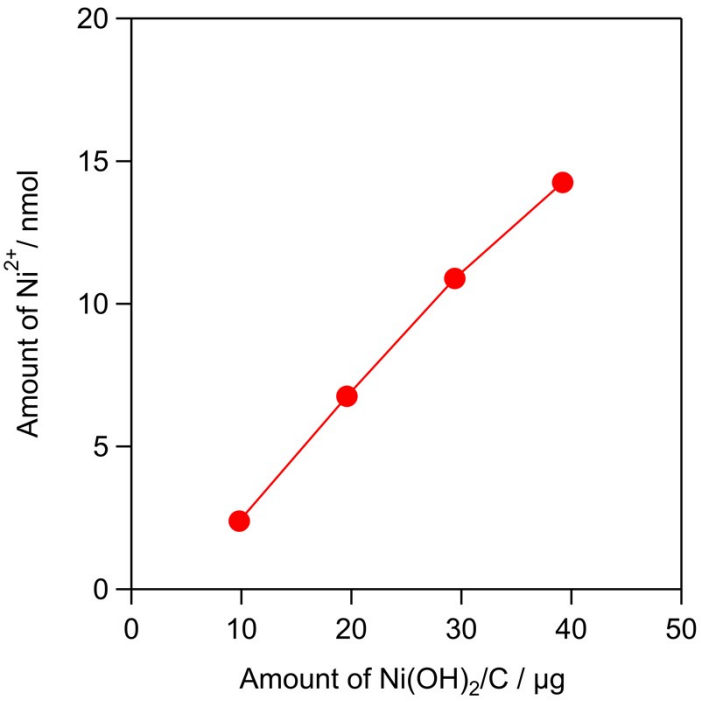
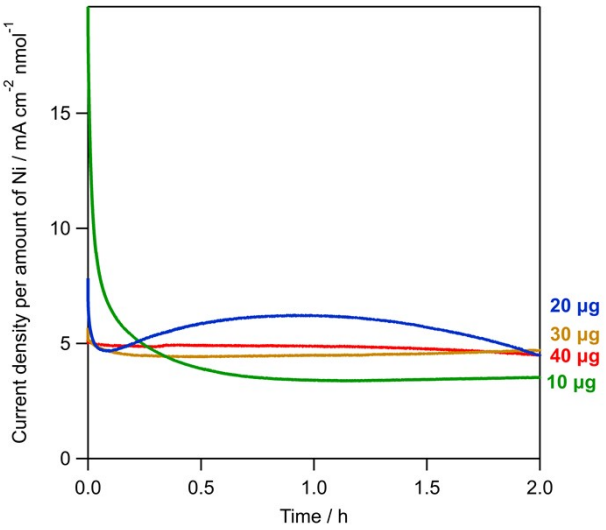
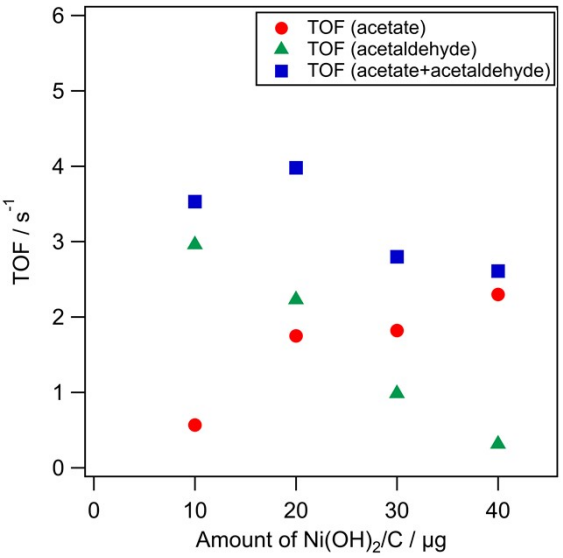


Fig. S9 Amount of electrochemically active Ni at different catalyst loadings.

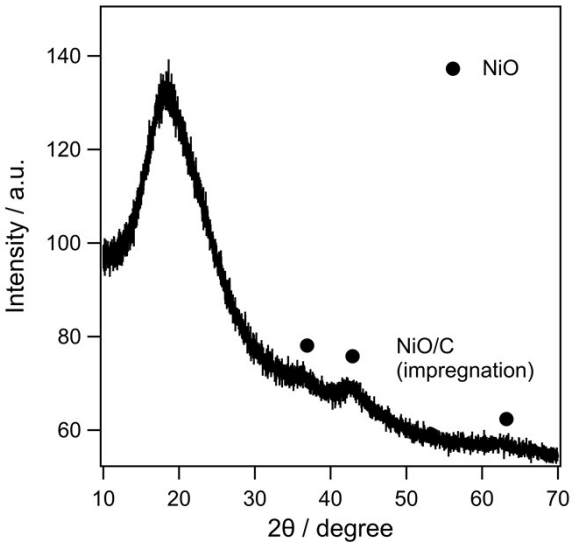


(a)

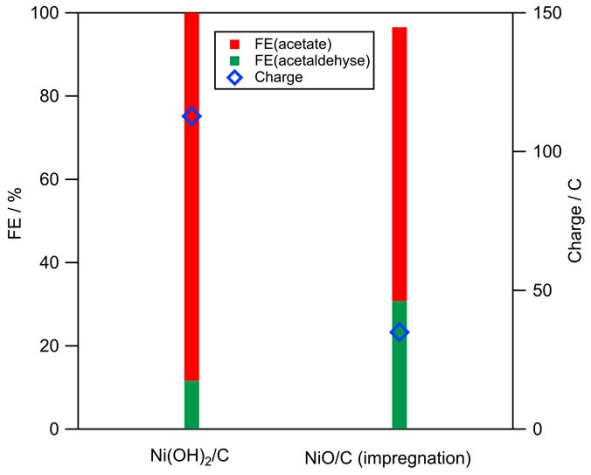


(b)

Fig. S10 (a) Current density and (b) TOF normalized by the electrochemically active Ni amount for $Ni(OH)_2$/C electrodes with different catalyst loadings (10–40 µg).



(a)



(b)

Fig. S11 (a) XRD pattern of NiO/C prepared by an impregnation method, and (b) comparison of EOR performance on $Ni(OH)_2$/C and NiO/C catalysts at 1.6 V vs. RHE in 1 M ethanol. The catalyst loading was adjusted so that the amount of Ni on the GC electrode was the same for both catalysts. To prepare the NiO/C catalyst, $Ni(NO_3)_2 \cdot 6H_2O$ (97.3 mg) was dissolved in ethanol (50 mL), after which KB (100 mg) was added. The mixture was stirred, and then ethanol was evaporated at 70 °C under stirring. The resulting sample was dried overnight and subsequently calcined in air at 250 °C for 3 h to obtain the NiO/C catalyst.

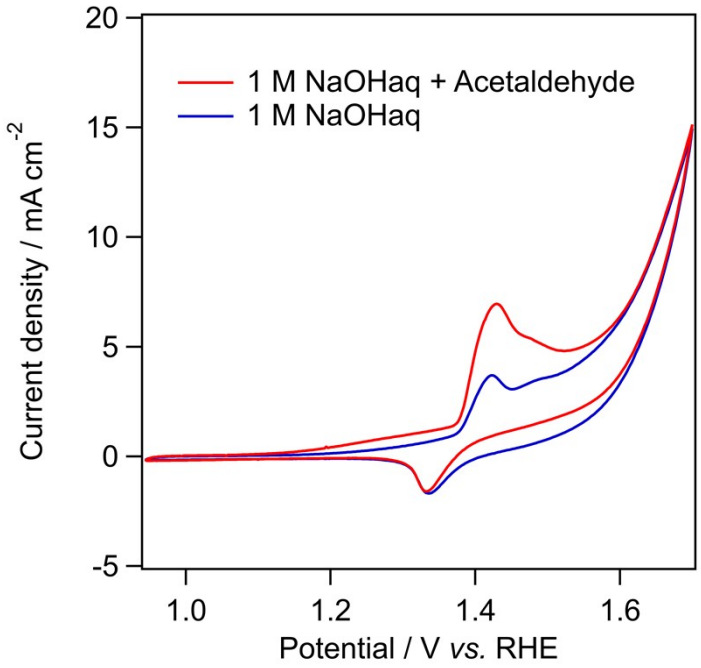


Fig. S12 CVs of $Ni(OH)_2$/C in 1 M NaOH and 1 M NaOH containing 22.7 mM acetaldehyde (catalyst loading: 40 μg).

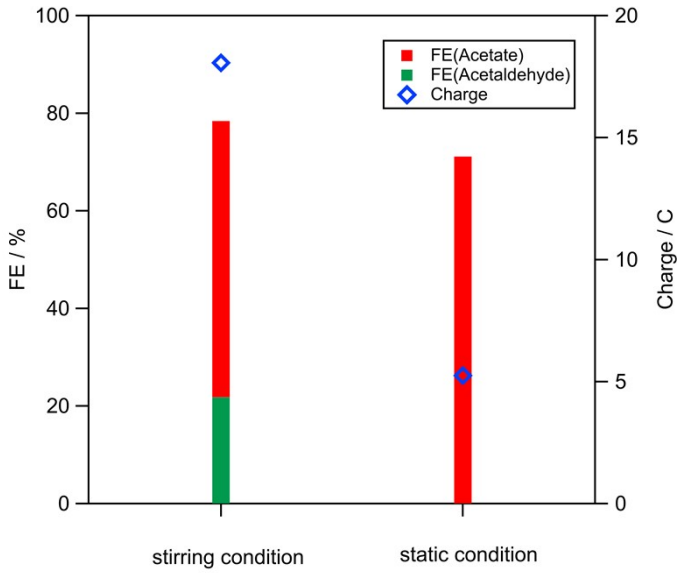


Fig. S13 Effects of stirring on EOR at 1.6 V vs. RHE in 0.05 M ethanol with a catalyst loading of 40 μg.

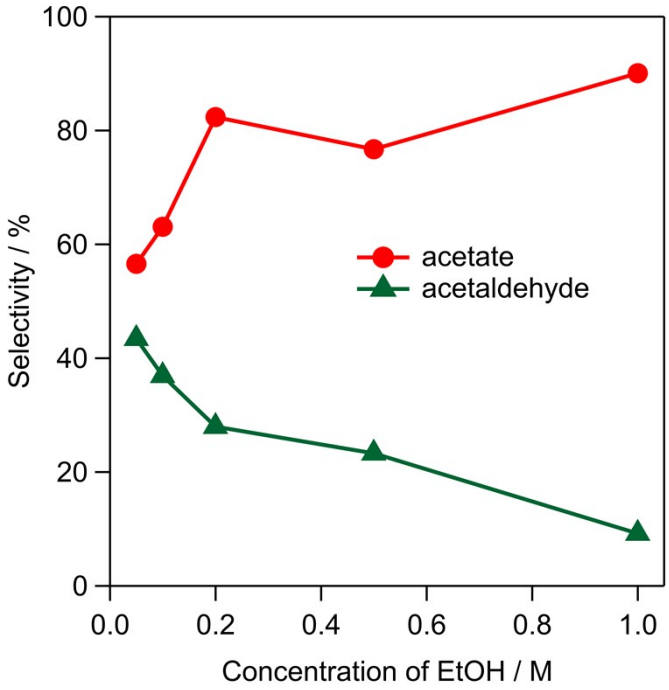
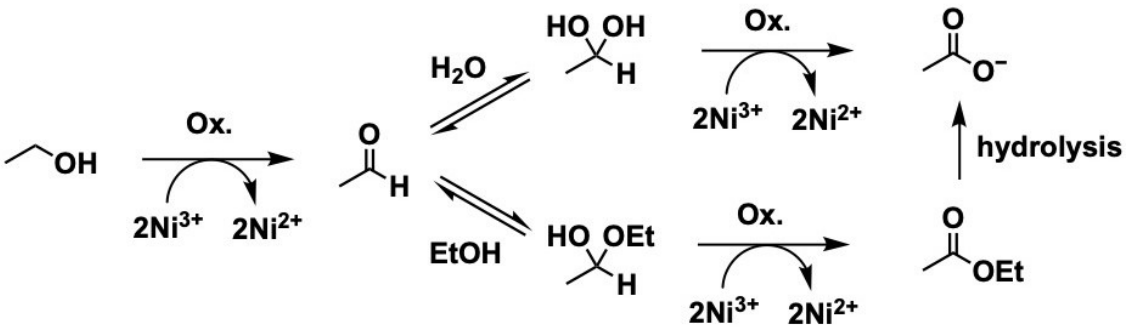


Fig. S14 Product composition (acetate and acetaldehyde) during EOR in 1 M NaOH containing 0.05–1.0 M ethanol.



Scheme S1 Reaction pathways for acetate formation during EOR.

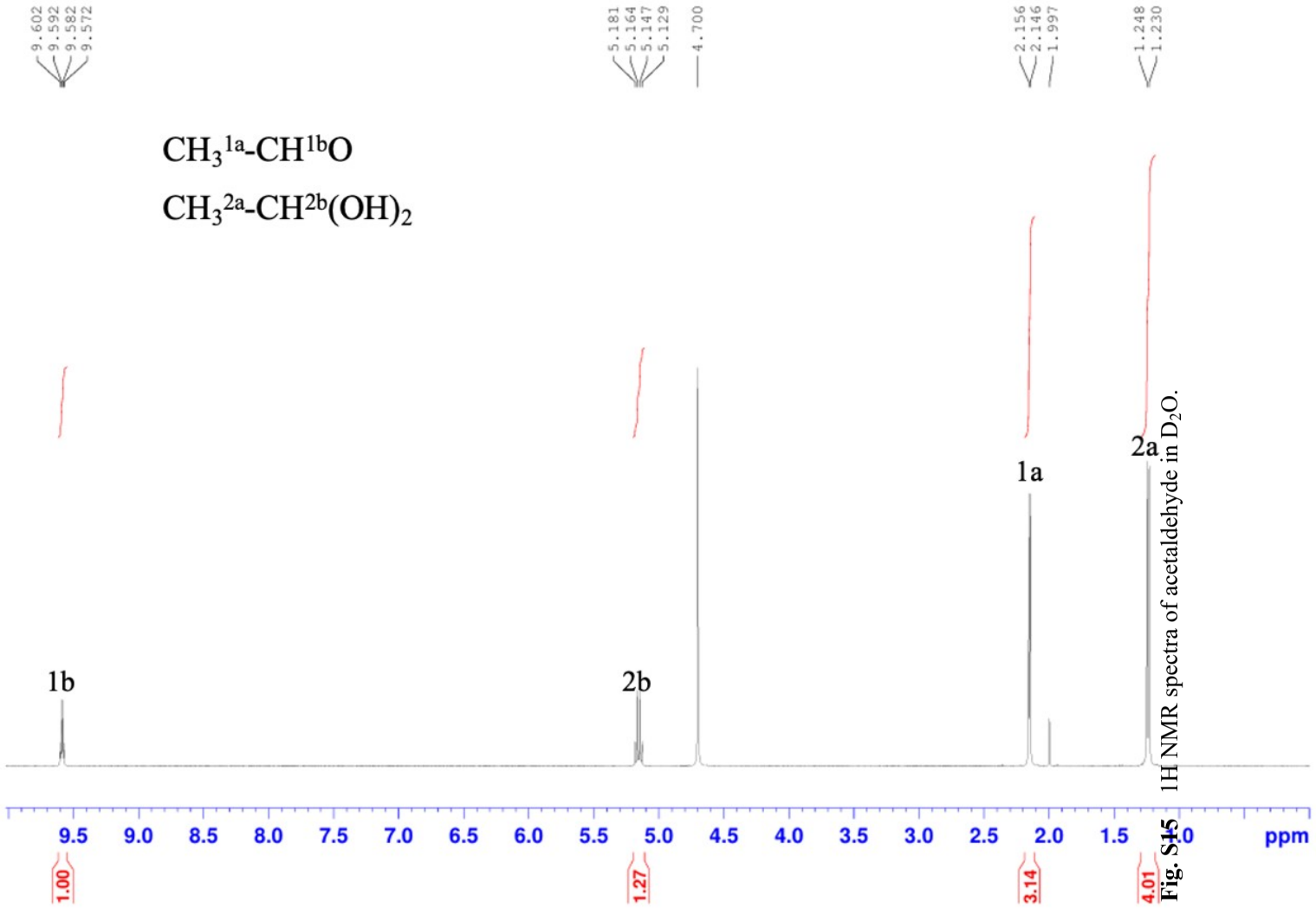


Fig. S15 1H NMR spectra of acetaldehyde in D_2O.

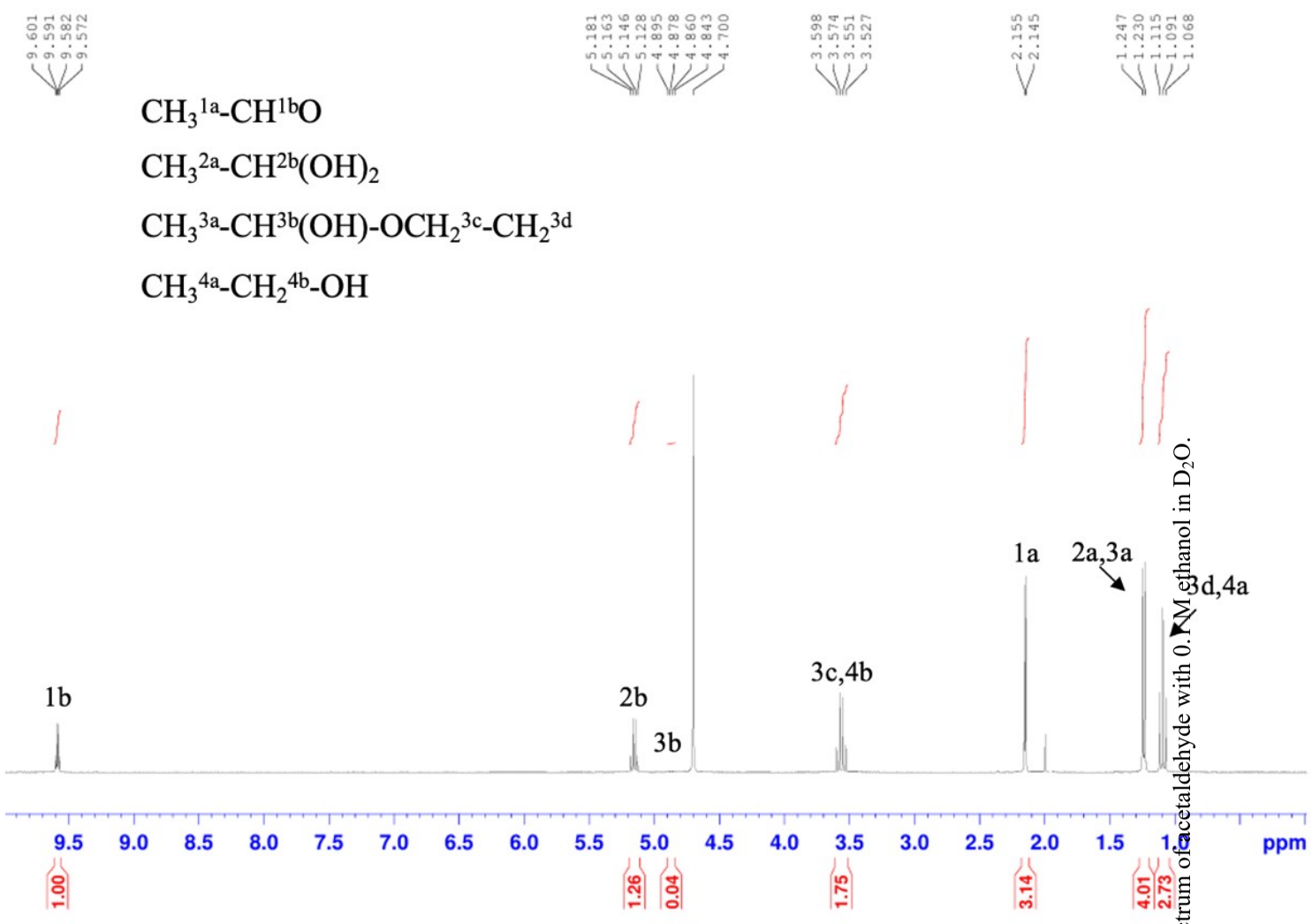


Fig. S16 ^{1}H NMR spectrum of acetaldehyde with 0.1 M ethanol in D_2O.

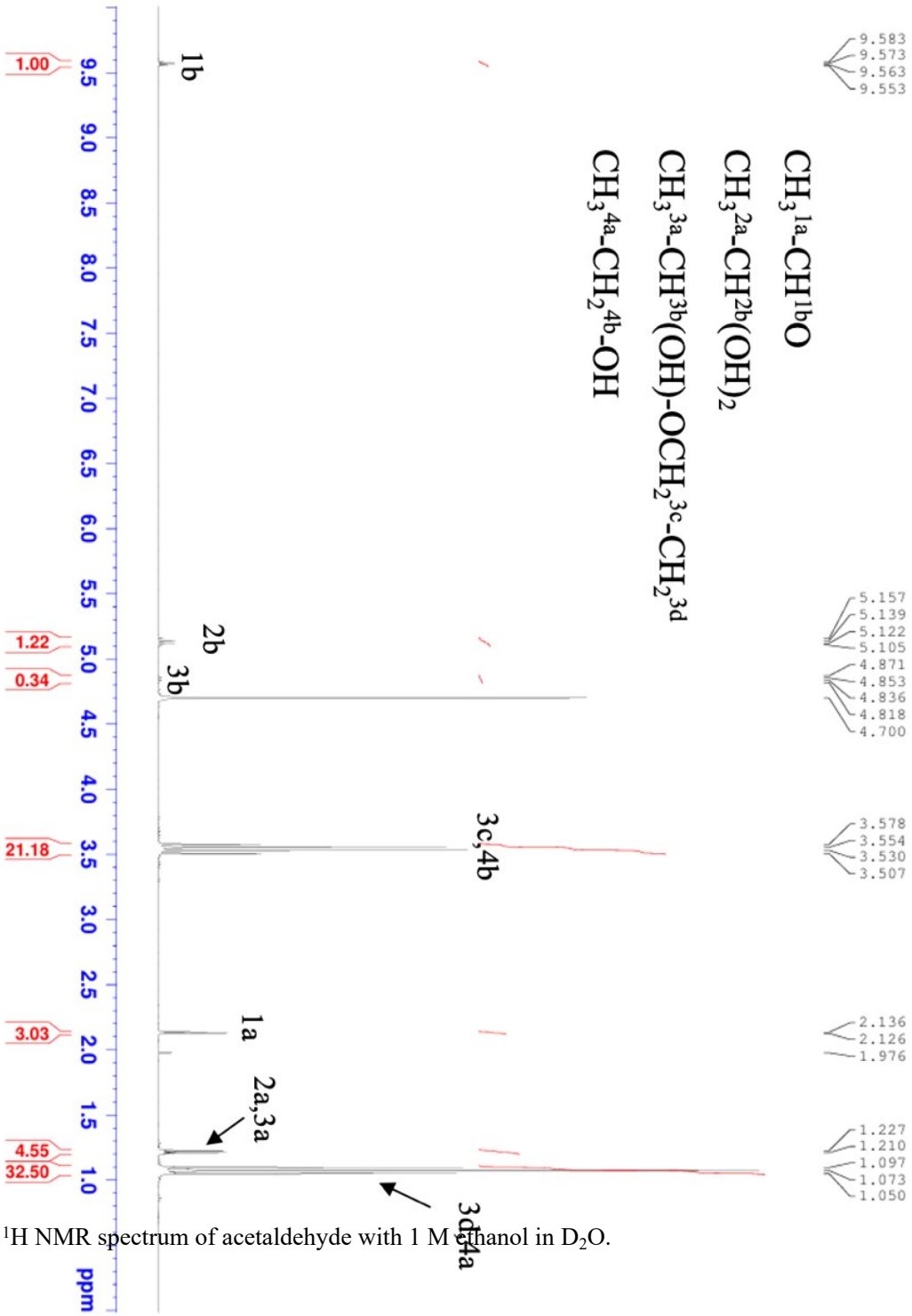


Fig. S17 ^{1}H NMR spectrum of acetaldehyde with 1 M ethanol in D_2O.