Electronic Supporting Information

Hydroxyl-mediated ethanol selectivity of CO₂ hydrogenation

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S1. Characterization details

1.1 Characterization methods

Powder X-ray diffraction (XRD) patterns were performed with 2θ values between 20° and 90° using a Bruker-D8 diffractometer (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) measurements were taken on a PHI 1600 ESCA instrument (PE Company) equipped with an Al Kα X-ray radiation source (hv = 1486.6 eV). Before measurements, all the samples were dried at 50°C for 6 h. The binding energies were calibrated using the C 1s peak at 284.6 eV as a reference.

The morphology of catalysts was characterized by transmission electron microscopy (TEM; FEI Tecnai G2 F20, 200 kV). The TEM was additional equipped with high-resolution electron energy-loss spectroscopy (EELS) for elemental analysis. Annular dark field scanning TEM (ADF-STEM) and energy dispersive X-ray (EDX) mapping were operated with an Oxford X-Max 80 SDD EDX detector at 200 kV. To investigate the molar ratio of different elements, the catalysts, 10 mg each, were dissolved in a perchloric/nitric acid mixture. The concentrations of Rh, Fe and Li in the leached solutions were measured by the inductively coupled plasma optical emission spectroscopy (ICP-OES; Varian 720-ES).

H2 temperature-programmed reduction (H2-TPR) and CO temperature-programmed desorption (CO-TPD) were performed on a Micromeritics AutoChem II 2920 apparatus equipped with HIDEN QIC-20 mass spectrometer (MS). For H2-TPR experiment, 100 mg sample was pretreated at 300°C for 1 h under flowing Ar to remove water and other contamination. After cooling to 50°C, 10 vol% H2/Ar was introduced for the reduction and the temperature was increased from 50°C to 800°C with the ramp rate of 10°C/min. The signal was recorded online by thermal conductivity detector (TCD). For CO-TPD experiment, 100 mg sample was pre-reduced at 400°C for 1 h under 10 vol% H2/Ar. When the temperature was cooled by liquid N2 and kept stable at -70°C, pure CO was introduced for 0.5 h. Subsequently, the purging was carried out by Ar for 1 h. Then the temperature was increased from -70°C to 500°C with the ramp rate of 10°C/min. The gas component in the effluent was monitored and recorded online by MS, and the signals for m/e of 44, 28 and 18 were monitored.

The Rh on the particle surface was studied by employing the CO chemisorption method. For each test, 200 mg sample was pre-reduced with 10 vol% H2/Ar at 400°C for 1 h, then cooled to 50°C. Subsequently, CO was admitted to the sample by injection pulses of 10 vol% CO/He (0.5082 mL) until the consumption peaks became stable. It can be assumed that the adsorption stoichiometry factor of Rh/CO = 1.1 The VCO is the active loop volume of CO adsorbed on Rh (mL), SF is the stoichiometry factor.

A Micromeritics Tristar 3000 analyzer was used to obtain the textual properties of catalysts by N2 adsorption-desorption at 77 K. Prior to the tests, all samples were degassed at 300°C for 6 h. The specific surface areas were calculated from the isotherms using the Brunauer-Emmett-Teller (BET) method, and the pore distribution and the cumulative volumes of pores (Vpore) were obtained by the Barret-Joyner-Halenda (BJH) method from the desorption branches of the N2 isotherms.

The Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used to record vibrational spectra of molecules adsorbed on the different catalysts. In situ DRIFTS experiments were performed on a Thermo Scientific Nicolet IS50 spectrometer, equipped with a Harrick Scientific DRIFTS cell and a mercury-cadmium-teelluride (MCT) detector cooled by liquid N2. About 100 mg finely ground sample was packed in the ceramic crucible of the in situ chamber. All the samples were pretreated at 400°C under a H2 flow (20 mL/min) for 1 h and cooled to the desired temperature to obtain a background spectrum, and the spectra for each measurement was then collected by subtracting the background spectrum. The spectra under reaction conditions were recorded with a
resolution of 4 cm\(^{-1}\). As for the Fourier Transform Infrared (FTIR) spectrum to characterize the surface hydroxyl, 1 mg of sample was mixed in an agate mortar with \(\sim\)300 mg of potassium bromide (KBr) followed by a thorough drying in a vacuum oven at 200 \(^{\circ}\)C. Before mixing, the KBr powder was dried at 500 \(^{\circ}\)C overnight to get rid of water. The mixture was then pressed into a pellet for 5 min using a force of 5 tons, and transparent pellets were obtained. All the pellets were dried in vacuum oven at 120 \(^{\circ}\)C for 3 hours to get rid of water before FTIR tests. We use the pure KBr pellet (\(\sim\)300 mg) as the background and integrate peak area of associative hydroxyl stretching vibrations at 3450 cm\(^{-1}\) to represent the amount of the hydroxyl. Furthermore, the peak area of hydroxyl groups normalized by BET surface area (S\(_{\text{BET}}\)) of catalysts was applied to represent the density of surface hydroxyls.

### 1.2 Reactivity test

CO\(_2\) conversion, C-containing gas products selectivity, ethanol yield, turnover frequency (TOF) were calculated as follow\(^2\)\(^-\)\(^4\):

\[
X_{\text{CO}_2} (%) = \frac{F_{\text{CO}_2,\text{out}} - F_{\text{CO}_2,\text{in}}}{F_{\text{CO}_2,\text{in}}} \times 100
\]

\[
S_i (%) = \frac{\%i \times n}{\sum \%i \times n} \times 100
\]

Ethanol yield(%) = \(X_{\text{CO}_2}(\%)) \times S_{\text{ethanol}}(\%) \times 100

TOF of ethanol = \(\frac{F_{\text{CO}_2,\text{in}} \times X_{\text{CO}_2} \times 60 \times S_{\text{ethanol}}}{V_{\text{CO}} \times S_{\text{F}}}(h^{-1})\)

TOF of CH\(_4\) = \(\frac{F_{\text{CO}_2,\text{in}} \times X_{\text{CO}_2} \times 60 \times S_{\text{CH}_4}}{V_{\text{CO}} \times S_{\text{F}}}(h^{-1})\)

Where \(i\) represents the carbon containing species in the products, including CH\(_4\), CO, C\(_n\)H\(_m\), CH\(_3\)OH and C\(_2\)H\(_5\)OH, and \(n\) is the number of carbon atoms in the carbon containing species. TOF of CH\(_4\) or ethanol was calculated as moles of CH\(_4\) or ethanol formed on per mole of surface Rh obtained from the CO chemisorption. TOF of CO\(_2\) was calculated as moles of CO\(_2\) converted on per mole of surface Rh. The Data for the catalytic activity were collected when the reaction reached stable conditions, and the repeated tests have been also carried out to confirm the reproducibility of the results. Besides, carbon balances closed to within \(\pm\)8\% for the data.
S2. Supporting tables and figures

2.1 Supporting tables

Table S1. Physicochemical properties of different catalysts.

| Catalyst                  | \( W_{\text{Rh}} \)\(^a\)/wt\% | \( S_{\text{BET}} \)\(^b\)/m\(^2\) g\(_{\text{cat}}\)\(^{-1}\) | \( V_{\text{pore}} \)\(^b\)/cm\(^3\) g\(_{\text{cat}}\)\(^{-1}\) |
|---------------------------|----------------------------------|---------------------------------|---------------------------------|
| RhFeLi/TiO\(_2\) NRs-400°C | 2.5                              | 22.5                            | 0.08                            |
| RhFeLi/TiO\(_2\) NRs-500°C | 2.4                              | 23.6                            | 0.08                            |
| RhFeLi/TiO\(_2\) NRs-600°C | 2.5                              | 21.8                            | 0.07                            |
| RhFeLi/TiO\(_2\) Com       | 2.4                              | 18.2                            | 0.06                            |
| RhFeLi/TiO\(_2\) NRs-CO    | 2.4                              | 23.1                            | 0.08                            |

\(^a\) ICP-AES.
\(^b\) N\(_2\) adsorption.

Table S2. Catalytic properties of different catalysts.

| Catalyst                  | \( d_{\text{Rh}} \)\(^a\)/nm | Active loop volume (CO, cm\(^3\)/g STP) | Ethanol yield /% | TOF of CH\(_4\) /h\(^{-1}\) | TOF of ethanol /h\(^{-1}\) |
|---------------------------|-------------------------------|----------------------------------------|------------------|-----------------------------|-----------------------------|
| RhFeLi/TiO\(_2\) NRs-400°C | 2.5                           | 0.50                                   | 3.1              | 0.58                        | 0.11                        |
| RhFeLi/TiO\(_2\) NRs-500°C | 2.3                           | 0.69                                   | 5.1              | 0.21                        | 0.12                        |
| RhFeLi/TiO\(_2\) NRs-600°C | 2.8                           | 0.42                                   | 0.9              | 0.02                        | 0.04                        |
| RhFeLi/TiO\(_2\) Com       | 4.0                           | 0.09                                   | 0.6              | 0.20                        | 0.08                        |
| RhFeLi/TiO\(_2\) NRs-CO    | 2.7                           | 0.67                                   | 0.1              | 0.01                        | 0.00                        |
| RhFeLi/SiO\(_2\)           | 7.1                           | 0.06                                   | 0.4              | 0.09                        | 0.08                        |

\(^a\) Diameter of Rh nanoparticles determined by the statistical results of TEM images.
**Table S3.** Compositions of different catalysts.

| Catalyst       | Rh:Fe (XPS) | Rh:Fe (ICP-AES) | Rh/wt% (ICP-AES) | Fe/wt% (ICP-AES) |
|----------------|-------------|-----------------|------------------|------------------|
| RhFeLi/TiO₂ NRs | 58:42       | 48:52           | 2.4              | 1.4              |
| RhFeLi/TiO₂ Com | 29:71       | 50:50           | 2.4              | 1.3              |

**Table S4.** Binding energies of Rh 3d and Fe 2p, and molar ratio of Rh:Fe for different RhFeLi/TiO₂ catalysts.

| Catalyst       | RhFeLi/TiO₂ NRs-400°C | RhFeLi/TiO₂ NRs-500°C | RhFeLi/TiO₂ NRs-600°C | RhFeLi/TiO₂ NRs-CO | RhFeLi/TiO₂ Com |
|----------------|------------------------|------------------------|-----------------------|--------------------|----------------|
| Rh 3d/2        | 307.1 eV               | 307.2 eV               | 307.1 eV              | 307.2 eV           | 306.8 eV       |
| Fe 2p/2        | 710.8 eV               | 711.0 eV               | 710.9 eV              | 711.0 eV           | 711.3 eV       |
| Rh:Fe (Atomic ratio) | 59:41              | 58:42                  | 56:44                 | 48:52              | 29:71          |
### Table S5. DRIFTS peak assignments of the surface species for the CO₂ hydrogenation reaction.

| Species     | Peaks/cm⁻¹ | Assignment               |
|-------------|-------------|--------------------------|
| Formate     | 1585-1610   | \( \nu_{as}(\text{OCO}) \) |
|             | 1361-1370   | \( \nu_{s}(\text{OCO}) \) |
|             | 2880-2886   | \( \nu(\text{CH}) \)     |
|             | 1379-1383   | \( \delta(\text{CH}) \)   |
|             | 2970-2977   | \( \delta(\text{CH})+\nu_{as}(\text{OCO}) \) |
|             | 2731-2738   | \( \delta(\text{CH})+\nu_{s}(\text{OCO}) \) |
| Carbonate   | 1520, 1300-1400 | CO₃²⁻                   |
|            | 2931-2821-2825 | \( \nu(\text{CH₃}) \)   |
| Methoxy     | 1045-1049   | \( \nu(\text{OCH₃}) \)   |
| Methyl      | 1450-1470   | \( \delta(\text{C-H}) \)  |

### Table S6. CO₂ conversion and product distribution of CO₂ hydrogenation over different catalysts.a

| Catalyst      | Conversion/% | Selectivity/% | CO | CH₄ | CH₃OH | C₂H₅OH | Other oxygenatesb |
|---------------|--------------|---------------|----|-----|-------|--------|-------------------|
| RhFeLi/TiO₂ NRs-300 °C | 22.0         | 5.4           | 84.7 | 1.9  | 7.5   | 0.5    |                   |
| RhFeLi/TiO₂ NRs-400 °C | 21.4         | 5.1           | 79.5 | 0.6  | 14.6  | 0.2    |                   |
| RhFeLi/TiO₂ NRs-500 °C | 15.7         | 12.5          | 53.9 | 2.2  | 31.3  | 0.1    |                   |
| RhFeLi/TiO₂ NRs-600 °C | 6.6          | 77.2          | 6.7  | 3.2  | 12.6  | 0.3    |                   |
| RhFeLi/TiO₂ Com | 4.5          | 43.9          | 36.8 | 3.3  | 15.7  | 0.3    |                   |
| RhFeLi/TiO₂ NRs-CO | 4.7          | 81.4          | 9.6  | 7.1  | 1.2   | 0.7    |                   |

a. Reaction conditions: 300 mg catalyst, P = 30 atm, T = 250 °C, GHSV= 6000 h⁻¹, CO₂/H₂/N₂ = 1/3/1.
b. Other oxygenates are mainly C₂⁺ oxygenates.
2.2 Supporting figures

Fig. S1. (a) TEM and (b) HRTEM of TiO$_2$ NRs. The scale bar represents 20 nm.
**Fig. S2.** Raman spectrum ($\lambda_{\text{excitation}} = 532$ nm) of 2.5 wt% RhFeLi supported on different TiO$_2$ after reaction. The supports include TiO$_2$ NRs-400°C, TiO$_2$ NRs-500°C, TiO$_2$ NRs-600°C, TiO$_2$ NRs-CO and TiO$_2$ Com. Raman spectra were recorded under ambient conditions using a 532 nm Ar ion laser beam.
Fig. S3. (a) H$_2$-TPR profile of 1 wt% FeO$_x$/TiO$_2$ NRs and 1 wt% FeO$_x$/TiO$_2$ Com. (b) H$_2$-TPR profile of 2.5 wt% RhFeLi/TiO$_2$ NRs and 2.5 wt% RhFeLi/TiO$_2$ Com.
Fig. S4. (a) FTIR spectra over 2.5 wt% RhFeLi/TiO₂ NRs, 2.5 wt% RhFeLi/TiO₂ Com and 2.5 wt% RhFeLi/SiO₂ after CO adsorption at 250 °C. (b) XPS spectra of Rh 3d obtained from 2.5 wt% RhFeLi/TiO₂ NRs, 2.5 wt% RhFeLi/TiO₂ Com and 2.5 wt% RhFeLi/SiO₂. (c) XPS spectra of O 1s obtained from 2.5 wt% RhFeLi/TiO₂ NRs and 2.5 wt% RhFeLi/TiO₂ Com. All the data were collected from the catalysts after H₂-reduction.

Note: The O 1s spectrum of RhFeLi/TiO₂ displays two peaks at 529.0 and 531.5 eV (Fig. S4c), which can be attributed to lattice oxygen and hydroxyl groups, respectively.²⁻⁶
Fig. S5. (a) The comparison of CO₂ conversion (Black symbol) and product distribution (Column) obtained over 1 wt% RhFeLi (Rh:Fe:Li = 1:1:1) supported on different supports. (b) The comparison of ethanol yield obtained over 1 wt% RhFeLi (Rh:Fe:Li = 1:1:1) supported on different supports. Reaction conditions: P = 30 atm, T = 250 °C, GHSV = 6000 h⁻¹, CO₂/H₂/N₂ = 1/3/1.
Fig. S6. The CO₂ conversion (Black) and product distribution obtained from 2.5 wt% Rh/TiO₂ NRs and Com (a), 2.5 wt% RhFe/TiO₂ NRs and Com (Rh:Fe=1:1) (b), 2.5 wt% RhLi/TiO₂ NRs and Com (Rh:Li=1:1) (c), 2.5 wt% RhFeLi/TiO₂ NRs and Com (Rh:Fe:Li=1:1:1) (d). Reaction conditions: P = 30 atm, T = 250 °C, GHSV = 6000 h⁻¹, CO₂/H₂/N₂ = 1/3/1.
Fig. S7. Stability test and product distribution obtained over 2.5 wt% RhFeLi/TiO$_2$ NRs (a), 2.5 wt% RhFeLi/TiO$_2$ Com (b), 2.5 wt% Rh 2.5 wt% FeLi/TiO$_2$ NRs (c), 2.5 wt% Rh 2.5 wt% FeLi/TiO$_2$ Com (d), 2.5 wt% Rh 5 wt% FeLi/TiO$_2$ NRs (e), 2.5 wt% Rh 5 wt% FeLi/TiO$_2$ Com (f). The molar ratio of Rh:Li is 1:1. Reaction conditions: P = 30 atm, T = 250°C, GHSV = 6000 h$^{-1}$, CO$_2$/H$_2$/N$_2$ = 1/3/1.
Fig. S8. (a) CO-TPD of pure TiO$_2$ support: TiO$_2$ NRs, TiO$_2$ Com. Pretreatment: H$_2$ reduction at 400°C for 1h. (b) FTIR spectra of 2.5 wt% RhFeLi supported on TiO$_2$ NRs, TiO$_2$ Com, TiO$_2$ NRs-CO and TiO$_2$ NRs-H$_2$ re-reduction after reaction. (c) FTIR spectra of 2.5 wt% RhFeLi supported on TiO$_2$ NRs-400°C, TiO$_2$ NRs-500°C and TiO$_2$ NRs-600°C after reaction.

Note: The hydroxyls over the surface of TiO$_2$ were characterized by CO-TPD and FTIR. The peak areas of hydroxyls showed in Fig. 4a and Fig. 6 are obtained from Fig. S8b, c. We integrated peak area of associative -OH stretching vibrations (3450 cm$^{-1}$) to represent the amount of hydroxyls.
Fig. S9. (a) DRIFTS of CO reduction at 350 °C versus time on the 2.5 wt% RhFeLi/TiO₂ NRs. (b) The amount of -OH at 3450 cm⁻¹ in DRIFTS spectra of 2.5 wt% RhFeLi/TiO₂ NRs versus time after feeding CO flow into *in situ* cell at 350 °C.
Fig. S10. (a) HRTEM, particle size distributions (Inset figures) and (b) HAADF-STEM images of 2.5 wt% RhFeLi/TiO2 NRs after CO reduction. (c, d, e) HRTEM, particle size distributions (Inset figures) of 2.5 wt% RhFeLi/TiO2 NRs-300 °C, RhFeLi/TiO2 NRs-400 °C and RhFeLi/TiO2 NRs-600 °C after H2 reduction. (f) HAADF-STEM images of 2.5 wt% RhFeLi/TiO2 NRs-600 °C after H2 reduction.
Fig. S11. (a) DRIFTS spectra over 2.5 wt% RhFeLi supported on TiO$_2$ NRs-CO, TiO$_2$ NRs-400°C, TiO$_2$ NRs-500°C and TiO$_2$ NRs-600°C after CO adsorption at 250°C. (b) XPS spectra of Rh 3d obtained from 2.5 wt% RhFeLi supported on TiO$_2$ NRs-CO, TiO$_2$ NRs-400°C, TiO$_2$ NRs-500°C and TiO$_2$ NRs-600°C. (c) XPS spectra of Fe 2p obtained from 2.5 wt% RhFeLi supported on TiO$_2$ NRs-CO, TiO$_2$ NRs-400°C, TiO$_2$ NRs-500°C and TiO$_2$ NRs-600°C.
Fig. S12. *In situ* DRIFTS spectra over 2.5 wt% RhFeLi/TiO₂ NRs (a, c) and 2.5 wt% RhFeLi/TiO₂ Com (b, d) after switching the CO₂+H₂+Ar (CO₂:H₂=1:3) flow to pure CO₂ flow at 250 °C.
Fig. S13. (a) *In situ* DRIFTS spectra over 2.5 wt% RhFeLi/TiO$_2$ NRs and 2.5 wt% RhFeLi/TiO$_2$ NRs-CO after CH$_3$OH+Ar adsorption followed by CO+H$_2$ adsorption at 250 °C. (b) The GC-FID spectra of gaseous and liquid products produced over 2.5 wt% RhFeLi/TiO$_2$ NRs with different reactants. Reaction conditions: P = 30 atm, T = 250 °C, CO/H$_2$ = 1/2, the feeding rate of H$_2$O or CH$_3$OH/H$_2$O (CH$_3$OH/H$_2$O = 1/10) is 0.5 mL/min.
Scheme S1. Conceivable reaction mechanism of CO₂ hydrogenation to ethanol on Rh-based catalyst.
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