Generation Oxide Surface Patches Promoting the H-spillover in Ru/(TiO\textsubscript{x})MnO Catalysts Enable CO\textsubscript{2} Selective Reduction

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Method Supplement

**Materials and chemicals.** The following chemical reagents were used without further purification: Potassium permanganate (KMnO₄, 99.5%, Tianjin Fangzheng Reagent factory), Manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, >99%, Sinopharm), Tetrabutyl titanate (C₁₆H₃₆O₄Ti, 98%, Macklin), Ruthenium(III) nitrosyl nitrate solution (Ru(NO)(NO₃)ₓ(OH)ᵧ, x+y=3, 1.5% w/v, Macklin), Anatase titanium dioxide (TiO₂(a), 99.8%, 10-25 nm, Aladdin), P₂₅ titanium dioxide (TiO₂(P), Acros Organics), Aluminium oxide (γ-Al₂O₃, 99.97%, Alfa Aesar), Silicon dioxide (SiO₂, 99%, Alfa Aesar), Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, >99%, Sinopharm), Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, >99%, Aladdin), Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, >99%, Sinopharm), Urea (H₂NCONH₂, >99%, Sinopharm).

**Preparation of Ti(a)/Mn or Ti(P)/Mn supports by mixing.** Two starting sources of TiO₂ NPs were used: commercial anatase TiO₂ and P₂₅ (Evonik). The 0.12 g commercial TiO₂ and 1.38 g MnOx were mixed in 30 ml deionised water, stirred for 6 h and dried at 60 °C overnight. The solid mixture was calcined at 450 °C for 3 h to obtain Ti(a)/Mn or Ti(P)/Mn.

**Preparation of CuZnAl.** CuZnAl catalyst was prepared by urea homogeneous precipitation method. Typically, an aqueous solution containing 3.02 g Cu(NO₃)₂·3H₂O, 0.93 g Zn(NO₃)₂·6H₂O, 0.78 g Al(NO₃)₃·9H₂O, 12.01 g urea and 100 ml deionised water was stirred at 95 °C for 2 h followed by aged for 24 h. The filter cake obtained after filtration was washed with deionised water and dried at 60 °C. CuZnAl catalyst was obtained after calcination at 350 °C for 3h.

**Temperature programmed experiments.**

**H₂-TPR.** The 50 mg samples were pretreated with N₂ at 300°C for 1 h, then ramped from 50°C to 600°C (10 °C/min) in 10% H₂/N₂ (27.6 ml/min), and TCD signals were recorded to obtain H₂-TPR curves.

**TPD.** The 200 mg catalyst was pretreated with 10%H₂/Ar at 500 °C for 1 h, then purged with Ar at 510°C for 30 min to remove of adsorbed H species. After decreasing to 50°C,
high-purity CO₂ or 10% H₂/Ar was pre-adsorbed for 30 min, then insert gas (30 ml/min, He for CO₂-TPD, and Ar for H₂-TPD) was purged to baseline to stabilise. The TPD curve was then recorded with the temperature ramping from 50 to 700°C (10 °C/min).

**CO₂+H₂-TPR.** The catalysts were pretreated with high-purity H₂ at 500°C for 2 h, then cooled to 50 °C. The 30 ml/min reaction gas composed of 72 Vol% H₂/24 Vol% CO₂/4 vol% N₂ was switched until the baseline was stabilised. The reaction temperature was ramped from 50 to 600°C (5°C/min), and the MS signals of m/z=44 and 28 were used to record the consumption of CO₂ and formation of CO.

**H-D exchange experiments.** After pre-reducing by H₂ at 500 °C, the H₂: D₂: Ar (1:1:4, 30 ml/min) gas mixture was passed through the catalyst bed until the baseline was stabilised, and the temperature was ramped from 50 to 500°C (10 °C/min). The MS signal intensity of H₂ (m/z=2), HD (m/z=3), and D₂ (m/z=4) was recorded.

**DFT calculation Method.**

All DFT calculations were performed with the plane wave-based pseudo-potential code in Vienna *ab initio* simulation package (VASP). ²,³ The projector augmented wave method (PAW) describes the electron-ion interaction. ⁴,⁵ The exchange and correction energies are described by the generalised gradient approximation using Perdew-Burke-Ernzerhof formulation (GGA-PBE). ⁶ The plane wave cutoff energy was specified by 400 eV, the electron smearing method with σ = 0.20 eV was used to ensure energies with errors due to smearing of less than one meV per unit cell. The convergence criteria for geometry optimisations of total energy and forces were 10⁻⁷ eV and 0.02 eV/Å. Spin polarisation was included. The 3×3×1 Monkhorst-Pack k-points sampling was used. The vacuum layer between periodically repeated slabs was set as 15 Å to avoid interactions among slabs. The transition state was located using the climbing image nudged elastic band (CI-NEB) method. ⁷ A stretching frequency analysis was also performed to verify whether a transition state is associated with a single imaginary frequency.

In our study, TiO₂ species were highly dispersed on the MnO surface for reduced
Ru/Ti/Mn catalyst (no obvious particles of TiO₂ exist in XRD and EDS mapping). Therefore, we constructed a MnO-supported nanoclusters model and calculated the H transport barriers on various sites. We used a 3-layer (4 × 4) MnO (100) slab model containing 96 atoms, where the top 2 layers, including adsorbates, were relaxed, and the bottom layer was kept fixed in their bulk positions. MnO(100) is used for this study because it is non-polar and thermodynamically stable. For all calculations, the initial magnetic moments of Mn²⁺ cations were configured to follow the AFM-II antiferromagnetic arrangement in bulk MnO, verified by powder neutron diffraction. The PBE+U using the method of Dudarev was used to also provide another estimate of the adsorption energy because of the highly correlated electronic structure of MnO. A U-J value of 4.0 eV yields the best energy of formation for bulk MnO, and is used in all calculations. According to the model size of MnO, a nine-atom TiO₂ cluster model was constructed.

The activation barrier \( E_a \) and reaction energy \( E_r \) are calculated as \( E_a = E_{TS} - E_{IS} \) and \( E_r = E_{FS} - E_{IS} \), respectively, where \( E_{IS} \), \( E_{TS} \), and \( E_{FS} \) are the energies of the corresponding initial state (IS), transition state (TS), and final state (FS), respectively.

**Calculation methods for kinetic parameter experiments.**

Activation energy and reaction order is calculated based on the rate equation for a chemical reaction (1) and Arrhenius equation (2).

\[
\begin{align*}
    r &= - \frac{d[CO_2]}{dt} = k[CO_2]^α[H_2]^β[CO]^γ[CH_4]^δ[H_2O]^ε \quad (1) \\
    k &= k_0e^{-\frac{E_a}{RT}} \quad (2)
\end{align*}
\]

The \( r \) represents CO formation rate (mol/h), \([M]\) represents M species partial pressure (kPa). \( R \) is the gas constant (8.314 J/K·mol). \( k_0 \) is the pre-exponential factor, independent of the catalyst's intrinsic activity. Equation (3) is obtained by substituting equation (2) into (1) and logarithmic transformations:

\[
lnr = -\frac{E_a}{RT} + lnk_0 + \alpha ln[CO_2] + \beta ln[H_2] + \gamma ln[CO] + \delta ln[CH_4] + \epsilon ln[H_2O] \quad (3)
\]

The latter five terms can be regarded as constants in the steady-state reaction with variable temperature and low CO₂ conversion (4):
\[ \ln r = -\frac{E_a}{R} \frac{1}{T} + C \quad (4) \]

\( \ln r \) and \( \frac{1}{T} \) are linear functions, and \( -\frac{E_a}{R} \) is the slope. By changing the temperature \( T \), a series of \( \ln r \) can be obtained, and the activation energy \( E_a \) can be calculated. The calculation of \( r \) is consistent with the Rate calculation method in the main text.

The reaction orders of the reactants were calculated using equation (3). Under constant temperature, keeping the concentration of other reactants unchanged, changing the partial pressure of the specified species, and \( \alpha \) and \( \beta \) were obtained, representing the reaction orders of CO\(_2\) and H\(_2\), respectively.
Figure S1. **a** Overview and **b** local magnification of XRD patterns for calcined and reduced Ti/Mn support without Ru loaded.
Figure S2. XRD patterns of Ru/Ti/Si-C and Ru/Ti/Si -R, C=Calcined and R=Reduced. When SiO₂ is used as the support rather than MnOₓ, the TiO₂ diffraction lines still are detectable after H₂ pretreatment at 500°C (Figure S2), nor do they indicate significant changes in size and dispersion.
Figure S3. *In-situ* XRD experiment for Ru/Ti/Mn catalyst during thermal treatment under 50% H₂/N₂ atmosphere. a. TiO₂ [101] plane, b. MnO [200] plane.
Figure S4. *In-situ* XRD experiment for Ti/Mn support during thermal treatment under 50% H2/N2 atmosphere. a. 20-50°, b. TiO2 [101] plane, c. MnO [200] plane.
Figure S5. In-situ XRD experiment for Ru/Ti/Mn during N₂ heat treatment. a. 20-50°, b. TiO₂ [101] plane, c. MnO [200] plane.
In-situ Raman spectra allow for analysing the change in Ti species during the H2 treatment process (Figure S6-S7). The bands at 146 (Eg), 399 (B1g), 518 (A1g), and 631 (Eg) cm$^{-1}$ corresponding to lattice vibrations of the TiO2 NPs drastically increase when the treatment temperature is above about 260° C. In particular, it enhances the symmetrical stretching vibration at about 146 cm$^{-1}$, confirming that the TiO2 redispersion occurs during the reduction process with increased surface-exposed TiO2 species. Figure S7b shows the surface composition changes during the reduction. The Raman bands at 580 and 638 cm$^{-1}$, corresponding to MnO$_6$ octahedra of MnO$_2$, are present in the sample treated at 50° C. These bands shift on increasing the reduction temperature.

A new weak Raman band also appears at 653 cm$^{-1}$ at a treatment temperature of 180° C. This band corresponds to the Mn-O breathing vibration of tetrahedrally coordinated Mn$^{2+}$ and thus indicates the partial reduction of MnO$_2$. Its intensity increases further at 220° C.

The Raman band at 562-581 cm$^{-1}$, assigned to Mn-O stretching vibration perpendicular to the direction of MnO$_6$ octahedral double chains, and the shift in the band indicates an interaction between TiO$_2$ and MnO$_x$. When the temperature increased, MnO$_x$ was completely reduced to MnO, which has a cubic rock salt structure with poor Raman activity.

The results above are consistent with a mechanism of in-situ transformation of TiO2 NPs during treatment with H2, leading to the spreading of the titania NPs to form XRD-amorphous patches on the MnO$_x$ surface.
**Figure S7.** *In-situ* H₂-reduction Raman results of Ru/Ti/Mn at 500 °C for 5-25 min compared to at 50 °C.

*In-situ* Raman spectra allow analysing Ti species' change during the H₂ treatment process (Figure S7). See main text for details.
Figure S8. HAADF-STEM images and corresponding EDS line scanning across Ru particle on reduced a-b, Ru/MnO$_x$ and c-d, Ru/Ti/Mn.
Figure S9. HR-TEM images of calcined Ru/Ti/Mn.

HR-TEM images of calcined Ru/Ti/Mn catalyst show that Ti species exist in the form of anatase TiO$_2$ nanoparticles on the MnO$_x$ surface (Figure S9), in agreement with the indication by electron energy loss spectroscopy (EELS) mapping images (Figure S10). See main text for details.
Figure S10. TEM image and EELS mapping of calcined Ru/Ti/Mn catalyst.
Figure S11. ADF-STEM image and corresponding EDS elemental mapping of reduced Ru/Ti/Mn catalyst.

TiO$_2$ species on the reduced sample are highly dispersed, as confirmed by the corresponding energy dispersive spectroscopy (EDS) elemental mapping images (Figure S11), which provided visual evidence for the dispersion process of TiO$_2$. 
Figure S12. a, b Ru 3d5/2 and Mn 3s XPS spectra of reduced Ru/MnOx and Ru/Ti/Mn by nearly *in-situ* XPS. c Ti 2p spectrum of calcined and reduced Ru/Ti/Mn by nearly *in-situ* XPS.

Ru 3d5/2 and Mn 3s spectra of nearly-*in-situ* XPS of reduced Ru/MnOx and Ru/Ti/Mn catalysts (Figure S12a and S12b). See main text for details.
**Figure S13.** *In-situ* HAADF-STEM images of a, unreduced Ru/Ti(P)/Mn and b, reduced Ru/Ti(P)/Mn. c, The EELS spectra over 400-700 eV and d, Ti L-edge spectra of unreduced and reduced Ru/Ti(P)/Mn.

The *in-situ* EELS signal of Ti L-edge and the energy loss decrease by H2 reduction (Figure S13) indicates the existence of Ti species in a partially reduced state.
Figure S14. a TEM image of commercial P25. b Particle size distribution of the P25.

TiO$_2$ (P25) NPs, with an average size of $21 \pm 6$ nm (Figure S14) were used instead of anatase TiO$_2$ NPs in preparing the Ru/Ti/Mn sample to check the role of the nature of titania. Ti(a) and Ti(P) indicate anatase TiO$_2$ and commercial P25 TiO$_2$ (Evonik), respectively. P25 is a mixture of anatase and about 20% rutile. The behaviour is rather similar in the two cases (Figure S15).
Figure S15. a, Overview and b, local magnification of Ru/Ti(a)/Mn XRD patterns. c, Overview and d, local magnification of Ru/Ti(P)/Mn XRD patterns. C=Calcined and R=Reduced.
In addition, we further check the final test conditions with the theoretical model, and prove that our relevant kinetic data have eliminated the influence of internal and external diffusion. Both the absence of internal and external diffusion was verified, which includes Weisz-Prater criterion ($C_{WP}$) for internal diffusion and Mears' criterion ($C_M$) for external diffusion. (Fogler H S. Elements of chemical reaction engineering. Chemical Engineering Science, 1987.)

\[
C_{WP} = \frac{r_{obs} \rho_c R_p^2}{D_{eff} C_s} < 1 \\
C_M = \frac{r_{obs} \rho_b R_p n}{k_c C_{Ab}} < 0.15
\]

Where $r_{obs}$ = observed reaction rate, mol/kg-cat·s

\[
n = \text{reaction order}
\]

\[
R_p = \text{catalyst particle radius, m}
\]

\[
\rho_c = \text{density of catalyst, kg/m}^3
\]

\[
\rho_b = \text{bulk density of catalyst bed, kg/m}^3
\]

\[
= (1-\Phi) \rho_c \quad (\Phi=\text{porosity})
\]

\[
D_{eff} = \text{effective diffusivity, m}^2/\text{s}
\]

\[
C_s = \text{gas concentration of A at the external surface of the catalyst, mol/m}^3.
\]

\[
C_{Ab} = \text{bulk gas concentration of A, mol/m}^3.
\]

\[
k_c = \text{external mass transfer coefficient, m/s}
\]
For the activity measurements, a total gas flow rate of 100 ml min⁻¹ and a catalyst particle size of 0.25-0.38 mm (40-60 mesh) were employed. The above-mentioned $C_{WP}$ and $C_M$ are calculated based on the Ru/Ti/Mn reaction activity.

$\rho_c \approx \rho_b \approx \rho_{cat} = 0.51$ g/cm³

$C_s \approx C_{Ab} = 1.07 \times 10^{-5}$ mol/cm³

$D_{eff} \approx 0.0156$ cm²/s

$k_e \approx 0.15$ m/s

$C_{WP} = \frac{r_{obs} \rho_c R_p^2}{D_{eff} C_s}$

$= [(25 \times 10^{-6}$ mol/gcat·s) $\times (0.51$ g/cm³) $\times (0.038$ cm)²] / [(0.0156$ cm²/s) $\times (1.07 \times 10^{-5}$ mol/cm³)]

$= 0.11 < 1$

$C_M = \frac{r_{obs} \rho_b R_p^n}{k_e C_{Ab}}$

$= [(25 \times 10^{-6}$ mol/gcat·s) $\times (0.51$ g/cm³) $\times (0.00038$ m) $\times 0.4] / [(0.15$ m/s) $\times (1.07 \times 10^{-5}$ mol/cm³)]

$= 0.001 < 0.15$

Therefore, internal and external diffusion effects could be neglected during the activity tests.
Figure S17. CO₂ hydrogenation performances of Ru/TiO₂(P), Ru/MnOₓ and Ru/Ti(P)/Mn as function of reaction temperature. a, CO₂ conversion. b, CO selectivity.

The CO selectivity of Ru on TiO₂ depends instead on the source of titania which may induce changes of adsorption and desorption of intermediate CO.¹³ Ru/Ti(P)/Mn (P25 TiO₂ as a precursor) and Ru/Ti/Mn (anatase TiO₂ as a precursor) synthesised with various Ti precursor possessed similarly enhanced RWGS activity (Figure S17), while the former also accompanied by TiO₂ redispersion shown in Figure S15.
Figure S18. CO formation rate of dual-bed or powder-mixing for TiO$_2$ and MnO$_x$ supported catalysts. (Numbers correspond to CO formation rate, mmol CO·g$_{\text{cat.}}$·h$^{-1}$)

Realising an intimate contact between TiO$_2$ and MnO$_2$ is important in obtaining a high conversion rate. A dual bed of Ru/TiO$_2$ and Ru/MnO$_x$ performs significantly poor than when intimate contact is achieved. While realising a direct contact between TiO$_2$ and MnO$_x$ during the preparation procedure lead to better catalysts, even an intimate physical mixture gives good results (Figure S18). During the pretreatment in H$_2$, TiO$_2$ may reduce and spread over the MnO$_x$ surface even when an intimate mechanical mixing of the two oxides is present. This strategy to improve the CO$_2$ hydrogenation performance by TiO$_x$ spreading over the oxidic support is not limited to Ru NPs (Figure S24).
Figure S19. a Overview and b local magnification of XRD patterns for spent Ru/MnO$_x$ and Ru/Ti/Mn.
Figure S20. CO formation rate on Ru/Ti/Mn-x catalysts with different Ti loading content for CO\textsubscript{2} hydrogenation at 400 °C. x represents the mass loading of Ti tested by ICP (ICP results can be found in Table S1).
**Figure S21.** XRD patterns for calcined Ru/Ti/Mn-x with different Ti loading content. 

x represents the mass loading of Ti tested by ICP (ICP results can be found in Table S1).
Figure S22. a Overview and b local magnification of XRD patterns for reduced Ru/Ti/Mn-x with different mass loading of Ti. x represents the mass loading of Ti tested by ICP.
The effect of H₂:CO₂ on CO₂ performance for Ru/MnOₓ and Ru/Ti/Mn catalysts. The H₂/CO ratio increase to 6 does not significantly lower the CO selectivity of Ru/MnOₓ and Ru/Ti/Mn catalysts. It remains above 96% (Figure S23).
Figure S24. CO2 hydrogenation performances of Ru, Pt and Pd loaded on Ti/Mn and MnOx as a function of reaction temperature. a, CO2 conversion. b, CO selectivity.

This strategy to improve the CO2 hydrogenation performance by TiOx spreading over the oxidic support is not limited to Ru NPs. Other metals NPs as Pt and Pd also show a similar effect (Figure S24).
Figure S25. CO$_2$ hydrogenation performances of MnO$_x$ and TiO$_2$/MnO$_x$ without metal loaded.

The activity of MnO$_x$ and TiO$_2$/MnO$_x$ without Ru loading are much lower than that of Ru/MnO$_x$ and Ru/Ti/Mn catalysts (Figure S25), even if reported previously as active substrates in CO$_2$ selective reduction.
Figure S26. HAADF-STEM image and Ru nanoparticles size distribution of reacted Ru/Ti/Mn for stability test.

Electron microscopy data show that the size of the Ru NPs in the Ru/Ti/Mn catalyst increases slightly to 5.4 nm (Figure S26), the reason for the initial slight decrease of activity. After this initial change, however, Ru NPs’ size and catalytic performances remain stable.
Figure S27. CO$_2$+H$_2$-DRIFTs of Ru/MnO$_x$ catalyst under CO$_2$:H$_2$=1:3 from 50 °C to 350 °C.

In-situ DRIFT spectra under the reaction atmosphere from 50 to 350 °C of the Ru/Ti/Mn and Ru/MnO$_x$ catalysts showed the same adsorption species or reaction intermediates (Figure S27). See text for details.
Figure S28. H$_2$-DRIFTs of Ru/Ti/Mn catalyst pre-reacted at 350 °C for 30 min under CO$_2$:H$_2$=1:3 followed by H$_2$ for 45 min.
Figure S29. H₂-DRIFTs of Ru/MnOₓ catalyst pre-reacted at 350 °C for 30 min under CO₂:H₂=1:3 followed by H₂ for 45 min.

In-situ DRIFT spectra. After reacting at 350°C for 30 min, reaction gas (CO₂+H₂) was switched to H₂. The DRIFTs results are presented in Figures S28-S29.

Surface bi-CO₃²⁻ species are largely unreactive in the H₂ atmosphere. This evidence indicates that the bi-CO₃²⁻ is a strongly adsorbed inactive (spectator) species. On the contrary, surface HCO₃⁻ might be the key active intermediate in the reaction process because fast disappears in the presence of H₂. This active intermediate was mainly derived from the CO₂ adsorbed on the hydroxyl group on the catalyst surface. Moreover, CO₂ directly dissociates to CO* and O* on the oxygen vacancy. The former further desorbs as gas phase CO, while the active H species remove the latter in the form of H₂O.
**Figure S30.** In-situ CO$_2$+H$_2$-DRIFTS of Ti/Mn support without Ru under CO$_2$:H$_2$=1:3 atmosphere from 50 °C to 350 °C.
Figure S31. In-situ DRIFTs of Ti/Mn support without Ru pre-reacted at 350 °C for 30 min under CO₂:H₂=1:3 atmosphere followed by H₂ for 30 min.
Figure S32. CO$_2$+H$_2$-DRIFTs of Ru/TiO$_2$(a) catalyst under CO$_2$:H$_2$=1:3 from 50 °C to 350 °C.
Figure S33. H₂-DRIFTs of Ru/Ti/Mn catalyst under H₂ flow for 30min at room temperature.

Ru/Ti/Mn show an enhanced number of hydroxy group (-OH, the wide infrared band between 3600-2800 cm⁻¹) than Ru/MnOₓ (Figure 5b). These surface -OH derive from H₂ dissociation on the surface of Ru NPs and migration to the support (H-spillover). A similar -OH peak appears in the 3600-2800 cm⁻¹ region when the catalyst is treated with H₂ at room temperature (Figure S33. These hydroxyl groups may react with CO₂ to form HCO₃⁻.)
Figure S34. Temperature programmed treatment under H₂ (H₂-TPR) flow of MnOₓ and Ti/Mn without Ru loading.
Figure S35. Temperature-programmed H-D exchange of Ru/MnOx and Ru/Ti/Mn with H₂+D₂ as the feed gas.
Figure S36. Time evolution of DRIFT spectra during the H-D isotopic exchange experiments recorded after exposing a freshly reduced sample of a, Ru/MnOx and b, Ru/Ti/Mn to D2 stream at 100 °C.
Figure S37. Integral area of H$_2$-TPD curve of Ru/MnO$_x$ and Ru/Ti/Mn catalysts.
**Figure S38.** Scheme of H adsorbed states of B1 (a), B2 (b) and B3 (c) on TiO$_x$ nanocluster. H (yellow spheres), O (red spheres), Ti (blue spheres), and Mn (grey spheres) atoms are shown.
**Figure S39.** Scheme of H adsorbed states of A1 (a) and A2 (b) on TiO\textsubscript{x}/MnO interface. H (yellow spheres), O (red spheres), Ti (blue spheres), and Mn (grey spheres) atoms are shown.
Figure S40. Scheme of H adsorbed states of C1 (a) and C2 (b) on MnO surface. H (yellow spheres), O (red spheres), and Mn (grey spheres) atoms are shown.
**Figure S41.** Scheme of CO$_2$ adsorbed and dissociated over MnO without active H species. a1-a2, initial state (IS) that CO$_2$ adsorbed on perfect MnO. b1-b2, transition state (TS). c1-c2, the formation of CO and O. H (yellow spheres), O (red spheres), and Mn (grey spheres) atoms are shown.
Figure S42. Scheme of CO$_2$ adsorbed and dissociated over MnO with active H species. a1-a2, initial state (IS) that CO$_2$ adsorbed around the H species. b1-b2, transition state (TS2). c1-c2, the formation of *COOH. d1-d2, transition state (TS3). e1-e2, the formation of CO and OH. H (yellow spheres), O (red spheres), and Mn (grey spheres) atoms are shown.
Table S1. ICP results of calcined Ru/MnOₓ and Ru/Ti/Mn-x catalysts.

<table>
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<th>Sample</th>
<th>Ru (%)</th>
<th>Ti (%)</th>
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<tr>
<td>Ru/MnOₓ</td>
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<td>-</td>
</tr>
<tr>
<td>Ru/Ti/Mn-0.9</td>
<td>0.31</td>
<td>0.86</td>
</tr>
<tr>
<td>Ru/Ti/Mn-2.8</td>
<td>0.42</td>
<td>2.83</td>
</tr>
<tr>
<td>Ru/Ti/Mn-4.9 (Ru/Ti/Mn)ᵃ</td>
<td>0.38</td>
<td>4.90</td>
</tr>
<tr>
<td>Ru/Ti/Mn-10.8</td>
<td>0.37</td>
<td>10.78</td>
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ᵃ The Ru/Ti/Mn-4.9 in table refers to the Ru/Ti/Mn in the main text.
Table S2. CO$_2$ hydrogenation performances for catalysts at 400 °C.

<table>
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<tr>
<th>No.</th>
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<th>CO$_2$ conversion (%)</th>
<th>CO selectivity (%)</th>
<th>CO rate (mmol/g/h)</th>
<th>Ref.</th>
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<td>1</td>
<td>Ru/Ti-MnO$_x$</td>
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</tr>
<tr>
<td>2</td>
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<td>3</td>
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<td>100</td>
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</tr>
<tr>
<td>4</td>
<td>Ru/5%P25/MnO$_x$</td>
<td>9.7</td>
<td>100</td>
<td>62.6</td>
<td>This work</td>
</tr>
<tr>
<td>5</td>
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<td>100</td>
<td>33.5</td>
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<tr>
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<tr>
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<tr>
<td>8</td>
<td>Ru/5%MnO$_x$/a-TiO$_2$</td>
<td>0.7</td>
<td>100</td>
<td>4.5</td>
<td>This work</td>
</tr>
<tr>
<td>9</td>
<td>Ru/SiO$_2$</td>
<td>40.5</td>
<td>49.0</td>
<td>127.6</td>
<td>This work</td>
</tr>
<tr>
<td>10</td>
<td>Ru/a-Al$_2$O$_3$</td>
<td>15.0</td>
<td>38.8</td>
<td>37.5</td>
<td>This work</td>
</tr>
<tr>
<td>11</td>
<td>Ru/P25</td>
<td>52.4</td>
<td>9.3</td>
<td>31.2</td>
<td>This work</td>
</tr>
<tr>
<td>12</td>
<td>Ru/CeO$_2$</td>
<td>16.5</td>
<td>92.4</td>
<td>97.9</td>
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</tr>
<tr>
<td>13</td>
<td>Ru/MgO</td>
<td>8.8</td>
<td>89.2</td>
<td>50.4</td>
<td>This work</td>
</tr>
<tr>
<td>14</td>
<td>CuZnAl</td>
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<td>100</td>
<td>74.5</td>
<td>This work</td>
</tr>
<tr>
<td>15</td>
<td>0.5%Ru/Al$_2$O$_3$</td>
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<td>22.5</td>
<td>14.5</td>
<td>14</td>
</tr>
<tr>
<td>16</td>
<td>0.01%Ru(sac)/FeO$_x$</td>
<td>14</td>
<td>100</td>
<td>3.8</td>
<td>15</td>
</tr>
<tr>
<td>17</td>
<td>1%Ru/a-TiO$_2$</td>
<td>22</td>
<td>100</td>
<td>37.7</td>
<td>13</td>
</tr>
<tr>
<td>18</td>
<td>0.8%Ru/MnO</td>
<td>20</td>
<td>87</td>
<td>35.0</td>
<td>16</td>
</tr>
<tr>
<td>19</td>
<td>0.4%Ru@mSiO$_2$-N</td>
<td>13.7</td>
<td>93.4</td>
<td>17.1</td>
<td>17</td>
</tr>
<tr>
<td>20</td>
<td>0.5%Ru/TiO$_2$</td>
<td>40</td>
<td>19</td>
<td>15.3</td>
<td>18</td>
</tr>
<tr>
<td>21</td>
<td>0.5%Ru/0.2%K/TiO$_2$</td>
<td>50</td>
<td>5</td>
<td>5.0</td>
<td>18</td>
</tr>
<tr>
<td>22</td>
<td>0.5%Ru/0.2%Na/TiO$_2$</td>
<td>55</td>
<td>2</td>
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<tr>
<td>23</td>
<td>0.5%Ru/0.2%Li/TiO$_2$</td>
<td>50</td>
<td>17.5</td>
<td>17.6</td>
<td>18</td>
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<tr>
<td>24</td>
<td>Au/TiO$_2$</td>
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<td>100</td>
<td>23.4</td>
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<tr>
<td>25</td>
<td>1%Pd+2.3%La$_2$O$_3$/MWCNT</td>
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<td>100</td>
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<tr>
<td>26</td>
<td>Rh@S-1(1MPa)</td>
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<td>90</td>
<td>5.5</td>
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<tr>
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<td>K80-Pt/L</td>
<td>14</td>
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</table>

*a* No. 4-14 were corresponding to Ref.-2 in Figure 3c, and they were prepared and tested by ourselves. No. 15-27 were corresponding to Ref.-1 in Figure 3c, which were originated from the previous literatures.

*b* The reaction temperature was 380 °C.


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