Supporting Information:

Transfer hydrogenation of CO_2 into formaldehyde from aqueous glycerol heterogeneously catalyzed by Ru bound to LDH

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Experimental Section

Preparation of Ca-Al layered double hydroxide (LDH)

LDH materials were prepared from an aqueous solution of high concentrations of metal salts through a homogeneous alkalization reaction triggered by propylene oxide. In one typical experiment run, 14 mmol of $CaCl_2 \cdot 2H_2O$ and 3.5 mmol of $AlCl_3 \cdot 6H_2O$ (The atomic ratio, $y = Ca^{2+}/Al^{3+}$ was equal to 4) were dissolved in a mixture of EtOH (3 mL) and ultrapure water (4 mL). 49 mmol of propylene oxide (PO, 99%, Macklin) was added to the mixture at 298 K and further stirred for 1 min to yield a homogeneous solution. Then, stirring was stopped, and the mixture was sealed and kept at 313 K. After aging for 24 h at

313 K, wet gels were submerged in 50 mL of isopropyl alcohol (IPA) and kept for >1 h at 313 K to exchange the liquid in pores with IPA. This solvent exchange process was repeated 3 times with fresh IPA to remove the remnants of precursors and by-products produced from PO. Then, the wet gels were collected and dried at 313 K for >72 h.

Deposition of Ru on LDH

The dissolved RuCl₃·nH₂O (35.0-42.0% Ru basis, Aladdin) in deionized water (0.4 g·L⁻¹) was diluted with water with the total volume of 50 mL. Ca-Al LDH (0.5 g) was added to the resulting precursor solution and stirred at 323 K for 12 h. The resulting slurry was then recovered by centrifugation and dried at 333 K overnight , yielding Ru/LDH as a gray powder. The loading amount of Ru changed in the range from 0.1%~3%.

Material characterization

The specific surface (BET) area of the sample was measured using a surface area and porosity analyzer (ASAP2460, Micromeritics). XRD patterns were acquired using a x'pert3 powder (PANalytical B.V., Netherlands) with Cu K radiation, operating at 40 kV and 40 mA. SEM images were obtained using a Nova NanoSEM 450 (FEI company, Netherlands) system. The accelerating voltage was 150 kV. Transmission electron microscopy and energy-dispersive X-ray spectroscopy were performed on a JEOL JEM-F200 and a JEOL JED-2300T, respectively. X-ray photoelectron spectroscopy (XPS) were conducted with AXIS-ULTRA DLD-600W (Shimadzu-Kratos company, Japan). Ru K-edge X-ray absorption fine structure spectra were collected at BL14W beamline in Shanghai Synchrotron Radiation Facility (SSRF). The storage rings of SSRF was operated at 3.5 GeV with a stable current of 200 mA. Using Si(111) double-crystal monochromator, the data collection were carried out in transmission mode using Lytle detector. All spectra were collected in ambient conditions. XAFS data were examined using the Athena program.

The Catalytic activity

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Catalytic activity measurements were performed in the batch reactor system. In the typical experiment for batch reactor, the catalyst (50 mg) and aqueous glycerol (0.2 M, 10 mL) were loaded into an autoclave. Subsequently, the reactor was sealed and the reaction mixture was purged with CO₂ gas several times. Finally, the reaction was loaded with CO₂ to a pressure of 1.0 MPa while gently stirring with 300 rpm. The temperature of the system was kept at 323 K and stirred for 12 h. The yields of products were determined by HPLC using a Agilent 1260 HPLC instrument (Agilent Technologies company, America) equipped with an Aminex HPX-87H Ion Exclusion Column. 5 mM H₂SO₄ (0.500 mL/min) was used as mobile phase at 308 K. For comparison, reductant H₂ gas (1.0 MPa) was also used in another catalytic reaction system. In this case, deionized water (10 ml) was used to replace 10 mL of aqueous glycerol (0.2 M). Following each reaction, 1,4-BDO (1,4-butandiol) was added to the reaction mixture as internal standards. Glycerol was determined by gas chromatography in conjunction with a flame ionization detector (GC-2010 plus, Shimadzu, Kyoto, Japan). The MBTH (0.5% w/v, Macklin), HCl (0.2 M) and ammonium ferric sulfate (0.5%) were used to determine formaldehyde.

Results



Figure S1. (a) SEM image of LDH, and (b) TEM image of Ru/LDH.



Figure S2 Nitrogen adsorption-desorption isotherm and pore size distribution of Ru/LDH.

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Figure S3. TEM and HRTEM images of Ru/LDH.

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Fitti	ng Coeffi	cient :	0.4590							
Eleme	nt	(keV)	Mass ⁸	Counts	Sigma	Atom%	Compound	Mass%	Cation	K
ΟK	(Ref.)	0.525	53.83	29460.37	0.57	73.01				1.0000
Al K	!	1.486	7.62	9061.81	0.18	6.13				0.4602
Ca K	!	3.690	38.55	18713.32	0.61	20.87				1.1272
Ru L			ND			ND				
Total			100.00			100.00				

Figure S4. The energy dispersive X-ray element mapping images of Ru/LDH.



Figure S5. Curve-fitting result for Ru/LDH.

Table S1. Results of curve-fitting analysis of Ru/LDH.

Sample	Path	CN	R(Å)	$\sigma^2(10^{-3} {\rm \AA}^2)$	$\Delta E_0 (eV)$	R-factor	
	Ru-O1	2.5±0.2	1.93±0.03	6.9±1.3	-14.2±1.4	0.005	
Ku/LDII F	Ru-O2	2.1±0.1	2.05±0.01	2.1±0.8	5.3±0.9	0.005	

CN, coordination number; *R*, bonding distance; σ^2 , Debye-Waller factor; ΔE_0 , inner potential shift

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Fig. S6 XP spectra of Ru (A), Ca (B) and Cl(C) for Ru/LDH and oxidized Ru/LDH (Ru/LDO-oxi for reference).

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Fig. S7 The photo of the solutions after adding MBTH, HCl and ammonium ferric sulfate, reacting at 308 K for 10 mins. Left: 0.2 M aqueous glycerol, right: the solution after reaction (reaction conditions: 50 mg of 0.5 wt% Ru, 10 ml of 0.2 M aqueous glycerol, 1 Mpa CO₂, 323 K, 300 rpm, 12 h).



Fig. S8 Effect of Ru amount on the oxidation activity and selectivity of glycerol. Reaction conditions: catalyst amount = 50 mg Ru/LDH, 0.2 M aqueous glycerol = 10 ml, CO_2 Pressure = 1 Mpa, Temperature =323 K, Stirring Speed = 300 rpm, Reaction time=12 h.



Fig. S9 Effect of reaction temperature on the oxidation activity and selectivity of glycerol. Reaction conditions: catalyst amount = 50 mg of 0.5 wt% Ru/LDH, 0.2 M aqueous glycerol = 10 ml, CO_2 Pressure = 1 Mpa, stirring Speed = 300 rpm, reaction time=12 h.

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Fig. S10 HPLC spectra of the solutions after reaction over Ru/LDH under different conditions: catalyst amount = 50 mg, 0.2 M aqueous glycerol = 10 ml, CO_2 Pressure = 1 Mpa, Temperature =323 K, Stirring Speed = 300 rpm, Reaction time=12 h.



Fig. S11 HPLC spectra of the solutions after reaction over 0.5 wt% Ru/LDH under conditions: catalyst amount = 50 mg, 0.2 M aqueous glycerol = 10 ml, CO_2 Pressure = 1 Mpa, Temperature =323 K, Stirring Speed = 300 rpm or 1000 rpm, Reaction time=12 h.



Fig.S12 Molar yield of HCHO with RuCl₃ as homogeneous catalyst (molar of Ru was equal to molar of Ru in 50 mg of 0.5 wt% Ru/LDH) and catalyst recyclability tests over 0.5 wt% Ru/LDH: catalyst amount = 50 mg, 0.2 M aqueous glycerol = 10 ml, CO_2 Pressure = 1 Mpa, Temperature =323 K, Stirring Speed = 300 rpm, Reaction time=24 h.



Scheme S1 CO_2 hydrogenation to produce formaldehyde with a Ru/LDH Catalyst via proposed pathway of glycerol oxidation.