Supplementary Information

Hydrogen generation by coupling methanol steam reforming with metal hydride hydrolysis

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1. Experiments

CaH$_2$ (Shanghai Titan Scientific Co., Ltd, ＞97%) and CuO (Beijing Beihua Fine Chemicals Co., Ltd, 99.0%) in the powder form are mixed with different molar ratios by ball milling (Fritsch Pulverisette 5) under Ar atmosphere. Other mixtures were prepared in a similar process. The materials are confirmed by powder X-ray diffraction (XRD, PANalytical X'Pert3 Powder, Cu Kα), scanning electron microscope (SEM, Hitachi S4800) with an energy dispersive X-ray spectrometer (EDX), X-ray photoelectron microscopy (XPS, Axis Ultra, Kratos, Al Kα radiation) and Fourier transformed infrared (FT-IR) spectroscopy (Bruker Tensor 27).

The hydrogen generation performance is measured in a 50 mL stainless steel autoclave (SLM 50, Beijing Century Senlang Co., Ltd.) with a high precision pressure gauge (accuracy 0.01 MPa, L61K, Hong Kong Huibang Technology Co., Ltd) and a gas flowmeter (50 mL/min, D07, Beijing Seven Star Flow Co., Ltd.). In a typical measurement, the CaH$_2$/CuO composite and a 10 mL crucible containing a CH$_3$OH-H$_2$O mixture is loaded into the autoclave. After purging with high purity Ar three times, the autoclave is sealed and is heated to 150-250 °C. CH$_3$OH and H$_2$O are vaporized and react with the solid and the pressure of the autoclave increases due to the formation of gaseous products. After 180 min, the autoclave is allowed to cool down to room temperature. The total amount of gas is determined by the pressure of the autoclave, which has been previously calibrated. The gas composition is analyzed by gas chromatography (GC7900, China). The H$_2$ yield is calculated using the total amount of gas times the H$_2$ purity from gas chromatography analysis.

To evaluation of the contribution of hydrolysis and methanol steam reforming in the H$_2$ generation, parallel experiments in the same setup by using pure hydrides (CaH$_2$ or MgH$_2$) and H$_2$O are carried out. The H$_2$ yield and purity is determined by the same method as noted above.

2. Estimation of the equilibrium CO partial pressure

The thermodynamic data of the matters involved in the calculation is retrieved from Ref 1 [1]. For estimation, the reaction enthalpy $\Delta_r H_m^{\circ}$ and entropy $\Delta_r S_m^{\circ}$ values are regarded as temperature invariant within the experimental temperature range. The Gibbs free energy change of the reaction $\Delta_r G_m^{\circ}(T)$ and equilibrium constate $K^{\circ}(T)$ are calculated using:

$$\Delta_r G_m^{\circ}(T) = \Delta_r H_m^{\circ} - T\Delta_r S_m^{\circ}$$

$$K^{\circ}(T) = e^{-\Delta_r G_m^{\circ}(T)/RT}$$

The results are summarized in

In the calculation, we assume that the reaction yields the same H_2 partial pressure 3 MPa. To calculate the equilibrium CO partial pressure in MSR using catalyst supported on non-CO_2 absorbing substrates, we start with a mixture gas of H_2: CO_2=3:1 in molar ratio (Here we assume full conversion of the stoichiometric CH_3OH and H_2O in the MSR to simplify the estimation). Thus, the CO pressure is determined by the equilibrium of the water-gas shift reaction with initial state $p(H_2)$ = 3 MPa and $p(CO_2)$=1 MPa.

When CO_2 is absorbed to yield $CaCO_3$, the CO_2 partial pressure is determined by the reaction $CaCO_3 \leftrightarrow CaO + CO_2$, which is 2.95×10^{-5} MPa at 250°C. Thus, the initial state is $p(H_2)$ = 3 MPa and $p(CO_2)$ = 2.95×10^{-5} MPa.

The results are summarized in .
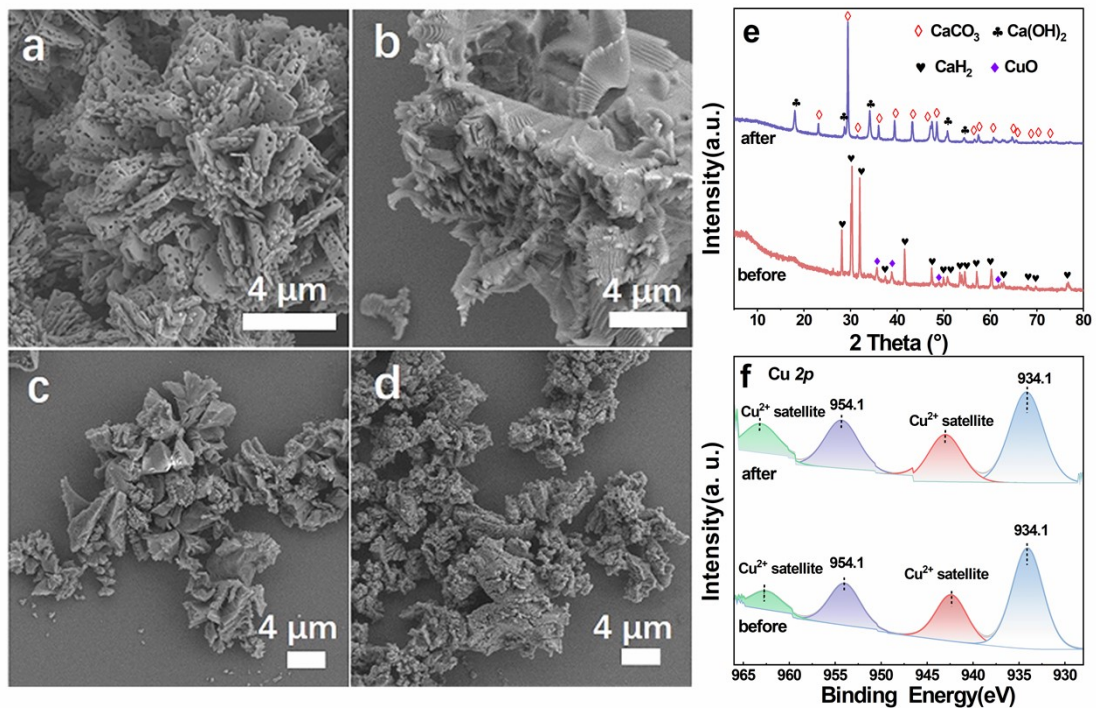
3. Supplementary figures and tables

SEM images of (a) CuO, (b) CaH_2, (c) CaH_2/CuO composite and (d) product of CaH_2/CuO after the coupled reaction; (e) XRD and (f) XPS spectrum of CaH_2/CuO composite before and after the coupled reaction.
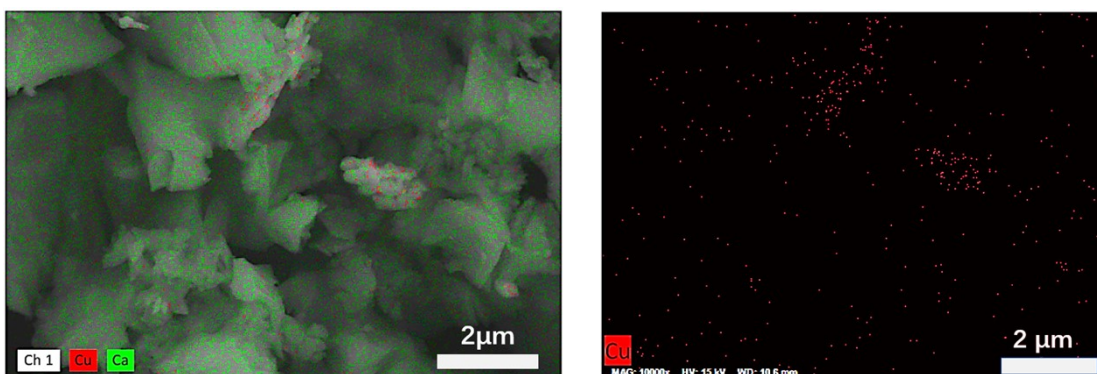
Fig. S2 Element mapping of the CaH$_2$-CuO composite (mass ratio CaH$_2$:CuO=10:1) prepared by ball milling before reaction.
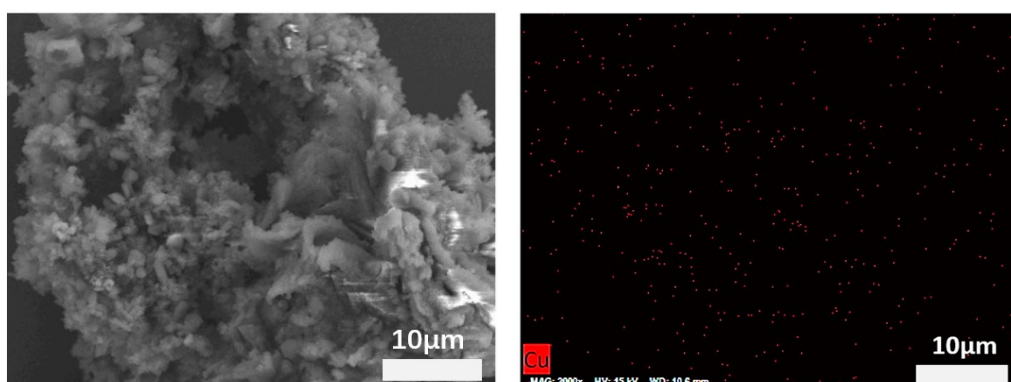

Fig. S3 Element mapping of the solid product of the CaH$_2$-CuO composite (mass ratio CaH$_2$:CuO=10:1) after coupling.
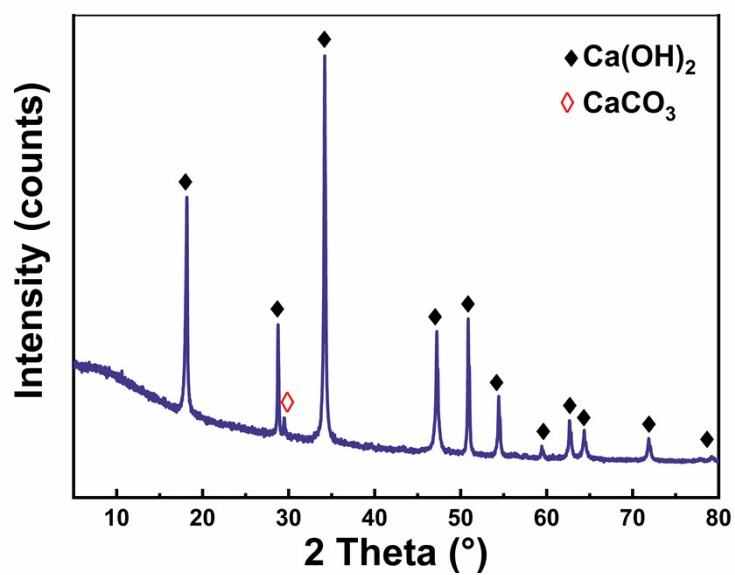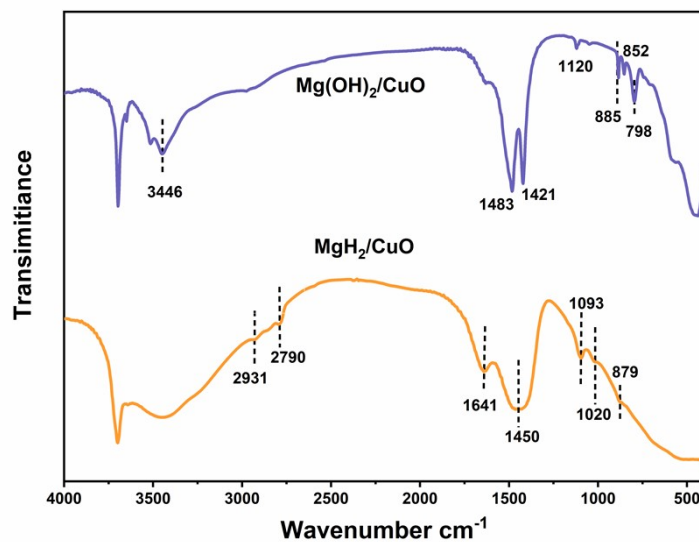
Fig. S5 IR spectrum of the product of the Mg(OH)$_2$-CuO and MgH$_2$-CuO composites after the coupled reaction. Peaks for $MgCO_3 \cdot 3H_2O$: 850 cm^{-1}, 1105 cm^{-1}, 1485 cm^{-1}, 1420 cm^{-1}.

Table S1. Experimental details of H_2 generation by coupling methanol steam reforming with hydrolysis of CaH_2.

Entry	x	$nCaH_2$ / mol	nCH_3OH /mol	nH_2O /mol	$V(H_2)$ /mL	$V_m(H_2)$ /mL	$V_h(H_2)$ /mL	CO /%	CH_4 /%	CO_2 /%
1	0	0	0.010	0.010	301	301	0	0.60	0.60	23.80
2	1/2	0.010	0.010	0.030	1188	756	432	0.00	0.08	6.64
3	3/5	0.015	0.010	0.040	1361	737	624	0.00	0.00	0.00
4	2/3	0.020	0.010	0.050	1681	761	920	0.00	0.00	0.00
5	3/4	0.030	0.010	0.070	2194	782	1412	0.00	0.00	0.00
6	1	0.010	0	0.020	432	0	432	0.00	0.00	0.00

The amount of CuO is 0.042 g and the reaction temperature is 250°C in all the experiments. In Entry 1, 0. 01 mol $CaCO_3$ is used as the support for CuO.

x: fraction of hydrolysis in the coupled reaction, determined by $x=n(CaH_2)/(n(CaH_2) + n(CH_3OH))$.

$V_m(H_2)$: Volume of H_2 from methanol steam reforming at 298 K, 101 kPa.

$V_h(H_2)$: Volume of H_2 from hydrolysis of CaH_2 at 298 K, 101 kPa.

Table S2 Experimental details, key results and calculation details for coupled reactions with different fraction of hydrolysis x (Data for Fig. 2 in the main text) [a]

Term	Note for the term	Fraction of hydrolysis in the coupled reaction x					
		$x=0$	$x=1/2$	$x=3/5$	$x=2/3$	$x=3/4$	$x=1$
$m(CuO)$/g	Amount of reactants	0.042^b	0.042	0.042	0.042	0.042	0
$n(CaH_2)$/mol		0	0.01	0.015	0.02	0.03	0.01
$n(CH_3OH)$/mol		0.01	0.01	0.01	0.01	0.01	0
$n(H_2O)$/mol		0.01	0.03	0.04	0.05	0.07	0.02
$V(H_2)_{exp}$/mL[c]	Experimental total H_2 volume at 298 K and 101 kPa	301	1188	1361	1681	2194	432
V_h/mL	H_2 volume from hydrolysis at 298 K and 101 kPa	0	432	624	920	1412	432
V_m/ml	H_2 volume from methanol steam reforming at 298 K and 101 kPa	301	756	737	761	782	0
$n(H_2)_{exp}$/mol	Experimental total H_2 moles	0.012	0.048	0.055	0.068	0.089	0.018
$\rho_{H, exp}$/%[d]	Experimental H density	1.60	7.38	6.53	6.56	6.25	4.54
$\rho_{H, h}$/%	Experimental H density from hydrolysis	0	2.68	2.99	3.59	4.02	4.54
$\rho_{H, m}$/%	Experimental H density from methanol steam reforming	1.60	4.69	3.53	2.97	2.23	0
$n(H_2)_{theo}$/mol	Theoretical total H_2 moles	0.03	0.05	0.06	0.07	0.09	0.02
$V(H_2)_{theo}$/mL	Theoretical total H_2 volume at 298 K and 101 kPa	736	1227	1473	1718	2209	491
$\rho_{H, theo}$/%	Theoretical H density	3.92	7.62	7.06	6.71	6.29	5.16
H_2(%)	Volume percentage of gases in the products	75.00	93.28	100.00	100.00	100.00	100.00
CO(%)		0.60	0.00	0.00	0.00	0.00	0.00
CH_4(%)		0.60	0.08	0.00	0.00	0.00	0.00
CO_2(%)		23.80	6.64	0.00	0.00	0.00	0.00

Note

a. The reaction is carried out at 250 °C. x is the fraction of hydrolysis in the coupled reaction, defined as $x=n(CaH_2)/(n(CaH_2) + n(CH_3OH))$

b. For x=0 (conventional methanol steam reforming), 0.042 g CuO is loaded on 0.010 mol $CaCO_3$

c. The experiment H_2 volume is calculated by the total gas volume at 298 K times the H_2 volume percentage from gas chromatography analysis.

d. The H density (both experimental and theoretical) is calculated based on all the reactants (CaH_2, CuO, CH_3OH and H_2O)

3 Experimental details, key results and calculation details for coupled reactions on CuO supported on different substrates (Data for Fig. 4 in the main text) [a]

Term	Note for the term	Substrates for CuO					
		Al_2O_3	$CaCO_3$	$Mg(OH)_2$	$Ca(OH)_2$	MgH_2	CaH_2
m(CuO)/g	Amount of reactants	0.042	0.042	0.042	0.042	0.042	0.042
$n(CaH_2)$/mol		0.010	0.010	0.010	0.010	0.010	0.010
$n(CH_3OH)$/mol		0.010	0.010	0.010	0.010	0.010	0.010
$n(H_2O)$/mol		0.010	0.010	0.010	0.010	0.030	0.030
$V(H_2)_{exp}$/mL[b]	Experimental total H_2 volume at 298 K and 101 kPa	144	301	76	674	799	1188
V_h/mL	H_2 volume from hydrolysis at 298 K and 101 kPa	0	0	0	0	440	432
V_m/ml	H_2 volume from methanol steam reforming at 298 K and 101 kPa	144	301	76	674	359	756
$n(H_2)_{exp}$/mol	Experimental total H_2 moles	0.006	0.012	0.003	0.027	0.033	0.048
$\rho_{H, exp}$/%[c]	Experimental H density	0.76	1.60	0.55	4.31	5.63	7.38
$\rho_{H, h}$/%	Experimental H density from hydrolysis	0	0	0	0	3.10	2.68
$\rho_{H, m}$/%	Experimental H density from methanol steam reforming	0.76	1.60	0.55	4.31	2.53	4.69
$n(H_2)_{theo}$/mol	Theoretical total H_2 moles	0.03	0.03	0.03	0.03	0.05	0.05
$V(H_2)_{theo}$/mL	Theoretical total H_2 volume at 298 K and 101 kPa	736	736	736	736	1227	1227
$\rho_{H, theo}$/%	Theoretical H density	3.87	3.92	5.37	4.71	8.65	7.62
H_2(%)	Volume percentage of gases in the products	73.88	75.00	76.20	95.77	89.55	93.28
CO(%)		0.72	0.60	0.00	0.00	0.00	0.00
CH_4(%)		0.13	0.60	0.00	0.00	0.12	0.08
CO_2(%)		25.28	23.80	23.80	4.23	10.33	6.64

Note:

a. The reaction is carried out at 250 °C. The mass ratio of CuO/substrate is 1/10. The molar ratio of H_2O/CH_3OH is 3 (i.e. x=1/2) for the hydrides and 1 for other substrates.

b. The experiment H_2 volume is calculated by the total gas volume at 298 K times the H_2 volume percentage from gas chromatography analysis.

c. The H density (both experimental and theoretical) is calculated based on all the reactants (CaH_2, CuO, CH_3OH and H_2O)

Table S4 Experimental details, key results and calculation details for coupled reactions on CuO-CaH$_2$ composite at different temperature (Data for Fig. 5 in the main text)[a]

Term	Note for the term	Reaction temperature/°C				
		150	180	200	220	250
m(CuO)/g	Amount of reactants	0.042	0.042	0.042	0.042	0.042
n(CaH$_2$)/mol		0.020	0.020	0.020	0.020	0.020
n(CH$_3$OH)/mol		0.010	0.010	0.010	0.010	0.010
n(H$_2$O)/mol		0.050	0.050	0.050	0.050	0.050
V(H$_2$)$_{exp}$/mL[b]	Experimental total H$_2$ volume at 298 K and 101 kPa	936	1037	1089	1608	1681
V$_h$/mL	H$_2$ volume from hydrolysis at 298 K and 101 kPa	920	920	920	920	920
V$_m$/ml	H$_2$ volume from methanol steam reforming at 298 K and 101 kPa	16	117	169	687	761
n(H$_2$)$_{exp}$/mol	Experimental total H$_2$ moles	0.038	0.042	0.044	0.066	0.068
ρ$_{H, exp}$/%[c]	Experimental H density	3.65	4.05	4.25	6.27	6.56
ρ$_{H, h}$/%	Experimental H density from hydrolysis	3.59	3.59	3.59	3.59	3.59
ρ$_{H, m}$/%	Experimental H density from methanol steam reforming	0.06	0.46	0.66	2.68	2.97
n(H$_2$)$_{theo}$/mol	Theoretical total H$_2$ moles	0.07	0.07	0.07	0.07	0.07
V(H$_2$)$_{theo}$/mL	Theoretical total H$_2$ volume at 298 K and 101 kPa	1718	1718	1718	1718	1718
ρ$_{H, theo}$/%	Theoretical H density	6.71	6.71	6.71	6.71	6.71
H$_2$(%)	Volume percentage of gases in the products	100	100	100	100	100
CO(%)		0	0	0	0	0
CH$_4$(%)		0	0	0	0	0
CO$_2$(%)		0	0	0	0	0

Note:

a.   The amount of reactants: CaH$_2$ 0.020 mol, CuO: 0.042 g, CH$_3$OH 0.010 mol, H$_2$O 0.050 mol, i.e. x=2/3.

b.   The experiment H$_2$ volume is calculated by the total gas volume at 298 K times the H$_2$ volume percentage from gas chromatography analysis.

c.   The H density (both experimental and theoretical) is calculated based on all the reactants (CaH$_2$, CuO, CH$_3$OH and H$_2$O)

Table S5 List of Enthalpies and Entropies of the related substances.

Substance	Physical state	$\Delta_f H_m^\ominus$/ (kJ/mol)	$S_m^\ominus$/ (J/mol K)
CO	g	-110.53	197.67
H_2O	g	-241.82	188.72
CO_2	g	-393.51	213.64
H_2	g	0	130.59
$CaCO_3$	c	-1207.60	91.70
CaO	c	-634.92	38.10

Table S6 Thermal and kinetic equilibrium calculation results.

	$\Delta_r H_m^\circ(298.15K)$ /(kJ/mol)	$\Delta_r S_m^\circ(298.15K)$ / (J/mol K)	$\Delta_r G_m^\circ(523.15K)$ /(J/mol)	$K^\circ(523.15K)$
$H_2+CO_2=CO+H_2O$	41.16	42.16	$1.91*10^4$	$1.23*10^{-2}$
$CaCO_3=CaO+CO_2$	179.17	160.04	$9.54*10^4$	$2.95*10^{-10}$

Table S7 List of the partial pressure calculation results.

MSR on conventional Cu based catalyst				
	H_2	CO_2	CO	H_2O
Initial partial pressure/MPa	3	1	0	0
Equilibrium partial pressure/MPa	2.83	0.83	0.17	0.17
Coupled MSR and hydrolysis on CuO/CaH$_2$				
	H_2	CO_2	CO	H_2O
Initial partial pressure/MPa	3	$2.95*10^{-11}$	0	0
Equilibrium partial pressure/MPa	3	$2.95*10^{-11}$	$1.04*10^{-6}$	$1.04*10^{-6}$

Reference

1.   A. P. Miller, *Lange's Handbook of Chemistry*, 1941.