Mechanism study on hydrogen generation from metal hydride coupled methanol steam reforming

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1. Supplementary Figures

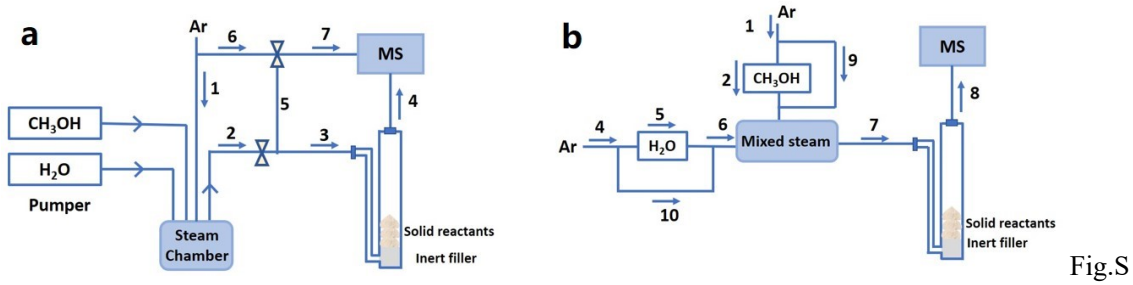

Fig.S1 Schematics of (a) online MS setup and (b) MS system for isotope labeling experiments

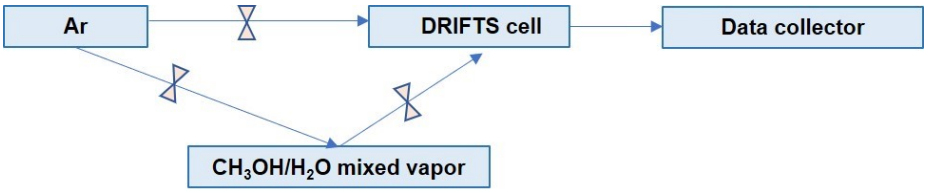

Fig.S2 Schematic of the in-situ IR experiment

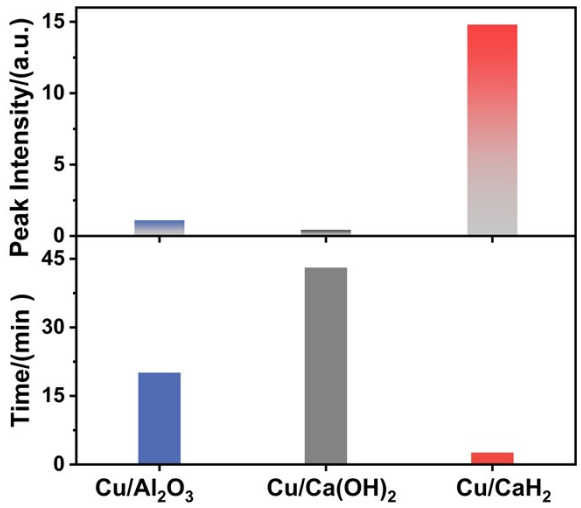

Fig.S3 MSR initiation time and H_2 signal peak intensity over Cu/Al_2O_3, $Cu/Ca(OH)_2$ and Cu/CaH_2. (Initiation time is defined as the first appearance of the H_2 signal; for Cu/CaH_2, it refers to the point where the signal starts to exceed that of pure hydrolysis. Peak intensity corresponds to the maximum H_2 signal at t = 25, 48 and 5 min, respectively.)

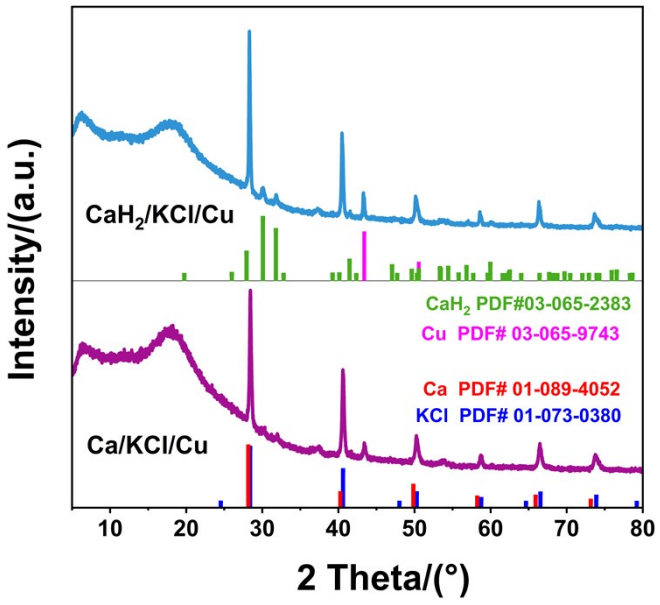

Fig. S4 XRD Patterns of Ca/KCl/Cu and CaH_2/KCl/Cu

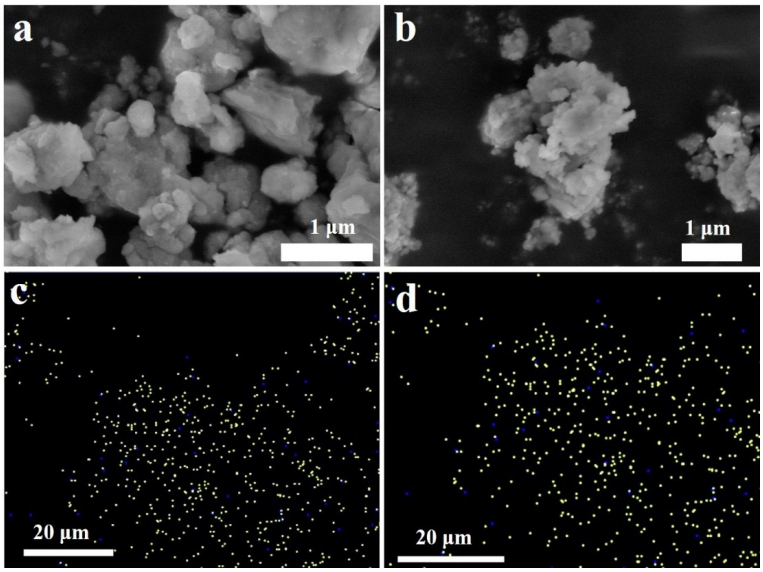

Fig.S5 (a, b) SEM images of Ca/KCl/Cu and CaH_2/KCl/Cu and (c, d) corresponding elemental mapping of surface Ca (yellow) and Cu (blue)

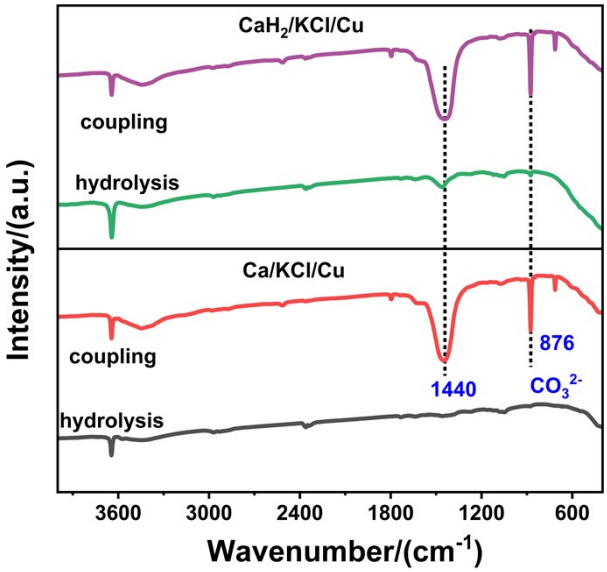

Fig. S6 Comparison of IR spectra of solid hydrogen production products from the coupling of Ca/KCl/Cu and CaH_2/KCl/Cu with MSR

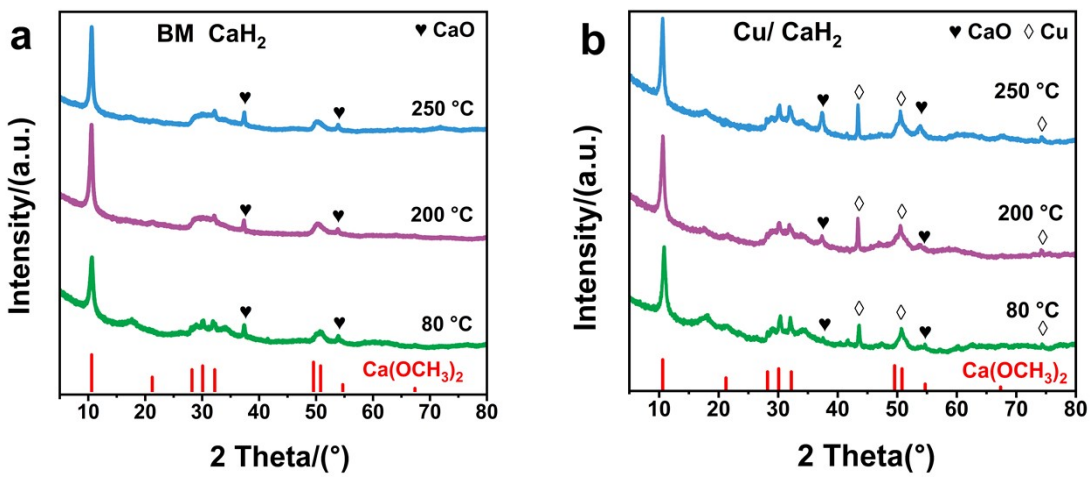

Fig. S7 Comparison of alcoholysis products of ball-milled CaH_2 (a) before and (b) after Cu incorporation under different temperature conditions

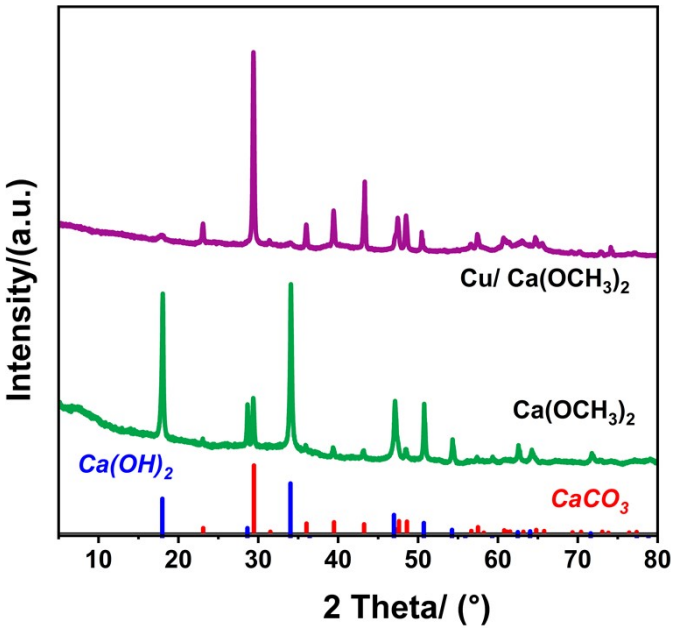

Fig.S8 XRD of solid products after reaction with water for samples of $(CH_3O)_2Ca$ before and after compositing with Cu, respectively

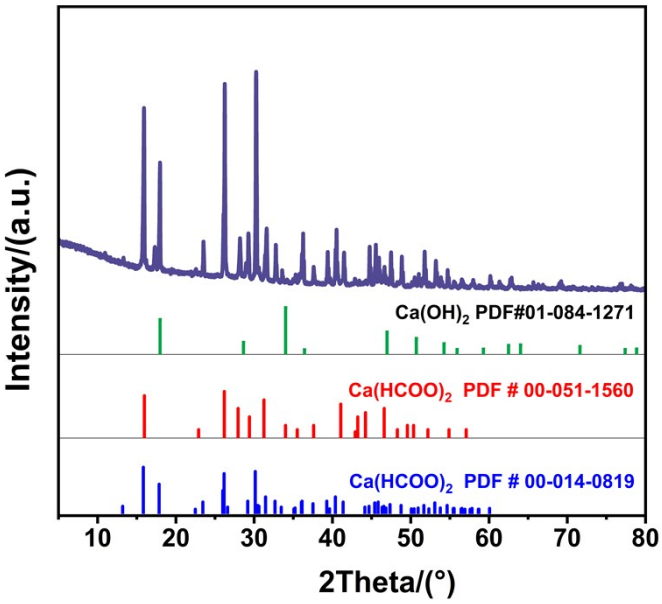

Fig.S9 XRD patterns of solid products obtained from the reactions of CaH_2/CuO with HCOOH solutions.

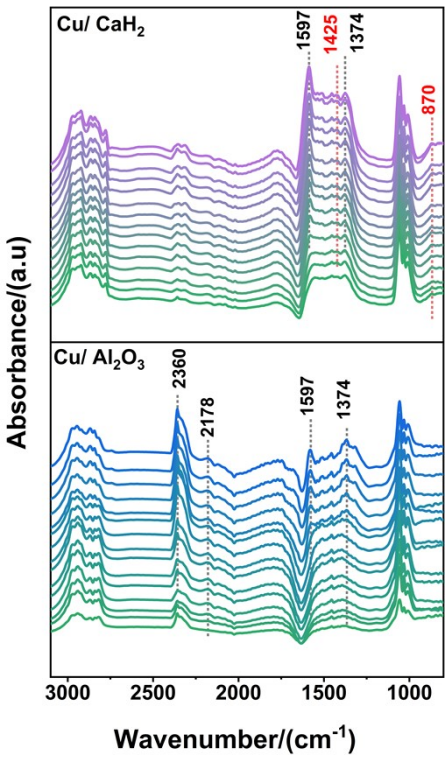

Fig.S10 In situ DRIFT spectra of Cu/Al_2O_3 and Cu/CaH_2 reacting with CH_3OH/H_2O mixed vapor (molar ratio 1:3) at 250 °C.

2. Supplementary Tables

Table S1 Summary of online MS experimental conditions for MSR over Cu supported on different carriers (CaH_2, $Ca(OH)_2$, Al_2O_3)

No.	Reactants	$m_{(solid\ reactants)}$ /g	T / °C	feed rate /(mmol·min^{-1})	
				H_2O	CH_3OH
1	**Cu/Al_2O_3 +H_2O +CH_3OH**	2.31	250	0.75	0.25
2	**$Cu/Ca(OH)_2$+H_2O+CH_3OH**	2.31	250	0.75	0.25
3	**Cu/CaH_2 +H_2O +CH3OH**	2.31	250	0.75	0.25
4	**Cu/CaH_2 +H_2O**	2.31	250	0.75	-

Table S2 Summary of experimental conditions for online MS of Cu/CaH_2 reaction under different methanol-to-water ratios

No.	*n* (CH_3OH): *n* (H_2O)	*x*(CH_3OH)	$m_{(Cu/CaH2)}$ /g	T / °C	feed rate /(mmol·min^{-1})	
					H_2O	CH_3OH
1	**0.2:1**	0.2	2.31	250	0.750	0.125
2	**0.3:1**	0.3	2.31	250	0.750	0.250
3	**0.6:1**	0.6	2.31	250	0.750	0.500
4	**CH_3OH**	1	2.31	250	-	0.250
5	**H_2O**	0	2.31	250	0.750	-

Table S3 Experimental details, key results and calculation details for comparison of Ca/KCl/Cu and CaH_2/KCl/Cu coupled with MSR (Data for Fig. 2a in the main text)

Terms			Ca/KCl/Cu	CaH_2/KCl/Cu
Reactants	$m_{(Ca)}$/g	Amount of reactants	0.40	0.00
	$m_{(CaH2)}$/g		0.00	0.42
	$m_{(KCl)}$/g		1.60	1.64
	$m_{(CuO)}$/g		0.20	0.21
	$n_{(CH3OH)}$/mol		0.01	0.01
	$n_{(H2O)}$/mol		0.03	0.03
H_2 Yield [a]	$V_{exp, total}$/mL	Experimental total H_2 volume at 298 K	719	828
	$V_{exp, h}$/mL	Experimental H_2 volume from hydrolysis at 298 K	240	340
	$V_{exp, m}$ /ml	Experimental H_2 volume from MSR at 298 K	479	488
	$V_{theo, m}$/ mL	Theoretical H_2 volume from MSR at 298 K	736	736
Methanol Conversion	C_m/%	$V_{exp, m}$/ $V_{theo, m}$	66.06	66.28
Gas Composition	H_2(%)	Volume percentage of gases in the products	99.90	99.84
	CO(%)		0.10	0.16
	CH_4(%)		0.00	0.00
	CO_2(%)		0.00	0.00

a. 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.

Table S4 Assignment of the main absorption peaks observed in the spectra

Substrates	functional group	Peak Position/cm^{-1}
CH_3OH	C-H	2970、2922、2862、2842
	-OCH_3	1030
	C–H vibration of methoxy group	2942、2820
HCOOH	$HCOO^-$	1580-1600、1367-1376
	C=O	1716
carbonates	CO_3^{2-}	1425、870
CO_2	-	2360、2340
CO	-	2178