Supplementary information

Bi-functional Ru/$Ca_3Al_2O_6$-CaO catalyst-CO_2 sorbent for the production of high purity hydrogen via the sorption-enhanced steam methane reforming

Sung Min Kim,[a] Paula M. Abdala,[a] Davood Hosseini,[a] Andac Armutlulu,[a]
Tigran Margossian,[b] Christophe Copéret,[b] and Christoph Müller*[a]

[a] Department of Mechanical and Process Engineering, ETH Zurich, Leonhardstrasse 21, 8092 Zurich, Switzerland
[b] Department of Chemistry and Applied Sciences, ETH Zurich, Vladimir Prelog Weg 1-5, 8093 Zurich, Switzerland

*Corresponding author. Tel.: +41 44 632 3440.
E-mail address: muelchri@ethz.ch (Prof. Christoph Müller)

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Table S1. EXAFS fitting results of calcined materials at Ru K-edge

Materials	Coordination shell	Coordination number	R [Å]	σ^2 [Å^2]	ΔE [eV]	R-factor
RuO_2	Ru-O	2	1.94 ± 0.02	0.0030 ± 0.0003		
	Ru-O	4	1.98 ± 0.02	0.0030 ± 0.0003		
	Ru-Ru	2	3.13 ± 0.02	0.0029 ± 0.0003	-3.73 ± 1.48	0.027
	Ru-O	4	3.22 ± 0.19	0.0029 ± 0.0003		
	Ru-Ru	8	3.54 ± 0.01	0.0029 ± 0.0003		
Ru/Al_2O_3	Ru-O	2	1.94 ± 0.03	0.0030 ± 0.0003		
	Ru-O	4	1.98 ± 0.02	0.0030 ± 0.0003		
	Ru-Ru	2	3.11 ± 0.01	0.0035 ± 0.0003	-3.61 ± 1.39	0.025
	Ru-O	4	3.17 ± 0.23	0.0035 ± 0.0003		
	Ru-Ru	8	3.54 ± 0.01	0.0035 ± 0.0003		
$CaRuO_3$	Ru-O	6	2.00 ± 0.01	0.0034 ± 0.0004		
	Ru-Ca	2	3.14 ± 0.02	0.0040 ± 0.0023		
	Ru-Ca	2	3.26 ± 0.02	0.0040 ± 0.0023	-1.71 ± 1.42	0.028
	Ru-Ca	2	3.37 ± 0.02	0.0040 ± 0.0023		
	Ru-Ca	2	3.61 ± 0.02	0.0040 ± 0.0023		
	Ru-Ru	5	3.84 ± 0.01	0.0037 ± 0.0011		
Ru/lime	Ru-O	6	1.96 ± 0.03	0.0070 ± 0.0004		
	Ru-Ca	2	3.12 ± 0.01	0.0075 ± 0.0034		
	Ru-Ca	2	3.31 ± 0.07	0.0075 ± 0.0034	-3.13 ± 1.27	0.021
	Ru-Ca	2	3.31 ± 0.07	0.0075 ± 0.0034		
	Ru-Ca	2	3.47 ± 0.14	0.0075 ± 0.0034		
	Ru-Ru	5	3.86 ± 0.01	0.0131 ± 0.0025		
Ru/CaO	Ru-O	6	1.95 ± 0.04	0.0067 ± 0.0004		
	Ru-Ca	2	3.10 ± 0.02	0.0086 ± 0.0061		
	Ru-Ca	2	3.23 ± 0.01	0.0086 ± 0.0061	-3.60 ± 1.28	0.020
	Ru-Ca	2	3.31 ± 0.06	0.0086 ± 0.0061		
	Ru-Ca	2	3.42 ± 0.19	0.0086 ± 0.0061		
	Ru-Ru	5	3.87 ± 0.03	0.0175 ± 0.0049		
$Ru/Ca_3Al_2O_6$-CaO	Ru-O	6	1.97 ± 0.02	0.0091 ± 0.0006		
	Ru-Ca	2	3.12 ± 0.01	0.0088 ± 0.0042		
	Ru-Ca	2	3.32 ± 0.08	0.0088 ± 0.0042	-3.47 ± 1.53	0.027
	Ru-Ca	2	3.32 ± 0.05	0.0088 ± 0.0042		
	Ru-Ca	2	3.42 ± 0.18	0.0088 ± 0.0042		
	Ru-Ru	5	3.76 ± 0.08	0.0091 ± 0.0006		

Table S2. Textural properties of bifunctional Ru-CaO after repeated carbonation and regeneration (in calcined form).

Catalyst	Cycles	N_2 physisorption		
		S_{BET} [m^2/g]	V_{Pore} [cm^3/g]	D_{pore} [nm]
Ru/lime	2	6	0.07	1.9
	10	1	0.01	1.8
Ru/CaO	2	8	0.10	1.9
	10	2	0.05	1.9
Ru/$Ca_3Al_2O_6$-CaO	10	18	0.23	2.0

Table S3. Physicochemical properties of bifunctional Ru-CaO after 10 cycles of SE-SMR and regeneration.

Catalyst	N_2 physisorption			Particle size[a] [nm]	H_2 chemisorption[b] [$\mu mol_{Ru}/g_{cat}$]	
	S_{BET} [m^2/g]	V_{Pore} [cm^3/g]	D_{pore} [nm]			
Ru/lime	5	0.06	1.8	34 ± 4	2.1	(0.7%)
Ru/CaO	6	0.07	1.9	23 ± 4	7.2	(2.4%)
Ru/$Ca_3Al_2O_6$-CaO	18	0.21	1.8	8 ± 2	31.5	(10.6%)

[a] average Ru particle size as determined by TEM, and [b] the quantity of surface Ru was calculated via H_2 chemisorption using a stoichiometry factor of 1.0 for H/Ru,[30-32] the parenthesis give the Ru dispersion

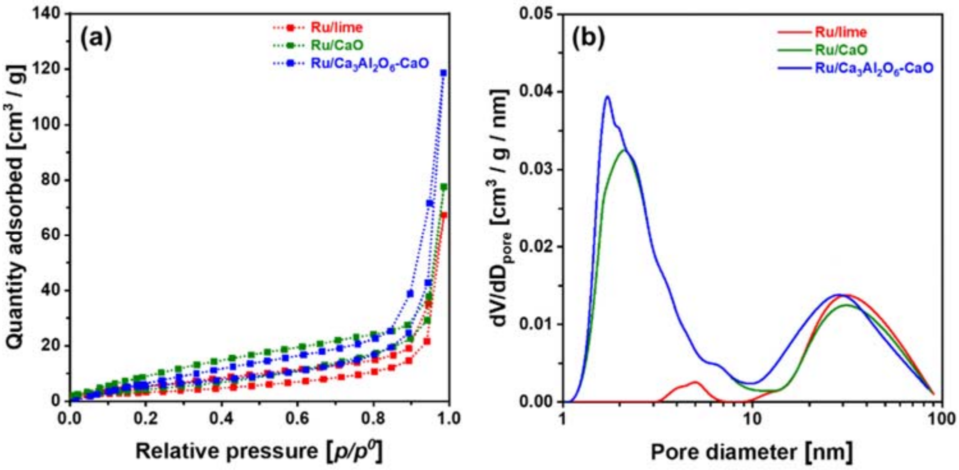

Figure S1. (a) N_2 physisorption isotherm and (b) BJH pore size distribution of Ru/lime, Ru/CaO and Ru/$Ca_3Al_2O_6$-CaO calcined at 850 °C.

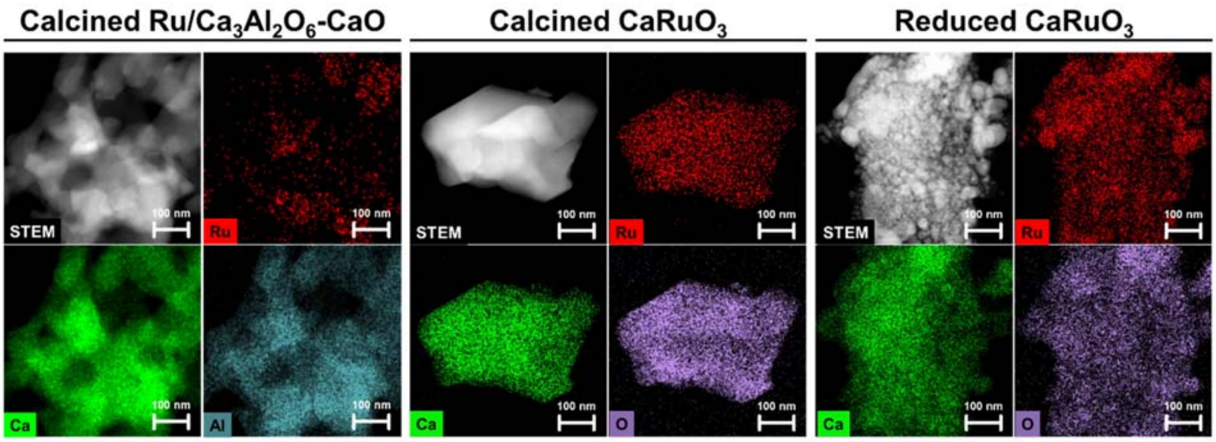

Figure S2. STEM EDX mapping of calcined Ru/$Ca_3Al_2O_6$-CaO, and calcined and reduced $CaRuO_3$.

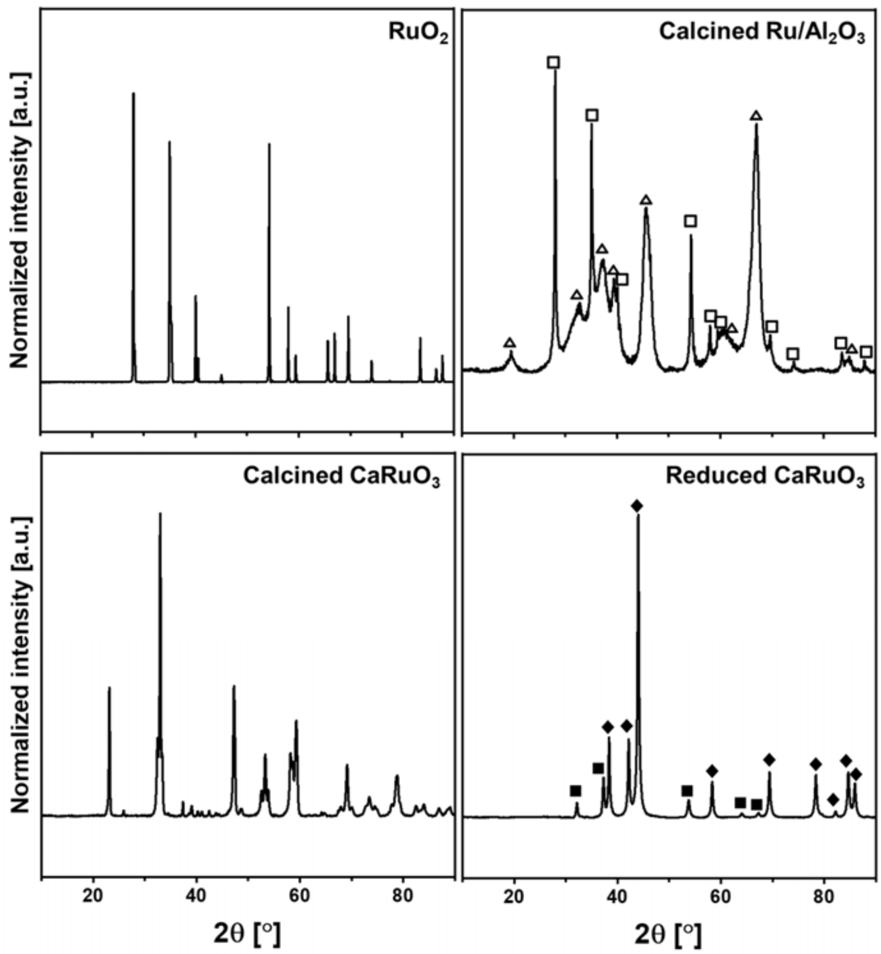

Figure S3. XRD of the reference RuO_2 (Sigma-aldrich), calcined Ru/Al_2O_3, calcined $CaRuO_3$ and reduced $CaRuO_3$: (□) RuO_2, (△) γ-Al_2O_3, (♦) Ru, and (■) CaO.

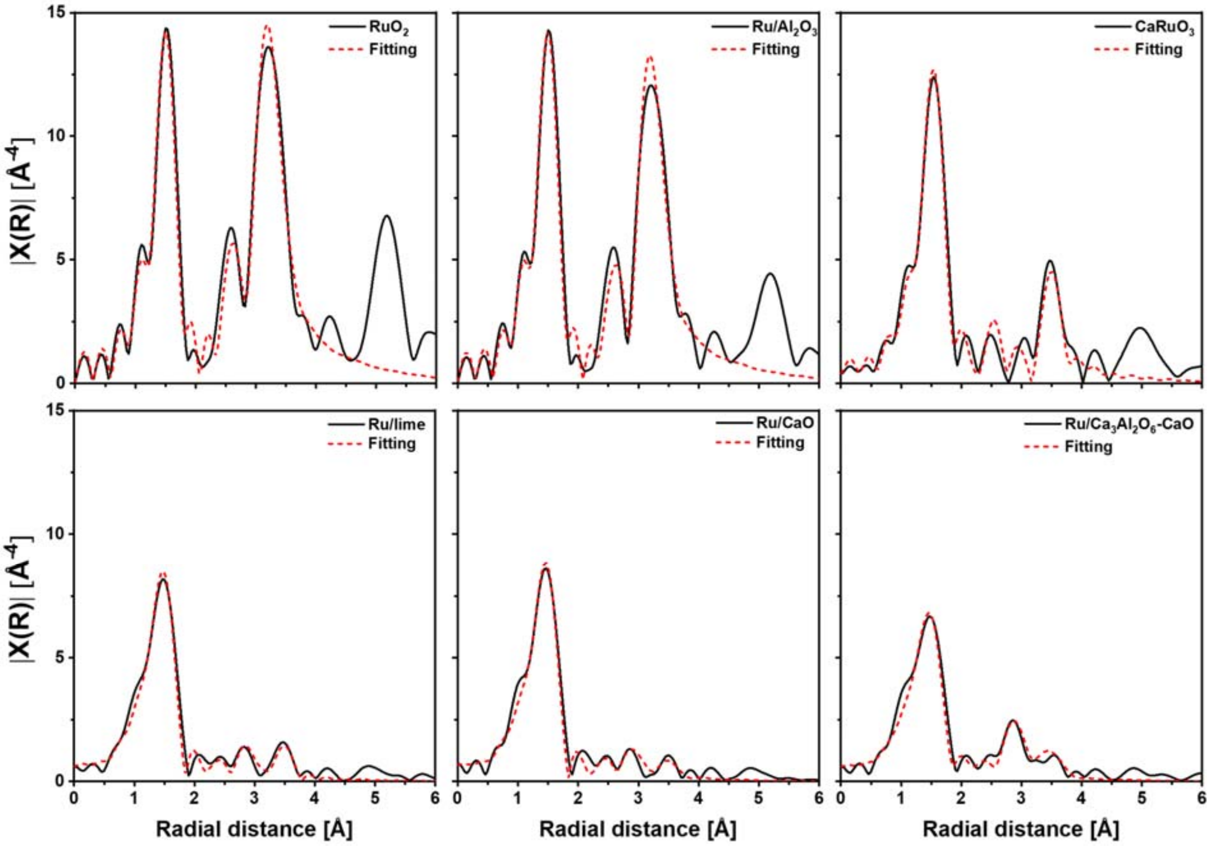

Figure S4. Fourier-transform of k^3-weighted EXAFS and fitting of the calcined reference and synthetic bifunctional materials.

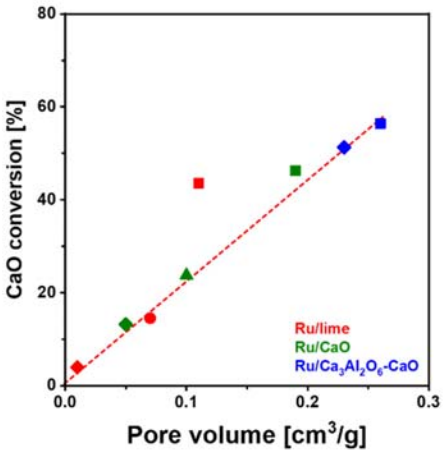

Figure S5. CaO conversion in the kinetically-controlled carbonation regime as a function of pore volume: (■) 1st, (●) 2nd, (▲) 5th and (◆) 10th cycle.

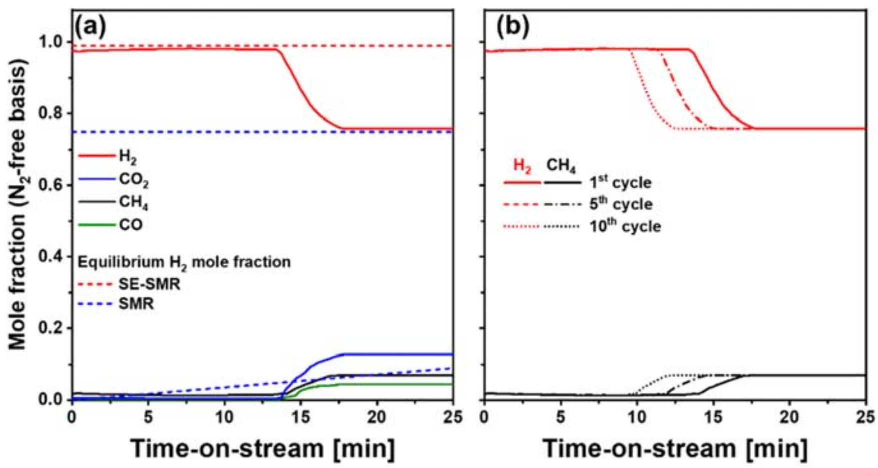

Figure S6. (a) Off-gas composition during the 1st cycle for Ca-Ni-ex-Htlc and (b) the breakthrough curves for H_2 and CH_4 in the 1st, 5th and 10th cycle.

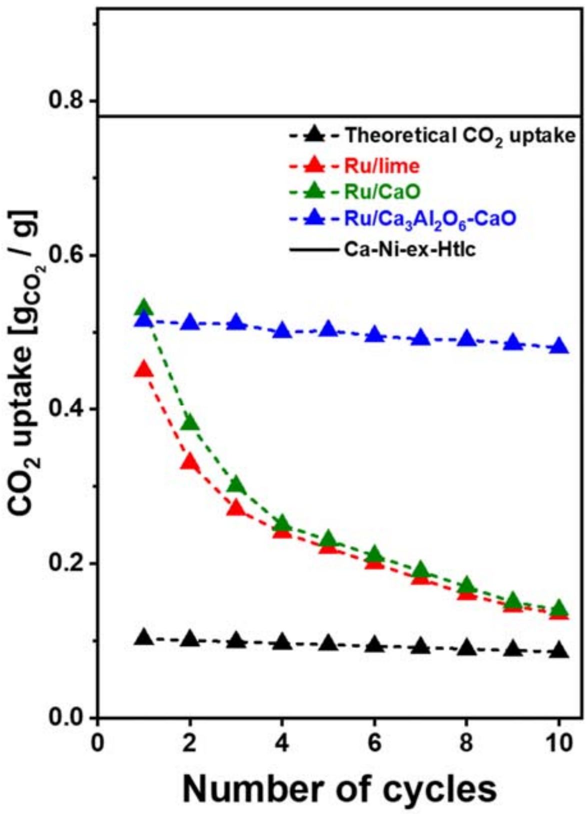

Figure S7. CO_2 uptake under SE-SMR-mimicking conditions (carbonation: 550 °C using 50 ml/min of 20 % CO_2/N_2, 2 h, and regeneration:750 °C, 50 ml/min of N_2, 15 min) as a function of number of carbonation-regeneration cycles. The solid line gives the theoretical CO_2 uptake of pure CaO, i.e., 0.78 g_{CO_2}/g.

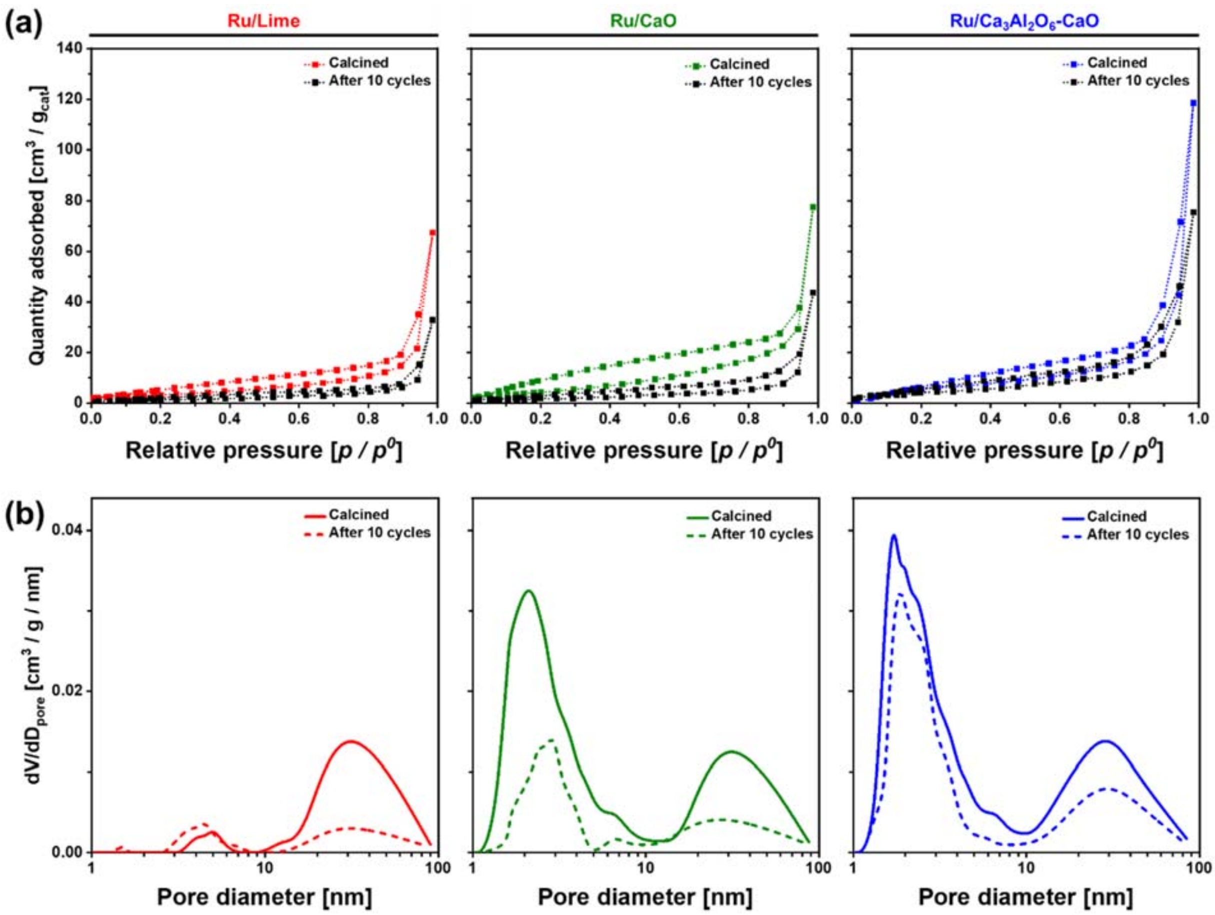

Figure S8. (a) N_2 physisorption isotherm and (b) BJH pore distribution for Ru/lime, Ru/CaO and Ru/$Ca_3Al_2O_6$-CaO freshly calcined and after 10 cycles of SE-SMR and regeneration.