Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

$Ce_{1-x}Sr_xO_{2-\delta}$ solid solution support cobalt-based catalysts for hydrogen production via auto-thermal reforming of acetic acid

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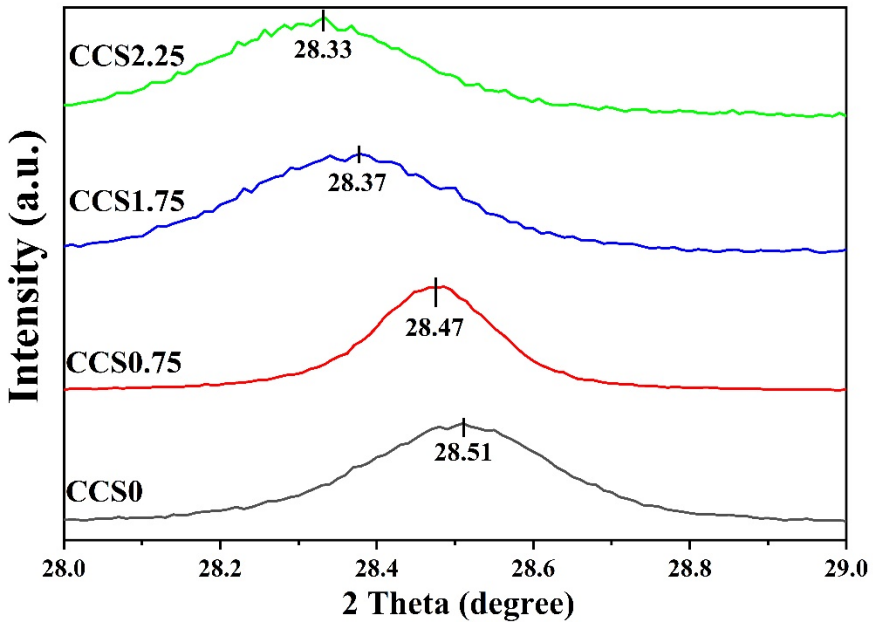

Fig. S1. Enlarged XRD patterns from 28° to 29°

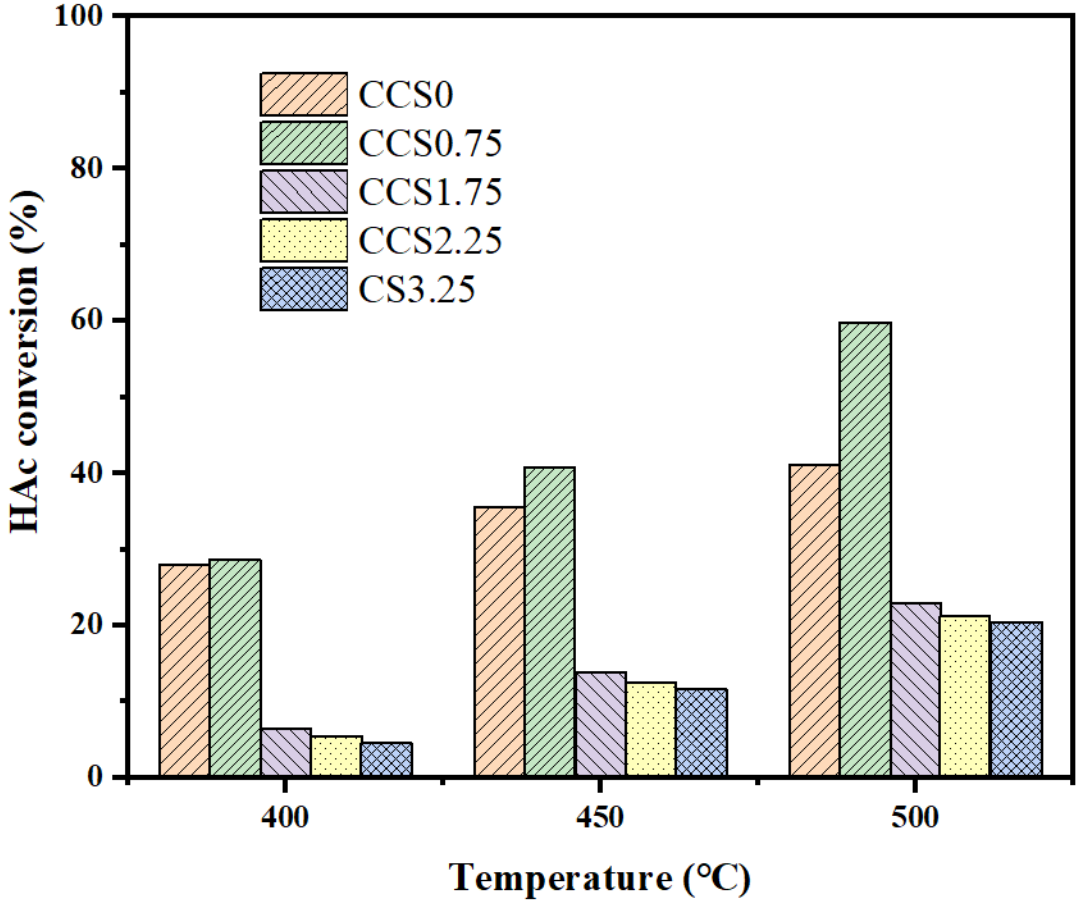

Fig. S2. Effect of temperature on the HAc conversion of the CCS_x catalysts at GHSV= 50000 $mL \cdot g_{catal}^{-1} \cdot h^{-1}$ in ATR

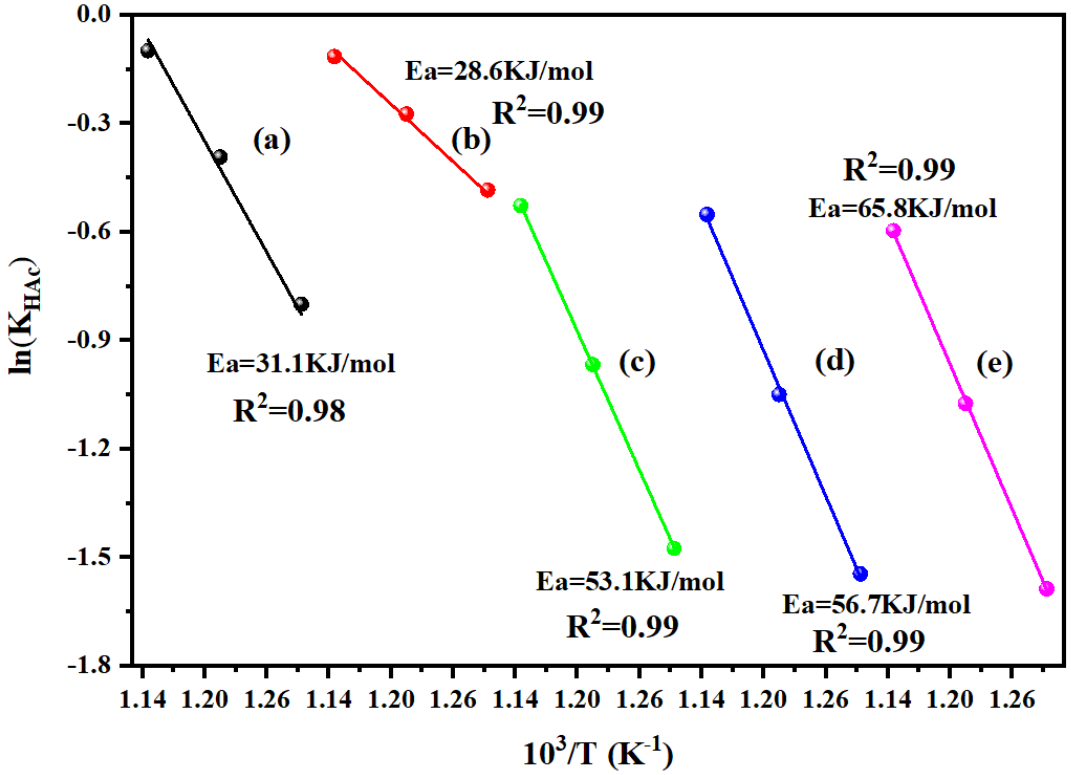

Fig. S3. Arrhenius plots of CCS_x catalyst: (a) CCS0, (b) CCS0.75, (c) CCS1.75, (d) CCS2.25 (e) CS3.25

Table S1. Cell parameters of CCS_x catalysts.

Catalysts	Main Phase composition	Space group	Cell parameters (Å)		
			a	b	c
CCS0	CeO_2	Fm-3m	5.411	5.411	5.411
CCS0.75	$Ce_{1-x}Sr_xO_{2-\delta}$	Fm-3m	5.423	5.423	5.423
CCS1.75	$Ce_{1-x}Sr_xO_{2-\delta}$	Fm-3m	5.430	5.430	5.430
CCS2.25	$Ce_{1-x}Sr_xO_{2-\delta}$	Fm-3m	5.425	5.425	5.425
CS3.25	$SrCO_3$	Pm-cn	5.107	8.421	6.028

Table S2. Hydrogen uptake and Co^0 reducibility from H_2-TPR

Catalysts	Hydrogen consumption (mmol/g)		Co^0 Reducibility (%)
	Peak 1	Peak 2	
CCS0	0.93	1.39	10.5
CCS0.75	1.03	2.01	15.4
CCS1.75	0.45	0.77	8.5
CCS2.25	0.37	0.35	7.2
CS3.25	0.11	0.23	4.3

Table S3. The Co^0 dispersion, hydrogen production rate, TOF-H_2 and E_a of CCS_x catalysts

Catalysts	Co^0 dispersion[a]	Hydrogen production rate (μmol-$H_2 \cdot s^{-1} \cdot gcat^{-1}$)[b]	TOF of H_2 (10^{-2} s^{-1})[c]	Activation energy (E_a) kJ*mol^{-1}
CCS0	0.066	7.57	12.8	31.1
CCS0.75	0.074	9.77	14.8	28.6
CCS1.75	0.046	0.58	1.5	53.1
CCS2.25	0.027	0.33	1.4	56.7
CS3.25	0.015	0.06	0.5	65.8

[a] Obtained from H_2-TPD by assuming $H_{ad}/Co^0_{surf}=1$

[b] Obtained from Eq. (14)

[c] Obtained from Eq. (15)

Table S4. The distances between Ce/Sr atom and its nearest O atoms.

	Ce-O1	Ce-O2	Ce-O3	Ce-O4	Ce-O5	Ce-O6
d(Å)	2.35	2.37	2.37	2.37	2.37	2.37
	Sr-O1	Sr-O2	Sr-O3	Sr-O4	Sr-O5	Sr-O6
d(Å)	2.59	2.57	2.60	2.58	2.60	2.57

Table S5. The calculated E_{vac}(in eV) for the $Ce_{1-x}Sr_xO_{2-\delta}$ (111) surface with one and two O vacancies. For the CeO_2(111) surface, the surface and subsurface O vacancy formation energies were 2.58 and 2.50 eV, respectively. V_{OI}-V_{OIII} were the surface vacancies and VO_{IV}-V_{OV} were the subsurface vacancies for the $Ce_{1-x}Sr_xO_{2-\delta}$ (111) surface; V_{OIV-1}-V_{OIV-2} were the surface vacancies and V_{OIV-3}-V_{OIV-4} were the subsurface vacancies.

$Ce_{1-x}Sr_xO_{2-\delta}$[a] ($Ce_{47}Sr_1O_{95}$)	V_{OI}	V_{OII}	$V_{OIII=OV}$	V_{OIV}	V_{OVI}
E_{vac}(eV)	-0.705	-0.704	-0.776	-0.804	-0.778
$Ce_{1-x}Sr_xO_{2-\delta}$[b] ($Ce_{47}Sr_1O_{94}$)	V_{OIV-1}	V_{OIV-2}	V_{OIV-3}	V_{OIV-4}	
E_{vac}(eV)	1.22	0.92	1.05	1.96	

[a] The unique structure of Sr-CeO_2 with one O vacancy

[b] The unique structure of Sr-CeO_2 with two O vacancy (based on O_{IV} structure by removing of the second structurally unique oxygen atoms)