Calcium Cobaltate: a Phase-Change Catalyst for Stable Hydrogen

Production from Bio-glycerol

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	Pre-breakthrough	Post-breakthrough	Glycerol
Catalyst	(5min) ^a	(20min) ^b	conversion
	H_2 %	H_2 %	(%) ^c
Ca _{0.33} Co _{0.67} O	88.48	55.46	99.48
Ca _{0.43} Co _{0.57} O	92.25	62.35	99.63
Ca0.50C00.50O	95.52	66.84	99.83
Ca _{0.57} Co _{0.43} O	94.24	82.26	99.73

Table S1 The effect of Ca/Co ratio on the performance of the SESRG reaction. Thecorresponding XRD and H2-TPR results are shown in Fig. S1.

^a The hydrogen purity at the 5th minute measured by GC.

^b The hydrogen purity at the 20th minute measured by GC.

^c The average conversion of glycerol for the first SESRG period for 20min.



Fig. S1 CO₂ absorption breakthrough curves over CaO, $Ca_{0.50}Co_{0.50}O$ (CCO) and reduced $Ca_{0.50}Co_{0.50}O$ (rCCO). The CaO was prepared by calcinating commercial CaCO₃ at 800°C for 4 h. CCO was reduced at 600°C for 1h in H₂ to obtain rCCO. The absorption on CaO and rCCO was performed in 10%CO₂/N₂ at 550°C for 30min, while the absorption on CCO was in 10%CO₂/H₂ at 550°C for 30min.

The relatively slower absorption kinetics of CCO material was investigated through comparing with the breakthrough curve with conventional CaO sorbent. As shown in Fig. S1, the reduced CCO materials displayed similar breakthrough period as the CaO derived from decomposing commercial CaCO₃, suggesting that the CaO derived from CCO materials afforded the similar absorption kinetics. However, it should be stressed that the CCO materials was subjected to the SESRG without the reduction in this work. The reduction of CCO was *in-situ* performed to release CaO and Co catalyst. The absorption of CO₂ by unreduced CCO showed an obviously slower breakthrough for about 7.5 min in the mixture of CO₂ and H₂, mimicking the reaction conditions. This result clearly indicates that the relatively slow kinetics of CO₂ absorption shown in Fig. 2a was resulted from the simultaneous formation and carbonation of CaO. In principle, it could be improved by pre-reducing the CCO before the SESRG stage, but it is obviously impracticable because of the extra H₂ consumption and complicated operation.



Fig. S2 (a) XRD patterns and (b) H_2 -TPR profiles of the calcined Ca_xCo_yO with different Ca/Co ratios.



Fig. S3 Effects of temperature (a) and S/C ratio (b) on H_2 purity in the pre-breakthrough and post-breakthrough stages and average conversion of SESRG over $Ca_{0.50}Co_{0.50}O$ catalyst. Reaction conditions: (a) 1atm, S/C=4, 0.02 ml/min, 30 ml/min Ar, 1.5g catalyst; (b) 1atm, 550 °C, 0.02 ml/min, 30 ml/min Ar, 1.5g catalyst.



Fig. S4 Effect of the decarbonization temperature on (a) H_2 purity and (b) average conversion of glycerol in the pre-breakthrough stages over Ca_{0.50}Co_{0.50}O. Reaction conditions: 1atm, 550 °C, 0.02 ml/min, 30 ml/min Ar, 1.5g catalyst; decarbonization conditions: 1atm, 30 ml/min air, 30min.



Fig. S5 XRD patterns of $Ca_{0.50}Co_{0.50}O$ with different calcination duration. Decarbonation (dec) conditions: 1atm, 30 ml/min air, 800 °C, for 0.5h, 3h and 5h. The crystallite sizes of CCO were determined with the Scherrer equation as 45.6 nm, 46.2 nm and 48.4 nm for 0.5, 3, 5 h, respectively. This result indicate the CCO was quite thermally stable against sintering at 800 °C.



Fig. S6 H₂ and CO₂ concentration profiles measured by online GC in (a) the second cycle of SESRG and (b) the ten reaction-decarbonation cycles over the Ca_{0.50}CO_{0.50}O catalyst. (c) Concentrations of gaseous products over the Ca_{0.50}CO_{0.50}O catalyst determined by GC during the ten reaction-decarbonation cycles. The product concentrations are represented by the values at 8 min and 20 min in every cycle, which represent the pre-breakthrough and post-breakthrough stage of SESRG, respectively. (d) Evolution of breakthrough time as a descriptor of the CO₂ sorption capacity and glycerol conversions during ten reaction-decarbonation cycles. Reaction conditions: 1 atm, 550 °C, S/C= 4, 0.02 ml/min, 30 ml/min Ar, 1.5 g catalyst; decarbonization conditions: 1atm, 30 ml/min Air, 900 °C, 30min.



Fig. S7 (a) STEM, (b) HRTEM images and (c,d) the EDS elemental mapping of the used catalyst after the first SESRG reaction. The insets in (b) show the lattice fringes of metallic cobalt and cobalt oxide, respectively, suggesting their coexistence.



Fig. S8 (a) FESEM images of the used $Ca_{0.50}Co_{0.50}O$ catalyst and (b) Binary image

generated from (a).



Fig. S9 FESEM images of Ca_{0.50}Co_{0.50}O during 120 SESRG-decarbonization cycles. The column 700 °C denotes that the sample was heated to 700 °C under an air atmosphere (30 Ncm³/min). The images show the morphological transition from dense bulk materials to small cubic particles and hierarchical *shinyleaf-pricklyash-like* structures.





Fig. S10 XRD patterns of the calcined Ca-M-O samples. The calcined samples are denoted as M-Ca-T-4h where M is the additional metal (Fe, Cu, or Ni) and T is the calcination temperature. These results suggest that calcium ferrates formed at 800 °C, while the formation of cuprate occurred at 850 °C. In the case of nickel, the calcium nickelate cannot be formed under the conditions in this work.