Supplementary Information

Ceria-trapped single-atom rhodium catalysts for efficient ethanol steam reforming to hydrogen

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Fig. S1: XRD pattern of Ce₅/Al₂O₃ catalyst.





Fig. S2: HAADF-STEM images of Rh/Al₂O₃ catalyst.



Fig. S3: HAADF-STEM images of Rh-Ce₁/Al₂O₃ catalyst.

5 nm



Fig. S4: HAADF-STEM image and particle size statistic of Rh-Ce₃/Al₂O₃ catalyst



Fig. S5: HAADF-STEM image and particle size statistic of Rh-Ce₅/Al₂O₃ catalyst.



Fig. S6: k³-weighted wavelet transforms for the Rh K-edge XAFS signals of Rh-Ce_x/Al₂O₃ catalysts and standards. (a) Rh foil, (b) Rh₂O₃, (c) Rh/Al₂O₃ and (d) Rh-Ce₃/Al₂O₃.



Fig. S7: EXAFS fitting curves at the Rh K-edge for Rh-Ce₅/Al₂O₃ catalyst.



Fig. S8: XPS spectra of Rh/Al₂O₃ and Rh-Ce₅/Al₂O₃ in the low-binding-energy region (0-35 eV).



Fig. S9: (a) Ce 3d XPS spectra of Ce₅/Al₂O₃ and (b) O 1s XPS spectra of Rh-Ce_x/Al₂O₃ catalysts.



Fig. S10: (a) Rh 3d spectra of Rh-Ce₅/Al₂O₃ at 4% poor H₂ and 10% rich H₂ reaction conditions. (b) Ce 3d spectra of Rh-Ce₅/Al₂O₃ at 4% poor H₂ and 10% rich H₂ reaction conditions.



Fig. S11. The correlation between different oxygen vacancy content and single-atom Rh content. (The oxygen vacancy content was obtained by calculating the ratio of $O_{sur}/(O_{sur}+O_{lat})$ in O 1s XPS spectra. The single-atom Rh content was determined by integrating the geminal-dicarbonyl CO adsorption peaks area at 2088 and 2012 cm⁻¹ in CO-DRIFTS, subtracting the corresponding peaks area from Rh/Al₂O₃ to eliminate the background contribution, the resulting value was then divided by the background-corrected peak area of the Rh-Ce₅/Al₂O₃ catalyst to obtain the relative amount of single-atom Rh.)



Fig. S12: H₂-TPR profiles of Ce₅/Al₂O₃ catalyst.



Fig. S13: (a) Ethanol conversion and **(b)** H₂ production rates over Rh-Ce_x/Al₂O₃ catalysts during the ESR reaction at different temperature. (reaction conditions: liquid feed of H₂O/ethanol = 8 at 27.1 μ L min⁻¹, with balance N₂ at 123 mL min⁻¹, 20 mg catalyst and 80 mg SiO₂).



Fig. S14: Carbon products production rate over Rh-Ce_x/Al₂O₃ catalysts during the ESR reaction at different temperature. (a) CO₂ production rate, (b) CO production rate, (c) CH₄ production rate, (d) C₂H₄ production rate. (reaction conditions: liquid feed of H₂O/ethanol = 8 at 27.1 μ L min⁻¹ with balance N₂ at 123 mL min⁻¹, 20 mg catalyst and 80 mg SiO₂)



Fig. S15: Stability test of ESR reaction on Rh/Al₂O₃ and Rh-Ce₅/Al₂O₃ catalysts. (reaction conditions: liquid feed of H₂O/ethanol = 8 at 27.1 μ L min-1, with balance N₂ at 123 mL min⁻¹, WHSV of ethanol = 37.02 h⁻¹, 10 mg catalyst and 90 mg SiO₂, 450 °C).



Fig. S16: Raman spectra of Rh/Al₂O₃ and Rh-Ce₅/Al₂O₃ after different ESR reaction times at 450 °C.



Fig. S17: Ethanol conversion on Rh/Al₂O₃ and Rh-Ce₅/Al₂O₃ catalysts in the C₂H₅OH/D₂O reaction. (reaction conditions: liquid feed of D₂O/ethanol = 8 at 27.1 μ L min⁻¹ with balance N₂ at 123 mL min⁻¹, 20 mg catalyst and 80 mg SiO₂, 450 °C).



Fig. S18: (a) *In situ* DRIFTS spectra of Rh/Al₂O₃ catalysts exposed to 0.3% CH₃CH₂OH/Ar. **(b)** The formation of H₂, CO₂, CH₄, CO, C₂H₄ and H₂O on Rh/Al₂O₃. **(c)** *In situ* DRIFTS spectra of surface intermediates on Rh/Al₂O₃ during ESR reaction. **(d)** The formation of H₂, CO₂, CH₄ and CO during ESR reaction.



Fig. S19: *In situ* DRIFTS spectra of **(a)** Rh/Al₂O₃ and **(b)** Rh-Ce₅/Al₂O₃ catalysts exposed to different reaction composition at 350 °C. The formation of H₂, CO₂, CH₄ and CO on Rh/Al₂O₃ exposed to **(c)** CH₃COOH/Ar and **(d)** H₂O. (rection conditions: pre-exposed to 0.075% CH₃COOH/Ar at 350 °C for 30 min, followed by Ar purging for 30 min, and finally exposed to 0.75% H₂O for 60 min)



Fig. S20: (a) The correlation between formate species (1588 cm⁻¹) and temperature change on Rh-Ce₅/Al₂O₃ exposed to 1%CO/1.2%H₂O/Ar. (b) The correlation between derivative of H₂ production and temperature change on Rh-Ce₅/Al₂O₃ exposed to 1%CO/1.2%H₂O/Ar.



Fig. S21: (a) *In situ* DRIFTS spectra of surface intermediates on Rh/Al₂O₃ during WGS reaction. (b) The formation of H₂ and CO₂ on Rh/Al₂O₃ during WGS reaction. (reaction conditions: 1% CO/1.2% H₂O/Ar from 200 °C to 500 °C at a rate of 10 °C min⁻¹). (c) *In situ* DRIFTS spectra of Rh/Al₂O₃ catalysts exposed to CO/H₂O/Ar and H₂O/Ar at 200 °C. (d) The formation of H₂, and CO₂ on Rh/Al₂O₃ exposed to H₂O/Ar. (rection conditions: pre-exposed to 1% CO/1.2% H₂O/Ar at 200 °C for 30 min, and finally exposed to 1.2% H₂O for 60 min)



Fig. S22: (a) *In situ* DRIFTS spectra of Rh/Al₂O₃ catalysts exposed to 1% H₂O/Ar. (b) *In situ* DRIFTS spectra of Rh-Ce₅/Al₂O₃ catalysts exposed to 1% H₂O/Ar. (c) The formation of H₂O on Rh/Al₂O₃ and Rh-Ce₅/Al₂O₃. (d) *In situ* DRIFTS spectra of Rh/Al₂O₃ catalysts exposed to 1% CO/Ar. (e) *In situ* DRIFTS spectra of Rh-Ce₅/Al₂O₃ catalysts exposed to 1% CO/Ar. (f) The formation of CO on Rh/Al₂O₃ and Rh-Ce₅/Al₂O₃.

Sample	Temperature (°C)	X _{EtOH} (%)	$ m R_{H2}$ (mmol $ m g_{cat}^{-1}$ min ⁻¹)	Ref	
Rh-Ce ₅ /Al ₂ O ₃	450	100	22.4	This work	
NiRh@NiO@SiO2	550	80	21.8	1	
Rh/LaCeAlO ₃	500	100	20.9	2	
Rh-Co/CeO ₂ -ZrO ₂	550	100	15.4	3	
$Rh@Ce_{0.2}Zr_{0.8}O_2-Al_2O_3$	700	100	21.9	4	
Rh-Fe/CaO-Al ₂ O ₃	600	100	14.4	5	
Rh-Pt/CeO ₂ /SiO ₂	550	100	17.2	6	
0.5RhNi/TiO ₂	400	100	20.3	7	
Rh/A	400	100	17.6	8	
Rh-La ₂ O ₃ -SiO ₂	500	100	11.1	9	
Rh/CeO ₂	550	100	13.1	10	

Table S1: Comparison study on catalytic performance for ESR reaction over reported catalysts and this work.

Sample	Shell	$R~(\mathring{A})^{\mathrm{a}}$	CN ^b	$\sigma^2 (\mathring{A}^2)^c$	$\Delta E0 \ (eV)^d$	R factor ^e
Rh-Ce ₅ /Al ₂ O ₃	Rh-O	1.7	5.6	0.005	-6.75	0.02
	Rh-O-Ce	2.8	1.5	0.154		

Table 2: EXAFS fitting parameters at the Rh K-edge for Rh-Ce₅/Al₂O₃ catalyst.

^abond distance; ^bcoordination number; ^cDebye-Waller factor; ^dthe inner potential correction; ^egoodness of fit.

References

- 1. Q. Xue, Z. Li, B. Yan, S. Ullah, Y. Wang and G. Luo, J. Catal. , 2024, 434, 115536.
- 2. A. H. Martínez, E. Lopez, L. E. Cadús and F. N. Agüero, Catal. Today. , 2021, 372, 59-69.
- 3. M. Araque, J. C. Vargas, Y. Zimmermann and A.-C. Roger, Int. J. Hydrogen Energy, 2011, 36, 1491-1502.
- 4. L. De Rogatis, T. Montini, M. F. Casula and P. Fornasiero, J. Alloys Compd., 2008, 451, 516-520.
- 5. L. Chen, C. K. S. Choong, Z. Zhong, L. Huang, T. P. Ang, L. Hong and J. Lin, J. Catal. , 2010, 276, 197-200.
- 6. B. Cifuentes, M. Hernández, S. Monsalve and M. Cobo, Appl. Catal. A-Gen., 2016, 523, 283-293.
- H. Meng, Y. Yang, T. Shen, W. Liu, L. Wang, P. Yin, Z. Ren, Y. Niu, B. Zhang, L. Zheng, H. Yan, J. Zhang, F.-S. Xiao, M. Wei and X. Duan, *Nat. Commun.*, 2023, 14, 3189.
- 8. P. Osorio-Vargas, C. H. Campos, R. M. Navarro, J. L. G. Fierro and P. Reyes, Appl. Catal. A-Gen., 2015, 505, 159-172.
- 9. L. Coronel, J. F. Múnera, A. M. Tarditi, M. S. Moreno and L. M. Cornaglia, *Appl. Catal. B Environ.*, 2014, 160-161, 254-266.
- 10. T. Hou, B. Yu, S. Zhang, T. Xu, D. Wang and W. Cai, *Catal. Commun.*, 2015, **58**, 137-140.