

Supporting Information

Tailoring the activity and selectivity of Rh/SiO₂ in the selective hydrogenation of phenol by CoO_x promotion

Fei Zhang,^{a, c} Chunzheng Wu,^b Shuibo Wang,^a Shiwei Wang,^a Tong Li,^a Laixi Zou,^{c, *}

Hongbo Yu,^{a, *} and Hongfeng Yin^{a, *}

^a Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo, Zhejiang 315201, P. R. China

^b Chemistry and Materials Engineering, Zhejiang A&F University, Hangzhou, Zhejiang 311300, P.R. China

^c School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, Jiangxi 341000, P.R. China

* Corresponding author: E-mail: yinhf@nimte.ac.cn; Fax: +86 0574 8668 5043

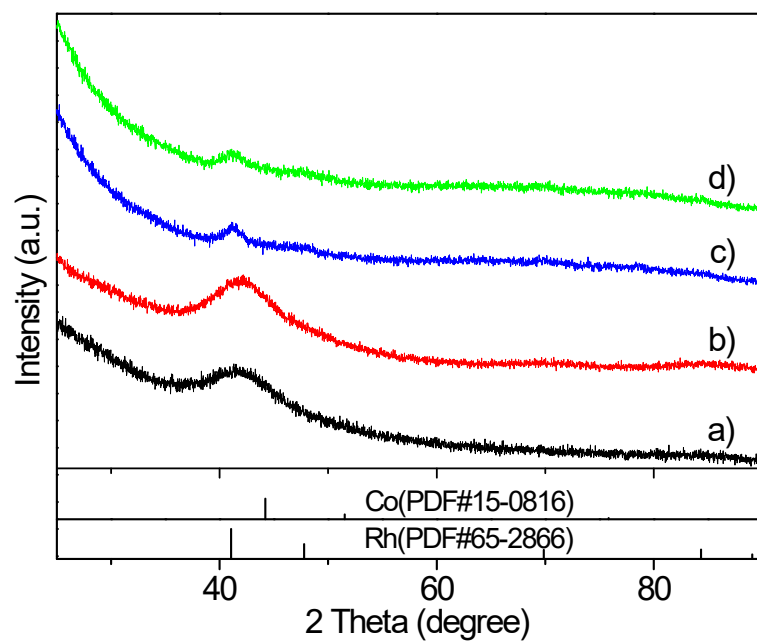


Fig. S1 XRD patterns showing: a) Rh_1Co_3 NPs; b) Rh_1Co_1 NPs; $\text{Rh}_1-(\text{CoO}_x)_3/\text{SiO}_2$ nanocatalysts; $\text{Rh}_1-(\text{CoO}_x)_1/\text{SiO}_2$ nano catalysts.

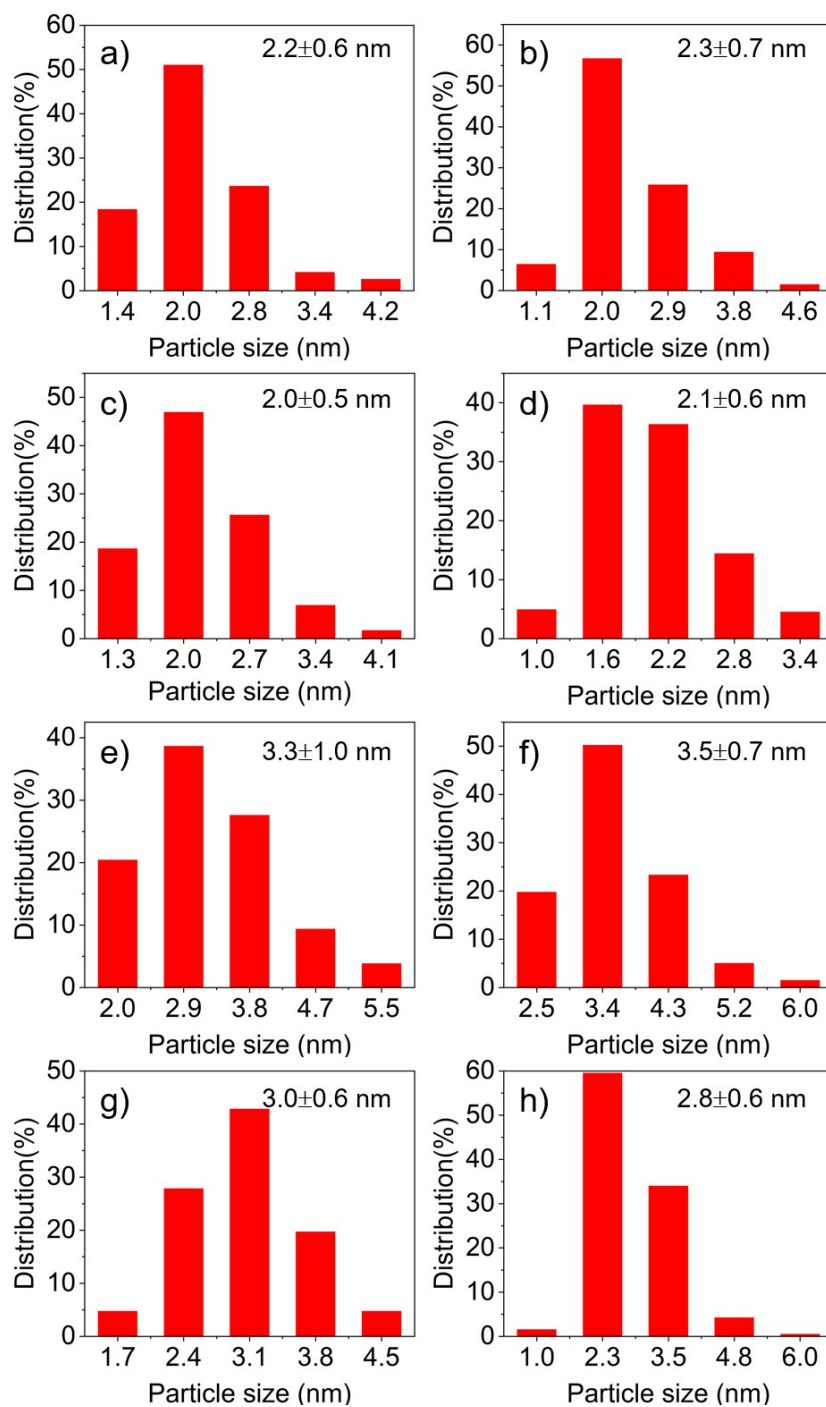


Fig. S2 Size distributions of as-synthesized nanomaterials showing: a), Rh NPs; b), Rh₃Co₁ NPs; c), Rh₁Co₁ NPs; d), Rh₁Co₃ NPs; e) Rh/SiO₂; f), Rh₃-(CoO_x)₁/SiO₂; g), Rh₁-(CoO_x)₁/SiO₂; and h), Rh₁-(CoO_x)₃/SiO₂.

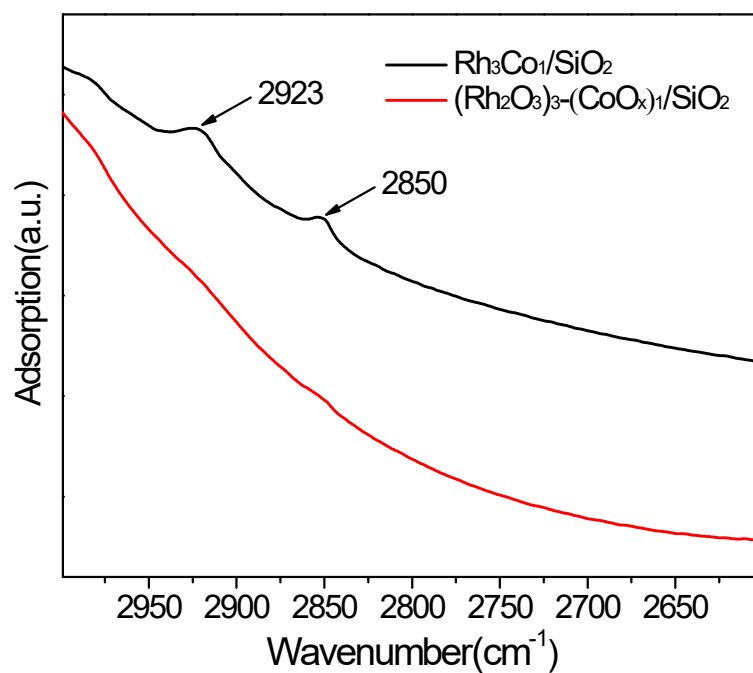


Fig. S3 FT-IR spectra of Rh₃Co₁/SiO₂ sample (without calcination) and (Rh₂O₃)₃-(CoO_x)₁/SiO₂ after calcination treatment.

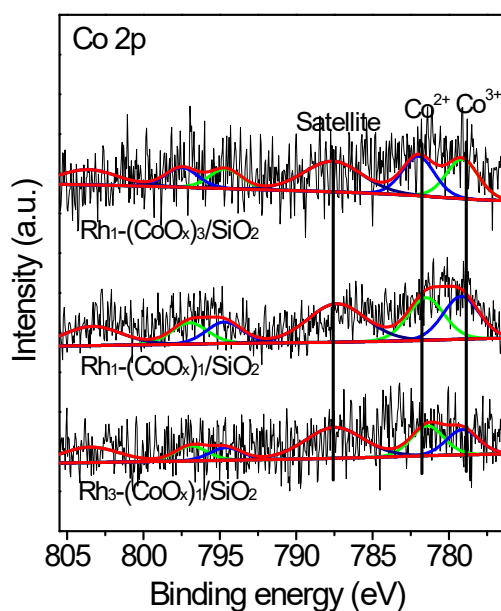


Figure S4 Co 2p XPS spectra of SiO₂ supported Rh-based nanocatalysts. (Rh loading, theoretical value 1 wt%).

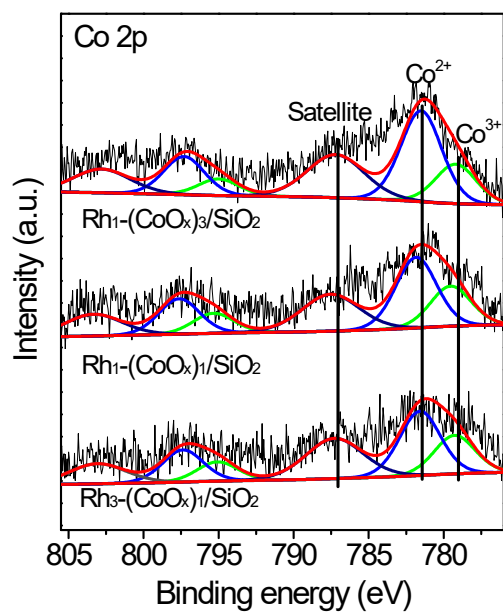


Figure S5 Co 2p XPS spectra of SiO₂ supported Rh-based nanocatalysts. (Rh loading, theoretical value 3 wt%).

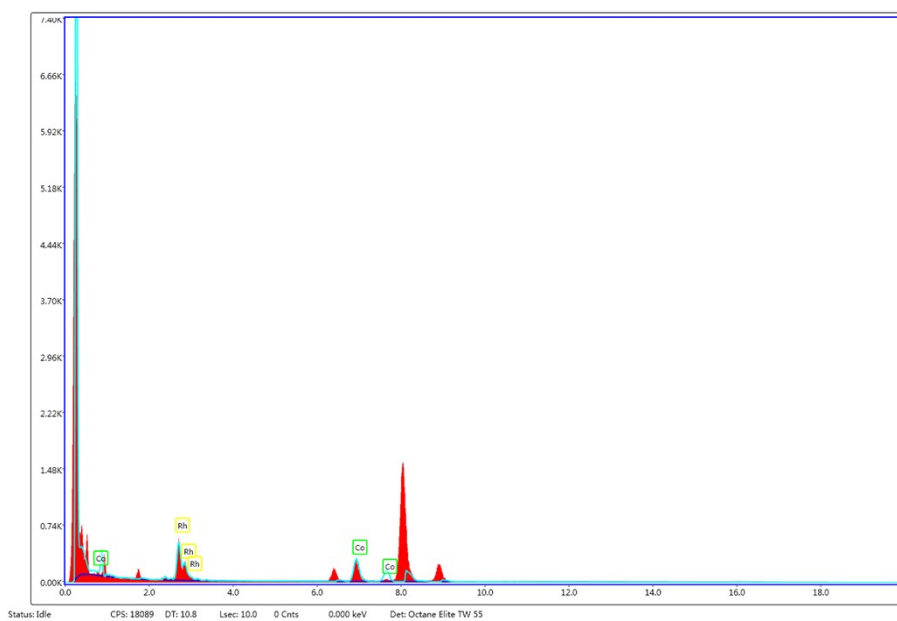


Fig. S6 EDS spectra of Rh₃-(CoO_x)₁/SiO₂ nano catalyst.

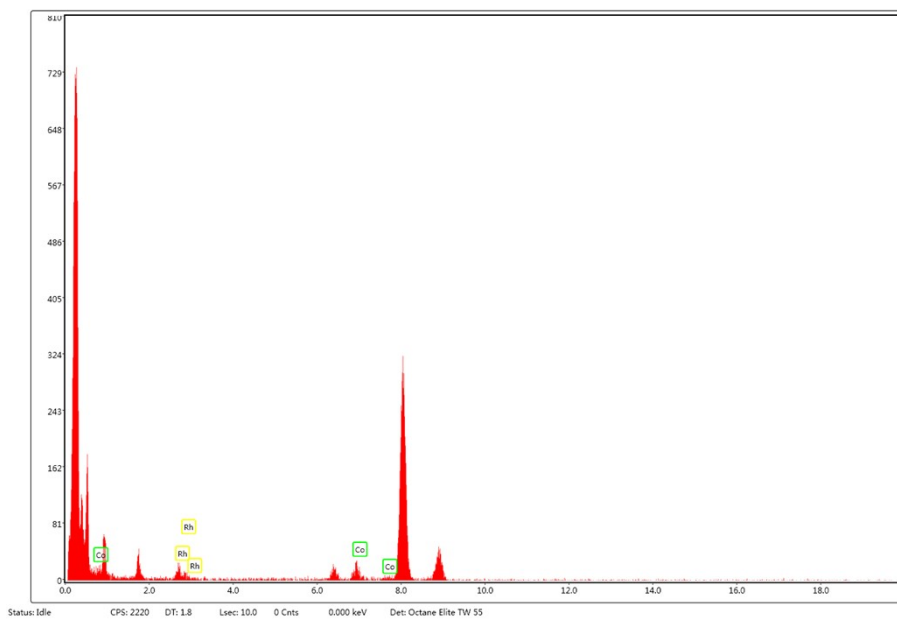


Fig. S7 EDS spectra of $\text{Rh}_1-(\text{CoO}_x)_1/\text{SiO}_2$ nano catalyst.

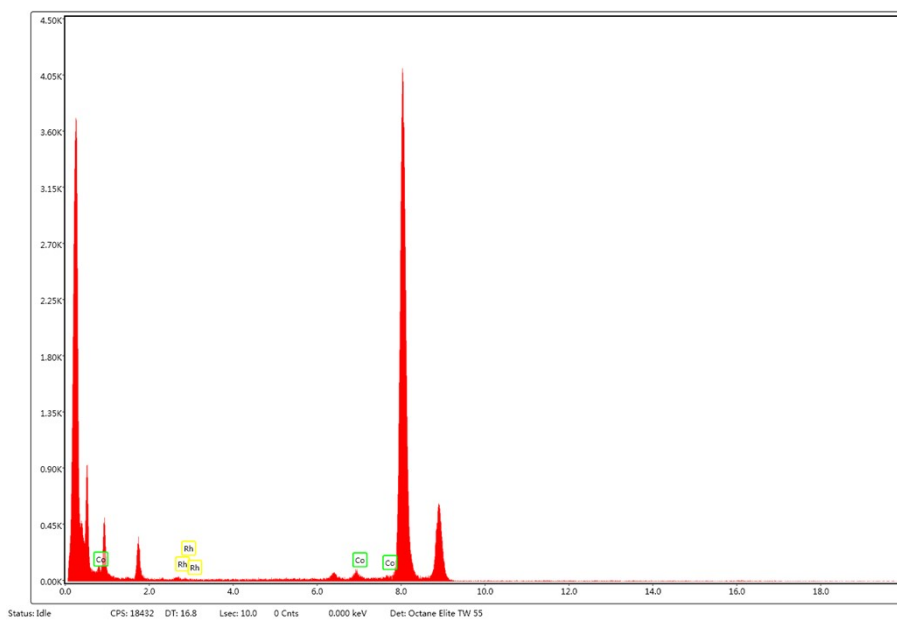


Fig. S8 EDS spectra of $\text{Rh}_1-(\text{CoO}_x)_3/\text{SiO}_2$ nano catalyst.

Table S1. The actual loadings of Rh and Co in Rh-CoO_x/SiO₂ catalysts analyzed by ICP-OES.

Sample	Rh loading (wt%)	Co loading (wt%)
Rh/SiO ₂	0.99%	-
Rh ₃ -(CoO _x) ₁ /SiO ₂	1.02%	0.18%
Rh ₁ -(CoO _x) ₁ /SiO ₂	1.08%	0.56%
Rh ₁ -(CoO _x) ₃ /SiO ₂	1.04%	1.65%

Table S2. The catalytic performance for hydrogenations of phenol over CoO_x/SiO₂ catalyst.

Catalyst ^a	Conversion (%)	Selectivity (%)	
		Cyclohexanol	Others
0.1000 g CoO _x /SiO ₂	0	N/A	N/A

^aReaction conditions: phenol, 0.1000 g; temperature, 60 °C; ethanol, 10.0 mL; H₂, 1.0 MPa; reaction time, 100 min; speed of agitation, 600 rpm/min.

Synthesis of CoO_x/SiO₂ catalyst.

The CoO_x/SiO₂ catalyst was prepared by a wet impregnation method. A certain amount of Co(NO₃)₂·6H₂O aqueous solution was impregnated on 1.0 g of SiO₂ to prepare the 1.0 wt % CoO_x/SiO₂ catalyst. After 4h of immersion, the sample was dried for 5h at 110 °C, and followed by calcining at 500 °C for 3h in air to obtain CoO_x/SiO₂ catalyst.

Table S3. Comparison of catalytic performance of Rh₃-(CoO_x)₁/SiO₂ and previously reported heterogeneous catalysts for the selective hydrogenation of phenol.

Catalysts	Conditions			Conv. (%)	Sel. (%)	TON ^a /h	Ref.
	T (°C)	P (MPa)	t (h)				
Rh ₃ -(CoO _x) ₁ /SiO ₂	60	1.0	1.7	98.1	99.4	213	This work
Rh/SiO ₂	25	0.1	9.0	100	18	18	1
Rh@HMSNs	45	0.5	3.0	90.6	96.6	28	2
Rh/CNF	300	2.0	0.2	51	40	89	3
Rh-PAA	80	4.0	0.5	40	100	40	4
FFSiRh	75	0.6	2.0	100	52	10.	5
Rh@S-MIL-101	50	0.5	2.0	80	35	33	6

^a Turnover number (TON) is measured as moles of products per total molar Rh atoms.

Reference

- 1 H. W. Zhang, A. J. Han, K. Okumura, L. X. Zhong, S. Z. Li, S. Jaenicke, G. K. Chuah, *J. Catal.*, 2018, **364**, 354-365.
- 2 P. J. Yan, P. F. Tian, K. J. Li, M. A. C. Stuart, J. Y Wang, X. H. Yu S. H. Zhou, *Chem. Eng. J.*, 2020, **397**, 125484-125495.
- 3 H. J. Wang, F. Y. Zhao, S. Fujita, M. Arai, *Catal. Commun.*, 2008, **9**, 362-368.
- 4 S. Kuklin, A. Maximov, A. Zolotukhina, E. Karakhanov, *Catal. Commun.*, 2016, **73**, 63-68.
- 5 L. L. R. Vono, C. Broicher, Karine Philippot, L. M. Rossi, *Catal. Today.*, 2021, **381**, 126-132.
- 6 I. E. Ertas, M. Gulcan, A. Bulut, M. Yurderi, M. Zahmakiran, *J. Mol. Catal. A: Chem.*, 2015, **410**, 209-220.

