Ligand-protected precipitation of cobalt over silica nanospheres for catalytic oxidation of toluene

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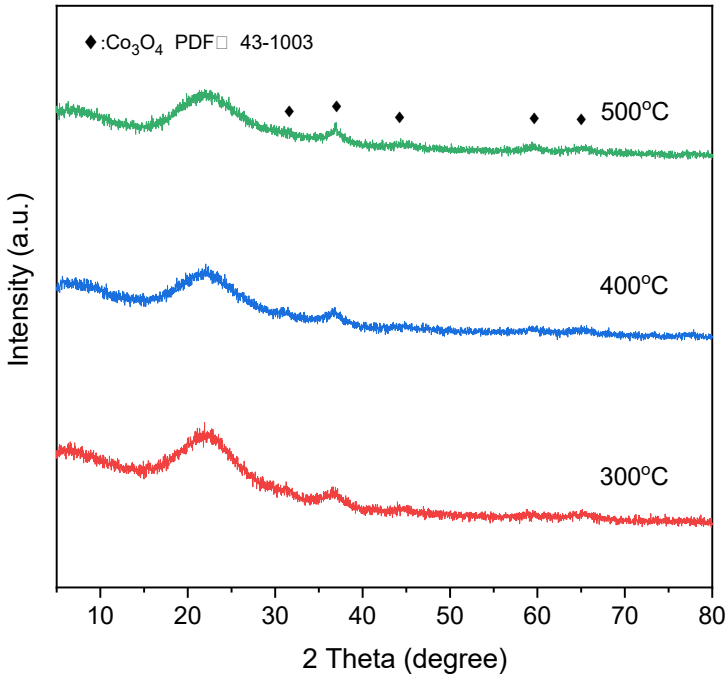

Fig. S1. XRD patterns of 10Co/SiO_2_LP calcined at various temperatures.

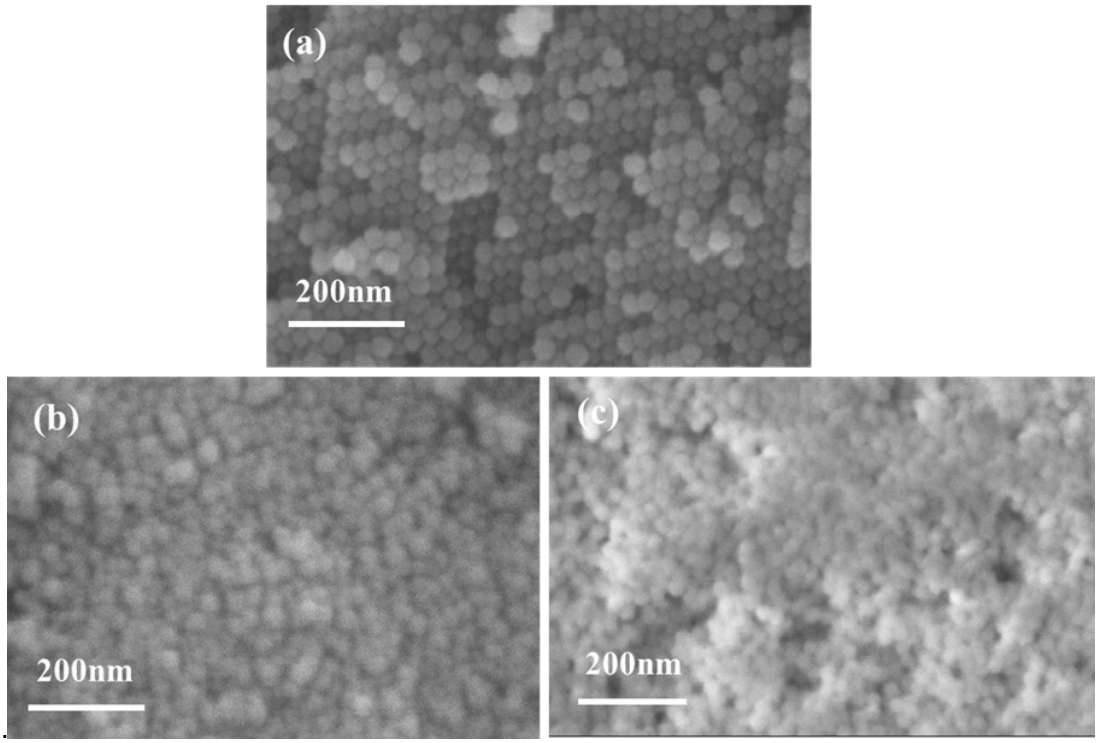

Fig. S2 SEM images of (a) SiO_2 support, (b) 10Co/SiO_2_IM, and (c) 10Co/SiO_2_LP

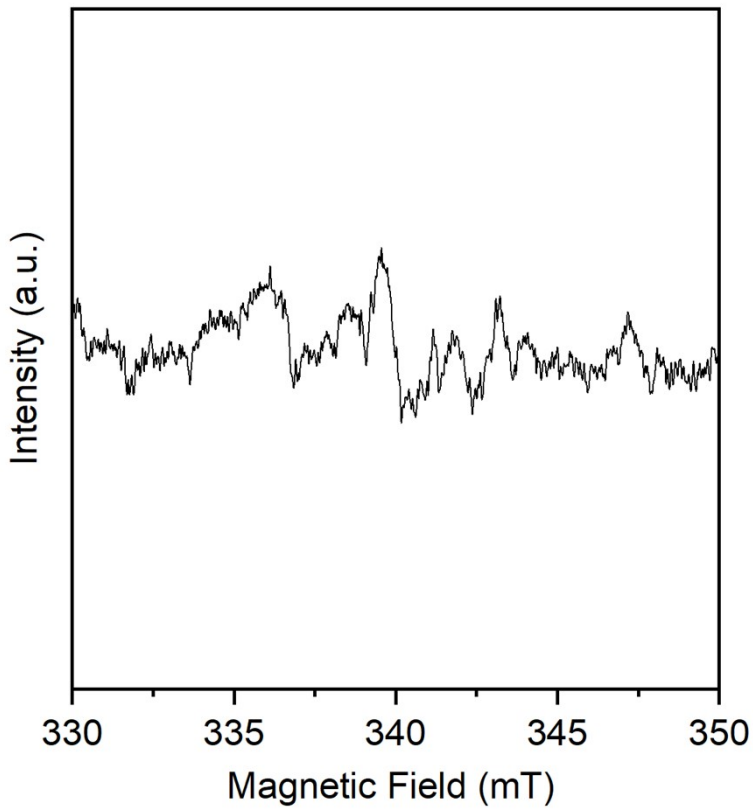

Fig. S3 EPR spectrum of the 10Co/SiO_2_LP sample calcined at 300°C

Table S1 Particles sizes of Co_3O_4 in 10Co/SiO_2_IM and 10Co/SiO_2_LP.

Sample	Co_3O_4 particle size (nm)	
	XRD	TEM
10Co/SiO_2_IM	12.1	8-20
10Co/SiO_2_LP	3.6	2-6

Table S2. Binding energies and Co^{3+}/Co^{2+} ratios of various Co/SiO_2 catalysts.

Catalyst sample	Binding energy (eV) Δ (Co $2p_{3/2}$−Co $2p_{1/2}$)	Co^{3+}/Co^{2+}	$Co^{3+}/(Co^{2+}+ Co^{3+})$
$6Co/SiO_2$_LP_400℃	15.3 (795.9-780.6)	0.88	0.47
$8Co/SiO_2$_LP_400℃	15.3 (795.7-780.4)	1.04	0.51
$10Co/SiO_2$_IM_400℃	15.3 (795.7-780.4)	0.87	0.47
$10Co/SiO_2$_LP_400℃	15.3 (795.4-780.1)	1.06	0.51
$12Co/SiO_2$_LP_400℃	15.2 (795.5-780.3)	0.94	0.48
$10Co/SiO_2$_LP_300℃	15.3 (795.7-780.4)	1.15	0.54
$10Co/SiO_2$_LP_500℃	15.3 (795.7-780.4)	0.86	0.46

Table S3. T_{10}, T_{50} and T_{90} values of toluene oxidation over various Co/SiO_2 catalysts.

Catalyst	T_{10}/℃	T_{50}/℃	T_{90}/℃
$6Co/SiO_2$_LP_400℃	188	240	260
$8Co/SiO_2$_LP_400℃	171	235	255
$10Co/SiO_2$_IM_400℃	206	250	271
$10Co/SiO_2$_LP_400℃	170	230	250
$12Co/SiO_2$_LP_400℃	166	230	250
$10Co/SiO_2$_LP_300℃	150	220	235
$10Co/SiO_2$_LP_500℃	176	232	254

Note: T_{10}, T_{50}, and T_{90} represent the temperatures corresponding to toluene conversion rates of 10%, 50%, and 90%.

Table S4. T_{10}, T_{50} and T_{90} values of toluene oxidation over 10Co/SiO_2_LP at various reaction conditions.

Toluene concentration	Space velocity (ml/g·h)	T_{10}/℃	T_{50}/℃	T_{90}/℃
100 ppm	45000	150	220	235
400 ppm	45000	200	230	240
700 ppm	45000	220	248	257
100 ppm	70000	160	225	237
100 ppm	120000	175	228	240

Note: T_{10}, T_{50}, and T_{90} represent the temperatures corresponding to toluene conversion rates of 10%, 50%, and 90%.

Table S5. Comparison of toluene oxidation performance of 10Co/SiO_2_LP with the reported Co-based catalysts.

Catalyst	Catalyst dosage (g)	Toluene concentration (ppm)	Space velocity ($ml \cdot g^{-1} \cdot h^{-1}$)	T_{90} (℃)	Long-term stability (h)	References
0.5CMO/3DOM-Al_2O_3	0.08 g(0.008 g),	1000	30000	274	-	[1]
ε-MnO_2	- (-)	500	60000	243	-	[2]
pompon-like Co_3O_4	- (-)	500	60000	298		[3]
10% CoOx/g-C_3N_4	0.05g(0.005g)	1000	156000	279	＞36	[4]
CuO/Co_3O_4-S	0.1g(0.02g),	500	10000	246	＞100	[5]
$CoCeO_x$/Beta	- (-)	1000	10000	307	-	[6]
Co_3O_4	0.1 g(0.1 g)	1000	60000	270	-	[7]
10Co/SiO_2_LP_300℃	0.2 g(0.02 g)	100	45000	235	＞100	**This work**
	0.2 g(0.02 g)	700	45000	257	＞100	**This work**
	0.2 g(0.02 g)	100	120000	240	＞100	**This work**

References

[1] J. Vélez, G. E. González, L. Urán, J. Arboleda, A. Echavarría, M. Velasquez, R. Molina, S. Moreno and C. Ostos, *Applied Surface Science*, 2025, **708,** 163736.

[2] M. T. Nguyen Dinh, C. C. Nguyen, T. L. Truong Vu, V. T. Ho and Q. D. Truong, *Applied Catalysis A: General*, 2020, **595**, 117473.

[3] W. Liu, R. Liu, H. Zhang, Q. Jin, Z. Song and X. Zhang, *Applied Catalysis A: General*, 2020, **597**, 117539.

[4] C. Miao, J. Liu, J. Zhao, Y. Quan, T. Li, Y. Pei, X. Li and J. Ren, *New Journal of Chemistry*, 2020, **44**, 11557-11565.

[5] W. Liu, H. Yu, S. Yang, Z. Song, X. Chen and X. Zhang, *Environmental Research*, 2024, **248**, 118411.

[6] Y. Wang, S. Wu, G. Wu, N. Fang, Y. Chu and J. Guo, *Microporous and Mesoporous Materials*, 2022, **343**, 112158.

[7] Rokicińska A, Natkański P, Dudek B, et al, *Applied Catalysis B: Environmental*, 2016, **195**, 59-68.