

## Supporting Information

### **Atomic Layer Deposition of Ru Nanoclusters on Ba-LaCeO<sub>x</sub>: A Highly Efficient Catalyst for Ammonia Synthesis under Mild Conditions**

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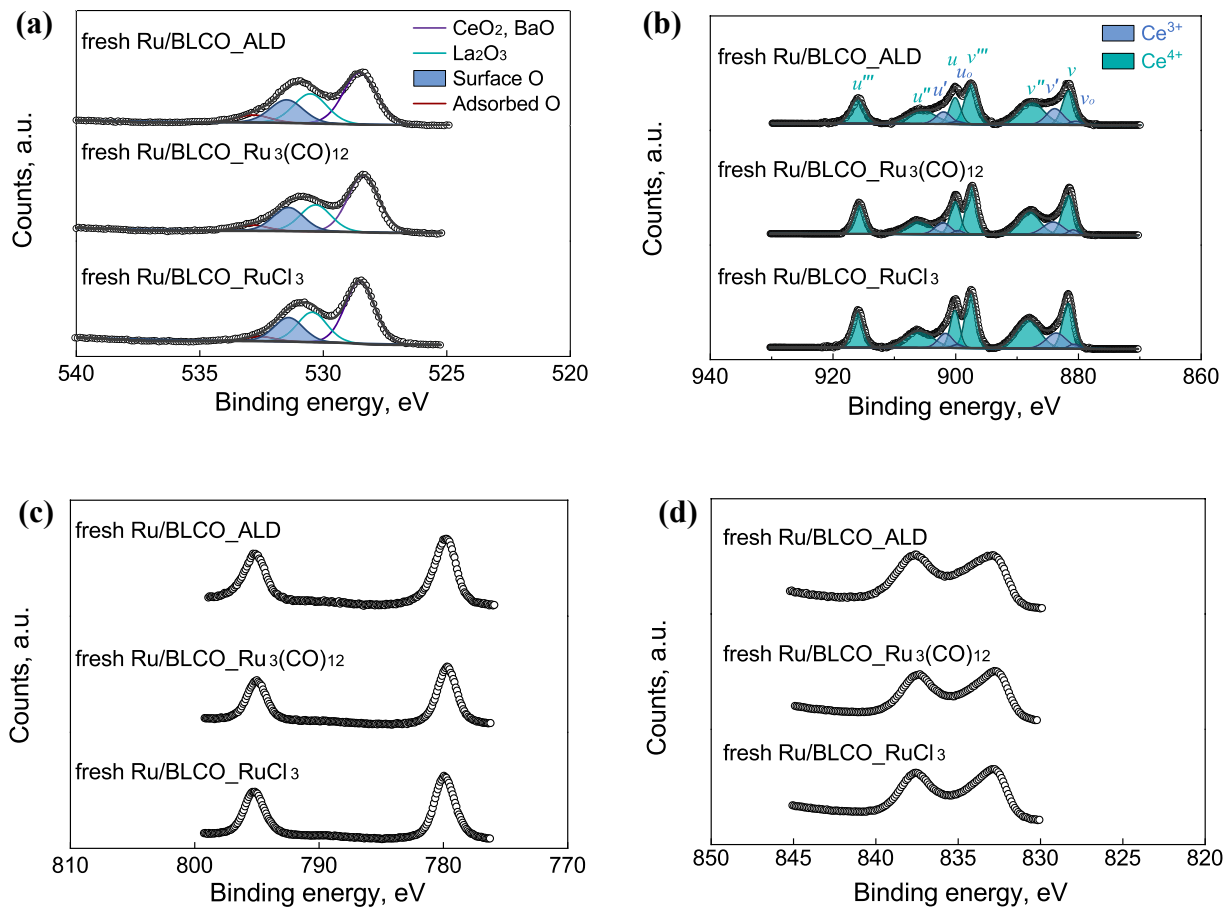


Figure S1. XPS spectra of (a) C 1s, (b) Ce 3d, (c) Ba 3d, and (d) La 3d<sub>5/2</sub> for the fresh Ru/BLCO\_ALD, fresh Ru/BLCO\_Ru<sub>3</sub>(CO)<sub>12</sub>, and fresh Ru/BLCO\_RuCl<sub>3</sub> catalysts.

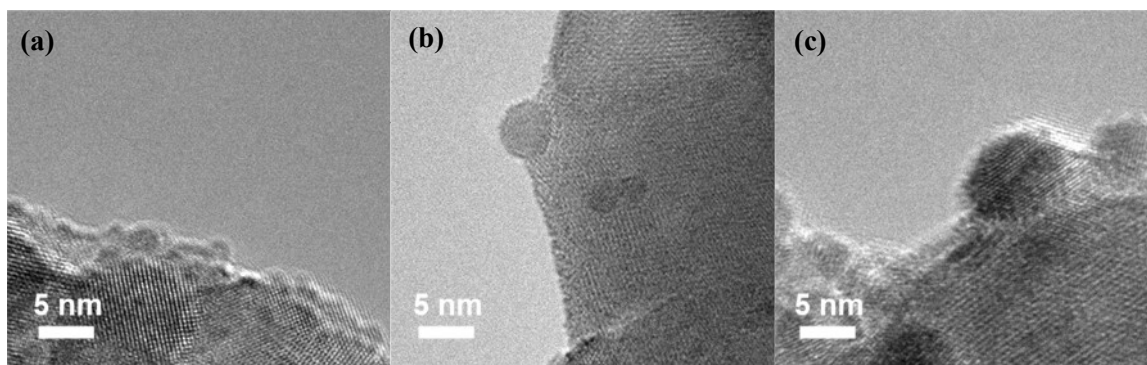


Figure S2. TEM images of (a) reduced Ru/BLCO\_ALD, (b) reduced Ru/BLCO\_Ru<sub>3</sub>(CO)<sub>12</sub>, and (c) reduced Ru/BLCO\_RuCl<sub>3</sub> catalysts.

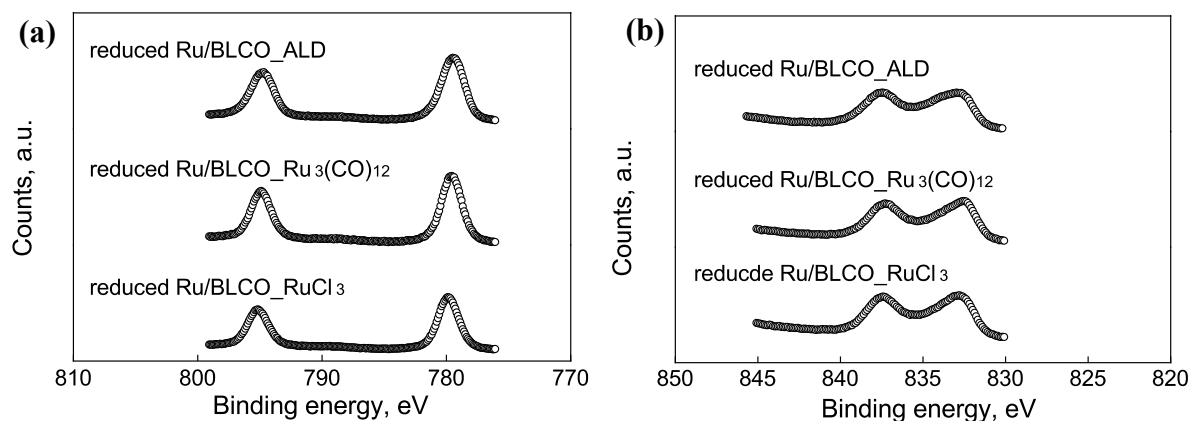


Figure S3. XPS spectra of (a) Ba 3d, and (b) La 3d<sub>5/2</sub> for the reduced Ru/BLCO\_ALD, reduced Ru/BLCO\_Ru<sub>3</sub>(CO)<sub>12</sub>, and reduced Ru/BLCO\_RuCl<sub>3</sub> catalysts.

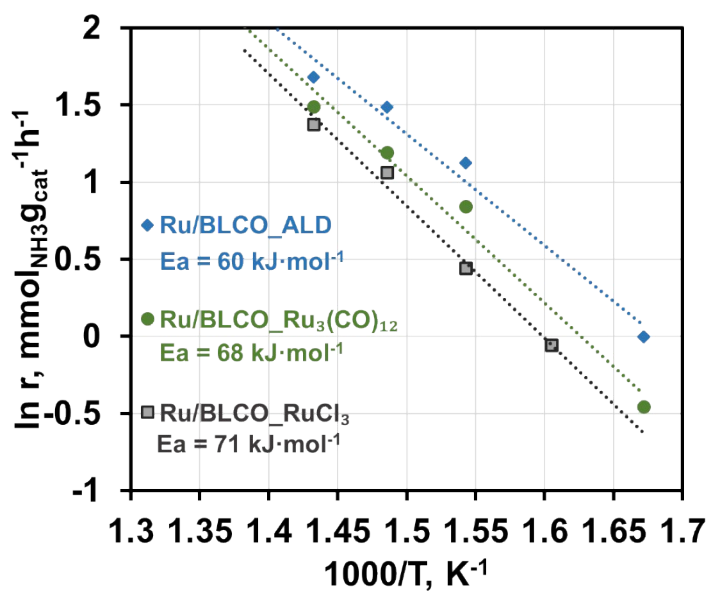


Figure S4. Arrhenius plots for ammonia synthesis reactions at 1.0 MPa and 6,000 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> over Ru/BLCO\_ALD, Ru/BLCO\_Ru<sub>3</sub>(CO)<sub>12</sub>, and Ru/BLCO\_RuCl<sub>3</sub> catalysts.

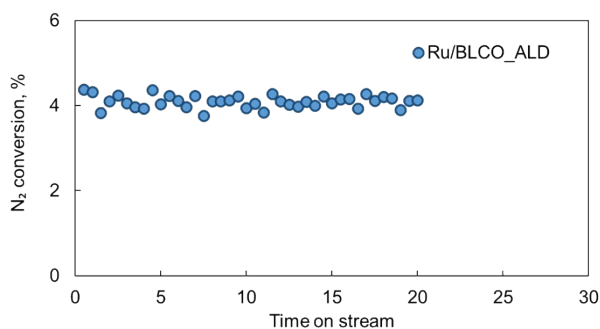


Figure S5. Second cycle stability test of Ru/BLCO\_ALD for ammonia synthesis under conditions of 350°C, 4.2 MPa, and 6,000 mL gcat<sup>-1</sup>h<sup>-1</sup>.

Table S1. Atomic composition results of different catalysts based on XPS.

Catalyst	Element, atom %						Ce/Ru	Ba/Ru
	Ba	La	C	Ce	Ru	O		
Fresh Ru/BLCO_ALD	3.76	6.60	39.77	4.82	2.27	42.78	2.1	1.66
Reduced Ru/BLCO_ALD	3.96	6.92	40.35	4.97	1.77	42.03	2.8	2.24
Fresh Ru/BLCO_Ru <sub>3</sub> (CO) <sub>12</sub>	3.63	6.39	49.56	4.51	1.84	34.07	2.5	1.97
Reduced Ru/BLCO_Ru <sub>3</sub> (CO) <sub>12</sub>	3.87	7.52	31.29	4.88	1.71	50.73	2.9	2.26
Fresh Ru/BLCO_RuCl <sub>3</sub>	2.84	6.93	37.06	4.63	1.97	46.57	2.4	1.44
Reduced Ru/BLCO_RuCl <sub>3</sub>	3.29	5.85	34.94	4.96	1.53	49.43	3.2	2.15

Table S2. Relative atomic concentrations of Ru and RuO<sub>2</sub> based on C 1s + Ru 3d and Ru 3p XPS peak deconvolution.

Catalyst	Based on C 1s+ Ru 3d		Based on Ru 3p	
	Ru%	RuO <sub>2</sub> %	Ru%	RuO <sub>2</sub> %
Fresh Ru/BLCO_ALD	72.3	27.7	74.2	24.8
Reduced Ru/BLCO_ALD	76.8	23.2	77.1	22.9
Fresh Ru/BLCO_Ru <sub>3</sub> (CO) <sub>12</sub>	-	100	-	100
Reduced Ru/BLCO_Ru <sub>3</sub> (CO) <sub>12</sub>	81.3	18.7	83.5	16.5
Fresh Ru/BLCO_RuCl <sub>3</sub>	-	100	-	100
Reduced Ru/BLCO_RuCl <sub>3</sub>	87.8	12.2	87.1	12.9