energies

Supplementary Materials: Stability studies of highly active cobalt catalyst for the ammonia synthesis process

Magdalena Zybert, Hubert Ronduda, Wojciech Patkowski, Weronika Rybińska, Andrzej Ostrowski, Kamil Sobczak, and Wioletta Raróg-Pilecka

Supplement to 2.1. Catalyst preparation

The data obtained during N_2 physisorption experiments were approximated using Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) isotherm models. The specific surface area (SSA) and total pore volume (V_P) for the catalyst precursors were determined (Table S1). The textural features of the prepared catalysts precursors show some differences depending on the Ba promoter addition method used. The specific surface area of the catalyst precursors was in the range of 37–54 m^2 g^{-1}, and the highest was for the material obtained using the deposition-precipitation method (DP sample). Figure S1 presents type IV isotherms with H1 hysteresis loop at P/P_0 = 0.65–1 characteristic for mesoporous materials consisting of agglomerates. The pore size distributions (Figure S2) for the WI and DP catalyst precursors show a clear dominance of pores with an average size of 10 nm and a small share of small mesopores of 2–3 nm. For the WM catalyst precursor, a larger number of smaller mesopores with a 2–3 nm diameter were observed.

Table S1. Physicochemical properties of the studied catalyst precursors.

Catalyst precursors	SSA (m^2 g^{-1}) [1]	V_P (cm^3 g^{-1}) [2]
WI	37	0.13
WM	43	0.14
DP	54	0.15

[1] SSA – specific surface area determined for the catalysts precursors based on the BET adsorption model.
[2] V_P – total pore volume determined for the catalysts precursors based on the BJH adsorption model.

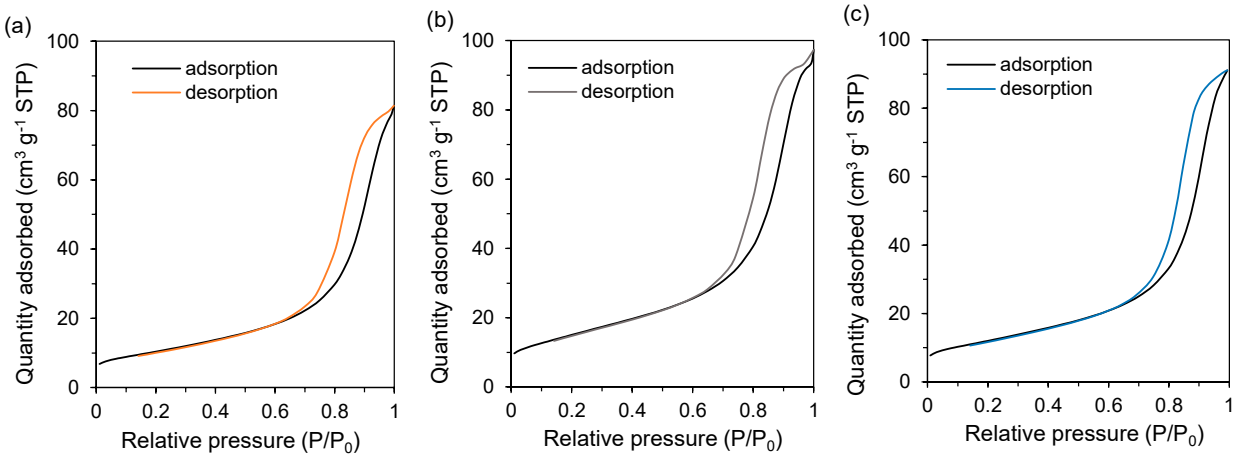

Figure S1. N_2 adsorption-desorption isotherms for (a) WI, (b) DP, and (c) WM catalyst precursors obtained based on the BJH adsorption isotherm model.

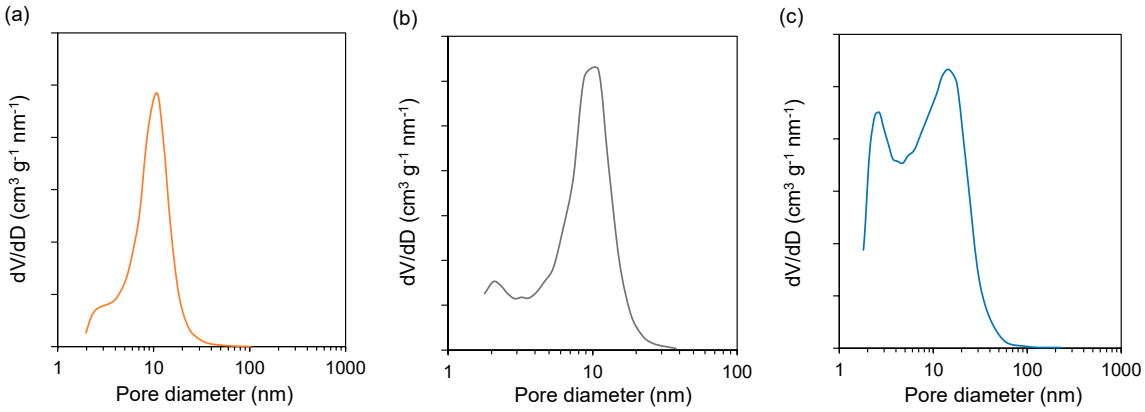

Figure S2. Pore size distribution curves for (a) WI, (b) DP, and (c) WM catalyst precursors obtained based on the BJH adsorption isotherm model.

The phase composition of the catalyst precursors was determined based on XRPD measurements (Figure S3). For all the studied catalyst precursors, two basic components were identified: intense reflections from the Co_3O_4 phase and few low-intensity reflections from CeO_2. Depending on the method used to introduce the promoter (Ba), other phases containing Ba promoter were also observed. Thus, for materials prepared by WI and WM methods, the main promoter phase visible in the diffractogram is barium(II) nitrate used to impregnate these materials. Single reflections of barium(II) carbonate, formed during the materials drying at 120 °C in air, are also visible. For the material obtained by the DP method, where Ba was introduced by precipitation of barium(II) carbonate on the surface of a mixture of Co_3O_4 and CeO_2 oxides, the main reflections derived from the Ba promoter phase are related to barium(II) carbonate.

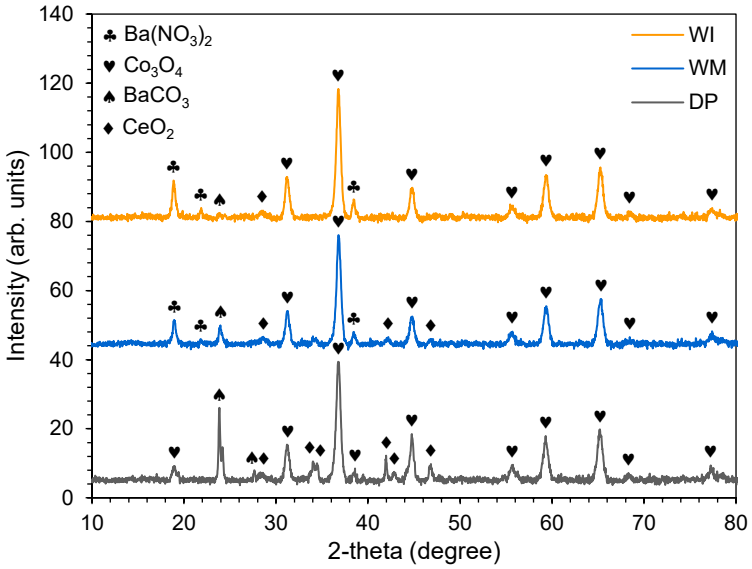

Figure S3. XRPD patterns of the WI, DP, and WM catalyst precursors.

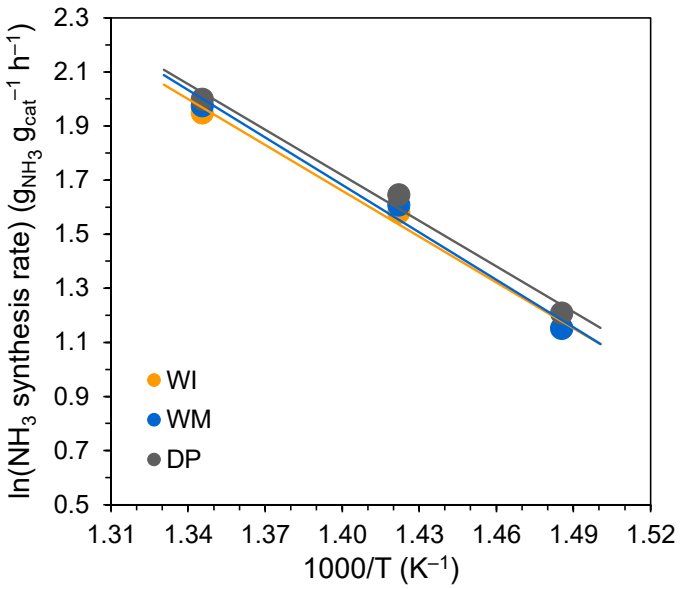

Figure S4. Arrhenius plots for the rate of ammonia synthesis at 6.3 MPa over the WI, DP, WM catalysts.

Table S2. Comparison of the catalytic performance for NH_3 synthesis of different catalysts.

Entry	Catalyst	Reaction temperature (°C)	Reaction pressure (MPa)	NH_3 synthesis rate (g_{NH_3} g_{cat}^{-1} h^{-1})	Reference
1	Ru/CeO_2-r	400	10	6.75	[34]
2	$Ru/La_2Ce_2O_7$	425	10	3.11	[35]
3	Fe_3O_4	430	3	0.53	[36]
4	$Fe_{1-x}O$	430	3	0.70	[36]
5	$Fe_{1-x}O$ (ZA-5)	400	10	1.12	[37]
6	Co/Ba	400	6.3	2.99	[38]
7	Co/CeO_2	400	10	0.70	[39]
8	$Ba\text{-}Co/CeO_2$	400	10	0.88	[39]
9	Co(40)/Mg-La	400	6.3	2.35	[40]
10	CoCeBa (WI)	400	6.3	3.17	This work
11	CoCeBa (WM)	400	6.3	3.17	This work
12	CoCeBa (DP)	400	6.3	3.35	This work

Table S3. Unit cell parameters and crystallite size of $BaCeO_3$ phase in the CoCeBa catalyst precursors.

Catalyst precursors	a (Å)	b (Å)	c (Å)	V (Å^3)	Crystallite size (nm)
WI	6.247	6.212	8.780	340.7	25.6
WM	6.267	6.208	8.765	341.0	24.3
DP	6.283	6.208	8.736	340.8	11.6

Table S4. Unit cell parameters and crystallite size of $BaCeO_3$ phase in the CoCeBa catalysts after overheating in H_2 (600 °C, 96 h).

Catalysts	a (Å)	b (Å)	c (Å)	V (Å^3)	Crystallite size (nm)
WI	6.271	6.215	8.776	342.1	30.0
WM	6.283	6.196	8.798	342.6	24.3
DP	6.215	6.180	8.725	335.1	46.2