Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

MOF-derived nanostructured catalysts for low-temperature ammonia synthesis

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Supporting information

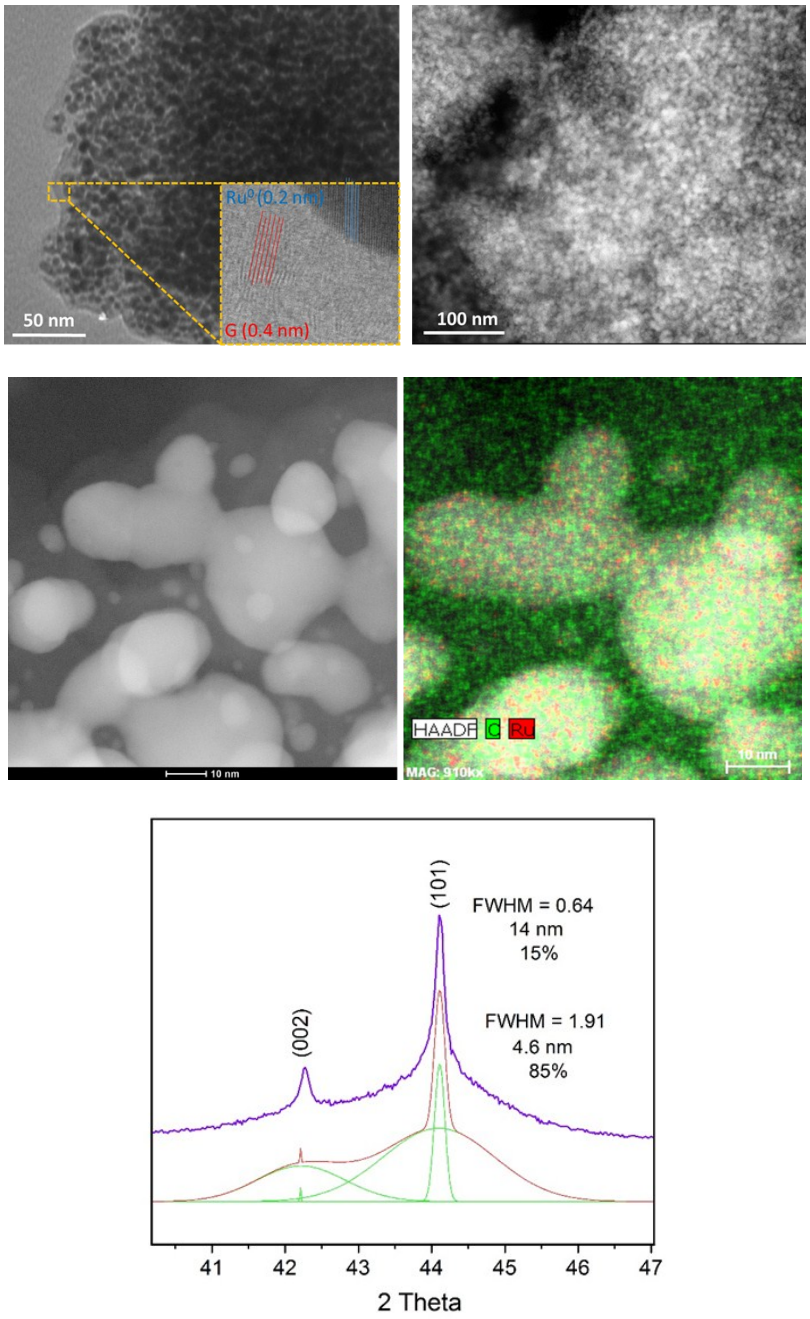

Figure S1. (above) STEM-HDAAF analysis of MOF-derived nanostructured catalysts obtained at 900 °C and 0 hour holding. (center) STEM image and elemental mapping analysis of nanostructured catalysts showing the presence of Ru and C after degradation upon long exposure to STEM beam. (below) Deconvolution of the XRD signal and calculation of the Ru nanoparticle size by Scherrer equation suggest the small concomitant formation (15%) of larger Ru nanocrystals.

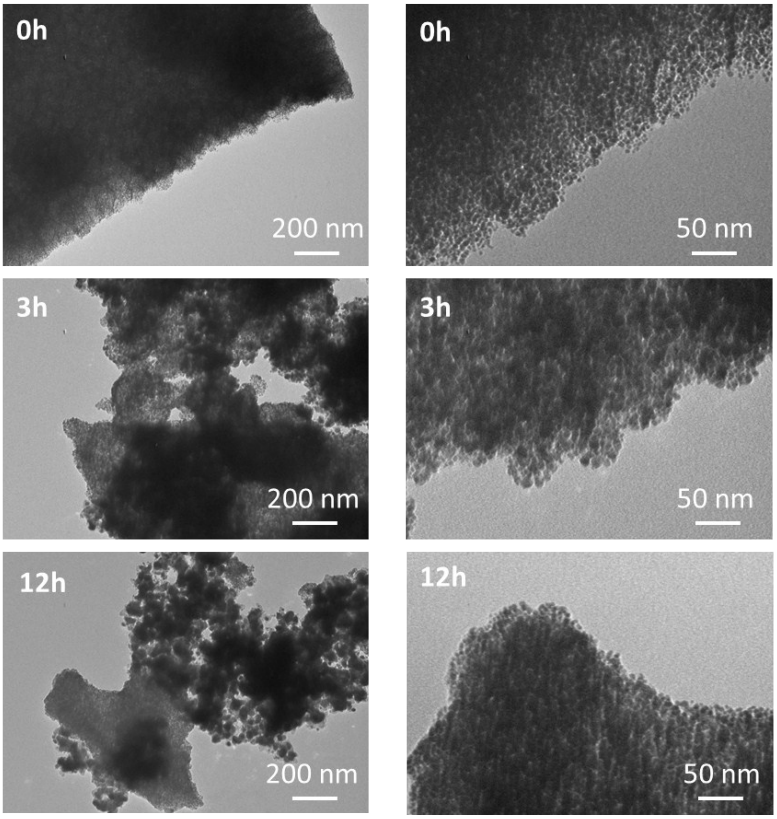

Figure S2. TEM analysis of the effect of the holding time on the microstructure of MOF-derived catalysts.

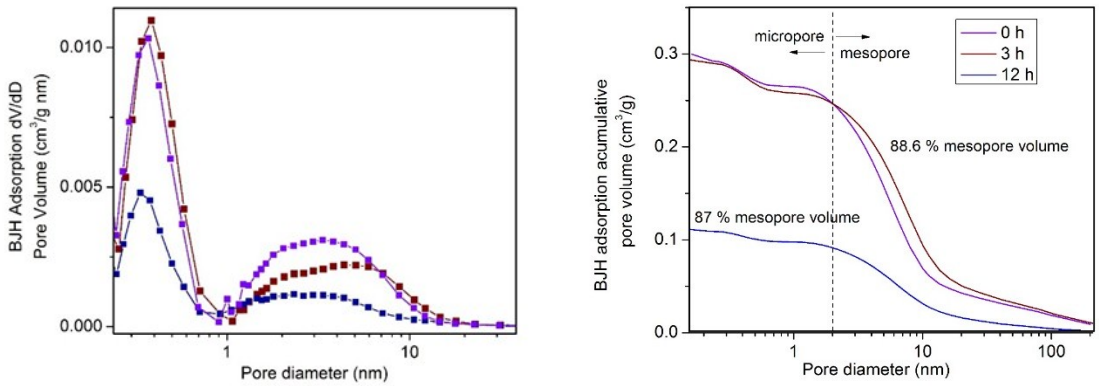

Figure S3. Pore size distribution of MOF-derived nanostructured catalysts prepared at 900 °C and varying holding times (0, 3 and 12h).

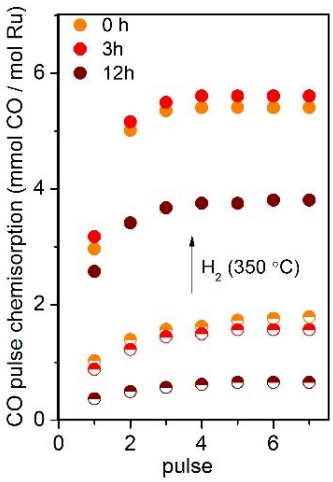

Figure S4. CO chemisorption before and after H_2 activation at 400 °C for MOF-derived nanostructured catalysts prepared at 900 °C and varying holding times (0, 3 and 12h).

Table S1: Effect of Ba and Cs promoter loading and ratio on ammonia production rates at GHSV of 15,000 h^{-1}, 350 °C and 95 barg

Ru:Ba:Cs (molar ratios)	NH_3 production rate ($mol_{NH3}/mol_{Ru}.h$)
1:0.05:0.10	4.71
1:0.05:0.15	10.35
1:0.05:0.20	**16.21**
1:0.025:0.10	0.18
1:0.10:0.40	5.34

Catalysts with Ba:Cs of 1:2, 1:3 and 1:4 were prepared at three different loading levels. Their activity was tested in the Microreactor at a gas hourly space velocity (GHSV) of 15,000 h^{-1} and 95 barg. Table 1 summarizes the results of the optimization study carried out at a reaction temperature of 350 °C. It was found that catalysts with Ru:Ba:Cs of 1:0.05:0.2 resulted in the highest ammonia production rate.

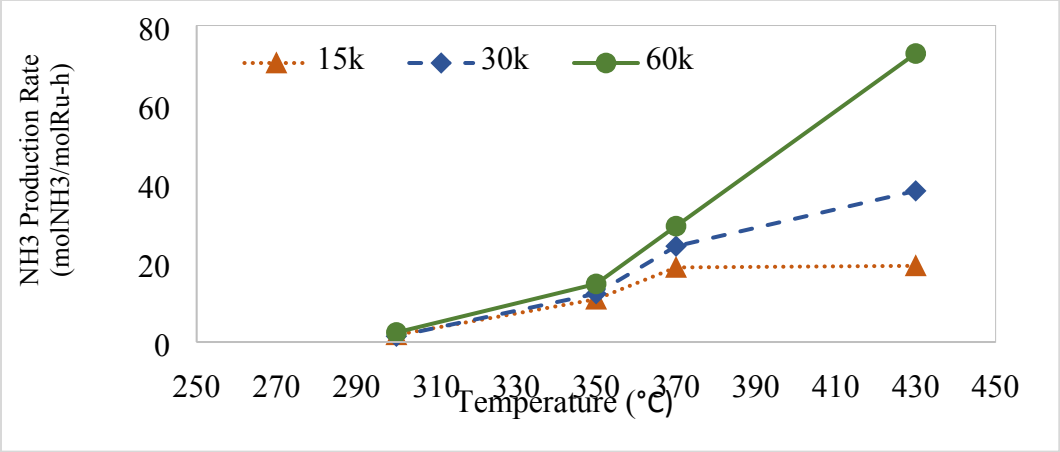

Figure S5. Effect of gas hourly space velocity (GHSV) on catalytic activity for ammonia synthesis. Tests carried out at 95 barg.

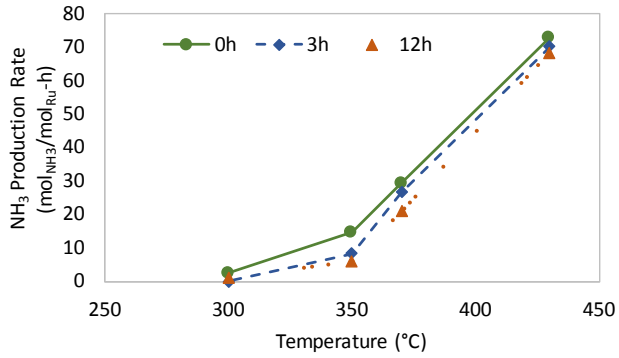

Figure S6. Effect of holding time on catalytic activity for ammonia synthesis. Tests carried out at GHSV of 60,000 h-1 and 95 barg

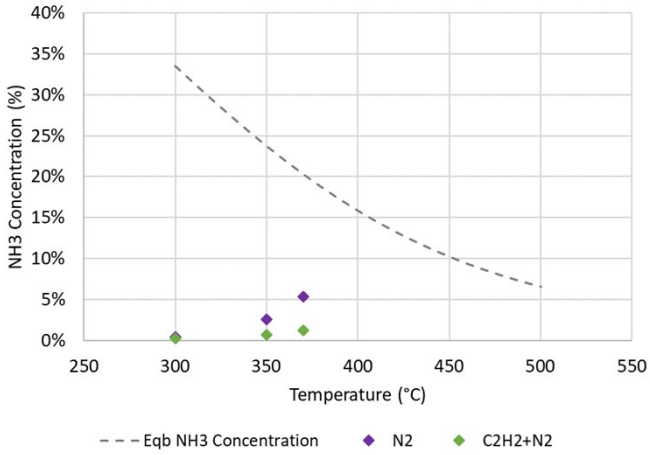

Figure S7. Ammonia conversions for the MOF-derived nanostructured catalysts prepared under N_2 and C_2H_2 reported at Table S2 compared to the thermodynamic equilibrium. Tests carried out at GHSV of 60,000 h^{-1} and 95 barg.

Table S2. Catalytic activity TOF (h^{-1}) for MOF-derived nanostructured catalysts prepared under N_2 at different holding times compared to pretreated with C_2H_2 at 500 °C.

Treatment	430	400	370	350	300
0h	**72.9**	**50.1**	**29.3**	**14.7**	**2.4**
3h	70.1	48.6	26.6	8.2	1.2
12h	68.4		21.0	6.1	1.0
C_2H_2	**173.5**	**95.0**	**32.8**	**18.0**	**5.8**

Table S3. Comparison to other reported Ru catalysts.

catalyst	P (bar)	S_{BET} ($m^2\ g^{-1}$)	Ru load (wt.%)	Dispersion (%)	Particle size (nm)	r_{NH3} ($g_{NH3}\ g_{cat}^{-1}\ h^{-1}$)		TOF (s^{-1}) 10^{-3}		E_a	ref
						300C	400C	300C	400C	(kJ mol^{-1})	
BaCs-RuC (N_2)[a]	95	210	58.5	0.6	3-4	0.25	4.89	0.7	13.8	108.7	This
BaCs-RuC (C_2H_2)[a]	95	126	23.1	3.5	<1	0.22	3.68	1.6	26.3	73.7	This
Ba-Cs-Ru/C	90	440	23.1	-	-	-	12.5	-	-	-	1
Ru/C12A7:e^-	1	1	0.3	4.1	32.9	-	-	-	270	40	2

[a] Ru:Ba:Cs = 1:0.05:0.2.

[1] Kowalczyk, Z., Krukowski, M., Raróg-Pilecka, W., Szmigiel, D., Zielinski, J. *Appl. Catal. A* **2003** *(248) 67–73.*

[2] Hara, M.; Kitano, M.; Hosono, H., *ACS Catalysis* **2017,** *7* (4), 2313-2324.