

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/131070/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Richards, Nia, Carter, James H., Parker, Luke A., Patisson, Samuel, Hewes, Daniel, Morgan, David John , Davies, Thomas E., Dummer, Nicholas F. , Golunski, Stanislaw and Hutchings, Graham J. 2020. Lowering the operating temperature of perovskite catalysts for N₂O decomposition through control of preparation methods. *ACS Catalysis* 10 (10) , pp. 5430-5442. 10.1021/acscatal.0c00698

Publishers page: <http://dx.doi.org/10.1021/acscatal.0c00698>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



Supporting Information

Lowering the Operating Temperature of Perovskite Catalysts for N₂O Decomposition Through Control of Preparation Methods

Nia Richards,¹ James H. Carter,¹ Luke A. Parker,^{1,2} Samuel Pattison,¹ Daniel G. Hewes,¹ David J. Morgan,¹ Thomas E. Davies,¹ Nicholas F. Dummer,¹ Stanislaw Golunski,¹ Graham J. Hutchings^{1*}

¹Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT UK

²Now at; Inorganic Chemistry and Catalysis Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584CG Utrecht (The Netherlands)

*Corresponding author: Hutch@cardiff.ac.uk

Table S1. Table of contents for electronic supplementary information

Page 2	Fig. S1. TGA profile and corresponding derivative as a function of temperature recorded in air (50 ml min ⁻¹) from 30 – 800 °C at 5 °C min ⁻¹ of various precursors. Legend: (a) Citric acid, (b) Oxalic Acid, (c) Barium Nitrate, (d) Praseodymium Nitrate, (e) Cobalt Nitrate, (f) Barium Acetate, (g) Praseodymium Acetate, (h) Cobalt Acetate.
Page 3	Table S2. Pre-treatment and calcination temperature of each catalyst
Page 3	Fig. S2. N ₂ O conversion of PBC SAS (▲) and PrO ₂ impurity as found in PBC SAS (◆) and quartz wool (x) over the temperature range of 200 to 600 °C. Reaction conditions: 1 % N ₂ O/He, total flow 100 ml min ⁻¹ .
Page 3	Fig. S3. SEM-EDX mapping of PBC Citric. Legend: Yellow: Pr, Red: Ba, Green: Co, Blue: O. All scale bars to 1 μm.
Page 4	Fig. S4. SEM-EDX mapping of PBC Oxalic. Legend: Yellow: Pr, Red: Ba, Green: Co, Blue: O. All scale bars to 1 μm.
Page 4	Fig. S5. SEM-EDX mapping of PBC SAS. Legend: Yellow: Pr, Red: Ba, Green: Co, Blue: O.
Page 5	Fig. S6. TEM of PBC SAS catalysts showing the structure of the catalyst as the same throughout the entire system.
Page 6	Fig. S7. Catalytic activity data as a function of time and temperature for the catalysts tested in the manuscript.
Page 6	Fig. S8. N ₂ O conversion of PBC SAS (▲) at the temperature of 450 °C for 22 hours. Reaction conditions: 1 % N ₂ O/He, total flow 100 ml min ⁻¹ .

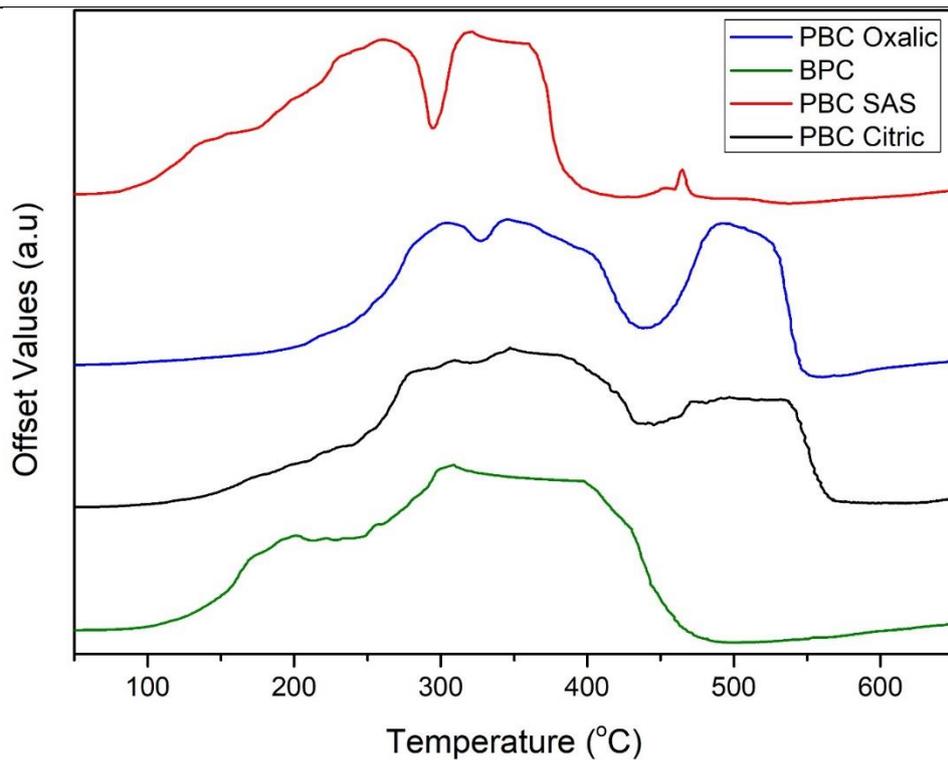


Fig. S9. Temperature programmed reduction of BPC and PBC catalysts, performed at 5 °C min⁻¹ up to 700 °C, under a flow of 10 % H₂/Ar. Legend: Green – BPC, Black – PBC, Blue – PBC Oxalic, Red – PBC SAS.

Fig. S10. Co 3p XPS spectra of PBC and BPC catalysts normalised to the same counts per second scale.

Table S3. Data showing the unit cell parameters of the catalysts discussed in the paper.

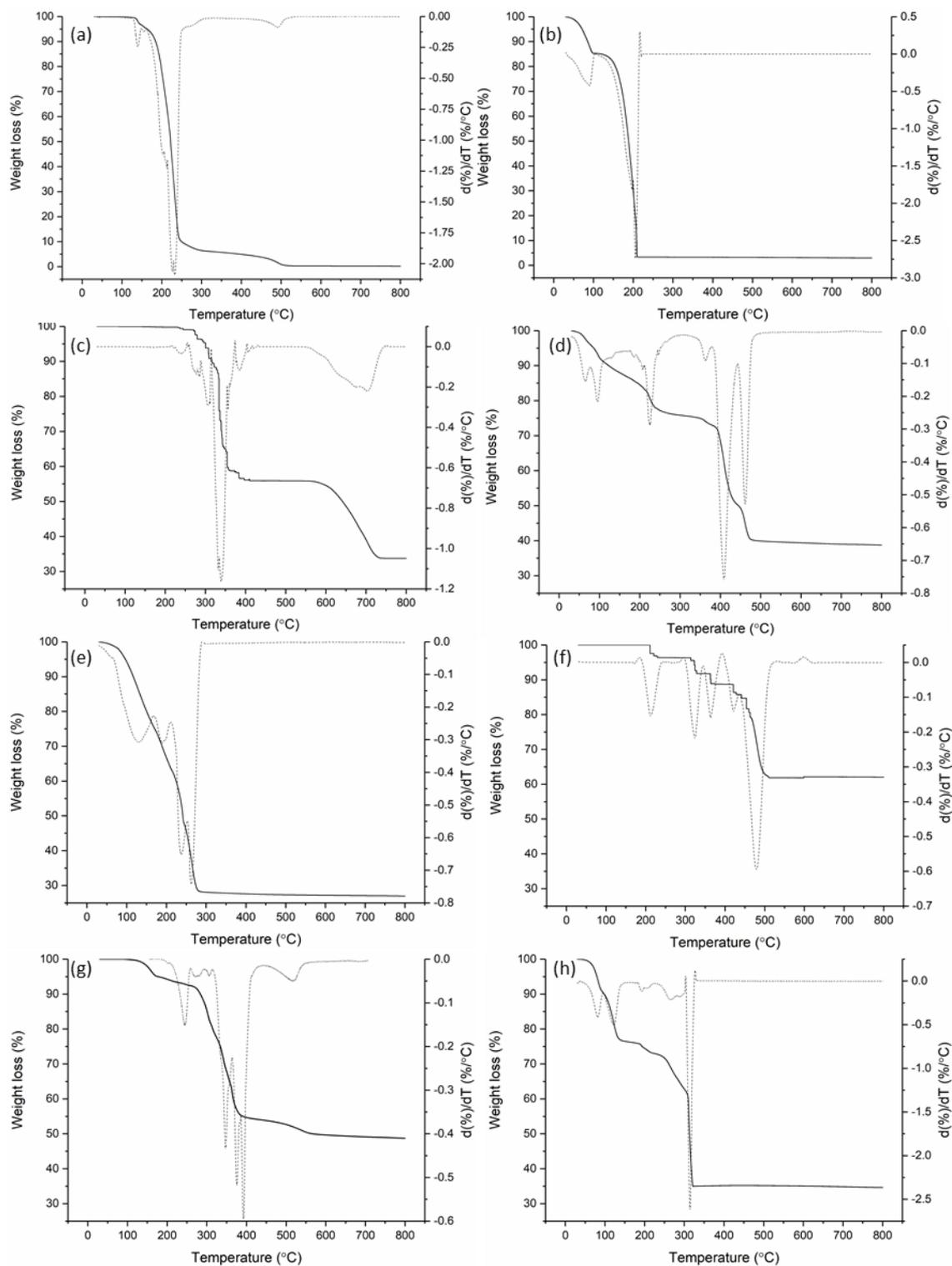


Fig. S1. TGA profile and corresponding derivative as a function of temperature recorded in air (50 ml min^{-1}) from $30 - 800 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C min}^{-1}$ of various precursors. Legend: (a) Citric acid, (b) Oxalic Acid, (c) Barium Nitrate, (d) Praseodymium Nitrate, (e) Cobalt Nitrate, (f) Barium Acetate, (g) Praseodymium Acetate, (h) Cobalt Acetate.

Table S2. Pre-treatment and calcination temperature of each catalyst

Catalyst	Prep method	Pre-treatment temperature (°C)	Calcination Temperature (°C)
BPC	Citric Acid	400	900
PBC	Citric Acid	500	550
PBC	SAS	300	700
PBC	Oxalic	300	700

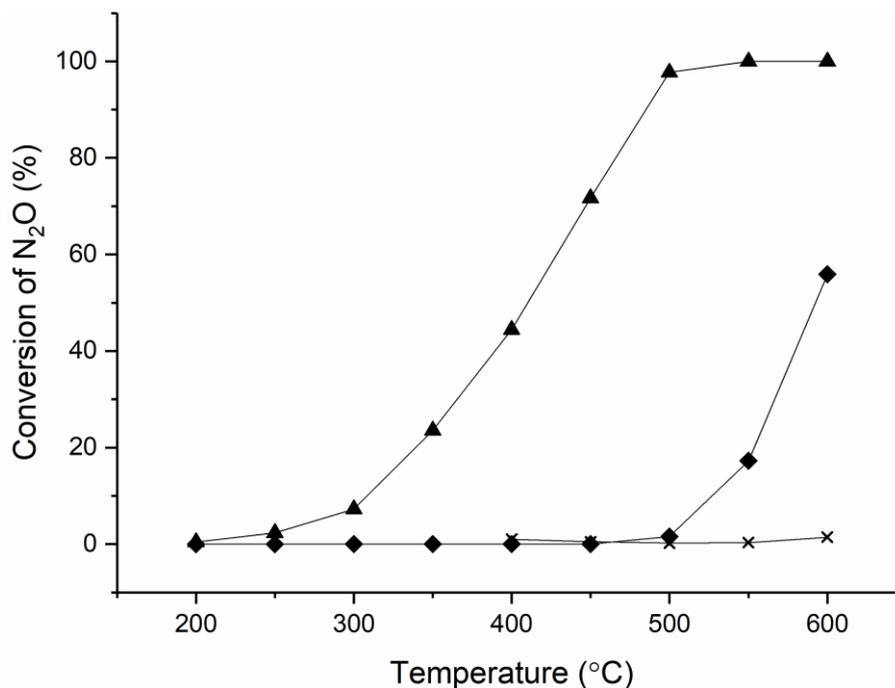


Fig. S2. N₂O conversion of PBC SAS (▲) and PrO₂ impurity as found in PBC SAS (◆) and quartz wool (x) over the temperature range of 200 to 600 °C. Reaction conditions: 1 % N₂O/He, total flow 100 ml min⁻¹.

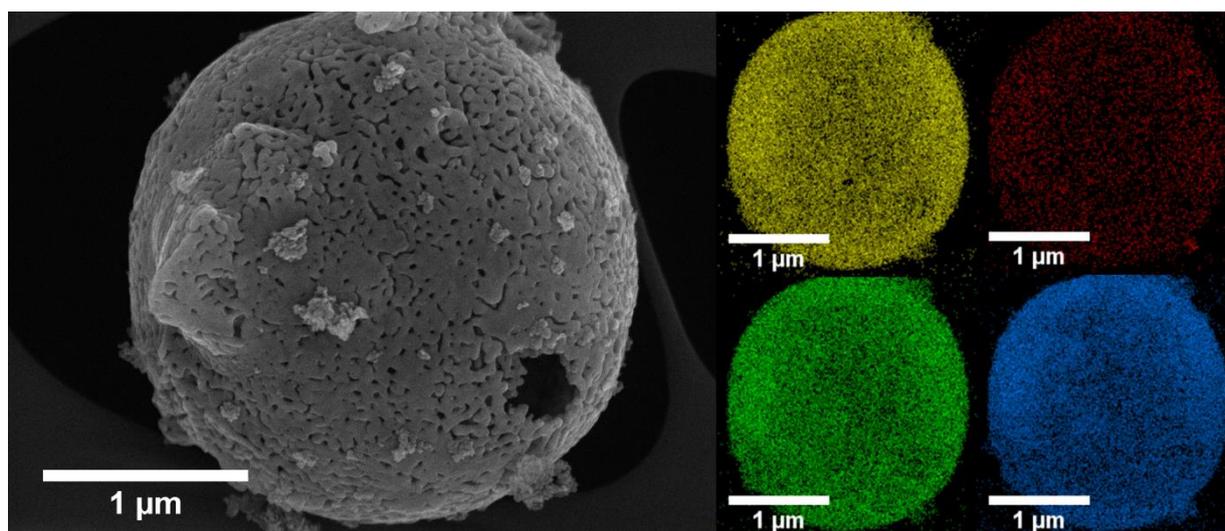


Fig. S3. SEM-EDX mapping of PBC Citric. Legend: Yellow: Pr, Red: Ba, Green: Co, Blue: O. All scale bars to 1 μm.

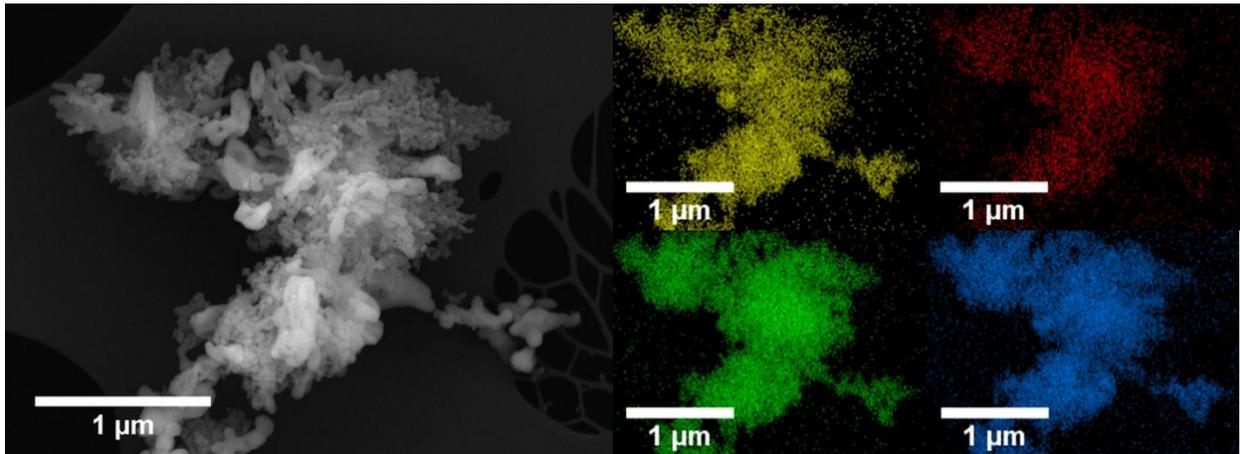


Fig. S4. SEM-EDX mapping of PBC Oxalic. Legend: Yellow: Pr, Red: Ba, Green: Co, Blue: O. All scale bars to 1 μm .

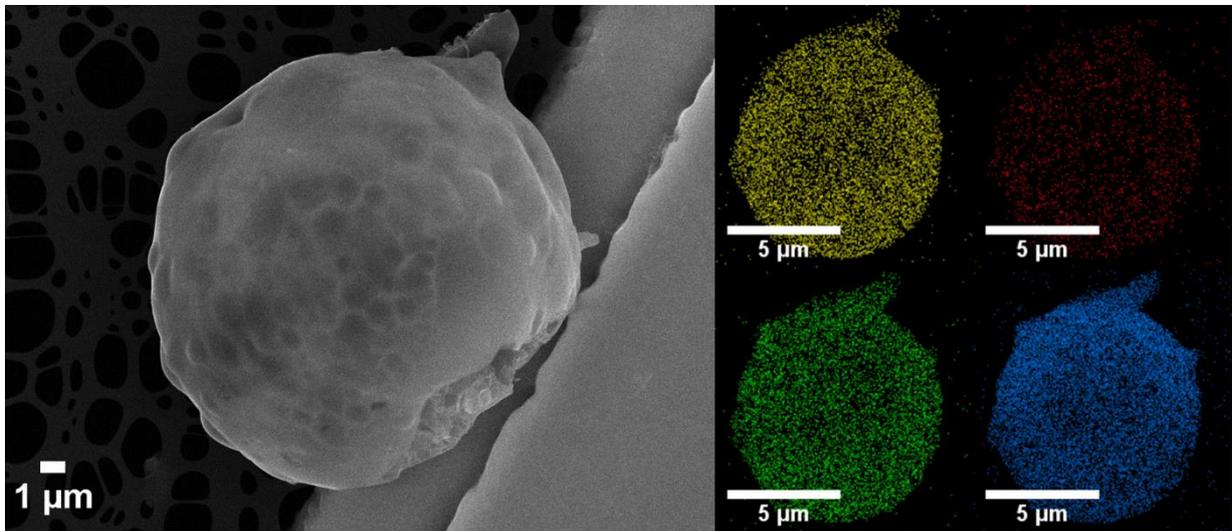


Fig. S5. SEM-EDX mapping of PBC SAS. Legend: Yellow: Pr, Red: Ba, Green: Co, Blue: O.

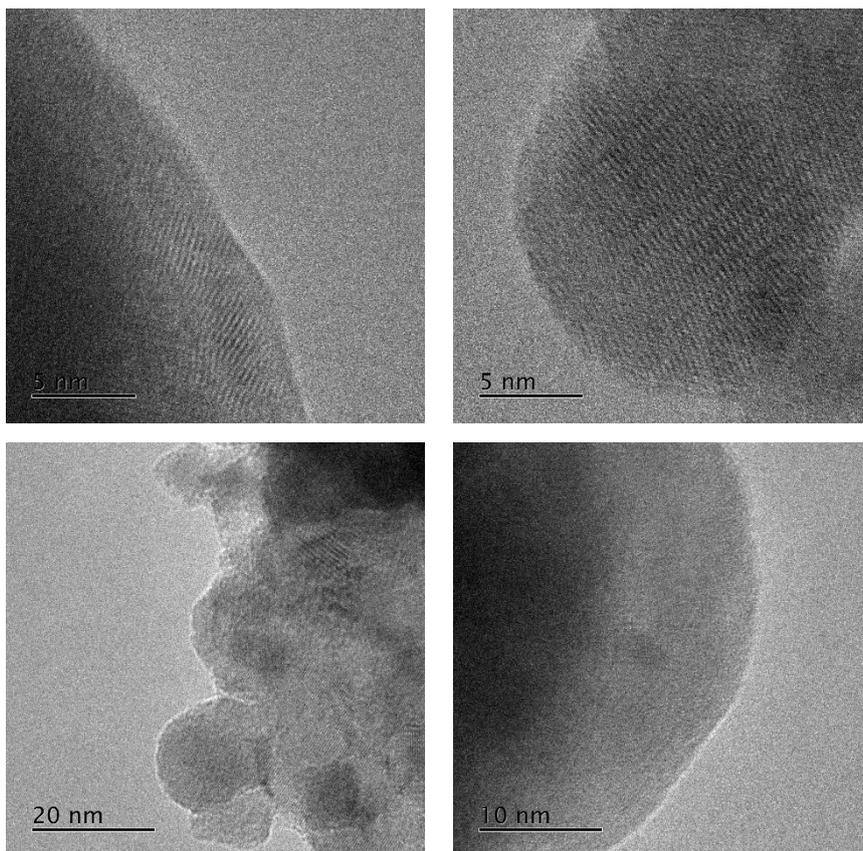


Fig. S6. TEM of PBC SAS catalysts showing the structure of the catalyst as the same throughout the entire system.

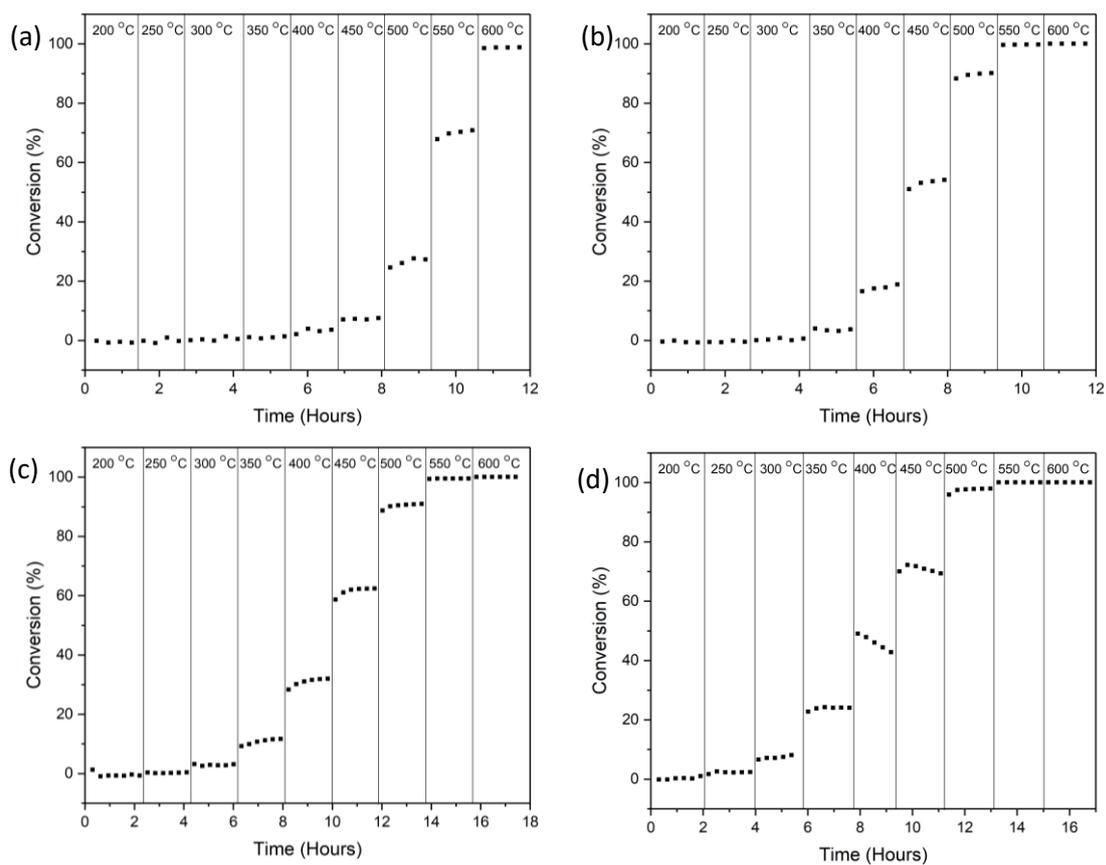


Fig. S7. Catalytic activity data as a function of time and temperature for the catalysts tested in the manuscript. Reaction conditions: 1 % N₂O/He, total flow 100 ml min⁻¹. Legend: a - BPC b - PBC Citric, c - PBC Oxalic, d - PBC SAS.

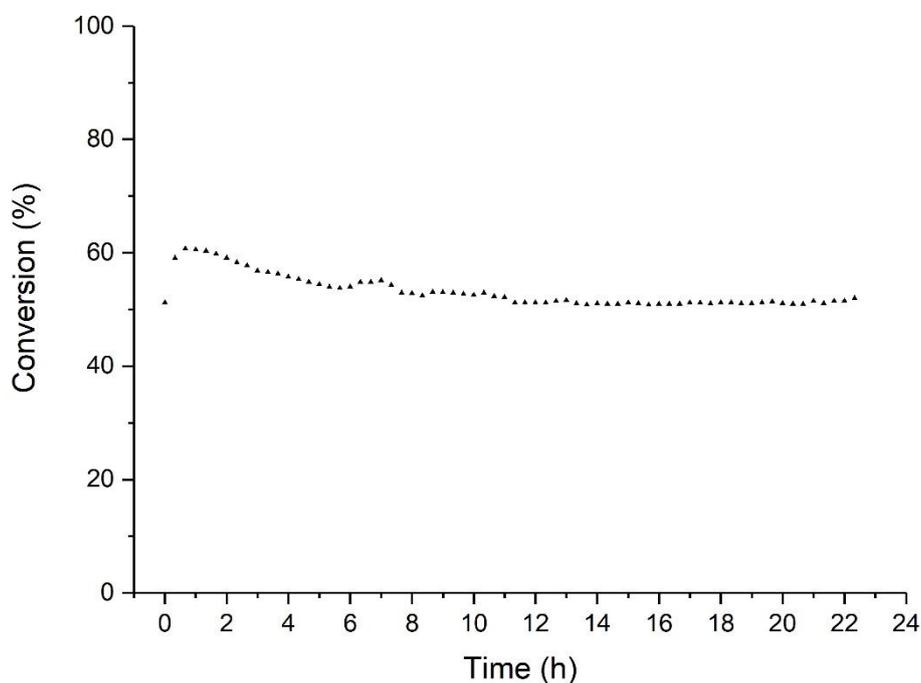


Fig. S8. N₂O conversion of PBC SAS (▲) at the temperature of 450 °C for 22 hours. Reaction conditions: 1 % N₂O/He, total flow 100 ml min⁻¹.

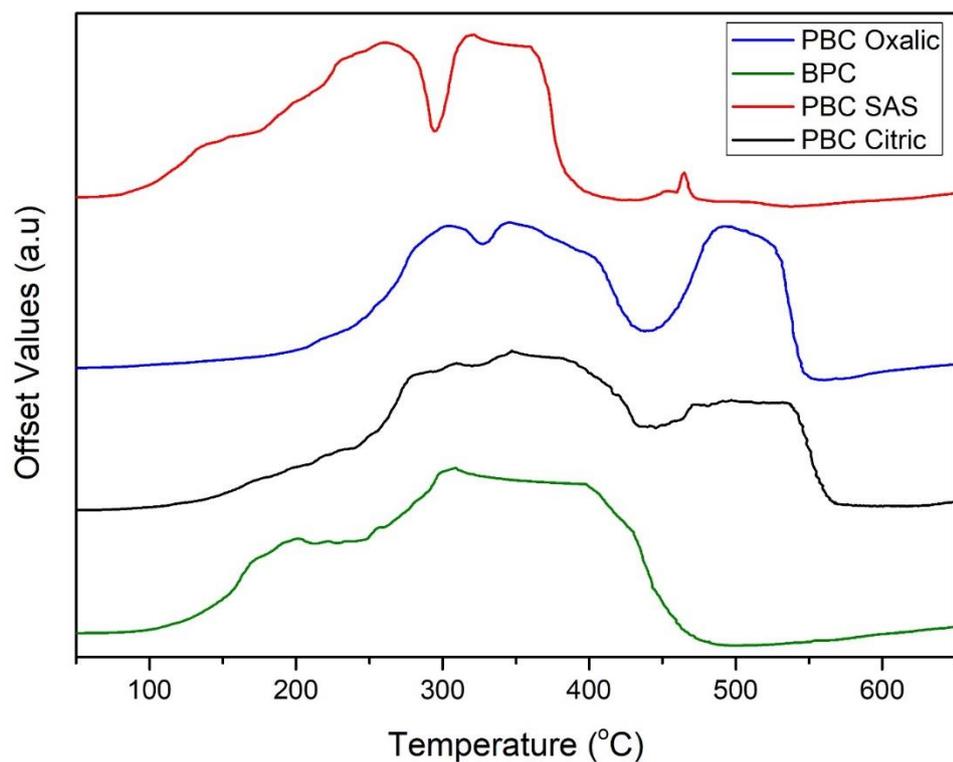


Fig. S9. Temperature programmed reduction of BPC and PBC catalysts, performed at $5\text{ }^{\circ}\text{C min}^{-1}$ up to $700\text{ }^{\circ}\text{C}$, under a flow of $10\% \text{ H}_2/\text{Ar}$. Legend: Green – BPC, Black – PBC, Blue – PBC Oxalic, Red – PBC SAS.

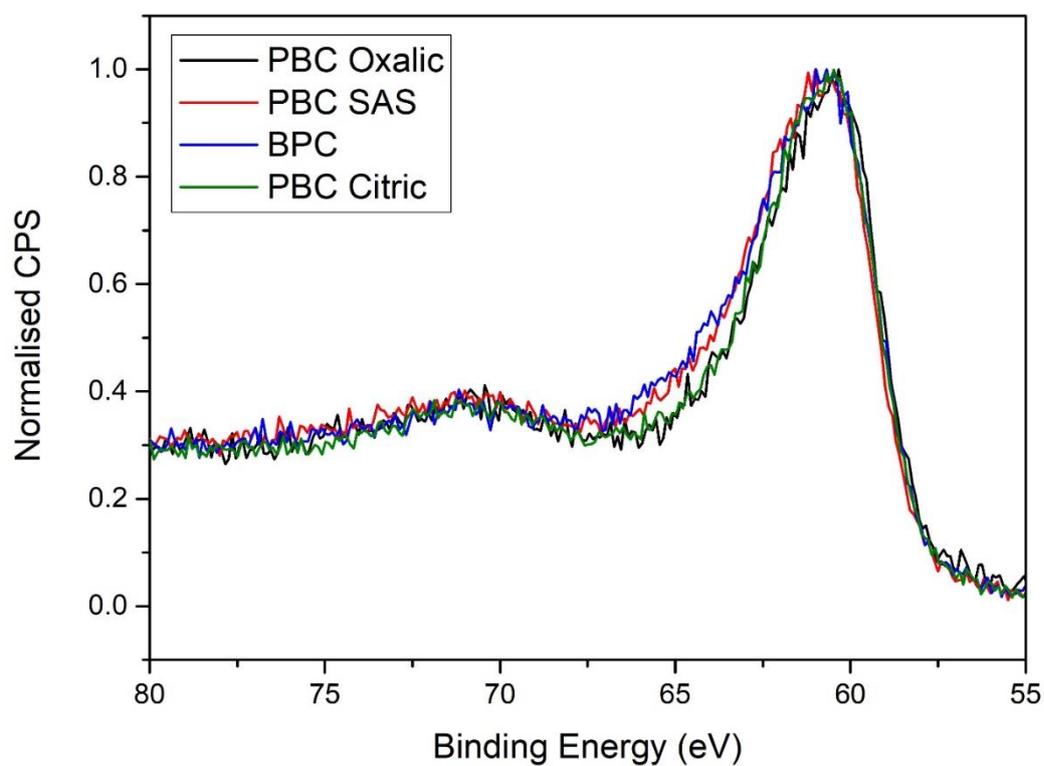


Fig. S10. Co 3p XPS spectra of PBC and BPC catalysts normalised to the same counts per second scale.

Table S3. Data showing the unit cell parameters of the catalysts discussed in the paper.

Compound	Structure	Space Group	Space Group Number [#]	a,b,c (Å)	α,β,γ (°)	Cell volume (pm ³)	Pseudo cubic cell a,b,c (Å)	Pseudo cubic volume (pm ³)
BPC	Orthorhombic	Pnma	62	a 5.34	α 90.0	215 x 10 ⁶	a 3.78	54.4 x 10 ⁶
				b 7.58	β 90.0		b 3.79	
				c 5.38	γ 90.0		c 3.80	
PBC Citric	Cubic	Pm-3m	221	a 3.78	α 90.0	54.0 x 10 ⁶	a 3.78	54.0 x 10 ⁶
				b 3.78	β 90.0		b 3.78	
				c 3.78	γ 90.0		c 3.78	
PBC Oxalic	Tetragonal	P4/mmm	123	a 3.89	α 90.0	116 x 10 ⁶	a 3.89	57.8 x 10 ⁶
				b 3.89	β 90.0		b 3.89	
				c 7.66	γ 90.0		c 3.83	
PBC SAS	Orthorhombic	Pnma	62	a 5.37	α 90.0	221 x 10 ⁶	a 3.80	55.3 x 10 ⁶
				b 7.61	β 90.0		b 3.81	
				c 5.41	γ 90.0		c 3.83	

[#] Space group number as assigned by the International Union of Crystallography.