

Electronic Supplementary Information

Stability vs. Reactivity: Understanding the Adsorption Properties of Ni₃(BTP)₂ by Experimental and Computational Methods

Greig C. Shearer^{a,b}, Valentina Colombo^{c,d,e}, Sachin Chavan^{a,b}, Elisa Albanese^a, Bartolomeo Civalleri^a, Angelo Maspero,^d Silvia Bordiga^{a}*

^a*Dipartimento di Chimica, Università di Torino, NIS Centre of Excellence and INSTM Centre of Reference, via Quarellino 15/A, 10135 Torino, Italy*

^b*(present address) inGAP centre of Research-based Innovation, Department of Chemistry, University of Oslo, Sem Saelandsvei 26, N-0315 Oslo, Norway*

^c*Department of Chemistry University of California, Berkeley, California 94720, United State*

^d*Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy*

^e*(present address) Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy.*

Table of Contents

Content	Page no.
Capillary powder X-ray diffraction	3
PXRD – Confirmation of Stability to Pellet Pressing	4
Sorption measurements	5
Table of the calculated and experimental FTIR vibrational frequencies of $\text{Ni}_3(\text{BTP})_2$ and their assignment	6
References	7

Capillary PXRD

The samples were prepared in a controlled atmosphere by first activating $\text{Ni}_3(\text{BTP})_2$ in the same conditions as in the FTIR measurements and placing the vacuum cell into a glovebox to transfer the powder into 1 mm boron-silicate capillaries. The patterns were collected with a PW3050/60 X'Pert PRO MPD diffractometer from PANalytical working in Debye-Scherrer geometry, using as source the high power ceramic tube PW3373/10 LFF with a Cu anode equipped with Ni filter to attenuate K_β and focused by a PW3152/63 X-ray mirror. Scattered photons were collected by a RTMS (Real Time Multiple Strip) X'celerator detector.

Figure S1 shows the capillary XRD patterns of $\text{Ni}_3(\text{BTP})_2$ before and after 573 K activation:

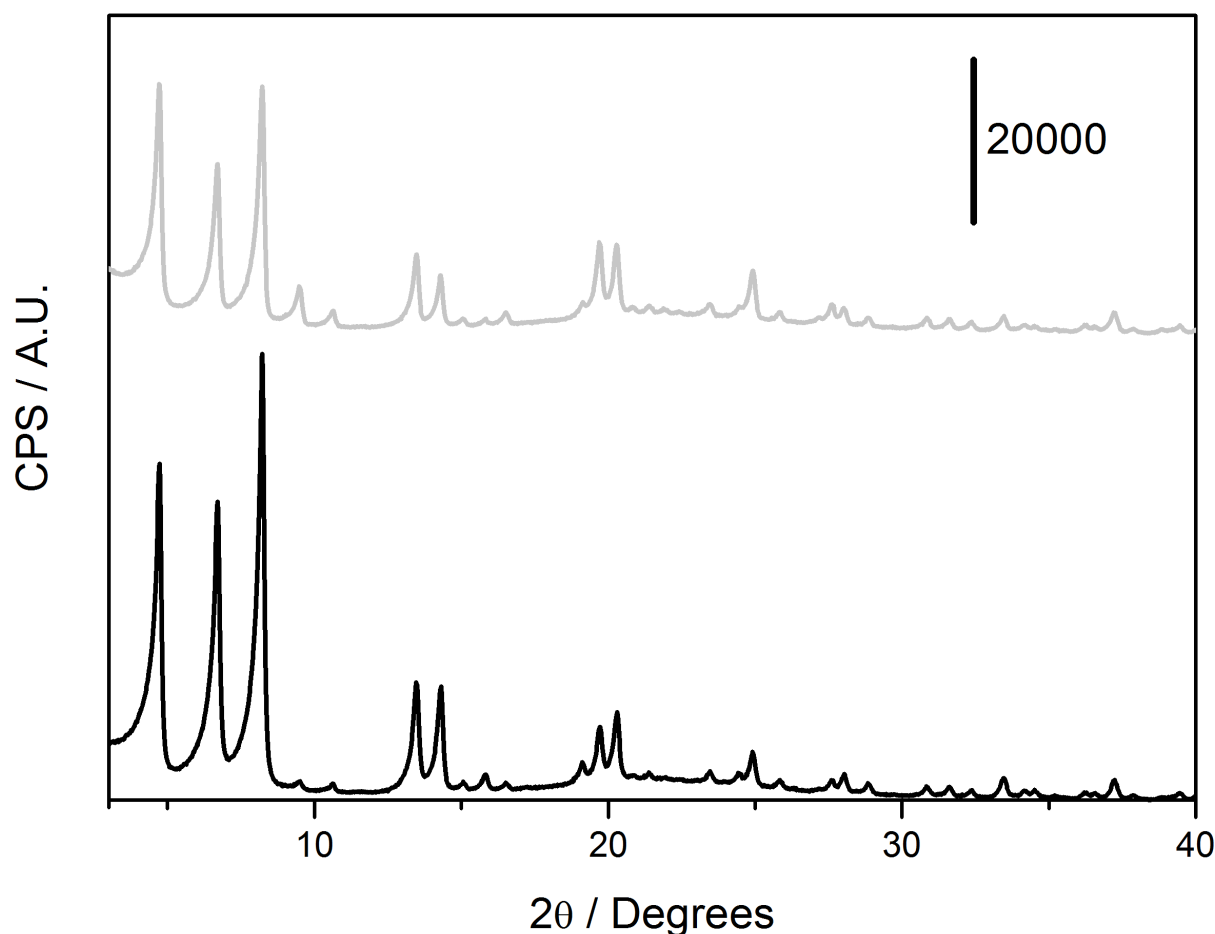


Figure S1 Capillary PXRD patterns of methanol exchanged $\text{Ni}_3(\text{BTP})_2$ as synthesised (top, grey) and activated at 573 K for 16 hours (bottom, black).

The figure shows that the patterns are identical with regards to the observed reflections and differ only in their relative intensities. It can therefore be concluded that the material survived the activation temperature of 573 K used throughout the work presented in this paper.

PXRD – Confirmation of Stability to Pellet Pressing

In order to verify that the structural integrity of $\text{Ni}_3(\text{BTP})_2$ is maintained when pressed into the self-supporting wafers used for the FTIR measurements, PXRD patterns were recorded before and after utilising a pellet press to apply pressures of up to 5 tons.

Figure S2 compares the PXRD pattern of as synthesised $\text{Ni}_3(\text{BTP})_2$ with those recorded after the application of pressures of 1 and 5 tons.

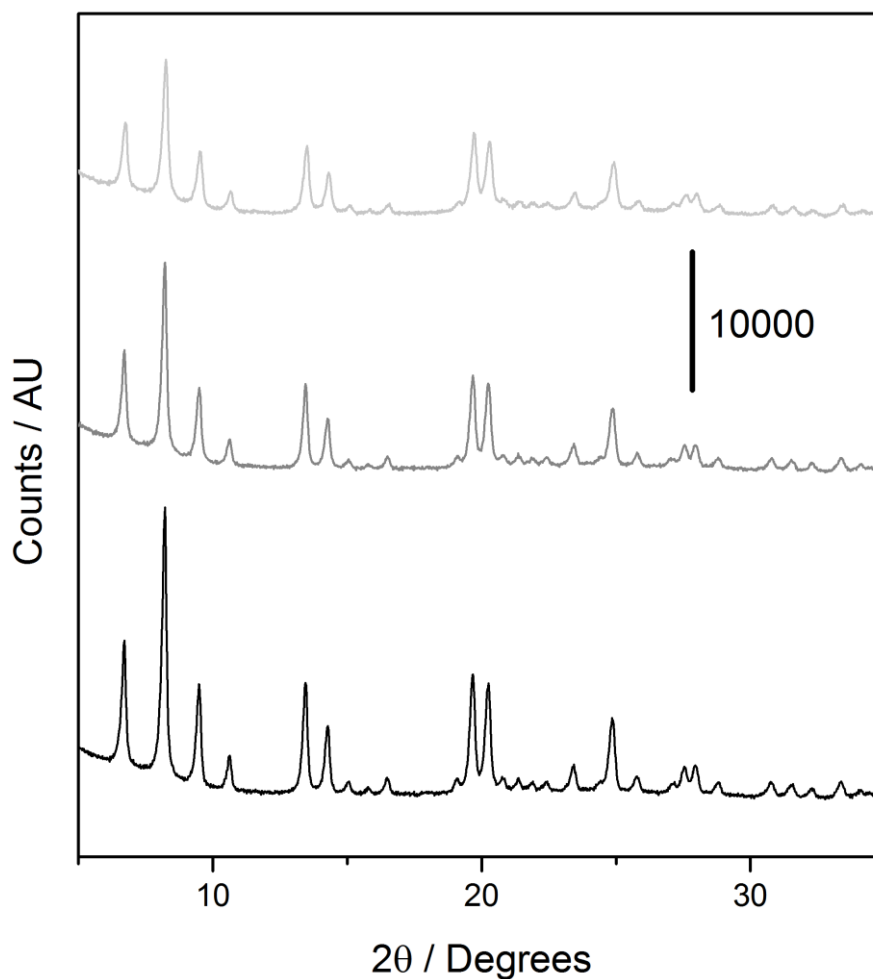


Figure S2 PXRD patterns of $\text{Ni}_3(\text{BTP})_2$: as synthesised (bottom, black); after the application of 1 ton of pressure (middle, dark grey); and after the application of 5 tons of pressure (top, light grey) .

The figure shows that all patterns are identical with regards to the observed reflections and differ only slightly in their relative intensities. It can therefore be concluded that $\text{Ni}_3(\text{BTP})_2$ maintains its structural integrity when pressed into the self-supporting wafers on which the FTIR measurements were made.

Sorption measurements:

Surface area, pore volume and pore size distribution were obtained by N₂ adsorption measurements carried out at 77 K on a Micromeritics ASAP 2020 sorption analyzer. The specific surface area of the materials were calculated using the Brunauer–Emmet–Teller (BET) method, while the micropore volume was determined with the t-plot method, adopting the Harkins and Jura equation of thickness.

Table S1 Shows a comparison of the results of surface area, pore volume, and pore size distribution measurements performed on Ni₃(BTP)₂ when activated overnight at 573 K as opposed to the temperature of 523 K recommended by Long et al.¹ The results compared are the calculated BET and Langmuir surface areas as well as the micropore surface area and volumes of the two samples.

Table S1: Surface area (m² g⁻¹) and pore volumes (cm³ g⁻¹) of Ni₃(BTP)₂ activated at 523 and 575 K

	S_{BET}^a	S_{Lang}^a	S_{micro}^b	V_{micro}^c
523 K	1026	1362	940	0.44
573 K	1024	1359	939	0.44

^aTotal area evaluated following the BET model in the standard $0.05 < P/P_0 < 0.25$ pressure range.

^cMicropore surface area and volume obtained from the t-plot. The micropore area is evaluated considering S_{BET} as the surface area of the material.

These results show that neither the surface area nor micropore volume of the material was affected when activating at 300 °C rather than the recommended 523 K. Combined with the capillary XRD measurements, it is confirmed that activating Ni₃(BTP)₂ at 573 K rather than 523 K does not impact the structural integrity of the material and that it also maintains its microporosity.

Table S2: Calculated and experimental IR active vibrational frequencies (cm^{-1}) of $\text{Ni}_3(\text{BTP})_2$ in the 1600-600 cm^{-1} range with description of the normal modes.

Exp	Calc	Description
462	452 (464)	N-Ni-N bend in plane
496	488 (500)	Ni-N asym stretch
632	627 (643)	C-C-C bending inter-ring
678	671 (688)	C-C-C bend op ^b out of plane phenylic
762	756 (775)	C-C-C bend op ^b in plane phenylic
857	833 (854)	C-H bend ip pyrazolic and bend ip ^a phenylic out of plane
1017	1011 (1037)	Ring deformation in plane pyrazolic
1075	1078 (1106)	N-C-H bend ip ^a in plane
1135	1134 (1163)	H-C-C bend ip ^a in plane phenylic
1188	1195 (1226)	N-C-H bending op ^b in plane
1253	1257 (1289)	N-N stretch + C-H bend in plane
1329	1326 (1360)	C-N sym stretch
1358	1354 (1389)	C-C symm Stretch + C-N asymm stretch
1402	1406 (1442)	C-N asymm stretch
1556	1553 (1593)	C-C stretch inter-ring
1598	1598 (1639)	Ring deformation in plane phenylic

^a ip = In phase

^b op = Out of phase

References

1. V. Colombo, S. Galli, H. J. Choi, G. D. Han, A. Maspero, G. Palmisano, N. Masciocchi and J. R. Long, *Chem. Sci.*, 2011, **2**, 1311-1319.