Electronic Supplementary Material

# Molybdenum blue nano-rings: an effective catalyst for the partial oxidation of cyclohexane

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## • GC/MS characterization of the reaction products from hydrocarbon oxidation using fresh MB, thermally treated MB and Co-naphthenate catalysts.

	Product	%
Conversion		6
	Cyclohexanol	52
	Cyclohexanone	40
	Adipic acid	1
	Hexyl esters	1.4
	Cyclohexyl esters	4.4
	Long chain carbon	0
	products (e.g. dimers, etc)	
	CO, CO <sub>2</sub>	0
Total selectivity		98.8%
Carbon balance		98.8%

Table S1: Catalytic performance of fresh MB in cyclohexane oxidation<sup>†</sup>.

†*Reaction conditions*: cyclohexane (8.5 g), 140 °C, 3 bar O<sub>2</sub>, 17 h reaction time, 6 mg MB.

	Product	%
Conversion		8.7
Selectivity	Cyclohexanol	44
	Cyclohexanone	41
	Adipic acid	2
	Hexyl esters	4.8
	Cyclohexyl esters	5
	Long chain carbon	1.8
	products (e.g. dimers, etc)	
	CO, CO <sub>2</sub>	0
Total selectivity		98.6%
Carbon balance		98.6%

**Table S2**: Catalytic performance of Co-naphthenate in cyclohexane oxidation<sup>†</sup>.

*†Reaction conditions*: cyclohexane (8.5 g), 140 °C, 3 bar  $O_2$ , 17 h reaction time, 6 mg cobalt naphthenate.

• NMR characterization of the reaction products from hydrocarbon oxidation using fresh MB, thermally treated MB and Co-naphthenate catalysts.





**Figure S1**: NMR profiles of products obtained from MB and Co-naphthenate catalysed oxidation of various cyclic hydrocarbons.

<sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>Cl) profiles of a) the liquid product of the MB-catalysed oxidation of cyclohexane, cyclohexane, cyclohexanol and cyclohexanone; and b) liquid products of cobalt naphthenate-catalysed cyclohexane oxidation; <sup>13</sup>C NMR profiles of c) liquid product of MB-catalysed oxidation of cyclohexane, cycl



**Figure S2**: <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>COD) profiles of the solid products from MBcatalysed oxidation of adipic acid and cyclohexane.

• Comparison between as-prepared MB and MB thermally treated in He

**Figure S3:** Raw XRPD patterns for (a) fresh MB, and (b) MB that has been heated in Heair at 180 °C for 48h.



**Figure S4**: XRPD patterns after signal filtering, smoothing and baseline correction for (a) fresh MB, and (b) MB that has been heated in Heat 180 °C for 48h.

The two XRD patterns (before and after thermal treatment of the MB) are very similar, suggesting that the self-assembled structure of MB nano-rings remained intact after the thermal treatment in He and if any change took place, it was related to the removal of a small amount of lattice oxygen only, which occurs without a catastrophic collapse of the superlattice or ring structure. This is an important point, as it is from this supposition, which is borne out by the STEM observations presented in Fig. S5 that a series of other further experiments were based.

Additionally, from the XRD patterns (Fig. 1 main body, and Figs. S3 & S4), it is not possible to detect any distinct reflections from more conventional molybdenum oxide phases (*i.e.* MoO<sub>3</sub> or MoO<sub>2</sub>). It should also be stressed that neither MoO<sub>3</sub> nor MoO<sub>2</sub> are expected to be present in our MB samples, due to the nature of the preparation procedure we have employed. In fact, MoO<sub>2</sub> is obtained *via* reduction of MoO<sub>3</sub><sup>1</sup> and since no reduction step has been used in our preparation, the possible presence of MoO<sub>2</sub> can be discounted. On the other hand the MoO<sub>3</sub> phase could be in principle be obtained from molybdate ions (MoO<sub>4</sub><sup>2-</sup>) in solution.<sup>2</sup> However, our preparation involves the oxidation of Mo powder with H<sub>2</sub>O<sub>2</sub> which leads to molybdate species. Moreover, all of the current protocols to obtain MoO<sub>3</sub> from molybdate species also need the presence of a highly acidic medium (*e.g.* 3M HCl),<sup>3</sup> and this methodology has deliberately not been employed in our work, precisely to encourage the assembly of molybdate chains to nano-rings, and not regular MoO<sub>3</sub> polymorph formation.

STEM characterization of MB material after thermal treatment



**Figure S5:** STEM-HAADF micrographs of the MB material after thermal treatment at 180 °C for 48 h in flowing He. Figs. (a) and (b) clearly demonstrate that the material still has a propensity to form a molecularly bonded superlattice structure after drop casting onto the grid. Figs. (c) and (d) show that the individual ring structures are still largely retained after the thermal treatment.

### References

- 1. J.-G. Choi and L.T. Thompson, Appl. Surf. Sci., 1996, 93, 14.
- 2. S. R. Bare, Langmuir, 1998, 14, 1500.
- 3. J. Jiang, J. Liu, S. Peng, D. Qian, D. Luo, Q. Wang, Z. Tiana and Y. Liu, J. Mater.

Chem. A, 2013, 1, 2588.