De novo design of microporous transition metal oxides

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***Ab initio* Hartree–Fock calculations are performed on the molybdenum and tungsten trioxides and bronzes, obtained by inserting alkali metal atoms or larger species in the MO_3 framework; we examine four known polymorphs and two new structures with a microporous architecture, and characterise their relative stability; we also explore the synthesis conditions under which the microporous polymorphs may be obtained, by designing potential organic templates.**

The structural chemistry of the Mo and W trioxides and bronzes comprises several known polymorphs, such as the perovskite (PV) structure of WO_3, $NaMoO_3$ and $NaWO_3$, the layered (L) α-MoO_3, hexagonal (Hex) $K_{0.33}WO_3$ and pyrochlore (PY) Cs_xWO_3. The bronzes are obtained by inserting extra species into the empty interstices of the host MO_3 lattice, and can be described as comprising an MO_3 framework, in whose pores are located the inserted, or extra-framework, cations.

In the PV, Hex and PY structures, the framework is built entirely of corner-sharing MO_6 octahedra, which connect into 4-membered rings in the PV, and 6-membered rings in the Hex and PY polymorphs. The 6-membered rings form hexagonal channels, which are parallel in the Hex, and intersect in the PY structure; the dimension of the extra-framework voids increases therefore in the order of PV < Hex < PY. In the L polymorph, the MO_6 octahedra connect corner- and edge-sharing in the *bc* plane, leaving a layered structure along *a*. Interstices are present in the interlayer region.

In recent work, we highlighted the importance of the M–O bonding pattern,[1–2] of Coulomb[2] and structural forces,[3] and of steric constraints[4] in the solid state chemistry of Mo and W oxides and bronzes. We now examine the relative stability of the framework structures in the insertion compounds.

A common feature of transition metal oxides (TMOs) are structural distortions due to off-centerings of the metal ions M in their coordination octahedra. In PV materials, the off-centering of M hybridises a set of levels, which in the cubic phase are of M–O non-bonding character, into π M–O bonding (in the valence band) and antibonding (in the conduction band) combinations.[1] When the metal ion has formal electronic configuration d^0, as in MoO_3 and WO_3, only the M–O bonding level is filled, and the distortion is stable; in the bronzes, the inserted atoms ionise and cede electrons to the host lattice, populating the M–O antibonding level at the bottom of the conduction band, which opposes the distortion. The PV-structured W bronzes are stable in the cubic phase.[1] The M–O bonding pattern in the valence and conduction bands is common to all the polymorphs examined, and a partial population of the conduction band will oppose off-centerings of M. Here, we are interested in the insertion compounds A_xMO_3, in which the metal ion has configuration d^x; we shall therefore consider only framework structures in which the M ions are on-centre in their coordination octahedra. We have optimised, under the above constraint, the structure of the four cited polymorphs of WO_3 and MoO_3, using a periodic restricted Hartree Fock Hamiltonian, as implemented in CRYSTAL95.[5] Basis set, tolerances and computational conditions are the same as described in refs. 2 and 3; a convergence criterion of 10^{-6} E_h was used in the geometry optimisation. From the calculated energies, we have constructed a scale of relative stability for the host MO_3 framework; results are summarised in Table 1. We note that the undistorted L polymorph is highly unstable with respect to the other three structures examined, suggesting that insertion compounds based on L-MoO_3 would not be stable following the cation insertion. The relative stability of the other three polymorphs (PV, Hex and PY) parallels their relative density, as higher electrostatic energies stabilise the densest structures.

Moving from the binary oxides to the insertion compounds, the relative stability of the polymorphs is altered; a balance between the Coulomb and steric effects stabilises the structures whose interstices have dimensions comparable with the size of the inserted ions. The experimentally reported crystal structures, for instance of the W bronzes, on increasing the size of the inserted ion, move from the cubic-PV form of $NaWO_3$ towards the Hex K_xWO_3 and Rb_xWO_3, to the PY structure obtained by insertion of Cs and of primary and secondary ammonium salts.[6] The importance of the short-range repulsion between the inserted ion and the MO_3 framework increases with increasing ionic size of the extraframework ion; in ref. 4 we estimated it as 0.52 eV for the relatively small K^+ ion in the hexagonal channels of Hex-WO_3. The energy arising from the short-range repulsion is therefore sufficient to offset the energy difference between the framework structures examined, shifting the stability towards the polymorphs with interstices of the appropriate dimensions. Extraframework ions present during the synthesis of the host MO_3 framework may therefore effectively act as inorganic templates, or structure-directing agents.

The use of organic cationic templates is a standard procedure in the synthesis of microporous aluminosilicates (zeolites), where the correlation between the shape of the organic cation and that of the pore structure obtained is now recognised.[7] The energy difference between the silica polymorphs is in the range of 0.1–0.2 eV per formula unit, much smaller than that we calculated in the Mo and W trioxides (excluding the L polymorph, the energy range of the PV, Hex and PY structures is of *ca.* 0.5 eV per formula unit). We attribute the higher energy difference in the trioxides to two effects: (i) the higher ionic charges, which increases the Madelung field, and (ii) the rigidity of the octahedral framework of TMOs, compared to the more flexible tetrahedral framework of silicates. We note however that the difference in framework energy is still in the range of the steric repulsion, and can be reversed, as confirmed by the different stable structures of the alkali W bronzes. We believe therefore that a template/host approach, similar to that employed in the synthesis of zeolites, can also be applied to obtain novel TMO frameworks. The advantages of TMOs with larger pores are manyfold: for example, such materials would better satisfy the requirement for high ionic conductivity and

Table 1 Relative energy (in eV per formula unit) of the MO_3 frameworks examined

Material	PV	Hex	PY	L	$H^{2\times1}$	$H^{2\times2}$
MoO_3	0.00	0.238	0.607	4.281	0.943	1.128
WO_3	0.00	0.315	0.725	5.471	0.902	1.393

structural stability, necessary in electro- and photo-chromic applications, and in Li batteries. Furthermore, if the pore sizes reach the dimension of small organic molecules, microporous TMOs would allow heterogeneous catalytic applications, and combine the molecular-sieve characteristics of zeolites with the higher acidic strength and redox properties of early transition metal cations.

Attempts to use organic cations, usually quaternary ammonium salts, to template novel TMO frameworks have been reported,[8] but resulted in the formation of inorganic polyanions, the Keggin structures, rather than extensive M–O frameworks. We now examine the topic with a more analytic approach, exploiting the insight that can be obtained from computer modelling to provide information on the relative stability and on the required synthesis conditions for new, microporous structures of TMOs. In particular, we employ a strategy recently developed for the *de novo* design of structure-directing agents in zeolites:[9] given a target microporous architecture, the organic template is gradually grown within the pores, to design molecules which provide optimal space filling and maximum interaction energy with the selected porous system, thus helping to direct the synthesis towards the target structure.

The method requires the knowledge of the porous TMO structure as starting point. This is a challenging task by itself, since microporous structures built up on MO_6 octahedra have so far never been reported; the only exceptions are the OMS sieves based on edge-sharing of $Mn^{IV}O_6$ units,[10] in which the framework has stoichiometry MO_2 and not MO_3 as required for the MO and W oxides. The first problem to solve is therefore that of designing a suitable target structure.

The PV and Hex structures can be imagined as a 2D arrangement, repeated by corner-sharing of the axial oxygens along the third direction; in the design of new structures we retained this 2D approach, as a useful starting point. If we define a new building block, as a chain of *n* aligned edge-shared octahedra, a series of new structures can be obtained from the same connectivity of the PV and Hex phases, replacing single octahedral units with alternating chains of *m* and *n* edge-shared octahedra. Given the method of construction, we denote the new structures $PV^{m\times n}$ and $H^{m\times n}$ (the 1×1 structures reproduce the PV and Hex polymorphs). All the new structures have an MO_3 framework stoichiometry. We have calculated the electronic distribution, geometry and energy of the first two members of the $H^{m\times n}$ series: $H^{2\times1}$ and $H^{2\times2}$ (Fig. 1). The new structures represent local minima in the potential energy surface; hence, if synthesised, they would have a non-zero activation barrier towards phase transformations. The calculated internal energy is compared in Table 1 with that of the known polymorphs. The new structures are unstable, as expected; the energy difference has nonetheless the same order of magnitude as that between the known polymorphs and is within the range of the steric energy. It may therefore be possible to overcome this difference with steric effects; given the relative instability of the framework, the template must be selected carefully, and must fit tightly in the porous structure to stabilise these particular polymorphs; which is probably why previous attempts with ‘randomly’ selected templates failed.

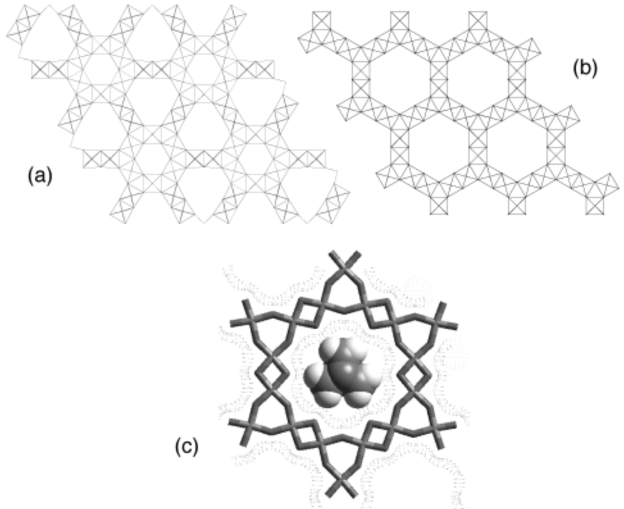

Fig. 1 Disposition of octahedra in the MO_3 framework of the $H^{2\times1}$ (a) and $H^{2\times2}$ (b) structures; diazobicyclooctane molecule, as located by the program ZEBEDDE[9] inside the pores of the $H^{2\times2}$ structure (c)

Finally, we applied the *de novo* method to design templating agents specific for the $H^{2\times1}$ and $H^{2\times2}$ structures. The interactions between the framework and the organic template were evaluted *via* interatomic potentials;[11] energy-minimised structures were obtained for each template in a rigid host MO_3 framework, ignoring the M-template terms. Candidate templates are ranked by their calculated binding energy (E_B) with the host lattice: the higher the E_B the more favourable the molecule is considered as a template.[7] The pores of the $H^{2\times1}$ structure have dimensions comparable to unsubstituted hydrocarbon chains, suggesting that *n*-amines or *n*-diamines, as used in zeolite synthesis may be suitable as templates. The pores of the $H^{2\times2}$ polymorph have a size comparable to the 12-membered rings in zeotypes, and allow the insertion of more structured organic moieties. Our calculations reveal that adamantane and diazobicyclooctane derivatives are of suitable dimensions, the latter [Fig. 1(c)] having the highest E_B. Future experimental studies will test the prediction of these calculations.

In summary, our computational study has shown the feasibility on energetics grounds of an extensive range of microporous chemistry based on octahedral MoO_3 and WO_3, and has suggested that such structures may be synthesised using a host/guest templating approach.

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Notes and References

1 F. Corà, M. Stachiotti, C. O. Rodriguez and C. R. A. Catlow, *J. Phys. Chem. B*, 1997, **101**, 3945; M. Stachiotti, F. Corà, C. O. Rodriguez and C. R. A. Catlow, *Phys. Rev. B*, 1997, **55**, 7508.
2 F. Corà, A. Patel, N. M. Harrison, R. Dovesi and C. R. A. Catlow, *J. Am. Chem. Soc.*, 1996, **118**, 12 174.
3 F. Corà, A. Patel, N. M. Harrison, C. Roetti and C. R. A. Catlow, *J. Mater. Chem.*, 1997, **7**, 959.
4 F. Corà and C. R. A. Catlow, *Solid State Ionics*, in press.
5 R. Dovesi, V. R. Saunders, C. Roetti, M. Causà, N. M. Harrison, R. Orlando and E. Aprà, *CRYSTAL95 User’s Manual*, Univ. of Torino, Italy, 1996.
6 P. J. Wiseman and P. G. Dickens, *J. Solid State Chem.*, 1976, **17**, 91; I. Tsuyumoto, A. Kishimoto and T. Kudo, *Solid State Ionics*, 1993, **59**, 211; T. Kudo, J. Oi, A. Kishimoto and M. Hiratami, *Mater. Res. Bulletin*, 1991, **26**, 779; P. Zavalij, J. D. Guo, M. S. Whittingham, R. A. Jacobson, V. Pecharsky, C. K. Bucker and S. J. Hwu, *J. Solid State Chem.*, 1996, **123**, 83.
7 M. E. Davis and R. F. Lobo, *Chem. Mater.*, 1992, **4**, 759; D. W. Lewis, C. M. Freeman and C. R. A. Catlow, *J. Phys. Chem.*, 1995, **99**, 11 194.
8 G. G. Janauer, A. Dobley, J. D. Guo, P. Zavalij and M. S. Whittingham, *Chem. Mater*, 1996, **8**, 2096.
9 D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas and G. J. Hutchings, *Nature*, 1996, **382**, 604.
10 Y. F. Shen, S. L. Suib and C. L. Oyoung, *J. Am. Chem. Soc.*, 1994, **116**, 11 020.
11 cff91_czeo molecular forcefield and Discover 4.0, Molecular Simulations Inc., San Diego, 1997.

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