CONTEMPORARY INORGANIC CHEMISTRY
22CMD111

Semester 2 22/23   Online Long-window Exam paper

This is an online long-window examination, meaning you have **23 hours** in which to complete and submit this paper. How you manage your time within the 23-hour window is up to you, but we expect you should only need to spend approximately **2 hours** working on it. If you have extra time or rest breaks as part of a Reasonable Adjustment, you will need to add this to the amount of time you are expected to spend on the paper.

It is your responsibility to submit your work by the deadline for this examination. You must make sure you leave yourself enough time to do so.

It is also your responsibility to check that you have submitted the correct file.

Exam Help
If you are experiencing difficulties in accessing or uploading files during the exam period, you should contact the Exam Helpline. For urgent queries please call **01509 222900**.
For other queries email examhelp@lboro.ac.uk

You may handwrite and/or word process your answers, as you see fit.

Answer **ALL** questions, Show **ALL** of your working.

1. a) A naturally occurring zeolitic material which intercalates alkali and alkaline-earth metal cations is shown in Figure 1. It has a particular affinity for caesium and strontium cations which enables clean-up applications in the nuclear industry e.g. at the SIXEP (Sellafield Ion Exchange Plant) where it is used as a sequestration agent for ^{90}Sr and ^{137}Cs.
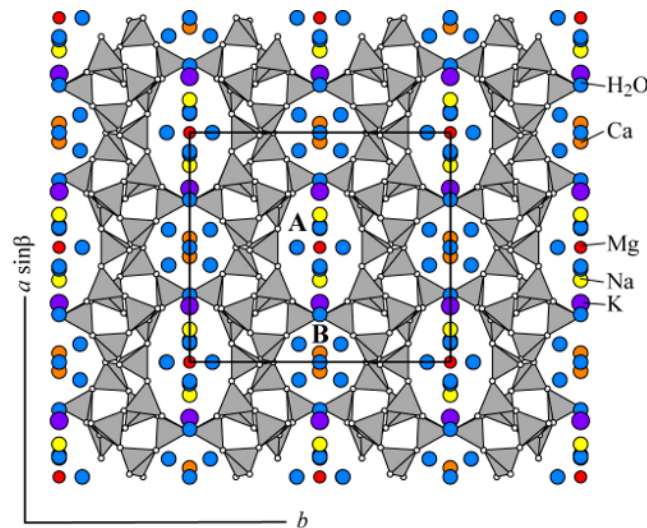

Figure 1: The crystal structure of clinoptilolite-Na (Agoura, California) with cation positions from the refinement of Koyama and Takéuchi (1977). Typically, clinoptilolite contains 4 to 7 cations per unit cell (Deer *et al*. 2004).

    (i) Identify the primary and secondary building units in clinoptilolite.

[2 marks]

    (ii) Explain why clinoptilolite is suitable as an ion exchanger and contrast its ion exchange behaviour with that of zeolite A. [5 marks]

    (iii) Why might ion exchange in an ammonia-rich solution effect the efficacy of the clinoptilolite to remove caesium? [1 mark]

    (iv) The SIXEP plant takes aqueous feed from high pH tanks which store nuclear waste. Why is it necessary to reduce the pH to near neutral before ion exchange can start? [2 marks]

b) Solutions of gadolinium nitrate and cerium nitrate were mixed and evaporated to dryness and then heated under oxygen to form material **X** that crystallises with the fluorite structure. Elemental analysis of **X** identified a material which contained 5.46% Gd and 76.28% Ce.

(i) Calculate the formula of **X** and explain whether or not this material might be expected to be a good oxygen ion conductor. [5 marks]

(ii) How could the limit of substitution of Gd_2O_3 in CeO_2 be determined experimentally? [4 marks]

(iii) Explain why manganese and aluminium would not be suitable choices of dopant to improve conductivity in CeO_2. [4 marks]

c) The image below shows a time-lapse sequence of crystals growing in a solution.
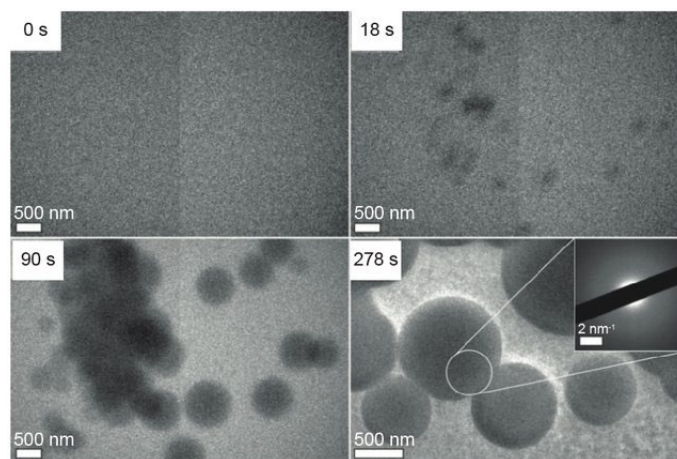
(i) Explain what is happening and why this process is not always desirable. [3 marks]

(ii) Framework structures can be prepared which consist of edge-linked silicon, aluminium, and phosphorus tetrahedra that are suitable for catalytic applications.
Explain how you would prepare the material $H_4Si_4Al_{20}P_{16}O_{80}$ using a microemulsion (micelle) technique, including careful removal of the template. [7 marks]

2. a) Assuming a general supramolecular equilibrium in solution produced between 2 molecular species, enumerate the possible alternatives for reducing the mixture of products. [3 marks]

   b) Rationalise the main differences between materials with amorphous pores and ordered pores. Give one example of an application that will benefit from using materials with amorphous pores and one where ordered pores are more relevant. [9 marks]

3. a) Consider a metal organic framework having hierarchical porosity. Are these structural characteristics going to affect the selectivity and permeability in mixed matrix membranes for gas separation applications? Why? [7 marks]

   b) What factors affect the performance of mixed matrix membranes containing metal organic frameworks as filler for water purification applications? Comment on any correlations. [6 marks]

   c) Consider 2 metal organic frameworks (MOF), MOF-1 and MOF-2, where MOF-1 is mesoporous with a surface area of 300 m^2/g and MOF-2 contains micro- and mesoporosity with a surface area of 2000 m^2/g. Comment on the advantages and disadvantages of choosing MOF-1 or MOF-2 for the encapsulation of nanoparticles (average diameter = 5 nm) for the catalytic reduction of nitro arenes. [8 marks]

4. a) Lanthanide elements are notoriously hard to separate due to their similar radii, exhibit little variation in common oxidation states, and mostly exhibit high coordination numbers. Consider a mixed lanthanide complex, e.g. containing both Nd and Sm. How might the separate metal sites be distinguished in a single crystal diffraction experiment? [3 marks]

   b) A single crystal of a lithium complex containing a chiral CHNO-containing organic ligand was found to diffract cleanly, but rather weakly, using a standard laboratory diffractometer equipped with a sealed Mo X-ray tube with the experiment run at room temperature. How might a better data set be obtained that enables the absolute structure to be determined? [7 marks]

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c)   Figure 1 below, shows part of the extended structure for benzene 1,3,5-tricarboxylic acid bis-methanol solvate (**1**). Key geometrical data are also provided.

Figure 1.

Selected bond lengths for (**1**):

C(9)–O(5) = 1.307(5) Å   C(9)–O(6) = 1.206(5) Å

Table of Hydrogen bonds for (**1**) [Å and °].

D–H···A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(1)–H(1)···O(8)	0.84	1.71	2.521(7)	162.4
O(7)–H(7)···O(4)	0.84	1.94	2.778(4)	176.0
O(3)–H(3A)···O(6A)	0.84	1.81	2.595(4)	154.2
O(5)–H(5A)···O(7C)	0.84	1.74	2.572(4)	171.4
O(8)–H(8)···O(1B)	0.84	1.97	2.766(7)	157.0

Symmetry operations for equivalent atoms:
A = x,y−1,z   C = x,y+1,z   B = −x+1,−y,−z+2

(i) Identify and name the unique graph sets in the extended structure of (**1**). You may wish to sketch the individual graph sets, or copy the figure above and annotate it. [6 marks]

(ii) Consider the two C–O bond lengths at C(9). Determine if they are statistically significantly different, and hence comment on the chemical nature of the group at C(9). [5 marks]

(iii) Looking at the hydrogen bond table, comment on how the O*H* atoms were refined. How were the H atoms on oxygen included in the model and how might the crystallographer have done better? [4 marks]

(iv) During the early part of the structure refinement, what would happen if atom O8 was incorrectly assigned as sulfur, and atom C7 incorrectly assigned as boron? [4 marks]

(v) Write an informative caption for Figure 1, suitable for inclusion in a journal publication. [5 marks]

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