Structural and activity investigation into Al^{3+}, La^{3+} and Ce^{3+} addition to the phosphomolybdate heteropolyanion for isobutane selective oxidation (2011)

$$M_x H_{3-3x}[PMo_{12}O_{40}]$$

$M = \text{Al, La or Ce}$

$H = \text{heteropolyanion (?)}$

$0 \leq x \leq 1$ (x is a continuous variable)

Methods

- XRD – x-ray diffraction
- Adsorption isotherm

Results

- *Additions*
  - Al^{3+} addition → causes primitive cubic phase
  - La^{3+} and Ce^{3+} addition → reduces surface area of PMo structure
- *Selective oxidation of isobutane* → temperature-programmed experiments yields:
  - methacrolein
  - lactone
  - acetic acid (<u>not</u> with Al compounds)
  - propene (<u>only</u> with Al compounds)
  - carbon dioxide
  - water
- *Preferential formation of propene* (over acetic acid) in Al^{3+} addition may be attributed to:
  - smaller cation size
  - primitive cubic structure
- *Product formation* achieved via two distinct reaction processes:
  - Category 1 → associated with surface formation of isobutane, with reaction rate governed by 'bulk migration' of charged particles
  - Category 2 → concerned with 'deep penetration' within the bulk of the substrate, and subsequent *desorbing* (?) in a series of bell-shaped humps

- *Product categorisation*
    - Methacrolein → forms via both Category 1 & 2
    - All other products → forms via Category 2 only
- *Kinetic analysis of activation barriers*

Product	**Category 1**	**Category 2**
Methacrolein	(67 ± 2) to > 350 kJ mol^{-1}	
Lactone	N/A	
Acetic acid	N/A	
Propene	N/A	
Carbon dioxide	N/A	
Water	N/A	

Summary

Metal cation addition to PMo anion results in:

- Increased thermal stability
- Decreased deactivation (increased activation?)
- Keggin structure remains intact (according to IR spectroscopy)

Questions:

1. Definitions:
    a. Heteropolyanion
    b. Desorb
    c. Primitive cubic phase
    d. Keggin structure
2. Atomic structures:
    a. Aluminium → period 3 metal – smaller cation sizes (?)
    b. Lanthanum and cesium → period 8 lanthanide elements
3. Quantum mechanical analysis (?)

4. Structural analysis:
    a. Use of other spectroscopic methods such as NMR or Raman
    b. Relevance of AFM ?
5. Particle size considerations and possible alternative methods:
    a. Laser diffraction
    b. Dynamic light scattering
    c. Automated imaging (dynamic and static)
    d. Resonant mass measurement
    e. Spatial filter velocimetry