**Structural and activity investigation into Al3+, La3+ and Ce3+ addition to the phosphomolybdate heteropolyanion for isobutane selective oxidation (2011)**

***Methods***

* XRD – x-ray diffraction
* Adsorption isotherm

***Results***

* *Additions*
  + Al3+ addition 🡪 causes primitive cubic phase
  + La3+ and Ce3+ addition 🡪 reduces surface area of PMo structure
* *Selective oxidation of isobutane* 🡪 temperature-programmed experiments yields:
  + methacrolein
  + lactone
  + acetic acid (not with Al compounds)
  + propene (only with Al compounds)
  + carbon dioxide
  + water
* *Preferential formation of propene* (over acetic acid) in Al3+ 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 |  |  |
| 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:
   1. Heteropolyanion
   2. Desorb
   3. Primitive cubic phase
   4. Keggin structure
2. Atomic structures:
   1. Aluminium 🡪 period 3 metal – smaller cation sizes (?)
   2. Lanthanum and cesium 🡪 period 8 lanthanide elements
3. Quantum mechanical analysis (?)
4. Structural analysis:
   1. Use of other spectroscopic methods such as NMR or Raman
   2. Relevance of AFM ?
5. Particle size considerations and possible alternative methods:
   1. Laser diffraction
   2. Dynamic light scattering
   3. Automated imaging (dynamic and static)
   4. Resonant mass measurement
   5. Spatial filter velocimetry