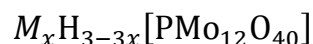


Structural and activity investigation into Al³⁺, La³⁺ and Ce³⁺ addition to the phosphomolybdate heteropolyanion for isobutane selective oxidation (2011)



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

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

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

Methods

- XRD – x-ray diffraction
- Adsorption isotherm

Results

- *Additions*
 - 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	(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