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Polyoxometalates, characterized by high reactivity and functionality, have attracted considerable attention for their application in the fields of catalysis, material science, and medicine. We have explored the behavior of polyoxometalate ion in solution with the help of multinuclear NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and isothermal titration calorimetry (ITC). Our present research interests are development of environmentally friendly oxidation catalysis. Now we have many trials to improve their catalytic activity and elucidate their process based on solution chemistry. Our recent results related to solution chemistry are as follows:

Cyclooctene epoxidation catalyzed by vanadium-substituted Lindqvist-type polyoxotungstate:[1] Tetrabutylammonium salts of Lindqvist $[VW_5O_{19}]^{3-}$ significantly promotes cyclooctene epoxidation with H_2O_2 in CH_3CN at 30 °C. The catalytic processes are discussed based on the UV/Vis, ESI-MS, ^{51}V NMR, and ^{183}W NMR spectra. Analysis of ESI-MS showed that the $[VW_5O_{19}]^{3-}$ anion retained a Lindqvist-type structure, and the multiple peroxidations occurred at both the V and W sites during epoxidation. With the synergistic effects provided by the W(peroxo) sites, the V(peroxo) site plays a catalytically active role in both epoxidation and H_2O_2 decomposition.

The formation of elliptical $\{Mo_{134}La_{10}\}$ ring by incorporating La^{3+} into the inner ring of circler

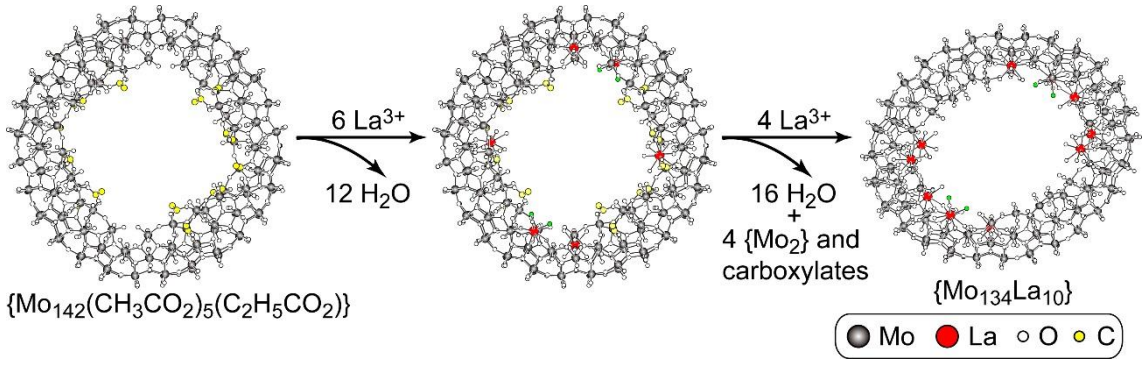

Figure. Two step of the coordination of $\{Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)\}$ to La^{3+} in aqueous solutions.

{$Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)$} ring in aqueous solution:[2] Modification of the Mo-ring from circle to ellipsoid was investigated using the ITC and ^{139}La NMR spectrometry coupled with the results of X-ray structural analysis of circler {$Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)$} ring and elliptical {$Mo_{134}La_{10}$} ring. {$Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)$} ring comprised of carboxylate-coordinated {Mo_2} linkers and six defect pockets in inner ring. Regarding the endothermic reaction of [La^{3+}]/{Mo_{142}}=6/1 with ΔH=22 kJ•mol^{-1}, ΔS=172 J•K^{-1}•mol^{-1}, and K=9.9×10^4 M^{-1} at 293 K, the results of ITC conclude that the coordination of the defect pockets to La^{3+} precedes the replacement of the {Mo_2} linkers with La^{3+}.

Catalytic hydrolysis of Adenosine Triphosphate (ATP) by polyoxomolybdate:[3, 4] Polyoxomolybdate ion, both of $[Mo_7O_{24}]^{3-}$ and $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$, show the antitumor activity against human gastric cancer and pancreatic cancer. These polyoxomolybdates also promote ATP hydrolysis to adenosine diphosphate (ADP). $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ is a photoreduction product obtained through the photolysis of $[Mo_7O_{24}]^{3-}$ at the pH range 5 to 7. The processes of ATP hydrolysis catalyzed by these polyoxomolybdates were investigated with ^{31}P NMR spectrometry, ESI-MS and ITC. $[Mo_7O_{24}]^{3-}$ ion exhibits high catalytic activity at the pH range 2 to 6. The resulst of ^{31}P NMR spectra and ITC suggested that ATP was decomposed through the formation of the ATP-molybdate complexes isostructural with $[(PO_4)_2Mo_5O_{15}]^{6-}$ and $[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ as intermediates. The ATP hydrolysis in the presence of $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ proceeds catalytically at the pH range 5 to 7.5. The $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ interacts weakly with ATP. The results of ESI-MS measurements suggest that ATP hydrolysis proceed retaining structure of $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ anion.

Reference

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