materials

Editorial

Molybdenum-, Vanadium-, and Tungsten-Containing Materials for Catalytic Applications

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As chemists, we are still fascinated by the magic of nature. Indeed, natural metalloenzymes can achieve a high number of chemical transformations without the action of humans [1]. From the chemist's point of view, the nature of coordination species and the environment around metals determine their activity [2]. Metalloenzymes are active in several reactions [3], particularly in oxidation processes with the assistance of molybdenum- [4], vanadium- [5], and tungsten-based compounds [6]. The activity of those species is quite large and the advantage lies in the stability of such complexes in aqueous media or under air [7]. According to the reported academic research known for decades, other metallic species are investigated to be active and are mainly composed of an inorganic part, such as as polyoxometalates (POMs) [8–13]. Among the several applications of POMs within several domains [8,9] and focusing on catalytic applications [10,11], POMs are considered as molecular models of metal oxides by mimicking the surface of metal oxides [12] present in nature (as rocks) and acting within some catalytic processes (mainly heterogeneous ones) [11].

Since our research domain is the catalytic applications of oxo-molybdenum and oxo-vanadium coordination complexes [14–18] and POMs [19–21], such as molecular [19,20] or supported catalysts [21], with emphasis on biomass-based substrate valorisation [22–24], we proposed to edit this Special Issue with the aim of collecting research of other international groups within the domain to show the diversity of possible catalyzed reactions using metal complexes. High catalytic activity with relatively low metal loading is an asset, from relatively low cost to more sustainable processes. Catalytic processes containing those elements are of a growing interest, notably heterogeneous ones, in terms of reuse and recycling.

The Special Issue highlights some recent advances in the development of Mo-, V-, and W-containing catalysts, including polyoxoanions and bulk materials (e.g., mesoporous materials, surfaces, etc.), with the involvement of those elements in catalytic materials. The emphasis is on recent trends, including materials processing (preparation and characterization) with their catalytic applications from simple reactions with model substrates to more complex and challenging ones.

The four original research papers collected in this thematic issue cover different aspects, dealing with processes using POMs non-supported and silica-supported (porous and non-porous) materials, managing different catalytic reactions, and exhibiting different approaches.

The article named "Vanadium-Substituted Phosphomolybdic Acids for the Aerobic Cleavage of Lignin Models—Mechanistic Aspect and Extension to Lignin" is a research article from Paris (France) [25]. Al-Hussaini, Launay, and Galvez developed a very interesting study based on lignin cleavage. Lignin is a polymer with several types of linkages between

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phenolic species. The authors used the ability of the heterometallic polyacid of general formula $H_6[PMo_9V_3O_{40}]$. This compound was synthesized using a variant of a known method under hydrothermal conditions. This POM was tested for the aerobic cleavage of two lignin models bearing a β-O-4 bond in lignin. The article points out the effect of several parameters for the reactions and application to a real case, using an organosolv wheat straw lignin. From the obtained results, a mechanism of cleavage was proposed.

Wang, Wang, Shang, Ren, Yue, and He from Fudan (China) presented, in the article titled "$H_3PMo_{12}O_{40}$ Immobilized on Amine Functionalized SBA-15 as a Catalyst for Aldose Epimerization" [26], the use of a heterogeneous catalytic system based on mesoporous silica (SBA-15) purposely functionalized with APTES for the immobilization of $H_3PMo_{12}O_{40}$. Several POMs loadings were investigated, and catalytic objects were used to epimerize glucose in water, aiming to valorize cheap sugar into high value ones. The aim was to transform glucose into mannose, and the results showed good selectivity with better activation energy (a gain of 16 kJ mol^{-1}) with immobilized catalyst vs. the molecular version. Other aldoses (among them mannose, arabinose, and xylose) were tested.

Another type of supported catalysts was presented in "Organic Solvent-Free Olefins and Alcohols (ep)oxidation Using Recoverable Catalysts Based on $[PM_{12}O_{40}]^{3-}$ (M = Mo or W) Ionically Grafted on Amino Functionalized Silica Nanobeads" [27]. Wang, Gayet, Guillo, and Agustin from LCC-CNRS Toulouse and Castres (France) showed how $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ could be immobilized on non-porous silica nanoparticles functionalized with APTES. The species were fully characterized by using different methods more specifically to quantify APTES and POM loading on the surface. The objects were tested for epoxidation of classical cyclic olefins, one terpene (limonene), and the oxidation of cyclohexanol. The catalysts could be recycled several times.

The last article of this Special Issue is a collaboration between Erlangen (Germany) and DTU at Lyngby (Denmark). "Ru-Doped Wells–Dawson Polyoxometalate as Efficient Catalyst for Glycerol Hydrogenolysis to Propanediols" written by Modvig, Kumpidet, Riisager, and Albert exhibits the valorization of glycerol in aqueous media using a Ru-doped Wells–Dawson polyoxometalate of general formula α2-$K_xP_2MW_{17}O_{61}$ (M = Ru, Pd, Pt). [28] Those species have been used to perform hydrogenolysis of glycerol into propanediols. The POM containing Ru was more active than Pd and Pt. In addition to catalysts loading, other parameters that influenced reactivity included H_2 pressure, stirring rate, etc.

In conclusion, the four articles published in this Special Issue show the richness of polyoxometalates as (supported/unsupported) catalysts for different reactions working in aqueous media or without organic solvent. The results presented exhibit important application, from the biomass valorization, downstream byproducts of industrial processes towards new materials, or cleaner processes. This is of crucial importance for a sustainable future in today's societies. We hope that this thematic issue can stimulate further research in the field.

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References

1. Leveson-Gower, R.B.; Mayer, C.; Roelfes, G. The importance of catalytic promiscuity for enzyme design and evolution. *Nat. Rev. Chem.* **2019**, *3*, 687–705. [CrossRef]
2. Ayipo, Y.O.; Osunniran, W.A.; Babamale, H.F.; Ayinde, M.O.; Mordi, M.N. Metalloenzyme mimicry and modulation strategies to conquer antimicrobial resistance: Metal-ligand coordination perspectives. *Coord. Chem. Rev.* **2022**, *453*, 214317. [CrossRef]
3. Ren, X.; Fasan, R. Engineered and artificial metalloenzymes for selective C–H functionalization. *Curr. Opin. Green Sustain. Chem.* **2021**, *31*, 100494. [CrossRef]

4. Kim, D.; Lee, J.; Seo, J. Molybdenum-containing metalloenzymes and synthetic catalysts for conversion of small molecules. *Catalysts* **2021**, *11*, 217. [CrossRef]
5. Plass, W.; Bangesh, M.; Nica, S.; Buchholz, A. Model studies of vanadium-dependent haloperoxidation: Structural and functional lessons. In *Vanadium: The Versatile Metal*; Oxford University Press: Oxford, UK, 2007; Volume 974, pp. 163–177. [CrossRef]
6. Torres, E.; Ayala, M. Biocatalysis by metalloenzymes. In *Comprehensive Inorganic Chemistry II*; Reedijk, J., Poeppelmeier, K., Eds.; Elsevier: Amsterdam, The Netherlands, 2013; p. 685. [CrossRef]
7. Fernandes, H.S.; Teixeira, C.S.S.; Sousa, S.F.; Cerqueira, N.M. Formation of unstable and very reactive chemical species catalyzed by metalloenzymes: A mechanistic overview. *Molecules* **2019**, *24*, 2462. [CrossRef] [PubMed]
8. Katsoulis, D.E. A survey of applications of polyoxometalates. *Chem. Rev.* **1998**, *98*, 359–388. [CrossRef] [PubMed]
9. Rhule, J.T.; Hill, C.L.; Judd, D.A.; Schinazi, R.F. Polyoxometalates in medicine. *Chem. Rev.* **1998**, *98*, 327. [CrossRef]
10. Kozhevnikov, I.V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem. Rev.* **1998**, *98*, 171. [CrossRef]
11. Mizuno, N.; Misono, M. Heterogeneous catalysis. *Chem. Rev.* **1998**, *98*, 199. [CrossRef]
12. Klemperer, W.G.; Wall, C.G. Polyoxoanion chemistry moves toward the future: From solids and solutions to surfaces. *Chem. Rev.* **1998**, *98*, 297. [CrossRef]
13. Omwoma, S.; Chen, W.; Tsunashima, R.; Song, Y.-F. Recent advances on polyoxometalates intercalated layered double hydroxides: From synthetic approaches to functional material applications. *Coord. Chem. Rev.* **2014**, *258*, 58–71. [CrossRef]
14. Pisk, J.; Agustin, D.; Vrdoljak, V.; Poli, R. Epoxidation processes by pyridoxal dioxomolybdenum(VI) (Pre)catalysts without organic solvent. *Adv. Synth. Catal.* **2011**, *353*, 2910. [CrossRef]
15. Morlot, J.; Uyttebroeck, N.; Agustin, D.; Poli, R. Solvent-free epoxidation of olefins catalyzed by "[MoO_2(SAP)]": A new mode of tert-butylhydroperoxide activation. *ChemCatChem* **2013**, *5*, 601. [CrossRef]
16. Pisk, J.; Daran, J.-C.; Poli, R.; Agustin, D. Pyridoxal based ONS and ONO Vanadium(V) complexes: Structural analysis and catalytic application in organic solvent free epoxidation. *J. Mol. Catal. A Chem.* **2015**, *403*, 52. [CrossRef]
17. Mrkonja, S.; Topić, E.; Mandarić, M.; Agustin, D.; Pisk, J. Efficient molybdenum hydrazonato epoxidation catalysts operating under green chemistry conditions: Water vs. decane competition. *Catalysts* **2021**, *11*, 756. [CrossRef]
18. Mihalinec, J.; Pajski, M.; Guillo, P.; Mandarić, M.; Bebić, N.; Pisk, J.; Vrdoljak, V. Alcohol oxidation assisted by molybdenum hydrazonato catalysts employing hydroperoxide oxidants. *Catalysts* **2021**, *11*, 881. [CrossRef]
19. Guérin, B.; Mesquita Fernandes, D.; Daran, J.-C.; Agustin, D.; Poli, R. Investigation of induction times, activity, selectivity, interface and mass transport in solvent-free epoxidation by H_2O_2 and TBHP: A study with organic salts of the $[PMo_{12}O_{40}]^{3-}$ anion. *New J. Chem.* **2013**, *37*, 3466–3475. [CrossRef]
20. Damjanović, V.; Pisk, J.; Kuzman, D.; Agustin, D.; Vrdoljak, V.; Stilinović, V.; Cindrić, M. The synthesis, structure and catalytic properties of the $[Mo_7O_{24}(\mu\text{-}Mo_8O_{26})Mo_7O_{24}]^{16-}$ anion formed via two intermediate heptamolybdates $[Co(en)_3]_2[NaMo_7O_{24}]Cl\cdot nH_2O$ and $(H_3O)[Co(En)_3]_2[Mo_7O_{24}]Cl\cdot 9H_2O$. *Dalton Trans.* **2019**, *48*, 9974. [CrossRef]
21. Pisk, J.; Agustin, D.; Poli, R. Organic salts and merrifield resin supported $[PM_{12}O_{40}]^{3-}$ (M = Mo or W) as catalysts for adipic acid synthesis. *Molecules* **2019**, *24*, 783. [CrossRef]
22. Loubidi, M.; Agustin, D.; Benharref, A.; Poli, R. Solvent-free epoxidation of himachalenes and their derivatives by TBHP using $[MoO_2(SAP)]_2$ as a catalyst, C.R. *Chimie* **2014**, *17*, 549. [CrossRef]
23. Wang, W.; Agustin, D.; Poli, R. Influence of ligand substitution on molybdenum catalysts with tridentate Schiff base ligands for the organic solvent-free oxidation of limonene using aqueous TBHP as oxidant. *Mol. Catal.* **2017**, *443*, 52. [CrossRef]
24. Runeberg, P.A.; Agustin, D.; Eklund, P.C. Formation of tetrahydrofurano-, aryltetralin, and butyrolactone norlignans through the epoxidation of 9-norlignans. *Molecules* **2020**, *25*, 1160. [CrossRef] [PubMed]
25. Al-Hussaini, L.; Launay, F.; Galvez, E. Vanadium-substituted phosphomolybdic acids for the aerobic cleavage of lignin models—Mechanistic aspect and extension to lignin. *Materials* **2020**, *13*, 812. [CrossRef] [PubMed]
26. Wang, H.; Wang, M.; Shang, J.; Ren, Y.; Yue, B.; He, H. $H_3PMo_{12}O_{40}$ immobilized on amine functionalized SBA-15 as a catalyst for aldose epimerization. *Materials* **2020**, *13*, 507. [CrossRef]
27. Wang, Y.; Gayet, F.; Guillo, P.; Agustin, D. Organic solvent-free olefins and alcohols (ep)oxidation using recoverable catalysts based on $[PM_{12}O_{40}]^{3-}$ (M = Mo or W) ionically grafted on amino functionalized silica nanobeads. *Materials* **2019**, *12*, 3278. [CrossRef]
28. Modvig, A.; Kumpidet, C.; Riisager, A.; Albert, J. Ru-doped wells–dawson polyoxometalate as efficient catalyst for glycerol hydrogenolysis to propanediols. *Materials* **2019**, *12*, 2175. [CrossRef]