

Višnja Vrdoljak, Edi Topić, Josipa Sarjanović,
Dino Kuzman, Tomica Hrenar, Jana Pisk

*University of Zagreb Faculty of Science, Department of Chemistry,
Zagreb, Croatia*



Engineering Nuclearity in Vanadium Assemblies: From metallosupramolecular isomerism to Tunable Oxidation Catalysis

ABSTRACT

Coordination-driven vanadium(V) assemblies were synthesized from aroylhydrazone ligands and NH_4VO_3 in the presence of various alcohols, using both conventional synthetic approaches and post-assembly structural transformations. They were systematically investigated to elucidate how reaction conditions and auxiliary alkoxide ligands control the formation of discrete tetranuclear complexes versus one-dimensional coordination oligomers, and how these structural motifs influence their stability and catalytic performance. Solid-state structures were elucidated by single-crystal and powder X-ray diffraction, supported by IR-ATR, NMR spectroscopy, and thermogravimetric analysis. Across all architectures, the monomeric building unit displays an ONO coordination environment around vanadium(V), provided by a doubly deprotonated hydrazone ligand. Oligomerization occurs via coordination of a pyridyl nitrogen atom to the sixth coordination site of the neighbouring oxovanadium center. Assemblies with alternating syn/anti motifs are thermodynamically preferred over those composed exclusively of syn or anti units. The functional consequences of the metallosupramolecular nuclearity were evaluated in the catalytic oxidation of substituted benzyl alcohols using tert-butyl hydroperoxide. The results highlight a fundamental trade-off between catalytic activity and selectivity: highly active catalysts tend to lose selectivity due to overoxidation, whereas highly selective systems operate more slowly.

Keywords: self-assembly, hydrazone ligands, metallosupramolecular; structure–property relationships; alcohol oxidation catalysis

BIOGRAPHY

Višnja Vrdoljak obtained her PhD in Inorganic Chemistry from the Faculty of Science at the University of Zagreb in 1996. After completing a post-doctoral fellowship at the University of Trieste, Italy, she joined the Faculty of Science at the University of Zagreb, Croatia. In 2015, she was appointed as a professor at the Department of Chemistry. Her current research focuses on developing hybrid organic-inorganic polyoxometalate-based materials and metallosupramolecular architectures of molybdenum, vanadium, and copper.