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Polymolybdates and Peroxomolybdates: Candidates for Catalysts in Industry

W. Lasocha^{1,2}, A. Szymanska², M. Oszejca¹, G. Appleby³, K. Pamin², J. Poltowicz²

¹Faculty of Chemistry, Jagiellonian University, Krakow, Poland, ²Jerzy Haber Institute of Catalysis & SC PAS, Krakow, Poland, ³Deutsches Elektronen-Synchrotron, Hamburg, Germany

Progress in catalysis depends on a full understanding of the role of the individual components of catalytic materials. Crystallographic studies offer insight into crystal structure, which enables the rational selection of reagents and better planning of the syntheses of novel materials and catalysts. In this paper we have studied the process of the oxidation of hydrocarbons and terpenes with oxygen from the air. Processes of this type are important in so-called "Green Chemistry." Their application can reduce the amount of environmentally harmful pollutants formed through conventional oxidation based on nitric acid. While investigating the catalytic activity of peroxy- and polymolybdates(VI) in the oxidation of cycloalkanes, we found a number of intriguing relationships. To explain them, we designed, synthesized and solved the crystal structures of the family of new peroxomolybdates, tri-, octa- and pentamolybdates of amines. Both single crystal and polycrystalline materials were investigated using laboratory as well as synchrotron radiation. Next, we used these compounds as catalysts in certain interesting for industry processes (e.g. oxidation of cyclic hydrocarbons). We have concluded that: – The activity of peroxocompounds is enhanced by the coordination of N-oxide groups to Mo atoms. – The activity of anionic polymeric trimolybdates decreases when 'surface of polymeric fiber' is blocked by cations. – The anionic layers of pentamolybdates are separated by cations of variable size. The distance between layers plays a role similar to that of the size of channels in zeolites. Summary: Peroxomolybdates and polyoxomolybdates show great prospects for new industrial uses (besides cracking and desulfurization).

[1] A. Szymańska, W. Nitek, D. Mucha, R. Karcz, K. et al. *Polyhedron*, 60 (2013) 39–46

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