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**SYNTHESIS AND CHARACTERIZATION OF SELECTED
POLYOXOMETALLATES AND THEIR APPLICATIONS IN CATALYSIS**

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ABSTRACT

Green processing is a central issue in both academia and industry, with regard to chemical synthesis because without this approach, industrial chemistry is not sustainable. Chemists are proud of their ability to create highly valuable compounds from inexpensive raw materials. In this thesis is presented green processing methods that were developed in the present study.

Highly efficient green processes for the epoxidation of olefins using molecular oxygen and hydrogen peroxide oxidants, catalysed by nanogold and silver catalysts supported on salts of polyoxometallate anions (POMs) are presented. These nanoparticles were stabilized in solution by the POMs and eventually supported onto their salts. The optimized supported catalysts were employed in the epoxidation of olefins using the above green oxidants. The gold catalysts supported on POMs are efficient in the epoxidation of olefins with air or pure dioxygen oxidant in the presence or absence of a solvent at 353 K. The method enjoys high conversions and selectivity, with no sacrificial reductants or promoters needed. For example, cyclooctene and 2-norbornene could be epoxidized with > 95% selectivity to the corresponding epoxides.

The silver catalysts supported on POMs are remarkably efficient in the epoxidation of olefins with hydrogen peroxide oxidant with or without a solvent at 333 K. The method enjoys >90% conversion and $\geq 99\%$ selectivity to the epoxide for a variety of olefins. In both cases the catalysts are easily recovered by filtration and are reusable several times. But the supported silver catalyst should be preferred from the economic point of view.

Methods for CO₂ coupling with epoxides to produce cyclic carbonates are also presented. Various transition metal substituted POMs (TMSPs) in conjunction with di-methyl amino pyridine (DMAP) base co-catalyst were found to be quite effective in the coupling of CO₂ with propylene oxide to form propylene carbonates at a CO₂ pressure of 30 bars and 140°C. In addition, tetraalkylammonium salts of TMSPs were investigated for the coupling of epoxides with CO₂ in the absence of DMAP. A number of these catalysts produced the cyclic carbonates in good yields and selectivity. For example, when using [(C₇H₁₅)₄N]₈ZnW₁₁O₃₉Co catalyst, the system enjoys >95% conversion and >96% selectivity to the corresponding cyclic carbonate for a variety of epoxides. Results of this study also showed that the catalytic activity is significantly influenced by the type of addenda transition metal and the counter ion. For example, cobalt- and manganese-substituted POMs showed higher activity whereas the copper one showed low activity.

A binary catalyst system composed of Ag/AgPOM and n-tetra butyl ammonium bromide (TBAB) was used in the direct synthesis of cyclic carbonates from olefins and CO₂ using 50% H₂O₂ as an oxidant in the presence of a base. This system produced the corresponding cyclic carbonates with >90% conversion and high selectivity to the cyclic carbonates for a variety of olefins. Results of this study also showed that both POM and TBAB were necessary for the reaction and no cyclic carbonate was formed without either catalyst or base co-catalyst. Further, these catalysts could be reused without loss of activity and selectivity.