Special Seminar
Department of Chemistry

**Thursday, January 18, 2018**
**Time 15:30**
**Bldg. 29 Room 307**

Yaniv Wolfer

**SUMMARY:**
The sol-gel process is relatively simple and has important applications; therefore its use is increasing. One example for using this process is entrapping catalysts in the sol-gel matrix. As a result of the entrapment, the catalyst was found to be recyclable and its catalytic activity, as well as its selectivity, sometimes increased. Moreover, it can be used in solvents where it is insoluble and often it is even more stable in the matrix than in the solvent.

The Nickel ions and their complexes, in different oxidation levels, are interesting catalysts, due to their ability to be found in several oxidation states. The tetravalent Nickel is usually used as a starting point for its oxidation-reduction reactions, so that the trivalent or monovalent complex is an intermediate product in the catalytic and electrolytic reactions. The different uses of the sol-gel method, the ease with which the active substances are entrapped, the advantages of heterogeneous catalysis and the importance of catalytic processes, in which transition metal complexes are used as catalysts, led us to investigate the activity of Nickel cyclam (1,4,8,11-tetraazacyclotetradecane), Nickel ethylene di-amine and Nickel nitrate as electrocatalysts entrapped in sol-gel matrices. The activity was examined in various reactions which we performed: water oxidation, oxidation of alcohols and de-halogenation.

The purpose of this study is to fix Nickel complexes in sol-gel matrices in various chemical processes for the formation of electrodes and columns and to
characterize the advantages of fixation of the complexes in sol-gel matrices, while finding optimal conditions for performing the processes.

A method was developed for the preparation of sol-gel electrodes. The electrodes were of different nature as a result of the use of different precursors with different residues (Methyltrimethoxysilane and Trimethoxyphenylsilane), containing the Nickel cyclam, Nickel ethylene di-amine or Nickel nitrate. The results obtained undoubtedly prove that we were able to perform the catalytic processes we studied. We found conditions for fixation of active species in the sol-gel electrodes in a simple method without covalently binding the catalyst to the matrix. In addition, we have shown that the electrodes can be recycled for further use in the processes studied.

The results indicate that with the electrodes created, we were able to oxidize ethanol and methanol at basic pHs, although the Nickel cyclam complex is sensitive to these conditions and decomposes immediately when it is in solution. We have shown that the Nickel-cyclam compound entrapped in the sol-gel matrix is eventually oxidized, but it occurs more slowly than in solution. Furthermore, we have shown that the material from which the electrode is made is of great importance to the reaction currents, the durability of the electrode and the rate of the catalytic process. In addition, we have shown that it is possible to entrap other Nickel complexes (such as Nickel ethylene di-amine and Nickel nitrate) that can also be used to perform oxidation of alcohols.

Another study that we performed was on finding the mechanism of the electrocatalytic for water oxidation, by Nickel cyclam. The results indicate that the phosphate and carbonate are stabilizing the trivalent Nickel complex which acts as a catalyst for the water oxidation. In addition, we proposed an alternative mechanism to that published in the literature for the water oxidation process, which is also supported by DFT calculations. We have shown that carbonate acts as a catalyst for water oxidation reactions by participating in reactions in a similar fashion to phosphates. However, unlike phosphates, the carbonate is also oxidized in the reaction and therefore in its presence the oxidation process begins with more cathodic voltages and involves higher currents. In addition,
we found that in the heterogenic catalysis, it is not possible to perform the water oxidation process in the presence of phosphates with the electrodes we created because it tends to be attached to the surface of the electrode. On the other hand, we were able to perform water oxidation with these electrodes in the presence of carbonate and to prove that the currents obtained as a result of water oxidation are directly proportional to the carbonate concentration in the solution. We assumed that in electrodes containing Nickel cyclam, the reaction mechanism was consistent with the mechanism we proposed in the homogenous system described above. However electrodes containing Nickel nitrate and Nickel ethylene di-amine were oxidized to Nickel hydroxide, which was used as the oxidizing agent in the reaction.

Using the sol-gel method above we also prepared a matrix from Tetramethoxysilane, in which the divalent Nickel cyclam complex were entrapped. We have shown that this complex can be reduced into a monovalent nickel that causes de-halogenation of alkyl halides. We used sodium borohydride, which was very effective in the system we worked on. Using ESR measurements, we showed that while the monovalent Nickel complex has a very short half-life in aqueous solutions, it is stable over time when trapped in the sol-gel matrix. In addition, we found that the entrapment of the complex in the sol gel matrix does not decrease its ability to reduce the alkyl halide we used. Although we have received low efficiencies, modifying the method we developed will enable the implementation of industrial processes using monovalent Nickel complexes.

In conclusion, in this study we have shown another layer in the properties and advantages of the sol-gel as a platform for fixation of active species and controlling the rate of the reaction, using various procures, in a wide variety of processes. This study makes it possible to understand how to select procedures and the method of preparing the sol-gel according to the characteristics required for performing the various processes needed. In addition, the study adds a lot of useful information about the catalytic processes that have been studied in this framework, thus greatly enhancing the ability to turn them into industrial applications.