SOL-GEL MATRICES IN REDOX PROCESSES
Ariela Burg,1 Dror Shamir,2 Dan Meyerstein,3,4 Yael Albo5

1Chemical Engineering Dept., Sami Shamoon College of Engineering, Beer-Sheva, Israel.
2Chemistry Dept., Nuclear Research Centre Negev, Beer-Sheva, Israel.
3Chemical Sciences Dept., Ariel University, Ariel, Israel.
4Chemistry Dept., Ben-Gurion University, Beer-Sheva, Israel.
5Chemical Engineering Dept., Ariel University, Ariel, Israel.

ABSTRACT

The fact that silica sol-gel matrices are inert to redox processes makes them an optimal medium for promoting a variety of redox processes by the entrapment of different redox agents. Thus it was shown that such matrices can be used as electron-exchange columns, as redox catalysts and as redox electro-catalysts. The results point out that the entrapment often affects the chemical properties of the entrapped species.

INTRODUCTION

Entrapment of reagents in sol-gel matrices has been reported for a variety of processes,1 e.g.: catalysis of a variety of processes;2,3 enzymatic processes;3,4 sensors;3 photonic processes;1 ion exchange;5 photocatalysis;6 membranes7 etc. However rarely for initiating desired redox processes. In this short review a variety of redox processes in sol-gel matrices studied by us recently are discussed.

The basic idea is based on the fact that the sol-gel matrices are redox inert and therefore are expected not to interfere with a redox process of an entrapped species. The results presented below point out that this is true for reduction processes. However, till now no strong oxidizing species was successfully entrapped in sol-gel matrices. This observation is probably due to the fact that sol-gel matrices formed via the hydrolysis of Si(OR)4 contain some –OR groups due to incomplete hydrolysis.8 The latter groups are reducing agents and seem to react with strong oxidizing species entrapped in the matrix.

EXPERIMENT

Four types of redox processes were successfully developed, and will be discussed in the following sections:


The basic idea is that a redox reagent, stable in two oxidation states, will be entrapped in the matrix and used as an electron exchange column.

First NiIII/L, L =1,4,8,11-tetraazacyclotetradecane or meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, were entrapped in a variety of sol-gel matrices made of Si(OCH3)4 and/or R-Si(OCH3)3.9 The results proved that indeed oxidizing electron exchange columns of this type can be made. However, some leaching of the complex with time affects the applicability of these columns.
The results also pointed out that the nature of R affects the leaching process. Furthermore, the results point out that silanol groups on the pore surfaces act as axial ligands to the Ni\textsuperscript{III} central cations, affecting their redox properties.\textsuperscript{9} In an effort to inhibit leaching of the nickel complex from the matrix Ni\textsuperscript{III}L\textsuperscript{2}, L\textsuperscript{2} = 1-propyl-1,3,5,8,12-pentaazacyclotetradecane, was covalently bound to a silica support.\textsuperscript{10} This procedure inhibits leaching. However, the observation that the Ni(III) complex is not very long lived, as it oxidizes the organic substituent used to bind it to the matrix, and reacts with O\textsubscript{2} limits its usefulness, and covalent binding of complexes that are stable in the oxidized form has to be achieved.\textsuperscript{10} Reducing electron exchange columns were prepared by entrapping POMs, polyoxometalates, in sol-gel matrices.\textsuperscript{8,11,12} The results point out that the POMs participate in the sol-gel formation process.\textsuperscript{8} As a result each POM is reduced by fewer electrons than the free POM in solution. NMR studies point out that nearly all the POMs in the matrix are available for the redox process.\textsuperscript{13} These matrices were shown to act as efficient electron exchange columns in the reduction of bromate\textsuperscript{12} and de-halogenation of aliphatic halo-organic compounds.\textsuperscript{13}

2. **Catalytic reductions.**

The POMs entrapped in the sol-gel matrices were shown to act also as catalysts in the reduction of aliphatic halo-organic compounds, p-nitro-phenol and bromate by borohydride.\textsuperscript{11,12} Cu\textsuperscript{II}L\textsuperscript{2+}, L\textsuperscript{2} =2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane, entrapped in a sol-gel matrix was shown to be an efficient catalyst for the de-chlorination of Cl\textsubscript{3}CCO\textsubscript{2} by ascorbate.\textsuperscript{14} However, the most efficient catalysts for de-halogenations developed are M\textsuperscript{o}-nanoparticles, M\textsuperscript{o}-NPs, entrapped in sol-gel matrices.\textsuperscript{13,15,16} The observed mechanisms of these reactions are surprising: In all cases the first product is a radical formed via reactions (1) – (5):

\[
\text{M}^\circ\text{-NP} + n\text{BH}_4^- + 6n\text{H}_2\text{O} \rightarrow (\text{M}^\circ\text{-NP})\text{-H}_{4n}^{4n} + n\text{H}_3\text{BO}_3 + 3n\text{H}_3\text{O}^+
\]

Followed by:

\[
(2) \quad (\text{M}^\circ\text{-NP})\text{-H}_{4n}^{4n} + n\text{H}_2\text{O} \leftrightarrow (\text{M}^\circ\text{-NP})\text{-H}_{4n+m}^{4n+(4n-m)} + m\text{OH}^-
\]

and:

\[
(3) \quad (\text{M}^\circ\text{-NP})\text{-H}_{4n+m}^{4n+(4n-m)} + X\text{H}_3\text{CH}_3\text{CO}_2^- \rightarrow \text{CH}_3\text{CH}_3\text{X}_k\text{-CO}_2^- + (\text{M}^\circ\text{-NP})\text{-H}_{4n+m}^{4n+(4n-m-1)} + X^-
\]

\(X = \text{Cl or Br, or } k\)

\[
(4) \quad (\text{M}^\circ\text{-NP})\text{-H}_{4n+m}^{4n+(4n-m)} + X\text{H}_3\text{CH}_3\text{CO}_2^- \rightarrow \text{CH}_3\text{CH}_3\text{X}_k\text{-CO}_2^- + (\text{M}^\circ\text{-NP})\text{-H}_{4n+m+1}^{4n+(4n-m-1)} + X^- + \text{H}^+
\]

The radicals ‘CH\textsubscript{3}\textsubscript{k}X\textsubscript{k-1}CO\textsubscript{2}’ thus formed react with the nanoparticles via:

\[
(5) \quad \text{CH}_3\text{CH}_3\text{X}_k\text{-CO}_2^- + (\text{M}^\circ\text{-NP})\text{-H}_{4n+m}^{4n+(4n-m-1)} \rightarrow \text{H}_{4n+m+1}^{4n+(4n-m-1)} + (\text{M}^\circ\text{-NP})\text{-CH}_3\text{X}_k\text{-CO}_2^- 
\]

However, the fate of the transients H\textsubscript{4n+m+1}\textsuperscript{+(4n-m-1)} + (M\textsuperscript{o}-NP)-CH\textsubscript{3}\textsubscript{k}X\textsubscript{k-1}CO\textsubscript{2} thus formed depends on the nature of M, \textsubscript{X}, \textsubscript{k}, \textsubscript{m}, and m. The results clearly point out that the de-halogenation mechanism is considerably more complex than usually assumed. Furthermore, the M\textsuperscript{o}-NPs, entrapped in sol-gel matrices are also good catalysts for the reduction of p-nitro-phenol and of bromate.\textsuperscript{13}

3. **Electro-catalytic processes.**

As sol-gel matrices are not conducting, special electrodes have to be prepared if such matrices are to be used as electro-catalysts. The electrodes were prepared by forming the sol-gel matrices in the presence of graphite powder and the active species to be entrapped in the matrix.\textsuperscript{14,17,18}
The results demonstrate that the electro-catalytic efficiency depends strongly on the nature of the pre-cursors used to prepare the sol-gel matrices: The highest catalytic currents are obtained when the matrix is prepared from Si(OR)₄, when the constituents of the matrix include also R'-Si(OR)₃ the catalytic current decreases with the increase in the hydrophobicity and volume of R'.


It was shown that Ni⁴⁺L⁻ is stabilized in sol-gel matrices. In homogeneous solutions Ni⁴⁺L⁻ is unstable, and has a lifetime of ca. 1 second. On the other hand, in a sol-gel matrix its lifetime is at least several hours. This effect is attributed to the observation that the mechanism of its decomposition in homogeneous is a second order one, and the entrapment inhibits this mechanism.

CONCLUSIONS

Three types of processes were studied:

a. The electro-catalytic oxidation of amines and alcohols by matrices with entrapped NiL²⁺, L = 1,4,8,11-tetraazacyclotetradecane. The results point out that the mechanism of the electro-catalytic process differs from that observed in homogeneous solutions and depends on the nature of the electrode. Thus for example N(CH₃)₃ is oxidized in the electro-catalytic process while it is not oxidized on GC electrodes. Furthermore the matrix protects NiL²⁺ against the oxidation of the ligand, thus the ligand is oxidized only after several catalytic cycles whereas in homogeneous solutions it is oxidized immediately.

b. The electro-catalytic de-chlorination of Cl₃CCO₂⁻ by matrices containing CuL₁²⁺, L₁ = 1,4,8,11-tetra-aza-cyclo-tetra-decane. Surprisingly oxalate is the main final product, though cathodic potentials are employed. The observed electro-catalytic current decreases when cyclic voltammetry is performed at high scan rates. This surprising result indicates that the mechanism of the electro-catalytic process depends on the scan rates. Plausible mechanisms at low and high scan rates are proposed.

c. Electro-catalytic water oxidation in the presence of bicarbonate: Sol-gel electrodes prepared from Si(OR)₄ were impregnated with Ni²⁺ cations and used as anodes in the presence of bicarbonate. The results prove that the bicarbonate acts as an electro-catalyst for water oxidation in neutral solutions. The electro-catalytic currents depend linearly on the concentration of the bicarbonate.

REFERENCES

4. V. V. Vinogradov, D. Avnir, Scientific Reports, 2015, 5:14411 | DOI: 10.1038/srep14411, 2015.