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Warsaw, Oct. 17th 2022

***Review of the Ph.D. thesis of Mrs. Alcina Johnson Sudagar***

The Ph.D. thesis by Mrs. Alcina Johnson Sudagar, entitled: “*Synthesis, characterization, and testing of catalytic nanomaterials – greener route to synthetic methods*” assigned to me for a review, was prepared at the Institute of Physical Chemistry, PAS in Warsaw in the Molecular Films Research group – a very well-known and renowned research group, under the supervision of Prof. dr hab. Włodzimierz Kutner and auxiliary supervision of Dr. Krzysztof Noworyta. The Ph.D. student, Ms. Alcina Johnson Sudagar carried out her research work within the International Studies in Chemistry framework, and in collaboration with the research group of Prof. Francis D’Souza at the University of North Texas.

The search for new, more selective, and “greener” routes, increasing the effectiveness of the chemical industry, simultaneously limiting energy consumption, the costs of processes, and the deteriorating impact on the environment is a must in a nowadays life. One of the most important pathways in this direction is to develop new catalysts, favoring less extensive, energy and material-wasting processes.

Ergo, as the author stated, the goal of the Ph.D. thesis was to enable greener routes in catalysis. This rather ardent goal was tackled in two rather loosely related approaches: one directed at the electrosynthesis of molecularly imprinted polymers (MIPs) mimicking the shape-selective catalysis of the C-C coupling reaction, and the other approach focusing on the use of brewery waste for the synthesis of silver-based nanomaterials toward their possible applications in photocatalytic OER (very briefly, 2 pages only) and catalysis of oxygen reduction reaction (ORR).

The Ph.D. dissertation was prepared according to a rather typical scheme and consists of an Abstract, an Introductory part (Chapter 1) together with Experimental techniques and methods (Chapter 2) on roughly 100 pages of text and figures, well balanced by the two chapters describing Ph.D. student's own experimental work on molecularly imprinted polymers for selective electrosynthesis (Chapter 3) and preparation and characterization of silver-based nanocomposites for catalytic applications (Chapter 4). The dissertation ends with Chapter 5 presenting and explaining again the motivation for this research, summarizing the achievements, and giving the synopsis for the future. It is supported by a large number of 440 literature positions, some of them referring to the web pages for basic information.

And so, Chapter 1 provides well-prepared and written information on homogeneous and heterogeneous catalysis with picturesque schemes illustrating the text, including two currently utilized models of enzyme catalysis (Scheme 1.3). The latter will be frequently referred to during the discussion on the mechanisms of workings of molecularly imprinted polymers. This chapter is based on the analysis of 274 well-selected literature references. Then, Ms. Alcina Johnson Sudagar describes the role of electrocatalysis and electrosynthesis as alternative routes in technological applications, where the electrode surface, specially adapted or tailored to the considered processes, acts as a controllable catalyst for energy conversion and storage. This part prepares the reader well for the subsequent part on molecularly imprinted polymers (MIPs) designed for selective electrosynthesis. I have only one comment on Scheme 1.4, as it is too simplified for the Ph.D. thesis and can be easily omitted without any harm to the clarity of the text. Next comes Section 1.3, which, apart from a historical outlook, gives an excellent review of the principles, and preparation methods, and points to the crucial factors affecting electrochemical MIP preparation. Ms. Sudagar shows also here the necessity of using various techniques, including simulation, providing better insight into the molecular interactions between the template and functional monomers, aiding in the successful MIP formation. However, some notions about the effects of progressive and simultaneous nucleation mechanisms that may affect the MIP (and NIP) film formation should be shown. Also, there is one sentence (p.23, last sentence of Section 1.3.5) that prepares for deeper discussion, yet it was left without it; it reads: "Electrochemical potential control is a significant parameter affecting the MIP films' morphology". This is a fundamental statement and as such it requires some thorough explanation. Moreover, I have a feeling, particularly due to the additive form of Eq. 1.1, that it can be discussed more deeply in this section, particularly in light of the subsequent Section 2.1.1a entitled: Theoretical simulations. Next, Section 1.3.6 gives also some

selected examples of catalysis and selective electrosynthesis that were enabled only in the presence of MIPs on the electrode surface. Finally, Section 1.3.7 explains why Ms. Alcina Johnson Sudagar has chosen DMBh as a representative candidate for selective electrosynthesis of TMBh – a significant component for catalytical hydroformylation. In her work of tentative selective electrosynthesis of TMBh, Ms. Sudagar was facing the main challenge of several side-reactions (Scheme 1.11), therefore the choice and preparation of a suitable MIP was a crucial step for subsequent establishing large-scale setups for industrial applicability and yield. With this chapter ends the part dedicated to the role of MIPs in selective electrosynthesis, biphenols in particular.

The next part of this Introductory chapter describes the use of nanomaterials (“green”) for catalysis, focusing on a somehow exotic procedure of using brewery wastes for the synthesis of silver-containing nanomaterials, both as reducing of Ag(I) ions and as capping agents, stabilizing the obtained nanostructures. These wastes contain a vast, mostly undefined mixture of amino acids, sugars, proteins, polyphenols, and other organics, differing from one brewery to another. Even though the author calls upon somehow similar studies on nanomaterial synthesis with help of various “green” organic extracts, the complexity of the system used renders the identification of the reactions that lead to the nanocomposite formation, stabilization, and elucidation of photocatalytic mechanisms, rather impossible. On this occasion, Ref. 198 does not describe the stabilized Mn<sub>3</sub>O<sub>4</sub> NPs with super-capacitive properties, but antimicrobial Ag nanoparticles, and it was published in 2015, not in 2019. Ms. Alcina Johnson Sudagar discusses next some basics of oxygen evolution reaction (OER), hydrogen evolution (HER), and oxygen reduction reaction (ORR) from the point of view of practical utilization of nanocatalysts, and photocatalysts and their effects on the electrocatalytic mechanisms involved in these reactions. She presents some textbook redox reactions involved, quoting the values of the equilibrium potentials vs. RHE (Eqs. 1.2-1.5), and the vs. SHE (line 5 from the top, p. 37). Is there any difference between these two reference electrodes, or not? It affects the consistency of the text. Also, discussing the ORR, it would be worth mentioning that one of the major problems in its practical use is oxygen limited dissolution in aqueous solutions and therefore - diffusion control of this reaction. This Introductory section is summarized by the thesis’s aims and scope, which helps understand the text that follows, bringing forth also the main points presented earlier in the Abstract.

Chapter 2 presents all experimental techniques, including theoretical simulations, and characterization techniques used by Ms. Alcina Johnson Sudagar during her Ph.D. research.

The first section (section 2.1) describes the use of simulation techniques aimed at predicting the formation of cavities suitable for MIP preparation selective toward the electrosynthesis of TMBh from DMPH. Density functional theory was used for prescreening functional monomers responsible for this selectivity and then QM and MM simulations for the cavity effect on the synthesis of TMPH. This modeling part allowed the selection of FM-2 (newly synthesized *p-Bis(2,2',5',2''-terhien-5'-yl)methyl benzoic acid*) functional monomer for MIP-2. This was important from the point of view of evaluating the standard Gibbs free energy and standard enthalpy changes, in the case of free molecules (DMPH radicals) as substrates and the same radicals within the MIP cavity in the synthesis of TMBh. The results of the simulations will show strong evidence of the catalytic capabilities of this particular MIP cavity toward the TMBh synthesis. This will be presented in Section 3.7.6, "Theoretical simulations of selective TMBh synthesis at MIP-2 films-coated electrodes (Table 3.5)". However, I have a feeling that it might be useful for the reader to have some basic set of equations used for the simulations, but also the general approach in modeling the effect of solvents used. From what I could understand, the additivity of dielectric permittivities of solvent components was assumed and this was the only parameter characterizing the environment.

The next sections describe the working electrode materials and surface preparation, enabling the deposition of NIP and MIP. In general, from the electrochemical point of view, these were the standard procedures, including the three-electrode glass cell for such investigations. This preparative part is followed by the procedures for MIPs (MIP-1 and MIP-2) and NIP preparative electrodeposition under potentiodynamic conditions with subsequent template extraction in the case of MIPs. As a source text for basic information on the techniques that were used for the characterization and evaluation of the performance of MIPs and nanocomposites toward the goals of the thesis, Chapter 2 is well-written, however, sometimes oversimplified. For instance, I do not understand the reason for placing Fig.2.1.b, because the "stagnant layer" suggests the motion between solid and liquid (plane of shear), and the diffuse layer should be defined since the next page contains the term "diffusion layer". There might be some misunderstanding without a precise distinction between these two. Also Fig. 2.1.c is very nice to look at, but the quantitative and qualitative practical information hidden in this graph is missing. The same is in Fig. 2.2.b. One typo (I guess) error is that "current  $I_1$  ...is applied" should read "voltage". Fig. 2.4.b: is there any quantitative description of current transients in chronoamperometry? Page 52, line 7 from top: is there a real band gap in metals? Fig. 2.5 does not give any information characteristic of a semiconductor electrode. It can be easily used in

any 2-electrode electrochemical cell, so what was the reason for placing it there? Fig. 2.7 uses  $1/j_{k,O}$ , whereas throughout the text, Equation 2.3, and in the figure caption it is  $1/j_{d,O}$ . The equilibrium condition is not mentioned when describing the adsorption phenomena and their theoretical analysis. Also, discussing the simplifications in Langmuir theory, the assumption of the maximum number of active sites is not listed. Discussing the section on silver nanocomposites, there is no mention of possible oxidation of Ag during drying in the oven. Anyway, these are small shortcomings that I should place in my review to show that I read it carefully. This whole part shows the large number of techniques that Ms. Alcina Johnson Sudagar had to master or at least become acquainted with to perform such vast experimental work during her Ph.D. research.

Now comes the experimental part, containing two separate lines of research under a common leitmotif: electrocatalysis for i) selective electrosynthesis of TMPH molecules with help of MIPs, and ii) “green” silver nanocomposites for ORR.

### **Selective electrosynthesis of TMPH**

In a challenging DFT simulation work, Ms. Alcina Johnson Sudagar prescreened (in a vacuum) various functional monomers for their non-covalent interactions with TMBh template molecules. The selection for future cavity synthesis was based on high negative Gibbs free energy gain. It occurred that the FM-1 monomer (*diphenylamine-2-carboxylic acid*) at molar ratio TMBh:FM-1 1:2 showed the highest negative energy gain, especially in its carboxylate form. Then, follows the sections containing thorough spectral analyses of the TMPH template and functional monomers binding, namely: UV-vis titration and FTIR studies on monomer and template interactions, keeping in mind the results of DFT simulation work. This section contains a large number of spectra and it would be very helpful if the characteristic wavelengths and wavenumbers are placed in these spectra; also *vide infra*. Otherwise, it is really difficult to follow the reasoning leading to the selection of the optimized molar ratio of TMBh and FM, as well as the comparison of FM-1 and FM-2. Anyway, I have found some discrepancies, such as in Fig. 3.3a, the FTIR spectrum of FM-1 shows only one band (at ca.  $3300\text{ cm}^{-1}$ ) in the range  $3200\text{-}3600\text{ cm}^{-1}$ , whereas in the text there is a discussion on the two bands of FM-1 in this region. Indeed, more bands appear, but only in the presence of TMBh. This can be discussed during the Ph.D. defense. There are also some mistakes such as “frequencies shifted by  $\sim 25\text{ cm}^{-1}$ ”, or “higher wavelengths” instead of wavenumbers (all in p. 111). After the spectral characterization, Ms. Alcina Johnson Sudagar presents the preparation of two types of MIPs, named MIP-1 and MIP-2, differing in the electropolymerization components (details shown in

Scheme 3.3 for MIP-1 and Scheme 3.4 for MIP-2). The results were confronted with the nonimprinted polymers – NIPs. What was important during the research work was the necessity of deprotonation of FM-1 and FM-2 molecules by the addition of TEA during the electropolymerization of MIPs, improving the film performance. However, there was an optimum concentration of 1 mM, because a further increase in TEA concentration restricted the film formation, particularly in the case of MIP-2. This section presents also the experimental optimizations of the ratios of molecular concentrations of film-forming components. One of the most important features of MIPs in general should be the possibility of maximum extraction of template molecules (TMBh) from the film cavities, leaving them ready for subsequent electrosynthesis of TMBh from DMBh. This process was also thoroughly investigated by the Ph.D. student and the results of such experiments allowed her to choose MIP-2 for further studies of selective TMBh synthesis. Further, these films were denoted as MIP-2a (thicker) and MIP-2b (thinner) During her experimental work, Ms. Alcina Johnson Sudagar found also that the quality of MIP films depends strongly on the freshness of the polymerization solution; she called it “aging” of the optimized pre-polymerization complex, adversely affecting the reproducibility of MIP films’ performance. Based on her results, she postulated that this effect may result from a decomposition/disaggregation of the complex over time. She supported this suggestion with UV-vis spectroscopy, DLS, and AFM techniques. generally, these studies were summarized in Table 3.3, which shows that the thicker, MIP-2a films, become even thicker after the extraction of template molecules, becoming also rougher and “stiff” (but the latter two parameters within the experimental error), whereas in the case of MIP-2b the films become thinner after the extraction, due to the removal of some aggregates present on the film surface. Having all this characterization of MIP-2 films ready, Ms. Sudagar proceeded toward their use for the selective TMBh electrosynthesis. For this, she used electrochemistry (for synthesis and optimization) and HPLC for the detection of products. By varying the mode (potentiostatic or galvanostatic) of the electrosynthesis, at pre-defined potential or current density and time, she was able to obtain a relatively high selectivity of MIP-2a films in comparison with the bare Pt electrode and NIP-2a electrodes under potentiostatic conditions (2V vs. Ag quasi-reference electrode, 2h reaction). The value of potential, was, however, questioned and lowered to 1.2 V, to preserve the film’s integrity and reusability. Next was an obvious step – the large-scale TMBh electrosynthesis, as was described in the synopsis of the Ph.D. research. The results are summarized in Fig. 3.23 and are quite good in terms of DMBh conversion and yield considered together because the DMBh conversion on bare Pt electrode was at least comparable to the other two, however, there was no TMBh desired product if Pt bare electrode was used. It was

also concluded by Ms. Alcina Johnson Sudagar, that the thinner MIP-2b films were slightly more selective toward the TMBh product electrosynthesis. As I already mentioned discussing the simulated values (*vide supra*) of the standard Gibbs free energy and standard enthalpy changes accompanying the TMBh synthesis, the Ph.D. student also presented 3D molecular structures of the MIP-2 cavities with skeleton models and molecular electrostatic potential surface, and the substrate (DMBh) positions within the cavity, facilitating the interactions between the reagents and favoring the TMBh product formation. This part confirmed the experimental results and supported the concluding remark that MIPs are promising electrode modifiers for selective electrosynthesis.

### **“Green” silver nanocomposites for catalytic applications**

This chapter (Chapter 4) is nicely summarized in Scheme 4.1, which guides the reader through the synthesis of silver nanocomposites with help of brewery wastes, the nanocomposites' characterization, and finally their use in catalysis toward ORR. In this respect, I should note, that the reactions leading to the formation of the Ag core, or the contents of the shells were not identified, except for the functional groups of the organics, via, e.g., the FTIR spectroscopy. As Table 4.1. (data obtained by Dr. D. Michałowska and Prof. M.Ł Roszko, Inst. of Agriculture and Food Biotechnology, State Res. Inst., Warsaw) shows, there are significant differences in Cl and P contents between brewery wastes denoted as BW7, BW9, and BW 5, used for the nanocomposite formation. And so, BW5 is characterized by the highest P and Cl, followed by BW9 and BW7. There are other significant differences pointed out by the Ph.D. student in her thesis, but I was surprised by these particular elements, taking into account the results of XRD diffraction analysis, Fig. 4.2. This was because, in the diffractogram of BW9 that contained a quite high content of P (ca. 149 mg/mL), there was no sign of  $\text{Ag}_3\text{PO}_4$  formation, that was quite evident in the diffractogram of BW7 (ca.97 mg/mL). I would be glad to hear the comments from Ms. Alcina Johnson Sudagar on this issue. Next comes the SEM analysis of nanocomposites, accompanied by EDXRF spectroscopy, and UV-vis analysis. In the case of the latter, it would be helpful to show also the spectrum of pristine Ag nanoparticles to identify its absorption band. Also, calling upon the semiconducting behavior of  $\text{Ag}_3\text{PO}_4$ , its properties from the literature data should be confronted with the rationale (and puzzle) presented in the thesis (p.164). A similar opinion I would like to share considering the sorption analysis presented in section 4.3.5: specific surface area shown in Table 4.5, should be at least compared with literature data for different Ag composites, otherwise, this section has an elusive value to me. Perhaps further studies on the adsorption of various compounds/environmental

contaminants are planned, because of the analysis of catalytic properties of the Ag nanocomposites that follows in the next sections 4.3.7a-c. Firstly, the ESR studies were carried out to characterize the electronic properties of the obtained nanocomposites aimed at elucidating their tentative catalytic and electrocatalytic behavior. The results were then compared with the photoelectrochemical studies of BW5Ag1, BW7Ag1, and BW9Ag1 in a classical system, after deposition on the FTO electrode. The latter results, presented in Fig. 4.13, show, that BW5Ag1 presents the highest photocurrent response (2 times higher than pristine FTO) in LSV experiments in the range 0.5-0.9 V vs. Ag quasi-reference electrode. Regardless of the relatively weak response (I assume, that for the calculations of photocurrent densities, the geometric area was used and the amount of deposit was strictly controlled), this figure shows that not only the photocurrent rises with potential, but also the shape of photocurrent responses differ with the potential, suggesting various mechanisms of the obtained response. I wonder why these results were not exploited further from the point of view of full characterization of the semiconducting behavior of nanocomposites and OER. Moreover, the highest response of BW5Ag1 was explained by the presence of Ag nanoparticles/nanoclusters (supported by ESR studies), however, the PXRD data show that in the case of BW5Ag1 the  $Ag_{met}$  phase content was very small, even though the Ag nanocrystallite size was the highest. Does this mean that increasing the density of Ag nanoclusters within the layer on the electrode would result in larger photocurrents? Leaving this topic, Ms. Sudagar considered the electrocatalytic oxygen reduction reaction, evaluating its mechanism with help of RRDE (GC disk). In the case of oxygen-saturated solution and in terms of the reduction current values, the obtained results are not spectacular, because the current value is ca. -0.8 V for bare GC ring and BW7Ag3-coated electrode are very similar. What was changed was the shape and the threshold value of the reduction current compared to the bare electrode. I would expect here at least a hint of a discussion on these differences. Then, the mechanism of the ORR reaction was evaluated using the Koutecky-Levich plots to assess the number of electrons involved as well as the kinetics of the overall ORR process in the neutral (0.1 M  $KNO_3$ ) and alkaline (0.1 M NaOH) solutions. Even though these plots yielded ca. 2e reduction reaction and the kinetic current densities are even the same in both solutions, the ring currents – a measure of hydrogen peroxide amount in the products were significantly lower in the alkaline solutions (exemplified by BW7Ag3). This observation was rather unexplained by Ms. Alcina Johnson-Sudagar in her Ph.D. thesis, and was left with the statement that to address this issue it is essential to explore it with techniques like ESR spectroelectrochemistry. Given the results, it was very good to summarize her efforts and give some summary and future perspective on the cost-effective and

environmentally friendly use of similar “green” Ag nanocomposites in catalysis and photocatalysis. Ms. Alcina Johnson Sudagar presented such synopsis in Chapter 5, which summarizes also her viewpoint on MIPs in selective electrosynthesis.

### **Concluding remarks**

Overall, my several critical comments are directed toward a vivid discussion during the Ph.D. defense and are by no means diminishing her research's cognitive and scientific value. The apparently distinct research areas of MIPs and nanocomposites were neatly connected by their catalytic functions. Ms. Alcina Johnson Sudagar co-authored 4 scientific publications in renowned journals (5 “in preparation”, perhaps already submitted at the time of this review), and two of the published ones are directly related to the topics in the dissertation.

Let me conclude, that the Ph.D. thesis of Ms. Alcina Johnson Sudagar, represents a valuable contribution to the existing state-of-the-art research on the catalytic synthesis of valuable industrial organics and “green” utilization of industrial (brewery) wastes as sources of catalytic nanocomposites. It complies with the conditions set forth by Polish law (art.187 ustawy z dnia 20 lipca 2011 r, Prawo o Szkolnictwie Wyższym i Nauce, Dz.U. z 2022 r., poz. 574 z późniejszymi zmianami). Therefore, I recommend it as the admission basis for the public Ph.D. defense of Ms. Alcina Johnson Sudagar, MSc. After completing all required subsequent steps, I propose awarding Ms. Alcina Johnson Sudagar the academic degree of Ph.D.

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