ABSTRACT OF THESIS

Tollens' reactions have been investigated for various transformations, as shown in the figure, and not limited to well known distinguishing test between aldehydes from ketones as a silver-mirror test. The present work revolves around an in-depth understanding of Tollens' reagent, as a novel oxidizing agent. The thesis is arranged into five chapters, in which 1st chapter presents a general history of Tollens' reaction along with an outline of the thesis.

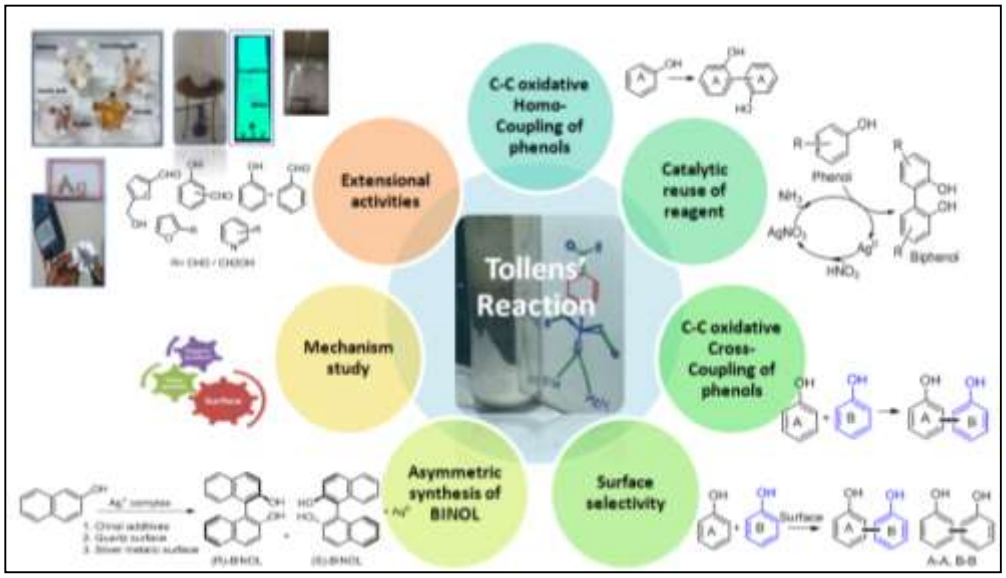

Figure: "Re-investigating Tollens' reaction"

Chapters 2, 3, and 4 report Tollens' reagent, to the best of our knowledge first time, for **C-C oxidative coupling** of phenol and 2-naphthol derivatives. One of the important findings is related to selective C-C oxidative **homo-coupling, cross-coupling, and/or asymmetric-coupling** using Tollens' reagent to obtain regio-, chemo-, or stereo- selectivity. The reagent was recycled efficiently (over 95%) similar to a catalyst and quantified using *conductometric* titration (> 95% up to 5th cycle). All C-C coupled products were characterized using mass-spectrometry, FT-NMR (^{1}H and ^{13}C), and FT-IR spectroscopic analysis and obtained with good yields (around ~90%). In one curious experiment, coupling reactions were carried out in a polypropylene vial (Eppendorf tube) resulted in the silver particle formation over the typical formation of a silver mirrored film. This prompted us to carry out a reaction, using plastic or teflon vessel instead of a typical borosilicate glass vessel, between 2,6-dimethoxyphenol and 2,6-di-*tert*butyl-phenol where the chemo-selective cross-coupling resulted in an isolated yield of 70% to 10%, respectively. To our surprise, oxidative coupling of 2-naphthol in a **Quartz** surface and freshly generated 'hypothetically-chiral' **silver-coated**

surface, (obtained from Traditional Tollens' Reaction with optically active *D*-glucose), resulted in stereo-selective BINOL formation (90-92 % isolated yield) and more importantly up to 57% enantiomerically enriched (*S*)-enantiomer (from polarimetry analysis). These results were led us to analyze concurrent precipitation of silver (in the form of silver mirror film or particles) using FE-SEM, SEM, microscopic image study, and P-XRD analysis. On analyzing FE-SEM showed changes in the morphology from truncated triangular pallets to cubical-rod shape due to change in the surface from teflon to polypropylene. Which resulted in selective homo- and cross-coupling product formation. Similarly, spherical shaped morphology was observed in the stereoselective reaction of 2-naphthol in quartz. The powder-XRD analysis of silver particles obtained from C-C coupling reaction shows the reflections at 2θ of 38.1º, 44.3º, 64.5º, 77.5º, and 81.5º, which can be indexed to the (111), (200), (220), (311) and (222) reflections of the FCC lattice system of silver particles in all these cases. We presently understand the origin of intensities difference and extra peaks in P-XRD data of these silver particles. The experimental results indicate oxidative **coupling** reaction, concurrent selective aggregation of silver particles on different surfaces resulted in chemo- and stereo-selectivity. On this basis, the thesis highlights a novel **surface-directed reaction mechanism** where chemo, as well as stereo-selectivity, gets driven by the growth of Ag-particles Ag^0-Ag^0 cohesive interactions and adhesive interaction between $Ag_{\text{-particle}}$ and surface.

Chapter 5 discusses three different aspects of Tollens' reactions- (i) the **selective oxidation** of aldehyde, phenols, and alcohols derivatives of hetero-aromatic and aromatic; (ii) interesting ways to mix reducing agents with $[Ag(NH_3)_2]^+$ as an activity not limited to **educational experiment**; (iii) synthesis and study of **silver nanoparticles**.

In short, the present investigation shows Tollens' reagent as a unique reagent for C-C coupling reactions, as shown in the figure. The study reveals an active role of macroscopic interaction in 'manipulating' molecular level interactions which results in chemo- and stereo-selectivity of the organic product formation.