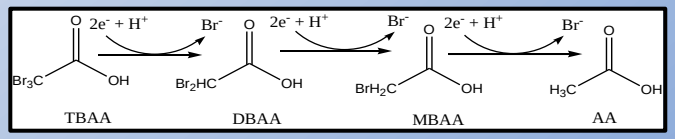
M° nano particles (M = Au, Ag) incorporated into silica matrices as catalysts for the reductive de-halogenation of halo-acetic acids

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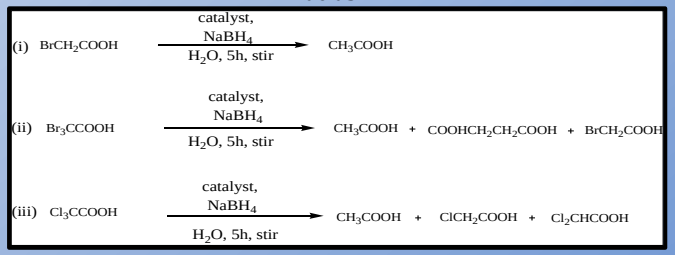
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Halogenated organic compounds are widely used as starting materials, intermediates, solvents in chemical industry, agricultural chemistry, medicinal chemistry and thus they are routinely found in waste water. These halogenated organic compounds are of great concern for their bio-accumulation, toxicity and persistence. In fact, most of the top hundred species in the list of hazardous compounds are halogenated organic compounds. Among these halo-organic compounds especially halo-acetic acids (HAAs) are harmful to many aspects of the environment and human life. Nowadays, researchers from all over the world are working on processes for the removal of these pollutants. However, noble metal nanoparticles have not been used extensively for the de-halogenation process though they have exceptional catalytic properties. Therefore, mono- bromo-acetic acid (MBAA), tri-bromo-acetic acid (TBAA) and tri-chloro-acetic acid (TCAA) were chosen as model substrates for the reductive de-halogenation by BH_4^- catalyzed by sol-gel entrapped Au° and Ag° nanoparticles. It was previously reported that TBAA undergoes consecutive de-bromination reactions to give di-bromo-acetic acid (DBAA), then MBAA and finally acetic acid (AA) (Scheme 1). Surprisingly, the results reported herein point out that Au^0 and Ag^0-NPs catalyze the de-bromination of TBAA through a different pathway to yield succinic acid (SA) along with acetic acid. However, the reduction of MBAA and TCAA proceeded through the mechanism reported in the literature (Scheme 2). Furthermore, even the rate of the addition of the reducing agent, $NaBH_4$, affects the relative yields of the products during the reduction of TBAA.

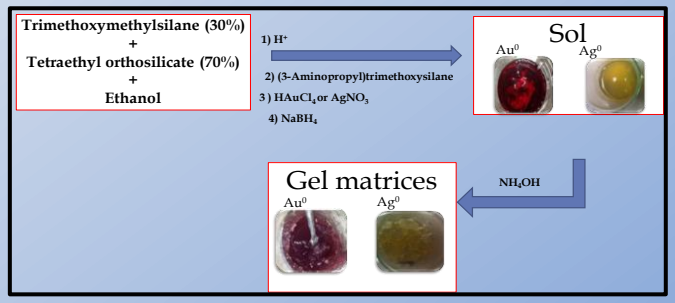
Scheme 1: The proposed pathway for the degradation of tri-bromo-acetic acid according to a literature report.



Scheme 2: Au° and Ag° -NPs entrapped in ORMOSIL catalysed de-halogenation of mono-bromo-, tri-bromo- and tri-chloro- acetic acids



Preparation of sol-gel silica matrices incorporated with gold and silver nanoparticles :



Characterization

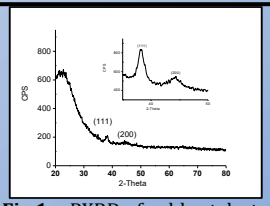


Fig.1a: PXRD of gold catalyst.

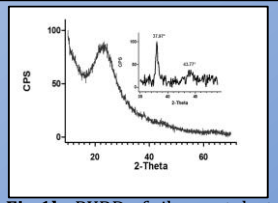


Fig.1b: PXRD of silver catalyst.

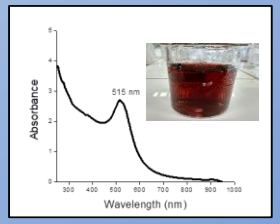


Fig.2a: UV-vis spectra of gold catalyst in sol state.

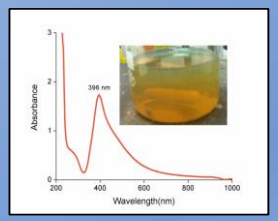


Fig.2b: UV-vis spectra of silver catalyst in sol state.

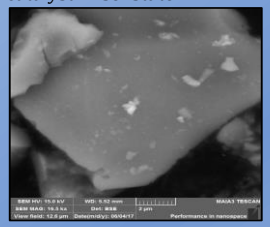


Fig.3a: SEM image of gold catalyst.

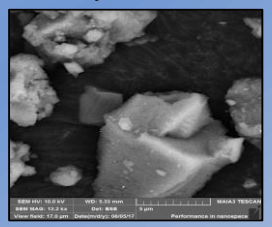


Fig.3b: SEM image silver catalyst.

Results and discussions

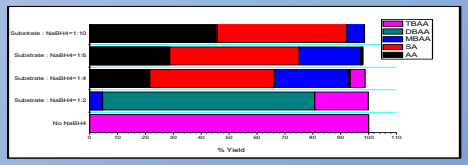


Fig. 4: Effect of the molar ratio of TBAA and $NaBH_4$ on the products distribution. Aqueous $NaBH_4$ solution was added in one portion.

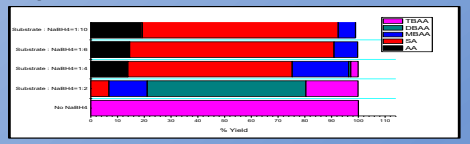
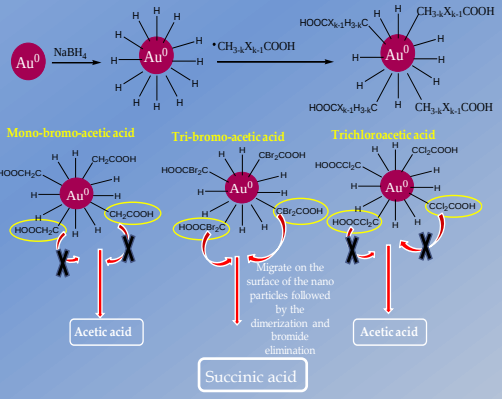
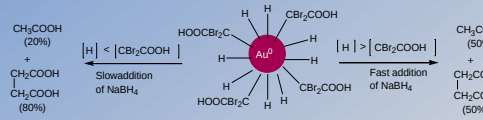


Fig. 5: Effect of the molar ratio of TBAA and $NaBH_4$ on the products distribution. Aqueous $NaBH_4$ solution was added dropwise over a period of 3.5 h.

The proposed mechanisms involved in the catalytic de-halogenation processes on Au°-NPs. :



Slow addition of the reducing agent facilitates the production of succinic acid as the major product



Conclusions

1) Radicals are intermediates in the catalytic de-halogenation process. 2) The detailed mechanism of the process differs for different substrates. 3) The rate of addition of the reducing agent, BH_4^-, has a major effect on the detailed mechanism of the de-halogenation of TBAA. The slower the addition the higher the yields succinic acid for TBAA reduction.