ENTRAPMENT OF Ag^o AND Au^o NANOPARTICLES IN SOL-GEL MATRICES FOR CATALYTIC APPLICATIONS

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Introduction

Sol-gel matrices can be efficiently utilized in heterogeneous catalysis [1-4]. The incorporation of a homogeneous catalyst into the matrix combines the specificity and reproducibility of the homogeneous catalyst with the advantages of heterogeneous catalysts (stabilization and easy separation of the catalyst) [5, 6]. The chemical behavior of these catalysts is affected by: the flexibility of the sol-gel cages and the accessibility of the entrapped species [7]. These properties can be controlled and tailored due to the large number of adjustable parameters of the sol-gel synthesis *e.g.* the nature and concentration of the precursors [8, 9] water concentration used [10], temperature, solvent [10, 11], catalyst used to accelerate the synthesis of the matrix [10, 12], aging and drying conditions. Furthermore, the catalyst can be used in solvents in which it is insoluble and is recyclable. Another important advantage is that the sol-gel entrapment takes place in the inner pores where the catalyst is protected and stabilized [13, 14].

In this study the catalytic ability of metal nanoparticles, that are embedded in SiO_2 matrices prepared by using the sol-gel synthesis route in order to prevent their agglomeration and thus reducing their catalytic activity, is investigated. All matrices contained M° nano-particles prepared by the reduction of 0.032 mmolof either $AgNO_3$ or $HAuCl_4$.

Results and Discussion

The catalytic efficiency of Ag^o and Au^o nanoparticles embedded in the prepared matrices, was examined by the investigation of reduction reaction of 4-nitrophenol, 4-NP, to 4-aminophenol by $NaBH_4$ [15-17]. The matrices prepared can be used as effective catalysts for the tested reduction reaction and the fixation of gold and silver nano-particles does not affect their catalytic activity. The reaction was followed by using a UV-vis absorption spectrophotometer. The effect of various parameters on the catalytic activity of the immobilized nanoparticles was investigated.

Effect of matrices composition

Matrices were prepared by using different compositions of the silane precurses: matrices containing only tetra-ethoxy-silane, TEOS, and matrices containing both tetra-ethoxy-silane and methyl-trimethoxy-silane, MTMOS, in 70:30 and 50:50 mole ratio. The effect of the addition of aminopropyl-triethoxy-silane, APS, to the components of the matrices was also examined. The percent of reduction of 4-nitrophenolwas calculated by measuring the absorption of 4-nitropheol solution (400 nm) before and after the reaction.

Fig. 1 shows the effect of the matrix composition on the decomposition of 4-nitrophenol, when matrices containing silver nanoparticles were used as the catalyst. Matrices prepared by using the precursors' mixture of M-TMOS and TEOS have better catalytic activity compared to matrices that contained only TEOS. This is attributed to the fact that the M-TMOS affects the final structure the matrix and the hydrophobicity of the gel obtained, and therefore is likely to affect both the dispersion of the particles in the matrix and the catalytic activity.

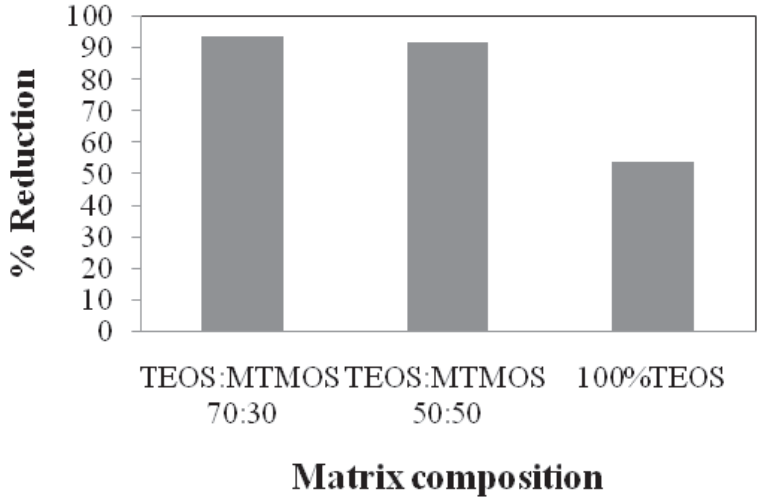

Fig. 1. Effect of Ag^{o} matrix composition.
The solution contained: 0.12 mM 4-NP, 1.2 mM $NaBH_4$ and 1.0 gram of matrix (suspended in the solution). The reaction medium was mixed for 12 minutes before filtration

The effect of the addition of APS to the precursors' solution was also investigated. As can be seen in Fig.2 the catalytic activity of the matrix prepared with APS is higher, this is attributed to the fact the amine groups contribute to the stabilization of gold nanoparticles in the matrix thus obtaining a higher catalytic efficiency [18, 19].

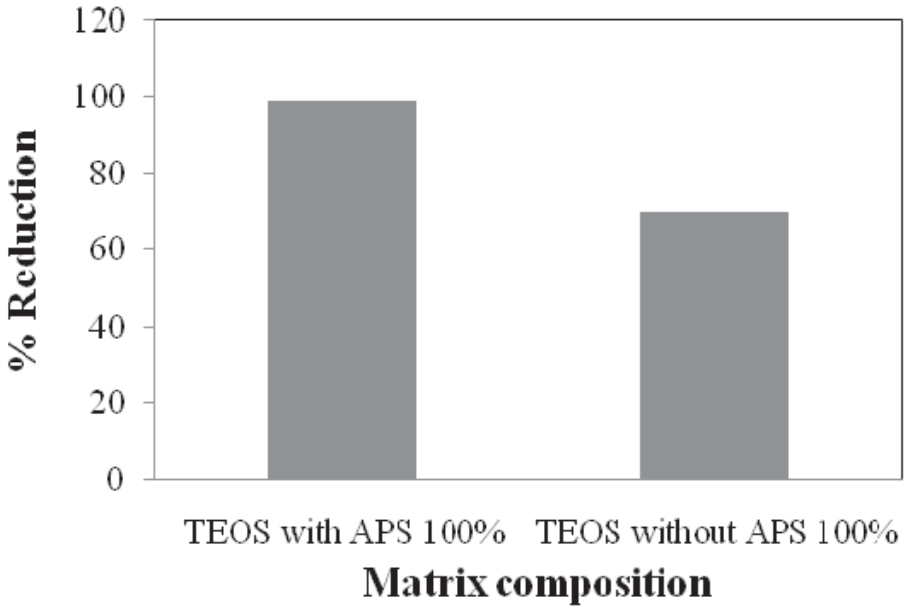

Fig. 2. Effect of APS addition in 100% TEOS Au^{o} matrices.
The solution contained: 0.12 mM 4-NP, 1.2 mM $NaBH_4$ and 1.0 gram of matrix (suspended in the solution). The reaction medium was mixed for 12 minutes before filtration

The relative catalytic activity of entrapped gold and silver nanoparticles in matrices was studied. As can be seen in Fig. 3 the gold matrix has a higher catalytic activity, this is attributed at least in part to the fact that the Ag°-NPs are considerably larger than the Au°-NPs and therefore the latter have a significantly larger surface area.

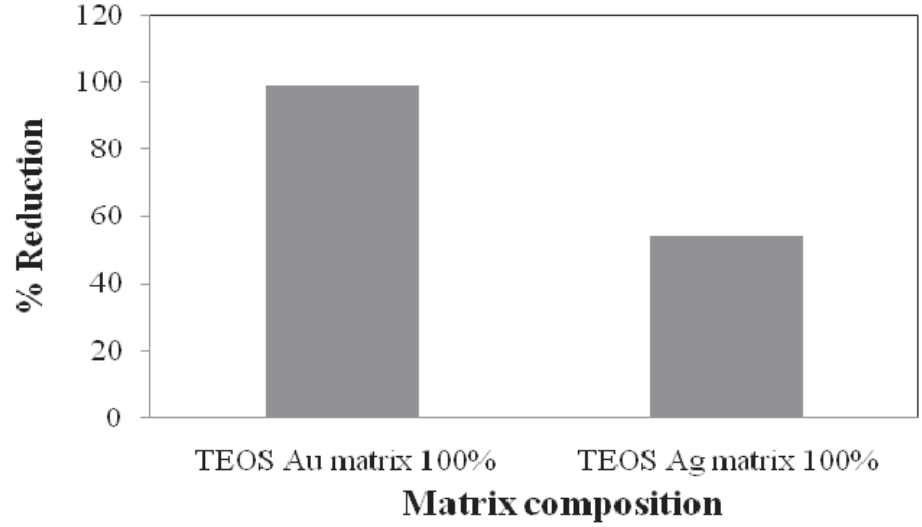

Fig. 3. Comparison of the catalytic activity of gold and silver nanoparticles.
The solutions contained: 0.12 mM 4-NP, 1.2 mM $NaBH_4$ and 1.0 gram of matrix (suspended in the solution). The reaction medium was mixed for 12 minutes before filtration

Reuse of matrices

In order to examine the stability of the gold and silver matrices, matrices that were used in one reaction cycle were washed and used for a second catalytic reduction. As shown in Fig. 4 reused matrices containing gold nanoparticles have demonstrated good catalytic activity as can be concluded from the disappearance of the absorption peak of 4-nitrophenolat 400 nm and the appearance of the 4 aminophenol peak at 300 nm.

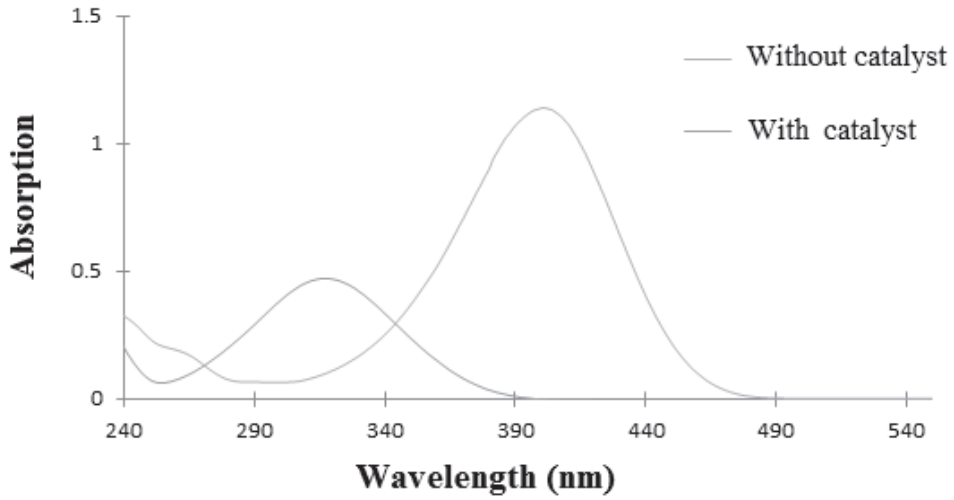

Fig. 4. Reduction of 4-nitrophenol in the presence of recycled Au° catalyst

In the case of recycled 100% TEOS matrix embedded with Ag° nanoparticles no catalytic activity was observed, while the matrix prepared with a mixture of TEOS and MTMOS showed partial activity.

Characterization of the matrices

Fig. 5 presents the FT-IR transmission spectra of 70:30 TEOS:MTMOS matrix (blank) and a 70:30 TEOS:MTMOS-Ag^{o} matrix. The band at 1392 cm^{-1} is attributed to the silver nanoparticles incorporated in the matrix [20, 21].

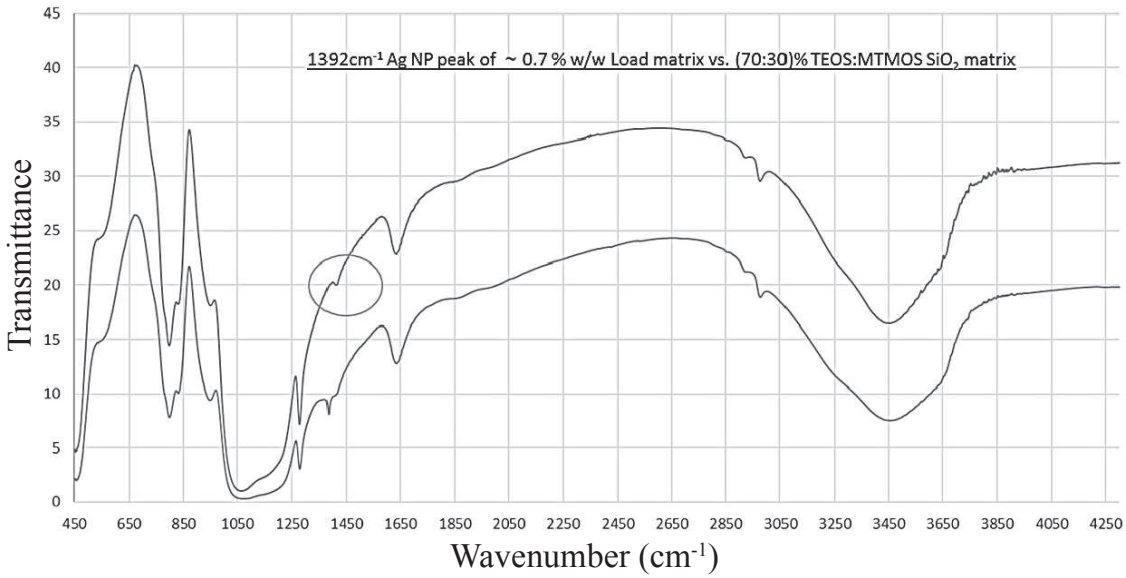

Fig. 5. FTIR transmission spectra of blank and Ag° incorporated matrices. The circle indicates the absorption band corresponding to 1392cm^{-1}

Concluding remarks

Gold and silver nanoparticles were successfully immobilized in silica matrices by using the sol-gel synthetic route. The supported nanoparticles have been successfully applied as a heterogeneous catalyst in the reduction 4-nitrophenol by $NaBH_4$ at a variety of conditions. The nature of the silane monomers used to prepare the matrices affects significantly their kinetic properties.

Acknowledgements

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