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Silica Nanospheres Coated by Ultrasmall Ag^0 Nanoparticles for Oxidative Catalytic Application

Svetlana V. Fedorenko[a,*], Michail E. Jilkin[b], Tatyana V. Gryaznova[a], Elizaveta O. Iurko[a,b], Olga D. Bochkova[a], Alsu R. Mukhametshina[a], Irek R. Nizameev[a], Kirill V. Kholin[a], Raffaello Mazzaro[c,d], Vittorio Morandi[c], Alberto Vomiero[e], Asiya R. Mustafina[a], Yulia H. Budnikova[a,b]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of Russian Academy of Sciences, Arbuzov st. 8, Kazan 420088, Russia
[b] Kazan (Volga Region) Federal University, Kremlyovskaya st. 8, Kazan 420008, Russia
[c] CNR-IMM, Bologna Section, Via Piero Gobetti 101, 40139 Bologna, Italy
[d] Chemistry Department "G. Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna, Italy
[e] Department of Engineering Sciences and Mathematics, Luleå University of Technology, 971 98 Luleå, Sweden

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ABSTRACT

The present work introduces optimal modification of core-shell composite nanomaterial, where small (2–8 nm) Ag^0 nanoparticles are deposited onto large (about 140 nm) silica spheres for application in oxidative catalysis. The size of Ag^0 and density of its deposition onto silica spheres was modified by the post treatment of initially deposited Ag^0 (about 30 nm) by hydrogen peroxide in specific conditions. The comparison of catalytic effect of the post-treated and initial SN-Ag^0 in electrochemical phosphonation of benzo(thia)oxazoles by diethyl phosphite in oxidative conditions revealed the difference between the composite nanoparticles. In particular, the post-treated SNs-Ag^0 nanoparticles exhibit efficient catalytic effect in oxidative conditions resulting in facile and green method for synthesis of phosphonated benzooxa(thia)zoles, while no catalytic effect is observed under the use of larger Ag^0 nanoparticles deposited onto silica spheres. The use of Ag^0-based nanomaterial in oxidative catalysis had been never demonstrated before.

Core-shell composite materials, where silica spheres are coated by a noble metal (mainly, gold and silver) shell, are of great interest in nanoscience due to their potential applications in medicine [1], biosensing [2], photonics [3] and catalysis [4]. The deposition of silver (Ag^0) nanoparticles onto larger-sized silica supports is a convenient tool to prevent their incontrollable agglomeration [5]. Thus, the choice of the core-shell morphology for colloid stabilization of Ag^0 nanoparticles is good alternative to their stabilization by another type of core-shell morphology, where Ag^0 cores are coated by polymeric or dendrimeric shell [6]. The choice of optimal core-shell morphology is of great impact in the catalytic application of silver nanoparticles.

An easy preparation, low cost, high monodispersity, and large particle size range of spherically shaped silica nanoparticles (SNs) are the reasons for their application as the cores for the deposition of Ag^0. Moreover, both chemical reactivity of Si—OH groups and adsorption capacity of silica surface are the factors facilitating a surface decoration of SNs [7]. The optimal surface decoration facilitates the deposition of Ag^0 nanoparticles through electrostatic attraction [8] or coordination bonds [9].

Silver nanoparticles have been of great interest as catalysts in organic synthesis among the metal-based nanoparticles, and their catalytic application has expanded rapidly in the past decade [10]. The applicability of the core-shell SN-Ag^0 nanomaterial in catalysis in great extent is exemplified in the literature by reductive capacity of Ag^0 [10], while, to the best of our knowledge, the applicability of Ag^0-based nanomaterial in oxidative catalysis has not been reported. Oxidative catalysis of C-H phosphonation reactions of aromatic compounds is of great impact in organic synthesis, although all documented examples including benzo(thia)oxazoles [11,12] represent homogeneous catalysis. Nevertheless, our previous reports are worth noting as successful application of nanoheterogeneous catalytic electrochemical transformations in organic synthesis [13].

Catalytic application of the core-shell composites based on Ag^0-deposition onto SNs (SN-Ag^0) requires optimal Ag^0 particle size and silica surface decoration density [10]. Nevertheless, a controllable optimization of both the parameters is still open for an improvement, although some fine literature examples are worth noting. The work [14]

* Corresponding author.
E-mail address: svetlana@iopc.ru (S.V. Fedorenko).

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