



ELSEVIER

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Reactions of methyl radicals with silica supported silver nanoparticles in aqueous solutions

Tomer Zidki^{a,*}, Andreas Hänel^{b,c}, Ronen Bar-Ziv^d^a Chemical Sciences Department, and the Schlesinger Family Center for Compact Accelerators, Radiation Sources and Applications, Ariel University, Ariel, Israel^b Department of Chemical Technology, Gdansk University of Technology, Gdańsk, Poland^c Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg, Freiberg, Germany^d Nuclear Research Centre Negev, Beer-Sheva, Israel

H I G H L I G H T S

- Silica supported silver NPs are efficient catalysts for dimerization of methyl radicals.
- Bare silica is inert towards the interaction with methyl radicals.
- Ethanol adsorbed on the SiO₂ surface changes the reaction path with CH₃.
- Adsorbed ethanol on the well-known Stöber silica prevents its precipitation.

A R T I C L E I N F O

Article history:

Received 16 October 2015

Received in revised form

23 November 2015

Accepted 27 November 2015

Available online 30 November 2015

Keywords:

Nanoparticles

Catalysis

Silver

Silica

Support

Radicals

A B S T R A C T

Silica supported silver nanoparticles (Ag⁰-SiO₂-NCs, NCs = nanocomposites) suspended in aqueous solutions are efficient catalysts for the dimerization of methyl radicals to produce ethane, while bare silica is quite inert towards the interaction with methyl radicals. In the presence of small amounts of ethanol adsorbed on the SiO₂ surface, the reaction path with methyl radicals is changed and methane is formed as the major product.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Metal nanoparticles are known as catalysts for various redox processes (Cuenya, 2010; Prieto et al., 2013). Much of these reactions involve radicals as key intermediates. The study of radical reactions near surfaces is relevant for many applications such as electrochemistry (Allongue et al., 1997; Andrieux et al., 1989; Kraeutler et al., 1978; Martínez-Huitle and Ferro, 2006; Shono, 1984; Stewart et al., 2004), photo-catalysis (Centi and Perathoner, 2009; Gaya and Abdullah, 2008; Han et al., 2009), energy storage (Centi and Perathoner, 2009), solar cells (Nowotny et al., 2007, 2008), etc.

Another practical utilization of this type of reactions is stemming from the compatibility of the radiation resistance of

materials serving in the nuclear industry especially in treatment of wet radioactive wastes where water is usually in an intimate contact with solid surfaces under radiation field in the storage containers. Knowledge of the long-term radiation effects of these heterogeneous systems is of much technological interest. It has been reported that methyl radicals (CH₃) react very fast with noble-metal and metal oxide nanoparticles (M⁰-NPs, M = Ag (Zidki et al., 2006), Au (Zidki et al., 2006), TiO₂ (Bar-Ziv et al., 2012a; Golberg-Oster et al., 2011) and CuO (Zidki et al., 2014a)) yielding ethane as a major product via a dimerization reaction catalyzed by the metal NPs surface (Bar-Ziv et al., 2012a; Golberg-Oster et al., 2011; Zidki et al., 2014b, 2006). This reaction involves a long-lived intermediate (M⁰-NP)-(CH₃)_n (Bar-Ziv et al., 2012a). When the metal NPs are Pt⁰, the major product is stable (M⁰-NP)-(CH₃)_n, i.e., a stable M-C bond in which the methyl radicals is bound to the metal NPs surface (Bar-Ziv et al., 2012b). Recently it was shown that coating Pt⁰-NPs surface with methyl groups affects their properties (Bar-Ziv et al., 2015). The high surface energy of metal

* Corresponding author.

E-mail address: tomerzi@ariel.ac.il (T. Zidki).

NPs makes them extremely reactive, and most systems undergo aggregation without protection or passivation of their surfaces (Raveendran et al., 2003). For utilization in industrial processes it is necessary to stabilize them onto a solid support, where silica is a typical example. This method has pros and cons: On one hand, the attached catalyst on the silica NP can be easily recycled by filtration and the ability of working at high metal NPs concentrations is achieved; on the other hand, unfortunately, with the immobilization of the metal NPs some changes in the catalytic activity occur posing a technological challenge (Zidki et al., 2014a, 2007). Recently we have reported that supporting metal NPs on silica nanoparticles (SiO_2 -NPs) affects the catalytic properties of the metals (Zidki et al., 2014b, 2007). It is well known that metal NPs such as silver and gold catalyze the one-electron reduction of water using the ketyl radicals, $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ (Henglein and Lilie, 1981; Henglein, 1979a, 1979b; Koppie et al., 1980). Our study has indicated that the “inert” SiO_2 -NPs have a significant effect on the catalytic water reduction mechanism (Zidki et al., 2014a, 2007) as the yield of H_2 production is changed appreciably after attaching the metal NPs to silica NPs. However, the bare SiO_2 -NPs are inert to ketyl radicals as the hydrogen yield equals to that formed from water blank (Zidki et al., 2014b, 2007). In some cases the molecular hydrogen yield decreases even lower than its yield from pure homogeneous water radiolysis, i.e., the hydrogen is consumed by reactions on the composite particles.

In this work the reactions of Ag° - SiO_2 nanocomposites (NCs) with $\cdot\text{CH}_3$ radicals in aqueous solutions with an emphasis on the interaction between the silica support and the silver NPs are investigated.

2. Experimental

2.1. Materials and instrumentation

Silver perchlorate (AgClO_4), tetraethyl orthosilicate (TEOS), (3-aminopropyl) trimethoxysilane (APS), and all other chemicals used were of the highest purity commercially available and were used as received. The water used was deionized and was further purified by a Millipore Milli-Q setup with a final resistivity of $R > 18 \text{ M}\Omega \text{ cm}$. Transmission electron microscopy (TEM) analyses were performed using a JEOL-TEM-100SX instrument. Specimens for TEM analysis were prepared on Lacey Formvar/carboncoated 300 mesh copper grid from Ted-Pella. Irradiations were carried out in a ^{60}Co gamma source of Noratom Gammacell, which emits γ rays of 1.25 MeV. The dose rate delivered to the sample by the ^{60}Co source, as determined by the Fricke dosimetry (Weiss et al., 1955), was 1.9 Gy min^{-1} . Doses were calculated assuming the radiation is absorbed only by the aqueous phase. The gases were analyzed using a HP 5890 GC fitted with a FID detector (Poropak QS GC column 10 Ft 1/8 in, Supelco). The carrier gas was He (30 mL min^{-1} , $T = 70^\circ\text{C}$).

2.2. Synthesis of SiO_2 nanoparticles and attachment of bridging molecules

Silica NPs were prepared according to the method of Stöber et al. (1968) as reported before by Zidki et al. (2007). Briefly, NH_4OH was added to dry ethanol followed by the addition of tetraethyl orthosilicate (TEOS) to give 0.28 M TEOS in the solution. The solution was stirred overnight to ensure that the reaction was completed. This procedure is reproducible, and it produces SiO_2 -NPs of approximately 45 nm in diameter at pH 10 (Zidki et al., 2007). As the stability of the silica particles is pH dependent (Korah et al., 2003), all dilutions throughout this study were done with pH 10 solutions (using NaOH in pure water). In order to

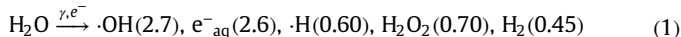
attach Ag° -NPs to the silica, the SiO_2 -NPs were functionalized with the bridging amino propyl silane (APS) molecules (Liz-Marzán et al., 1996; Makarova et al., 1999; Ung et al., 1999). The SiO_2 -NPs suspension was mixed with a quantity of APS sufficient to cover the SiO_2 -NPs with half a monolayer of APS (not more to avoid self-condensation), giving APS- SiO_2 . The detailed procedure was described elsewhere (Zidki et al., 2007). The resultant suspension was centrifuged subsequently and re-dispersed by sonication in water (pH 10) to clean the NPs from their precursors.

2.3. Attachment of silver NPs onto the silica

A 1.0 M aqueous solution of AgClO_4 was added to the functionalized silica particles solution (APS- SiO_2) to produce a 10 mM solution of Ag^+ . A reducing solution, sodium borohydride (10 mM in ice-cold water at pH 10) was added dropwise. The total volume of the reducing solution added was the same as the volume of functionalized silica suspension prior to the addition. The resulting nanocomposites solution (Ag° - SiO_2 -NCs) was centrifuged and re-dispersed in water at pH 10 by sonication to produce a solution of the desired concentration (up to 20 wt% of SiO_2 -NPs in the composite solution). The silver concentration was determined by inductively coupled plasma and the exact silica concentration was calculated from the Ag/SiO_2 ratio which equals 17. Fig. 1 shows the TEM image of the obtained Ag° - SiO_2 -NCs. The silver NPs are clearly visible as islands on the silica. These silver islands cover only a fraction (ca. 25%) of the SiO_2 -NPs. The SiO_2 -NPs size is $\sim 45 \text{ nm}$ and the size of the supported Ag° -NPs is $\sim 10 \text{ nm}$.

2.4. Irradiation experiments

The CH_3 radical are produced by irradiation of N_2O -saturated aqueous solutions containing dimethylsulfoxide (DMSO or $(\text{CH}_3)_2\text{S}=\text{O}$, 0.1 M during the course of this work) according to the Veltwisch et al. procedure (Veltwisch et al., 1980). When ionizing radiation (γ -radiation) is absorbed by a dilute aqueous solution the following initial products are formed (Dorfman and Matheson, 1969):



the numbers given in parentheses are G values (G values are defined as the number of molecules or radicals of each product per 100 eV of radiation absorbed by the solution). In N_2O -saturated solutions the hydrated electron is converted into the hydroxyl-

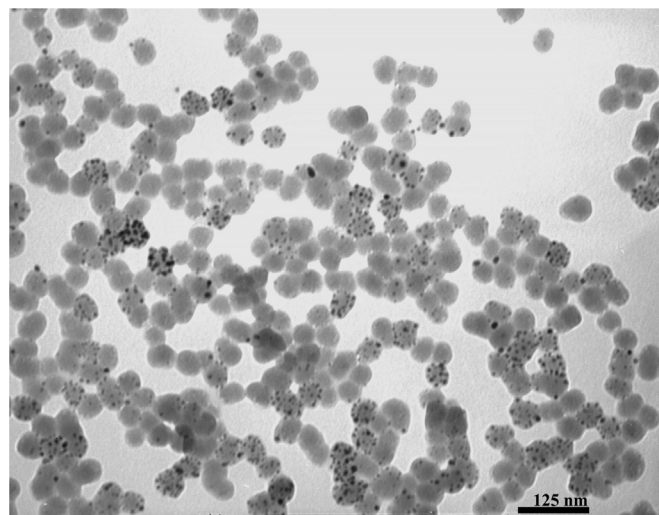


Fig. 1. TEM image of the Ag° - SiO_2 -NCs.

Download English Version:

<https://daneshyari.com/en/article/1891016>

Download Persian Version:

<https://daneshyari.com/article/1891016>

[Daneshyari.com](https://daneshyari.com)