Propylethylenediamine Decomposition in the Presence of Ag Nanoparticles in Silica-Gel Network

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1. Introduction

The mechanisms responsible for the extraction of methyl iodide (MeI) using well-known silver metal (Ag) or ion (Ag^+) doped adsorbents are still under investigation regardless of their early application in filters and wet scrubbers for decontamination or safety concerns [1]. In addition, in a previous published paper [2], it was estimated that gaseous wet MeI was bound to Ag nanoparticles, which are embedded into a propylethylenediamine ($NH_2CH_2CH_2NHCH_2CH_2CH_2$-, PEDA) anchored silica gel, by forming a complex that differs from silver iodide (AgI). However, more data are necessary to support this hypothesis and understand the binding properties between the gaseous wet MeI and Ag nanoparticles under the controlled experiment conditions.

2. Methods and Results

2.1 Sample Preparation

As described in a previous published paper [3], bare silica gels (Blank gel, TMOS:MeOH:water = 0.24 mol:0.888 mol:1.2 mol) and PEDA ligand anquored organic-inorganic silica gels (PEDA gel, TMSen:TMOS:MeOH:water = 0.0192 mol:0.24 mol:0.888 mol:1.2 mol) were prepared at room temperature and dried at 120 ^oC. Gel particles with sizes between 180 and 600 μm were selected after washing and drying the gels at room temperature. Ag nanoparticles (Ag NP) were produced in $AgNO_3$ solutions containing the prepared gels, by electron-beam (e-beam) irradiations (operating conditions: 0.2 MeV energy, 1 mA current, 15 min duration, total 270 kGy dose). The reduced Ag nanoparticles from Ag^+ were embedded into some prepared silica gels, which was already confirmed based on the transmission electron microscopy (TEM) results [3].

2.2 Gaseous Wet Methyl Iodide Preparation

Forty-eight μm sized monodisperse water droplets (operating conditions: 20 μm orifice diameter, 40 kHz frequency, 20 cm^3 water-syringe capacity, 8.2 x 10^{-4} cm/s syringe-pump run speed, and 0.139 cm^3/min liquid feed rate) were generated and dispersed (at a 15 × 100 cm^3/min air feed rate for dispersion and a 35 L/min air feed rate for dilution) using a Model 3450 Vibrating Orifice Aerosol Generator (VOAG, TSI Incorporated, USA) [4]. MeI gas was introduced at a 5 cc/min volumetric flowrate into the water line producing the 48 μm sized water droplets. The water droplets containing MeI gas (gaseous wet MeI) were continuously flowed and contacted into 0.50 g of each prepared gel placed in a bottle connected to the VOAG through a silicon tube for 30 min [2]. The concentration of the volatile MeI in the water droplets was about 195 ng/L based on the measurements using gas chromatography-mass spectrometry (GC-MS, Clarus 680/ATD-TurboMatrix, PerkinElmer). Other volatile organic compounds (VOCs) released by thermalizing the examining gels to 150 ^oC were analyzed using GC-MS combined with a headspace (HS).

2.3 FT-Raman Measurements

Vibration of O_3SiOH tetrahedra was observed at around 485 nm as a band in Silica-MeI, PEDA gel, and PEDA gel-MeI, as shown in Figure 1. However, the relative intensity of the band was decreased significantly in the Ag NP-PEDA gel, and disappeared even in the Ag NP-PEDA-MeI. Each of the intense CH stretching bands at 1049 cm^{-1} in the PEDA gel and the PEDA gel-MeI was slightly shifted to 1043 and 1057 cm^{-1} in the Ag NP-PEDA gel and the Ag NP-PEDA gel-MeI, and decreased in relative peak intensity. In addition, the relative band intensity and width of the overlapping amine stretching and non-specific organic -CH_2 stretching modes shown in the PEDA gel and the PEDA gel-MeI at the region of 2859 to 2990 cm^{-1} were significantly decreased owing to the interaction between amine and Ag nanoparticles in the Ag NP-PEDA gel and the Ag NP-PEDA gel-MeI. A peak shift was also observed from Ag NP-PEDA gel to Ag NP-PEDA gel-MeI within the above range. Furthermore, overall intense Raman bands were found for the Ag NP-PEDA gel and the Ag NP-PEDA gel-MeI, which include Ag NP, while bare silver nanoparticles show weak bands, particularly in the 700 − 1600 cm^{-1} region. It can be explained that the interactions between Ag nanoparticles and PEDA enhance the Raman signals, and the wet MeI layer around the PEDA and the Ag NP-PEDA decrease the Raman signals. In the 700 − 1600 cm^{-1} region, organic material decomposition on the silver nanoparticles with e-beam irradiation appeared as a large number of peaks. Another intense band at 223 cm^{-1}, which is known to be Ag-N stretching mode, was

observed in the Ag NP-PEDA gel and the Ag NP-PEDA gel-MeI.

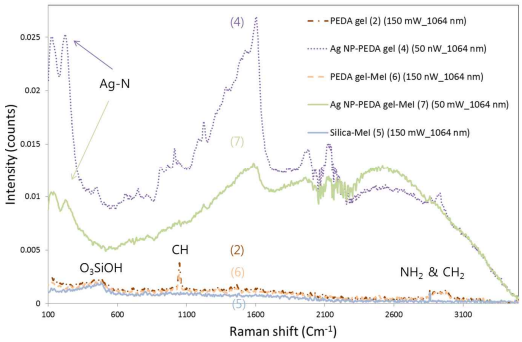

Fig. 1. FT-Raman spectra of PEDA-anchored SiO_2 gel (PEDA gel), Ag nanoparticle-embedded PEDA-anchored SiO_2 gel (Ag NP-PEDA gel), PEDA-anchored SiO_2 gel in gaseous wet MeI (PEDA gel-MeI), Ag nanoparticle-embedded PEDA-anchored SiO_2 gel in gaseous wet MeI (Ag NP-PEDA gel-MeI).

2.4 VOC Releases

It was observed that VOCs from silica, silica-MeI, PEDA gel, PEDA gel-MeI, and Ag NP-PEDA gel-MeI were all from a silicone tube used to flow gaseous wet MeI, but several VOCs from Ag NP-PEDA gel were detected, as shown in Figure 2. Propanoic acid, Pyrazine, 2,3-butanediol, tetramethyl oxirane, 2-ethyl-6-methylpyrazine, and 2-ethyl hexanoic acid were produced. This indicates that, although organic-inorganic hybrid silica gels are stable at over 200 ^{o}C, 270 kGy ionizing radiation of the e-beam used for Ag-nanoparticle production causes them to fragment into small organic molecules. The smaller organic fragments can be recombined with each other and released as VOCs during thermalization at 150 ^{o}C for a GC-MS-HS analysis. The pore sizes are fairly big enough to contain the organics. However, these organics were not released in gaseous wet MeI (ex. Ag NP-PEDA gel-MeI). They may be formed as organic compounds or complexes, which could not escape from the pores of the gel even at 150 ^{o}C.

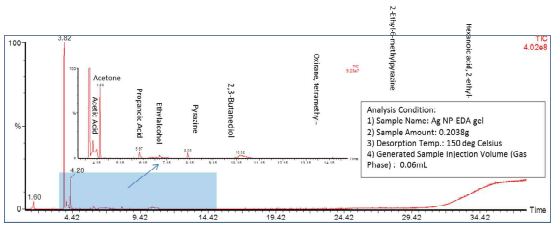

Fig. 2. Volatile organic compounds (VOCs) released from Ag nanoparticle-embedded PEDA-anchored SiO_2 gel (Ag NP-PEDA gel) using GC-MS combined with a headspace (HS).

3. Conclusions

Electron-beam irradiation (270 kGy), applied for Ag-nanoparticle production, caused the chain cleavage of propylethylenediamine in the silica-gel network to release some volatile organic compounds (VOCs). The introduced wet MeI can be entrapped in interstitial positions and can surround the Ag nanoparticles, the remaining organics, or the Ag NP-amine in a silica-gel network, and another MeI was found to bind to silanol groups (≡Si-OH) to form methoxy species, ≡Si-OMe, with the iodine leaving group (I^-) not being chemically detected.

Acknowledgements

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