Utilization of Sigle-site Photocatalyst and Photo-assisted Deposition Method for Synthesis of Nano-sized Metal Catalyst on Zeolite Materials

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Introduction

The transition metal oxide moieties such as tetrahedrally coordinated titanium oxide incorporated and isolated within zeolite and mesoporous silica have been named as "single-site photocatalysts" [1-4]. Under UV-light irradiation, these single-site photocatalysts form charge transfer excited state which can show the highly active and selective photocatalytic performance. Although the previous studies for the utilization as photocatalyst have mainly been focused on its phtotocatalytic activity [1-4], the applications of single-site photocatalyst for the synthesis of conventional catalysts such as nano-sized metal catalysts have not been investigated. On the other hand, the nano-sized metal catalysts such as Pd and Pt have been used widely for various reactions [5]. Achieving the precise control of particle size is one of the most important challenges. In the present study, nano-sized Pd metal catalyst has been deposited on the Ti-containing silicalite zeolite (TS-1) using the photo-assisted deposition (PAD) method (Fig.1). This synthesized catalyst (Pd loaded on TS-1) possesses two types of active sites, the nano-sized Pd metal for the synthesis of H_2O_2 from H_2 and O_2 gas and the tetrahedral coordinated titanium oxide moieties for the partial oxidation of organic compounds using H_2O_2 as oxidizing reagent. Using this combination of effective catalytically active sites, in this study, the partial oxidation of phenol has been carried out in a flow of mixture with H_2 and O_2 gas.

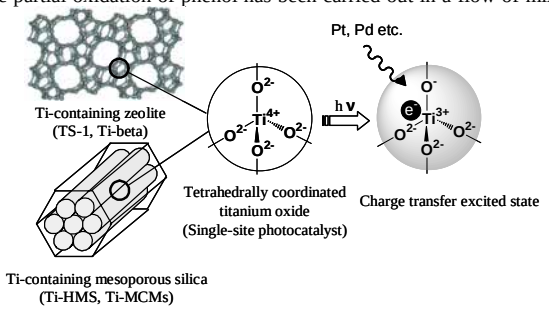

Figure 1. Scheme for the preparation of nano-sized metal catalyst using the sigle-site photocatalysts (Ti-containing zeolites) and photo-assisted deposition (PAD) method.

Materials and Methods

The synthesis of the Ti containing slicaalite zeolite (Si/Ti ratio : 60) was carried out by using tetraethylorthosilicate and titaniumisopropoxide as the starting materials and TPAOH as template. The Pd loaded on TS-1 (PAD-Pd/TS-1, 1.4 wt% as Pd metal) was prepared using the PAD method: Pd metal was deposited on TS-1 from aqueous solution of $PdCl_2$ under UV-light irradiation at 295 K. The samples were dried at 378 K and reduced by H_2 (20ml/min) at 473 K. The impregnated catalyst (imp-Pd/TS-1) was also prepared. The Pd K-edge XAFS measurements were recorded at 295 K in transmittance mode at BL01B1 of SPring-8.

Results and Discussion

The results from XAFS and UV-Vis measurements indicate that Ti exists as the tetrahedrally coordinatd Ti-oxide moieties (tetra-Ti-oxide) within the framework of TS-1. Under UV-light irradiation of the slurry of TS-1 in aqueous $PdCl_2$ solution, the Pd metal can be deposited on the TS-1. The Fourier transforms of Pd K-edge EXAFS spectra of the catalysts are shown in Fig. 2. The presence of the smaller peak assigned to the Pd–Pd bond of Pd metal indicates that the smaller Pd metal was formed on the photodeposited catalyst (PAD-Pd/TS-1). Under the flow of H_2 and O_2 in water, the formation of H_2O_2 was observed on the Pd/TS-1 catalysts (Fig. 3). The PAD-Pd/TS-1 can exhibit the higher reactivity than the imp-Pd/TS-1. Furthermore, the presence of phenol in this reaction system led the formation of the products from the partial oxidation of phenol with the formed H_2O_2. The micro-pores and the tetra-Ti-oxide moiety of TS-1 zeolite are suitable for the structure sensitive reaction to produce the oxidized products.

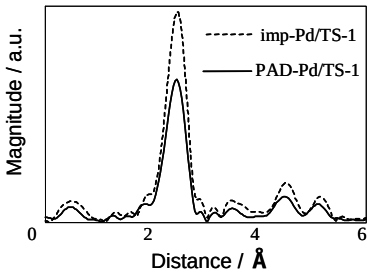

Figure 2. Fourier transforms of the Pd K-edge EXA FS spectra for PAD-Pd/TS-1 and imp-Pd/TS-1 catalysts.

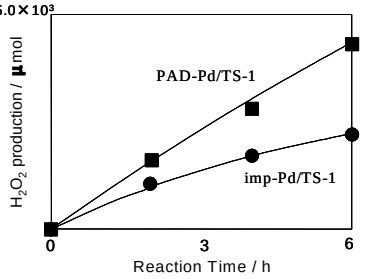

Figure 3. Reaction time profile for the H_2O_2 production from H_2 and O_2 gas on PAD-Pd/TS-1 and imp-Pd/TS-1 catalysts.

Significance

Using the single-site photocatalyst (TS-1) and the PAD method, Pd metal particles with high dispersion state can be deposited on the tetra-Ti-oxide of TS-1. The direct interaction between nano-sized Pd metal and the photo-excited tetra-Ti-oxide realized by the PAD method lead the possibility to design the unique and active nano-sized metal catalyst.

References

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