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Active site design in a core-shell nanostructured catalyst for one-pot oxidation reaction

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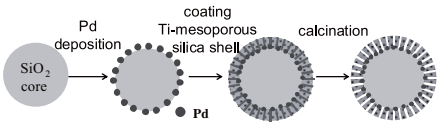
Introduction

One-pot oxidation reaction consisted of direct synthesis of hydrogen peroxide (H_2O_2) from H_2 and O_2 gases and oxidation reaction using *in situ* generated H_2O_2 is promising synthetic method, because it is possible to use the unstable H_2O_2 immediately without isolation/purification steps, which would contribute to energy and time saving as well as avoid the risk of transportation of the concentrated H_2O_2. The one-pot oxidation reaction requires the catalysts for product H_2O_2 (e.g. Pd nanoparticle) and for oxidation reaction (e.g. TiO_2), respectively. Until now, the conventional catalyst for one-pot oxidation reaction was physical mixture of both components or Pd supported TiO_2 zeolite. However using such catalyst, the synthesized H_2O_2 on the Pd catalyst will diffuse to the solvent before contact to Ti site and most of them will be decomposed to water in the solvent. To improve the efficiency of H_2O_2, we present a new type of core-shell structured catalyst to enable the one-pot oxidation of sulfide to sulfoxide with high efficiency and selectivity, in which a uniform SiO_2 core supporting Pd nanoparticles was covered with a Ti-containing mesoporous silica shell (Pd/SiO_2@TiMSS). Meanwhile, it is well accepted that the formation of tetrahedral Ti species is crucial to achieve selective oxidation using H_2O_2, while octahedral Ti species and bulk TiO_2 promote the decomposition of H_2O_2. Thus, local structure of Titanium species within the mesoporous silica shell was investigated by X-ray absorption fine structure (XAFS).

Experimental

The procedure for the synthesis of Pd/SiO_2@Ti-containing mesoporous silica shell (Pd/SiO_2@TiMSS) is schematically illustrated in scheme 1. Colloidal SiO_2 particles were firstly prepared by the Stöber method. The Pd nanoparticles were then successfully deposited on the surface of SiO_2 particle using electroless deposition technic. The Pd nanoparticles supported on SiO_2 were further coated with Ti-containing mesoporous silica shell using cetyltrimethyl ammonium bromide as structure directing agent (SDA), tetraethoxysilane (TEOS) as silica source, and tetrapropyl orthotitanate (TPOT) as Ti source. The final core-shell structure was obtained after calcination at 823 K in air to remove the SDA. [1]



Scheme 1. Schematic illustration of the procedure.

Results and discussions

The HR-TEM images of Pd/SiO_2@TiMSS show that the spherical NPs consist of nonporous SiO_2 cores, Ti-containing mesoporous shells with channels oriented perpendicular to the core surface, and Pd NPs. The thickness of the shell was determined to be approximately 30 nm. The Pd NPs were apparently present at the intended sites; the boundary between the SiO_2 core and mesoporous silica shell.

Fig. 1 shows the results of Ti K-edge XAFS analyses of TPOT and TiO_2 anatase crystal as reference samples and Pd/SiO_2@TiMSS. One sharp pre-edge peak at around 4970 eV observed in the XANES spectrum of Pd/SiO_2@TiMSS originate from the isolated titanium oxide species surrounded by four oxygen atoms in the mesoporous silica shell framework.

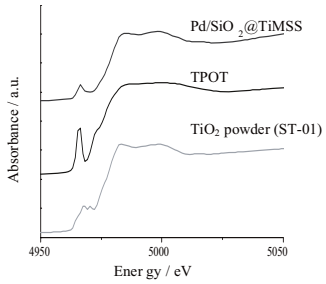


Figure 1. Ti K-edge XANES of Pd/SiO_2@TiMSS, TPOT and TiO_2 powder (ST-01).

The catalytic activity of Pd/SiO_2@TiMSS was investigated for the one-pot oxidation of methyl phenyl sulfide into methyl phenyl sulfoxide, catalyzed by isolated Ti-oxide moieties using in situ generated H_2O_2. The activity of Pd/SiO_2@TiMSS is significantly higher activity compared to conventional catalyst (physical mixture of Pd/SiO_2 and Ti-containing mesoporous silica particle or Pd supported Ti-containing zeolite (TS-1)).

Conclusions

The designed architecture offers a simple and efficient catalyst system to enable the one-pot oxidation of sulfide in the presence of H_2 and O_2, in which both Pd nanoparticles and isolated Ti oxide moieties within the frameworks are active sites for the formation of H_2O_2 and the oxidation of sulfide, respectively.

References

[1] S. Okada, K. Mori, T. Kamegawa, M. Che, H. Yamashita, *Chem. Eur. J.* in press

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