Synthesis of Bifunctional Metal-doped Silicas Supported Palladium Nanoparticles by Strong Electrostatic Adsorption

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Introduction

Ordered mesoporous materials with tunable pore structure and high surface are attracting extensive attention. Compared with materials having a one-dimensional array of pores, 3D mesoporous silicas such as KIT-5 with interconnected cage-type pores and KIT-6 owning ultra-large-pore network are preferred as bulky reaction intermediates can be accommodated in their pores [1]. It has been reported that tungsten, zirconium and niobium can be applied to provide catalytically active species due to their acidic properties [2,3,4]. Metal (W, Zr, Nb)-doped KIT-5 and KIT-6 materials are interesting because of their 3D pore structure and the acidic species as well as the facile synthesis method.

Pd is applied extensively as metal active species in the fields of petroleum refining, electrochemistry, catalysis, sensing, etc. The synthesis of highly dispersed nanoparticles is of great interest as it could greatly improve the utilization of metals. Strong electrostatic adsorption (SEA) is a relatively simple and effective method to prepare ultra-small nanoparticles(<1.5nm) even at high metal loadings (15wt% for Pd on carbon), whereby charged metal precursors are strongly adsorbed onto the oppositely charged supports [5]. Bifunctional materials with active metal sites and acid sites might be obtained by synthesizing Pd nanoparticles on metal (W, Zr, Nb)-doped silicas. Bifunctional materials open the door for carrying out cascade- and sequential-type reactions in a single reactor, where the number of isolation or purification steps can be lessened or eliminated so that the removal of unwanted by-products becomes unnecessary [6].

Materials and Methods

Metal (W, Zr, Nb)-doped KIT-5 or KIT-6 materials were prepared by hydrothermal synthesis method. Tetraethyl orthosilicate (TEOS 98%, Aldrich), sodium tungstate (Acros Organics), Zirconium (IV) oxychloride octahydrate (99.5% Sigma–Aldric), Niobium(V) chloride (99%, Strem Chemicals) were used as silicon, W, Zr and Nb sources respectively. Pd (2.5wt%) nanoparticle on the metal-doped silicas were prepared by strong electrostatic adsorption (SEA) method and wet impregnation with tetraamminepalladium (II) chloride monohydrate (PdTACl) (Sigma-Aldrich 99.99%) being used as cationic metal precursor.

Uptake survey of Pd on the meta-doped silicas will be simulated by RPA model. Hydrothermal stability test was carried out in the stainless autoclave reactor. Average particle size was obtained by deconvoluting X-ray diffraction and calculated by Scherrer equation as well as hydrogen-chemisorption using Micromeritics 2920 equipped with a TCD. NH_3-TPD was used to determine the acidity of metal-doped silicas as well as corresponding catalysts.

Results and Discussion

The Point of Zero Charge (PZC), nanoparticle size obtained from hydrogen chemisorption and by XRD using the Scherrer equation after fitting metal diffraction patterns were listed in Table 1. It can be seen that the metal dopants decreased the PZC of KIT-5 and KIT-6 silicas with tungsten lowering it the most.

Figure 1 shows Pd uptake surveys on representative doped and undoped KIT-5 supports and X-ray diffraction patterns of reduced Pd nanoparticles supported on metal-doped KIT-5. With the exception of Nb, the metal dopant does not substantially change the uptake curve as observed in the past for alkali dopants [7]. In the XRD data of Figure 1b, broad palladium peaks indicate very small particles on the undoped and W and Zr-doped support, whereas sharp peaks appeared on Nb-doped KIT-5. Particle sizes obtained from hydrogen chemisorption (<2nm) are consistent with the XRD data. These are summarized in Table 1.

Table 1 Particle sizes of 2.5wt% Pd catalysts on KIT-5, KIT-6 and metal-doped silicas calculated from hydrogen-chemisorption and X-ray diffraction.

Sample	Pd/KIT5	Pd/W-KIT5	Pd/Zr-KIT5	Pd/Nb-KIT5	Pd/KIT6	Pd/W-KIT6	Pd/Zr-KIT6	Pd/Nb-KIT6
PZC	3.4	1.2	2.4	2.1	3.6	1.3	2.4	2.2
Chemi. size (nm)	1.5	1.4	1.7	5.4	2.0	1.6	1.8	3.4
XRD size (nm)	0.82	0.86	0.82	4.8	0.73	0.75	1.3	4.8

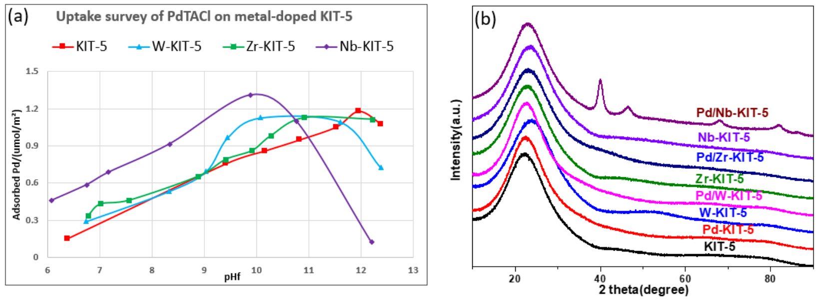

Figure 1. Uptake survey of PdTACl (a) and XRD plots (b) for 2.5wt% Pd catalysts on KIT-5 and metal-doped KIT-5 materials.

Significance

Bifunctional materials can be synthesized by depositing Pd on metal-doped silicas. Except for the Nb-doped support, over which a different deposition mechanism may operate, SEA is a simple and effective method to prepare ultra-small nanoparticles on metal-doped silicas.

References

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