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Preparation of Carbon Nano-fiber Washcoat on Porous Silica Foam as Structured Catalyst Support*

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Abstract This paper reports how a hairy layer of carbon nano-fibers can be prepared on the macro-porous silica foam produced by the sphere templating method. Firstly, three-dimensional close-packed crystals of polystyrene spheres are assembled on porous disk substrate by vacuum filtration or evaporation. The polystyrene template is annealed slightly above the glass transition temperature in order to strengthen the colloidal crystal and ensure interconnection of the spheres so as to obtain porous materials with open structure. Following the treatment of hexdecyltrimethylammonium bromide, the polystyrene template is filled with silica colloidal solution, which solidifies in the cavities. Then the polystyrene particles are removed by calcination at 843K, leaving behind porous silica foam. Scanning electron microscopy images demonstrate that silica foam has uniform and open structured pores. Nickel particles were deposited on porous silica foam layer by the dipping method and porous carbon nano-fiber washcoat was prepared by catalytic decomposition of ethene over small nickel particles.

Keywords sphere template, colloidal crystal, silica foam, carbon nano-fiber, washcoat

1 INTRODUCTION

Fast gas-liquid phase reactions over solid catalysts easily cause concentration gradient in reactors and catalysts because of relatively slow diffusion as well as the frequent occurrence of low concentration when gasses are dissolved. Such concentration gradient caused by the limitation of mass transfer influences the reaction rate as well as selectivity. Conventional strategies for gas-liquid-solid phase catalytic reactions comprise slurry reactors and trickle bed reactors. In trickle bed reactors, reactions easily end up in diffusion limitation because of the relatively large catalyst particle size that is necessary because of hydrodynamic reasons. In slurry reactors, although very small catalyst particles used are suitable for fast reactions, along with this it is at the high cost of removal of the catalysts from the products. Therefore, quite some research efforts are focused on developing structured catalyst to combine the advantages of slurry reactors and trickle bed reactors, which own large liquid-solid surface as well as short diffusion distance inside the catalyst without needing a difficult separation step. Carbon nano-fibers are potentially an alternative catalyst support because of their high surface area and macroporosity. However, carbon nano-fibers used as catalyst support in the form of powder[1—3] generally encountered the problem of agglomeration and separation from the products. Some researchers have been trying to develop a structured catalyst support such as wash-coated monolith with a hairy layer of carbon nano-fibers[4,5].

This paper mainly presents how thin macro-porous silica foam on a substrate is produced by the sphere templating method and carbon nano-fiber washcoat on this porous material is prepared. Nickel particles are deposited on porous silica foam and carbon nano-fiber washcoat is formed by subsequent catalytic vapor decomposition of carbon-containing gas. The carbon nano-fiber washcoat grown on the macro-porous silica foam as structured catalyst support presented here may overcome mass transfer limitation because of their high surface area and macroporosity. As a result, improved performance may be possible in application in gas-liquid phase catalytic reactions.

2 EXPERIMENTAL

2.1 Materials

Porous disks (Small Parts, Inc., USA) were used as substrate. The substrate is made from α-alumina and it is physically robust, chemically inert and

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resistant to high temperatures and corrosion with consistent pore structure. The diameter of the substrate is 29mm and it is 7mm thick with pore size of 0.5μm. The monodisperse polystyrene (PS) (Polysciences, Inc., Germany) was used to form template on porous disks. The polybeads with particle size of 0.75μm were packaged as 2.5% aqueous suspension. Tetraethoxysilane with purity of 99.9% (TEOS, Aldrich) was used to prepare silica colloidal. The surfactant hexadecyltrimethylammonium bromide (HTAB) with purity of 99% was obtained from Aldrich. Nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] (>98%, Merck, Darmstadt) and ammonium nitrate (>98%, Merck, Darmstadt) were used to prepare nickel solution. Hydrogen and nitrogen with purity 99.999% (INDUGAS), and ethene with purity 99.95% (PRAXAIR) were used for growing carbon nano-fibers on macro-porous silica foam.

2.2 Methods

The monodisperse polystyrene suspenstions were filtered through or evaporated on porous disk substrate to form template. Firstly, 0.2g 2.5% polystyrene suspension was diluted to 0.1% (by volume) by deionized water. Then it was placed in a cylinder which uses the porous disk substrate as bottom board. Under the aid of vacuum filtration, the water penetrated through the porous substrate and the polystyrene particles were hold back on the upside of the substrate to form the template. The template was vacuum dried 30min at 333K and then annealed 18min at 383K. After treated with $0.02 \mathrm{mol} \cdot \mathrm{L}^{-1}$ HTAB, the spaces between the polystyrene spheres were filled with silica colloidal solution, and subsequently the composite materials obtained were dried in a vacuum oven for 60min at 333K and then calcined at 843K in an air atmosphere in a programmable furnace. A TGA/SDTA 851 thermogravimetric analysis was used to characterize the calcination process. The typical amount of sample studied in a single TGA run was around 12mg. After removal of the polystyrene spheres in the composite, an ordered three-dimensional silica porous structure was obtained.

Nickel was supported on the obtained porous silica foam by the dipping method. Porous silica foam with area of 6.6 square centimeter was dipped in a pH-neutral $0.1 \mathrm{mol} \cdot \mathrm{L}^{-1}$ nickel solution for 15min. Nickel solution is obtained by dissolving 29g $Ni(NO_3)_2 \cdot 6H_2O$ and 80g NH_4NO_3 into a liter of water by adding 4ml of ammonia solution [25% (by mass)][4].The silica foam was placed downward to the bottom of the vessel and the substrate was facing upward. After washed by deionized water, the sample was dried over night in air at room temperature and subsequently at 373K for 12h with a ramp of $1 \mathrm{K} \cdot \mathrm{min}^{-1}$, followed by calcination in air atmosphere at 873K for 5h with a ramp of $5 \mathrm{K} \cdot \mathrm{min}^{-1}$.

Carbon nano-fiber washcoat was prepared in a quartz reactor(diameter of 3cm, 30cm long) with a porous quartz plate at the bottom to support the sample. About 12g sample was placed in the reactor and reduced in $20 \mathrm{ml} \cdot \mathrm{min}^{-1}$ of H_2 and $80 \mathrm{ml} \cdot \mathrm{min}^{-1}$ of N_2. The temperature was raised at the rate of $5 \mathrm{K} \cdot \mathrm{min}^{-1}$ from room temperature to 873K for 2h. Then it was decreased at the rate of $5 \mathrm{K} \cdot \mathrm{min}^{-1}$ to 723K and the carbon nano-fiber washcoat was grown in $30 \mathrm{ml} \cdot \mathrm{min}^{-1}$ of C_2H_4 and $150 \mathrm{ml} \cdot \mathrm{min}^{-1}$ of N_2.

The morphology of the macro-porous silica foam on porous disk substrate and the carbon nano-fiber washcoat were studied with scanning electron microscopy (SEM) (LEO 1550 FEG SEM, Germany). The structure of polystyrene template, the composite of polystyrene/silica, the macro-porous silica foam on porous substrate and carbon nano-fiber on porous silica foam were characterized.

3 RESULTS AND DISCUSSION

3.1 Macro-porous silica foam

3.1.1 *Polystyrene template*

Macro-porous silica foam is produced by the sphere templating method. The template can be formed by gravitational sedimentations, centrifugation, filtration and the convective assembly method[6—8]. We prepared the polystyrene arrays by filtration and evaporation. As to the filtration method, it allows easy washing and subsequent infusion with different media. The filtration and evaporation method allows easy control of the thickness of the layer. In a typical experimental run, the polystyrene suspensions were diluted to 0.1%—0.2% (by volume) and slowly filtered through or evaporated under vacuum on a smooth porous disk substrate. The polystyrene particles accumulated on the substrate surface in 5—8h, building closely packed three-dimensional ordered layers of thickness 4—10μm.

Figure 1 is the SEM micrographs of the surface of the polystyrene template. The thickness of the template is easily controlled by changing the amount of the polystyrene suspension. There are about ten layers in these template. The SEM image in Fig.1(a) depicts