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Phosphosilicate nanosheets for supported palladium nanoparticles as a novel nanocatalyst

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ABSTRACT

Inspired by the high accessibility and low diffusion limitations of fibrous silica nanoparticles (KCC-1), fibrous phosphosilicate (FPS) was engineered using a microemulsion system. In this work, we report design and synthesis of high-surface-area FPS using tripolyphosphate (TPP) and tetraethyl orthosilicate (TEOS). The FPS nanocatalyst was thoroughly characterized by Fourier transform infrared spectra (FTIR), Powder X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), and N_2 adsorption/desorption study. Considering the large ionic internal character, high mechanical and thermal stability as well as long-term colloidal stability, this system could be considered as perfect nanocatalyst by using the host–guest approach. Then palladium nanoparticles (Pd NPs) supported on fibrous phosphosilicat to the cycloaddition of CO_2 to epoxides.

1. Introduction

The field of nanocatalysis involving the use of catalysts having at least one nanoscale dimension, either externally or in terms of internal structures, with excellent activity, acceptable stability, and high selectivity is undergoing an explosive development. These specifications can be easily achieved by tailoring the size, morphology, composition, electronic structure, as well as thermal and chemical stability of the nanomaterial [1–17].

Among various nanocatalysts, silica-based nanomaterials are continuously growing due to their valuable features including their high surface areas, tunable nanoscale pore dimensions and sizes, and variable morphologies. However, the progress of the structure to real-world applications requests addressing of various scientific challenges such as control of multifunction alization, toxicity and efficiency of the synthesis protocol. A recent review on mesoporous silica nanocarriers has emphasized the current need of synthetic methods capable to produce truly dispersible uniform-sized nanoparticles with wide distributions of pore sizes [18–31].

The phosphosilicate (PS) system is of importance due to the simultaneous presence of phosphate and silicon groups in the system. Many researches have been devoted to the synthesis and characterization of PSs, most of them concerning the study of these compounds in the glassy state. PSs have been widely studied for their possible applications in optical fibers, electrolytes for high-energy density batteries as well as medical domain [32–39].

Recently, palladium (Pd) nanoparticles have been studied as catalysts due to their high catalytic activity for many organic catalytic reactions. Various supporting materials have been utilized to load Pd NPs as catalysts for organic catalytic reactions, including Pd/Al_2O_3 [18], $Au@Pd@TiO_2$ [40], Pd/SBA-15 [41] and Pd/C nanospheres [42]. All the listed above substances have great specific surface areas and pores leading to the homogeneous dispersion of the catalytic sites; thus avoiding the aggregation of NPs and improving the catalytic activity of the system. However, poor accessibility to these active sites inside the pores limits their applications for which significant mass transport is essential. Therefore, new supports with easily accessible high surface areas, not due to the pores, are highly desirable.

Nowadays, lots of energy originates from fossil fuels which results in increasing emission of carbon dioxide into the atmosphere. It increases the greenhouse effect [43,44]. More attention is focused to the capture, storage and utilization of carbon dioxide, which is anticipated to help alleviate the intense problem [45]. Carbon dioxide can be changed into some chemical compounds, for example organic carbonates, urea derivatives, oxazolidinone, solar fuels, formic acid and other organic compounds. The use of carbon dioxide reduce carbon dioxide levels in the atmosphere and provide commercially precious chemical supplies. The reaction of carbon dioxide with epoxides to produce cyclic

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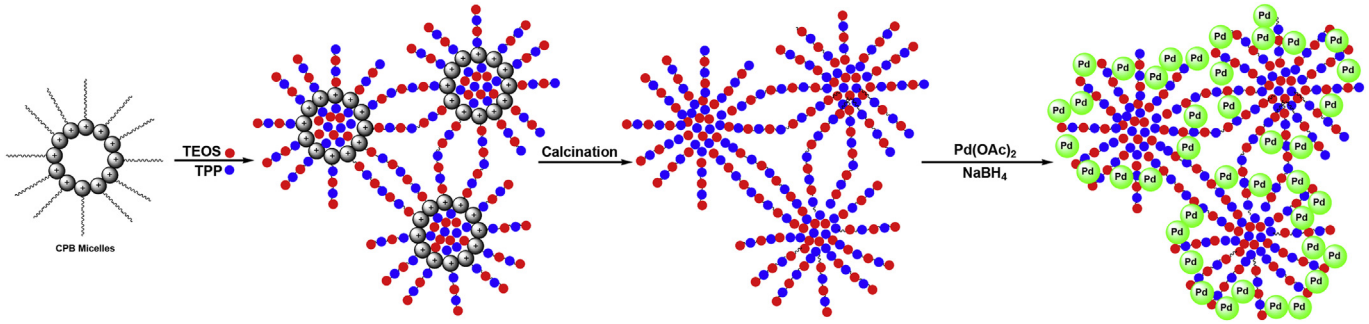

Scheme 1. Schematic illustration of the FPS preparation.

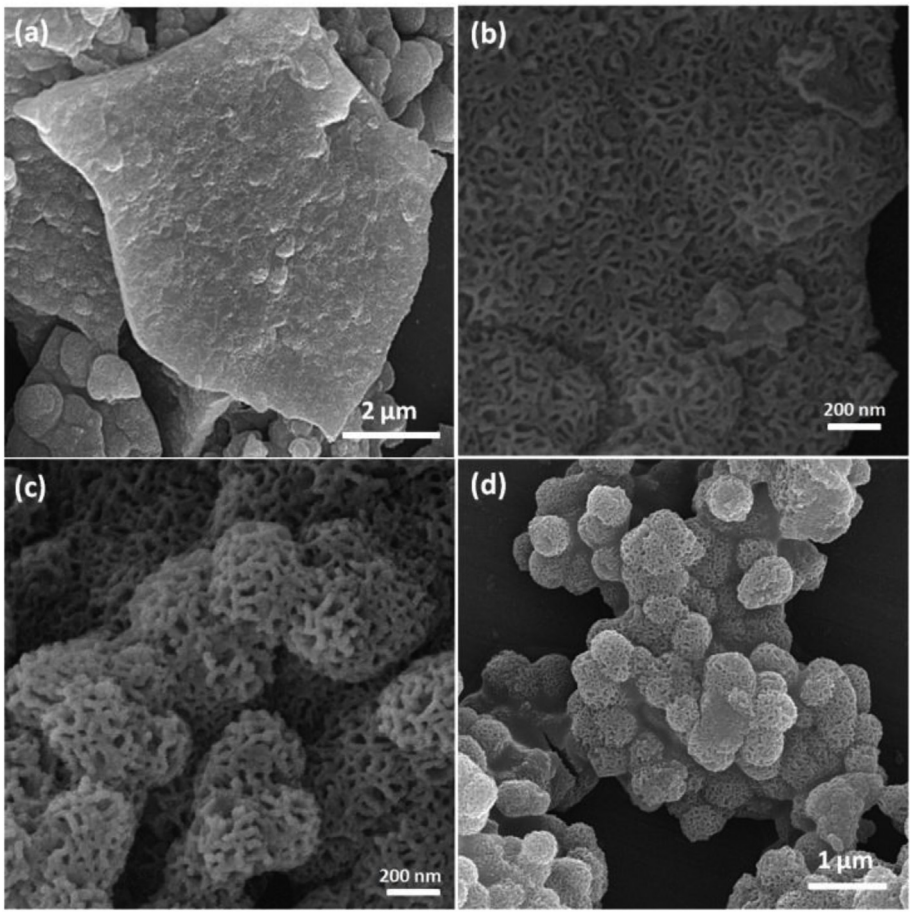

Fig. 1. FESEM images of FPS with a) 1.0 mol, b) 1.0 mol in high magnification, c) 0.8 mol, and d) 0.6 mol of TPP per 1 mol of TEOS and 0.5 g of urea.

carbonates is one of the most engaging effort, which has “100% atom utilization” and is satisfied with the required of “green chemistry” and “atomic economy” [46,47]. Moreover, cyclic carbonates are significant chemical products in many areas such as intermediates of chemical raw materials, electrolytes for lithium-ion cells and polar aprotic solvents [48–50].

In this work, a novel fibrous phosphosilicate nanostructures (FPS) having valuable properties were synthesized then palladium nanoparticles (Pd NPs) supported on fibrous phosphosilicat and used as a catalyst for the cycloaddition of CO_2 to epoxides. Microemulsion system led to the formation of a new morphology of mesoporous phosphosilicate having dendrimeric fibers expanded radially outward providing a high surface area and high accessibility of the reactant to the functional materials. To the best of our knowledge, phosphosilicate nanostructure with this type of fibrous morphology is unprecedented.

2. Experimental

2.1. Materials and methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus and are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. The particle size and structure of nano particle was observed by using a Philips CM10 transmission electron microscope operating at 100 kV. Powder X-ray diffraction data were obtained using Bruker D8 Advance model with Cu ka radiation. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min^{-1} under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.46 MHz, BRUKER DRX-400