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Short communication

Mesoporous MgO synthesized by a homogeneous-hydrothermal method and its catalytic performance on gas-phase acetone condensation at low temperatures

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ABSTRACT

Mesoporous MgO micro-particles (20–80 μm) with crystalline phase framework wall were synthesized through a simple hydrothermal homogeneous precipitation route using urea as precipitating reagent. It possesses high specific area (278 m^2/g), pseudo parallel pore and wall arrangement and large amount of basic sites and exhibits excellent catalytic activity for acetone condensation to mesityl oxide and isophorone even at low temperatures (<200 °C).

1. Introduction

Aldol condensation of acetone is one of the most important industrial processes for the synthesis of mesityl oxide (MO) and isophorone (IP). Currently, the industrial procedure for IP production is performed in a high-pressure autoclave with homogeneous aqueous-base catalysts such as KOH and NaOH [1]. This process generates significant waste water streams that must be neutralized and properly disposed, while re-use of the catalyst is not practical. Some of these problems might be avoided in gas -phase procedure, which could simplify the production process significantly, and minimize or possibly eliminate pollution. Developing an active and selective heterogeneous catalyst is the key to this process. At the laboratory scale, many basic catalysts have been proposed. Among them, pure or promoted MgO was considered to be one of the most prosperous catalyst due to its excellent hydrothermal stability [2–6]. However, these MgO-based catalysts are only active and selective at high temperatures (240–450 °C), because they do not have rich basic sites at low temperatures (<200 °C). It must be emphasized that if high conversions of acetone can be reached with these catalysts, the yields of MO and IP are generally modest. Besides the desired reaction, several side-reactions can also take place, leading to a poor products distribution and fast deactivation of the catalysts. This limitation has traditionally thwarted the potential of solid bases to replace environmentally problematic and corrosive liquid bases.

Mesoporous MgO maybe a feasible solution to above problem. [7–9] Compared to acidic SiO_2 and neutral Al_2O_3, MgO is more popular in basic catalysis area for its broad applications as industrial catalysts and catalyst supports employed in CO_2 adsorption, aldol addition, Claisen–Schmidt condensation, transesterification, and so on [10–17]. One of the most fruitful methods for preparing mesoporous MgO was "template" method, in which carbon aerogels, hexagonal arrays of mesoporous carbon or tri-block copolymer has been employed as hard or soft template for the formation of MgO during thermal decomposition of magnesium salt. These templates have resulted in ordered mesoporous MgO that mimic the structure of the templates and have a surface area of 100–300 m^2/g [18–20]. However, these synthesis procedures require expensive templates, multiple steps and are time-consuming. Another economic strategy for preparing mesoporous MgO is the so called "Template-free" method, in which the mesopores of MgO are formed by thermal decomposition of magnesium hydroxide or carbonate precursor. Using precipitation, solvothermal or hydrothermal methods, mesoporous MgO with all kinds of morphology such as nano-wires, nano-tubes, nano-rods, nano-plates and micro-polyhedrons were synthesized [21–24]. Unfortunately, the specific area of these MgO-materials is normally too low (<100 m^2/g) for potential industrial application. From the viewpoint of synthesis, it is still a significant challenge to obtain mesoporous MgO with high specific area via a one-step, simple, and economic approach.

Herein, we present an easily accessible, reproducible, and high-throughput method to synthesize mesoporous MgO with crystalline phase framework wall through a simple hydrothermal homogeneous

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precipitation route using urea as precipitating reagent. With this strategy, mesoporous MgO with high specific area is readily obtained. More important, the mesoporous MgO possesses a large amount of surface basic sites and can catalyze acetone condensation to MO and IP at low temperatures.

2. Experimental

2.1. Catalyst preparation

To obtain mesoporous MgO, $Mg(NO_3)_3 \cdot 6H_2O$ (AR grade, J&K Corp.) was used as the Mg^{2+} source. In a typical run, 0.01 mol of $Mg(NO_3)_3 \cdot 6H_2O$ and 0.10 mol of urea were dissolved in 50 mL of deionized water. Then, the solution was poured into a 100 mL Teflon bottle. Subsequently, the Teflon bottle with this solution was held in a stainless steel vessel autoclave, and the autoclave was sealed tightly. Finally, the autoclave was transferred into a temperature-controlled electric oven, and was subjected to hydrothermal treatment at temperatures in the range of 200 °C for 24 h. After the hydrothermal treatment, fresh white precipitates were separated by centrifugation, followed by drying at 110 °C in air and calcining at 500 °C for 5 h. The as-obtained white powder was mesoporous MgO (denoted as MM).

2.2. Catalyst characterization

The particle size distribution was determined by laser light scattering (Malvern, MS2000, USA). Scanning electron microscope (SEM) image was obtained on the Hitachi S-4100 FE-SEM instrument (Japan) operated at an accelerated voltage 10 kV. Transmission electron microscope (TEM) image to observe the morphology and Selected Area Electron Diffraction (SAED) pattern to confirm the crystallinity were obtained on Analytical Transmission Electron Microscope (Hitachi H-9000, Japan) with an accelerating voltage 120 kV (The fragments of MM that could be detected by TEM were prepared by spreading an ultrasonicated suspension (4 h) in ethanol on carbon-coated copper grids.). Small-angle and wide-angle X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) using Cu Kα radiation (λ = 1.5406 Å). N_2 adsorption/desorption isotherm at −196 °C was performed with a Quantachrome Autosorb 1-C system, the specific area and pore size distribution were obtained using the BET and BJH (DFT) methods, respectively.

The CO_2-temperature programmed desorption (CO_2-TPD) was performed on Chemisorption Analyzer AutoChem II 2920 (America). 50 mg of the sample was heated in a flow of pure He stream at a rate of 10 °C/min to 500 °C and kept for 1 h. Prior to adsorption of CO_2 at 30 °C, a blank TPD process was carried out from 30 °C to 500 °C to confirm no desorption occurred. After the adsorption of CO_2, CO_2-TPD was performed up to 800 °C at the rate of 10 °C/min.

2.3. Catalytic activity evaluation

Gas-phase aldol condensation of acetone was performed at 50–300 °C in a flow system with a down-flow fixed-bed quartz-tube reactor (6 mm diameter). About 1.0 g of catalyst was packed in the reactor placed in a vertical furnace. Prior to reaction, the catalyst was pretreated in nitrogen at 500 °C for 1 h to remove adsorbed water and carbon dioxide. The feed of acetone (5 μL/min) was admitted to the reactor by means of syringe pump and vaporized in a flow of nitrogen (1 ml/min). The pressure loss of the experiment is about 0.02 MPa. Standard catalytic tests were carried out at a space velocity (WHSV) of 0.24 g acetone/h/g catalyst. After 2 h, the products were collected and then analyzed with a gas chromatograph (Fuli 9720, with a FID detector). The yields of the products (Yield = mole of C of product/mol of C of acetone × 100%) were calculated by area normalization method on a carbon atom basis and the carbon balances are within 100 ± 2%. The turn over frequency (TOF) was denoted as Number of acetone molecules converted/Reaction time/Number of basic sites (O) on the surface of MM. Here, Number of basic sites was calculated by BET surface area of MM/Area of one crystal plane of one unit cell of MgO (0.42 nm × 0.42 nm)/Number of Oxygen atoms on one crystal plane of one unit cell of MgO (2 oxygen atom per crystal plane).

3. Results and discussion

Fig. 1a shows a typical SEM image and particle size distribution of MM. It can be observed that MM exhibits a micro-rod like morphology

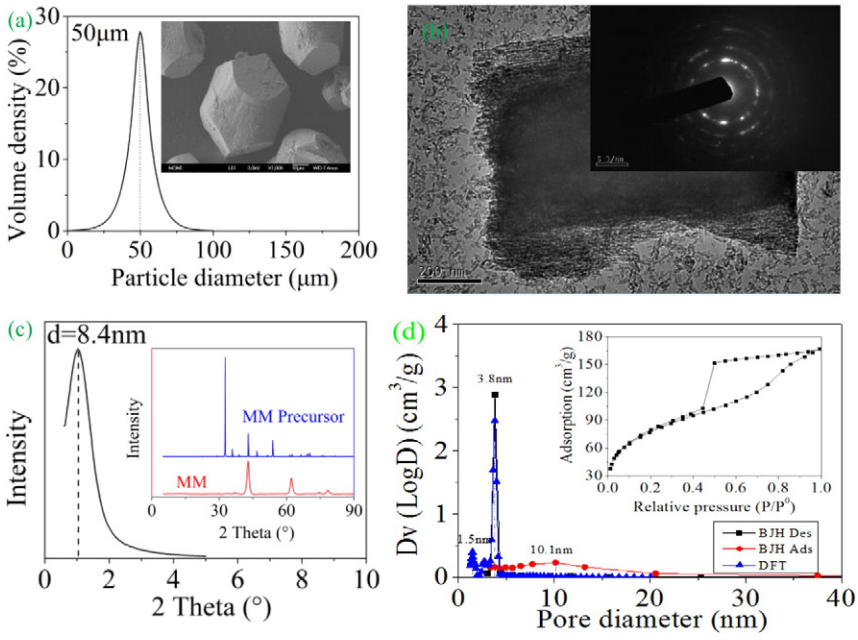

Fig. 1. (a) Particle size distribution and SEM image (inset) of MM; (b) TEM and SAED (inset) images of MM fragments; (c) Small-angle and wide-angle XRD patterns of MM and MM precursor (inset); (d) Pore size distribution and N_2 adsorption–desorption isotherm (inset) of MM.