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A novel and simple strategy for the direct synthesis bimetallic mesoporous materials Zr–La-SBA-15

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ABSTRACT

A series of Zr and La incorporated SBA-15 mesoporous materials (ZLS) were synthesized through a direct hydrothermal route without addition of mineral acids and characterized by FT-IR, XRD, TEM and N_2 adsorption–desorption isotherm techniques. The results indicated that the heteroatoms were successfully incorporated into the framework of SBA-15 after modification. The modified materials still preserved a desirable ordered two-dimensional *P6mm* hexagonal structure and possessed high specific surface area, large pore volume and narrow pore size distribution.

1. Introduction

Ordered mesoporous silica materials have become increasingly popular in chemistry, physics and materials since the discovery of mesoporous silica materials M41S [1], SBA-15 [2], KIT-1 [3], FSM -16 [4], HMS [5], MSU [6] and FDU [7]. Due to their high surface area, large pore volume, regular structure, and uniform pore size distribution, these materials have attracted considerable attention in the field of separation, adsorption and catalysis [1,8]. Many investigations have indicated that heteroatoms incorporated into the framework of mesoporous materials could create more active sites, so nearly all kinds of transition metals have been impregnated into mesoporous materials [9,10].

The SBA-15 material, a kind of ordered mesoporous silica material discovered in 1998 by Zhao et al. [2], had wide and important potential applications. However, it was difficult to introduce other metal ions directly into the framework of SBA-15 because of strong acidic conditions [2]. Recently, several papers have reported that some heteroatoms, for example, Al, Ti, V and Mn [11–14], were incorporated into the framework of SBA-15 by simply adjusting the pH values in hydrothermal procedures. However, little attention has been paid to the synthesis and application of the SBA-15 materials containing binary or ternary heteroatoms without addition of mineral acids. It has been known that the introduction of multi-heteroatoms into mesoporous SBA-15 framework could create new active sites compared with that of mono-heteroatom [15]. Hence, Zr–La-SBA-15 mesoporous materials (ZLS) were directly synthesized through a one-step hydrothermal route without addition of mineral acids in this paper. The main strategy of this method was to utilize the acid self-generated

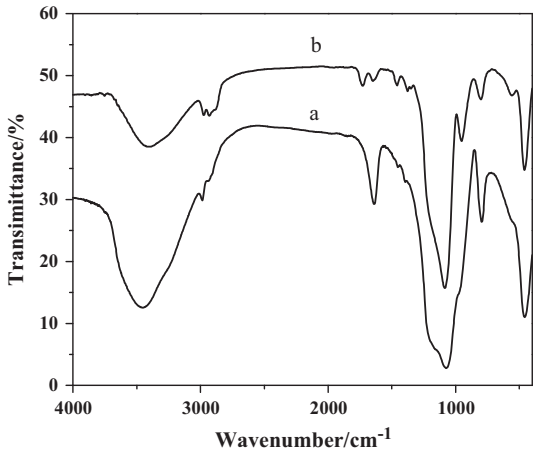

Fig. 1. FT-IR spectra of ZLS(n(Zr)/n(Si)=0.05) (a), SBA-15 (b).

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from the hydrolysis of inorganic salts in aqueous solutions where no addition of mineral acids was necessary.

2. Experimental procedure

ZLS materials were synthesized by the following procedure. 2 g of pluronic P123, as template agent, was dissolved in 100 g of deionized water under vigorous stirring at 35 °C for 2 h. Then appropriate amounts of tetraethyl orthosilicate TEOS (silica source), $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ (precursors) were added into above solution under vigorous stirring. The molar ratio of P123/TEOS/H_2O/ $ZrOCl_2 \cdot 8H_2O$/ $La(NO_3)_3 \cdot 6H_2O$ were kept as 0.01:1:170:*X*:*Y* (*X*:*Y*=1: 1, *X*=0.03, 0.05, 0.1). The mixed solution was continuously stirred for 20 h, and finally crystallized in a teflon-lined autoclave at 100 °C for 24 h. The white product was filtered, washed abundantly with deionized water and absolute ethanol to pH 7, and dried at 60 °C in a vacuum oven for 8 h. The template agent was removed from the as-synthesized product through a solvent extraction procedure using HCl/EtOH solution (1 g of sample in 5 mL/150 mL) for 24 h. The obtained sample was dried at 60 °C in the vacuum oven for 6 h. For comparison, conventional SBA-15 was also prepared according to Zhao's synthesis procedure [2].

FT-IR spectra were recorded on a Digilab FTS3000 FT-IR spectrometer using KBr pellets. XRD patterns were obtained with an X'Pert/PRO diffractometer in the reflection mode using Cu Kα radiation source. N_2 sorption isotherms were measured on a Micromeritics ASAP 2020 analyzer. TEM images of the samples

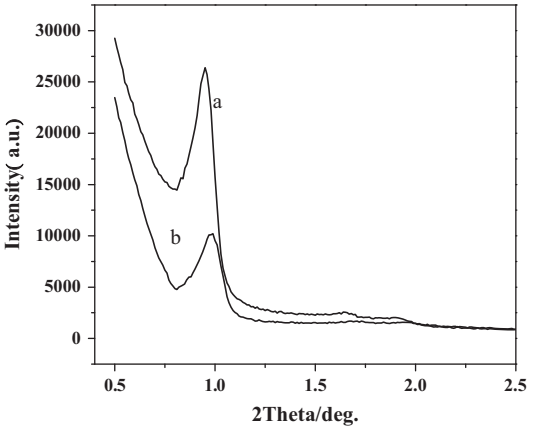

Fig. 2. Small angle XRD patterns ZLS(*n*(Zr)/*n*(Si)=0.05) with different methods removing the template. (a) Extraction method using a HCl/EtOH solution, (b) calcination method.

Table 1
Textural properties of the samples.

Sample name	BET surface area (m^2/g)	Pore size diameters[a] (nm)	Pore volume[b] (cm^3/g)	d_{100} (nm)
SBA-15	874	9.2	0.97	9.0
ZLS	828	9.0	0.94	9.3

[a,b] Calculated from the N_2 adsorption branch of the isotherms by the BJH method with Halsey equation.

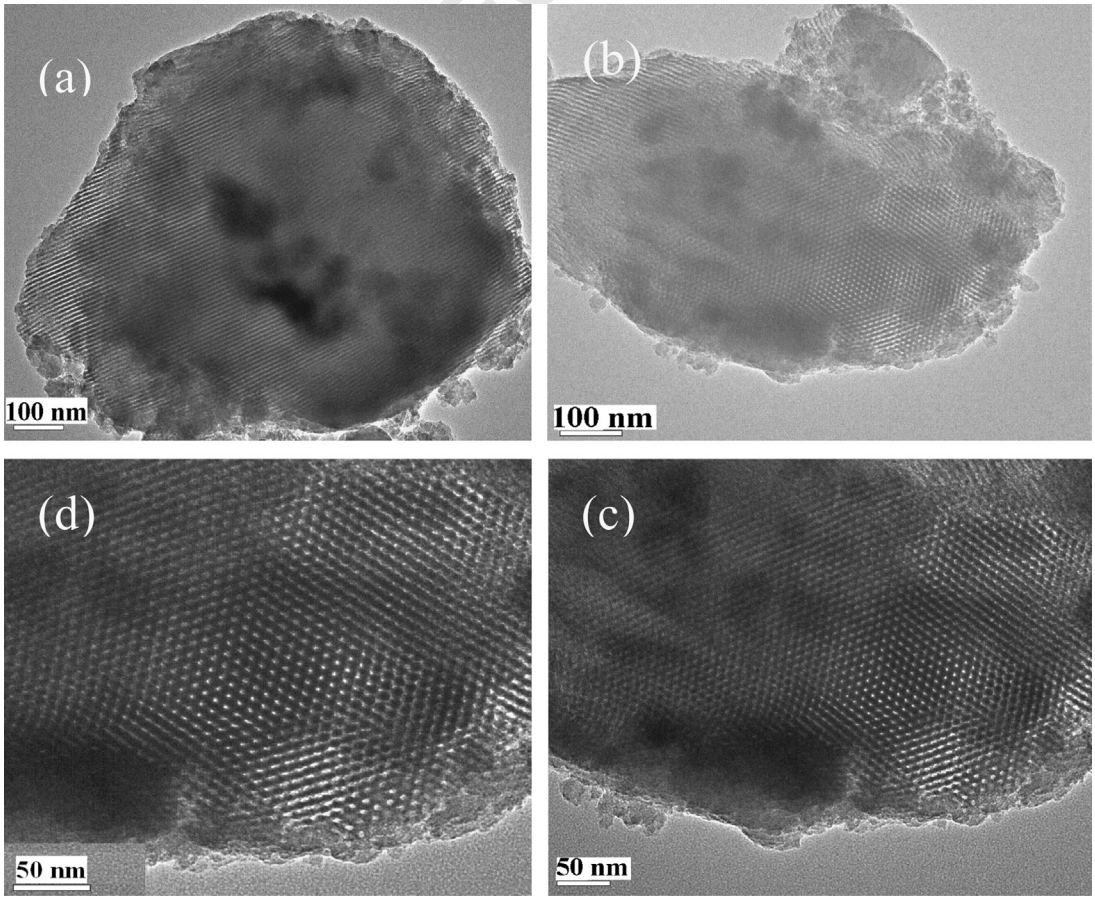

Fig. 3. TEM images of ZLS(*n*(Zr)/*n*(Si)=0.05). (a) In perpendicular direction, (b–d) in parallel directions; (a, b) the original TEM images of ZLS, (c, d) the partially enlarged images of ZLS.

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