Microporous and Mesoporous Materials 190 (2014) 240–247

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Niobium incorporated mesoporous silicate, Nb-KIT-6: Synthesis and characterization

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ARTICLE INFO

Article history:
Received 24 November 2013
Received in revised form 4 February 2014
Accepted 8 February 2014
Available online 18 February 2014

Keywords:
KIT-6
Niobium
Acidity
Mesoporous
Si MAS NMR

ABSTRACT

The direct incorporation of niobium into ordered cubic large pore mesoporous silicate with *Ia3d* structure, KIT-6, is demonstrated via hydrothermal synthesis using a Pluronic P123 triblock copolymer as the structure directing agent and *n*-butanol as additive. The synthesized materials, denoted as Nb-KIT-6, were characterized by analytical techniques such as XRD, elemental analysis, N_2 sorption, HR-TEM, ^{29}Si cross polarization (CP) magic angle spinning (MAS) NMR, Diffuse reflectance UV–Vis, NH_3-TPD, pyridine-FTIR and H_2-TPR. The Nb-KIT-6 materials, prepared with various Nb contents, possess high specific surface area (997–804 m^2/g) and pore volume (1.46–1.12 cm^3/g) with uniform pore diameter centered around 9.3 nm. The incorporation of most of the Nb in the framework was confirmed by Diffuse reflectance UV–Vis spectra, and contributes to an increase in total acidity. Pyridine FTIR measurements confirm the presence of both Brønsted and Lewis acidic sites, with the total acidity increasing nearly linearly with Nb content.

1. Introduction

Ever since the discovery of M41S silicas, there has been a growing interest in the synthesis of ordered mesoporous silicates, motivated primarily by the desire to extend the pore sizes into the mesoporous regime [1]. The unique properties of ordered mesoporous silicates, such as large surface area, high pore volume and tunable pore size, make them suitable for incorporating transition metal ions into their framework and imparting catalytic properties. In this context, mesoporous silica materials such as MCM-41, MCM-48 and SBA-15 have attracted much interest in recent years because of their potential applications in catalysis, sorption, sensors and biomedicine [2–9]. Transition metal ions have been incorporated into these materials via a direct hydrothermal synthesis route that allows uniform distribution of the heteroatoms in the entire framework avoiding pore-blockage that occurs when they are incorporated as metal-oxide particles. While most of the attention has focused on MCM-41 and SBA-15 type silicas, we have recently shown that metals such as W [10] and Zr [11] can be easily incorporated into KIT-6 structures that have ordered 3D mesoporous silicate with cubic *Ia3d* symmetry, tunable pore size, improved wall thickness and excellent thermal/hydrothermal stability. The Zr-KIT-6 materials were shown to be highly active, selective and stable for alcohol dehydration [12].

Nb-containing porous materials have been receiving increased attention as solid acid and oxidation catalysts. For instance, microporous AM-11 crystalline niobium silicates were studied as solid acid catalysts for the dehydration of xylose [13]. In another application, Nb-containing MCM-41 was shown to be active for transesterification of sunflower oil with methanol [14] and the Beckmann rearrangement of cyclohexanone oxime [15]. Nb-containing SBA-15 was shown to be active for sucrose hydrolysis [16] and glycerol esterification [17]. Nb-based SAPO-11 materials are shown to generate Lewis acid sites [18]. Nb-incorporated porous silicates have also been shown to be active in the epoxidation of substrates such as 1-hexene [19], cyclohexene [19–22], cylcooctene [23], propylene [24] and in the oxidation of methanol [25], *m*-toludine [26] and cyclopentene [27].

Based on these reported studies and advantages, we were motivated to investigate the direct incorporation of Nb species into the mesoporous KIT-6 framework in a one-pot synthesis using triblock copolymers as the structure-directing agent in the presence of *n*-butanol and a suitable niobium source. Various characterization techniques such as XRD, N_2 sorption, diffuse reflectance-UV–Vis, ^{29}Si-CP/MAS-NMR, H_2-TPR, NH_3-TPD and pyridine-FTIR reveal that

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http://dx.doi.org/10.1016/j.micromeso.2014.02.019
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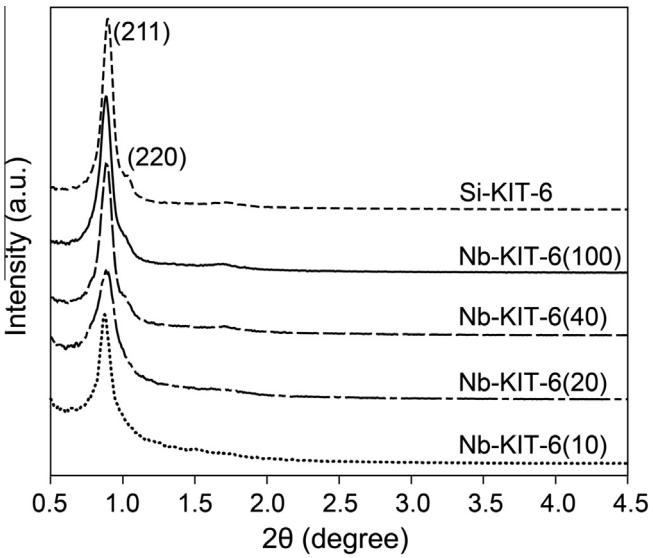

Fig. 1. Small angle X-ray scattering patterns of calcined Nb-KIT-6(Si/Nb) samples.

the Nb is incorporated in the KIT-6 framework as mostly tetrahedrally coordinated species, generating both Lewis and Brønsted acid sites.

2. Experimental

2.1. Materials

Tri-block co-polymer (Pluronic P123, EO_{20}–PO_{70}–EO_{20}, with an average molecular weight ~5800, Aldrich) and *n*-butanol (Aldrich) were used as received, as the structure-directing reagent and co-solvent, respectively. Tetraethyl orthosilicate (TEOS) (98%, Acros organics) and Niobium(V) chloride (99%, Strem Chemicals) were used as silicon and niobium sources, respectively, and were also used as received.

2.2. Synthesis of Nb-KIT-6

Nb-KIT-6 materials with different Si/Nb atomic ratios were synthesized using Pluronic P123 tri-block co-polymer and *n*-butanol for forming a cubic *Ia3d* mesophase. In a typical synthesis, 5.0 g of P123 were dissolved in 190 g 0.5 M hydrochloric acid solution at 35 °C. After complete dissolution, 5.0 g of *n*-butanol were added and the resulting mixture was stirred for another 1 h at 35 °C. Subsequently, 10.6 g of TEOS and the required amounts of Niobium(V) chloride were added to this mixture, and the stirring was continued for another 24 h. Finally, the reaction mixture was transferred to a 300 mL Teflon-lined SS autoclave and subjected to hydrothermal treatment for 24 h at 100 °C. The solid product was filtered off without washing and then dried at 100 °C overnight. The remnants of the structure-directing agent were removed by calcination in a flow of dry air at 550 °C for 5 h.

Table 1
Textural properties of Nb-KIT-6 samples.

Sample[a]	Si/Nb[b]	Nb[b] wt%	a_0[c] nm	S_{BET}[d] m^2/g	$V_{P,DFT}$[e] cm^3/g	$D_{P,DFT}$[f] nm	W[g] nm
Si-KIT-6	–		24.1	1013	1.30	8.5	3.6
Nb-KIT-6(100)	98	1.5	24.4	997	1.35	8.5	3.8
Nb-KIT-6(40)	41	3.4	24.4	991	1.20	8.5	3.8
Nb-KIT-6(20)	21	6.1	24.4	926	1.16	8.5	3.8
Nb-KIT-6(10)	9.8	10.9	24.7	804	1.01	8.5	3.9

$V_{P,DFT}$ is the total pore volume, and $D_{P,DFT}$ is the mesopore diameter calculated using NLDFT kernel developed for equilibrium capillary condensation isotherms of N_2 at 77 K on silica.

[a] Numbers in parenthesis represent Si/Nb ratio in synthesis gel.

[b] ICP-OES analysis.

[c] $a_0 = d_{211}/\sqrt{(h^2+k^2+l^2)}$.

[d] S_{BET} = specific surface area calculated from the adsorption branch of the isotherm in the relative pressure range of 0.05–0.25 using BET model.

[e] $V_{P,DFT}$ = cumulative pore volume by NLDFT method.

[f] $V_{P,DFT}$ = NLDFT pore diameter.

[g] W = wall thickness evaluated by $a_0/2 - D_{P,DFT}$.

2.3. Characterization of the catalysts

Small Angle X-ray Scattering patterns of Nb-KIT-6 samples were collected on a Rigaku system with a S-MAX 3000 instrument using a Bede Scientific microfocus tube source operating at 45 kV and 0.66 mA. X-ray powder diffraction (XRD) patterns in the high angle (2θ = 10–80°) were collected on a Bruker Proteum Diffraction System equipped with Helios multilayer optics, an APEX II CCD detector and a Bruker MicroStar microfocus rotating anode X-ray source operating at 45 kV and 60 mA. Elemental analysis was

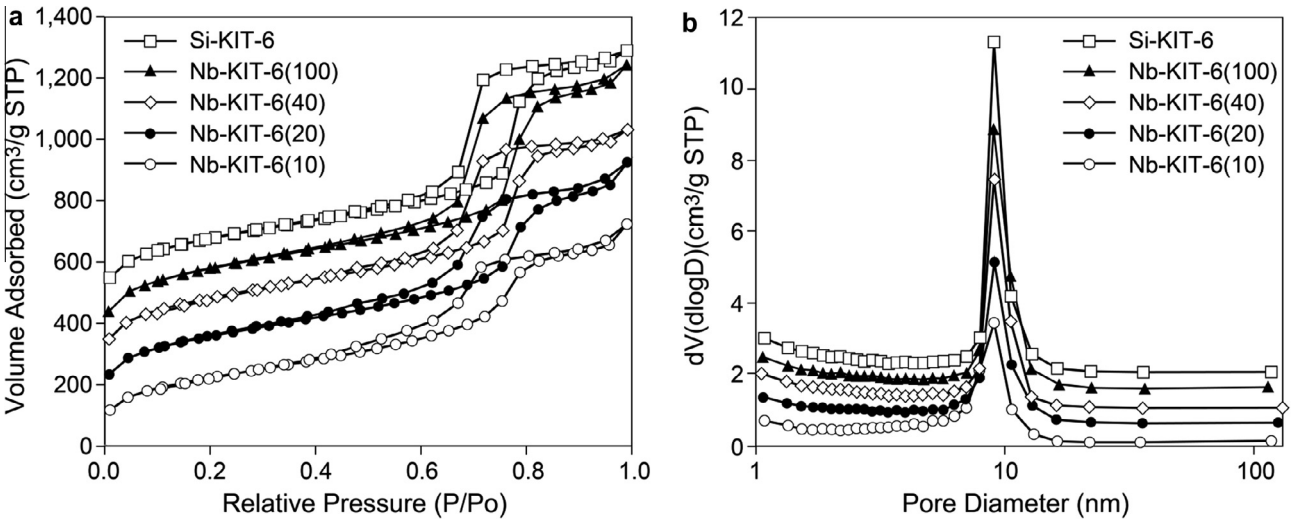

Fig. 2. (a) N_2 sorption isotherms and (b) pore size distribution of Nb-KIT-6(Si/Nb) samples.