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ScienceDirect
Microporous and Mesoporous Materials 112 (2008) 621–626
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Synthesis and characterization of chromium oxide nanocrystals via solid thermal decomposition at low temperature

Li Li [a], Zhonghua Zhu [a,*], Xiangdong Yao [a], Gaoqing Lu [a], Zifeng Yan [b]

[a] *ARC Centre of Excellence for Functional Nanomaterials and Division of Chemical Engineering, University of Queensland, St Lucia, Brisbane QLD 4072, Australia*

[b] *State Key Laboratory of Heavy Oil Processing, CNPC Key Laboratory of Catalysis, China University of Petroleum, Dongying 257061, China*

Received 2 August 2007; received in revised form 25 October 2007; accepted 29 October 2007
Available online 1 November 2007

Abstract

Chromium oxide nanocrystals were synthesized by solid thermal decomposition using cetyltrimethylammonium bromide (CTAB) or a triblock copolymer (P123) as template agent at low temperature. The chromium oxide nanocrystals possess lamellar phase with disordered mesopore. The template surfactants (P123 or CTAB) and hydrated water play an important bridging role in the aggregation of inorganic chromium species in the thermal decomposition of chromium nitration. The mesopores of chromium oxide are formed by eliminating CTAB or P123 from the Cr-surfactants composites with small shrinkage.

Keywords: Chromium oxide; Solid thermal decomposition; Mesopores; Lamellar phase; Nanocrystals

1. Introduction

The design and synthesis of mesostructured/mesoporous transition metal oxides have attracted considerable interests because of their potential applications in the fields of catalysis, sorption, chemical and biological separation, photonic and electronic devices, and drug delivery [1–4]. However, unlike silica and aluminosilicates, mesoporous transitional metal oxides are rather difficult to prepare due to hydrolysis, redox reactions, or phase transitions and a number of different coordination numbers and oxidation states [5]. So far, well-ordered mesoporous oxides of Al, Mn, Ti, V, Zr, Sn, Nb and Ta have been reported [6–11]. The popular synthetic routes are sol–gel method and hydrothermal method in the aqueous or non-aqueous solution [12–14]. Due to fast hydrolysis and aggregation in the solution, many synthetic methods have been developed for transitional metal oxides such as solvo-thermal method [15] and nanocasting method [16–20].

In our previous work, disordered nanoporous chromium oxides were prepared by solid thermal decomposition using citric acid (CA) as template and the relationship between the structure and the reaction conditions of chromium oxide was investigated [21]. The Cr_2O_3 materials obtained using CA as template possessed lamellar disordered mesopore structure with a broad pore size distribution. This might be caused by the weak template effect of CA and weak interaction between chromium precursors and CA. Although it is possible to prepare unstable lamellar phases, however, the preparation of uniformed mesoporous chromium oxide nanocrystals is more difficult.

In this study, a triblock copolymer (P123) or cetyltrimethylammonium bromide (CTAB) was used as template to synthesize mesoporous chromium oxide nanocrystals by solid thermal decomposition and the synthetic mechanism of mesoporous chromium oxide was explored. Compared to the Cr_2O_3 materials synthesized by CA, the Cr_2O_3 samples synthesized by CTAB or P123 possessed

* Corresponding author.
E-mail address: z.zhu@uq.edu.au (Z. Zhu).

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.10.044

uniform pore size and more ordered structure caused by the strong interaction between templates and precursors.

2. Experimental

2.1. Synthesis

Chromium oxide nanocrystals were synthesized by solid thermal decomposition method using a triblock copolymers (P123) or cetyltrimethylammonium bromide (CTAB) as template and chromium nitration as the precursor of chromium. In a typical synthesis, chromium nitration was fully mixed with P123 or CTAB surfactants. The mixtures were put into autoclave and heated in the oven at 140–200 °C for 24 h. After heating, the obtained samples were washed by distilled water and dried at 100 °C in the oven. The chromium oxide samples obtained were marked as Cr_2O_3-template-T.

2.2. Characterization

Nitrogen adsorption–desorption isotherms were obtained on a NOVA 1200 adsorption analyzer at 77 K. Specific surface areas of chromium oxides (S_{BET}) were determined by the BET method in the relative pressure range from 0.05 to 0.25. The total pore volume is derived from the amount of vapor adsorbed at the relative pressure of P/P_0=0.98, by assuming that the pores are then filled with liquid N_2. The pore size distribution was calculated using the N_2 desorption branch by the BJH method. The average particle size, D_p, was estimated using the equation $D_p=6/\rho S_{BET}$, where S_{BET} is the BET surface area of calcined Cr_2O_3 samples and ρ is the density of the primary bulk phase (ρ=5.21 g/cm^3) [22].

X-ray diffraction patterns were performed on a Bruker D8 advance diffractometer at 40 kV and 30 mA with Cu Kα radiation at a scanning rate of 2°/min in the 2θ range from 10 to 80 . Thermogravimetric analysis (TGA) was done on a Shimadzu TGA-50 by heating sample from room temperature to 773 K at 5.0 K/min in air gas. FT-IR analyses were performed on Shimadzu spectrometers in the range of 500–4000 cm^{-1}.

The morphology and structure were determined by scanning electron microscope (SEM) and transmission electron microscopy (TEM). SEM was conducted on a JEOL 8900 electron microscope on Pt-coated samples. The TEM images were obtained from JEOL-1010 electron microscope at 200 keV. Before the TEM measurements, the specimens were ground in ethanol and supported on holey carbon films located on Cu grids.

3. Results and discussion

To identify the decomposition temperature of chromium nitrate, the thermogravimetric analysis was conducted on the chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$) powder under flowing air, as shown in Fig. 1. The weight loss below

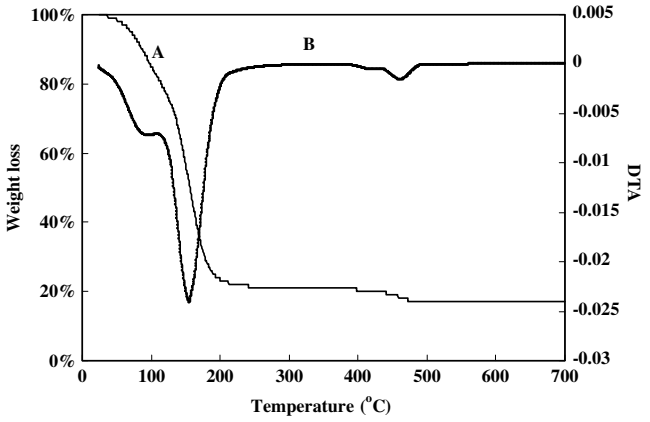

Fig. 1. TGA–DTA plot of chromium nitrate.

100 °C is assigned to the removal of hydration water in the salt. The big weight loss from 100 to 217 °C is mainly attributed to the thermal decomposition of $Cr(NO_3)_3$ to form Cr_2O_3 with the 64% weight loss. A slow and steady weight loss above 450 °C is ascribed to the deoxygenation of Cr_2O_3. Thus, synthesis of Cr_2O_3 samples from $Cr(NO_3)_3{\cdot}9H_2O$ via thermal decomposition method should be performed at the temperatures in the range of 140–200 °C.

The XRD patterns of as-synthesized Cr_2O_3 samples at different temperatures using CTAB as template are shown in Fig. 2. The XRD studies showed that all samples have the diffraction peaks at 33.6°, 36.2° and 54.8°, indicating formation of rhombohedra α-Cr_2O_3 eskolaite. The crystallize sizes of these samples calculated by Scherrer's equation are around 10–15 nm, suggesting that the inorganic framework consists of Cr_2O_3 nanocrystallites. One can see that the crystalline size increased with the increase in decomposition temperature, which means that the crystal growth is faster at higher decomposition temperature.

Nitrogen adsorption–desorption isotherms of Cr_2O_3 samples synthesized at different decomposition temperature using CTAB as template are shown in Fig. 3. The samples exhibit a typically IV isotherm with H3 hysteresis

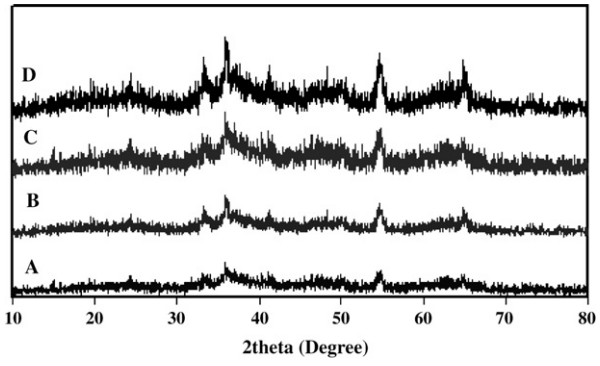

Fig. 2. The XRD patterns of as-synthesized Cr_2O_3 samples at different temperatures by solid thermal decomposition using CTAB as template (A. Cr_2O_3-CTAB-140, B. Cr_2O_3-CTAB-160, C. Cr_2O_3-CTAB-180, D. Cr_2O_3-CTAB-200).