



Influence of thermal treatments on phase composition and acidity of mesoporous tungsten oxide



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ABSTRACT

We report on the synthesis of mesoporous tungsten oxides via hard templating method using silicotungstic acid as W precursor and having surface areas and pore diameters up to 68 m²/g and 12.8 nm, respectively. The relation between thermal treatments (calcination temperature of W-KIT-6 composites and reductive treatment of tungsten oxides), crystalline structure and acidity has been systematically investigated. The acidity of mesoporous tungsten oxides was investigated using common pyridine adsorption methods and chemisorption of probe molecules (CO, H₂). Combination of XRD and FTIR techniques showed that monoclinic and orthorhombic phases of crystalline wall structure coexist in the calcination temperatures 550–800 °C. Increasing the calcination temperature and decreasing the W/Si mass ratio of composites favors the transformation of orthorhombic phase to more stable monoclinic. Moreover, the acidity as well as ability to chemisorbs CO decreases when the calcination temperature increases. The concentration of acid sites also depends on the temperature of reductive treatment of tungsten oxides: CO uptakes increase twice at the 250 °C and decrease by four times when the temperature increases to 450 °C.

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1. Introduction

Tungsten trioxide WO₃ has attracted much attention because of its unique photo-, thermo-, gaso- and electrochromic [1–4] properties. Tungsten trioxide nanomaterials have been used in many areas including catalysis [5,6], gas sensing application (detection of NO₂), for monitoring environmental pollution resulting from combustion or automotive emissions [7–9]), as “smart windows” [10] and field emission displays [11]. Mesoporous WO₃ can be synthesized by sol–gel [12,13], modified sol–gel with additives like poly(methyl methacrylate) spheres or carbon hollow spheres [6,14] and hard templating [15,16] methods. Techniques such as laser ablation [17], anodic oxidation [18], spray pyrolysis [19], sputtering [20,21], electrodeposition [4] and evaporation-induced-self-assembly (EISA) [22,23] have also been used to prepare mesoporous WO₃ materials. Most of the applications of such materials require both a high crystallinity and large surface areas. The

hard templating method has many advantages, i.e. it is inexpensive, simple and reproducible, and it can be carried out under normal atmosphere, with a huge number of adjustable synthesis parameters. Additionally, the hard templating strategy has afforded synthesis of mesoporous tungsten oxides with high surface area, many of which were unavailable by the above-mentioned preparation methods [24,25]. Although the synthesis of mesoporous WO₃ using hard templating method was performed by several groups, phosphotungstic acid H₃[W₁₂PO₄₀]·xH₂O was almost the unique tungsten source used [24,26], in contrast with sol–gel methods for which a variety of W precursors have been reported.

It is well known that many physico-chemical properties of materials, including crucial properties such as acidity, strongly depend on their phase structure. Sallard et al. [27] have reported that only WO₃ materials with highly crystalline structure exhibit long-term stability of electrochemical/electrochromic behavior (coloration efficiency, charge capacity, etc.) at high temperatures, in contrast to amorphous and partially crystalline materials which suffer from irreversible performance degradation due to structural modifications. Structure and catalytic properties of materials based on tungsten oxides are influenced markedly by thermal treatment and tungsten oxide content [28]. It has been shown that controlling the crystallinity and surface area are important to improve the

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photocatalytic activity [6]. High crystallinity was required to reduce the recombination of photoexcited electrons and holes while large surface area allowed the density of active surface sites to be increased. Despite numerous examples showing that the crystalline wall structure of metal oxides plays an important role for their applications, no systematic study on the effect of thermal treatments on phase composition and acidity of the resultant tungsten oxides has been carried out. For example, Wang et al. [29] studied and optimized the variables that influence the mesostructure, including heating conditions to synthesize thermally stable tungsten oxide materials. Zhou et al. [24] studied the effect of calcination temperature of W-hard template composites on crystalline phases present in resultant mesoporous tungsten oxides. In most of the articles, XRD and Raman spectroscopy are the main methods used to characterize such materials. Chemisorption of probe molecules on calcined samples with or without reduction treatment have also been used to estimate the density and type of active sites on WO_3 -based materials [28] together with the common pyridine adsorption methods [30].

Most of the studies on mesoporous WO_3 focus on its applications, and discussions about the influence of synthesis conditions and thermal treatments on phase composition and acidity are scarce. Herein, we report a detailed synthesis of mesoporous tungsten oxide prepared from silicotungstic acid hydrate $\text{H}_4[\text{W}_{12}\text{SiO}_{40}] \cdot x\text{H}_2\text{O}$ as tungsten precursor and following a hard templating method. Our aim was to investigate the influence of thermal treatments (calcination temperature of composites and treatment of tungsten oxides in reducing environment) on the phase composition and acidity of mesoporous tungsten oxide materials. The surface and acid properties were studied using probe molecules (pyridine, CO, H_2).

2. Experimental

2.1. Synthesis of hard template

The synthesis of KIT-6 was performed following a literature procedure [31]: 2.64 g of Pluronic 123 was dissolved in 4.48 ml HCl (37 wt.%) and 96.1 ml H_2O at 35 °C, and then 3.23 ml of n-Butanol was added. 6.24 g of tetraethyl-orthosilicate (TEOS) was added after 1 h of stirring. The resulting solution was stirred for 24 h, then transferred into a Teflon-lined stainless-steel autoclave and kept in an oven at 98 °C for 24 h under static conditions. The solid was filtered, washed with distilled water, dried at 80 °C and calcined at air at 550 °C for 5 h (heating rate 2 °/min).

2.2. Synthesis of mesoporous tungsten oxides

Impregnation of KIT-6 was carried out using silicotungstic acid hydrate $\text{H}_4[\text{W}_{12}\text{SiO}_{40}] \cdot x\text{H}_2\text{O}$ as W source. 1.5 or 4 g of $\text{H}_4[\text{W}_{12}\text{SiO}_{40}] \cdot x\text{H}_2\text{O}$ was added to 1 g of KIT-6 dispersed in 50 ml of ethanol. After 2 h of vigorous stirring the mixture was left in air under stirring until complete evaporation of the solvent. W-KIT-6 composites thus obtained were calcined at different temperatures (550–850 °C, 5 h, heating rate 2 °/min). After calcination samples were stirred with 20% HF during 40 min to remove silica. The final product was washed with water and ethanol and dried at 80 °C. The samples were labeled as WO_3 -meso-W/Si-T, where W/Si – mass ratio of W source to silica template (1.5 or 4), T – calcination temperature.

2.3. Characterization and chemisorption

X-ray powder diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer in the Bragg–Brentano geometry

with $\text{CuK}\alpha$ radiation. FTIR spectra of skeletal vibrations were recorded on a FTIR spectrometer Perkin Elmer Spectrum One using KBr pellets. Acidity of the samples was investigated by adsorption of pyridine as a probe molecule followed by FTIR spectroscopy. A self-supporting wafer was prepared, placed in a thermostated cell with NaCl windows connected to a vacuum line, and evacuated for 1 h at 400 °C. The adsorption of pyridine was carried out at temperature 150 °C and investigated on a Spectrum One (Perkin Elmer) spectrometer with a resolution of 1 cm^{-1} . Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Q-1000 thermal analyzer (MOM, Hungary) from room temperature to 1000 °C with a heating rate of 10 °C min^{-1} under flowing air.

Nitrogen adsorption–desorption isotherms were measured at liquid nitrogen temperature using a Sorptomatic 1990 apparatus after degassing the samples at 250 °C for 4 h. The surface area S_{BET} was calculated by the Brunauer–Emmett–Teller (BET) method in the P/P_0 range 0.05–0.1. The pore-size distribution was calculated on the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) model. Before CO and H_2 chemisorption measurements, samples were evacuated at 250 °C for 4 h. A CO adsorption isotherm was first measured at –196 °C up to a pressure of 304 Torr. A second run was performed after evacuation at 25 °C ($P \sim 10^{-3}$ Torr) for 1 h. CO adsorption isotherm related to the strong interactions was calculated by subtraction of these two analyses [32]. This isotherm was extrapolated to zero pressure to obtain the concentration of strong sorption sites [33].

2.4. H_2 treatment at 250 °C

Samples were treated in H_2 atmosphere at 250 °C before CO chemisorption measurements in order to modify WO_x surface properties. These chemisorption experiments include the following steps. The samples were first evacuated at 250 °C for 4 h and treated in H_2 atmosphere at 250 °C up to pressure 760 Torr for 4 h. Samples were then evacuated at 250 °C for 4 h, and a CO isotherms were measured to obtain the concentration of strong sorption sites similar to described above.

2.5. H_2 treatment at 450 °C

Sample WO_3 -meso-1.5-550 was then used for H_2 treatment at 450 °C before the CO chemisorption measurements similar to described above. After these measurements, the sample was evacuated at 250 °C for 4 h and additionally H_2 adsorption isotherms were measured at –196 °C up to pressure 760 Torr.

3. Results and discussions

3.1. Structure and surface characterization

Hard templating method for the preparation mesoporous materials includes the following steps: (1) impregnation of silica template with element source; (2) calcination of prepared composite; (3) removal of silica matrix. Mesoporous tungsten oxides were prepared using silicotungstic acid $\text{H}_4[\text{W}_{12}\text{SiO}_{40}] \cdot x\text{H}_2\text{O}$ (HSiW) as W source. This W precursor is not as widely used as WCl_6 and phosphotungstic acid $\text{H}_3[\text{W}_{12}\text{PO}_{40}] \cdot x\text{H}_2\text{O}$ (HPW). To the best of our knowledge, only one group reported on the synthesis of mesoporous tungsten oxides with optimal W/Si mass ratios of 3–4 using HSiW as W precursor; mesostructure was preserved up to 600–750 °C calcination temperatures [34]. HSiW has a lower decomposition temperature to tungsten oxide (523 °C, Fig. SI-1) compared to phosphotungstic acid HPW (603 °C), so the

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