



# A nanocellulose template strategy for the controllable synthesis of tungsten-containing mesoporous silica for ultra-deep oxidative desulfurization



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## ABSTRACT

Nanocellulose is a sustainable and ecofriendly nanomaterial derived from renewable biomass. Herein, we developed a novel controllable method for the synthesis of tungsten-containing mesoporous silica catalysts by using nanocellulose templates. Disordered worm-like mesoporous catalysts with a high dispersion of tungsten species were obtained by this method. In particular, the as-prepared catalysts presented high specific surface areas (344–535 m<sup>2</sup>/g), and their pore sizes could be efficiently tuned from 2 nm to 10 nm by adjusting the amount of bio-template in the synthesis system. The resultant samples were used as a catalyst for oxidative desulfurization (ODS) without any organic solvents as an extractant. The results showed that the catalysts with a large pore size (10 nm) and an optimal Si/W mol ratio (20) exhibited high catalytic activity, and dibenzothiophene could be completely removed at 60 °C in 10 min. The catalytic activity on different sulfur compounds increased in the order of benzothiophene < 4,6-dimethyldibenzothiophene < dibenzothiophene. GC–MS analysis of the oxidation products revealed that the catalysts simultaneously acted as both a catalyst and an adsorbent. Moreover, after recycling for five times, the removal of the oxidation desulfurization system could still reach 94%. As this method is sustainable, facile and controllable, the as-prepared catalysts could have potential for practical applications.

## 1. Introduction

Sulfur in transportation fuels remains a major source of air pollution. Environmental regulations have limited the level of sulfur in fuels to less than 15 ppm in many countries [1–3]. Thus, deep desulfurization of liquid fuels has been an important and challenging subject for industrial and environmental reasons in recent years. Currently, the conventional process for the removal of most sulfur compounds in industry is known as hydrodesulfurization (HDS), which is highly efficient at removing aliphatic and acrylic sulfur-containing compounds (thiols, sulfides, and disulfides) [4,5]. However, it is not efficient at removing bulky aromatic organosulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives [6]. This limitation originates from the steric hindrance of the methyl groups on the bulky aromatic sulfur species, which restricts access to the catalyst active sites [7]. Consequently, the removal of these aromatic organosulfur compounds using the HDS process is expensive and not very efficient.

To obtain ultra-low sulfur fuels, selective catalytic oxidative desulfurization (ODS) is considered to be a promising method [8–11]. In particular, ODS can efficiently remove bulky aromatic organosulfur

compounds and produce gasoline with ultra-lower sulfur under mild conditions [12]. In the ODS process, aromatic organosulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives, are oxidized to their corresponding sulfones and can be easily removed by extraction or adsorption. Recently, selective oxidation of such sulfur-containing compounds has been performed by using mesoporous catalysts due to their large specific surface area, high stability and easy to regeneration [13–20]. Various types of transition metal-containing mesoporous catalysts have been generally investigated, such as M-SBA-type [8,17,21–24], M-MCM-type [2,4,5] and M-HMS-type materials [25], where M is a transition metal (W, Mo, Ti, Fe, V, etc.), and they have shown activity and selective for the heterogeneous catalytic oxidation of sulfur compounds. However, their conventional hydrothermal syntheses with meso-template materials are often complicated. Moreover, the traditional meso-templates usually include cationic, anionic and non-ionic surfactants are all from non-renewable petroleum-based feed stocks and expensive, which limits their large-scale application. Therefore, it is still of great significance to develop green and cost-effective renewable template materials as an environmentally benign alternative.

Cellulose is the most abundant biomass material on the planet and is

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renewable, biodegradable and inexpensive [26,27]. Native cellulose consists of crystalline and amorphous regions. The amorphous region makes it sensitive to acid hydrolysis. When native cellulose is subjected to acid hydrolysis, the amorphous regions will be disrupted and form individual nanocellulose fibrils with lengths ranging from 50 to 1000 nm and widths ranging from 3 to 50 nm [28]. Nanocellulose is a promising biomaterial for use as an alternative template [29]. In addition, it is different from traditional template agents. It has a high aspect ratio, low density and an active surface of hydroxyl groups. Thus, it possesses the advantages of both traditional soft template and hard templates at the same time.

In the present work, we demonstrate for the first time a facile route to synthesize tungsten-containing mesoporous silica by using a sustainable, eco-friendly and inexpensive nanocellulose as a mesoporous template. By optimizing the synthesis conditions, a series of samples with different tungsten contents, specific surface areas (350–540 m<sup>2</sup>/g) and pore size (2–10 nm) has been systematically prepared and characterized. Finally, the resulting catalysts were tested in the oxidative desulfurization of sulfur compounds in the presence of hydrogen peroxide.

## 2. Experimental section

### 2.1. Chemicals and materials

Cellulose from absorbent cotton, sulfuric acid, tetraethylorthosilicate (TEOS), H<sub>2</sub>O<sub>2</sub> (aqueous solution, 30%), silicotungstic acid (AR grade), WO<sub>3</sub> (AR grade), isooctane (AR grade) and ethanol (AR grade) were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). Benzothiophene (BT, 99%), dibenzothiophene (DBT, 98%) and 4,6-dimethylidibenzothiophene (4,6-DMDBT, 99%) were purchased from Sigma-Aldrich.

### 2.2. Synthesis of the catalysts

Suspensions of nanocellulose (NC) were prepared as our previous work [30]. In brief, 10 g of cotton was treated with 100 ml of 65% (w/w) H<sub>2</sub>SO<sub>4</sub> at 45 °C for 120 min under vigorous stirring. After that, the obtained nanocellulose suspension was diluted 5-fold with deionized water to stop the hydrolysis. The final aqueous suspensions were sonicated for 20 min. The final aqueous suspensions were approximately 1.2% NC concentration by weight.

One-pot synthesized mesoporous tungsten-silica catalysts: Typically, 20 ml of ethanol, 10 ml of TEOS, and silicotungstic acid were thoroughly mixed at room temperature. The molar composition of the mixture was 1 TEOS:0.0125–0.1 W:7.2 ethanol. To this solution, specified masses of as-prepared nanocellulose suspensions were added with vigorous stirring. The final solution was further stirred at room temperature for 2 h and formed a gel in an oven at 80 °C for 6 h. Finally, the obtained products were calcined at 600 °C for 2 h in air. For comparison, various tungsten-silica materials with different Si:W molar ratios and pore size were prepared using this method and were denoted as SwX-Y, where X = 10, 20, 40 and 80, corresponding to the Si:W molar ratio, and Y = 0.5, 1.5 or 3.0 corresponding to the mass ratio of the nanocellulose suspensions to TEOS.

### 2.3. Characterization

FT-IR spectra were recorded on a Nicolet iS5 spectrometer (Thermo fisher, USA). The X-ray powder diffraction (XRD) patterns were recorded on an Ultimate IV (Rigaku, Japan) spectrometer. Raman spectra were measured on a DXR (American Thermo Electron) Raman spectrometer with a He-Ne laser (632.8 nm) as the light source. The nitrogen adsorption and desorption isotherms were measured on an ASAP 2020 system (Micromeritics, USA) in static measurement mode. The pore size distribution was obtained from the adsorption branches of the

isotherms using the Barrett-Joyner-Halenda (BJH) method. The morphologies and surface composition of the samples were observed with SEM and EDS (ZEISS SIGMA, Germany), respectively. The microstructures were studied by TEM (Tecnai Spirit (T12), Netherlands). XPS experiments were performed with an EscaLab 250Xi system (Thermo fisher, USA).

### 2.4. Experiments of oxidative desulfurization

The model oils were prepared by dissolving BT, DBT or 4,6-DMDBT in isooctane with a corresponding content of 500 ppm. The oxidative desulfurization catalytic tests were performed in a 10 ml flask equipped with a stirrer. In a typical run, 25 mg of catalyst and 5 ml of a model oil were added to the reactor and preheated to the reaction temperature. Then, H<sub>2</sub>O<sub>2</sub> was injected into the flask and stirred for a period. After the reaction, the remaining sulfur content of the model oil was analysed using an Agilent 7890 GC. To investigate its reusability, the catalyst was separated by centrifugation, washed with ethanol three times, dried at 100 °C, and then recycled for another time. The aromatic organosulfur compounds conversion was determined by the following equation, C% = (C<sub>0</sub> - C<sub>t</sub>)/C<sub>0</sub> × 100%, where C<sub>0</sub> is the aromatic organosulfur compound concentration at time zero and C<sub>t</sub> is the aromatic organosulfur compound concentration at time t.

## 3. Results and discussion

### 3.1. Characteristics

The FT-IR spectra for all the samples are shown in Fig. 1. The broad bands at approximately 3500 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> can be assigned to the symmetric stretching and bending vibrations of the surface hydroxyl group and absorbed water. The broad bands at 1080 cm<sup>-1</sup>, 810 cm<sup>-1</sup> and 470 cm<sup>-1</sup> are assigned to asymmetric stretching vibrations, symmetric stretching vibrations and bending vibrations of Si-O-Si bonds, respectively [31]. The band at approximately 960 cm<sup>-1</sup> has been widely used to characterize the substitution of Si by metal ions in the silica framework as the stretching Si-O vibration mode perturbed by the neighbouring coordination metal ions (like the Si-O-W bond) [32,33]. Thus, the presence of the band at approximately 960 cm<sup>-1</sup> in all samples can be ascribed to the framework of Si-O-W vibrations [9,34,35]. This result indicates that the presence of tungsten species incorporating into mesoporous silica framework were detected in all

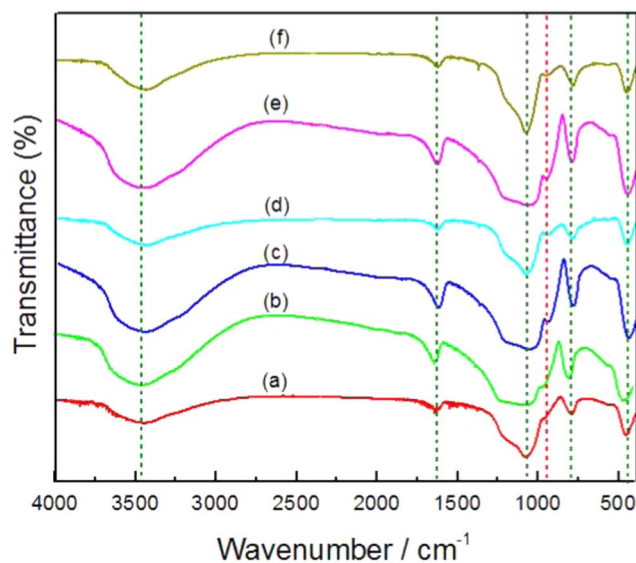


Fig. 1. FT-IR spectra of as-prepared samples. (a) Sw80-3.0; (b) Sw40-3.0; (c) Sw20-3.0; (d) Sw10-3.0; (e) Sw20-0.5; (f) Sw20-1.5).

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