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Flame aerosol synthesis of WO_3/CeO_2 from aqueous solution: Two distinct pathways and structure design

Shuhao Wang [a,b], Yun Huang [a,*]

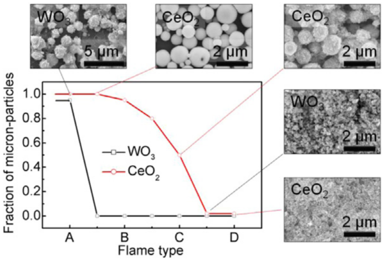
[a] State Key Laboratory of MultiPhase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences (CAS), Beijing 100190, China
[b] University of Chinese Academy of Sciences (UCAS), Beijing 100049, China

HIGHLIGHTS

- Flame temperature is adjusted by diluting fuel and oxidant synchronously.
- Droplet-particle and droplet-vapor-particle pathways are verified.
- Competition between flame temperature and vapor pressure plays the core role.
- Nanoparticle mixing and decorated structure are designed.

GRAPHICAL ABSTRACT

The competition between these critical parameters determined the pathway, the sublimation level, and the size distribution of final particles. Therefore, such conversion influenced by temperature and different sensitivity make it possible to design particle structure by elaborate control of flame temperature.



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ABSTRACT

Flame aerosol synthesis is a continuous one-step method to obtain metal oxides. However, production of uniform particle is considered an inherent challenge for flame aerosol synthesis from aqueous solution. It is necessary to fully understand the synthesis route and the essential governing factors to break through the barrier. A series of flames with different temperatures were employed to synthesize WO_3, CeO_2 and the WO_3/CeO_2 composite powders. Flame temperature and precursor concentration were investigated to determine the synthesis pathways from aqueous droplet to particle. Size distribution of the powders indicated that they were homogeneous (unimodal) micron particles at low temperature flame process, nanopowders at high temperature, and inhomogeneous (bimodal) particles in between. Two distinct pathways (droplet-particle and droplet-vapor-particle) were generalized from experiments and verified by size statistics. It was the competition between the temperature of flame and the vapor pressure of precursor solute that played an important role on selection of pathways. Based on the different response to temperature, the nanosized WO_3/CeO_2 mixture and nanoparticle-decorated $WO_3@CeO_2$ were designed. Furthermore, this generalized method was applicable for other tungsten oxide nanostructured catalysts, e.g. $WO_3@Al_2O_3$, $WO_3@ZrO_2$.

1. Introduction

Transition metal oxide and their composites are promising in wide applications. Taking WO_3 for example, it plays an important role as catalytic, photocatalytic and gas sensing material (Nandiyanto et al., 2013; Rey et al., 2015; Zheng et al., 2011). In addition, the tungsten-based composites doped or supported by other metal oxides, such as CeO_2 (Michalow-Mauke et al., 2015a), CuO (Widiyandari et al., 2012), TiO_2 (Arutanti et al., 2014), SiO_2 (Righettoni et al., 2010), Sb_2O_3 (He et al., 2013), ZnO (Siriwong et al., 2009), have been proved of excellent properties. Tungsten composites

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* Corresponding author.
E-mail address: yunhuang@ipe.ac.cn (Y. Huang).

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have been synthesized by various methods, e.g. hydrothermal (He et al., 2013), sol-gel (Sajjad et al., 2010), co-precipitation (Siriwong et al., 2012) and flame-assisted synthesis (Arutanti et al., 2014; Righettoni et al., 2010; Widiyandari et al., 2012; Xu et al., 2006). Among these approaches, flame-aerosol synthesis is considered as a scalable, continuous, and cost-effective method (Nandiyanto and Okuyama, 2011; Ren et al., 2015; Rosebrock et al., 2013; Teoh et al., 2010; Zhang et al., 2013).

In flame aerosol synthesis, the liquid precursors were often meticulously prepared according to the diverse composite required. The flammable solvent and metal-organic or organometallic compounds were commonly used, which were rarely economic or ecological. In contrast, as a combination of cheap solute and green solvent, the inorganic salt in water system is of consistent attraction (Rudin et al., 2013). However, the water in solution was considered to disturb the gas-phase reaction, even the stability of the flame (Tani et al., 2002). Therefore, uniform particle is an inherent challenge for flame-aerosol synthesis from aqueous solution (Seo et al., 2003; Tani et al., 2005). Efforts were made to improve the homogeneity and other properties, such as adding dimethylformamide or methanol into water solution (Cho et al., 2009), employing H_2 or C_2H_2 as fuel, and developing advanced flame reactor (Rudin et al., 2013). However, to break through the inherent challenge of flame aerosol synthesis from aqueous solution, it is necessary to fully understand the synthesis route and the essential governing factors.

The flame aerosol synthesis with aqueous solution is usually a flame-assisted spray pyrolysis process, because the enthalpy content in aqueous solution is much less than 50% (criterion) of the total combustion energy (Schimmoeller et al., 2011; Teoh et al., 2010). It was recognized that conventional spray pyrolysis might follow two pathways: droplet to particle and gas to particle. The enthalpy of precursor was considered as a governing factor in the process. When low enthalpy precursors were used, submicron particles with inhomogeneous morphology and size were usually obtained by droplet to particle conversion, while the high enthalpy precursor converted to nanoparticles by gas to particle pathway (Strobel and Pratsinis, 2007). This is helpful to understand the synthesis pathway from aqueous droplet to particle during flame aerosol synthesis. In flame aerosol synthesis from aqueous solution, droplet process(evaporation of solvent and precipitation of solute)has occurred before reaction and sublimation, due to the distinguishing volatilities of solute (inorganic salt) and solvent (water) (Wang et al., 2016). Therefore, the supporting flame plays a key role in flame-assisted synthesis according to the importance of the enthalpy of precursor in flame spray pyrolysis.

In this work, WO_3 and CeO_2 were synthesized with aqueous solution as precursor to study the effect of flame temperature on particle size distribution. A co-flow diffusion burner was used, which was robust enough to tolerate the aqueous droplets. The flame temperature was elaborately controlled by adjusting the fraction of CH_4 and O_2 in fuel and oxidant streams, respectively. According to the size statistics of the particles prepared at different flame temperature or precursor concentrations, two distinct pathways were verified, which depended on the competition between flame temperature and vapor pressure. With such guidelines, WO_3/CeO_2 nanoparticles mixture and nanoparticle-decorated $WO_3@CeO_2$ were designed. The design of nanoparticle-decorated structure was applicable for other tungsten oxide nanostructured catalysts, e.g. $WO_3@Al_2O_3$, $WO_3@ZrO_2$.

2. Experimental

2.1. Apparatus and material

Schematic of the flame aerosol synthesis experimental setup is illustrated in Supplemental Material Fig. S1. The detailed parameters were described in the previous experimental work of WO_3 powder synthesis (Wang et al., 2016). In this work, the system was upgraded by introducing inert gases to control the flame temperature.

The precursors were prepared by dissolving AMT ($[(NH_4)_6H_2W_{12}O_{40}] \cdot 4H_2O$, 99.5%, Xingbang Tungsten and Molybdenum Co., Ltd.) and cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.5%, Aladdin) in deionized water, respectively. Precursors of various concentrations were prepared ranging from 0.25 to 1.50 mol/L based on metal atoms. The feeding rate of the precursor was 0.15 mL/min, and the carrier gas (N_2) was fixed at 0.5 L/min. The basal flame (named Flame-A) was obtained by methane and oxygen (CH_4=1.6 L/min, O_2=4.8 L/min). The flame temperature was adjusted by diluting fuel and oxidant with inert gas (Ne and Ar) synchronously. All the gases are from Beijing Qianxi Gas Industry, with purity of 99.99%. The powder was synthesized at various operating conditions and then characterized by a series of analysis to determine the role of flame temperature in flame aerosol synthesis process. The employed experimental conditions are summarized in Table 1.

2.2. Characterization

Thermal gravimetric analysis was performed by the thermal analyzer (NETZSCH, STA449C) to determine the thermal properties of AMT and cerium nitrate. X-ray diffraction (XRD, SMARTLAB-9) patterns and scanning electron microscope (SEM, JSM-7001F) were used to check the crystallinity and morphology of the as-prepared powders. The flame temperature was deduced by an analytical solution and then measured by a 0.2 mm Pt-6%Rh/Pt-30%Rh B-type thermocouple.

Table 1
Experimental parameters of synthetic conditions for various samples.

Sample	Precursor (mol/L)			Flame configurations (L/min)
WO_3	AMT	0.25	0.50	Flame-A: Oxidant: O_2 1.2+Ar 3.6; Fuel: CH_4 0.4+Ne 1.2
		1.00	1.50	Flame-D: Oxidant: O_2 4.8; Fuel: CH_4 1.6
	AMT	1.00		Flame-B: Oxidant: O_2 2.4+Ar 2.4; Fuel: CH_4, 0.8+Ne 0.8
				Flame-C: Oxidant: O_2 3.6+Ar 1.2; Fuel: CH_4 1.2+Ne 0.4
CeO_2	Cerium nitrate: 1.00			Flame-A; Flame-B; Flame-C; Flame-D
WO_3/ CeO_2	AMT: 0.25; Cerium nitrate: 1.5			Flame-B; Flame-D

Molecular mass: CH_4, 16; O_2, 32; Ne, 20; Ar 40.