Applied Catalysis A: General 482 (2014) 171–178

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Effect of calcination temperature of the support and the catalyst of WO_3/SnO_2 on the catalytic oxidation of 1,2-benzenedimethanol by H_2O_2

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ARTICLE INFO

Article history:
Received 22 March 2014
Received in revised form 23 May 2014
Accepted 26 May 2014
Available online 2 June 2014

Keywords:
Tungsten oxide
Tin dioxide
Calcinations temperature
1,2-Benzenedimethanol
Catalytic oxidation

ABSTRACT

A series of WO_3/SnO_2 composite catalysts for the catalytic oxidation were prepared by co-precipitation-impregnation method and characterized with various techniques. The characterization results showed that the calcination temperature of the catalyst and the support was essential to the structural evolution of the WO_3/SnO_2. The studies of the catalytic behavior of WO_3/SnO_2 catalyst in the selective oxidation of 1,2-benzenedimethanol to phthalide using aqueous H_2O_2 as the oxidant suggested that the optimized calcination temperature of the support and the catalyst was 1023 K and 823 K, respectively, which was mainly attributed to the high dispersion of tungsten species and few W^{6+} ions entered into SnO_2 lattice. The latter will decrease inevitably the amount of surface active tungsten species.

1. Introduction

The metal oxide, due to its simple preparation, strong surface acidic sites, high thermal stability and better catalytic activities, has been considered as a kind of useful material in the catalysis field [1]. Tin dioxide (SnO_2) has been widely used as one of the most important smart and functional materials for technological and industrial applications because of its unique chemical and mechanical stabilities as well as two specific characteristics: variation in valence state and oxygen vacancies defects [2], such as transparent conductive electrodes, anode materials for lithium-ion batteries, solar energy conversion, electrochromic devices, antistatic coatings and catalysis [3–9]. So far, there are many studies on the nanocrystalline composites of SnO_2 with doping WO_3, and it has been reported that WO_3–SnO_2 composites were mainly applied in gas sensor [10–13], acid catalysis [14–18], and functional materials [19,20]. Bai et al. has investigated a novel preparation method of WO_3–SnO_2 nanocomposites by a two-step sol-precipitation method, and studied the effect of the preparation parameters, such as precipitation pH value, aging conditions and calcination temperature on the grain size and specific surface area of the nanocomposites [13]. They found that the incorporation of WO_3 could inhibit the grain growth of SnO_2, markedly enhancing the thermal stability of SnO_2, conversely, the addition of SnO_2 could also control the size growth of WO_3 nanocrystals and improve the gas sensitivity in the SnO_2/WO_3 powder synthesized by chemical co-precipitation [19]. In other words, these investigations confirmed the strong interaction between WO_3 and SnO_2. Ma et al. found that WO_3/SnO_2 could catalyze the hydrolysis of dichlorodifluoromethane, which was used as solid acid catalyst, and more effective than WO_3 or SnO_2 [14]. Sarkar et al. used synthetic mesoporous WO_3/SnO_2 for the esterification of oleic acid and ethanol to produce ethyloleate, which exhibited a comparable activity [15]. Recently, Kamata et al. have reported a heterogeneous catalyst with tungsten and zinc oxides supported on SnO_2 (W–Zn/SnO_2), which was proved efficient for the selective oxidation of various alkenes, amines, silanes, and sulfides with aqueous H_2O_2 as the green oxidant [21]. It was notable that the catalyst could be recovered from the reaction mixture and reused for several times without any obvious loss of catalytic performance. Several reports have implied that WO_3/SnO_2 composite has a fairly promising application prospect in the field of catalytic oxidation. However, to the best of our knowledge, there is no report about the effect of the calcination temperature of support and catalyst on the structure of WO_3/SnO_2. Additionally, the available related research on the selective oxidation of diols with WO_3/SnO_2 as the catalyst and H_2O_2 as the oxidant has been rarely reported so far.

Phthalide is commonly used in the manufacturing of dyes, pharmaceuticals, bactericides, etc. The traditional synthesis process of phthalide usually resulted in serious environmental pollution, and obtained a low yield of phthalide, or required high

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http://dx.doi.org/10.1016/j.apcata.2014.05.030
0926-860X/

reaction temperature, which consumed a large amount of energy [22]. However, the oxidation of 1,2-benzenedimethanol with aqueous H_2O_2 as oxidant could be called as a green process for the synthesis of phthalide, owing to the avoidance of waste or pollutant. Therefore, the oxidative lactonization of 1,2-benzenedimethanol to phthalide can be taken into account as a probe reaction to evaluate the catalytic performance of the catalysts. In our previous study, WO_x species have been proven to be efficient active sites for oxidation reactions [23], WO_3/ZrO_2 catalyst displayed good activity to the oxidation reaction of 1,2-benzenedimethanol, but the cyclic efficiency of the catalyst was not desired due to the weak interaction between W species and ZrO_2. However, the WO_3/SnO_2 showed super stability in the oxidation reaction with aqueous H_2O_2 as the green oxidant, and the catalyst could be reused for several times without obvious decrease of catalytic performance due to the strong interaction between W species and SnO_2 [21]. In this work, a series of WO_3/SnO_2 catalysts were synthesized by using co-precipitation-impregnation method and the effect of calcination temperature on the structure and catalytic performance of the WO_3/SnO_2 catalysts was firstly investigated. The relationship between the structure and catalytic activity of the WO_3/SnO_2 catalyst has been briefly discussed based on characterizations including BET, TEM, XRD, UV–vis DRS, Raman and XPS. The catalytic activity results showed that the catalyst (25%WO_3/SnO_2-1023, 823 K) exhibited the optimal catalytic performance for the oxidation of 1,2-benzenedimethanol, suggesting that proper calcination temperature of the support and the catalyst was necessary to good catalytic performance of WO_3/SnO_2.

2. Experimental

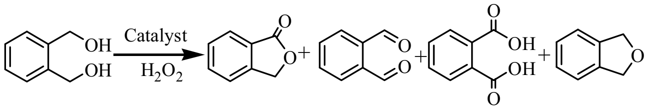
2.1. Catalyst preparation

$Sn(OH)_4$ was prepared by co-precipitation method as described elsewhere [24]. In a typical procedure, an aqueous solution of tin tetrachloride (50 mL, 0.64 M) was added dropwise to a solution of sodium hydroxide (150 mL, 0.90 M) under vigorous stirring. The mixture was kept vigorous stirring at 353 K for 40 min, and the produced precipitate ($Sn(OH)_4$) was obtained by filtration, washed with distilled water for several times, and finally dried at 373 K in air. The obtained support samples were finally calcined at certain temperature for 3 h in air, and the calcined samples were denoted as SnO_2-T_1, where T_1 (K) represents the calcination temperature of the support.

The procedure for the synthesis of $WO_3/Sn(OH)_4$ and WO_3/SnO_2-T_1 by wetness impregnation method was similar to the literature [23]. A certain amount of tungstic acid was added into aqueous solution of oxalic acid (0.2 M) at 363 K with vigorous stirring. When the mixture turned to be a transparent solution, the as-prepared support (2.0 g) was added into the above solution. The mixture was kept stirring at 363 K for 5 h and the excessive water was completely evaporated at the same temperature. The catalyst was finally obtained after drying at 373 K and calcined at a set temperature in air for 3 h. The calcined samples were denoted as WO_3/SnO_2-T_1, T_2, where T_2 (K) represents the calcination temperature of the catalyst (WO_3/SnO_2-R, R: room temperature, T_2: calcined at T_2 of $WO_3/Sn(OH)_4$).

2.2. Catalyst characterization

The specific surface area of samples was measured by nitrogen adsorption at 77 K with Micromeritics Tristar ASAP 3000 using the BET method. TEM images were obtained using a JOEL JEM 2010 microscope operating at accelerating voltage of 200 kV. The ethanol-dispersed sample was mounted on a lacey carbon formvar coated Cu grid. XRD patterns of the samples (2θ ranges from 20° to 90°) were conducted on a Bruker D8 Advance X-ray diffractrometer with Cu Kα radiation operated at 40 kV and 40 mA. UV–vis DRS was performed with a SHIMADZU UV-2450 instrument using $BaSO_4$ as the reference. The Raman experiments were taken by using a Jobin Yvon DiLor LabRAM I Raman spectrometer equipped with a holographic edge filter, a CCD detector and a He–Ne laser irradiated at 632.8 nm. XPS spectra were obtained on a Perkin-Elmer PHI 5000C ESCA system equipped with an Mg Kα (1253.6 eV) anode and a hemispheric energy analyzer. All binding energies were calibrated by using contaminant C 1s (284.6 eV) as a reference.



Scheme 1. The oxidation products distribution of 1,2-benzenedimethanol by H_2O_2.

2.3. Activity test

The activity test was carried out at 353 K in a round-bottom flask equipped with a reflux condenser using 50% hydrogen peroxide as the oxidant and t-BuOH as the solvent. In a typical experiment, a mixture of 1,2-benzenedimethanol (0.690 g), t-BuOH (10 mL) and a certain amount of catalyst were stirred in a flask for several minutes at 353 K. Then, the reaction was started after adding 50 wt.% aqueous H_2O_2 (0.67 mL) into the above mixture and was stirred for a desired time. The product distribution of the catalytic oxidation of 1,2-benzenedimethanol was identified by means of GC–MS method and was shown in Scheme 1. The catalytic performance of the catalysts was based on the yield of phthalide. Formation of products and consumption of substrate were detected by means of GC method.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET

As we all know, specific surface area is an important factor that affects the catalytic activity, because catalyst with larger surface area can provide more active sites that are beneficial for catalytic reactions. BET specific surface areas of SnO_2 and WO_3/SnO_2 composites calcined at different temperatures were shown in Table 1. It was interesting that uncalcined $Sn(OH)_4$ had the highest surface area. As the calcination temperature increased, the BET area of the as-obtained SnO_2 decreased substantially. When the calcination temperature was increased up to 1273 K, the surface area of SnO_2 was reduced to 5 m^2/g. After loading WO_3 species, the BET areas

Table 1
BET areas of different catalysts and supports.

Entry	Catalyst	Calcinations temperature of support (K)	Calcinations temperature of the catalyst (K)	BET (m^2/g)
1	$Sn(OH)_4$	–	–	98
2	SnO_2-823	823	–	44
3	SnO_2-1023	1023	–	26
4	SnO_2-1123	1123	–	18
5	SnO_2-1273	1273	–	5
6	25%WO_3/SnO_2-R	–	823	16
7	25%WO_3/SnO_2-823	823	823	12
8	25%WO_3/SnO_2-1023	1023	823	18
9	25%WO_3/SnO_2-1123	1123	823	13
10	25%WO_3/SnO_2-1123	1273	823	5