



Synthesis of acetyl salicylic acid over WO_3/ZrO_2 solid superacid catalyst

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ABSTRACT

Solid superacid WO_3/ZrO_2 was prepared by co-precipitation of an aqueous zirconyl chloride and ammonium metatungstate solution. The as-prepared catalysts were characterized by using XRD, Laser Raman spectroscopy and BET. Acetyl salicylic acid was synthesized from salicylic acid and acetic anhydride using as-synthesized WO_3/ZrO_2 . The effects of WO_3 concentration, reaction time, reaction temperature, molar ratio of reactants, as well as dosage of catalysts on synthesis of acetyl salicylic acid were investigated, and the reaction conditions were therefore optimized. The excellent yield (91.0%) of acetylsalicylic acid was obtained under optimized reaction conditions. The catalyst has been easily recovered and reused repeatedly with a consistent high yield.

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1. Introduction

Acetyl salicylic acid, also known as aspirin, is a common non-steroidal analgesic, antipyretic and anti-rheumatism drug. Aspirin in body also has anti-thrombotic function that can effectively inhibit the aggregation of blood platelets. It has been widely used for the prevention and treatment of cardiovascular and cerebrovascular diseases. Today aspirin is one of the most commonly used medicines around the globe. Furthermore, its application is continuously being expanded and a large number of its derivative drugs have been synthesized. Acetyl salicylic acid is commercially prepared by acetylation reaction with salicylic acid and acetic anhydride in presence of concentrated H_2SO_4 or H_3PO_4 [1,2]. The use of concentrated sulfuric or phosphoric acid as catalysts has, however, resulted in low production yield (65–67%) and poor selectivity as well as strong reactor corrosion and severe environmental pollution. An environmentally more friendly catalyst with high activity, high selectivity and no corrosion is, therefore, in high demand.

In recent years, many alternative catalysts for acetyl salicylic acid synthesis have been explored. It was reported that using aminosulfonic acid as the catalyst at reaction temperature 81–85 °C, 93.4% yield of acetyl salicylic acid was obtained [3]. Aminosulfonic acid showed high activity and less pollution, but it was easily dissolved in water and needed to be refilled throughout the production process, which will limit its wide acceptance in industrial applications. $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacid as catalyst was also used to synthesize acetyl salicylic acid, and showed very high catalytic activity. For example, a very high yield (95%)

of acetyl salicylic acid was obtained by using $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst under optimal conditions [4]. Furthermore, $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacid has emerged as a potential alternative catalyst to the conventional homogeneous acid catalyst due to its ease of being recycled for repeated usage without resulting in difficulty of waste disposal. However, $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ catalysts in heterogeneous reaction system slowly lose the sulfate radical on their surface so that the acid strength is clearly decreased over time, resulting in rapid decline of reaction activity. It is also found that the thermal stability of the catalysts cannot meet the requirements for industrial application [5]. Comparing to $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$, the acid strength of WO_3/ZrO_2 catalyst is slightly lower, while its thermal stability is better, undergoing significantly less deactivation in the presence of H_2 , O_2 , and steam atmosphere [6]. It has been viewed as a greener catalyst. WO_3/ZrO_2 catalyst has also shown a higher activity and better selectivity for some of acid catalyzed reactions [6–10]. In this report, solid superacid WO_3/ZrO_2 was prepared by co-precipitation method, and was characterized by XRD, Raman spectroscopy and BET. Its catalytic properties for synthesizing acetyl salicylic acid was investigated in details.

2. Experimental

2.1. Catalyst preparation

An aqueous zirconyl chloride and ammonium metatungstate solution at pre-determined concentration was heated to the boiling temperature, and was kept at reflux conditions for 2 h and then cooled. The pH of the resulting solution was adjusted to 8–9 by drop-wise addition of aqueous ammonia with magnetic agitation. A jelly precipitate was formed, which was aged for 24 h at ambient conditions. The aged precipitate was filtered and washed with

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distilled water until the absence of chlorides. Then the collected solid was dried at 100 °C overnight, and calcined in air at either 700 or 800 °C for 3 h to produce respective WO₃/ZrO₂ solid superacids. This series of catalysts was denoted by their weight percentage of WO₃ and calcination temperature. For example, 10-WO₃/ZrO₂ (700 °C) represents the catalyst containing 10 wt.% WO₃ and calcined at 700 °C.

2.2. Catalyst characterization

The crystalline structure of the catalyst samples was determined by X-ray powder diffractometer (XRD, D8-Super Speed, Bruker company, Germany) at 40 kV × 30 mA, and CuKα radiation was used with a scanning speed of 2.4°/min and scanning range of 10–70°; Raman spectra of the samples exposed to ambient conditions were acquired with Renishaw Raman In Via spectrometer. The 514 nm line of laser was used as excitation source and a laser power of approximately 17 mW was applied. The Raman scattering was collected in a static-scan mode in the 200–1200 cm⁻¹ spectral region with a resolution >4 cm⁻¹, and a total scanning time for each spectrum is 50 s.

2.3. Synthesis of acetyl salicylic acid

The acetylation of salicylic acid with acetic anhydride was conducted in a batch reactor that was equipped with magnetic agitation using the as-prepared WO₃/ZrO₂ catalyst. The mixture was elevated to pre-determined temperatures in a water bath and kept at the same temperature for pre-set times. Then the catalyst was recovered by filtration at reaction temperature and washed thoroughly with hot water. The washing water was added to the filtrate. The filtrate was hydrolyze in water to remove unreacted acetic anhydride to acetic acid, and was slowly cooled to room temperature in icy water bath without agitation to obtain white acetyl salicylic acid crystals. The crystals were collected by filtration, and washed with chilled water to obtain acetyl salicylic acid (crude product). The crude crystals were purified by re-crystallization in ethanol–water solution. The crystal was confirmed to be acetyl salicylic acid by melting point measurement, FT-IR and UV–vis spectra. The yield of the re-crystallized pure products was calculated as below:

$$\text{Yield (wt.\%)} = \frac{\text{obtained wt. of product}}{\text{theoretical wt. of product}} \times 100$$

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Crystalline structure of catalyst

Either tetragonal (t) or monoclinic (m) zirconia crystal phases or both are found in as-prepared catalysts. The phase transition of both crystal phases is dependent on the calcination temperature and the tungsten oxide content. For WO₃/ZrO₂ catalysts, the presence of tetragonal zirconia is required to become superacid, whereas it is hardly to form the strong acid site on monoclinic zirconia [11,12]. Consistent with previous studies, our experiments showed that an amorphous zirconia is obtained by calcining pure Zr(OH)₄ below 300 °C, a two-phase mixture of the tetragonal and monoclinic is formed between 350 and 600 °C, and a monoclinic phase with a minor amount of tetragonal zirconia at 700 °C [13,14] (curve a in Fig. 1). In 5-WO₃/ZrO₂ calcined at 700 °C as shown in Fig. 1, only tetragonal phase is with no noticeable diffraction peaks from monoclinic phase. Our experimental results further show that tetragonal zirconia increases with concentration of tungsten oxide.

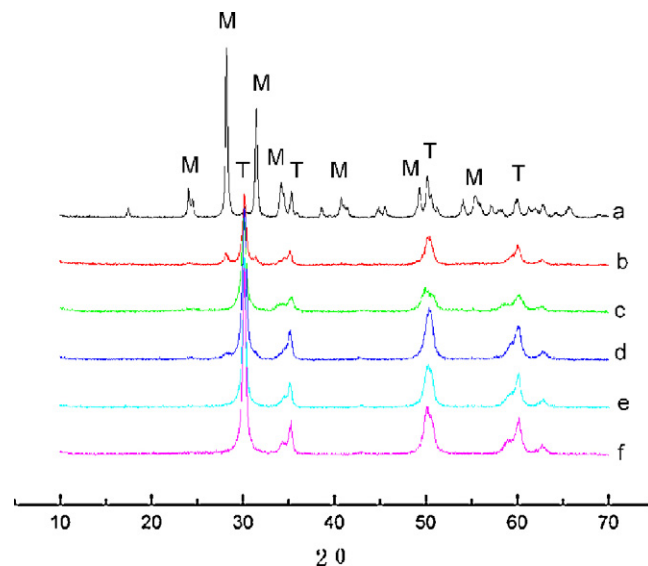


Fig. 1. XRD patterns of catalysts calcined at 700 °C with different WO₃ concentration. a–0, b–5%, c–10%, d–15%, e–20%, f–25%, M–monoclinic ZrO₂, T–tetragonal ZrO₂.

For WO₃/ZrO₂ with WO₃ concentration at 15 wt.%, it is interesting to note that XRD peaks corresponding to monoclinic phase have been totally eliminated, and only peaks from tetragonal phase are found. Simultaneously, neither diffraction peak corresponding to crystalline WO₃ is observed nor are peaks corresponding to any new crystal phases. The observation indicates the structure stabilizing effect of highly dispersed surface tungsten oxide by co-precipitation method (Fig. 1).

Traces of monoclinic zirconia were observed in the samples calcined at 800 °C; when the concentration of tungsten oxide was reached beyond 15 wt.%, diffraction peaks corresponding to crystalline WO₃ become apparent, and their intensities increase with tungsten oxide (Fig. 2). From the literatures it has been seen that tungsten oxide concentration and calcination temperature must be strictly controlled to eliminate monoclinic zirconia and to avoid formation of crystalline WO₃ in the catalysts [15,16].

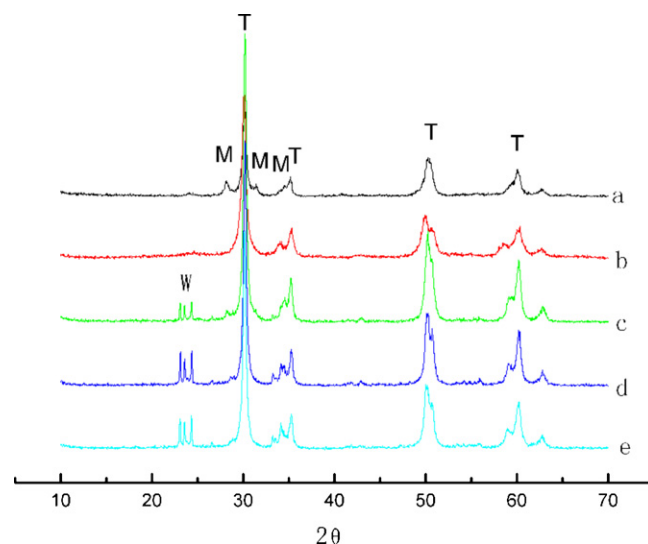


Fig. 2. XRD patterns of catalysts calcined at 800 °C with different WO₃ concentration. a–5%, b–10%, c–15%, d–20%, e–25%, M–monoclinic ZrO₂, T–tetragonal ZrO₂, W–monoclinic WO₃.

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