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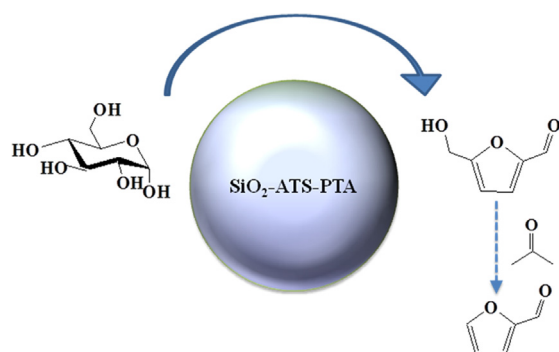
Preparation of 5-hydroxymethylfurfural from glucose catalyzed by silica-supported phosphotungstic acid heterogeneous catalyst



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GRAPHICAL ABSTRACT



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ABSTRACT

Conversion of carbohydrates into 5-hydroxymethylfurfural (HMF) is a valuable reaction for biomass efficient utilization. The silica-supported phosphotungstic acid (PTA) heterogeneous catalyst (SiO₂-ATS-PTA) was prepared and characterized by XRD, FT-IR, pyridine-FTIR and SEM. The SiO₂-ATS-PTA was used to catalyze the conversion of glucose, and it afforded 78.31% yield of HMF at 160 °C for 140 min. The SiO₂-ATS-PTA could be reused for five runs without significant loss of catalytic activity. Furfural was the main byproduct. A kinetic analysis was carried out and the values of the activation energy and the pre-exponential factor for the reaction were 30.25 kJ mol⁻¹ and 1.08 × 10⁷ min⁻¹, respectively.

1. Introduction

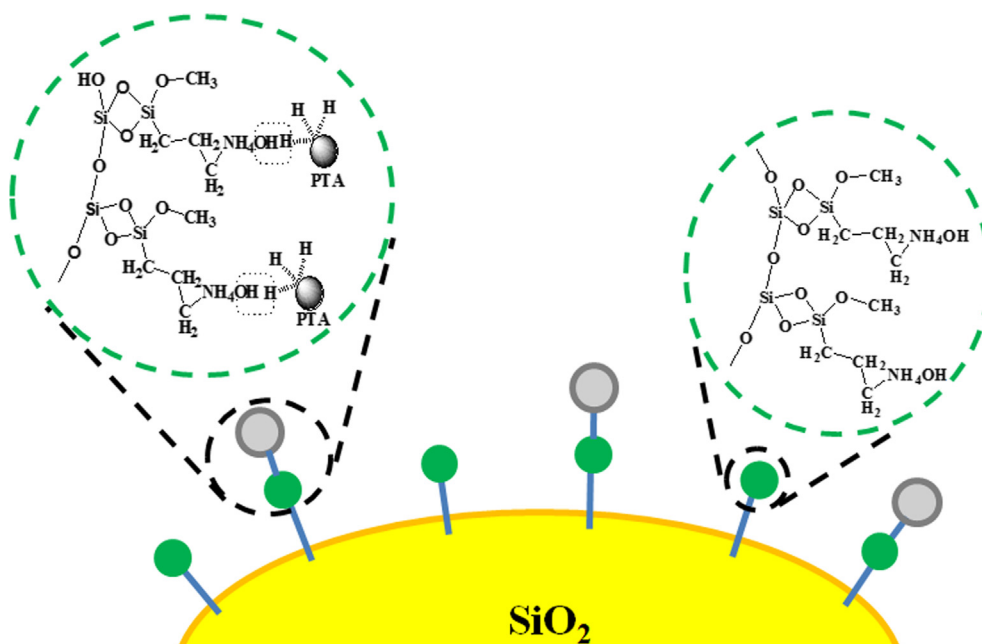
Recently, biomass is attracting much attention as promising new resource due to their availability and abundance [1,2]. Practical pathways were developed to transform biomass-derived carbohydrates into a broad range of value-added compounds [3]. 5-Hydroxymethylfurfural (HMF) has received significant attention as one of the priority chemicals on the list of “ten bio-based chemicals” published by the U.S. Department of Energy [4–6]. Rapid progress in the development of

efficient catalytic approaches for HMF production has been witnessed over past few years [7–10].

Homogeneous catalysts, such as inorganic acid [11], CrCl₂ and CrCl₃·6H₂O etc. [12,13] usually bring excellent yield of HMF while they also cause environmental pollution, equipment corrosion and hard catalyst separation, which limit the industrial application process of them. Recently, heterogeneous catalysts draw researches' attention with basic characteristic of easy separation [14,15] and varies of heterogeneous catalysts were investigated [16], such as mesoporous

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Scheme 1. The structure diagram of target catalyst SiO₂-ATS-PTA.

aluminum doped MCM-41 silica [9], zeolite [17], amorphous Cr₂O₃, SnO₂, SrO [7], and modified tin oxide [18] etc. However, severe reaction conditions were usually employed in heterogeneous catalytic reaction process [19]; ionic liquid and polar organic solvent were usually used as solvent, which would cause environmental pollution [20,21]. So, researchers have turned their attentions to more promising heterogeneous catalysts with sustainability and environmental friendliness, to explore mild, effective and green catalytic reaction processes.

Heteropoly acid was studied extensively because its chemical properties can be varied considerably due to the structural characteristics [22,23]. Heteropoly acid could be converted into heterogeneous catalyst when it was supported on certain supporter [24]. Gomes [25] discovered that the heterogeneous catalyst with Phosphotungstic acid (PTA) supporting on MCM-41 was effective for HMF production from fructose. However, silica gel was suggested to be a more suitable supporter for PTA than MCM-41 [26]. In this work, the catalyst SiO₂-ATS-PTA with PTA supporting on silica gel was synthesized and used to catalyze the conversion of glucose, which is considered as a more ideal starting material than fructose, while it is simultaneously more difficult to be converted because of its molecular structure [27]. The catalytic performance of SiO₂-ATS-PTA for HMF formation from glucose was studied and a kinetic analysis was carried out.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade and used as received without any further purification. X-ray diffraction (XRD) of the catalyst SiO₂-ATS-PTA were recorded with Cu K α (D2 PHASER) radiation ($\lambda = 0.1541$ nm) using a PANalyticalXpert Pro instrument (BRUKER) at 25 °C with a silicon mono-crystal sample holder at step size of 0.017°. The intensity (Miller indices) as a function of 2θ was measured while the angle range was 5–40°. Fourier-transform infrared (FTIR) spectrum (4000–500 cm^{−1}) of the catalyst SiO₂-ATS-PTA was recorded by a Bruker Vertex 80 V FTIR vacuum spectrometer (Ettlingen, Germany) with a resolution of 2 cm^{−1} and 32 scans per sample. Field emission scanning electron microscope (FESEM; Hitachi SU8010, accelerated voltage: 15 kV) was used to study the morphology of the catalysts. Pyridine Fourier-transform infrared (Py-FTIR) experiments were

performed using a USA PE Frontier FT-IR Spectrometer. The concentrations of the Brønsted and Lewis acidic sites on the samples were determined using the FT-IR spectra of adsorbed pyridine; the sample was pressed into a self-supporting wafer (10–15 mg/cm^{−2}, diameter = 10 mm) and was inserted into a measurement cell with KBr windows that was connected to a vacuum apparatus. The wafer was treated at 350 °C under vacuum for 2 h and was subsequently cooled to room temperature to collect the background spectra. The pyridine adsorption was performed by equilibrating the wafer for 30 min at room temperature. To calculate the weak acidic sites and the medium and strong acidic sites, the IR spectra for the samples were recorded after degassing for 60 min at 473 K. The specific surface areas of the target catalyst were examined via nitrogen adsorption at 77 K (Quantachrome Instruments, Quadrasorb SI, America). The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method.

2.2. Catalyst preparation

The target catalyst SiO₂-ATS-PTA was prepared as: 4.00 g SiO₂ was added into 40 mL HNO₃ aqueous (30%) under 70 °C with water reflux for 70 min, then the reaction mixture was filtered, washed with water for three times, dried under 65 °C in a vacuum oven, collected and denoted as SiO₂-A; 3.00 g SiO₂-A was added in 6 mL toluene with 1 g aminopropyltrimethoxysilane (ATS) as adhesive, then was placed in an ultrasound generator under 80 MHz for 10 min, followed by being heated for 70 min at 70 °C with stirring at 500 rpm, dried under 65 °C in a vacuum oven, collected and denoted as SiO₂-ATS; 1 g SiO₂-ATS was mixed with 1.5 g PTA and 6 mL methanol was used as solvent. The reaction mixture was stirred for 2000 rpm under 30 °C for 20 h, then was filtered, washed with methanol for three times, dried at 65 °C in a vacuum oven, denoted as SiO₂-ATS-PTA. The structure diagram of the catalyst SiO₂-ATS-PTA was shown in Scheme 1. The mass proportion of SiO₂:ATS:PTA in the 1.75 g target catalyst SiO₂-ATS-PTA was 0.75 g:0.25 g:0.75 g.

2.3. Typical procedure for the catalytic conversion of glucose into HMF

Qi et al. proved the dehydration of HMF was restricted and the steady of HMF increased in water when acetone was used as co-solvent with water [28]. So acetone/water mixture solution

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