Warsaw, 22 November 2023

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Title of the doctoral dissertation: **Titania-based photocatalysts prepared by sonication in understanding the selective oxidation of lignin-inspired molecules to phenolics**

Abstract

Lignin is considered as a vast and abundantly available renewable resource for the production of various aromatic compounds. Green and economical approaches, such as catalytic selective transformation of lignin-based model compounds to high value products by avoiding the addition of oxidizing agent and the harsh experimental conditions, are still a challenging and highly interesting research tasks. In general, titania-based materials showcase great photocatalytic performances towards the decomposition of a plethora of emerging organic pollutant. However, some dominant drawbacks such as low porosity, fast recombination of photogenerated electron-hole pairs, and an unselective photoreactivity limit the potential application for selective catalytic conversions. This research work focused on the synthesizing the novel titania based photocatalysts with the assistance of ultrasound (US) to overcome the above mentioned drawbacks and the nanomaterials to be utilized for the catalytic selective transformation of lignin based model compounds. US irradiation during the synthesis can lead to various physical and chemical effects, such as the enhanced mass transfer, de-passivation, formation of free radicals like hydroxyl etc., due to the nano-jets, localized hotspots where the temperature and pressure can reach up to 5000 °C and 1000 bars, respectively, which in result can tune the physiochemical features of the synthesized nanomaterials on demand. The physical and chemical effects depend on the utilized US frequency. Therefore, US irradiations of different frequencies (22, 40, 80 and 500 kHz) and with different amplitudes were utilized during the synthesis of titania photocatalyst via a simple slow precipitation method under ambient conditions. For the sake of comparison and to shed light on which physicochemical features are affected upon US irradiation, a titania sample was also synthesized in "silent conditions", using magnetic stirring instead of US, while keeping all other parameters same. The synthesized photocatalysts were characterized by various techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), nitrogen sorption (for the porosity), and

diffused reflectance spectroscopy to estimate the optical band gap. The synthesized photocatalysts were tested for the additives-free photocatalytic selective conversion of lignin inspired model compounds such as the benzyl alcohol and 2-phenoxy-1-phenylethanol in the bath catalytic reactors. The photocatalysts synthesized by using the low amplitude (30 μm) of low frequency (22 kHz) (22kHz-3) showed the highest photocatalytic conversion of benzyl alcohol (75 %) to benzyl aldehyde (67 %) as compared to all other US assisted synthesized photocatalysts. This best performing US-assisted synthesized sample (22kHz-3) showed also the highest yield of the valuable products such as benzyl aldehyde, phenyl formate and 2-phenoxy-1-phenylethanone from the catalytic conversion of 2-phenoxy-1-phenylethanol as compared to the sample synthesized in silent conditions as well as benchmark commercial titania P25 sample. These photocatalytsts were reused for up to five runs of photocatalytic experiments with the similar photoreactivity being intact and without Ti leaching to be observed. The sonophotocatalytic studies revealed that 22kHz-3 sample showed higher selective sonophotocatalytic conversion of 2-phenoxy-1-phenylethanol than photocatalytic process, resulting in an elevated aromatic balance of the reaction. The photogenerated holes were identified as the most reactive species for this photocatalytic reaction revealed by the scavengers studied. This research work showed that utilization of US after optimizing the frequency and amplitude during the synthesis steps can lead to desired materials and specific physicochemical features in order to achieve elevated selective redox photocatalytic performance.

22-11-2023