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Title: Nanoengineering of thin layers of semiconductor photocatalysts in a microreactor environment for lignin-based model compounds valorization

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Abstract

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This thesis aims to synthesize novel thin layers of materials assisted by ultrasound techniques with optocatalytic properties on the internal wall of fluoropolymer microtube reactor for selective oxidation of lignin-based model compounds. The materials was further modified with metals like Fe, Cu, and Co for advance studies. It was expected that such materials will exhibit high surface areas and interesting properties. The critical step was to deposit sol-gel synthesized semiconductor metal oxides (TiO_2, ZnO) layer on the internal wall of polymeric (copolymers of tetrafluoroethylene and perfluoroethers - perfluoroalkoxy alkane) PFA microtube by a method assisted by ultrasounds. Oxidation reactions conducted in micro spaces can allow precise control of parameters like reaction time, temperature, mixing, reproducibility and safety. Continuous flow reactions may also prevent or reduce side reactions and decomposition caused by over irradiation. Irradiation can be easily controlled by controlling of the flow rate of the pumping system. These above kind of controls are expected to increase selectivity, conversion, and yield.

The research plan includes the synthesis of nanoparticles modified with metals via the sol-gel method. Various characterization like N_2 physisorption, X-ray diffraction analysis, UV-Vis diffuse reflectance spectroscopy, etc., is part of the initial step. Doping of titania with metals for the application in heterogeneous photocatalysis improve the visible light response of the TiO_2. The synthesized catalysts were deposited onto the wall of microreactor and the characterization of microtubes was done through scanning electron microscope, optical microscope, to visualize immobilized catalyst layer. Microflow photocatalytic oxidation tests proved that the Fe-TiO_2 material has the highest photocatalytic conversion (28 %) of benzyl

alcohol compared with the other TiO_2 samples under visible light irradiation. The next goal was to investigate the photocatalytic performance of all the synthesized nanoparticles for the selective oxidation of different lignin-based model compounds such as benzyl alcohol, coniferyl alcohol, cinnamyl alcohol, and vanillyl alcohol in liquid phase under different light sources (UV and Visible). The alcohols containing hydroxyl and methoxy groups (coniferyl and vanillin alcohol) showed high conversion (93 % and 52 %, respectively) with 8 % and 17 % selectivity towards their respective aldehydes, with the formation of other side products. The results offer an insight into the ligand-to-metal charge transfer (LMCT) complex formation, which was found to be the main reason for the activity of synthesized catalysts under visible light.