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Direct synthesis of hydrogen peroxide over Au–Pd catalyst in a wall-coated microchannel

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ABSTRACT

Hydrogen peroxide production via direct hydrogenation of molecular oxygen offers many challenges for both catalyst and reactor development to have a high selectivity. An important advantage of using a capillary channel microreactor is the possibility to use H_2/O_2 concentrations that would be considered explosive in traditional reactors. Au–Pd bimetallic catalysts prepared by impregnation or two-phase synthesis procedure were deposited in a form of thin catalytic film in a capillary microchannel. This coated catalyst performed identical to a comparable slurry catalyst tested in a classical batch autoclave. Operating the microreactor within what would have been the explosive regime in a conventional reactor results in a higher selectivity and productivity.

1. Introduction

Efforts to make chemistry "greener" and more sustainable require innovation in chemical processes and chemicals used. Hydrogen peroxide is considered as an environmentally friendly oxidant, since water is the only by-product remaining after its degradation. However, the anthraquinone auto-oxidation (AO) process that is currently used for large-scale production of hydrogen peroxide cannot be listed as green. Besides its complexity, the main disadvantage of the AO process is waste generation that occurs during the hydrogenation step and results in the formation of hydroanthrahydroquinones, oxanthrones, and anthrones [1]. Its green alternative, the direct synthesis method offers many challenges for both catalyst and reactor development to have a high selectivity to the desired peroxide, since conditions suitable for the synthesis of hydrogen peroxide are the same leading to its decomposition or to a non-selective formation of H_2O. The development of a small scale on demand direct synthesis process for production of ultra-pure grade hydrogen peroxide in desirable concentrations without addition of stabilizers and preservatives is of significant interest for fine chemical industry [2,3].

Direct synthesis of hydrogen peroxide is a complex three-phase process, which uses solid catalyst, H_2/O_2 mixtures supplied in a gas state and a solvent. An obvious drawback for the direct formation of hydrogen peroxide from H_2 and O_2 is the very wide explosive region. Reactor miniaturization provides an opportunity to safely handle the direct hydrogenation of molecular oxygen. The safety of this reaction in a wall-coated microchannel is influenced by the combination of temperature and pressure applied. The safety considerations of working with potentially explosive hydrogen and oxygen mixtures in a wall-coated microchannel are discussed in detail by Chattopadhyay and Veser [4]. Upon addition of the catalyst, ignition is shifted towards lower temperatures. Both the homogeneous high temperature dominated and the heterogeneous catalyst initiated ignition branch were taken into account. Simulations showed that a reactor diameter of 300 μm can be considered intrinsically safe (temperature independent) at 1 bar pressure. With increasing pressure in the system, homogeneous reactions tend to accelerate, scaling with the square of reactor pressure, due to the dominance of bimolecular collisions, in contrast to surface reactions, which show linear dependence on pressure. However, at higher pressures, surface reactions will be limited by diffusion of reacting species from the bulk face to catalytic surface, considering that $D \sim P^{-1}$. This means that consumption of reactants is accelerated near the catalytic wall, but delayed in the bulk phase. Chattopadhyay and Veser clearly show that for pressures as high as 10 bar, even in case of extremely small reactor diameters, ignition is dominated by the homogeneous reaction pathway. To operate a wall-coated catalytic reactor safely at higher pressures, it is crucial to stay below the critical ignition temperature, below which homogeneous ignition (explosion) can no longer occur for

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the desired channel diameter. Performing the reaction in a two-phase gas–liquid flow additionally diminishes the possibility for radical or/and hot-spot formation. The liquid separates the gas in small bubbles and acts as a large heat sink.

A catalytic microreactor for direct synthesis can be realized as packed-bed column [5–7], or the catalyst can be immobilized on the walls of the microchannel [8]. Catalyst deposition in the form of a catalytic film on the walls of gas–liquid microreactors is preferred over a catalyst bed due to the high-pressure drop [5,6] and poor catalyst wetting and contacting [9] associated with a packed bed. Kobayashi et al. [10] first introduced the method to deposit a colloidal solution of Pd encapsulated in copolymer micelles with polystyrene backbone on the walls of a microchannel creating thin layers covalently bonded to the glass surface. However, the acidic conditions applied in the direct hydrogen peroxide synthesis are unfavorable for the stability of this kind of liquid film.

In this work, the focus is on the preparation of well-adhered and uniform catalytic layers inside closed capillary channels which are embedded subsequently with bimetallic Au–Pd nanoparticles. Supports with a low isoelectric point, such as SiO_2, are favorable for peroxide formation as this results in lower subsequent hydrogenation rates [11]. For this reason, we used silica wash-coated layer as support. The main benefit of the application of porous films with a large internal surface area as a catalyst support in general is the considerably enhanced surface available for catalyst deposition compared to the geometric surface area of the microchannel wall only. The reaction rate per unit volume of microchannel in case of heterogeneously catalyzed reactions is directly determined by the available catalytic surface area [12], since microchannels possess excellent mass and heat transfer properties.

2. Materials and methods

2.1. Preparation of microchannel wash-coats

Uncoated fused silica capillaries 320 μm in diameter were wash-coated by displacing a plug of the coating slurry using N_2. The coating slurry contains fumed silica, silica gel, and sodium silicate and colloidal silica as binders. The most critical aspect of the coating is maintaining the film uniformity during and after the displacement of the coating fluid. The uniformity of the coating thickness is greatly affected by the ability to maintain the coating parameters such as coating velocity, temperature, and solvent evaporation rate constant during and after the displacement of the coating solution. Disregarding those parameters often results in severe coating non-uniformity with often an order of magnitude high variation in layer thickness along the capillary length. To accurately control those critical coating parameters and prevent the formation of layer non-uniformities, coating setup was built (Fig. S1). The layer thickness and uniformity were assessed using scanning electron microscopy (SEM). Additional ultrasonic adherence tests were performed to ensure mechanical stability of the wash-coated layer under reaction conditions. No loss of coating layer was observed after ultrasonic testing or after reaction performed.

2.2. Catalyst preparation

A gold–palladium catalyst was chosen for the direct hydrogen peroxide synthesis, since Pd alloyed with Au shows an enhanced activity to peroxide formation compared to the traditionally employed Pd catalyst [13–16]. The silica layer coated on the reactor walls or dried wash-coated powder material was functionalized with active Au–Pd metallic species by impregnation with aqueous solutions of $HAuCl_4$ and $PdCl_2$ or deposition of stabilized Au–Pd nanoparticles prepared using a two-phase synthesis method. Au–Pd nanoparticles were synthesized in dichloromethane following the protocol described elsewhere [17]. This two-phase synthesis approach, originally introduced by Brust and co-workers [18], involves transfer of tetrachloropalladate and tetrachloroaurate ions from water to the organic phase by means of tetraoctylammonium chloride as a phase-transfer agent and subsequent reduction using $NaBH_4$. The application of dichloromethane in the catalyst preparation enables a fast evaporation of solvent, thus making the catalyst preparation process faster and more efficient. The concentrations of the metal precursors were adjusted to give an approximately 5 wt% total loading of the bimetallic catalyst with a variable Au/Pd molar ratio with respect to SiO_2 wash-coated material. The catalytic layers were dried at 120 °C for 12 h and calcined at 380 °C for 4 h, since this is the upper temperature limit for the protective polymer film on the outside of the capillary.

Catalysts prepared by traditional wet impregnation were prepared by impregnating SiO_2 coated layer with a solution containing dissolved the required amounts of $HAuCl_4$ and $PdCl_2$ to achieve an approximately 5 wt% loading calculated on the amount of support coated. After water removal, the capillary was dried at 120 °C and calcined at 380 °C. Subsequently, the impregnated catalyst was reduced in a H_2 flow at 300 °C prior to use. Deposition of active metallic species onto the preformed silica layer ensures that the catalyst remains accessible on the silica surface. The metal loadings were verified by inductively coupled plasma (ICP).

Details about catalyst preparation and characterization are provided in the Supplementary information.

2.3. Catalytic testing

Catalytic testing was done in a conventional titanium batch autoclave reactor and in a microcapillary setup (Fig. 1). The catalyst performance in the microchannel was investigated using both pure and diluted hydrogen–oxygen mixtures in order to study the effect of higher reactant partial pressures.

2.3.1. Slurry catalyst testing

The Au–Pd catalyst used in autoclave testing was immobilized on dried and sieved SiO_2 slurry particles in order to have an identical silica support in both types of experiments. The total loading of Au and Pd was approximately 5 wt%. The direct H_2O_2 synthesis is a three-phase process, which involves H_2/O_2 mixtures as a gas phase, a solvent, and the solid catalyst phase. The role of the liquid phase supplied is to collect and solubilize hydrogen peroxide formed, since pure hydrogen peroxide is highly unstable and decomposes into water and oxygen. To additionally minimize hydrogen peroxide decomposition, a water solution containing 0.05 M of sulfuric acid containing approximately 9 ppm of NaBr was used in all experiments as a liquid phase. Acids such as sulfuric or phosphoric decelerate based-catalyzed decomposition of peroxide, while bromide ions even at very low concentrations poison catalytic sites that promote O_2 dissociation and the direct formation of water [19,20].

Semi-batch experiments were carried out in a 300 ml titanium Gr2 autoclave. The reactor is equipped with magnetic impeller designed to stir up to a maximum 3000 rpm and electrical heating. The pressure in reactor is controlled by back-pressure controller (BPC). Gas mixture containing 4 vol.% of H_2 and O_2 was supplied through the stirrer shaft. Typically, 1/3 of the total autoclave volume was filled with the liquid phase containing catalyst powder. All experiments were done at 30 °C, while pressure was maintained at 20 bar. After the desired temperature and pressure were reached, stirring was started. The rotation speed was varied in a range of 800–1500 rpm to determine the optimum agitation speed. Both gas- and liquid-phase analyses were conducted using online