

Performances and deactivation of Pd supported on N-doped CNT in the direct synthesis of H₂O₂

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Introduction

The direct synthesis of H₂O₂ from H₂/O₂ is increasing of interest with starting of operations for new large scale processes using H₂O₂ as reactant (synthesis of caprolactame and propene oxide). One major problem in the direct synthesis of H₂O₂ is the presence of parallel and consecutive reactions leading to the formation of water, which dramatically affects the selectivity. A possible approach to limit this problem regards the possibility to modify the nature of the active particles (Pd) by forming an alloy especially with gold [1]. Another problem derives from the need to operate with diluted H₂ and O₂ gaseous feeds to be outside the explosion range of the O₂/H₂/inert mixture. The problem can be overcome using a microreactor technology, where the high ratio between the internal wall to volume, allows an efficient quenching of radical reactions and thus safe operations inside the explosion region. For this reason, we have focused our attention on the development of novel catalysts based on N doped carbon nanotubes (N-CNT). Here we reported the performance of these catalysts in direct synthesis of H₂O₂ and the analysis of their recyclability. Experimental tests and TEM characterization data indicate that the use of CO₂-expanded methanol allows improving the catalytic performances in H₂O₂ direct synthesis due to the enhanced solubility of H₂ and O₂, but induces a fast catalyst deactivation due to an enhanced mobility and sintering of the supported Pd particles.

Experimental

Palladium and Pd-Au supported catalysts with metal loading of 2% wt were prepared by sol immobilization technique [2] using N-CNTs, prepared by post-treatment of commercial CNTs using NH₃ at 873 K. Catalytic oxidation tests of H₂ to H₂O₂ were carried out in a stirred stainless steel reactor coated with Teflon (capacity 250 ml), containing 35 mg of catalyst in a fine powder form and 125 ml of anhydrous CH₃OH as a reaction medium. A gas mixture containing 9 vol% of H₂ with a H₂/O₂ ratio in a range 1:2 to 1:7 and CO₂ was bubbled continuously through the reaction medium under vigorous stirring at room temperature until the pressure reached the set value (pressure range 10-30 bar). The reaction products were analysed

by potentiometric titrations of H₂O₂ (Metrohm, 794 Basic Trino) and H₂O (Metrohm, 831 KF Coulometer), respectively.

Results/Discussion

CNT materials show excellent properties as support for Pd nanoparticles to prepare catalysts for the direct synthesis of H₂O₂. The introduction of N functionalities in CNT materials further enhances the productivity of the catalyst. However, they have also a negative effect on the rate of H₂O₂ consecutive conversion to water [2]. The N functional groups will have not only a positive effect in stabilizing smaller Pd nanoparticles but also an electronic effect. It may be tentatively suggested that more electron-rich Pd nanoparticles would favor O₂ surface coverage and the rate of H₂O₂ synthesis. The presence of PVA contribute to give an optimal dispersion, key parameter to get a high activity, but it also covered the Pd nanoparticles reducing the initial activity (until 13 min) after this time the lost of PVA involve a fast increase in terms of productivity but at the same time the Pd nanoparticles mobility increase with subsequent sintering. It has been confirmed by the tests of used catalysts which shown a marked decrease of productivity (more than 60%) than fresh sample. The Pd nanoparticles (average diameter 2-3 nm) were observed by TEM investigation on all fresh samples. The STEM picture (fig. 1a) of the used catalyst shown the sintering of the Pd nanoparticles. In a previous work [2] we reported a comparison, in terms of productivity and selectivity, of these materials with a selected literature results, it may be concluded that the productivity obtained by our N-CNT based catalysts is rather high, also taking into account the mild reactions conditions. The selectivity to H₂O₂ is initially high (about 98%) and after about 10 min go down reaching values of 15-20% (fig. 1b). The presence of gold improve the selectivity but only for short reaction time. Finally the performances of these materials are promising for the direct synthesis of H₂O₂ but further study are necessary to improve their stability.

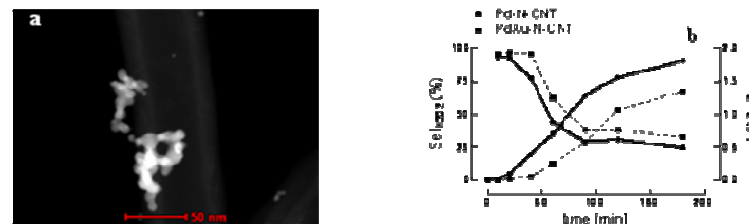


Figure 1. a) STEM image of PdAu/N-CNT after reaction; b) Catalytic behavior of Pd/N-CNT and PdAu/N-CNT catalysts in the direct synthesis of H₂O₂

References.

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