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Pd nanoparticles supported on N-doped nanocarbon for the direct synthesis of H_2O_2 from H_2 and O_2

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ABSTRACT

Pd nanoparticles deposited by sol-immobilization on N-doped nanocarbon are studied in the direct synthesis of H_2O_2 and compared with undoped catalysts or prepared by the same Pd deposition method on active carbon (Vulcan XC-72). The Pd on N-CNT-like gives high productivities to H_2O_2, comparable to the best literature results. The introducing of nitrogen in the CNT-like material favors not only the dispersion of Pd (with a consequent improvement of the activity), but also the specific turnover. However, the introduction of these N functionalities on the surface has also a negative effect on the rate of H_2O_2 consecutive conversion to water.

1. Introduction

The direct synthesis of H_2O_2 from H_2/O_2 is increasing of interest with the starting of operations of new large scale processes using H_2O_2 as the oxidant: synthesis of caprolactame and propene oxide [1]. One major problem in the direct synthesis of H_2O_2 derives from the need to operate with diluted H_2 and O_2 gaseous feeds to be outside the explosion range of the O_2/H_2/inert mixture, with consequent low productivities. In order to overcome this problem, high pressure operations (ca. 10 MPa) are typically reported in most of the patents [2–4].

The reaction of direct synthesis of H_2O_2 using Pd-based catalysts is known from long time. In the 80s it was an intense research activity in many companies on this reaction [4], but after the explosion of a pilot-scale reactor at DuPont the research declined. In the last 5–10 years, a return of interest on this reaction from both companies and academic groups derived from the need of using cleaner oxidation reactants, and reduce the environment impact of various large scale processes, such as those indicated above and the direct benzene hydroxylation to phenol [1]. Although most, but not all, of the more recent studies have been made using low H_2 concentrations (close to lower explosivity limit of the H_2:O_2:inert mixture), still major safety problems remain. In fact, high selectivities in the reaction require to use large O_2 to H_2 ratios and organic solvents, between which methanol is one of the most common. In these conditions, e.g. using volatile organic solvents such as the alcohol, high oxygen concentrations and pressures, the mixture is still potentially explosive. Industrial operations using large reactors are thus potentially unsafe, even if considering technical advances in reactor safety design. In addition, the cost of operations with high pressure significantly reduces the potential economic advantage of the direct synthesis of H_2O_2 with respect to the commercial antraquinone route.

In the past, we explored the possibility of using catalytic membranes/diffusors for intrinsically-safer operations in the direct synthesis of H_2O_2 [5–8]. The limit, however, was the low overall productivity (per reactor volume) and high cost of the membrane.

An alternative approach for intrinsically-safer operations is to use microchanneled reactors [9], where the high surface to volume ratio allows an effective quenching of radical-chain reactions, thus allowing operating safely inside the explosivity range. This solution is particularly suited for small-scale applications.

One of the limits still present in the use of microreactors is that they require the development of new catalysts. The first motivation is that the catalyst in powder form, such as used in the slurry-type reactor typically adopted in most of the studies, cannot be used due to microchannels plugging problems. The deposition of a thin film on the microchannels walls is not optimal in terms of amount of catalyst and fluidodynamic aspects, particularly for gas–liquid reactions such as the case of the H_2O_2 direct synthesis. In wall-coated microchannels, Reynold number may be not enough to guarantee good turbulence or Taylor flow regimes may establish. If the catalyst is instead present in the form of nanofibres filling the void space of the microchannels, the potential advantages are: (i) better wall-to-volume ratio (more

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effective quenching of radical-type explosive reactions), (ii) increase in the surface to volume catalyst ratio (reduced mass transfer limitations which favor decomposition of H_2O_2), (iii) increase in the catalyst loading per volume of microreactor, (iv) increase in the microturbulence (better performances and safety), (v) reduced problems related to gas cap over the catalyst surface.

The use of the catalyst in the form of nanofibres filling the void space of the microchannels has thus many advantages in terms of reactor design.

Several types of supports (acid oxides, resins, mesoporous materials) have been reported in literature [2–4], but essentially no data on the use of carbon nanotubes or similar materials are given.

Nanocarbon materials (nanofibres, nanotubes, etc.) are the natural choice as support to prepare 1D-type catalysts suitable for use in microchanneled reactors. The aim of this work is thus an exploratory investigation on the use of carbon nanotube like (CNT-like) materials as a support for Pd nanoparticles in the direct H_2O_2 synthesis and the analysis of the effect of modification of the surface properties of the CNT-like support by doping with nitrogen via gas phase amination.

Tests were made at lower pressure (1 MPa) than that typically reported in patents or literature data (in the 4–10 MPa range), because low pressure operations are a target for microchanneled reactors to reduce the costs of operations. However, to simplify the study and have results more comparable with literature, catalytic tests have been made in batch- or semi-continuous autoclave reactors. Catalytic tests have been made in the presence of CO_2 as ballast, because as shown earlier [1,10], the presence of CO_2 modifies the properties of the solvent (methanol) improving in particular the solubilization of oxygen. We refer for this reason as CO_2-expanded methanol as the solvent.

2. Experimental

Commercial carbon nanotube-like materials used in this study have been supplied by Pyrograf Products, Inc. The nomenclature used by the company, PR24PS, refers to the specific grade, PS stays for "Pyrolytically Stripping" which is the post-treatment applied to the as-produced nanotubes-like materials in order to remove the polyaromatic hydrocarbons from the surface. Scanning electron micrograph (SEM) images show morphology of the fibres with an average diameter of 88 ± 30 nm. Although a carbon nanotube (CNT) structure is present, we prefer to indicate these materials as CNT-like, because high-resolution transmission electron images show that the inner layer is composed of angled graphite sheets, e.g. "herringbone" morphology [11]. The external layer is instead due to deposited pyrolitic carbon, so called turbostratic graphite. The general morphological characteristics of this nanocarbon are thus similar to carbon nanotubes (CNTs), but the effective nanostructure is different. This sample is indicated hereinafter as CNT-like. These nanocarbon materials are available in relative large amounts at low cost, and they are thus a good suitable choice to develop the aimed catalysts for H_2O_2 direct synthesis. The presence of catalyst impurities was determined by X-ray fluorescence. Only traces of Fe and S and in very low amounts Mg, Cl, Ca and Cr are present. The surface area, determined by full BET method, is $55\,m^2\,g^{-1}$ and a dominant macroporous texture is present.

N-doped CNT-like support was prepared by post-synthesis treatment of the pristine CNT-like by using NH_3 flow ($0.2\,L\,min^{-1}$) at 873 K for 4 h. Before this procedure, the CNT-like was pretreated with nitric acid (20 g of CNTs per liter of HNO_3) at 373 K for 2 h under continuous stirring. Then they were rinsed until the washing water turns on neutral pH. The sample was then dried at 343 K overnight. This sample is indicated hereinafter as N-CNT-like. The nature of nitrogen functionalities on the CNT-like surface, and its graphite structure, were evaluated by XPS synchrotron radiation [12] as well as by elemental analysis (Leco TC-300/EF-300 N/O analyzer). The amount of N introduced after treatment with ammonia at 873 K is 1.1 wt% as bulk value, and about 8% on the surface.

The palladium was then deposited on CNT-like and N-CNT-like using sol-immobilization procedure [13]. Na_2PdCl_4 (0.093 mmol) was dissolved in 100 ml of H_2O, and PVA (poly vinyl alcohol) was added to the solution in the Pd/PVA (w/w) ratio of 1:1. The solution was stirred for 5 min, after which 0.37 mmol of $NaBH_4$ was added under vigorous magnetic stirring. The brown Pd(0) sol was formed immediately. The sol was immobilized by adding the support (acidified at pH 2 by sulphuric acid) under vigorous stirring. After 30 min the slurry was filtered and the catalyst washed thoroughly with distilled water and dried at 353 K overnight.

In addition to CNT-like and N-CNT-like, a reference acid, graphitic and low surface area active carbon (Vulcan XC-72 from Cabot; surface area, $254\,m^2\,g^{-1}$; average particle diameter, 30 nm; 0.3%, sulphur) was used as the support. The characteristics of this active carbon make it a suitable type of material for the comparison with CNT-like materials. This sample is indicated hereinafter as C.

The wt% of the metal deposited on the support after the preparation was determined by atomic absorption spectroscopy (AAS) performed with a Perkin–Elmer Analyst 200 apparatus. Samples for analysis were prepared dissolving 20 mg of the dried catalyst in an aqua regia solution. The amount of Pd in the samples was respectively 0.90 wt% and 0.91 wt% for Pd/CNT-like and Pd/N-CNT-like catalysts, while 3 wt% for Pd/C. A further reference sample was prepared by incipient wetness impregnation using γ-Al_2O_3 SasolPuraloxSCCa-30/200 as the support. The amount of Pd was 2.7 wt%. This sample is indicated hereinafter as Pd/A.

Palladium particles morphology, size distribution and dispersion, were determined by transmission electron microscopy and statistical analysis. HRTEM investigations have been carried out with a Philips CM200 TEM FEG. The samples were dry-deposited on a holey carbon film supported on a Cu grid.

All catalysts were tested at room temperature in the catalytic oxidation of H_2 to H_2O_2 in a stirred stainless steel reactor coated with Teflon (capacity 300 ml) containing 30 mg of catalyst in a fine powder form and 125 ml of anhydrous CH_3OH as a reaction medium, in order to improve both solubility of H_2 and particularly O_2. Two hundred and fifty microliter of H_2SO_4 were added for H_2O_2 stabilization as reported in previous papers [4,5]. Batch- and semi-batch operations (e.g. continuous feed of the gas to the batch slurry reactor containing the solvent) tests were made. In batch-type tests, a gas mixture containing 10 vol% of H_2 with a H_2/O_2 ratio of 1:2 and 50% CO_2 was bubbled continuously through the reaction medium at room temperature until the pressure reaches the set value of 1 MPa, after which the feed was stopped. These conditions permit to work outside the explosion range of H_2/O_2 mixtures. In semi-batch tests, the gas feed was continuous during the experiments. Stirring (1300 rpm) was started after reaching the desiderate pressure, and experiments were carried out for 90 min (batch operations) or longer times (semi-continuous operations). Data were corrected to take into account the initial mixing time. Gas analysis for H_2 and O_2 was performed using a gas chromatograph unit (Agilent 3000 A equipped with a Molsieve 5 Å column using argon as carrier gas). Conversion of H_2 was calculated by gas analysis before and after reaction. The reaction products were analysed by potentiometric titrations of H_2O_2 (Metrohm, 794 Basic Trino) and H_2O (Metrohm, 831 KF Coulometer), respectively.

Tests in H_2O_2 decomposition were analogous to those of direct synthesis (batch reactor), but introducing already a methanol solution containing a determined amount of H_2O_2 and using a gas feed in which O_2 was substituded with N_2. These tests were also made at room temperature.