



Design of catalytic carbon nanotube-based reactor for water denitration – The impact of active metal confinement

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ABSTRACT

The catalytic reduction of nitrate to N_2 represents the efficient water remediation technique in terms of the achieved nitrate depletion, but still with a main drawback – the production of ammonia as the undesired product. Therefore, efforts are undertaken to solve the problem, in terms of both reactor and catalyst design. Usage of internal cavities of carbon nanotubes (CNTs) may be a solution, both as a catalyst support and chemical nanoreactor. The aim of this work was to examine the activity and selectivity of Pd-Cu active phase located inside the carbon nanotubes – the confinement effect. Due to more accurate analysis of this effect, catalytic behavior of the metal nanoparticles deposited on the CNT exterior walls was also tested. Positioning of the active metal phase, *i.e.* exclusively inside or outside the CNTs, was promoted by previous CNTs cutting (*via* catalytic oxidation) and using solvents of different surface tension. The results of catalytic tests revealed the hindering effect of confined metal nanoparticles, while the externally deposited ones can be portrayed by superior performances in terms of both their activity and selectivity. The unexpected result was explained by a negative impact of confined particles due to their electron deficiency, as well as their size determining the second step of denitration reaction as a structure sensitive one.

1. Introduction

Since their discovery in 1991, the unique tubular morphology of carbon nanotubes (CNTs) represents a great research challenge for many scientists over the world. The possibility of using the inner cavity of CNTs for depositing various materials is still under extensive exploration. The well-defined channels of nanotubes restrict the size of encapsulated materials creating a reactor with nanometer or even subnanometer particle sizes. The early developed synthesis techniques were successfully applied for complete filling of CNTs and production of metallic nanowires [1]. Later, the further development of these methods enabled the selective confinement of a large range of materials in the form of discrete nanoparticles. The confinement phenomenon has been intensively examined in the field of catalysis offering a lot of possibilities for designing new catalysts and/or nanoreactors based on CNTs. It has been evoked in the literature that due to the curvature of CNT walls, the π electron density is shifted from the concave inner to the convex outer surface, which affects the electronic structure of the metal particle sitting in the tube interior, consequently changing the activity and selectivity of the corresponding catalyst [2]. So far, a broad range of catalytic chemical reactions have been conducted in order to

study the possibility of tailoring the catalyst properties and performances by nanoscale confinement, eventually leading to different reaction pathways and distribution of products. Most of the obtained results have confirmed that metal confinement inside CNTs results in enhanced catalytic behavior compared to the tubes with particles dispersed on their exterior surface [3–5]. This might be partially assigned to the lower rate of particle agglomeration resulting in the prevention of catalyst deactivation [6]. However, negligible or even hindering impact of inner position of the metal particles was observed in a few reports as well [7–9]. These results are also considered very important from the perspective of further catalyst design and the development of new nanoreactor methodologies.

Nowadays, among all literature reported filling techniques, wet chemistry methods seem to be the most applicable due to their simplicity and versatility [10,11]. Many metals and metal oxides can be deposited inside the CNTs from inorganic or organic solutions of their precursors by capillary forces. Since the filling extent depends on the surface tension of the liquid and the CNT walls wettability, the position of nanoparticles can be additionally tailored by choosing the appropriate solvent [11]. However, the homogeneous distribution of particles exclusively on interior or exterior surface of the tubes is still difficult to

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achieve, especially with CNTs with diameters less than 10 nm [12]. Consequently, in order to improve the selectivity of the process, several strategies have been developed. The most common ones imply the CNT cutting [13], resulting in enhanced particles deposition within CNT interior due to the minimization of mass transport restrictions. Another approach might be asymmetric modification (functionalization) of the concave and convex tube surfaces [14].

The water denitration is of great environmental significance since the pollution of underground water, an important source of potable water, has become a widespread concern in many countries due to excessive use of chemical fertilizers. High level of nitrate in drinking water is known to be a potential risk to human health causing various diseases. Among the current available remediation processes, catalytic denitration has an advantage compared to the other methods being an eco-friendly and economically viable process [15]. However, the main drawback of this process is the production of ammonia as the undesired product. Up to now, numerous bimetallic catalytic systems comprising of a precious metal (Pd, Pt, Rh) and a promoting transition metal (Cu, Ni, Fe, Sn, In) have been widely tested in order to establish the catalyst with enhanced performances. Among them, the Pd-Cu active phase has been emphasized in many reports as the most effective system, but still inadequate in terms of selectivity to nitrogen [16,17]. According to the accepted mechanism, bimetallic Pd-based entities are essential for the conversion of nitrate to nitrite, while the further nitrite reduction occurs solely on Pd monometallic sites [18,19].

The exploration of the catalysts in the form of carbon nanoreactors has been mainly focused on various hydrogenation and oxidation reactions. This paper is the first one dealing with the CNT-based catalyst confinement effect in water denitration reaction. The main idea behind the confinement effect is the possibility of lenient reaction conditions practice and consequent achievement of higher selectivity. In addition, the size of active metal particles in a carbon nanotube-based reactor offers advanced catalytic activity due to higher active sites dispersion. The last, but not the least, correlation of denitration reaction selectivity and active metal particle size (pointed by the tube channels confinement effect) might be important. Namely, there are few papers dealing with denitration reaction selectivity focusing on its second step structure sensitivity [20–22], however the results are diverse depending on applied active metals (Pd or Pt). Therefore, the activity and selectivity of Pd-Cu active phase placed inside the carbon nanotubes were examined in this paper, with special emphasis on nitrogen selectivity. In order to favor the filling of the tube interior, the original long multi-walled carbon nanotubes were catalytically shortened (and consequently opened) prior to the metal deposition. The confinement effect study implied a control sample test, assuming the same metal nanoparticles dispersed entirely on external surface of the same carbon nanotubes.

2. Experimental

2.1. Synthesis and functionalization of multi-walled carbon nanotubes (MWCNTs)

MWCNTs synthesis was carried out for one hour in a flow of ethylene/nitrogen mixture (1:1) at 700 °C, using an *in situ* pre-reduced 5% Fe-Co/Al₂O₃ catalyst in a home-made reactor setup that was described earlier [23,24]. The obtained raw material was boiled under reflux for 6 h in diluted NaOH and concentrated HNO₃ solutions, respectively, in order to remove the catalyst remains and functionalize the MWCNT surface. The resultant sample was collected on a filter and rinsed with distilled water until a pH neutral followed by drying at 110 °C for 24 h. The obtained long nanotubes, labeled as LMWCNTs (L = long), have been proved as free from any catalyst remains [24].

2.2. Oxidative cutting of MWCNTs

The catalytic oxidation of previously prepared LMWCNT sample was performed in the presence of Ag as a catalyst, selected based on the well-known fact that it catalyses the oxidation of hydrocarbon compounds [25]. Among the other transition metals (Au, Cu, etc.) with the same ability, Ag is the most efficient one [26,27]. The catalytic role of Ag nanoparticles in oxidative cutting has also been confirmed by the reduction of CNT oxidation temperature [28].

The nanotube sample was ultrasonically impregnated with aqueous AgNO₃ (Centrohem, Serbia) solution in order to achieve the nominal 5 wt.% Ag. The obtained suspension was further treated for 3 h at 40 °C followed by vacuum evaporation of the excess solvent. The solid residue was dried in an oven at 120 °C for 24 h. Silver nanoparticles were obtained by decomposition of AgNO₃ heated in an oven at 2 °C/min up to 300 °C in N₂ flow and maintained at the final temperature for the next 3 h. The catalytic oxidation of CNTs was carried out by switching the gas stream from N₂ to air and subsequently cooling the sample rapidly after 90 min of reaction time. The used Ag nanoparticles were removed from nanotubes by additional ultrasonic treatment in 2 M HNO₃ for 3 h at 40 °C. After filtration, washing and drying, the prepared nanotube sample was labeled as SMWCNTs (S = short).

2.3. Synthesis of Pd-Cu catalysts for water denitration

The SMWCNT sample was used for the synthesis of two bimetallic 2% Pd – 1% Cu catalysts (weight based) with metal nanoparticles deposited inside and alternatively outside of SMWCNTs. PdCl₂ (Alfa Aesar GmbH & CoKG, Germany) and Cu(NO₃)₂·3H₂O (Centrohem, Serbia) were the corresponding metal precursors and acetone or xylene were used as alternative solvents for inside and outside deposition, respectively. The applied preparation protocols were adopted from the literature with some modifications [29,30]. The filling approach is based on lower surface tension of acetone as a metals solvent, which easily fills the tube interior providing both metals within the tubes confinement. The procedure involved the ultrasonic-assisted wet coimpregnation of both precursors dissolved in acetone for 4 h, following an extended mechanical stirring for 16 h at ambient conditions. The primary removal of the solvent was performed by heating at 50 °C, followed by slow heating to 120 °C by a step of 1 °C/min and kept at this temperature for 6 h in 110 cm³/min flow of air. Prior to use, the Pd-Cu catalyst was heat treated in N₂ flow at 200 °C for 2 h and activated by reduction in H₂ flow at 200 °C for 3 h. The prepared sample was denoted as Pd-Cu_{IN}. The procedure for the deposition of metal nanoparticles on the exterior surface of short nanotubes was based on the application of xylene as a temporary blocker of MWCNT channels. This organic solvent is immiscible with the water solution of metal precursors and it prevents them from entering the nanotube channels. The procedure included mixing of nanotubes and xylene in an ultrasonic bath for 4 h at room temperature, followed by the simultaneous addition of water solutions of both metal precursors and a commercial buffer providing pH 10. After continuous stirring for 24 h, the two-layered mixture was heat treated at 80 °C until the complete evaporation of the liquid phase. The synthesized catalyst was then subjected to static drying and additionally purified by ultrasonic treatment in order to remove the buffer remains. The heat treatment and reduction steps were performed under the same conditions as for the catalyst having metals inside the nanotube channels. The obtained catalyst was denoted as Pd-Cu_{OUT}. EDS analysis was performed in order to examine the metals present in the catalyst samples, both qualitatively and quantitatively. The results of elemental analysis indicate that both catalyst samples have both metals loading close to the nominal one, *i.e.* 0.26 at.% (2.23 wt.%) and 0.24 at.% (1.23 wt.%), for Pd and Cu, respectively for the Pd-Cu_{IN} sample, and 0.25 at.% (2.15 wt.%) and 0.22 at.% (1.13 wt.%), for Pd and Cu, respectively, for the Pd-Cu_{OUT} sample.

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