

Pd nanoparticles for their application in catalysis and H₂ detection systems

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Objectives and novelty

Nowadays the use of H₂ is one of the most promising alternatives to replace fossil fuels in the energy industry. However, due to its properties, safety issues concerning H₂ generation, transport, storage and use must always be considered.

Regarding H₂ usage as a fuel, the most important method for obtaining H₂ is hydrocarbon reforming. However, the H₂ streams that are produced by this methodology contain pollutants that must be removed prior to its application in devices such as fuel cells. Fuel cells are electrochemical devices where energy is obtained from the reaction between O₂ and H₂, being water the only generated by-product. For these applications, the H₂ streams used need to be free of CO since this is a compound that poisons the electrocatalysts of the cells. For this reason, the design of active and selective catalysts is mandatory to carry out this process, which is called Preferential Oxidation of CO (PrOx CO).

Also, related to the use of H₂ in different fields, it is necessary to develop safety systems adapted to these new technologies. In this sense, H₂ is a colorless and odorless gas, highly flammable and explosive above certain concentrations (4% in air). Therefore, the development and application of H₂ sensors is mandatory when working with this gas.

The objectives of this work are the synthesis, characterization and application of novel materials for their application as catalysts for the PrOx CO reaction and also as active sensors for H₂ detection systems. The materials prepared are based on Pd nanoparticles and some Pd-based bimetallic alloys and CNTs have been used as support for the heterogeneous catalysts and also for the preparation of the gas sensors.

Results and conclusions

Regarding the Preferential Oxidation of CO reaction, different catalysts have been prepared using Pd as the active phase and materials with different properties as supports (mainly Al₂O₃, SiO₂ and CNTs). For these materials, the influence of several experimental parameters (related to the synthesis of the metal nanoparticles) over the catalytic performance has been evaluated. These parameters include the synthesis temperature, the metal precursor concentration in solution, the amount of capping agent and also the aging time of the colloid.

The experimental conditions of the synthesis of the metal nanoparticles have a great influence on the size of the nanoparticles in the final colloidal suspension. Also, the deposition of the nanoparticles on the supports brings forth a slight increase in the metal particle size in all cases. The particle size, in turn, greatly affects the performance of the nanoparticles

when tested as catalysts in the PrOx reaction, with the best results obtained for catalysts with 2.5-3.5 nm Pd particle size. The colloidal-based catalysts display a much better performance in this application than the equivalent Pd catalyst prepared by direct impregnation with the metal precursor. This difference has been attributed to the presence of a capping agent (PVP) on the surface of the metal nanoparticles in the colloid. It has been found that this capping agent interacts with the metal surface, affecting its electronic density and therefore modifying the catalytic performance, mainly increasing the selectivity with respect to that of the standard (i.e. impregnated) catalyst. Also, this electronic interaction has been found to be time-dependent and progressively disappears as the nanoparticles are kept in the colloid before their deposition on the supports. For this reason, the aging time of the nanoparticles in the colloid is a parameter that negatively affects the performance of the catalysts when applied in this particular reaction. The heterogeneous catalysts prepared from recently synthesized Pd colloids perform very efficiently for the PrOx CO reaction, with complete CO removal from the gas stream without deactivation during several hours and also in the presence of CO₂ and H₂O.

Together with powder catalysts, the active phase has been also incorporated within the confined dimensions of silica capillaries, in order to prepare capillary microreactors for the same application. The use of microreactors has the advantage of the reduced dimensions of the systems (which makes them suitable for on-board applications and small devices) and also the inherent higher safety and better performance of the devices, as compared to conventional powder catalysts. In these microreactors, the active phase has been deposited as a thin layer on the inner walls of the channels, and also as a highly porous monolithic structure within the capillary. In both cases, a continuous deposit of the active phase has been obtained throughout the length of the capillary (that varies from 20 cm to 2 m), with a homogeneous distribution of the metal phase on the supports in both configurations. Concerning the catalytic behaviour, a very important influence of the capillary length has been observed, as expected, since the modification of the residence time of the gases in the reactor affects both the activity and selectivity of the active phase. As a general trend, an increase in the residence time reflects in an increase in the CO conversion but is, in all cases, associated to a decrease in selectivity. Also, the microreactors where the active phase has been deposited as a filling present a much better performance than those where the catalysts was deposited as a coating on the channels. This is due to the gas-solid interaction being favored in the case where the porous filling structure is used. From the comparison of the catalytic activity of the microreactors with the

same active phases tested as powder catalysts, the results indicate that the catalysts behave more efficiently when incorporated in the channels of the microreactors. This is due to the fact that mass and heat transfer processes are favored in the reduced dimensions of the microchannels. As a conclusion of these types of materials, the microreactors where the catalyst is incorporated as thin coating are not very appropriate for the PrOx CO application. However, when the catalyst is incorporated as a filling within the structure, the gas-solid interact is much better and the microreactors perform successfully for this application. The catalysts in this configuration display selectivity values close to 50% under the experimental conditions used and these results, together with their high flexibility, stability and easy handling make them very good candidates for small-scale H₂ purification applications. In addition, these microreactors have shown an outstanding performance when tested for CO removal in H₂-free gas streams, opening a new field of application for these materials.

In this work, different materials have been prepared for the development of H₂ detection systems. These systems are based on metal nanoparticles (with different metal compositions) deposited on Multi-Wall Carbon Nanotubes (MWNTs) and the devices developed have proven to perform very successfully for the intended application.

The preparation of the sensors, based on drop-casting of the different materials directly from a previously prepared suspension, is a very simple and reproducible methodology for the synthesis of this kind of materials. The composition of the MWNTs suspension has a very important influence over the performance of the sensors, with the best results obtained for the sensors prepared from a MWNTs suspension in H₂O and with the addition of some surfactants. Also, both the metal loading and nanoparticles composition have a great influence on the performance of the devices. The best results have been obtained for the samples with higher metal loading and when pure Pd nanoparticles were used. The incorporation of Ni in the metallic structure did not improve in any case the performance of the sensors. The devices prepared are active for the detection of H₂ in the concentration interval from 0.2 - 5% vol. H₂ and with low response and recovery times (20 s and 140 s, respectively). Finally, for these samples, the presence of O₂ has been found to be mandatory for the reversible behaviour of the sensors. Also, it has been established that the H₂ detection mechanism is related to the nanoparticles increasing in size when they are exposed to the analyte gas and a modification of the resistance of the system when this process takes place. Evidences of other processes occurring at the same time on the metal surfaces, such as H₂O formation, have been also observed.

Related Publications

- [¹] I. Miguel-García, Á. Berenguer-Murcia, D. Cazorla-Amorós. *Applied Catalysis B* 98 (2010) 161-170.
- [²] I. Miguel-García, Á. Berenguer-Murcia, T. García, D. Cazorla-Amorós. *Catalysis Today* 187 (2012) 2-9.
- [³] J. García-Aguilar, I. Miguel-García, Á. Berenguer-Murcia, D. Cazorla-Amorós. *Carbon*, 66 (2014) 599-611.

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<http://rua.ua.es/dspace/handle/10045/36384>