Thesis Review. Synthesis of metallic and zeolite nanoparticles for catalysis and gas separation.

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Objectives and novelty

The object of the presented PhD Thesis is, on the one hand the development of catalytic systems based on metallic nanoparticles supported on a broad variety of supports, including nanostructured materials, which present good catalytic properties both in terms of activity and selectivity. With the aim to design new catalysts the synthetic procedures for both nanoparticles and nanostructured materials will be integrated to give rise to a new family of catalysts. These will be employed in a selective hydrogenation reaction in order to determine their catalytic behavior. The second objective of this PhD Thesis is to synthesize thin zeolite films on carbon materials for their use in the separation of gases with similar sizes for processes such as air or hydrogen purification. From 2000, the Carbon Materials and Environment research group (CME) of the Inorganic Chemistry Department at the University of Alicante has carried out an intensive study on the synthesis of zeolite membranes and the application of nanoparticles in catalysis.

As with the objectives, the novelty of this PhD Thesis is two-fold: first, the combined synthesis of a nanostructured material in the presence of metallic nanoparticles yielded a new series of materials which are synthesized by a simple one-pot route. These new composites have been successfully applied in selective hydrogenations with outstanding results. Secondly, the development of carbon-supported zeolite membranes using the seeding procedure known as electrophoretic deposition employing colloidal suspensions of nanocrystalline zeolite seeds has yielded composites that possess good permeation properties combined with moderate O_2/N_2 separation factors.

Results

This PhD Thesis represents a landmark in catalysts preparation for the development of highly active, selective and robust systems. The combination of a nanostructured material synthesis with metallic nanoparticles incorporated in the same synthesis vessel yielded materials with a markedly different porous structure and particle size distribution (Figure 1). This novel methodology called “simultaneous synthesis” not only simplifies the preparation of heterogeneous catalysts, but also broadens the scope of applicability of both mesoporous materials and metallic nanoparticles. The synthesized colloids have been also deposited on a large selection of inorganic supports, from carbon materials with different structures and porous textures, to ceramics with different chemical nature.

The prepared materials were screened for their catalytic properties in the semihydrogenation (i.e. selective hydrogenation) of phenylacetylene, yielding very interesting results:

- The TurnOver Frequency (TOF) of the Pd nanoparticles supported on “classical” inorganic materials (i.e. alumina) was not significantly different from the value found for the homogenous catalysts.
- Carbon materials are good supports for Pd nanoparticles, although samples with a low external surface area present significant agglomeration of the catalyst.
- Mesoporous materials do not differ markedly from microporous inorganic oxides such as zeolite or commercial alumina in the semihydrogenation of phenylacetylene.
- The prepared catalysts are stable for 5 catalytic cycles, thus showing their robustness.
- Phenylacetylene conversion and selectivity towards styrene values ranged from 90 to 98%, clearly showing the potential of the prepared systems.
- TOF values for the samples prepared following the “simultaneous synthesis” protocol were the highest for all the catalyst series, indicating that the chosen reaction may be structure sensitive.

In this PhD Thesis the preparation of zeolite membranes on carbon supports by seeding of the supports by electrochemical methods based on the electrical/conductive properties of carbon has been analysed. In this manner, by using the carbon support as an electrode in an electrophoresis process, we have managed to deposit a coating of colloidal zeolite crystals on the carbon starting material, in such a way that the process that takes place is an ElectroPhoretic Deposition (EPD). These crystals act as *seeds* or crystallization nuclei so that the synthesis of continuous layers of zeolite on our support by hydrothermal treatment is significantly improved. Hydrothermal synthesis is performed on the resulting materials giving rise to a continuous

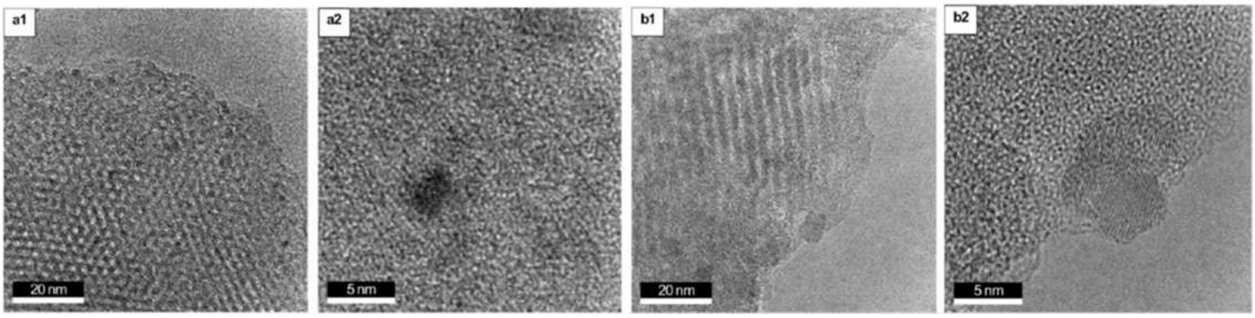

Figure 1. HR-TEM micrographs of (a) Pd nanoparticles impregnated on a nanostructured MCM-41 support and (b) Pd nanoparticles prepared on MCM-41 by “simultaneous synthesis”.

zeolite layer covering to totality of the surface of the carbon support. The resulting composites have been tested for their permeation properties in a Wicke-Kallenbach cell (Figure 2), showing both high permeation fluxes and good O_2/N_2 separation factors.

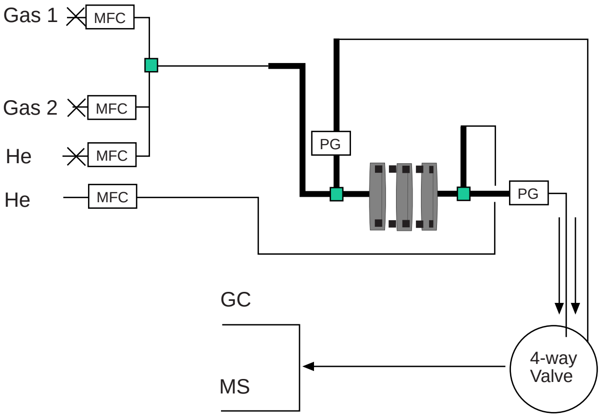

Figure 2. Scheme of a Wicke-Kallenbach cell. MFC: Mass Flow Controller; PG: Pressure Gauge; GC: Gas Chromatograph; MS: Mass Spectrometer.

Conclusions

A novel methodology has been developed for the direct incorporation of metallic nanoparticles inside mesoporous matrices, which we have named “simultaneous synthesis”. The prepared catalysts have shown excellent activity and selectivity in a selective hydrogenation reaction (phenylacetylene semihydrogenation). Catalysts prepared following the simultaneous synthesis protocol showed the highest activity values (expressed as TOF) for all the analyzed samples, which clearly reveals the importance of not only the support, but also the catalyst preparation method.

Focusing on the improvement of membrane characteristics, from the preparation of the first membrane reported in our research group, our interest focused on the improvement of the preparation of these materials, applying the secondary growth methodology, which consists on the seeding of the support with zeolite crystalline seeds prior to hydrothermal treatment. Nevertheless, the way this seeding was applied was by the electrophoretic deposition of colloidal LTA (i.e. zeolite A) crystals, thus not only opening new possibilities with regards to the preparation of membranes, but also making it possible to better control the conditions under which it was possible to grow continuous layers of zeolite on carbon discs. Furthermore, when the carbon support is seeded prior to hydrothermal treatment, the oxidation of the support is no longer a critical issue to obtain a zeolite membrane, having the composites good membrane properties.

Related publications

[1] Dominguez-Dominguez S, Berenguer-Murcia A, Cazorla-Amoros D, Linares-Solano A, Semihydrogenation of phenylacetylene catalyzed by metallic nanoparticles containing noble metals, Journal of Catalysis, 2006; 243(1), 74-81.

[2] Dominguez-Dominguez S, Arias-Pardilla J, Berenguer-Murcia Á, Morallón E, Cazorla-Amoros D, Electrochemical deposition of platinum nanoparticles on different carbon supports and conducting polymers, Journal of Applied Electrochemistry, 2008; 38(2), 259-268.

[3] Dominguez-Dominguez S, Berenguer-Murcia A, Pradhan BK, Linares-Solano A, Cazorla-Amoros D, Semihydrogenation of phenylacetylene catalyzed by palladium nanoparticles supported on carbon materials, Journal of Physical Chemistry C, 2008; 112(10), 3827-3834.

[4] Dominguez-Dominguez S, Berenguer-Murcia A, Linares-Solano A, Cazorla-Amoros D, Inorganic materials as supports for palladium nanoparticles: Application in the semi-hydrogenation of phenylacetylene, Journal of Catalysis, 2008; 257(1), 87-95.

[5] Dominguez-Dominguez S, Berenguer-Murcia A, Morallón E, Linares-Solano A, Cazorla-Amoros D, Zeolite LTA/carbon membranes for air separation, Microporous and Mesoporous Materials, 2008; 115(1-2), 51-60.

Full Thesis can be downloaded from http://hdl.handle.net/10045/24115