

EFFECT OF THE SUPPORT ON THE CATALYTIC ACTIVITY OF PALLADIUM NANOPARTICLES: CARBON NANOTUBES VERSUS ALUMINA

Izaskun Miguel-García, Ángel Berenguer-Murcia and Diego Cazorla-Amorós

Department of Inorganic Chemistry, University of Alicante, Ap.99, E-03080, Alicante, Spain

Introduction

The design of catalysts for specific applications requires a wide knowledge of the parameters affecting their behaviour. Among these parameters, the influence of the active phase (usually metallic) and the support are of paramount importance [1]. Recently, in the field of catalysis with nanoparticles, it has been demonstrated that the capping agent used in the nanoparticles synthesis might present an electronic interaction with the support that can affect the catalytic activity of the materials [2]. In this work, the effect of the support has been analyzed in the preferential oxidation of CO (PrOx) reaction, catalyzed by palladium nanoparticles. This is an important reaction, used in the industry for the purification of the H₂ streams that feed the fuel cells [3].

Experimental

For this work, several Pd-nanoparticles based catalysts have been prepared by the wet-impregnation method, using alumina and carbon nanotubes (CNT) as supports. The nanoparticles were synthesized by the reduction-by-solvent method, by dissolving the appropriate amount of precursor (Pd(ac)₂) in ethylene glycol, and reducing it under inert atmosphere. The synthesis is carried out in the presence of a capping agent (PVP, polyvinylpyrrolidone, 40K) that prevents aggregation of the nanoparticles [4]. The purified nanoparticles are then deposited onto the catalytic supports. For comparison purposes, a standard catalyst was prepared by the conventional impregnation method [5].

The nanoparticles and catalysts synthesized have been characterized by several techniques, including ICP and TEM to determine the loading and dispersion of the catalysts.

The catalysts have been tested in the PrOx reaction. Prior to reaction, the samples were reduced in 10% H₂/He flow, for 2 hours at 200°C. The gas composition fed to the reactor was 2% CO, 2% O₂, 30% H₂ in He. CO conversion and selectivity were analyzed under non-isothermal conditions, up to 200°C.

Results and Discussion

Stable colloidal palladium nanoparticles have been synthesized by the reduction-by-solvent method, and deposited onto alumina and CNT. Figure 1 shows the TEM images of the as-synthesized catalysts, and the precursor colloidal suspension. It includes the Pd nanoparticles-based catalysts (samples Pd/CNT and Pd/Al₂O₃) and the Pd catalyst prepared by classical impregnation method.

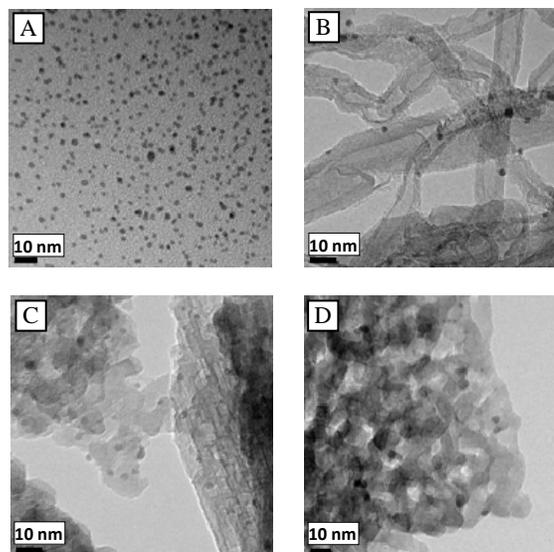


Fig. 1 TEM images of the following samples: (a) colloidal Pd nanoparticles, and catalysts (b)Pd/CNT, (c)Pd/Al₂O₃, (d)Pd/Al₂O₃-Impregnated.

Table 1 shows the characterization results of the catalysts prepared for this work, and the colloidal Pd nanoparticles. It can be observed that the nanoparticles average size slightly increases from the colloid to the final catalysts. Comparing the Pd-particles size among the different catalysts, the average size is smaller in the case of the colloidal catalysts than in the impregnated one, showing a very narrow size distribution. There are no significant differences among the colloidal catalysts synthesized, both showing similar loading and dispersion.

Table 1. Results of the colloidal nanoparticles and catalysts characterization. The loading has been determined by ICP, and the size (d,nm) and Dispersion (D,%) of the nanoparticles has been estimated by TEM micrographs.

	% Pd	d (nm)	D (%)
Pd/CNT	0.55	2.6 ± 0.6	34
Pd/Al₂O₃	0.40	2.8 ± 0.6	32
Impregnation	0.52	3.9 ± 1.5	23
Pd Colloid	x	2.2 ± 0.4	x

Figure 2 shows the results of the catalytic activity of the catalysts synthesized for this work, where CO conversion and selectivity are represented as a function of temperature. As it can be observed, the impregnated catalyst shows moderate activity, although its selectivity is very low, barely reaching 10%. With this low value of selectivity, CO oxidation is not a viable process to carry out with this catalyst. However, both colloidal catalysts show better selectivity than the impregnated

sample. These samples exhibit very high selectivity for the process under study, with values above 50%. Interestingly, sample Pd/CNT shows much higher activity than the alumina supported sample. For the carbon supported catalyst, the maximum CO conversion is achieved at a temperature of 130°C, whereas the alumina supported catalyst reaches the maximum CO conversion around 200°C. T_{50} , defined as the temperature at which CO conversion reached 50% for each sample, is then ~50°C lower for the carbon supported catalyst. This is an important parameter, since these catalysts are designed to operate at the exit of a water-gas-shift reactor, and must work within the temperature window of 80-200°C. Therefore, both colloidal catalysts are highly active and selective for the reaction under study.

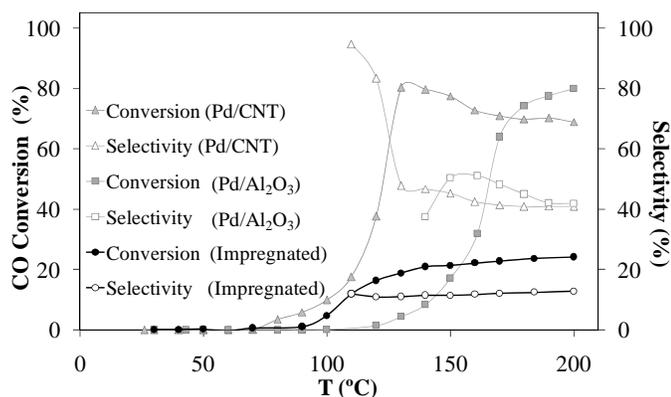


Fig. 2 Results of the catalytic activity of the samples synthesized for this work. Solid symbols represent CO conversion, and hollow symbols represent selectivity to CO oxidation. $GHSV = 30000h^{-1}$.

However, there are important differences in the catalytic behaviour of these two catalysts that cannot be explained in terms of the active phase. These differences might be due to the different electronic interaction of the PVP surrounding the nanoparticles and the supports used in each case. Being the PVP a pyrrolidone substituted ring, its interaction with the support would be stronger with the carbon nanotubes than with the alumina, due to the presence of electronic π -interactions. The different electronic environment of the Pd particles, depending on the support, would be therefore responsible for the different catalytic behaviour observed.

Conclusions

In this work palladium nanoparticles have been synthesized by the reduction-by-solvent method, displaying a very narrow distribution in the particles size. The catalysts synthesized from these nanoparticles have shown high selectivity towards CO oxidation in the PrOx reaction, although differences in the activity have been observed depending on the nature of the catalytic support. The results obtained with the CNT as support are remarkable on terms of

both activity and selectivity. The electronic interactions between the PVP surrounding the nanoparticles and the support might be responsible for the different catalytic behaviour reported.

Acknowledgments. The authors would like to thank the Spanish Ministerio de Ciencia e Innovación and Plan E (project CTQ2009-10813) and the Generalitat Valenciana (project Prometeo/2009/047) the financial support for this work.

References

- [1] Ertl G, Knözinger H, Weitkamp J. Handbook of heterogeneous catalysis. Wiley-VCH; 1997.
- [2] Park JY, Aliaga C, Renzas JR, Lee H, Somorjai GA. The role of organic capping layers of platinum nanoparticles in catalytic activity of CO oxidation. *Catal Lett* 2009;129:1-6.
- [3] Farrauto R, Hwang S, Shore L, Ruettinger W, Lampert J, Giroux T, Liu Y, Ilinich O. New material needs for hydrocarbon fuel processing: generating hydrogen for the PEM fuel cell. *Annu Rev Mater Res* 2003;33:1-27.
- [4] Miguel-García I, Berenguer-Murcia Á, Cazorla-Amorós D. Preferential oxidation of CO catalyzed by supported polymer-protected palladium-based nanoparticles. *Appl Catal B*. Submitted.
- [5] Son IH, Shamsuzzoha M, Lane AM. Promotion of Pt/ γ - Al_2O_3 by new pretreatment for low-temperature preferential oxidation of CO in H_2 for PEM Fuel Cells. *J Catal* 2002;210:460-465.