

Seed-Mediated Synthesis of Nanostructured Supported Pd Catalysts and Applications in Selective Hydrogenation Reactions

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Introduction

The tremendous development of nanomaterials offers the opportunity to obtain new “tools” with interesting properties in various domains of application including sensors and catalysis. In this respect, the synthesis of well-defined nanoparticles (NPs) with controlled morphology provides a way to modify the proportion of different crystallographic planes and to tune the activity and/or the selectivity for surface-structure sensitive catalytic reactions. This shape-controlled synthesis can be achieved through a “bottom-up” approach using colloidal techniques with structuring agents. These agents (surfactants or polymers) selectively stabilize facets, thus restricting the crystal growth along certain crystallographic directions. This leads to nano-objects with well-defined morphology.

Different catalytic applications (mainly selective hydrogenations or oxidations) have been considered using such nanostructured metallic catalysts and results showed that selective catalysts can be obtained [1]. Up to now, all these studies used polymers to selectively control the crystal growth. Polymers are however difficult to remove from the surface of the NPs before using them in catalytic reactions. Their presence could modify the selectivity results and prevents any definite conclusion on structure-reactivity relationships between crystallographic planes exposed and catalytic properties. We then developed synthesis techniques producing well-defined Pd NPs using easily removable surfactants instead of polymers [2]. The Pd nanostructured catalysts were tested in the selective hydrogenation of buta-1,3-diene (liquid and gas phase [3]) and of cinnamaldehyde. Results clearly established that the preferential exposition of crystallographic planes allowed tuning the catalyst selectivity in a large extent.

Materials and Methods

In a first step, small Pd NPs (3–4 nm in diameter) were synthesized using Na_2PdCl_4 , cetyltrimethylammonium bromide (CTAB), and NaBH_4 as a strong reducing agent. The as-formed Pd nanoparticles were then used as “seeds” in a second step to control nucleation. The “growth” solution was therefore prepared using Na_2PdCl_4 , CTAB, and a weak reducing agent, L-ascorbic acid. The choice of metallic precursor, surfactant, and seed concentration directly influences the final morphology. Deposition of the NPs onto $\alpha\text{-Al}_2\text{O}_3$ was performed using classical impregnation techniques (incipient wetness or in excess). Liquid-phase hydrogenation of buta-1,3-diene was carried out at 20°C under 20 bars of H_2 . Complementary information was also acquired in gas-phase conditions using a surface-science static-reactor setup which allowed varying the initial partial pressures of H_2 and diene. Hydrogenation of cinnamaldehyde was performed at 50°C under 10 bars of H_2 . Catalysts were characterized using (HR)TEM, SAED and XPS.

Results and Discussion

Seed-mediated synthesis of Pd NPs selectively leads to the formation of well-defined Pd nano-objects whose proportions can be controlled through the tuning of the nucleation and growth processes. The different nano-objects obtained include: nanorods presenting (100) lateral facets and (111) extremities (Fig. 1A), nanocubes (only (100) facets), bipyramids (only (100) facets), or prisms (only (111) facets). The proportion of the different crystallographic planes was then modified in order to evaluate their influence on selective hydrogenation properties. Butadiene hydrogenation experiments reveal that the increasing proportion of (111) planes on well-defined Pd NPs leads to highly efficient catalysts for the formation of butenes without further hydrogenation to butane (Fig. 1B).

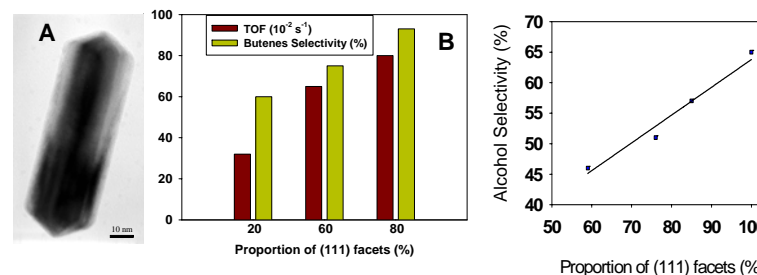


Figure 1. A) Example of a Pd nanorod exposing mainly (100) facets; B) Turnover frequency and butene selectivity versus fraction of (111) facets, in the gas-phase hydrogenation of buta-1,3-diene (298 K, P_{H_2} = 5 Torr, P_{diene} = 0.5 Torr at $t=0$).

Figure 2. Change in alcohol selectivity with the increasing proportion of (111) facets in the liquid-phase hydrogenation of cinnamaldehyde (50°C, 10 bar H_2).

In the hydrogenation of cinnamaldehyde, a complete reversal of selectivity is observed (from the saturated aldehyde, hydrocinnamaldehyde, to the saturated alcohol) with increasing proportion of (111) facets (Fig. 2). Moreover, very high turnover frequencies are obtained as compared to a commercial Pd/ Al_2O_3 catalyst ($\text{TOF} = 2 \text{ s}^{-1}$).

Significance

Shape-controlled Pd nanoparticles preferentially expose specific crystallographic facets unlike classical isotropic catalysts. These supported particles are highly selective hydrogenation catalysts. This approach brings (or confirms) mechanistic information on structure sensitivity under realistic experimental conditions.

References

- Chimentao, R.J., Kirm, I., Medina, F., Rodriguez, X., Cesteros, Y., Salagre, P., and Sueiras, J.E *Chem. Comm.* 246 (2004).
- Berhault, G., Bausach, M., Bisson, L., Becerra, L., Thomazeau, C., and Uzio, D. *J. Phys. Chem. C* 111, 5915 (2007).
- Piccolo, L., Valcarcel, A., Bausach, M., Thomazeau, C., Uzio, D., and Berhault, G., *Phys. Chem. Chem. Phys.* 10, 5504 (2008).