

# Selective hydrogenation of the C=O group in unsaturated aldehydes by Pd-based catalytic systems

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## Introduction

Selective hydrogenation of organic substrates, containing different functional groups, is a key reaction in chemistry. In particular, hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols is of outmost importance in fine chemicals and perfumery industry.

Transition metals, such as Ni, Pt, Ru and Rh, supported on carbon or inorganic carriers and opportunely promoted, are able to hydrogenate the C=O group, giving unsaturated alcohols with a good selectivity [1, 2]. By contrast, palladium systems catalyze almost exclusively hydrogenation of the C=C bond, affording saturated aldehydes. The minor electrostatic repulsion between the Pd surface and the C=C bond, due to a significantly reduced d-band width compared with other metals, favoring the substrate adsorption and hydrogenation via the C=C bond, was proposed to be the key factor for the intrinsic low selectivity towards unsaturated alcohols of palladium [3].

Recently, we have focused our attention on a new route planned to modify the Pd reactivity towards C=O hydrogenation in unsaturated aldehydes [4]. In this work, results obtained with supported Pd catalytic systems, prepared through impregnation or co-precipitation and by using different supports, dopants and activation procedures, are reported.

## Materials and Methods

Hydrogenation of campholenic aldehyde was carried out in liquid phase in a five-necked flask, equipped with a reflux condenser at constant temperature ( $343 \pm 0.5$  K), in cyclohexane as solvent and under H<sub>2</sub> flow (50 cc/min) at atmospheric pressure. Pd/MeO<sub>x</sub> (MeO<sub>x</sub> = SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>) catalysts were prepared by the wetness impregnation (series I) and the co-precipitation method (series CP). A characterization of the structural and redox properties of all the catalysts by transmission electron microscopy (TEM), X-ray diffraction (XRD) and temperature programmed reduction (TPR) was performed.

## Results and Discussion

Results of the kinetic tests in hydrogenation of campholenic aldehyde, chosen as a model substrate, show that products distribution on Pd/MeO<sub>x</sub> catalysts strongly depends on the nature of the support, preparation method, activation procedure and dopants (Fig. 1). The highest selectivity value to the desired unsaturated alcohol naturanol is registered on the Pd/Co<sub>3</sub>O<sub>4</sub> catalyst prepared by co-impregnation. On this catalyst a maximum yield to the unsaturated alcohol > 85 % is obtained.

Catalytic and characterization data suggest that a high interaction degree between Pd and supports and/or dopants play a key role to obtain high selectivity values through formation of new surface (bimetallic) sites, serving as adsorption centers for the carbonyl group. Therefore, the resulting modification of the noble metal electron properties changes the interaction of surface Pd atoms with adsorbed reactant species.

Characterization results evidence also that a geometric effect could be an additional factor contributing to the modification of the Pd reactivity towards the C=O hydrogenation. In fact, the substrate molecule approach to the active surface sites is indeed fundamental, and conditions disfavouring the interaction with the more sterically hindered C=C group leads consequently to a higher selectivity towards C=O hydrogenation.

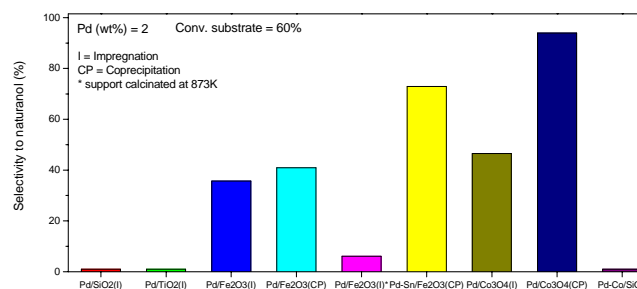


Figure 1. Selectivity to naturanol on different Pd catalysts.

## Significance

Naturanol is a valuable intermediate for perfumes and flavors. Conventional supported Pd catalysts are not selective towards the unsaturated alcohol. The search for Pd catalysts having high selectivity in the selective hydrogenation of the carbonyl group in unsaturated aldehydes is therefore of great interest both for scientific and industrial reasons. Optimizing the preparation of different Pd/MeO<sub>x</sub> catalysts, we were able to develop Pd catalysts with un-precedent high selectivity and yield to naturanol (> 85%).

## References

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