

Supported platinum catalysts prepared by photochemical deposition

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Photochemical deposition of noble metals in different supports is gaining importance because of its simplicity and advantages. Its main advantage is the ability of spreading very effectively the metal throughout the support, thus leading to very high dispersions, resulting in higher molecular control, with a positive effect on both activity and selectivity. This type of catalysts prepared by this and other methods are currently being used in industrial preparation of fine chemicals. A common synthetic route in these processes is the selective catalytic hydrogenation of organic substrates containing unsaturated functional groups, like in cinnamaldehyde.

In the present study, hydrogenation catalysts prepared by photochemical deposition are compared against the usual incipient wetness catalysts. The nature of the support was also investigated as MWNT were compared against TiO₂. Catalyst loads are also varied in order to achieve the desired conversion and selectivity.

Pt catalysts supported on titania (1 and 5%wt) and on MWNT (1%wt Pt) were prepared by the photochemical deposition method. The metals were dispersed on the surface by liquid phase photodeposition of dihydrogen hexachloroplatinate (IV). The procedure employed for the deposition was adapted from that described in the literature (Zhang, *et al*). A catalyst with 5% wt Pt loading prepared by incipient wetness over MWNT (5Pt/MWNT-623) and a commercial 1% wt Pt supported in charcoal (1Pt/C, Johnson Matthey, Charcoal type 18 powder) were used in hydrogenation of cinnamaldehyde in a well-stirred stainless steel reactor. The reaction mixture contained heptane (solvent), cinnamaldehyde, decane (as an internal standard for gas chromatography) and the catalyst. The temperature was set at 363K and the reaction started by feeding the reactor with hydrogen to a 10bar pressure. Small aliquots of the reaction mixture were taken throughout the reaction to perform quantitative analysis (conversion and product selectivity). The analysis was performed in a GC DANI 1000, equipped with a WCOT Fused Silica column.

Table 1 – Initial reaction rates (mmol g_{Pt}⁻¹ min⁻¹), cinnamyl alcohol selectivity (%) and oxidation states of Pt obtained by XPS.

Catalyst	r _{CNAL,0} (mmol g _{Pt} ⁻¹ min ⁻¹)	S _{CNOL} (%)	Pt ⁽⁰⁾ (%)	Pt ^(II) (%)
1Pt/MWNT-773	10.6	43.6	54	47
1Pt/TiO ₂ -773	7.1	53.5	59	41
5Pt/TiO ₂ -773	2.5	67.3	92	8
5Pt/MWNT-623	8.4	43.1	52	48
1Pt/C	23.8	6.1	-	-

There is a visible correlation between the selectivity and the fraction of metallic platinum at the surface of the catalyst. The photodeposition method is able to produce active catalytic materials for selective hydrogenation of cinnamaldehyde. Metallic dispersion and particle size are currently being determined in order to establish more specific relations between the preparation method and the performance of the catalysts.

References

Zhang, Z. B., Wang, C. C., Zakaria, R., Ying, J. Y. (1998). Role of particle size in nanocrystalline TiO₂-based photocatalysts. *Journal of Physical Chemistry B*, 102(52), 10871-10878.