

Novel Nanocatalysts on the Base of Ultra Thin Polyelectrolyte Layers in Selective Hydrogenation of Acetylenic Alcohols

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Introduction

Nanocomposites containing metal nanoparticles are widely developed to replace regular catalysts for many organic reactions. Catalysts on the base of metal nanoparticles have large surface area-to-volume ratio of the metal. It allows utilizing effectively the expensive metals and providing the higher activity and selectivity compared to the traditional catalysts. However, without a suitable support the metal nanoparticles aggregate reducing the surface area and restricting the control over the particle size [1]. Both natural and synthetic polyelectrolytes (PE) can be used for nanoparticles stabilization in ultra thin polymeric layers.

This study is devoted to the investigation of the reaction of selective hydrogenation of acetylenic alcohols using palladium nanoparticles stabilized in ultra thin layers of polydiallyldimethyl ammonium chloride (PDADMAC), poly(sodium 4-styrenesulfonate) (PSS) and chitosan (CS) deposited on alumina. The reaction of triple bond hydrogenation is one of the most widely used reactions in fine chemistry. Here the selective hydrogenation of dehydrolinalool (DHL) to linalool (LN) (which is used as a composite of many cosmetics and perfumes and as an intermediate in synthesis of vitamins (A, E, K)) will be discussed in more detail. The scheme of the reaction is shown in Figure 1.

Materials and Methods

PDADMAC (Mw 400 000 – 500 000), PSS (Mw 70,000) and CS low molecular weight (viscosity 20-200 cP, 1 % in 1% acetic acid, Brookfield, 75-85% deacetylation) were purchased from Sigma-Aldrich. DHL (99%) was supplied by pharmaceutical company PC "Belgorodvitaminy" (Belgorod, Russia). Solvent – propanol-2 (99.5%) and hydrazine (98%) were purchased from Aldrich. Water was deionized before use.

Following catalysts were synthesized: (i) Pd-PDADMAC (PDADMAC - 5 g/l), (ii) Pd-CS (CS), (iii) Pd-PSC-1 (PSS – 5 g/l, CS – 5 g/l), (iv) Pd-PSC-2 (PSS – 1 g/l, CS – 5 g/l), (v) Pd-PSC-3 (PSS – 1 g/l, CS – 1 g/l), (vi) Pd-PSC-4 (PSS – 0.5 g/l, CS – 5 g/l), (vii) Pd-PSC-5 (PSS – 0.5 g/l, CS – 0.5 g/l). For the preparation of the above mentioned catalysts two methods were used: monolayered deposition (Pd-PDADMAC and Pd-CS) and "layer-by-layer" deposition (Pd-PSC-1,2,3,4,5). During the preparation of multilayered systems the PSS was used as a polyanion for isolation of palladium nanoparticles containing layers of polycation (CS).

Catalytic experiments were carried out in the isothermal glass batch reactor at ambient pressure. The influence of the PE concentrations, substrate/catalyst amount ratio, reaction temperature was investigated. Physical-chemical investigations of the catalysts, substrate and product were conducted via GC, TEM, XPS and BET.

Results and Discussion

It was found that during Pd-CS preparation by monolayered deposition method the recharge of alumina surface can't provide strong attaching of CS, so the part of CS is washed out from the surface decreasing the activity of the catalyst. The use of "layer-by-layer" preparation method allows creating favorable conditions for CS deposition due to the existence of negative charged PSS on alumina surface. The optimal amounts of PSS and CS providing the higher stability of palladium nanoparticles were determined. It was found that the optimal content of PSS should exceed 1 g/l. If PSS content lower than 1 g/l there are sites on alumina surface, which doesn't covered with PE (Pd-PSC-5). Catalytic activity of this catalyst was found to decrease during repeated catalytic cycles, which is due to the low stability of the metal nanoparticles. Besides it was determined that if CS content exceed the PSS content (Pd-PSC-2 and Pd-PSC-4) some part of CS remains free and the catalysts change their activity during repeated catalytic cycles. However if PSS to CS ratio was equal to one, the catalysts revealed the highest stability and didn't loose their activity. Pd-PSC-3 was found to have the highest stability and selectivity (95%). Pd-PDADMAC showed the selectivity of 98% at 98.3% of DHL conversion.

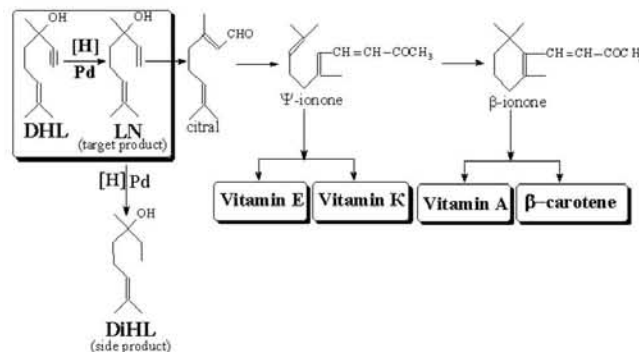


Figure 1. The scheme of selective hydrogenation of DHL to LN.

Significance

New catalysts on the base of PE were synthesized. Multilayered deposition was shown to provide higher stability of metal nanoparticles than the monolayered one.

References

1. Kidambi, S., Bruening, M.L. *Chem. Mater.* 17, 301 (2005).