Hydrogenation of acetylene alcohols with novel Pd colloidal catalysts prepared in block copolymers micelles

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Abstract

Hydrogenation of the triple bond of acetylene alcohols to the double one of olefin alcohols (linalool, isophytol) was studied with Pd colloids prepared in polystyrene-poly-4-vinylpyridine micelles in toluene and deposited on Al_2O_3. The high selectivity (99.8% for linalool and 99.5% for isophytol) of such catalyst is explained by durable modification of the Pd nanoparticle surface with 4-vinylpyridine units. The activity of the Pd catalyst studied is determined by high reactivity of small Pd nanoparticles. Maximum relative rate was found to be in methanol, but the highest selectivity was achieved in toluene because the latter is a selective solvent for polystyrene-poly-4-vinylpyridine micelles and provides the better accessibility of reactive sites. © 1999 Elsevier Science B.V. All rights reserved.

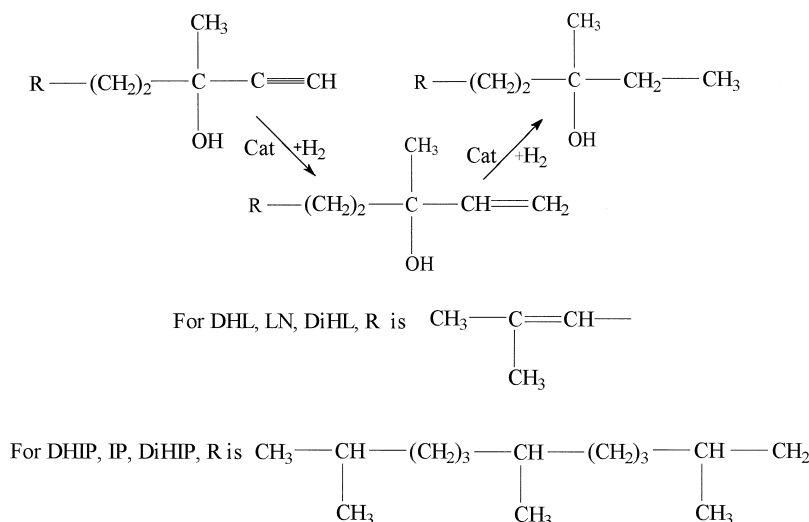*Keywords:* Acetylene alcohols; Selective hydrogenation; Pd colloids; Polymer micelles

1. Introduction

Polymeric catalysts, both organometallic polymers and polymer-protected, colloidal noble metals are of great interest since they are very promising for many catalytic applications [1–3]. Pd-, Rh-, and Pt-containing polymer systems have been studied as catalysts for olefin hydrogenation [4,5], but no paper is related to polymer catalysts dealing with hydrogenation of long chain acetylene alcohols which are intermediate products in the preparation of some important vitamins and fragrant substances.

Linalool (LN, 3,7-dimethyl-octadiene-1,6-ol-3), the product of selective hydrogenation of dehydrolinalool (DHL, 3,7-dimethyl-octaene-6-yne-1-ol-3) is a fragrant substance of terpenic series. This is also a part of many cosmetic preparations and a number of scent compositions. Isophytol (IP, 3,7,11,15-tetramethyl-hexadecene-1-ol-3), the product of dehydroisophytol (DHIP, 3,7,11,15-tetramethylhexadecyne-1-ol-3) selective hydrogenation, is the intermediate substance in vitamins E and A synthesis. The selective hydrogenation of the triple bond to a double one is one of the steps of LN and IP syntheses (see Scheme 1). When hydrogenation goes on non-selectively, LN transforms into dihydrolinalool (DiHL, 2,6-dimethyl-octen-2-ol-6), while IP converts into dihydroisophytol (DiHIP), which are possible side products of these reactions.

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Scheme 1. Acetylene alcohols hydrogenation processes: (a) DHL, LN, DiHL; (b) DHIP, IP, DiHIP.

Selective hydrogenation of acetylene compounds to olefins (including, alcohols) has mainly been carried out with supported Pd catalysts, such as Pd/C, Pd/SiO$_2$, Pd/CaCO$_3$, Pd/Al$_2$O$_3$ and others, modified with organic (for example, pyridine, quinoline) and inorganic (Zn, Cd, Pb and other salts) substances [6–12]. Such a modification allowed to increase the selectivity of hydrogenation, but resulted in polluting the end products with the modifiers.

Another imperfection of this way of modification was poor stability of such catalysts: modifiers adsorbed on the catalyst surface often left the surface during usage, thus decreasing the catalyst selectivity. Previously we have developed for the first time the synthesis of Pd-containing polymers derived from polystyrene–polybutadiene triblock copolymers (SBS) and bis(acetonitrile) palladium chloride (SBS-Pd) [13,14]. These polymers deposited on Al$_2$O$_3$ seemed to be catalytically active in hydrogenation of dehydrolinalool [14] and allowed to reach 98.7% selectivity without any modification. Recently a novel type of Pd-polymer catalysts was elaborated [15,16] via synthesis of Pd colloids in cores of block copolymer micelles derived from polystyrene-poly-4-vinylpyridine (PS-b-P4VP) in selective solvents (toluene, THF). The

catalytic properties of Pd colloids perfectly stabilized in block copolymer micelles (PS-b-P4VP-Pd) were demonstrated in hydrogenation of cyclohexene, 1,3-cyclohexadiene and 1,3-cyclooctadiene both as homogeneous and heterogeneous catalysts [16]. The present paper is focused on the study of Pd colloidal catalyst synthesized in PS-b-P4VP micelles and deposited on Al$_2$O$_3$ in preparations of commercially valuable linalool and isophytol.

2. Experimental, results and discussion

The preparation of Pd colloids stabilized in block copolymer micelles in toluene has been described elsewhere [15]. The reactor for hydrogenation has been described in Ref. [14]. DHL (DHIP) concentration (C_o), catalyst amount (C_c) and hydrogenation temperature (T_h) have been varied: C_o from 33.4 to 250.8 g/l for DHL and from 83.3 to 116.7 g/l for DHIP, C_c from 1.67 to 5.00 g/l for DHL and 1.67 to 3.33 g/l for DHIP and T_h from 50 to 95°C. The experiments were carried out at atmospheric pressure. The optimal conditions for hydrogenation were chosen experimentally. The best selectivity in DHL hydrogenation (99.8%) was achieved at $C_o =$

Table 1
The relative rates of DHL and DHIP hydrogenation over different Pd catalysts (20% hydrogen uptake, solvent—toluene)

Catalyst	DHL hydrogenation rate, m^3 H_2 / (g Pd mol DHIP s)	DHIP hydrogenation rate, m^3 H_2 / (g Pd mol DHIP s)
Pd colloidal catalyst	0.55	0.16
Pd/Al$_2$O$_3$	3.2×10^{-2}	2.9×10^{-2}
Pd/CaCO$_3$	5.9×10^{-3}	4.8×10^{-3}

66.6 g/l, $C_c = 3.33$ g/l in toluene at 90°C. The maximum selectivity in DHIP hydrogenation was obtained in the same solvent at 90°C for $C_o = 100$ g/l and $C_c = 2.3$ g/l.

Based on kinetics, relative rates, r, of DHL and DHIP hydrogenation which are the relation of reaction rate at 20% of hydrogen uptake to catalyst and DHL (DHIP) amounts were calculated. Table 1 includes these values for the processes carried out both over the catalyst studied and conventional Pd catalysts under the same optimal conditions. Comparing these results one can see that the reaction rates are much smaller for traditional catalysts. As for selectivity, the latter catalysts require the additional modification by modifiers described above to achieve a selectivity of 99.5%.

For DHIP, the activity of catalyst is about three times smaller as compared to DHL hydro-genation that can be explained by longer hydro-carbon tail of DHIP (Scheme 1).

The mathematical treatment of kinetic data carried out in the way depicted in Ref. [17] shows that formally all experimental results both for DHL and DHIP can be well-described by Eq. (1):

$$W = \frac{kx_1}{x_1 + Qx_2},\tag{1}$$

where k is the kinetic parameter; x_1 is the acetylene alcohol concentration; x_2 is the olefin alcohol concentration; Q is the adsorption parameter. $Q = K_2/K_1$ where K_2 and K_1 are the adsorption equilibrium constants of olefin alcohol (linalool, isophytol) and acetylene alcohol (dehydrolinalool, dehydroisophytol), respectively.

Thus, the denominator of Eq. (1) characterizes the substrate adsorption. For graphic construction of the curves the parameter θ was used which is a relative time: $\theta = \tau'/q$, $\tau' =$ current reaction time, $q = C_o/C_c$ (see Figs. 1 and 2). These figures demonstrate a good agreement of calculated curves and experimental data. For each q value the total time τ required for the reaction completion is also shown.

The influence of solvent nature on catalytic properties of Pd colloidal catalyst was studied.
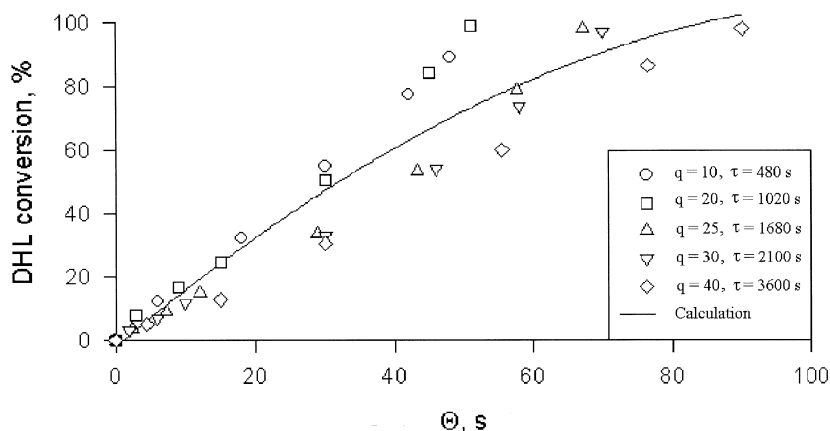

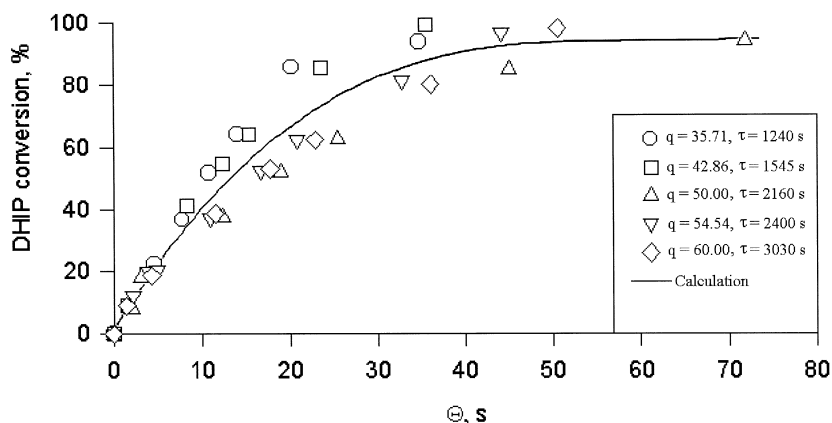Fig. 1. Dependence of DHL conversion on relative time.

Fig. 2. Dependence of DHIP conversion on relative time.

Maximum relative rate was found to be in methanol, but the highest selectivity was achieved in toluene. Indeed, toluene is a selective solvent for PS-b-P4VP providing a complete dissolution of PS corona and maximum accessibility of active centers located in micelle cores.

It should be noted that the initially observed catalytic activity and selectivity of the catalyst studied remain unchanged after 10 cycles, i.e., the catalyst can be recycled without its activity loss.

3. Conclusion

Pd colloids prepared in PS-b-P4VP block copolymer micelles and deposited on Al_2O_3 exhibited high activity and selectivity in hydrogenation of the triple bond of acetylene alcohols to the double one of olefin alcohols that can be explained by carrying out the hydrogenation with very reactive small Pd colloids surrounded by 4VP units. Control experiments carried out over conventional catalysts (Pd/Al_2O_3, $Pd/CaCO_3$) exhibit much smaller hydrogenation rates than those observed for colloidal catalyst.

For DHIP hydrogenation the catalyst activity was found to be much lower which for DHL can be explained by the much longer hydrocarbon tail of the former substrate.

The influence of solvent nature on catalytic properties of Pd colloidal catalyst in DHL and DHIP hydrogenation was studied. Maximum relative rate was found to be in methanol, but the highest selectivity was obtained in toluene, so the latter is suggested to be a preferable medium for acetylene alcohols hydrogenation.

Acknowledgements

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