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Porous membrane catalysts with Pd–M-clusters for liquid phase hydrogenation of dehydrolinalool

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Abstract

New membrane catalysts with less than 1.5% of Pd in porous stainless steel have been prepared for liquid phase hydrogenation of unsaturated organic compounds. Ultradispersed Pd modified with catalytically active Pb, Mn, or Bi was prepared using Metal Vapour Synthesis techniques. Rates of over 12 mol/m^{2}h with selectivities of up to 96% in hydrogenation of dehydrolinalool into linalool under atmospheric pressure of H_2 were observed. The ease of separation of this catalyst from reaction products, its regenerability, along with its corrosion, thermal stability, and mechanical strength give good prospects for these materials.

1. Introduction

The selective hydrogenation of acetylenic compounds into ethylenic ones is widely used in fine organic synthesis and is usually performed over Pd-containing catalysts. The activity and the selectivity of this catalyst are increased by combining Pd with a number of transition metals and by choosing the right type of the catalyst support. Catalytic Pd-containing membranes possess additional advantages for both the selectivity and activity control. Independence from the organic feedstock and simple control of hydrogen content in the catalyst, and uniformity of hydrogen concentration along the layer of the catalyst results in increases in selectivity. The high rate of hydrogen transport through the membrane to the catalyst surface increases the catalyst's activity. These reasons suggest study of an active and selective catalytic membrane for liquid phase hydrogenation of acetylenic compounds into ethylenic ones.

2. Catalysts preparation

Catalytic membranes were prepared out of 0.20 mm thick porous cermet stainless steel foil. The effective pore diameter was 2–3 μm. Pd and bimetallic Pd–M-clusters were obtained in the cryochemical unit with the stationary reactor using Metal Vapour Synthesis technique (MVS) [1]. The metals were evaporated resistively and then cocondenced into the toluene matrix precooled by liquid N_2. After heating the matrix to room temperature, we obtained the sol for imbedding the active components into the cermet stainless steel membrane. Fixation of Pd-and Pd–M-clusters in the pores of the support was carried out in the special reactor under ultrasonic treatment. Without ultrasonic treatment, the major part of the

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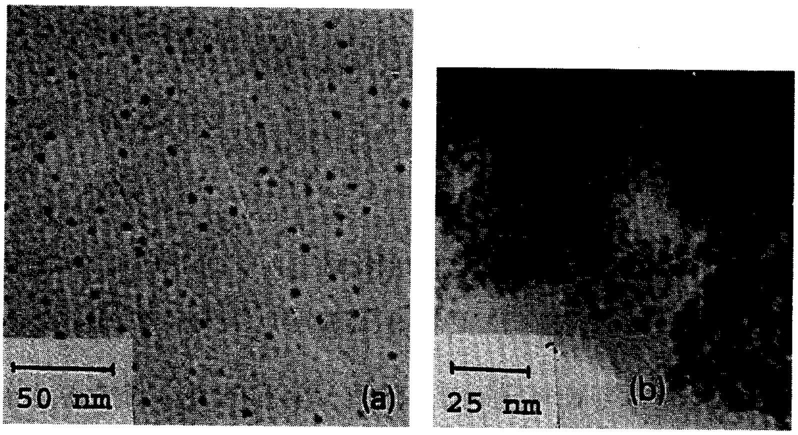

Fig. 1. Transmission electron micrographs of Pd-clusters prepared by cryosynthesis.

ultradispersed metals was supported on the outer surface of membrane in the form of a uniform black layer which displayed weak adhesion to the membrane. The ultrasonic treatment at a frequency of 22 kHz provided a uniform and stable Pd–M-active phase distributed in the pores of the membrane.

The investigation of the Pd–M-clusters in the toluene suspension was performed using Transmission Electron Microscopy. A droplet of sol was placed on a clean mica in a special container. After quenching in liquid N_2, the sample was dried under high vacuum within 5–7 hours and then covered with a layer of carbon. The resulting carbon film with the incorporated Pd-particles was investigated in TEM under the voltage of 75 kV in the range of magnifications of 10 000–500 000×. One could observe particle sizes of 10–30 Å (a) and the assemblies of separate particles (b) (see Fig. 1). It is necessary to note that after deposition of Pd–M-clusters on the membrane and its activation, the particle sizes can change [2].

Differential Thermal Gravimetric Analysis has shown that the samples of Pd–M-black (dried in vacuum at room temperature) still lose 12–15% of their weight while heated in flowing Ar from room temperature to 500°C. This weight loss results from the degradation of the organic layer which stabilizes ultradispersed metallic particles.

Chromato-Mass-Spectrometric Analysis (performed with Kratos MS 25 RF spectrometer) indicates that the decomposition of the organic layer in vacuum proceeds mostly in the temperature range of 150–200°C. $C_6H_5^+$, $C_6H_5CH_3^+$, $C_6H_5CO^+$, and $C_6H_5COOH^+$ ions were detected. At lower temperatures more toluene was evolved, and at higher temperatures, benzoic and phthalic acids. In the conditions of catalytic reaction after imbedding the Pd–M-clusters into the pores of the stainless steel membrane, this organic layer of clusters can behave itself in a different way.

The content of Pd + M active phase in the catalyst was investigated by means of Atomic Absorption Spectroscopy and was found to be almost constant at the level of 1.5 wt.-%.

3. Procedure of catalytic experiments

Membrane catalysts with the imbedded Pd–M-clusters have been tested in the liquid phase hydrogenation of dehydrolinalool (3,7-dimethyloctyn-1-en-6-ol-3) into linalool (3,7-dimethyloctadien-1,6-ol-3). The reaction products were analyzed by GLC using an Apiezon-L column.

The 20 × 110 mm membrane catalyst was configured in the reactor such that it separated the inner volume of the reactor into two chambers. A constant stream of 2–10 ml/hour of liquid dehydrolinalool was introduced into one chamber, and slightly more than stoichiometric amount of hydrogen (under somewhat excessive pressure) into the other. The hydrogenation reaction of acetylenic alcohols was most likely to occur in the course of hydrogen diffusion through the moistened with dehydrolinalool catalyst pores to the hydrogenation chamber.

After hydrogenation, the catalyst was regenerated in situ. At first it was washed with ethanol and then heated for 1 hour at 400°C in flowing air, then hydrogen.

4. Results and discussion

Among the most selective catalysts for liquid phase hydrogenation of dehydrolinalool are membrane catalysts of Pd–Ru-alloys in a foil [3]. The disadvantage of these catalysts is the high content of noble metals in the reactor and low productivity with respect to Pd-weight. Supported Pd–Ru-catalysts with low noble metals concentration are not selective in the hydrogenation of acetylenic alcohols into ethylenic ones [4]. Among the supported catalysts with low concentration of noble metals, Pd–Pb-, Pd–Mn-, and Pd–Bi-systems are most promising for selective hydrogenation [5–7]. On the basis of the above reasoning we have prepared and tested Pd, Pd–Pb, Pd–Mn, and Pd–Bi supported membrane catalysts.

After the first activation at 400°C first in flowing air and then under H_2, all the catalysts displayed stable activity in the temperature range between 90 and 180°C. The regeneration frequency depended on the reaction temperature, but it was not necessary to regenerate the catalyst more often than once every 8–10 hours. Successive regenerations did not lower catalyst activity.

Table 1
Hydrogenation of dehydrolinalool to linalool at 150°C, under atmospheric hydrogen pressure on the mixed metal catalysts on porous steel membranes

Active component of the catalyst	Pd/M (wt. ratio)	Selectivity (%)	Activity (mol/m^2 h)
Pd		80	13
Pd + Pb	1/2	95	2
Pd + Mn	2/1	96	9
Pd + Bi	3/1	95	10

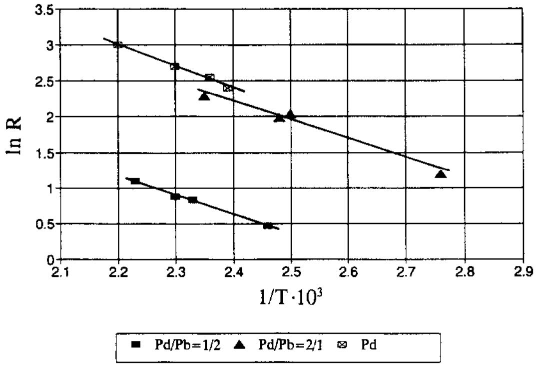

Fig. 2. Temperature dependence of reaction rates for Pd-and Pd–Pb-catalysts.

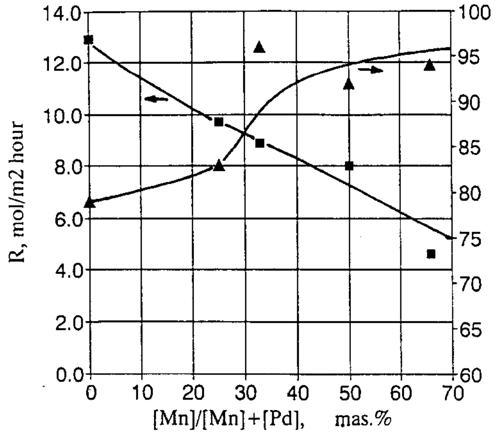

Fig. 3. Reaction rate and selectivity of Pd–Mn-catalysts in hydrogenation of dehydrolinalool at 150°C. (□) rate; (▲) selectivity.

The reaction was zero order with respect to the substrate. The activities and selectivities of dehydrolinalool hydrogenation at 150°C are shown in Table 1. With constant Pd + M concentration in the catalyst, the activity of the catalyst goes down. Temperature dependence of reaction rates for Pd- and Pd–Pb-catalysts is shown in Fig. 2. Activation energies for all these catalysts are about 6 kcal/mol. With diminishing Pd concentration and increase of the transition metal concentration, increases the selectivity. Fig. 3 shows the activity and selectivity of Pd–Mn-catalysts dependence on Mn concentration. According to [8], the solubility of Mn in Pd does not exceed 20 wt.-%. In our case we observed more or less stable selectivity of Pd–Mn-catalysts with Mn-concentrations higher than 30 wt.-%. That could indicate that with higher Mn-concentrations the active phase of the catalyst has the same composition, but the increasing the Mn-concentration only blocks some of the active surface. In any case, using porous membrane catalysts with Pd–Mn-clusters for liquid phase hydrogenation of dehydrolinalool results in a productivity of 10–12 mol/m^2 h. This productivity is equal to that of the best membrane catalysts made of Pd-alloys in foil or tube form [3]. That means of about 30 times increase in activity with respect to Pd-weight. The rest of the advantages of membrane catalysts are retained.

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