

## Design of Nano-Sized Polymer-Palladium Catalysts for Hydrogenation

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### Abstract

Nanoscale palladium/oxide catalysts stabilized with poly-2-methyl-5-vinylpyridine (P2M5VP) have been prepared and tested in the reaction of 3,7,11-trimethyldodecyne-1-ol hydrogenation in ethanol at 50°C and hydrogen atmospheric pressure. The catalysts showed high activity, stability and selectivity. Chemical interaction of  $\text{PdCl}_2$  with pyridine groups of P2M5VP on oxides (ZnO and MgO) promotes formation of even distribution of uniformed metal particles. Polymer chains prevent agglomeration of active phase of Pd and deactivation of catalysts during hydrogenation reaction.

### Introduction

The effective immobilization of metal catalysts is a particularly important methodological target, especially for metal complex based catalysts. Catalytic activity is mainly affected by the size and the dispersion of metal particles. It is known that ultradispersed metal particles supported on inorganic oxides can be produced by using organometallics including metal carbonyls [1,2]. The other way to produce active, selective and stable catalysts is to use functionalized polymers as carriers. Increasing exploitation of polymer-supported catalysts is occurring both in academic and industrial laboratories [3-5]. However, the drawbacks of polymer supports are diffusion problems, low thermal and mechanical stability. Coating inorganic carriers by functional polymers can lead to minimization of these disadvantages. At the same time such types of catalysts will possess advantages of polymer-metal catalysts such as stable activity and selectivity. It is important to obtain catalysts that have maximum accessible surface where the polymer does not shield metal particles from the substrate. High selectivity and stability of the catalysts is pointed out in papers, but there are only few reports concerning selective hydrogenation of long chain acetylene

compounds on supported nano-sized catalysts [6-8]. The present paper has deal with investigation of designed 5% Pd-P2M5VP supported on ZnO and MgO in hydrogenation of 3,7,11-trimethyldodecyne-1-ol.

### Experimental

#### *Catalytic process*

Hydrogenation of 3,7,11-trimethyldodecyne-1-ol (TMD) were carried out in thermostatic glass vessel with constant shaking. The reaction was carried out in ethanol (0.025 l) at 50°C and atmospheric pressure of hydrogen. Catalysts were treated with hydrogen during 0.5 hour before reactant was added into the reactor.

To study the stability of catalysts some portions of TMD were injected into reactor one after another.

The analysis of hydrogenation products was carried out on Crom-4 chromatograph (Czechoslovakia) using a flame ionization detector and 3.5 m length column filled with 10% Apiezon-L + 2% PEG-20M on Chromaton-N-AW-DMCS. Argon was used as a carrier gas. Based on the chromatographic analysis the selectivity of hydrogenation ( $S_{\text{hydr.}}$ ) of TMD were determined by following equations:

$$S_{\text{hydr.}} = \frac{[3,7,11\text{-trimethyldodecene-1-ol}]}{[3,7,11\text{-trimethyldodecene-1-ol}] + [3,7,11\text{-trimethyldodecane-1-ol}]} \times 100\%$$

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### Catalysts preparation

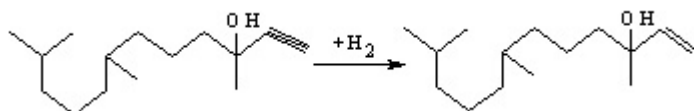
5% Pd-P2M5VP/ZnO and 5% Pd-P2M5VP/MgO have been prepared. Oxides (ZnO or MgO) were treated with ethanol solution of P2M5VP and then with ethanol solution of PdCl<sub>2</sub>. Obtained catalysts were dried in the air and used in catalytic hydrogenation.

5% Pd/ZnO and 5% Pd/MgO have been prepared by the same way but without P2M5VP coating. Catalysts

were tested in hydrogenation reaction to determine influence of polymer additive on properties of the obtained catalysts.

### Results and discussion

Hydrogenation of TMD on all prepared catalysts is carried out with formation of 3,7,11-trimethyldodecene-1-ol:



The latter is converted into the 3,7,11-trimethyldodecane (Fig.1). The yield of olefin alcohol is nearly

the same on all tested catalysts. Selectivity of the process is within the range of 82-85% (Table 1).

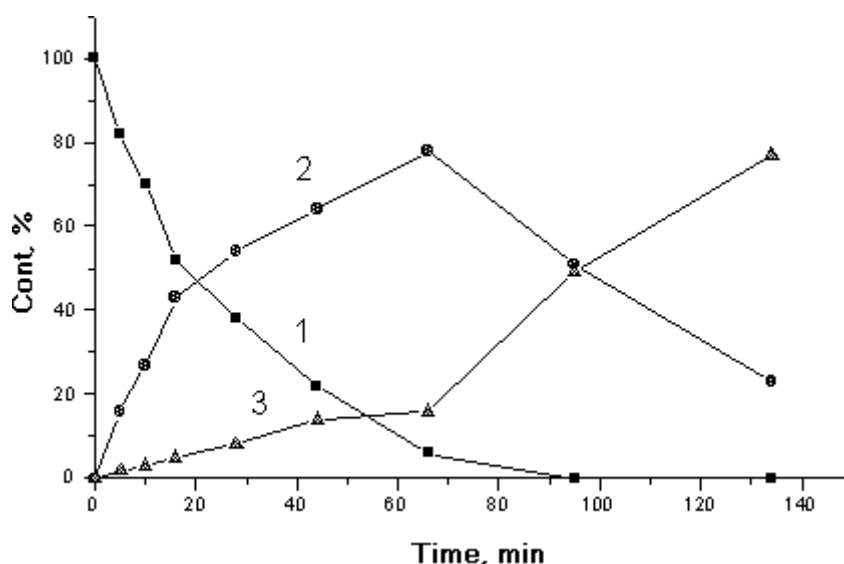


Fig.1. Diagram of TMD (5.8 ml) hydrogenation over 5% Pd-P2M5VP/ZnO (0.5 g) at 50°C and 1 atm hydrogen pressure in ethanol (25 ml)  
1-TMD, 2- 3,7,11-trimethyldodecene-1-ol, 3- 3,7,11- trimethyldodecan-1-ol

**Table 1**

Hydrogenation of TMD (0.58 ml) on palladium (5%) supported catalysts (0.05 g) in ethanol (25 ml) at 50°C and 1 atm hydrogen pressure and characteristics of supports

Catalysts	Surface area, m <sup>2</sup> /g	Isoelectric point of oxides	Particle sizes, nm	W 10-5 mole/l sec	S <sub>c=c</sub> , %	TON
Pd/MgO	6,8	12,1-12,7	7-10, 20-25	25.6	82	800
Pd-PMVP/MgO			5-7	21.8	85	4800
Pd/ZnO	88	7,0-9,0	30-35	16.5	85	400
Pd-PMVP/ZnO			6-8	21.4	85	6700

The results of TMD hydrogenation over all prepared catalysts are presented in the Table 1. The results showed that activity and selectivity of the catalytic process are not affected very much on the methods of catalysts preparation as well as oxide nature.

Polymer additive plays an important role in catalysts' formation and their stability during hydro-

genation. Comparison of turnover numbers (TON) of catalysts with and without P2M5VP showed that polymer promotes catalysts' stability more than 10 times (Table 1). These catalysts characterized with small sizes of Pd particles - 6-8 nm and their even distribution on the oxide surfaces. It is visible on the micrograph of the Pd-P2M5VP/MgO catalyst (Fig.2,3)

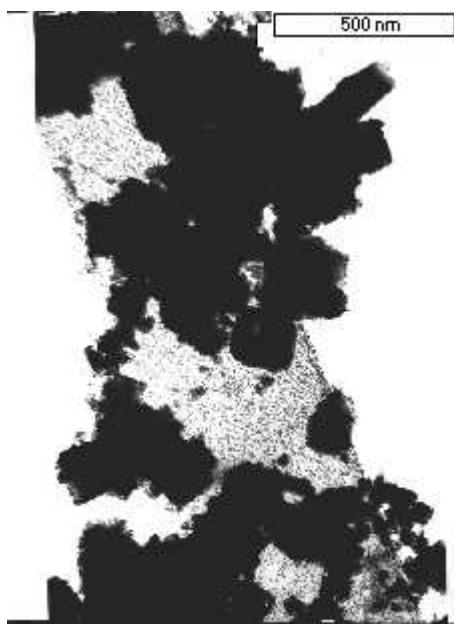


Fig.2. Micrograph of 5%Pd-P2M5VP/MgO catalyst

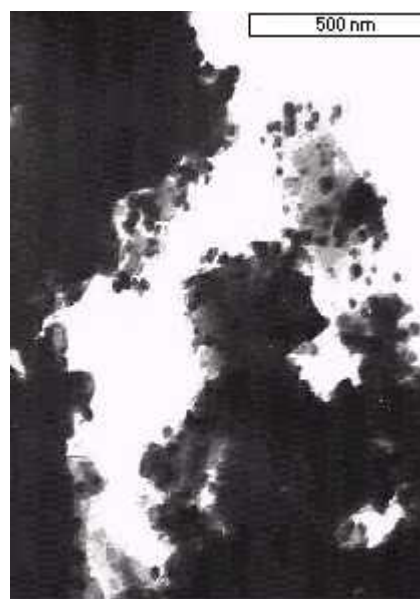


Fig.3. Micrograph of 5%Pd-P2M5VP/MgO catalyst

It is known [8,9] that  $\text{PdCl}_2$  forms complexes with poly(vinylpyridine)s, that are active, stable and selective catalysts for hydrogenation. High stability of these complexes used as catalysts are explained by preventive function of polymer chains. It is proposed, that ZnO and MgO coated with polymer are able to coordinate Pd(II) ions through nitrogen of pyridine groups of P2M5VP. It leads to even distribution of Pd particles on the oxide surfaces. This supposition is proved by electron microscopy study of Pd/MgO catalyst without polymer coating (Fig 3). This catalyst is characterized with particles of different shapes and sizes and occasional their distribution on oxide surface.

Thus, soluble functional polymers can be use for preparation of catalysts. Chemical interaction of transition metal salts with functional groups of polymers on oxide surfaces promotes formation of even distribution of metal particles. Polymer chains prevent

agglomeration and deactivation of catalysts.

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