

# EXAMINATION OF CATALYSTS CONTAINING PALLADIUM IN OXIDATION OF CARBOHYDRATES IN AIR

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In course of our experimental work several catalysts containing different quantities of palladium were prepared and investigated for the influence of the production process on their activity and lifetime. The catalysts were examined in the oxidation of 2,3-4,6-di-isopropylidene-L-sorbose (DAS), then in the oxidation of several carbohydrates and their derivatives and in each case monocarboxylic acids were obtained. The experiments concerning the procedure of oxidation and the experimental methodology will be described in future publications.

Scientific literature enumerates cases of obtaining different monocarboxylic acids from carbohydrates or from their derivatives in the course of oxidation in air, mainly in the presence of platinum and sometimes of palladium catalysts.

BUSCH [1] prepared D-glyconic acid from D-glucose in the course of oxidation in air in the presence of palladium catalyst on calcium carbonate carrier. OKNI [2] and KOROTKY [3] applied Pt catalyst for this reaction. SHEEDEN and TURNER [4] produced 2-keto-L-gulonic acid from L-sorbose by platinum-on-carbon catalyst. TRENNER [5, 6], MEHLTRETTER et al. [7] and COLON et al. [8] also produced the equivalent glucuronic acid from 1,2-*o*-isopropylidene- $\alpha$ -D-glucopyranose (MAG) in the presence of platinum catalysts.

Starting from (MAG) BAKKE and THEANDER [9] got hexofuranolactone-5-ulose by oxidation in the presence of Pd catalyst. HEYNS [10] and others [11, 12] obtained the equivalent 2-keto-L-gulonic acid from the 2,3-4,6-di-*o*-isopropylidene-L-sorbose in the presence of platinum-on-carbon catalyst and with palladium catalyst, respectively.

HEYNS and POUTTON [13] stated the precious metals to be the best catalysts for the oxidation of carbohydrates and derivatives in air (Pt, Pd) and the most suitable carrier to be bone coal. The first step in preparation of palladium-on-carbon catalysts is the impregnation of the bone coal by a water-soluble salt of palladium, mainly a chloride. This is followed by reducing to metal. There are several requirements for the quality of bone coal [14] and a

lot of admixtures are known. Different methods have been put down for reducing the metal compound, too. In a Soviet patent [15] formaldehyde is employed, HARTUNG [16] uses a formaldehyde solution buffered with sodium acetate, ZELINSKY and GLINKA [17] use formic acid in alkaline solution, in a patent of Hoechst [18] hydrazine is applied for the reduction of the metal compound. There are several descriptions where palladium compounds are reduced by hydrogen suspended in alkaline or acidic solution.

In the last decade interest has been concentrated on metal boride catalysts. BROWN [19] prepared a palladium-boride catalyst with and without bone coal carrier having a composition of  $\text{Pd}_2\text{B}$  (he reduced the palladium salt carried on bone coal by sodium-boro-hydride). For the preparation of colloidal palladium catalysts before reducing the palladium salt, NORD [20] proposed the dosage of polyvinyl alcohols as protective colloid. TYRENKOVA and BONDERJAK [21] used polyvinyl alcohols as carrier for palladium catalysts.

The catalysts mentioned above were elaborated for hydrogenation. By these catalysts carbohydrates can be oxidized in air in thin water solutions (4 to 5%) only within 18 to 50 hours of reaction time. Neither yields, nor lifetime of catalysts are satisfactory. Therefore we examined how to improve the preparation of catalysts.

First, hydroxides of different metals were precipitated on bone coal carrier but as they proved to be inactive they were promoted with palladium and palladium boride. In this way more active catalysts could be prepared than before. Their activity was proportional with their palladium contents, hence subsequently exclusively the preparation of palladium and palladium-boride-on-carbon catalysts has been examined.

#### *Metal hydroxides-on-carbon catalysts promoted by Pd ( $K_F$ )*

Hydroxides of Cr, Mn, Fe, Co, Ni and Cu were prepared on bone coal carrier with Pd admixture. In all cases the catalysts contained 20% of metal. The amount of Pd in catalysts varied between 0.5 and 10%. These catalysts were effective in the oxidation of DAS (2,3-4,6-di-o-isopropylidene-L-sorbose). The reactions were made in all cases in a 10% aqueous solution in the presence of  $\text{NaHCO}_3$  at 85 °C but even with the best catalysts the yield did not exceed 20% in a five-hour reaction time (Figs 1, 2, 3). Pd can be stated to have no accelerating effect and the yield to vary with the Pd content of the catalyst.

#### *Metal hydroxides-on-carbon catalysts promoted by Pd-boride ( $K_{FB}$ )*

In the last decade metal boride catalysts were used mainly in hydrogenation with success. Therefore Pd-boride catalysts (Figs 4, 5) were prepared by keeping the quoted Pd—bone coal proportions by weight. These significantly improved the oxidation yield of DAS compared to the catalysts without borides. The catalysts containing Fe and Mn were especially active (Fig. 6).

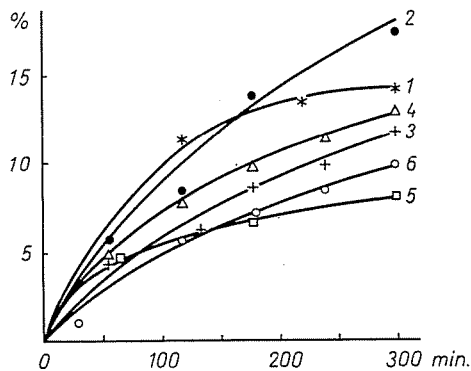


Fig. 1. Pd content 1%, yield vs. reaction time

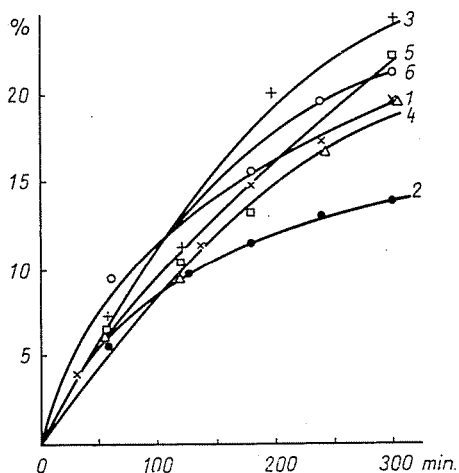


Fig. 2. Pd content 10%, yield vs. reaction time

### *Palladium-on-carbon catalysts (K)*

Assuming that palladium-on-carbon catalysts prepared in a suitable way result in better yields than before, we examined the applicability of palladium-on-carbon catalysts in the oxidation of DAS depending on the way of preparation and on the Pd contents. The catalysts were prepared as follows:  $\text{Pd}(\text{OH})_2$  was precipitated on bone coal with alkali from  $\text{PdCl}_2$  solution of known concentration, then the obtained  $\text{Pd}(\text{OH})_2$ -on-carbon suspended in water was hydrogenated. Only in this way could reproducible catalysts, convenient for the oxidation be produced. During the precipitation of  $\text{Pd}(\text{OH})_2$  the exact adjustment of the pH was very important [22]. Palladium-hydroxide-on-carbon was hydrogenated at atmospheric pressure until the hydrogen absorp-

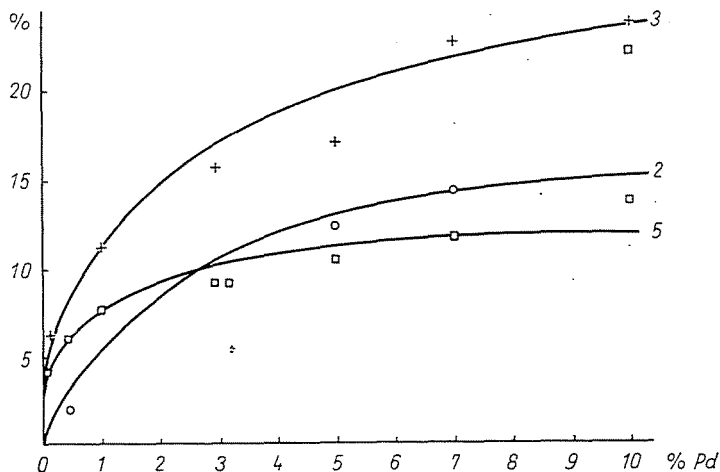


Fig. 3. Yield vs. Pd content of catalyst. Marks on curves: 1. chrome; 2. manganese; 3. iron 4. cobalt; 5. nickel; 6. copper

Figs 1, 2, 3. Metal hydroxide-on-carbon catalysts promoted by palladium ( $K_F$ )

tion was complete. The yield increased with the Pd content of the catalysts: The catalyst containing 30% by weight of Pd caused the oxidation of the 10% DAS solution to yield 90 to 100% in five hours (Fig. 7).

Oxidation results did not improve upon hydrogenating at 20 atm pressure under otherwise identical conditions (Fig. 8).

#### *Palladium-on-carbon catalysts with polyvinyl alcohol admixture ( $K_{PVA}$ )*

Further experiments aimed at decreasing the Pd content. Publications on Pd catalysts quote polyvinyl alcohols to have a colloid protective effect [20, 21].

Catalysts were prepared by adding polyvinyl alcohol to the suspension of  $PdCl_2$  and bone coal before the precipitation of  $Pd(OH)_2$ , followed by the alkali precipitation and hydrogenation. In this way several palladium-on-carbon catalysts were prepared with different Pd contents. Among these we already succeeded in oxidizing the 10% DAS solution with the 5% Pd catalyst in four hours at a yield of nearly 100%. Then 5% Pd-on-carbon catalysts were prepared with different polyvinyl alcohol admixtures. Among these the best were those with a 0.066 to 0.038 g dosage of PVA admixture for 1 g Pd (Fig. 9).

Presumably the polyvinyl alcohol is sorbed on the bone coal and the linking Pd is more active or rather it assumes superfine dispersion on the surface of bone coal.

Catalysts prepared in polyvinyl alcohol solution without bone coal did not prove suitable (Fig. 10).

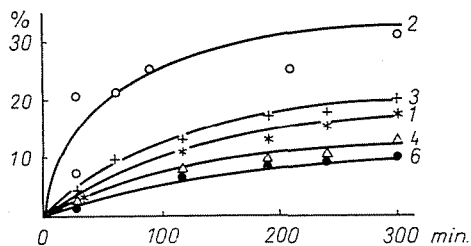


Fig. 4. Pd content 1%, yield vs. reaction time

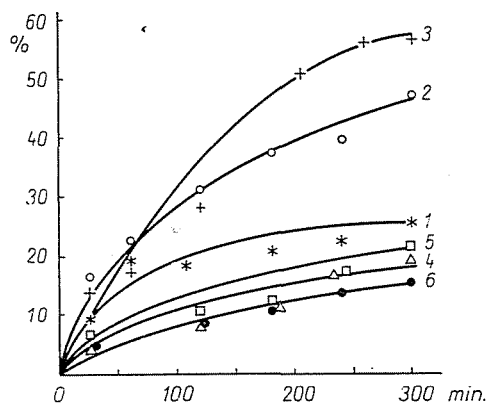


Fig. 5. Pd content 10%, yield vs. reaction time. Marks on curves: 1. chromium; 2. manganese; 3. iron; 4. cobalt; 5. nickel; 6. copper

Figs 4, 5. Metal hydroxide-on-carbon catalyst promoted by palladium boride ( $K_{FB}$ )

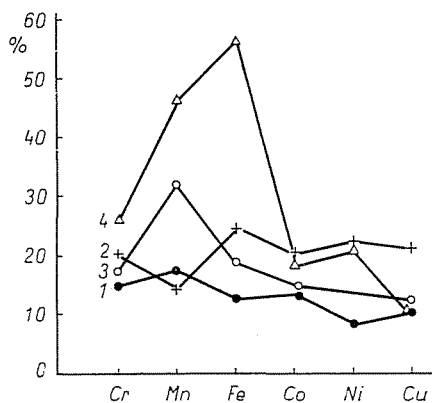


Fig. 6. Comparison of metal hydroxide-on-carbon catalysts promoted by palladium and palladium boride. Marks on curves: 1. Pd content 1%, with catalyst  $K_F$ ; 2. Pd content 10%, with catalyst  $K_F$ ; 3. Pd content 1%, with catalyst  $K_{FB}$ ; 4. Pd content 10%, with catalyst  $K_{FB}$

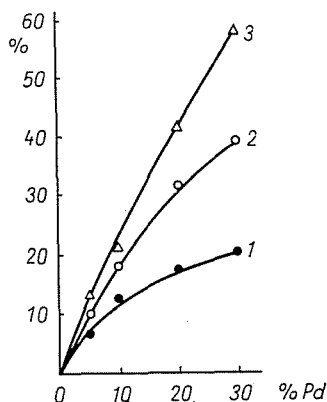


Fig. 7. Catalysts hydrogenated at atmospheric pressure

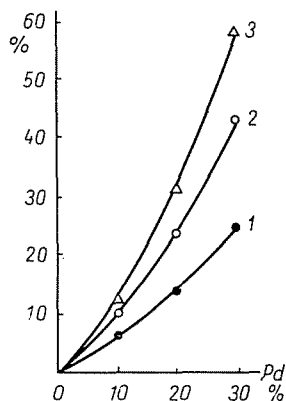


Fig. 8. Catalysts hydrogenated at 20 atm pressure

Figs 7, 8. Effect of palladium-on-carbon catalysts (K) on the yield vs. Pd content

#### *Palladium-boride-on-carbon catalysts with polyvinyl alcohol admixture (K<sub>B</sub>)*

Among the metal hydroxide-on-carbon catalysts admixed with Pd the Pd-borides proved to be the best. Therefore the Pd-boride-on-carbon catalysts were also examined.

Pd catalysts of 5% were prepared with the optimum amount of polyvinyl alcohol so that after the precipitation of Pd(OH)<sub>2</sub> different amounts of NaBH<sub>4</sub> were added to the mixture filtered and its water suspension hydrogenated at atmospheric pressure (at least three mols of NaBH<sub>4</sub> are needed for one Pd atom) (Fig. 11).

The optimum PVA proportion measured on Pd-boride-on-carbon catalysts appeared to be 0.083 g for 1 g Pd (Fig. 12); this agrees well with the proportion measured on Pd-on-carbon catalysts.

Such catalysts prepared without carrier were better than the equivalent Pd catalyst but worse than that on bone coal carriers (Fig. 13).

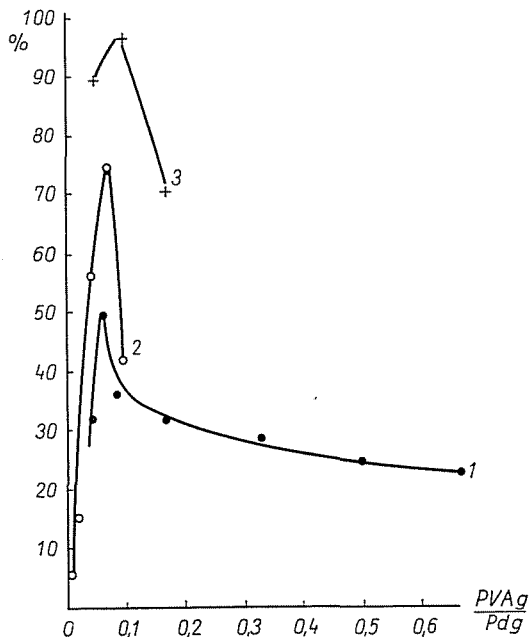


Fig. 9. Yields possible with 5% Pd catalysts type  $K_{PVA}$  vs. PVA/Pd ratio by weight. Reaction time: 1. two hours; 2. four hours; 3. six hours

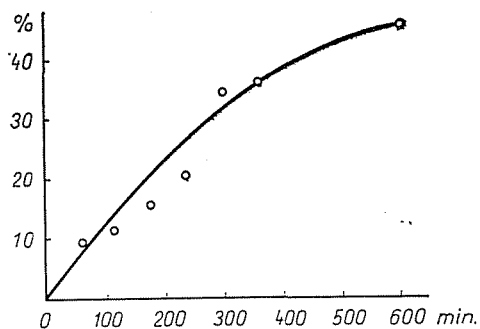


Fig. 10. Effect of palladium catalyst without carrier admixed with polyvinyl alcohol vs. reaction time

#### Catalysts-on-carbon in polyvinyl alcohol solution with trace amount of $NaBH_4$ ( $K_N$ )

Catalysts were prepared by adding a small amount of  $NaBH_4$  before hydrogenation to the  $Pd(OH)_2$ -on-carbon [0.04 mol to one mol of  $Pd(OH)_2$ ]. This procedure much improved the 5% Pd catalysts. Such catalysts were also prepared with different PVA admixtures. Catalysts containing 0.043 g PVA were found to be optimal (Fig. 14).

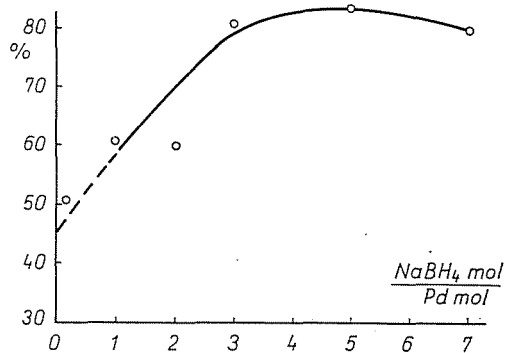


Fig. 11. Yields possible in two hours with a 5% Pd catalyst type  $K_B$  vs. ratio by mol of  $\text{NaBH}_4/\text{Pd}$  used for preparation

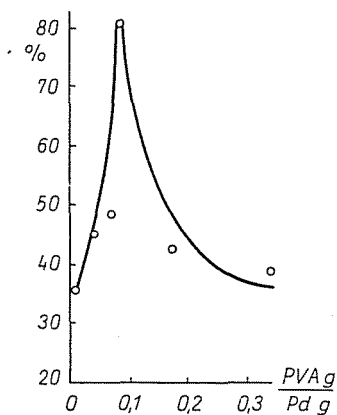


Fig. 12. Yields possible in two hours with a 5% Pd catalyst type  $K_B$  vs. PVA/Pd ratio by weight

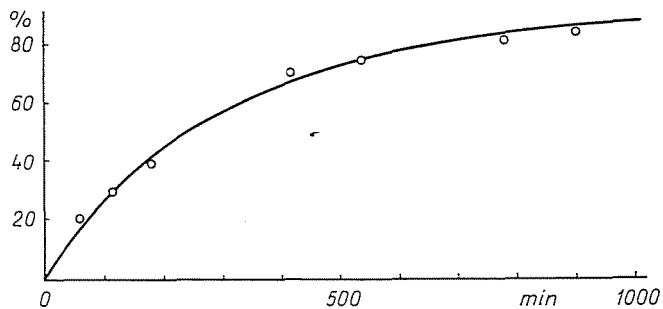


Fig. 13. Effect of palladium boride catalyst without carrier admixed with polyvinyl alcohol on the yield vs. reaction time



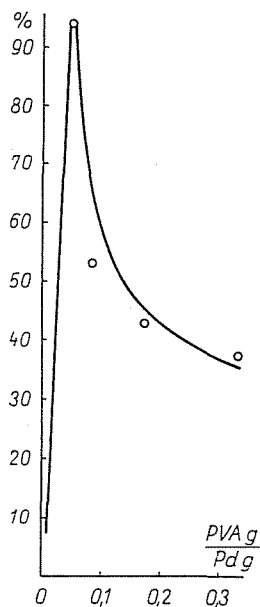


Fig. 14. Yields possible in two hours with a 5% Pd catalyst type  $K_N$  vs. PVA/Pd ratio by weight

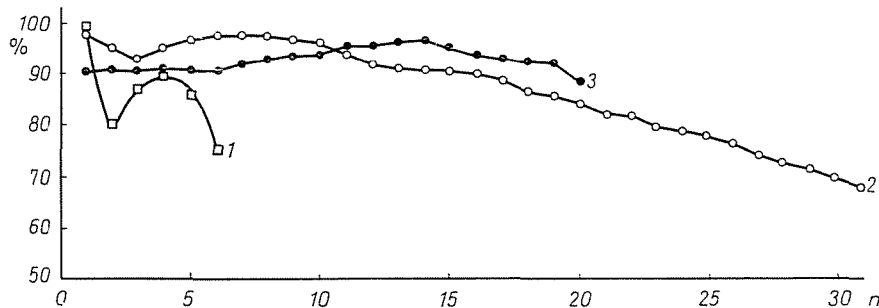


Fig. 15. Average yields possible with catalysts type  $K_N$  vs. number of utilizations. The Pd contents of the catalyst are: 1. 5%, 2. 15%, 3. 30%

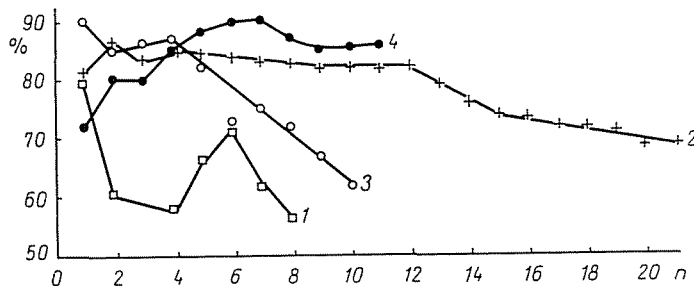


Fig. 16. Average yields possible with catalysts type  $K_B$  vs. number of utilizations. The Pd contents of the catalyst are: 1. 5%, 2. 10%, 3. 15%, 4. 20%

### The pot life of $K_B$ and $K_N$ catalysts

The 5% Pd catalysts of  $K_B$  and  $K_N$  type are very active in oxidation. Their pot life, of great importance in industrial utilization, was examined, too.

DAS solutions of 10% were oxidized repeatedly with the catalysts, for two to five hours each. Results with catalyst types  $K_N$  and  $K_B$  are shown in Figs 15 and 16, respectively.

It is conspicuous that the 5% Pd catalysts exhibited a single time the same activity as the higher Pd catalysts. Thus for industrial uses only catalysts of at least 10% Pd may be reckoned with. Among the 15% Pd catalysts that of type  $K_N$  produced 15 times an 85% average yield; the type  $K_B$  only 10 times; the type  $K_N$  had 30 times 70% average yield, the type  $K_B$  21 times.

Catalysts type  $K_N$  did not recede in yield after as many as 400 oxidations of furan derivatives and D-glucose.

The most effective catalysts for the required oxidations at an industrial scale were those produced in the presence of polyvinyl alcohol with a small amount of  $\text{NaBH}_4$  admixture (type  $K_N$ ) [22].

### Summary

Production of catalysts suitable for oxidizing carbohydrates in air has been examined. Improved Pd and Pd-boride catalysts could be produced by precipitating  $\text{Pd}(\text{OH})_2$  on bone coal carrier in presence of polyvinyl alcohol from aqueous  $\text{PdCl}_2$  solution and in case of boride types reacted with  $\text{NaBH}_4$  suspended in water and hydrogenated at atmospheric pressure. For industrial applications the Pd catalyst on bone coal carrier produced by adding traces of  $\text{NaBH}_4$  to  $\text{Pd}(\text{OH})_2$  is the most suitable. Among these, the catalyst with 20% Pd content can be used over 30 times for the oxidation of di-O-isopropylidene-hexoses and over 400 times for the oxidation of hexoses and of furan, i.e. tetrahydrofuran containing oxymethyl or aldehyde groups in  $\alpha$ -position. The substrate can be oxidized to mono-carboxylic acid in 2 to 5 hours at a nearly 90% yield, even in 20% aqueous solutions.

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