

# Hydrogenation on Granular Palladium-containing Catalysts: I. Hydrogenation of Tertiary Acetylene Alcohols

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**Abstract**—Commercial granular palladium catalyst (0.5% of Pd on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was modified by treating with zinc acetate (type 1) or successively with zinc acetate and ammonia (type 2). The treatment significantly increased the hydrogenation selectivity for a triple bond into a double bond: to 85.3–93.1% with the type 1 catalyst and to 96.3–97.8% with the type 2 catalyst. A construction of an autoclave with a fixed bed of the granular catalyst is described.

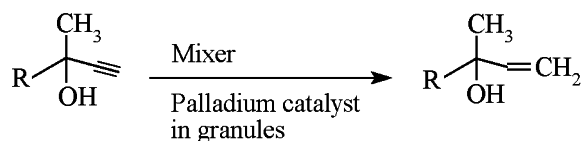
The hydrogenation in agitated reactors is usually carried out with palladium on carbon or homogeneous catalysts. The obvious advantage over the above of the granular palladium catalysts (GPC), e.g., 2% of Pd on granulated carbon or 0.5% Pd on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (ShPAK-0.5), is in the ease of separation of the reaction mixture from the catalyst. However to the use of GPC in a common rotating autoclaves stands in the way the abrasion of the catalysts providing fine particles hard to filter off and appearing in the product as an impurity. In the industry the GPC are commonly used in upflow reactors but at small-scale production, from 10 to 1000 g, they are inconvenient since the process requires prolonged adjustment.

We describe here a construction of an agitated reactor with a fixed bed of GPC and its application to

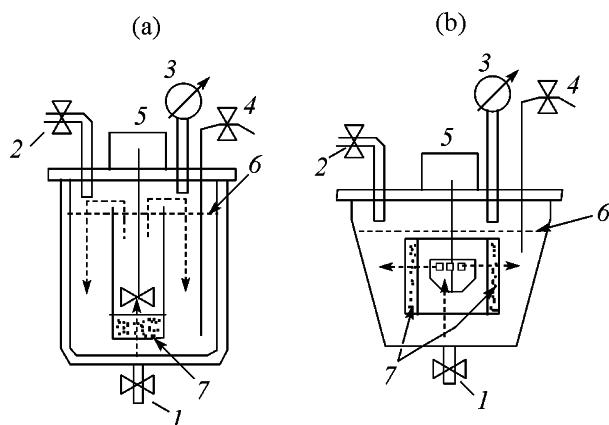
large-scale syntheses. A reactor of 10 l capacity is shown on Fig. 1a. It is equipped with bottom discharge, manometer, a valve for hydrogen input, and a capillary for sampling. The pumping of the fluid through the catalyst bed is ensured by the operation of a turbo-type agitator and by an efficient motor (3000 rpm). The flow of the fluid is shown by arrows.

For test experiments with small charge of substances was manufactured a reactor of 1 l capacity shown in Fig. 1b. In this reactor is used an agitator of centrifugal type (the fluid flow is also indicated by arrows) and vertical and not horizontal position of catalyst bed: the catalyst is packed into a latticed bowl. Although it turned out that the construction of reactor with the turbo-type agitator and horizontal catalyst bed was somewhat better, in both reactor types the granulated catalyst did not suffer fragmentation (no mechanical abrasion was observed).

The said reactors were used in hydrogenation of acetylene alcohols within the framework of refining a production process for isophytol preparation, the key product in the vitamin E synthesis.



I-III, R = CH<sub>3</sub> (a), Me<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>2</sub> (b), Me(MeC=CHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (c), Me(CHMeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (d).



(a) Reactor of 10 l capacity, (b) Reactor of 1 l capacity. (1) bottom discharge, (2), hydrogen input valve, (3) manometer, (4), capillary for sampling, (5), high-speed motor, (6), fluid level, (7) net with GPC.

Since unmodified palladium catalysts are known to possess a moderate selectivity with respect to hydrogenation of the triple and double bonds we

**Table 1.** Hydrogenation of acetylenes **Ia-d**

| Compd. no. | Catalyst type | Conversion, % | Selectivity, % | Pressure, at | Temperature, °C | Reaction time, h | Dilution with <i>i</i> -PrOH | Charge type <sup>a</sup> |
|------------|---------------|---------------|----------------|--------------|-----------------|------------------|------------------------------|--------------------------|
| <b>Ia</b>  | 1             | 98.2          | 93.1           | 16–20        | 24–27           | 16               | –                            | A                        |
|            | 2             | 99.7          | 97.8           | 16–20        | 45              | 6                | –                            | A                        |
| <b>Ib</b>  | 1             | 97.8          | 91.1           | 12–16        | 26–28           | 8.5              | –                            | A                        |
|            | 2             | 99.1          | 96.6           | 10–16        | 65              | 3.5              | –                            | A                        |
| <b>Ic</b>  | 1             | 99.3          | 89.7           | 10–12        | 25              | 6                | 1:1                          | B                        |
|            | 2             | 98.9          | 96.3           | 7–10         | 60              | 4                | 1:1                          | B                        |
| <b>Id</b>  | 1             | 99.1          | 85.3           | 5–8          | 24–26           | 4                | 1:1                          | B                        |
|            | 2             | 99.5          | 97.5           | 1–2          | 50              | 5                | 1:1                          | B                        |

<sup>a</sup> A Reactor of 1 l capacity, 400 ml of initial compound, 20 ml of catalyst; B Reactor of 10 l capacity, 3.5 l of initial compound, 120 ml of catalyst.

studied two catalysts prepared from a commercial catalyst ShPAK-0.5 (0.5% of Pd on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) by treatment with zinc acetate (type 1) or by successive treatment with Zn(OAc)<sub>2</sub> and gaseous ammonia (type 2).

The experimental results are presented in Table 1. As seen, the type 2 catalyst shows considerably higher selectivity as compared with the type 1 catalyst (85.3–93.1% for type 1, 96.3–97.8% for type 2). Both gaseous ammonia and zinc acetate were formerly used to poison palladium catalysts [1], but they were not used in preparation of catalysts, and were just added into the reactor. We found that the catalyst prepared by treatment with gaseous ammonia showed good reproducible activity, and besides these catalysts were relatively stable (probably the ammonia molecules were retained in the pores by adhesion forces).

The experimental conditions are somewhat different. In the series of compounds **Ia-d** the rate of hydrogen absorption considerably increased: for instance, under conditions where dimethylethynylcarbinol (**Ia**) was hydrogenated to olefin **Ila**, dehydroisophytol (**Id**) bypassed the stage of isophytol (**IId**) and gave at once dihydroisophytol (**IIId**). Therefore in the series **Ia-d** the pressure and reaction time should be reduced. Note that with no agitation the hydrogen absorption virtually stopped. Thus an efficient stirring in the reactor type described is necessary for sufficient hydrogenation rate. Therefore in hydrogenation of compounds **Ic, d** the reaction mixture was diluted with 2-propanol (1:1) to reduce viscosity of the solution.

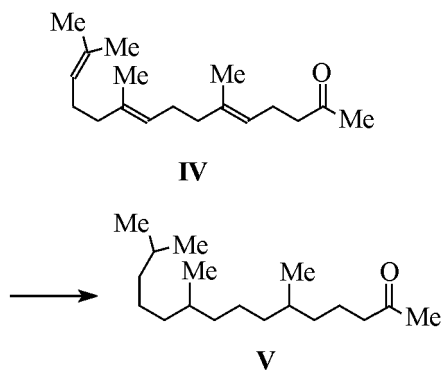
Since olefins **II** under the reaction conditions are further hydrogenated to compounds **III**, the yield of the latter grows (and the selectivity consequently decreases) with growing conversion of acetylenes **I** (and with the overall reaction time). These data are directly illustrated in Table 2 (hydrogenation on type 1 catalyst). Similarly in the experiment at larger scale (charge 7 l) at the hydrogenation of compound **Ia** into **Ila** on the type 2 catalyst with conversion of the initial substrate of 80% the selectivity was 99%, and the yield with respect to the isolated product after rectification was 94.4% (taking into account that some initial compound was recovered). In the experiment carried out to 99.2% conversion of the initial compound the selectivity amounted to 97.5%, the yield of the target product was 96.7% as determined by GLC, and 92.8% after distillation. Thus the yield of the target compound with respect to consumed initial substrate is somewhat higher at conversion of 80%, and the catalyst under study (type 2) is comparable in selectivity with homogeneous hydrogenation catalysts [2] but also possesses the same advantages as palladium catalysts immobilized on the polymer supports [3].

Thus, in comparison of catalysts of types 1 and 2 as the parameter that determined the comparable conditions we used the degree of conversion (and the overall reaction time) and not the temperature. Since the activity of catalyst 2 was somewhat lower than that of catalyst 1 the comparable time of reaction with catalyst 2 was attained by applying higher temperature (by 20–49°C). Although at higher temperature usually decreases the selectivity, the data in Table 1 show that even at higher temperature the selectivity on catalyst 2 is better.

**Table 2.** Variation of selectivity with time of hydrogenation of compound Ia on type 1 catalyst (23–27°C, 16–20 at)

| Time, h | Conversion, % | Yield of compound, % |      | Selectivity, % |
|---------|---------------|----------------------|------|----------------|
|         |               | IIa                  | IIIa |                |
| 1.5     | 18.6          | 17.9                 | 0.7  | 96.2           |
| 4.5     | 27.0          | 25.8                 | 1.2  | 95.5           |
| 8       | 48.6          | 46.5                 | 2.1  | 95.7           |
| 12      | 74.7          | 71.2                 | 3.5  | 95.3           |
| 14.5    | 90.9          | 85.5                 | 5.4  | 94.1           |
| 16      | 98.2          | 91.4                 | 6.8  | 93.1           |

At exhaustive hydrogenation of farnesylacetone (**IV**) into phyton (**V**) the problem of selectivity is lacking, and the catalyst ShPAK-0.5 can be used without modification. Phyton (**V**) was obtained with the help of unmodified catalyst ShPAK-0.5 in 97.8% yield.



#### EXPERIMENTAL

Chromatographic analysis of compounds **IIa–d**, **IIIa–d**, **IV** was carried out on chromatograph LKhM-8MD (capillary column 25 m, stationary phase SE-30, 22°C).

**Catalyst preparation.** (1) Catalyst on alumina support for exhaustive hydrogenation. Commercial catalyst ShPAK-0.5 (0.5% of Pd on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was placed in a porcelain dish and calcined in a muffle for 2 h at 350–450°C. The catalyst was cooled, placed into a round-bottom flask equipped with a reflux condenser and a capillary for hydrogen input. To the catalyst was poured 2-propanol, the flask was heated to 70°C, and a hydrogen flow through it was passed

for 2 h (in 0.5 h the catalyst turned black). Then the 2-propanol was decanted, and the catalyst was dried at 80°C.

(2) Preparation of the catalyst poisoned with zinc acetate (type 1). To 100 g of the catalyst prepared as above was added 0.5 l of 15% solution of Zn(OAc)<sub>2</sub>, and the mixture was boiled at reflux for 2.5 h, then the catalyst was filtered off, washed with distilled water, and dried at 80–100°C.

(3) Preparation of the catalyst poisoned with ammonia (type 2). The catalyst prepared along procedure 2 was placed into a desiccator and evacuated by a water-jet pump. Then ammonia was introduced into the desiccator to atmospheric pressure, and the vessel was left standing for 10 h. The catalyst thus treated was flushed with air and put into the reactor.

**General method of hydrogenation in a reactor with a fixed-bed catalyst.** Into the reactor of 10 l capacity was charged a cell with 120 g of granular catalyst, then in a vacuum through the bottom discharge valve was charged into the vessel 7 l of liquid [2,2-dimethyl-3-butyn-2-ol (**Ia**) and dehydrolinalool (**Ib**) were used without dilution, 3.5 l of dehydronerolidol (**Ic**) or dehydroisophytol (**Id**) for hydrogenation were diluted with 3.5 l of 2-propanol]. The flow of hydrogen was passed into the reactor, the agitator was switched on, and the reactor was heated to the required temperature (the catalyst type, temperature of the process, and hydrogen pressure are listed in Table 1). As the hydrogen was consumed, it was added to the initial pressure value. The reaction mixture in the reactor was sampled through a capillary and analyzed every hour. On completion of the process the reactor was cooled to room temperature, and the reaction product was discharged under hydrogen pressure. The compound obtained was analyzed by GLC and subjected to rectification.

#### REFERENCES

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