

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PRODUCING CATALYSTS

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As known, porous carrier substances impregnated with zinc- and cadmium salts of organic acids, above all those with an active surface like active carbon, silicagel and the like are catalysts for various chemical reactions especially for the thermal production of organic vinyl esters of acetylene and the corresponding organic acids, but they may also be used f. i. for the thermal production of vinyl chloride from acetylene and hydrogen chloride, whereby the catalyst is formed in the course of the process. Such catalysts were produced hitherto in such a way that an aqueous solution of the zinc or cadmium salt was absorbed by active carbon or if necessary by silicagel, pumice stone or the like whereby generally in order to concentrate the metal salt in the carrier an amount of the solution was added in excess and hereafter the water was extensively removed by drying. In order to get a catalyst having little water, a long drying in the vacuum was necessary by which in consequence of the unavoidable escaping of acid vapors the material of the vacuum dryer was corroded and basic zinc or cadmium salts were formed, the equal regeneration of which in the highest active form is very difficult because of the influence of the acid on the catalyst being employed. Besides, such a drying under technical conditions does not yield only an approximately anhydrous catalyst. Consequently, at the beginning of producing vinyl acetate e. g. important amounts of acetic acid-water mixtures are formed, corroding the walls of the reaction room and of the accessory apparatus, causing a partly decomposition of the formed vinyl acetate into acid and acetaldehyde and making difficult the isolation of the vinyl acetate from the raw reaction product.

It has now been found that catalysts, absolutely free from water, may be easily produced whereby the above mentioned process of drying the catalyst which is connected with difficulties in materials and an expense of time and costs is not necessary.

The new method of producing consists in impregnating the carrier substances with a melting consisting of a mixture of the organic zinc- or cadmium salts to be employed with the corresponding salt of a basic nitrogen compound, whereby, if necessary, an excess of the free basic nitrogen compound may be present. Generally, anhydrous meltings of this kind will be employed; a melting not absolutely free from water however, yields—according to the points of view demonstrated in the introduction—a still much more suitable catalyst than that one obtained

by impregnating the carrier with aqueous solutions of zinc- and cadmium salts. If using as starting material zinc- or cadmium oxides and carbon acids which contain no or small amounts of water, the formed or given amount of water may be easily bound partly or wholly by adding corresponding quantities of acid anhydride.

The impregnation of the porous carrier substances, like f. i. active carbon, with such meltings proceeds surprisingly well. The melting is simply mixed with the active carbon by stirring resp. by mixing thru, whereby it is best, if the melting is added to the active carbon which is moved in a rotating drum heated if necessary. Then the catalyst may be applied directly e. g. for producing vinyl acetate.

It is surprising that the impregnation in a compact form yields catalysts which—containing the same amount of zinc- or cadmium salts—are as active as those produced in a troublesome way with aqueous solutions. Further it is surprising that such high concentrations of the zinc- and cadmium salts can be obtained with the salts of basic nitrogen compounds at temperatures lying below those for the dissociation or splitting off of ketone of the metallic salts as the following examples show. It is further surprising that the nitrogen compounds brought into the catalyst do not injure the activity of the catalyst. Hereby also the possibility is given to produce catalysts containing specially large amounts of zinc- or cadmium salt whereby they are especially capable.

Example 1

Basic ammonium acetate, produced by leading ammoniac into glacial acetic acid until saturation at 100° solves—heated up to 140°—the 1,8 fold of its weight of zinc acetate. Well suited additions to the catalysts are e. g. the following:

(a) 12 kg of glacial acetic acid are saturated with ammoniac at 100°. At about 140° 18,6 kg of glacial acetic acid and 12,4 kg of zinc oxide are gradually added at the same time and solved in the melting.

(b) 12 kg of glacial acetic acid are saturated with ammoniac at 100°. At about 140° 10,6 kg of zinc oxide and a mixture of 15,0 kg of glacial acetic acid and 4,5 kg of acetic anhydride are gradually added at the same time and solved in the melting.

(c) 12 kg of glacial acetic acid are saturated with ammoniac at 100°. At about 140° 12,4 kg of zinc oxide and 15,6 kg of acetic anhydride are

gradually added at the same time and solved in the melting.

In all cases homogeneous meltings are formed, being sufficient thin liquid as to be absorbed equally by 30-35 kg of active carbon and thereby yielding a catalyst directly to be applied for producing vinyl acetate being at least equivalent to a catalyst produced with aqueous solutions. Not mentioning that the concentration and drying process was omitted, the catalyst yielded according to (a) at the beginning of producing vinyl acetate much less aldehyde and aqueous reaction product than the catalyst produced with aqueous solutions dried as far as possible in a troublesome way. In the production of the catalyst according to (b) the forming of aldehydes and the contents of water still more declined; in the catalyst obtained according to (c) these undesired secondary reaction products were completely lacking.

Example 2

A solution of 60 g of urea in 120 g of glacial acetic acid solved at 100° 60 g of anhydrous zinc acetate, at 130-150° further 180 g more, at 160° once more 60 g. On the whole the fivefold of the weight of the urea was solved, resp. a 62,6%ic solution of zinc acetate was obtained. This too

was easily absorbed by the active carbon and yielded a special active catalyst.

Example 3

5 The neutralization product of 79 g of pyridine and 30 g of glacial acetic acid solves at 80° 79 g of anhydrous zinc acetate, at 125° once more the same quantity and at 150° further 79 g, wholly 237 g that is the threefold quantity of the applied pyridine.

Example 4

15 A solution of 35 g of hexamethylen tetramine in 60 g of glacial acetic acid solves till 150° 70 g of anhydrous zinc acetate.

Example 5

20 30 g of glacial acetic acid were neutralized with 50,5 g of triethanol amine. At 120° this melting solved 50,5 of anhydrous zinc acetate, at 140° once more 50,5 were nearly completely solved.

Example 6

25 The neutralization product of 93 g of aniline and 60 g of glacial acetic acid solves at 140° about the same weight of anhydrous zinc acetate.

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