ISSN NO: 2770-0003
Date of Publication: 02-12-2021

Modern Acetylene Hydrochlorination Catalysts

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Abstract: The paper presents the results of the analysis of patent literature on the development of mercury-free catalysts for the process of hydrochlorination of acetylene. Catalysts based on gold chloride and base metal chlorides are considered, and a comparative analysis of these catalysts is carried out.

Key words: vinyl chloride, acetylene hydrochlorination, gold chloride, vinyl chloride, acetylene, hydrochloride, catalyst, base metals.

Introduction.

At the moment in Russia, almost a third of vinyl chloride is obtained by hydrochlorination of acetylene [1]. There are two methods using acetylene as raw material:

1. Hydrochlorination of acetylene, where the raw material is pure acetylene and hydrogen chloride;
2. Combined method, where the raw material is pyrolysis gas with an acetylene content of at least 8% and hydrogen chloride.

The latter method involves carrying out the process in several stages, the first of which is the direct chlorination of ethylene from pyrogas to 1,2-dichloroethane, which is then cracked to obtain vinyl chloride and hydrogen chloride.

$CH_2=CH_2 + Cl_2 \rightarrow CH_2Cl\text{-}CH_2Cl$

$CH_2Cl\text{-}CH_2Cl \rightarrow CH_2=CHCl + HCl$

At the second stage, the formed hydrogen chloride enters the acetylene hydrochlorination stage.

$CH\equiv CH + HCl \rightarrow CH_2=CHCl$

The hydrochlorination process uses a catalyst consisting of mercury (II) chloride on activated carbon. Mercury chlorides are toxic (hazard class 1), and they also form a mobile complex with hydrogen chloride, which is carried away from the catalyst surface.

Since 2013, the number of studies and patents on mercury-free catalysts for the hydrochlorination of acetylene has skyrocketed. As a result of the analysis it was revealed that the chlorides of gold, iridium, platinum and palladium are the most active in relation to the hydrochlorination reaction (Fig. 1). Since catalysts based on gold salts have shown the greatest activity, most patents on non-mercury catalysts for the hydrochlorination of acetylene suggest using gold chlorides as an active substance [2].

With the new catalyst, the conversion of acetylene and the selectivity of the process were more than 99.9% [3], higher than that of the mercury catalyst. The disadvantage of this catalyst is its rapid deactivation due to gold reduction.

This problem is solved by introducing various additives: copper salts, salts of other noble metals, organic compounds such as phenanthroline, thiourea, etc. Also, additives can reduce the gold content in the catalyst, thereby reducing its cost.

The addition of thiourea [4] to gold salts makes it possible to reduce the gold content in the catalyst to 0.25 wt%, but the acetylene conversion and selectivity also becomes lower (90% and 95%, respectively).

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Salts of ruthenium, palladium, or platinum [5, 6] as additives to the catalyst exhibit a stabilizing effect - the catalyst service life increases from 200 h without loss of activity to 500 h. Using this catalyst, the acetylene conversion is 98%, and the selectivity is 99%. The disadvantage of these additives is the high price of precious metals.

The most promising are catalysts based on gold and copper chlorides [7, 8]. Copper chloride can catalyze the hydrochlorination reaction without gold chloride, which can reduce the amount of noble metal used and reduce the cost of the catalyst. Also, the addition of copper chloride makes it possible to increase the life of the catalyst, acting as a stabilizer that prevents the reduction of Au^3 + to Au^0.

Since gold is an expensive noble metal, there has been an increased interest in the catalytic ability of base metals in relation to the hydrochlorination reaction of acetylene.

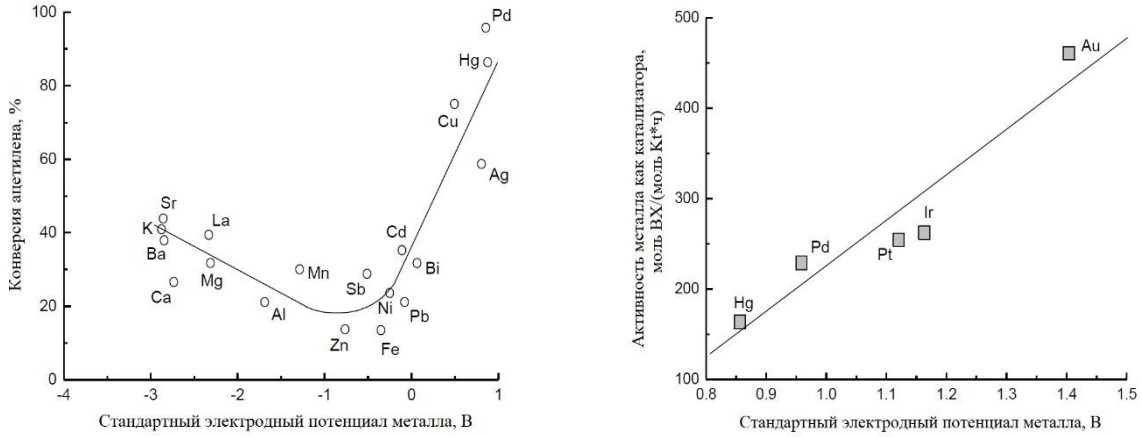

Fig. - Activities of different metal chlorides on AC for the process of acetylene hydrochlorination

Copper or barium is used as a catalyst component based on base metals [9, 10]. In this case, the conversion of acetylene is reduced to 30%.

Various additives increase the conversion of acetylene to 80-90%, but the catalyst life is less than 100 hours without loss of activity. Such additives include: phosphoric acid, nitrogen-containing activated carbon, fatty organic acids, complexes of rubidium chlorides with ammonia, etc.

At the moment, the investigated catalysts without the addition of noble metals are less active than catalysts containing gold.

The most promising is a catalyst containing gold and copper chlorides on activated carbon [11], where the total metal content is 3 wt%, and the Au: Cu ratio is 1: 5. This catalyst is more active, safer than mercury (hazard class 3, and for mercury - 1) and has the ability to regenerate.

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ISSN NO: 2770-0003
Date of Publication: 02-12-2021

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