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Thus the catalysts with composition Pd-Cu/sibunite were active in a case of selective obtaining 4,4'-diaminostilbene-2,2'-disulfonic acid (DAS) by hydrogenation of 4,4'-dinitrostilbene-2,2'-disulfonic acid (trans-DNS) in water. The product of the reaction, amine, 4,4'-diaminostilbene-2,2'-disulfonic acid (DAS) is used in photographic technology to produce phosphorescent whiteners for fibers and paper and as a bleach.

The starting molecule contains functional groups and C = C-multiple bonds. In the initial DNS, either two NO₂ groups can be reduced with the formation of a diamine and a C = C bond, with the formation of dibenzyl derivatives, destruction of the stilbene bond with the formation of p-aminotoluene sulfonic acid. Alternatively, hydrogenolysis of the sulfo groups is also possible. Therefore, the development of catalysts for the selective reduction of DNS for the preparation of DAS in a high yield is very important both from a theoretical and practical point of view.

We have known that the simultaneous hydrogenation of both the nitro groups and the stilbene C=C bond occurs on Pd catalysts deposited on sibunite and Al_2O_3 . X-ray diffraction and electron microscopy (Fig.-4a, b) have demonstrated that Al_2O_3 has a stronger interaction with the active phase compared to sibunite, which causes a higher activity of aluminum oxide during the hydrogenation of DNS. The formation on the surface of mixed active centers of the type of solid solutions of the Cu₃Pd composition with a particle size of 5 nm and massive PD clusters of 100 nm is established, which causes sufficient uniformity of both the surface and the adsorbed hydrogen. This is probably the reason for the high selectivity of the Pd-Cu/sibunite catalyst in the hydrogenation of DNS (Fig.-4c).

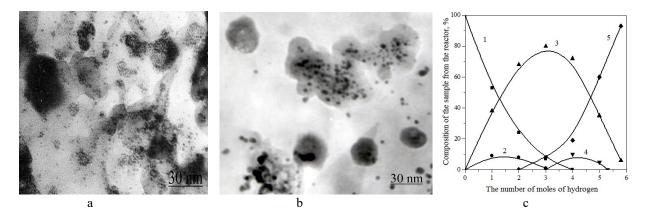


Fig-4: Hydrogenation of 4,4'-dinitrostilbene-2,2'-disulfonic acid (trans-DNS) in water to 4,4'-diaminostilbene-2,2'-disulfonic acid (DAS) on Pd-Cu/sibunite catalyst: a) TEM image of Pd-Cu/Al₂O₃; b) TEM image of Pd-Cu / sibunite; c) change in the composition of the sample during the hydrogenation of DNS on Pd-Cu / sibunite at 25°C and 1.5 MPa according to the results of thin-layer chromatography: 1-DNS, 2-nitrosonitrostilbene; 3-nitroaminostilbene (NAS); 4-nitrosoaminostilbene; 5-diaminostilbene (DAS)

The addition of copper to palladium in an amount of more than 3:7 significantly reduces the rate of hydrogenation of the DNS up to a complete stop. Varying the copper content from 1 to 3 decreases the reaction rate, but increases the selectivity of the process. The optimal catalyst Pd-Cu/sibunite allows to reach the maximum yield of the desired product is up to 91-92% in an aqueous medium. The developed catalyst is stable during hydrogenation of 7-8-fold portions of DNS.

CONCLUSION

The possibility of using nitro compounds in industry and agriculture as relatively inexpensive chemicals in the production of various valuable chemical products is currently attracting chemists. A special place among the chemical transformations of nitro compounds is occupied by the hydrogenation reaction in the liquid phase up to aromatic amines. In a frame of short review adsorption of nitro compounds under conditions of liquid-phase hydrogenation using palladium catalysts, theoretical and experimental aspects of data from literature and patent sources are discussed. The authors also have described their experiments with the selective hydrogenation of 4,4'-dinitrostilbene-2,2'-disulfonic acid over Pd-Cu catalysts