The influence of the 1,2-dichloroethane hydrodechlorination on the physicochemical properties of bimetallic Ag-Cu loaded BEA zeolite

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Abstract: $Ag_{2.0}Cu_{2.0}$HAlBEA and $Ag_{2.0}Cu_{2.0}$SiBEA zeolites were prepared by conventional wet impregnation and two-step postsynthesis methods, respectively, and investigated in the gas phase hydrodechlorination (HDC) of 1,2-dichloroethane at atmospheric pressure, at 523 K. The state of silver and copper in catalysts at different stages of their biography was characterized by different physicochemical methods such as: low-temperature N_2 sorption, TPR, TEM, XRD, XPS, and TPH. We have shown that after catalytic run both agglomeration of metal particles and their re-dispersion took place and the cause of this phenomenon is the formation of chlorine containing species in spent zeolite catalysts.

Keywords: hydrodechlorination, 1,2-dichloroethane, physicochemical characterization.

1. Introduction

Our earlier works[1-3] clearly show that depending on the kind of synthesis method, zeolite catalysts more or less change upon hydrodechlorination conditions. Prepared by two-step postsynthesis method nickel, silver, nickel - silver and nickel – copper containing SiBEA catalysts have shown resistance for changes in aggressive reaction conditions. On the other hand Ni, Ni-Cu, Ag, Ni-Ag containing HAlBEA catalysts synthesized by conventional wet impregnation were more sensitive for sintering and poisoning by carbon and chlorine containing deposits during HDC process[1-3]. Inspired by our earlier works, we would like to investigate the effect of two-step postsynthesis method of preparation and conventional impregnation on physicochemical properties of zeolite catalysts containing Ag-Cu at various stages of their biographies.

2. Experimental

A tetraethylammonium Beta (TEABeta) (Si/Al = 17) zeolite provided by RIPP (China) was calcined at 823 K for 15 h in air to remove template. Organic-free HAlBEA zeolite was treated with 13 mol L^{-1} nitric acid (353 K, 4 h) to obtain dealuminated SiBEA zeolite, with Si/Al ratio higher than 1300, and then washed several times with distilled water and dried at 363 K overnight. Both forms of BEA zeolite (dealumined SiBEA and acidic HAlBEA) were used as support for the synthesis of metallic catalysts. $Ag_{2.0}Cu_{2.0}$HAlBEA and $Ag_{2.0}Cu_{2.0}$SiBEA were prepared by co-impregnation method of HAlBEA and SiBEA, respectively, and investigated in hydrodechlorination of 1,2-dichloroethane at atmospheric pressure, at rather low reaction temperature. Bimetallic zeolite catalysts were characterized by low-temperature N_2 sorption, TPR, TEM, XRD, XPS, and TPH.

3. Results and discussion

TEM measurements were carried out for Ag-Cu zeolite catalysts at different stages of their biography. The correlation of the samples composition and nanoparticles sizes for the catalysts before and after catalytic reaction leads to classify particles in two categories: small bimetallic nanoparticles slightly monodisperse in size (3-5 nm) with heterogeneous composition, and larger nanoparticles, heterogeneous in size (from 10 to 50 nm) but with homogenous composition (95 % Ag) (**Fig.1**). Additionally, in the case of spent-red-C-$Ag_{2.0}Cu_{2.0}$HAlBEA, third category: monometallic copper small nanoparticles with an average particles diameter from 2 to 5 nm were found. It seems that small copper nanoparticles were formed by aggregation of very small copper clusters that could not be observed for red-C-Ag$_{2.0}$Cu$_{2.0}$HAlBEA due to resolution limits of the microscope. On the other hand, in the case of spent-red-C-Ag$_{2.0}$Cu$_{2.0}$SiBEA we could observe only one category of slightly monometallic (95 % Ag) nanoparticles with diameters from 3 nm to 50 nm. It seems that bimetallic nanoparticles lost Cu and became Ag nanoparticles under hydrodechlorination conditions. The TEM data are in agreement with XRD results obtained for red- and spent- catalysts. Catalytic hydrodechlorination of 1,2-dichloroethane involves changes in the structure of the zeolite catalysts. Except the peaks related to the presence of Ag and Cu nanoparticles, they contain reflections related to AgCl and $CuCl_2$ salts which is a signature of the formation and agglomeration of silver and copper chlorine in both catalysts. This could be the reason of rapid deactivation of these catalysts during hydrodechlorination of 1,2-dichloroethane.

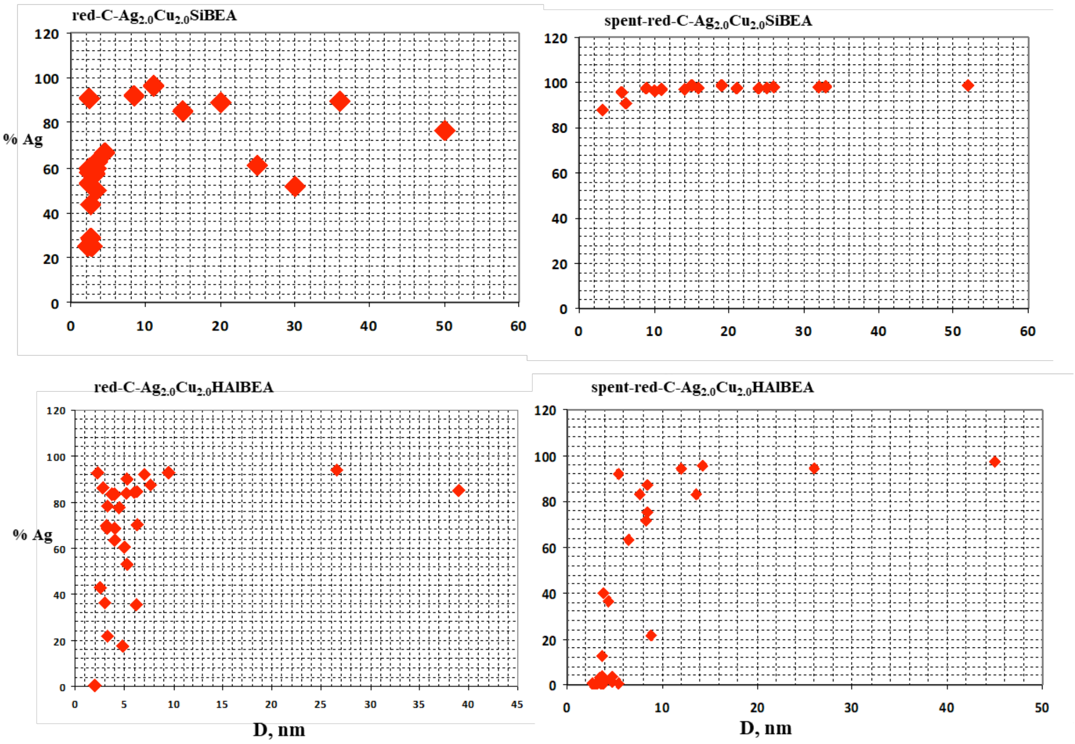

Figure 1. Correlation diagram for composition and size of nanoparticles for Ag-Cu zeolite catalysts.

4. Conclusions

The investigation realized in this work clearly shows that the Ag$_{2.0}$Cu$_{2.0}$SiBEA and Ag$_{2.0}$Cu$_{2.0}$HAlBEA contain mainly very small, Ag and Cu nanoparticles in reduced form of the catalyst. Under hydrodechlorination process on the both catalysts carbon and chlorine species are deposited. We have shown that Ag and Cu nanoparticles agglomerate and transform into AgCl and $CuCl_2$.

References

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