Preparation of metal-containing zeolites by plasma modification

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Zeolite porous materials now become widely used. They are used as adsorbents for drying and purification of gases and liquids, obtaining a high vacuum, etc. In organic synthesis, zeolites are used as catalysts or catalyst supports. In the last case, metal is usually the active component.

Production of metal-containing zeolites, namely recovery and control of metallic groups, is quite difficult process [1,2]. Injection of active metal into the porous structure is usually implemented due to exchange of zeolite cations and ions of corresponding metal from solution of its salt. As a result metal which is located in zeolite exists there in oxidated form. Subsequent usage of this material as catalysts implies the necessity of its thermal reduction. The processing of metal-containing catalysts in the conditions of high temperatures can lead to partial destruction of porous structure. On the other hand, negative influence on the homogeneity of metal distribution takes place, namely it leads to clusters agglomeration and its migration to the external surface of the matrix with blockage of pores and reduction of catalyst's efficiency.

We believe that the application of low-temperature plasma allows to exclude thermal activation stage from the process of metal containing catalysts preparation. This method allows realizing a dehydration of zeolite, its transfer to hydrogenic form and metal reduction at the same time. The process takes place at about room temperature, while thermal reduction requires the temperature up to 823 K.

In low-temperature plasma conditions, zeolite water decomposes as follows:

$$H_2O \rightarrow e^-, H_3O^+, H^\bullet, O^\bullet, H_2, H_2O_2, O_2.$$

Hydroxonium ion created can substitute metal in ion-exchange positions:

$$M_n^+Zt^{n-} + H_3O^+ \rightarrow H_n^+Zt^{n-} + H_2O + nMe^+,$$

while the ions of metal reduce through addition of electrons that are created during water decomposition:

$$Me^+ + e^- \rightarrow Me^0.$$

As a result, metal-containing zeolites with the specified concentration and regular distribution of metal can be obtained. Metal concentration is controlled at the pre-stage of ion-exchanging and is limited by the charge of the zeolite framework. If process needs higher metal concentration, immobilization of metal can be carried from the gas phase in low-temperature plasma conditions, using special compounds as the source of metal. Howsever, in this case the surface of granules is modified to a greater extent than the porous structure of zeolite, due to the non-equilibrium modification process.

Thus, the application of low-temperature plasma for metal-containing catalyst synthesis leads to several advantages. The first is the achievement of homogenous and finally dispersed distribution of metallic clusters on. The other advantage of plasma chemical method is fast and cheap way of zeolites modifying.

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