Novel Method of Preparation of Gold Nanoparticles by Ion Exchange

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Introduction

Last 15 years gold was studied intensively as a catalyst since it shows big potential for many important reactions such as CO oxidation, H2+O2 reaction, reduction of NO by H2 etc.¹-³. It was proved that gold is active when it is in form of small particles (less than 5 nm). The size of gold particles depends on the support used for the preparation and on method of preparation³.

The cation exchange by which protons or other cations on the surface or within the structure of the support are replaced by cations of the active metal leads, with the nobel elements of Groups 8-10, first to the atomically dispersed species, and then after an optional calcinations and careful reduction with hydrogen to extremely small metal particles. The procedure is especially effective with zeolites. It is therefore at first sight surprising that it has not been used more widely or to greater effect for preparing small particles of gold. One possible explanation is limited number of cationic gold complexes available; although the ethylenediamine complex [Au(en)2]³⁺ is known, the ammine of Au⁺, [Au(NH3)2]⁺ has only recently been described. The literature does, however, record a number of attempts to put gold species into zeolites, the Y form being most often used³.

Gold has been introduced into HY zeolite by cation exchange using the [Au(en)2]³⁺ ion, followed by thermal decomposition at 423 K. The 80% of obtained particles had size between 1 and 4 nm³.

Au/NaY and Au-Fe/NaY catalysts were prepared by ion exchange from a HAuCl₄ solution. On pure gold containing sample, they obtained gold particles of 10-40 nm diameter, while in the presence of iron, the mean diameter decreased to 5-8 nm⁴.

In this paper the novel method of preparation of gold/zeolite samples by ion exchange with Au(NH3)₄(NO3)₃ complex and their characterization is described. We could not find the literature data on zeolite by cation exchange using the

Fig.1. TEM images of Au/M24 sample reduced at 50°C.
utilization of this complex for Au/zeolite preparation.

Results and discussion

H-mordenites with various SiO$_2$/Al$_2$O$_3$ molar ratio 10 (M10), 15 (M15), 24 (M24), 206 (M206) were used.

The gold samples were produced by ion exchange method. The solution of [Au(NH$_3$)$_4$](NO$_3$)$_3$ complex for ion exchange was prepared by reaction of HAuCl$_4$ with NH$_4$OH$^5$. After ion exchange the samples were undergone to hydrogen reduction at different temperatures for 2.5 h. The concentration of gold in samples measured by EDS was about 1-2 wt. % for all samples.

Three absorption bands of gold species (Fig. 2) with UV-Vis. diffuse reflectance spectroscopy were detected. The band at 195-205 nm corresponds to Au$^{1+}$ ion$^2$; band at 250-380 nm is suggested to be assigned with Au$_n^{m+}$ clusters$^6$; the band at 500-550 nm is attributed to the gold nanoparticles on external surface of zeolite$^2$.

Increase of reduction temperature (Fig. 2) leads to decrease of relative intensity of Au$^{1+}$ peak and to rise of relative intensity of peak of metal clusters and particles showing that contribution of gold cations was decreased and the one of reduced species increased. Maximum band shifts to the blue side of spectra and it is correlated with increasing of nanoparticle size according to Mie theory. The XRD data confirmed that size of metal particles was increased with increasing the reduction temperature. The size of gold particles in prepared samples estimated by Mie theory is less than 5 nm. The TEM image (Fig. 1) shows as that gold particles less than 2.5 nm in diameter can be obtained by this method for low reduction temperature.

Further analysis of optical spectra revealed that SiO$_2$/Al$_2$O$_3$ molar ratio influenced significantly on contribution of gold clusters in the samples due to change of acid properties.

Peak assigned to Au clusters in the spectra recorded is most stable and its relative intensity does not change with temperature of reduction. It is probably due to the strong interaction this species with the support. The clusters seems to be located inside the zeolite channels that prevents their aggregation.

References