eTEM investigation of gold nanoparticle formation in recrystallized zeolite silicalite-1

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1 Introduction

Supported gold nanoparticles, since the first report on their high catalytic activity in low-temperature CO reduction, have been used extensively in organic chemistry reactions [1]. However, supported nanoparticles are prone to sintering which is causing a thermal deactivation of the catalyst [2]. The stability might be improved by encapsulation of individual nanoparticles inside the porous inorganic material. Such materials were proven to be size-selective and stable under extreme temperature conditions [3].

The preparation of gold nanoparticle encapsulated zeolite silicalite-1 is reported. The zeolites are modified by a recrystallization process (desilication), which creates voids and mesopores inside the crystal structure of individual particles. This additional porosity facilitates the formation of gold nanoparticles inside the zeolite channels upon wet impregnation. Environmental Transmission Electron Microscopy (eTEM) is applied for the characterization of the material with the emphasis on the process of *in-situ* nanoparticle formation inside the zeolite channels, sintering stability at elevated temperatures, and the reactivity of the material in the simple oxidation reaction. Furthermore, the influence of degree of desilication and temperature of desilication on the recrystallized material is investigated. Variation in choice of gold precursor and water content for impregnation of the recrystallized silicalite-1 are examined in terms of size of nanoparticles and their distribution inside the zeolite framework.

2 Experimental

All the reported materials were synthesized form commercially available chemicals. Zeolite silicalite-1 was prepared using traditional synthesis method. Preparation of gold recrystallized silicalite-1 was based on impregnation of recrystallized silicalite-1 prepared by an alkaline dissolution-reassembly process in the presence of the surfactant [4]. Obtained materials were investigated using HRTEM in terms of *ex-situ* nanoparticle formation and eTEM for the *in-situ* formation under the atmosphere of hydrogen at elevated temperature. Other analytical techniques like BET, ICP-MS, and XRD were applied for the standard characterization.

3 Results and discussion

eTEM imaging of the gold recrystallized silicalite-1 was performed under elevated temperature and hydrogen atmosphere in order to investigate the *in-situ* formation of gold nanoparticles. Figure 1 depicts recrystallized zeolite crystals with encapsulated gold nanoparticles. Immediate *in-situ* formation of Au-NP was observed under the irradiation with electron beam in vacuum (right side Figure 1). In this case, nanoparticles were located at the surface of the inner voids in the crystals. Gradual reduction of metal nanoparticles was performed using blanked-beam, where specimen was exposed to the electron beam only for the time to sample an image (left side Figure 1). In this case, distribution of nanoparticles is more uniform between the voids surface and channels of the zeolite.

Stability against sintering was monitored *in-situ* in oxygen atmosphere at elevated temperatures in eTEM and showed promising results. Catalytic activity was confirmed based on simple oxidation reaction.

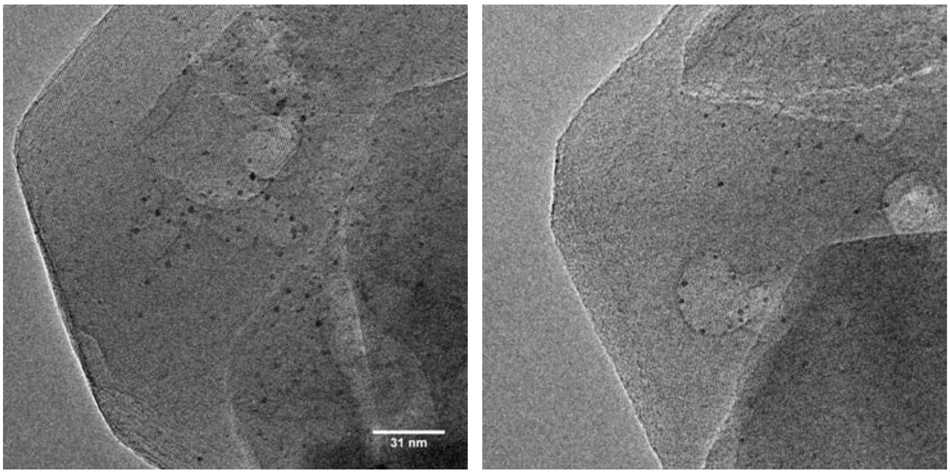

Fig. 1. eTEM image of recrystallized silicate-1 with encapsulated Au nanoparticles. Left: beam-blanked specimen; right: constant-illumination specimen. Cavities inside the zeolite crystal are visible as large voids localized in the centre of the crystal. Nanoparticles are visible in the matrix of zeolite – in the channels and at the edges of cavities. Gold nanoparticles are 3nm in size. The channels structure of silicate-1 is visible.

4 Conclusions

Environmental Electron Transmission Microscopy was used as a main tool for *in-situ* investigation of nanoparticle formation in the recrystallized zeolite silicalite-1. Various parameters influencing the characteristics of material were examined using above technique. Stability for sintering and catalytic activity were proven and observed.

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