Crystal structure of Ag^+-exchanged low silca X-type zeolite and its structural and chemical changes under moderate pressure and temperatrue

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Faujasite is one of the natural zeolites and occurs with olivine in basaltic volcanic rocks or augite in limburgite. Faujasite crystallizes in $Fd\bar{3}$ space group containing sodalite cages arranged in the diamond structure via double 6-membered ring. This results in forming supercages outlined by 12-membered rings. Faujasite-type zeolites have been used in industrial applications for ion exchange, molecular sieving and catalysis. One of the synthetic faujasites with lowest silica content is called low-silca X (LSX, Si/Al =1.0), which has been studied intensively because of its ion exchange performance. Amongst exchangeable cations, Ag^{2+} is known to be strong oxidizer but difficult to synthesize. We have, however recently shown that Ag^{2+}-form of zeolite can be stabilized via pressure and temperature treatment in small-pore zeolite, natrolite. In order to develop a potentially novel catalytic property in large-pore zeolite, Ag^+-exchanged LSX (Ag-LSX:$Ag_{96}Al_{96}Si_{96}O_{384}\cdot nH_2O$) has been prepared and treated under moderate pressure and temperature conditions. We observe the formation of zero-valent silver particles at 1.4GPa which is recovered after pressure release. We have derived structural models of the as-prepared Ag-LSX and pressure- and temperature-treated Ag-LSX using high-resolution synchrotron X-ray diffraction data. We found 96 silver cations and 245 water molecules distributed at seven and five distinctive sites, respectively, in the as-prepared Ag-LSX model. On the contrary, pressure- and temperature-treated Ag-LSX exhibits reduced amount of silver cations by 47.4% and increased amount of water molecules by 40.8% at six and seven distinctive sites, respectively. Electron paramagnetic resonance (EPR) and scanning electron microscopy (SEM) measurements indicate that charge-disproportionation has occurred via pressure- and temperature-treatment to turn the original monovalent silver cations to divalent silver cations and zero valent silver nanoparticles. Ethylene epoxidation measurements are underway to test novel catalytic performance of pressure- and temperature-treated Ag-LSX.