Local Geometry and Electronic Properties of Nickel Nanoparticles Prepared via Thermal Decomposition of Ni-MOF-74

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Metal-organic framework (MOF) provides high selective catalytic activity resulting from the porous crystalline structure[1]. Particular interest is in M-MOF-74 class (M = Mg, Mn, Fe, Ni *etc.*) due to the high density of unsaturated M^{2+} cations sites that can selectively interact with different gases. However, these compounds possess poor thermal/chemical stability and limited electrical conductivity. Recently, it was shown that a composite material containing metal nanoparticles and MOFs composite (NP/MOF) would act as a multifunctional material which mitigates the limitation of MOFs[2, 3] and also enhances catalytic properties[1-3]. In our recent work, Ni-NP@Ni-MOF-74 composite was prepared *via* partial decomposition method, which shows evidence of phase separation into fcc-Ni with raising temperature[4]. The NPs synthesized *via* this method generally accompanies cleavage of the ligand-metal bonds that could have a significant impact on the structure which in turns could affect their catalytic properties. In this regards, investigation of the local structure and electronic properties are of paramount importance to gain insightful information on the functioning of these materials.

In this work, we have investigated local geometries and electronic properties of thermally decomposed Ni-MOF-74 at different heat treatment conditions. The samples subjected to different heat treatment condition [623K-12hrs., 673K-12hrs., 673K-400hrs.] were *ex-situ* characterized using different techniques; that is, pair distribution function (PDF) analysis using high energy X-ray diffraction was performed at BL04B2 beamline, XAFS measurements at the Ni-*K* edge was performed at the BL01B1 beamline and hard X-ray photoelectron spectroscopy (HAXPES) was performed at the NIMS BL15XU beamline, SPring-8, Japan.

Our PDF study reveals the formation of fcc-Ni nanoparticles with a mixture of MOFs phase in the sample heated at 623K for 12hrs. Raising the heat treatment condition led to complete precipitation of fcc-Ni nanoparticles in the matrix of MOFs. The local structure and valence state investigated using XAFS show evidence of ligand to metal charge transfer process and reduction of Ni^{2+} for the sample heated above 623K-12hrs., additionally, the Ni lattice is found to be slightly compressed resulting from surface stresses in nanosized particles/surface ligand environment. The electronic structure measurement results using HAXPES show a significant narrowing of the valence band and a decrease in *d*-band centering with increasing temperature indicating effective catalytic properties of the Ni-NP@Ni-MOF-74 composite.

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