Supplementary Information

Enhanced hydrogen chemisorption and spillover on non-metallic nickel subnanoclusters

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Fig. S1 Detailed procedures of *in situ* XAFS measurements for (a) NC-loaded ZTCs and (b) NN-loaded ZTC. Each measurement was aimed to obtain the XAFS spectra of the arrowed samples.



Fig. S2 TEM-SAD analysis results on (a-c) ZTC-NN(L)H, (d-f) ZTC-NC(L)H, and (g-i ZTC-NC(V)H. (a,d,g) TEM images. The area used for the SAD analysis is highlighted with a red circle. (b,e,h) TEM images on the ranges used for the SAD analysis. (c,f,i) SAD patterns. In (c), spots corresponding to Ni(111) and Ni(200) are indicated by arrows. The weak white ring overlapping on Ni(111) corresponds to carbon (10) diffraction derived from the ZTC matrix.

In ZTC-NN(L)H, it is possible to find several weak diffraction spots corresponding to Ni(111) and Ni(200), indicating that Ni nanoparticles in this sample exist as metal crystals. On the other hand, in ZTC-NC(L)H and ZTC-NC(V)H, no diffraction spot was found, indicating that Ni species in these samples are amorphous.



Fig. S3 EDX mapping images of (a,b) ZTC-NN(L)H, (c.d) ZTC-NC(L)H, and (e,f) ZTC-NC(V)H. (a,c,e) and (b,d,f) are C- and O-mapping, respectively. The mapping area is the same as that for Ni-mapping (Fig. 3c,f,i). Scale bars are 20 nm.

C- and O-mappings of ZTC-NN(L)H and ZTC-NC(L)H do not display apparent overlapping at the positions of the Ni species. A possible reason is the insufficient resolution of C- and O-mappings, because of the strong background signal derived from the ZTC matrix which consists of carbon and also includes a large amount of oxygen (as high as 8.4 wt%). Thus, the O signal distributed at the positions of Ni species might be hidden by the background. Nevertheless, XAFS results clearly indicate that Ni species in ZTC-NC(L)H and ZTC-NC(V)H are not metallic and in unique oxidized conditions (Fig. 5).



Fig. S4 High-magnification STEM-HAADF image of ZTC-NC(V)H.



Fig. S5 A snap shot of the Supplementary Movie (ZTC-NC(V)H), showing a scale bar.



Fig. S6 *K*-edge XANES spectra of ZTC-NC(V)H, ZTC-NC(V)H-H₂, and ZTC-NC(V)H-H₂ treated in H₂ flow at 353 K for 25 min (denoted ZTC-NC(V)H-H₂-353K).



Fig. S7 Pore-size distributions of ZTC and Ni-loaded ZTCs calculated by the density functional theory (DFT) method, in which the equilibrium model of carbon slit pores was used. A sudden drop at 0.8 nm is an artifact inevitable in the DFT method.²

References

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