Electronic Supporting Information (ESI)

A simple and convenient approach for preparing core-shell-like silica@nickel species nanoparticles: highly efficient and stable catalyst for dehydrogenation of 1, 2-cyclohexanediol to catechol

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S1 Regarding the X-ray photoelectron spectroscopy (XPS) results of the Si-20Ni(Y) catalysts

X-ray photoelectron spectroscopy (XPS) was performed by a PHI Quantum 2000 XPS system with a monochromatic Al Kα source and a charge neutralizer. The binding energy (B.E.) was referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon.

Fig. 1 S shows the Ni $2p_{3/2}$ XPS spectra of Si-20Ni(Y) prepared at various G-D-P time. The Ni $2p_{3/2}$ peak in the range of 850 to 858 eV comprises two component peaks with B. E. at *ca.* 854.4 and 856.3 eV, which can be assigned to the nickel ions in the NiO and nickel phyllolicates, respectively [1]. Both the NiO and nickel phyllosilicates are present over the surface of Si-20Ni(4) and Si-20Ni(24); however, with increasing the G-D-P time, the peaks for NiO decrease and those for nickel phyllosilicates increase. This consequence supports the conclusion observed in TEM (Fig. 6) that, the generated nickel phyllosilicates are mainly located on the external surface of core-shell-like silica@nickel species nanoparticles.

S2 Regarding the change of mean diameter of nanoparticles during the G-D-P process

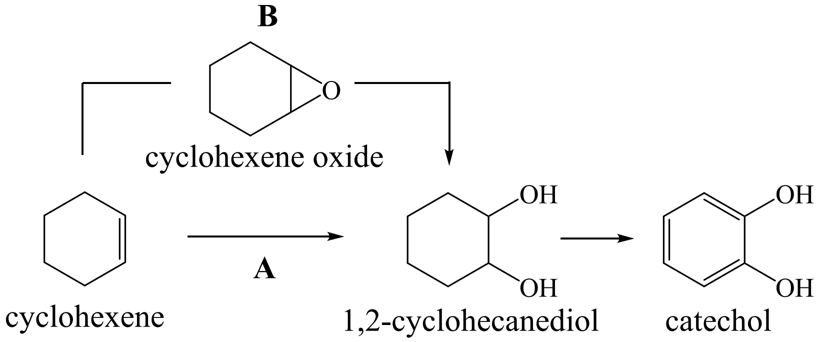
Field emission scanning electron microscopy (FE-SEM) image was performed using a JSM 6700F scanning electron microscope. First, the catalyst was ground and ultrasonically suspended in alcohol; then, it was doped on a silicon chip. Before the measurement, the catalyst was coated by Au film through evaporation to increase its electric conductivity.

Fig. 2 S shows the change of mean diameter of silica@nickel species nanoparticles as a function of G-D-P time measured by FE-SEM. The mean diameters of these particles are estimated by *ca.* 500 particles. The variation of mean diameter of silica@nickel species nanoparticles can be divided into three periods: (a) from the beginning to 2 h of G-D-P time, the mean diameter of silica@nickel species nanoparticles increases steeply from *ca.* 25.4 nm to *ca.* 30.5 nm; (b) from 2 h to 12 h of G-D-P time, the mean diameter of silica@nickel species nanoparticles increases slowly from *ca.* 30.5 nm to *ca.* 30.8 nm; (c) from 12 h to 24 h of G-D-P time, the mean diameter of silica@nickel species nanoparticles increases at a quick speed from *ca.* 30.8 nm to *ca.* 34.6 nm. One can see that, the period (a) can correspond to the stage (3) in Fig. 1 b. During this period, the increase of the mean diameter of nanoparticles can be attributed to the deposition-precipitation of Ni over the silica support. The period (b) can correspond to the stage (4) in Fig. 1 b. During this period, first, silica cores are dissolved into monomeric silicic species gradually; then, these monomeric silicic species generated transfer into the aqueous solution and react with the depolymerized nickel hydroxides, generating nickel phyllosilicates over the outside of silica@nickel species nanoparticles. Generally, the diameter of nanoparticles would decrease with the depolymerization of nickel hydroxides, but increase with the generation of nickel phyllosilicates layers. However, the depth of the nickel phyllosilicates layer generated is probably similar as that of the nickel hydroxides layer consumed, resulting in the essentially unchanged mean diameter value of nanoparticles during the period (b). However, after 12 h of G-D-P time (period c), the mean diameter increases with increasing the G-D-P time. This period can correspond to the stage (5) in Fig.1 b. We have known that, in period (c), almost all of the nickel hydroxides have transformed into nickel phyllosilicates, or the nickel phyllosilicates generated embrace the nanoparticles, and thus prohibit the further transformation from nickel hydroxides to nickel phyllosilicates. Thus, nickel phyllosilicates are aging in this period. It is suggested that the aging probably increases the size of crystal particle of nickel phyllosilicates, leading to the increase of diameter of silica@nickel species nanoparticles.

S3 Regarding the reduction of nickel species during the STEM analysis

Fig. 3S shows the HAADF-STEM image of Si-20Ni(24) catalyst after a long time irradiation of electron beam. We can see that, some dark dots emerge over the surface of core-shell-like silica@nickel species nanoparticles after a long-time direct irradiation during the STEM measurement, which probably ascribed to the reduction of nickel species due to the high energy electrons[2].

Scheme 1S



Scheme 1

Figure 1 S

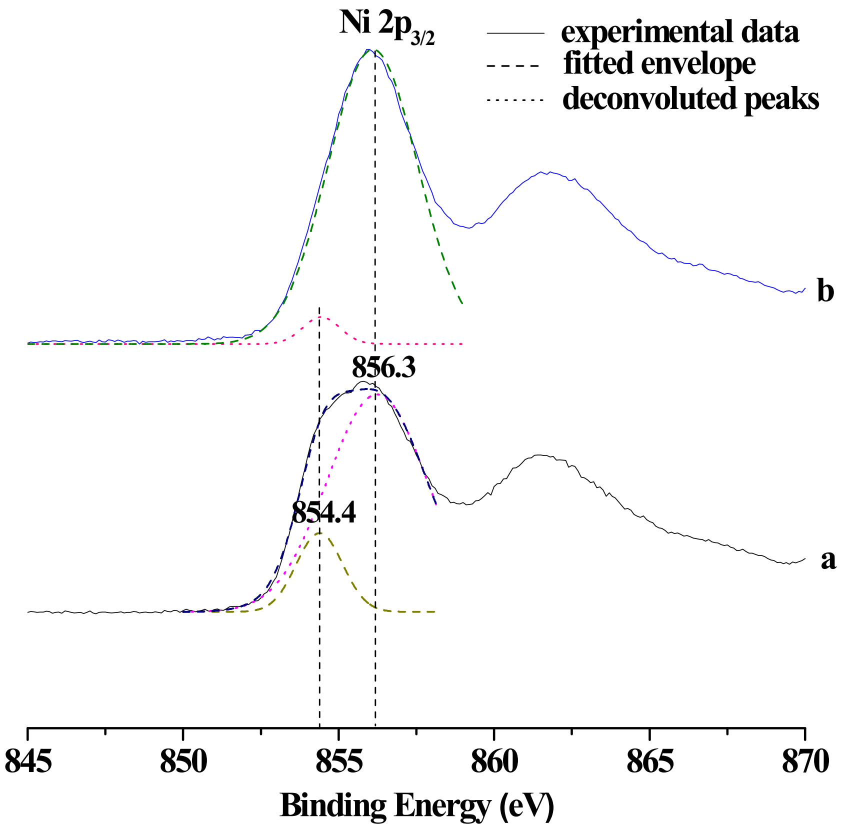


Fig. 1 S Ni2p XPS spectra for Si-20Ni(Y) prepared at various D-P time; Y = (a) 4, (b) 24, respectively.

Figure 2 S

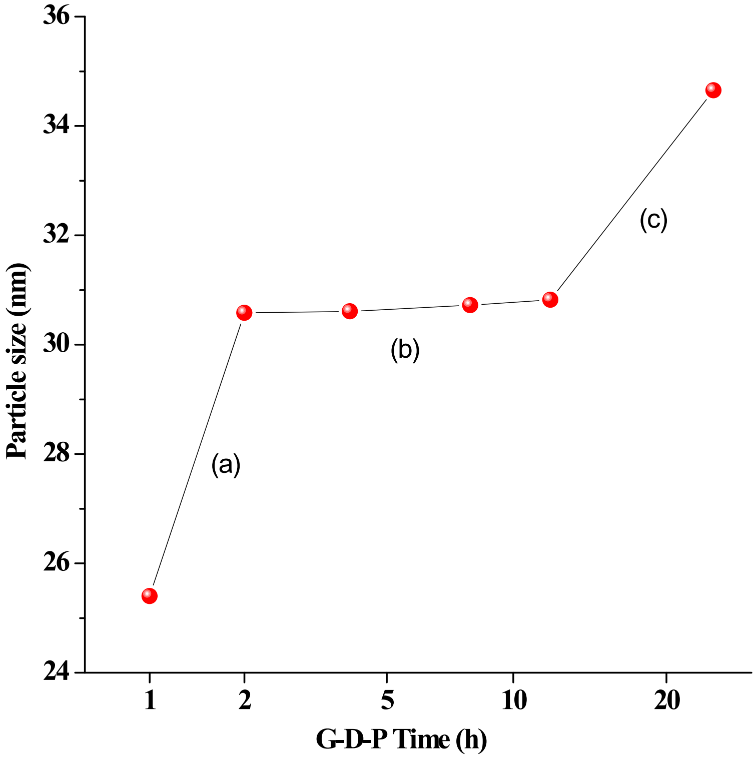


Fig. 2 S Change of mean particle diameter of Si-20Ni (Y) nanoparticles as a function of G-D-P time Y measured by FE-SEM.

Figure 3 S

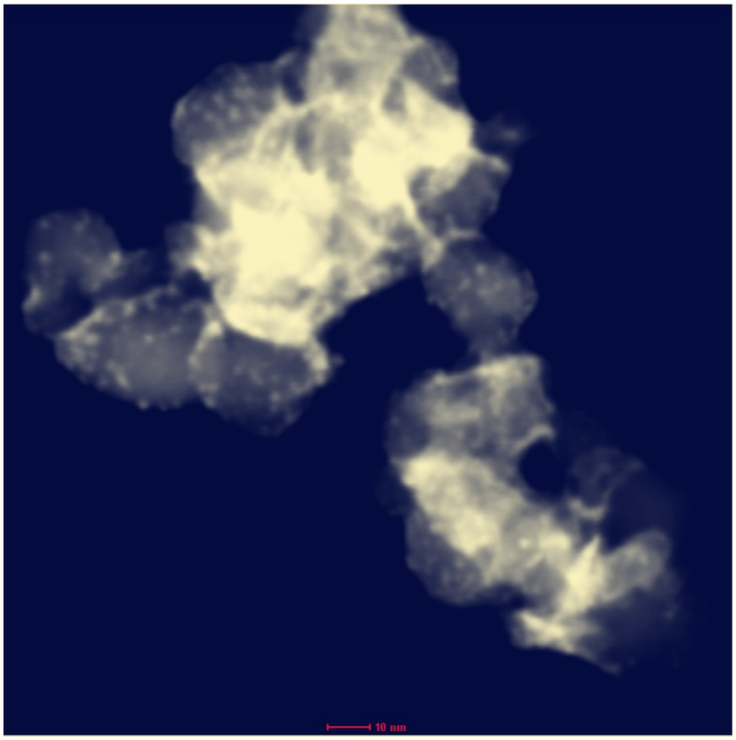


Fig. 3 S HAADF-STEM image of Si-20Ni(24) catalyst after a long time irradiation of electron beam.

Reference：

(1) Lehmann, T.; Wolff, T.; Hamel, C.; Veit, P.; Garke, B.; Seidel-Morgenstern, A. *Micro. Meso. Mater.,* 2012, ***151***, 113-125.

(2) Park, J. C.; Lee, H. J.; Bang, J. U.; Park, K. H.; Song, H. *Chem. Commun.* 2009, 7345.