Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Development of nickel-incorporated MCM-41-carbon composites and their application in nitrophenol reduction

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Experimental

Synthesis of MCM-41 and MCM-41-carbon composites

MCM-41 was synthesized at room temperature using the recipe reported by Grün *et al*.[1] To the solution of 120 mL of deionized water and 9.65 mL of aqueous ammonia (28%), 2.4 g of CTAB was added under continuous stirring. After complete dissolution of CTAB, 10.63 mL of TEOS was added slowly. The molar composition of the resulting solution was 1 TEOS:0.137 CTAB:2.95 NH_3:138.99 H_2O. The solution was stirred for another one hour. The resultant white precipitate was filtered, washed repeatedly with DI water and dried at 90 °C for 24 hours. Finally, the white powder was heated to 600 °C at a rate of 1 °C/min and kept at this temperature for 5 hours under flowing N_2 to remove the template.

The synthesis of MCM-41-carbon composites was exactly the same as that of MCM-41 except that various amounts (0.250. 0.500, 0.750, 1.000 and 1.500 g) of resorcinol were added into the CTAB-water-ammonia solutions and the resultant solutions were then stirred for 30 minutes, followed by the addition of 10.63 mL of TEOS and given amounts of HCHO. The moles of HCHO added were twice those of resorcinol. The samples obtained were labelled as MCM-41-C-x, where x = 0.05, 0.10, 0.15, 0.20, and 0.30, and represents the molar ratio of resorcinol to TEOS.

1. M. Grün, K. K. Unger, A. Matsumoto and K. Tsutsumi, *Microporous and Mesoporous Materials*, 1999, **27**, 207-216.

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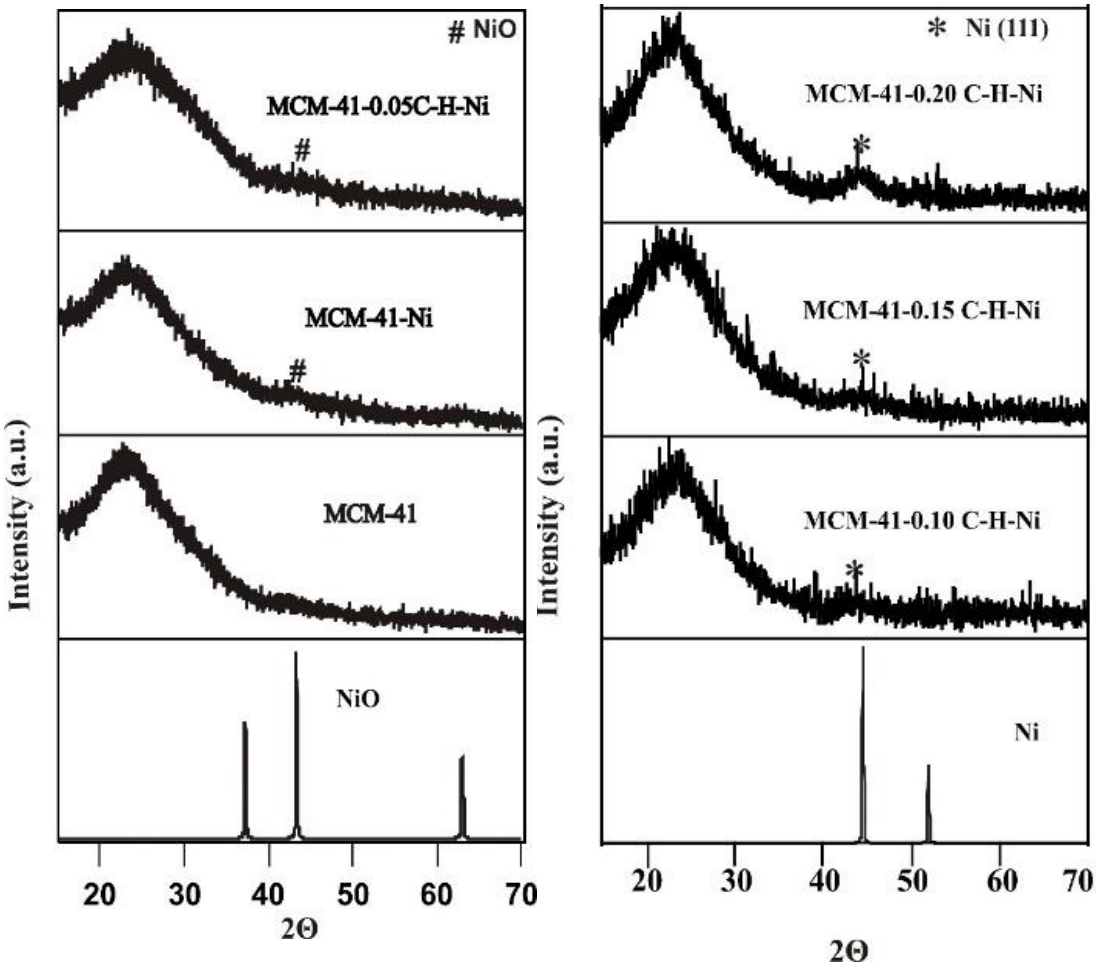

Figure S1. Wide-angle XRD patterns of MCM-41, MCM-41-Ni, MCM-41-x C-H-Ni, Ni [Powder Diffraction File (PDF) 04-0850) and NiO (PDF 47-1049*).*

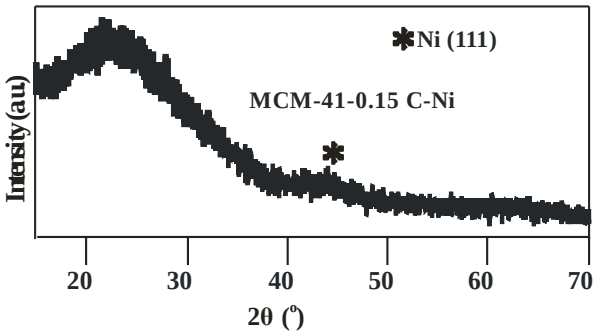

Figure S2: XRD pattern of MCM-41-0.15 C-Ni.

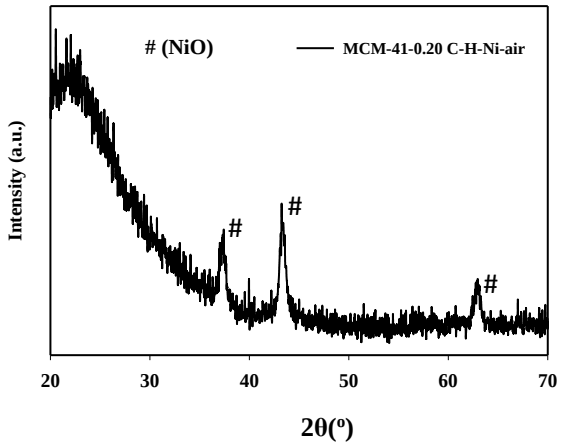

Figure S3: XRD pattern of MCM-41-0.20 C-H-Ni-air obtained after oxidation of MCM-41-0.20 C-H-Ni in air.

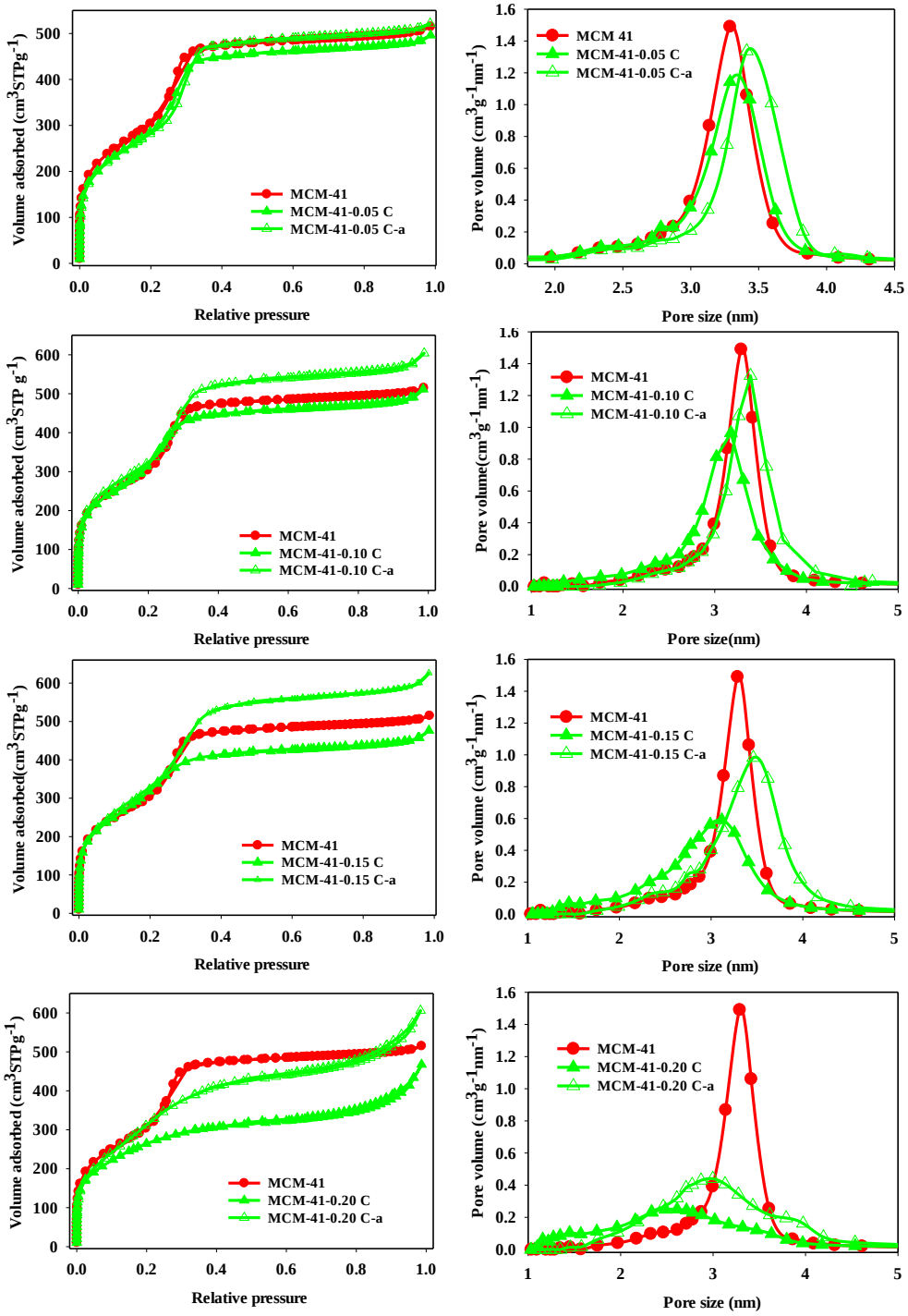

Figure S4: Nitrogen adsorption-desorption isotherms (left) and pore size distributions (right) for MCM-41, MCM-41-x C and MCM-41-x C- a.

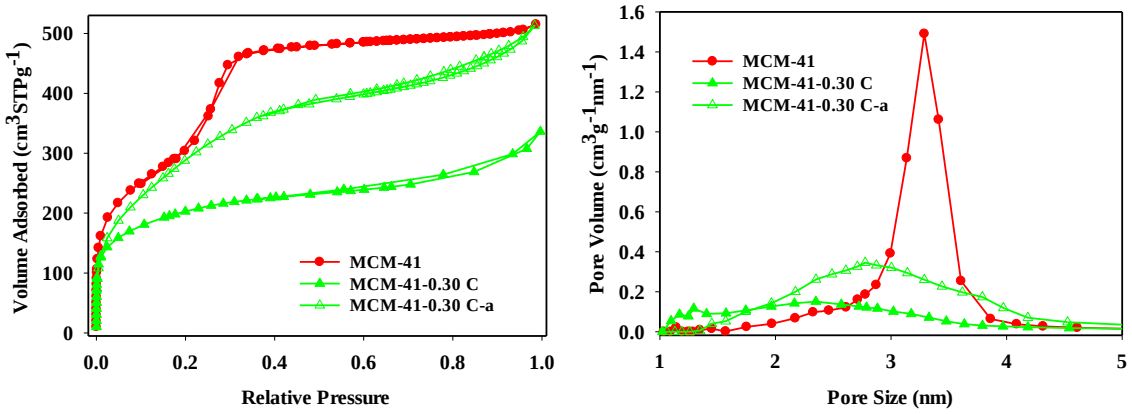

Figure S5: Nitrogen adsorption-desorption isotherms (left) and pore size distribution of MCM-41, MCM-41-0.30 C and MCM-41-0.30 C-a.

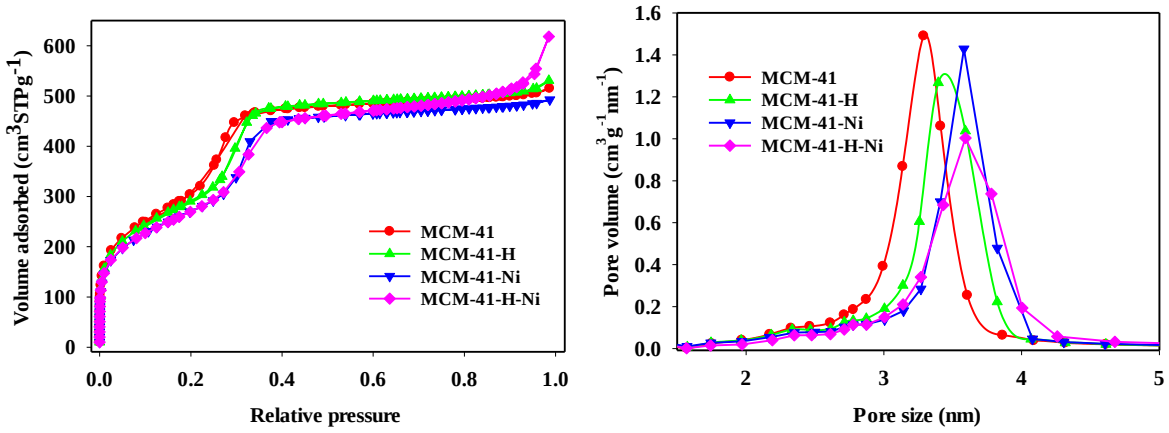

Figure S6: Nitrogen adsorption-desorption isotherms (left) and pore size distributions for MCM-41, MCM 41-H, MCM-41-Ni and MCM-41-H-Ni.

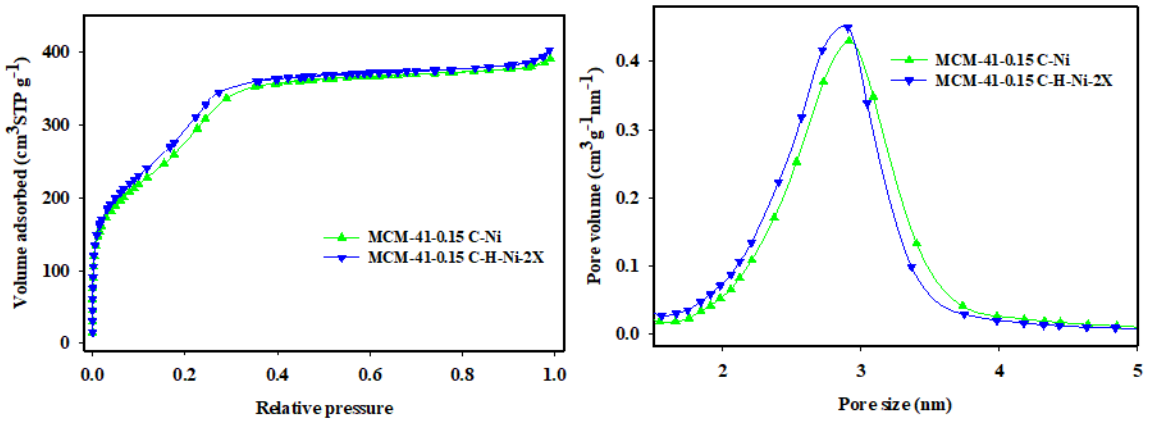

Figure S7: Nitrogen adsorption-desorption isotherms (left) and pore size distribution (right) for MCM-41-0.15 C-Ni and MCM-41-0.15 C-H-Ni-2X.

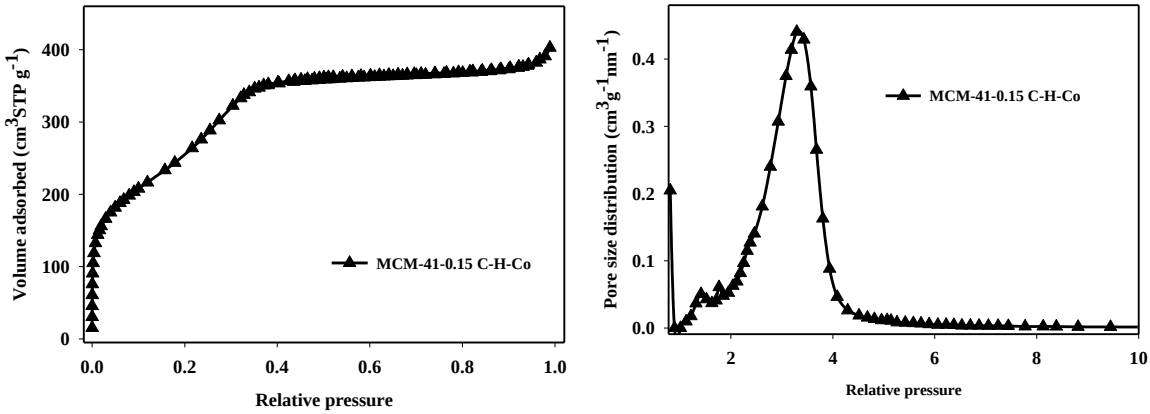

Figure S8: Nitrogen adsorption-desorption isotherm (left) and pore size distribution (right) for MCM-41-0.15 C-H-Co synthesized by a similar protocol as that used for MCM-41-0.15 C-H-Ni except cobalt nitrate was added instead of nickel nitrate.

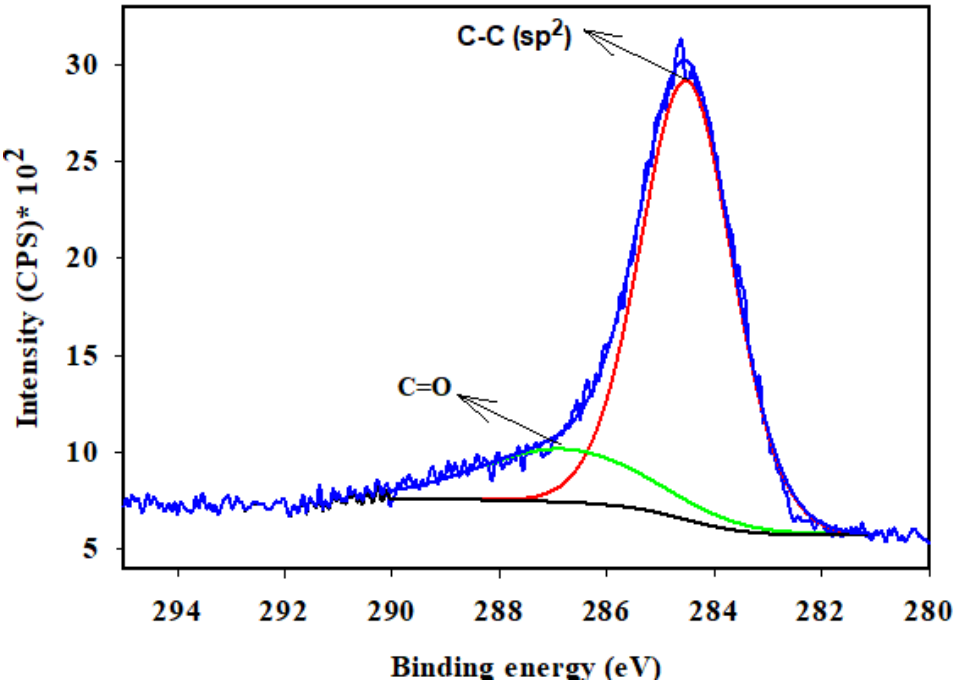

Figure S9: The high-resolution C1s XPS spectra of MCM-41-0.15 C-H-Ni.

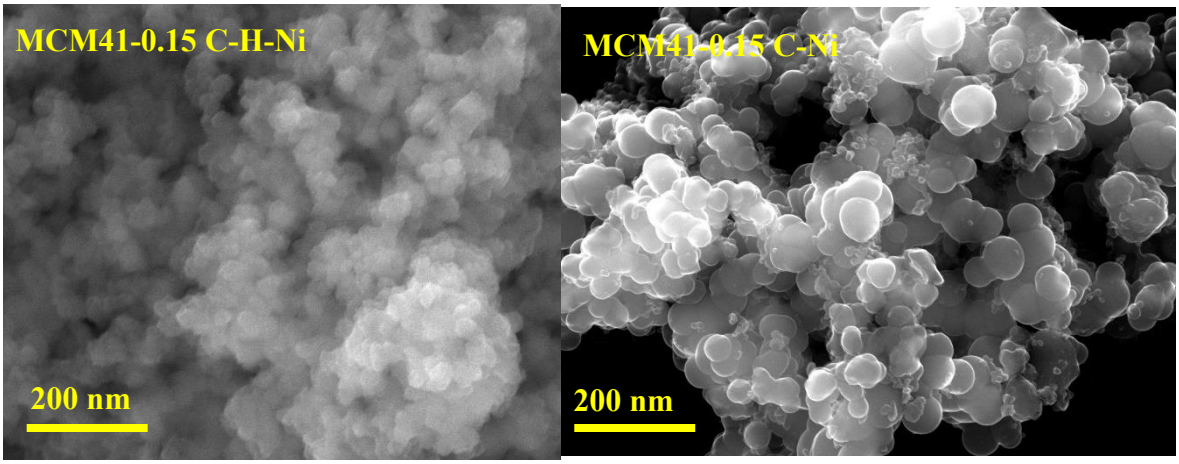

Figure S10: HR-SEM images of MCM-41 0.15 C-Ni (left) and MCM-41 0.15 C-H-Ni (right).

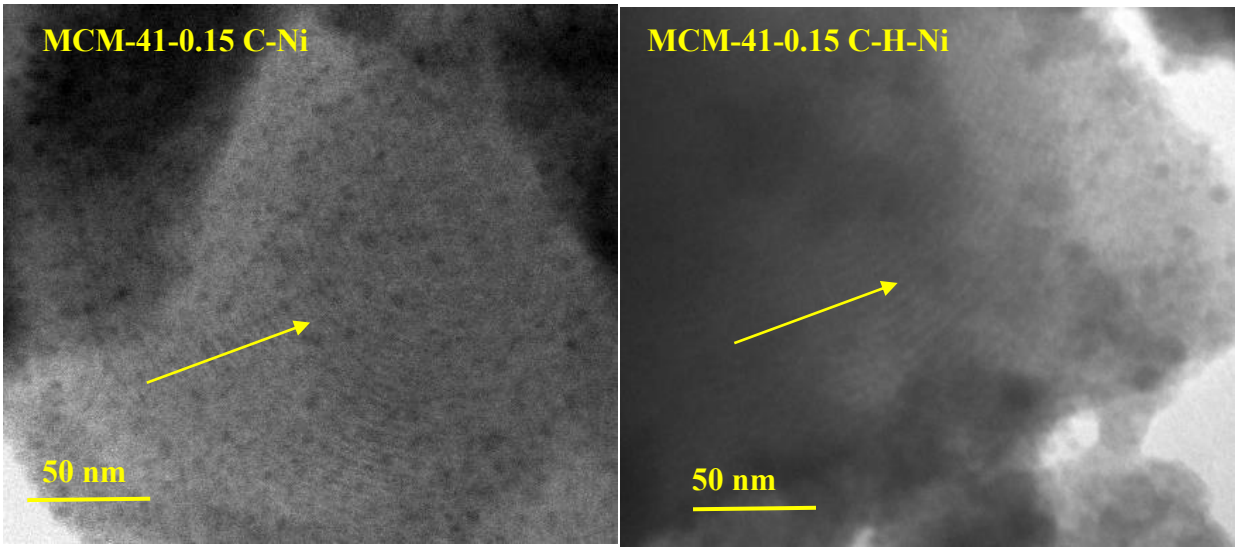

Figure S11: TEM images of MCM-41-0.15 C-Ni (left) and MCM-41- 0.15 C-H-Ni showing ordered channel-like mesopores even after nickel incorporation.

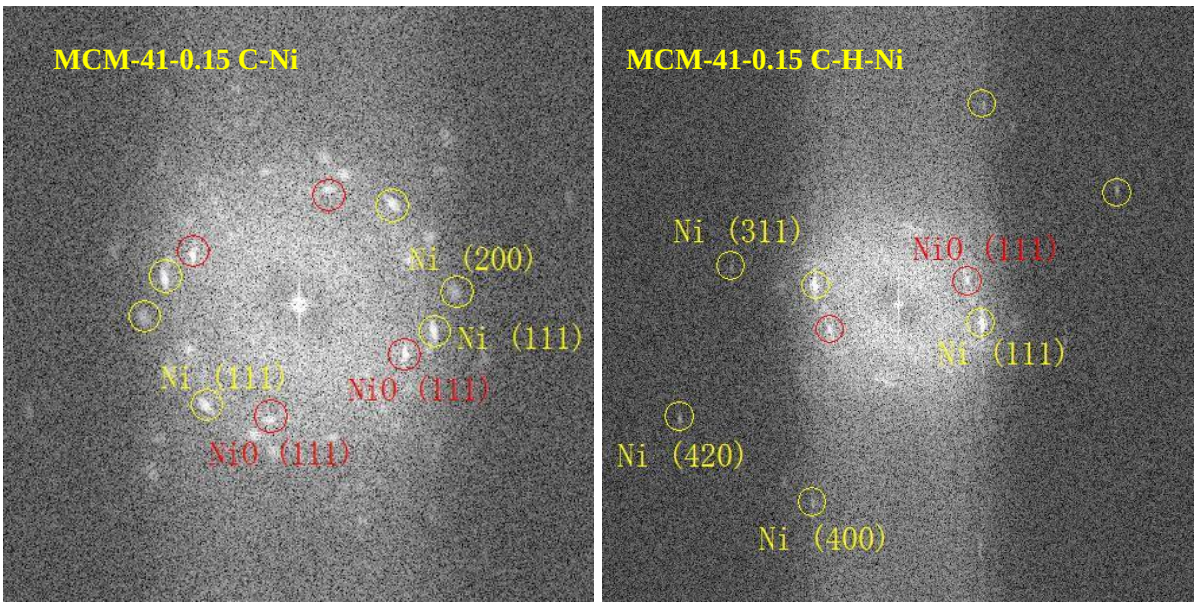

Figure S12: Fast Fourier transform images of the selected area (the cyan-colored frames in Figure 6) of MCM-41-0.15 C-Ni and MCM-41-0.15 C-H-Ni. Note: yellow circles for metallic nickel and red circles for NiO crystalline phases.

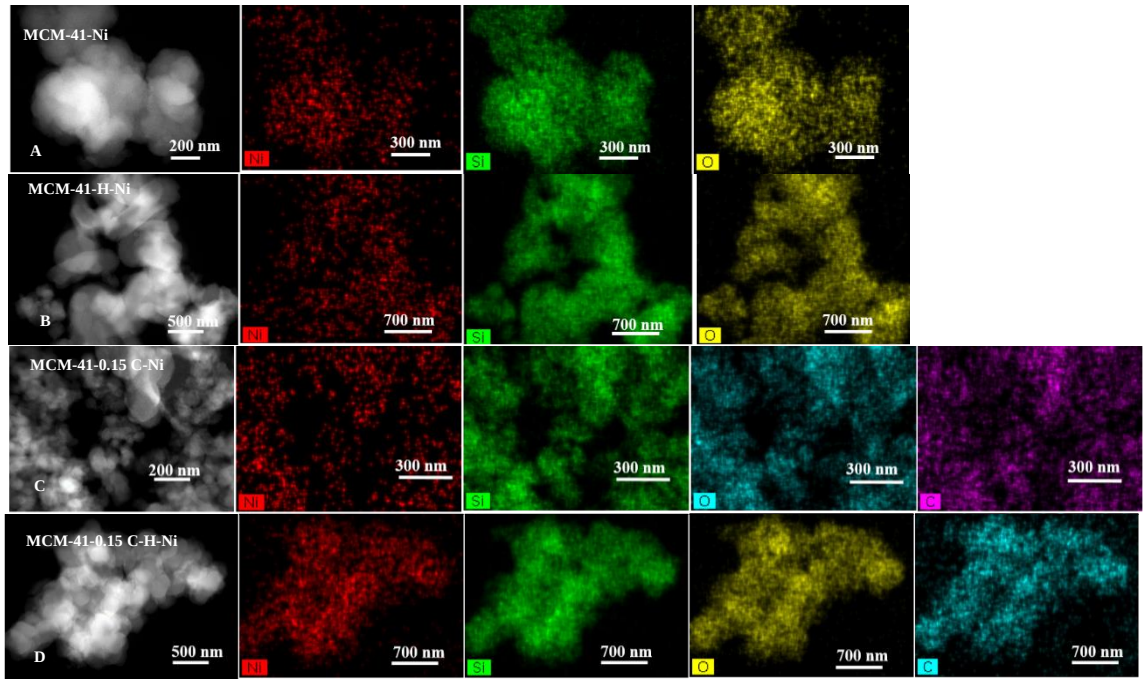

Figure S13: High angle annular dark-field STEM (HAADF-STEM) images with corresponding EDS elemental maps of MCM 41-Ni (Row A), MCM-41-H-Ni (Row B), MCM 41-0.15C- Ni (Row C) and MCM-41-0.15C-H-Ni (Row D).

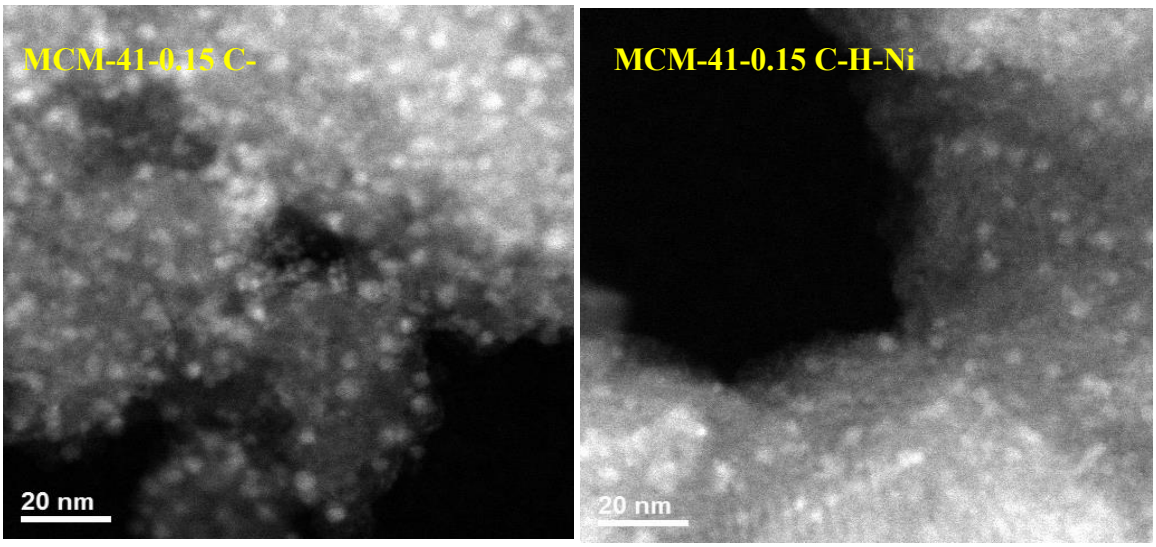

Figure S14: HAADF-STEM images of MCM-41-0.15 C-Ni and MCM-41-0.15 C-H-Ni showing size of Ni/NiO nanoparticles.

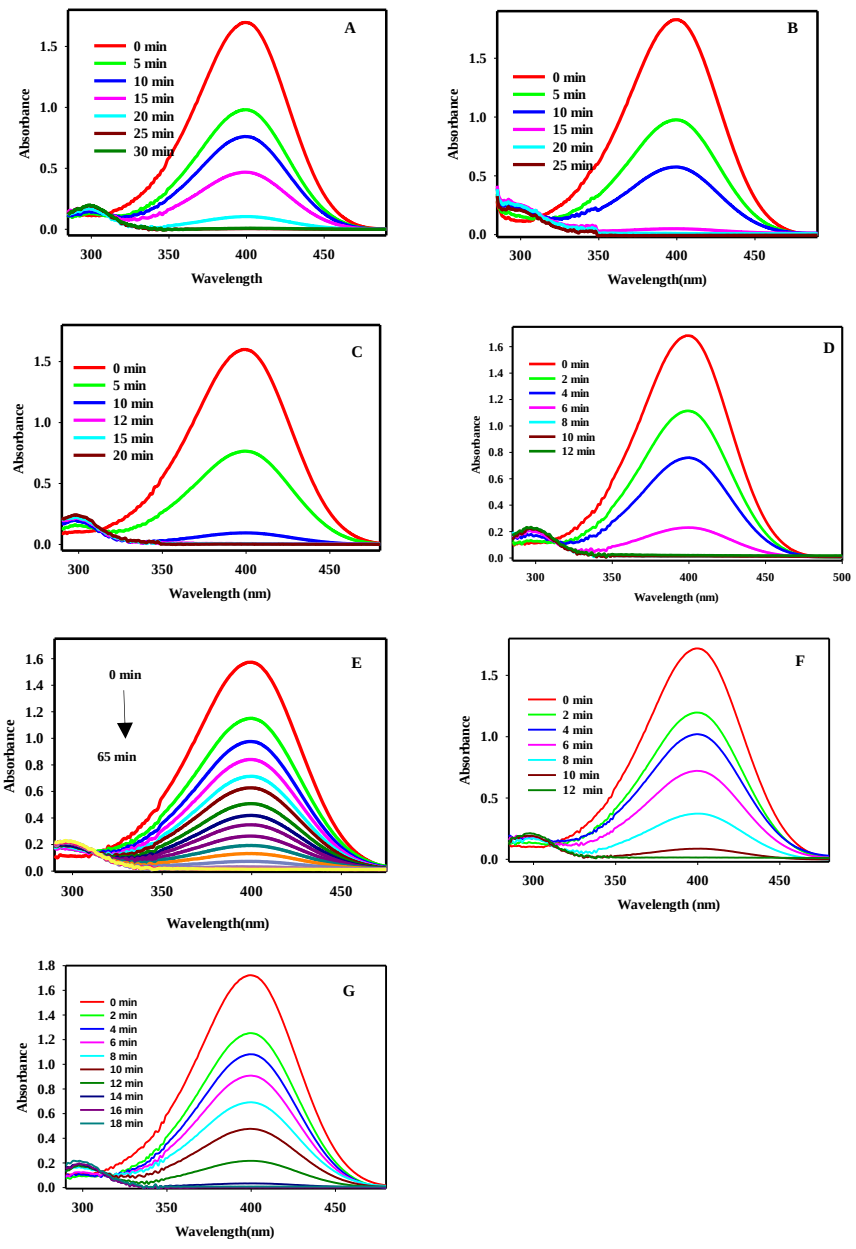

Figure S15: Time dependent absorption spectra for catalytic reduction of 4-nitrophenol by $NaBH_4$ in the presence of (A) MCM-41-Ni, (B) MCM-41-0.05 C-H-Ni, (C) MCM-41-0.10 C-H-Ni, (D) MCM-41-0.15 C-H-Ni, (E) MCM-41-0.20 C-H-Ni, (F) MCM-41-0.15 C-Ni and (G) MCM-41-0.15 C-H-Ni-2X.