New Journal of Chemistry

Preparation of Mesoporous TiO_2-C Composites as an Advanced Ni Catalyst Support for Reduction of 4-Nitrophenol

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Experimental Section

Chemicals. Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly (ethylene oxide) triblock copolymer Pluronic F127 ($PEO_{106}PPO_{70}PEO_{106}$, M_w = 12600) was purchased from Acros Chemical Inc. Phenol (C_6H_5OH, 99.98 wt%), formalin solution (HCHO, 37.0 – 40.0 wt%), hydrogen chloride (HCl, 36.0 – 38.0 wt%), sodium hydroxide (NaOH, 96.0 wt%), ethanol (C_2H_5OH, 99.7 wt%), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98 wt%), 4-nitrophenol(4-NP, 99.0 wt%) were obtained from Shanghai Chemical Company. Titanium tetrachloride ($TiCl_4$, 99.5 wt%), sodium borohydride ($NaBH_4$, 98.0 wt%) were purchased from Aladdin Industrial Inc. All

chemicals were used as received without any further purification. Deionized water was used in all the experiments.

Preparation of phenolic resol precursors

Phenolic resol was prepared from phenol and formaldehyde in a base-catalyzed process. For a typical preparation, phenol (8.0 g) was melted at 40 – 42 °C in a flask and then NaOH aqueous solution (1.7 g, 20 wt%) was added slowly under stirring. After 10 min, formalin (14.1 g) was dropped into it. The mixture was further stirred at 70 °C for 1 h. Upon cooling the mixture to room temperature, the pH value was adjusted to about 7.0 using HCl solution (2 M). Water was removed by vacuum evaporation at 50 °C. The final product was dissolved in ethanol (20 wt%).[1]

Preparation of mesoporous carbon

Pluronic F127 (0.846 g) and ethanol (5.0 g) were stirred at 40 °C for 10 min, resol (5.0 g) obtained above was added to the solution and stirred at 40 °C for 15 min. Then the solution was poured into several dishes. After ethanol evaporation at 40 °C for 5 – 8 h and thermopolymerization at 100 °C for 24 h, the membranes peeled off from the dishes. The as-prepared sample was heated at 600 °C for 2 h under nitrogen to obtain mesoporous carbon.[1]

Characterization. The small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U SAXS system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The d-spacing values were calculated by the formula: $d = 2\pi/q$. X-ray

diffraction (XRD) measurements were carried out on a Bruker D8 Powder X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100F microscope (JEOL, Japan) operated at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Energy-dispersive X-ray spectroscopy (EDX) was performed using a JEM-2100F EDX instrument. Field-emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4800 microscope. Thermogravimetric analysis (TGA) was carried out by using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 30 to 800 °C under air with a heating rate of 5 °C min^{-1}. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Before measurements, samples were degassed in a vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The pore size distribution (PSD) was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) model. The total pore volume (V_{total}) was estimated from the adsorbed amount at P/P_0 = 0.995. The UV-vis spectra were recorded on Shimadzu UV-2550 (Shimadzu, Kyoto, Japan). Temperatures were manually regulated with a water-jacketed cell holder. The Ni contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an IRIS Advantage Duo ER/S (Thermo Fisher Scientific).

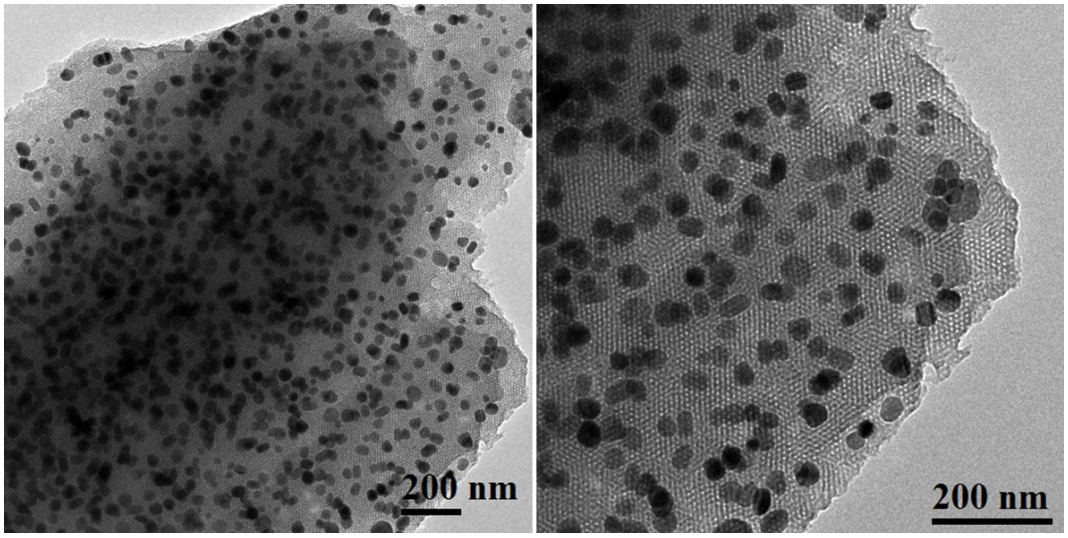

Fig. S1 TEM images of the mesoporous Ni/C sample synthesized by loading Ni nanoparticles on the mesoporous carbon *via* an impregnation method.

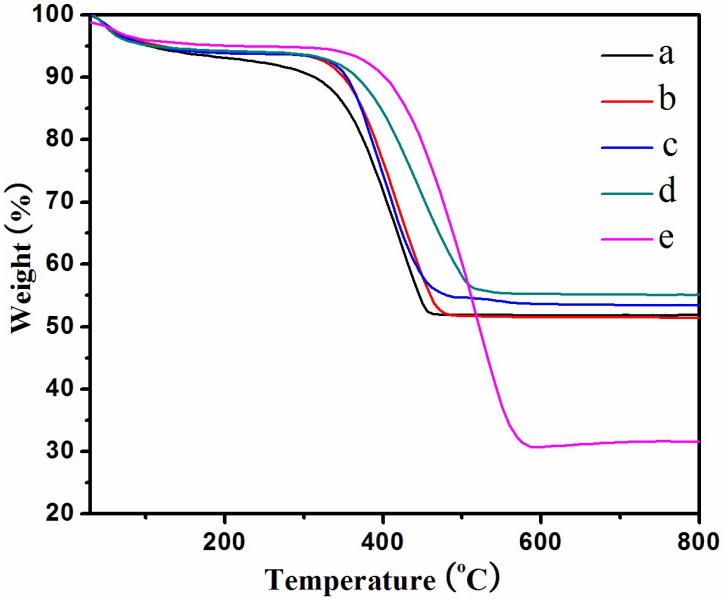

Fig. S2 Thermogravimetric (TG) analysis curves in air of the mesoporous Ni/TiO_2-C composites prepared by using a multi-component co-assembly method with different Ni contents: (a) Ni/TiO_2-C-0, (b) Ni/TiO_2-C-2, (c) Ni/TiO_2-C-5, (d) Ni/TiO_2-C-13, (e) Ni/C sample, respectively, the Ni/C sample synthesized by loading Ni nanoparticles on mesoporous carbon *via* an impregnation method.

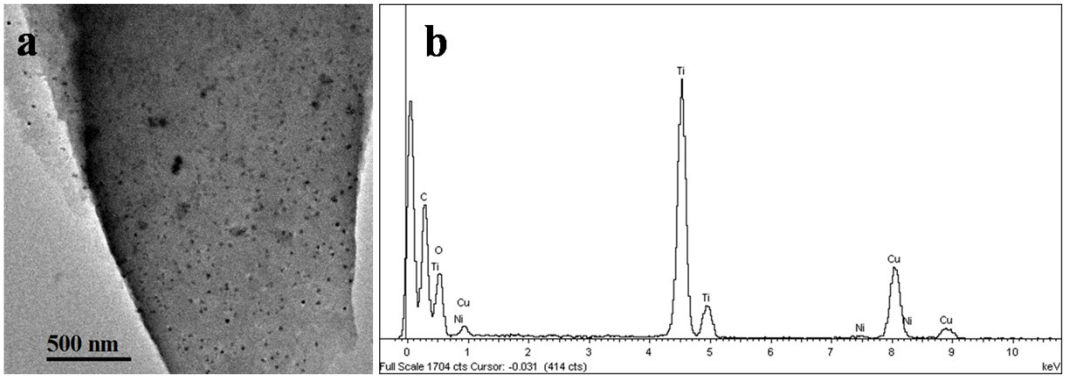

Fig. S3 (a) TEM image and (b) EDX pattern of the mesoporous Ni/TiO_2-C-5 composite with ~ 5 wt% of Ni.

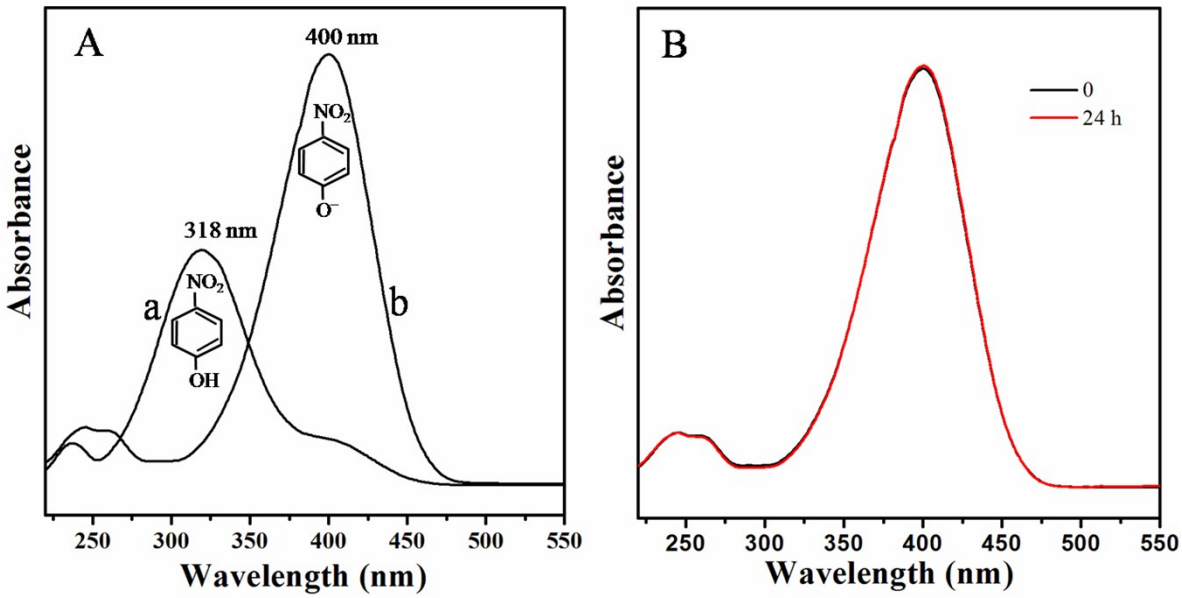

Fig. S4 (A) UV-vis absorption spectra of 4-nitrophenol (4-NP) before (a) and after (b) the addition of $NaBH_4$ solution (318 nm: 4-NP, 400 nm: 4-nitrophenolate ion), (B) UV-vis absorption spectra of 4-NP after the addition of $NaBH_4$ solution 0 and 24 h.

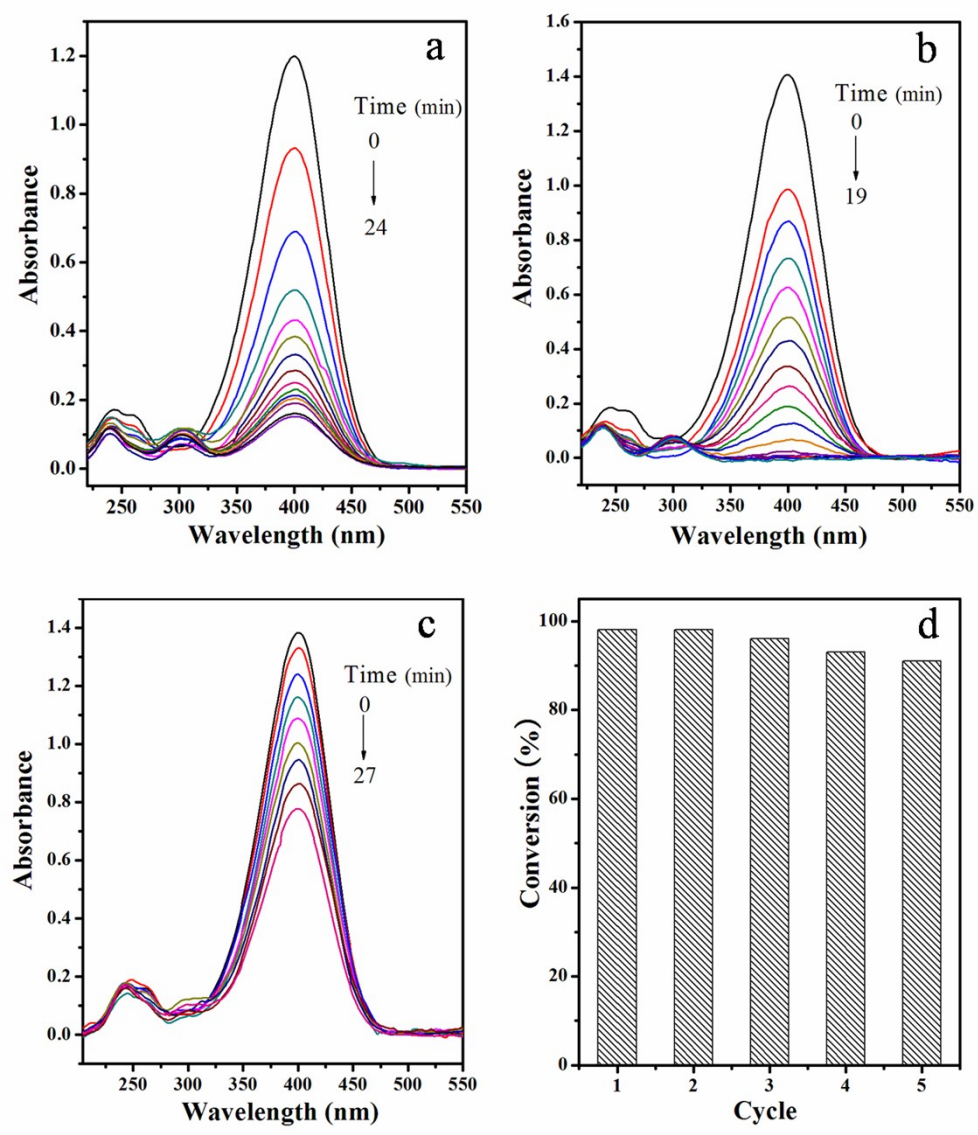

Fig. S5 UV-vis absorption spectra of the reaction solutions containing different catalysts at 25 °C : (a) the mesoporous Ni/TiO_2-C-2 composite with ~ 2 wt% of Ni, (b) the mesoporous Ni/TiO_2-C-5 composite with ~ 5 wt% of Ni, (c) the mesoporous Ni/TiO_2 synthesized by loading Ni nanoparticles on mesoporous TiO_2 *via* an impregnation method. (d) the recyclability of the mesoporous Ni/TiO_2-C-13 composite as the catalyst for the reduction of 4-NP.

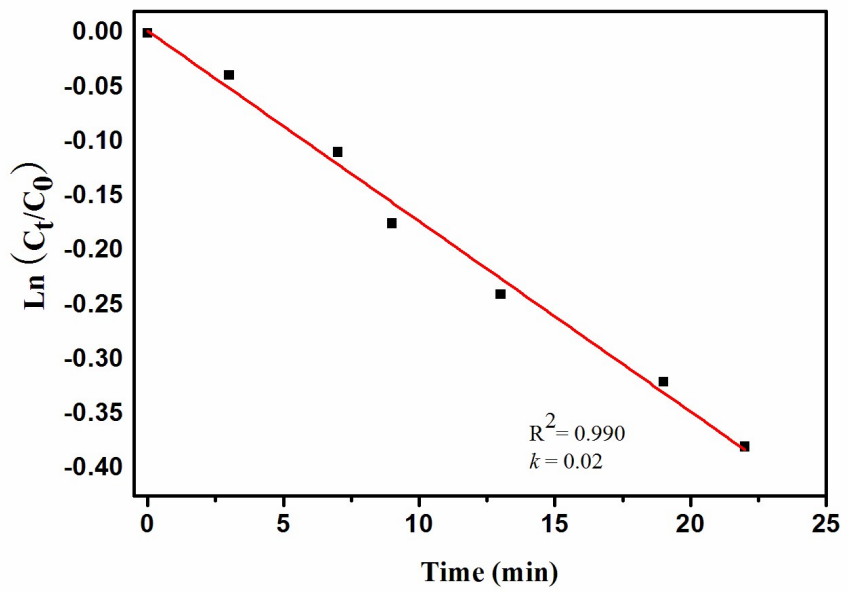

Fig. S6 The relationship between $\ln(C_t/C_0)$ and reaction time for the Ni/TiO_2 as the catalyst for the catalytic reduction of 4-NP at 25 °C, the Ni/TiO_2 sample synthesized by loading Ni nanoparticles on mesoporous TiO_2 *via* an impregnation method.

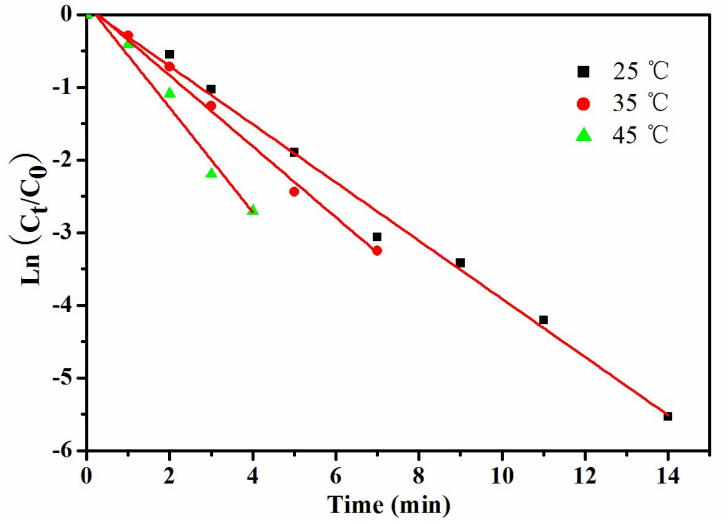

Fig. S7 The relationship between $\ln(C_t/C_0)$ and reaction time for the Ni/TiO_2-C-13 as the catalyst for the catalytic reduction of 4-NP at different temperatures.

Table S1 Rate constants for the catalytic reduction of 4-NP to 4-AP by Ni/TiO_2-C-13 composite at different temperatures.

Catalyst	K (min^{-1})	Temperature (°C)
Ni/TiO_2-C-13	0.40	25
Ni/TiO_2-C-13	0.49	35
Ni/TiO_2-C-13	0.72	45

Table S2 Comparison of the catalytic performance of the different catalysts for the reduction of 4-NP to 4-AP.

Catalyst	K (min^{-1})	Reference
Ni/TiO_2-C-13	0.40	This work
$Ni_{33.8}Co_{66.2}$ alloys	0.073	19 (a)
Modifiers-assisted Ni NPs	0.144	19 (a)
Ni@mesoporous-silica-35	0.33	19 (c)
Ni/graphene	0.70	2e
Ni_xP_y (6 h)	0.57	20

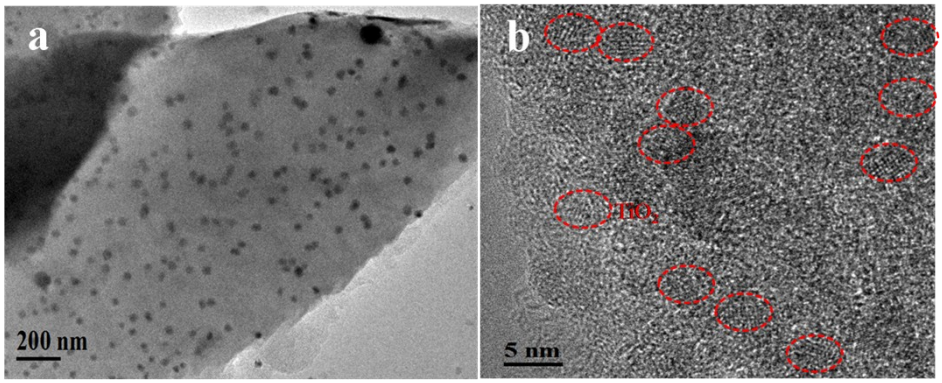

Fig. S8 TEM (a) and HRTEM (b) images of the mesoporous Ni/TiO_2-C-13 composite after being used as a catalyst for five times.

1. Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, L. Cheng, D. Feng, Z. X. Wu, Z. X. Chen, Y. Wan, A. Stein and D. Y. Zhao, *Chem. Mater.*, 2006, **18**, 4447.