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Facile route fabrication of nickel based mesoporous carbons with high catalytic performance towards 4-nitrophenol reduction[†]

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Novel nickel based mesoporous carbons are firstly *in situ* fabricated *via* pyrolysis of CTAB-chitosan-nickel supramolecular aggregates, which are pre-constructed by CTAB-directed self-assembly of 8-quinolinol modified chitosan and nickel acetate under basic conditions. This facile route fabrication method renders smart and homogeneously dispersed Ni nanoparticles (NPs) on the mesoporous carbonaceous framework without using any stabilizer and additional reductant, verified by high-energy X-ray diffraction, TEM, X-ray absorption fine structure, N₂ adsorption/desorption and Raman spectroscopy. Moreover, it is found that the morphology of Ni NPs, the textural property of carbonaceous supports, and the corresponding catalytic performance towards 4-nitrophenol reduction vary with the pyrolysis temperature. It is suggested that the nickel based mesoporous carbon pyrolyzed at 750 °C (Ni/MC-750) simultaneously possessing uniform spherical Ni NPs (24.5 nm) and bottle-neck mesopores exhibits the largest activity factor of 20.9 s⁻¹ g⁻¹ of any nickel catalysts.

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1. Introduction

Nickel nanoparticles (Ni NPs) have received considerable attention recently because of their low cost and remarkable catalytic performances in hydrogenation of nitrobenzene and nitrophenol, reduction of oxygen, and oxidation of olefins.¹⁻⁸ To facilitate catalyst recovery, Ni NPs are commonly dispersed onto solid matrices to prepare heterogeneous nickel catalysts. Thus various materials have been used as supporting matrices, including silica, alumina, titania, zirconia, magnesia, carbon, etc.⁹⁻¹⁴ Amongst them, porous carbonaceous supports are the most frequently used, and proved to be superior to oxide carriers, due to their chemical inertness and excellent stability under both acid and basic conditions. Mesoporous carbons (MC) are much favored since they offer great advantages over conventional activated carbons (AC) owing to their wellcontrolled mesopore structures which are favorable to transportation of large molecules.¹⁵ Recent advances in the fabrication of nickel based mesoporous carbons focus on the synthesis of MC by a conventional hard-templating approach first, followed

^aState Key Laboratory of Heavy Oil Processing, China University of Petroleum, Changping, Beijing 102249, China. E-mail: catalyticscience@163.com; Tel: +86-10-89734979 by wetness impregnation of nickel ions and reduction under an inert atmosphere.¹⁶ This tedious post-synthetic method renders instable catalysts with unevenly dispersed Ni NPs on the external surface or near pore mouths, resulting in a significant loss of reactivity during recycling because of the weak interaction between Ni NPs and the MC support.¹⁷ To replace such conventional "low efficient" preparations, pyrolysis of metal coordination polymers or metal organic frameworks under an inert atmosphere is proved to be step-economic to in situ construct homogeneously dispersed metal NPs firmly attached inside the carbonaceous matrix,18,19 since the metal NPs are in situ reduced and deposited onto the carbonaceous matrix formed almost simultaneously during pyrolysis. However, the resulting carbonaceous frameworks are always disordered and lack in uniform pore size distributions, thus blocking mass transportation. Despite continuous efforts, to fabricate the homogeneously dispersed Ni NPs firmly attached on MC via a step-economic method remains a challenge.

From the latest research on the synthesis of MC, we know that MC can be facilely fabricated *via* direct pyrolysis of supramolecular aggregates constructed by self-assembly of block copolymer templates and polymerizable precursors.^{20–23} Inspired by this methodology, we hypothesize that if the polymerizable precursors were substituted by nickel coordination polymers, homogeneously dispersed Ni NPs may be *in situ* fabricated into the MC matrix. However, the present polymerizable precursors, like widely studied phenolic resin and its derivatives, are hard to chelate metal ions to form metal



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coordination polymers due to the absence of chelating sites. It is known that chitosan is a very abundant biodegradable and biocompatible polysaccharide obtained by the alkaline deacetylation of chitin,²⁴ and possesses rich hydroxyl and amine moieties with strong affinity for metal ions.²⁵ Therefore, it is speculated that chitosan may be a suitable chelating agent for constructing chitosan-nickel coordination polymers.

We herein report novel nickel based mesoporous carbons in situ fabricated by direct pyrolysis of CTAB-chitosan-nickel supramolecular aggregates, constructed via CTAB-directed selfassembly of 8-quinolinol modified chitosan (CTS-HQ) and nickel acetate under basic conditions. In this study, chitosan was firstly modified by 5-chloromethyl-8-quinolinol to enhance its chelation with nickel ions and interaction with surfactant CTAB via electronic attraction, facilitating the formation of CTAB-chitosan-nickel supramolecular aggregates (or precursor composites). Owing to the difference in chemical and thermal stability between the chitosan and surfactant CTAB, as well as the reducibility of carbons, the following pyrolysis is a unique "one stone, three birds" strategy to remove CTAB, carbonize CTS-HQ and reduce nickel ions in a single step. The resulting nickel based mesoporous carbons with homogeneously dispersed Ni NPs on the mesoporous carbonaceous framework are confirmed by various characterization techniques, and screened as catalysts with a large activity factor of 20.9 $s^{-1} g^{-1}$ towards 4-nitrophenol reduction.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used as received without any further purification. Cetyltrimethylammonium (CTAB), chitosan, 8-quinolinol, nickel acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O), concentrated hydrochloric acid, 37% formaldehyde, 4-nitrophenol, sodium borohydride, triethylamine, acetic acid (CH₃COOH), ether, aqua ammonia (25 wt%), zinc chloride hexahydrate (ZnCl₂·6H₂O), acetone and ethanol were commercially available.

2.2. Preparation

The synthetic procedures for nickel based mesoporous carbons are depicted in Scheme 1. Chitosan was first modified by 5-chloromethyl-8-quinolinol to afford 8-quinolinol modified chitosan, CTS-HQ, involving a two-step chemical transformation from 8-quinolinol (see ESI and Fig. S1–5, ESI†). Then the precursor composite, Ni/CTS-P, was prepared by CTAB-directed self-assembly of CTS-HQ and Ni(CH₃COO)₂·4H₂O under basic medium. The molar ratio of the precursor gels used in the preferred preparation is 1CTS-HQ: $0.5Ni(CH_3COO)_2\cdot4H_2O: 0.12$ CTAB: $8.0NH_3$ (25 wt%): 114 H₂O: 10 EtOH. In a typical synthesis, 0.5 g CTAB was dissolved in 18.5 ml of water, and 7.2 ml EtOH combined with 6.8 ml NH₃·H₂O were added and stirred for 10 min. Then 1.6 g of CTS-HQ combined with 0.6 g



Scheme 1 Schematic illustration of nickel based mesoporous carbon preparation. (a) 5-Chloromethyl-8-quinolinol hydrochloride (1^{C} -HCl) and 8-quinolinol modified chitosan (CTS-HQ) preparation. (b) Precursor composite Ni/CTS-P synthesized *via* CTAB-directed self-assembly was pyrolyzed to yield Ni/MC-t.

of Ni(CH₃COO)₂·4H₂O was added and the resulting green mixture was stirred at room temperature for another 2 h, and then transferred into a polypropylene bottle and reacted at 100 °C under static conditions for 1 d. The precursor composite was recovered by filtration, dried overnight, and pyrolyzed in a tubular furnace under a N₂ atmosphere for 2 h. The heating rate was 2 °C min⁻¹ below 250 °C and 5 °C min⁻¹ above 250 °C. Samples pyrolyzed at 550, 750 and 950 °C correspond to Ni/MC-550, Ni/MC-750 and Ni/MC-950, respectively.

2.3. Characterization

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N₂ adsorption/desorption isotherms were recorded at 77 K with a Micromeritics Tristar II 3020. Before measurements, the samples were outgassed at 300 °C for 3 h. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distributions were measured by Barrett-Joyner-Halenda (BJH) analysis from the desorption branch of the isotherms. Morphology and microstructure were analyzed using a FEI Tecnai G2 F20 transmission electron microscope equipped with an energy dispersive X-ray spectroscopic analyzer operated at a voltage of 200 kV. Samples were sonicated for 5 min in EtOH, one drop of the suspended sample was dripped on a holey carbon film supported on a 300 mesh copper grid. Synchrotron X-ray diffraction measurements were performed at the 11-ID-C beamline of the Advanced Photon Source at Argonne National Laboratory. High-energy X-rays of 115 keV energy and 0.6 mm × 0.6 mm beam size were used to obtain two-dimensional (2D) diffraction patterns in the transmission geometry using a Perkin-Elmer large area detector placed at 1.6 m from the sample. Small-angle X-ray scattering (SAXS) measurements were performed at the 12-ID-C station at the Advanced Photon Source (APS, Argonne National Laboratory, Argonne, IL). The X-ray energy was 12 keV, which corresponds to a wavelength of 1.0332 Å. The sample-to-detector distance was about 2 m. X-ray absorption fine structure (XAFS) was carried out on a beamline at the 20-ID and 20-BM at Advanced Photo Source (APS) at Argonne National Laboratory. The XAFS data were obtained in the transmission mode at the Ni K-edge (8333.0 eV). For the Ni K-edge scan, a Ni foil was placed between the transmission and reference ion chambers. The XAFS data were processed using the Athena software for background removal, post-edge normalization, and XANES analysis. The extended X-ray absorption fine structure (EXAFS) data were analyzed using the Artemis software, which implemented FEFF (ESI[†]). Raman spectra were recorded with a HORIBA Jobin Yvon HR800 with a microscope attachment. The laser wavelength of 633 nm was focused using a diffraction limited spot, and the scan time was 2 s for each sample. Metal content was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a Perkin Elmer emission spectrometer. The dispersion of Ni was checked by H₂ chemisorption and carried out on a Micromeritics AutoChem II 2920 instrument. The sample (0.2 g) was firstly pretreated in argon (30 ml min⁻¹) at 250 °C for 1 h and the catalyst was cooled to room temperature and H₂ pulses were injected from a calibrated on-line sampling valve. H_2 adsorption was assumed to be complete after three successive peaks showed the same peak areas.

2.4. Catalytic reduction of 4-nitrophenol

The reduction of 4-nitrophenol (4-NP) was carried out in a quartz cuvette and monitored using UV-vis spectroscopy (Lambda 650s) at room temperature. For comparison, the aqueous 4-NP solution (0.01 M) was prepared and measured prior to monitoring the change of absorption. Then a total of 25 μ l of aqueous 4-NP solution was mixed with 2.5 ml of a fresh NaBH₄ (0.01 M) solution. Subsequently, a given amount of nickel catalyst was added to start the reaction, and the UV spectrometry was employed to *in situ* monitor the reduction by measuring the absorbance of the solution at 400 nm as a function of time at intervals of 1.25 min. After the reaction was finished, the mixture was centrifuged, and washed with ethanol and water three times. The resulting catalyst was re-dispersed in 25 μ l of aqueous 4-NP solution and 2.5 ml of fresh NaBH₄ solution, and the test was repeated to probe the stability.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the high-energy X-ray diffraction patterns of various Ni-containing samples. As expected, the precursor composite Ni/CTS-P exhibits no diffractions as compared to nickel acetate, indicating the coordination of nickel ions with CTS-HQ.^{26,27} Upon pyrolysis, all Ni/MC-*t* (*t*, pyrolysis temperature) samples display characteristics of fcc-structured Ni (JCPDS file 04-0805) at (111), (200), (220), (311) and (222) diffractions, indicating the formation of Ni nanocrystallites.^{28,29} However, the Ni/MC-750 catalyst exhibits the strongest diffraction intensity, suggesting most Ni nanocrystals formed when pyrolyzed at 750 °C. The small angle X-ray scattering pattern for Ni/MC-750 shows three weak peaks at *q* values of 0.212, 0.324 and 0.440 with a ratio of $1:3^{1/2}:2$ (Fig. S6, ESI†), associated with 10, 11 and 20 reflections of low 2D hexagonal symmetry with *p*6*m* space group.³⁰ A TEM image of Ni/MC-550



Fig. 1 High-energy X-ray diffraction patterns of (a) $Ni(CH_3COO) \cdot 4H_2O$, (b) Ni/CTS-P, (c) Ni/MC-550, (d) Ni/MC-750 and (e) Ni/MC-950.



Fig. 2 TEM images and the corresponding particle size distributions of (a, d) Ni/MC-550, (b, e) Ni/MC-750 and (c, f) Ni/MC-950, and the selected area electron diffraction (g), single electron microdiffraction (h) and high-resolution TEM (i, with its FFT pattern, inset) images of Ni/MC-750.

shows some mesoporous carbon nanotubes with homogeneously dispersed spherical NPs centered at *ca.* 23.6 nm (Fig. 2a and d). Ni/MC-750 exhibits slightly larger NPs embedded into the mesoporous carbons with an average diameter of 24.5 nm (Fig. 2b and e). However, Ni/MC-950 does not inherit the spherical shapes of pure Ni NPs, but rather displays irregularly congregated NPs with increased average diameter (Fig. 2c and f). Selected area electron diffraction (SAED) pattern of Ni/MC-750 exhibits diffraction rings with fcc polycrystalline (Fig. 2g), and the electron microdiffraction of single Ni NP demonstrates the $fm\bar{3}m$ symmetrical structure (Fig. 2h). The HRTEM image combined with the FFT pattern for Ni/ MC-750 displays clear lattice fringes throughout the whole particle, and the fringes in the (111) direction are 0.203 nm (Fig. 2i), confirming XRD findings.

Nickel specific XAFS was carried out to explore the electronic structure and the local structure ranged from 1 to 3 Å. As illustrated in Fig. 3, compared to Ni/CTS-P, the Ni/MC-tseries show decreased white line intensity along with the newly present pre-edge peak at *ca*. 8320 eV, suggesting that the



Fig. 3 (A) Ni K-edge XANES and (B) the corresponding Fourier transformed EXAFS spectra for (a) Ni/CTS-P, (b) Ni/MC-550, (c) Ni/MC-750, (d) Ni/MC-950 and (e) Ni foil.

Ni(+2) species are mostly reduced.^{31,32} In the corresponding *k* space, Ni/MC-*t* series show clear oscillations at a higher *k* region of k > 8 Å⁻¹ as compared to Ni/CTS-P (Fig. S7, ESI†), indicating the dominance of high Z backscatters, which would be Ni in our system. Correspondingly, the Fourier transformed EXAFS data (*r* space) exhibit one prominent peak at *ca.* 2.2 Å from the Ni–Ni contributions for Ni/MC-*t* series, different from

 Table 1
 Best fit parameters obtained from the analysis of the Ni K-edge EXAFS spectra^a

Materials	Shell	Fitting range $\Delta r [Å]$	CN	R [Å]	$\sigma^2 [{ m \AA}^2]$	$\Delta E \left[\text{eV} \right]$	R factor (%)
Ni/MC-550	Ni–Ni	1.25-2.95	4.8	2.49	0.00560	5.64	1.841
Ni/MC-750	Ni–Ni	1.00-2.94	7.4	2.48	0.00584	5.22	0.014
Ni/MC-950	Ni–Ni	1.18-2.95	7.7	2.48	0.00586	4.94	0.295
Ni foil	Ni-Ni	—	12	2.48	—	—	—

^{*a*} CN = coordination number, R = coordination distance, σ^2 = Debye–Waller factor, and ΔE_0 = inner potential correction.

the dominated Ni–O/C pairs at *ca*. 1.6 Å for Ni/CTS-P. On the other hand, the Ni–Ni peak intensity, proportional to the coordination number, varies with the pyrolysis temperature. Owing to the disordering in the higher shells, only the first shell ranging from 1.0 to 3.2 Å was curve-fitted. As illustrated in Table 1, the Ni–Ni coordination number increases from 4.8 to 7.7 as the pyrolysis temperature was elevated from 550 to 950 °C, indicating larger Ni NPs formed. However, all Ni/MC-*t* samples possess smaller coordination numbers than that of a Ni foil (CN = 12), suggesting that most Ni NPs are coordination.

The FT-IR spectrum of Ni/CTS-P shows CH_2 stretches at 2925 and 2855 cm⁻¹ from the surfactant CTAB, and characteristic phenyl and pyridyl vibrations between 1600 and 1300 cm⁻¹ (Fig. S8, ESI†), suggesting that CTS-HQ has been incorporated into the precursor composite *via* CTAB-directed self-assembly.³³⁻³⁵ However, these peaks disappear for Ni/MC-750 and Ni/MC-950 after the simultaneous CTAB removal and CTS-HQ carbonization, though there is some residue for Ni/MC-550.



Fig. 4 (A) N_2 adsorption/desorption isotherms and (B) BJH pore size distributions of (a) Ni/MC-550, (b) Ni/MC-750 and (c) Ni/MC-950.

 N_2 adsorption reveals that all Ni/MC-*t* samples exhibit a type IV isotherm with a sharp inflection step at P/P_0 ranging from 0.25 to 0.35 (Fig. 4A), characteristic of mesoporous materials.^{36,37} However, different from the H₄-type hysteresis loop in Ni/MC-550, Ni/MC-750 and Ni/MC-950 exhibit H₂-type hysteresis loops in the medium P/P_0 range, corresponding to bottle-neck pores.³⁸ It is observed that the surface area and the pore volume decrease with an increase of the pyrolysis temperature (Table 2). The S_{meso}/S_{micro} and V_{meso}/V_{micro} ratios increase gradually from 0.27 to 0.47 and from 1.62 to 2.24, respectively, suggesting that more mesoporous structures are created when elevating the pyrolysis temperature from 550 to 950 °C. All Ni/MC-*t* samples show pore sizes around 4.30 nm (Fig. 4B), suggesting that Ni NPs are mainly distributed on the carbonaceous framework.

The local structure of carbonaceous supports was investigated by Raman spectroscopy. As illustrated in Fig. 5, Ni/MC-*t* samples exhibit D and G bands centered at *ca*. 1355 and 1585 cm⁻¹, respectively, arising from the disordered carbon and ordered graphene sheet.³⁹ The Ni/MC-750 shows the largest I_G/I_D (relative ratio of the G band to the D band) value of 1.08 among the Ni/MC-*t* series (0.71 for Ni/MC-550 and 0.88 for Ni/MC-550), owing to the most developed graphene sheet formed when pyrolyzed at 750 °C.

The physical properties of the catalysts such as Ni content, dispersion and crystallite size for different Ni/MC-*t* catalysts calculated from ICP-AES and H₂ irreversible adsorption are shown in Table 3. It is clear that the H₂ uptake (Fig. S9, ESI[†]) amount decreases sharply from 48.3 to 11.7 μ mol g⁻¹ cat with a decline in Ni loading from 1.49 to 0.33 wt%. However, the Ni dispersion does not follow this trend, and the Ni/MC-750 catalyst shows the highest dispersion of 4.7% of any Ni/MC-*t* catalysts. On the other hand, the average Ni crystallite diameter

Table 2 Characteristics of Ni/MC-t series, BET surface area, S_{BET} (m² g⁻¹); external surface area, S_{ext} (m² g⁻¹); micropore surface area, S_{micro} (m² g⁻¹); pore volume, V_p (cm³ g⁻¹); micropore volume, V_{micro} (cm³ g⁻¹) and pore diameter, D_p (nm)

Materials	$S_{\rm BET}^{\ a} \left({\rm m}^2 \ {\rm g}^{-1}\right)$	$S_{\rm ext} \left({\rm m}^2 \ {\rm g}^{-1} \right)$	$S_{\rm micro} \left({\rm m}^2 {\rm g}^{-1}\right)$	$S_{\rm meso}/S_{ m micro}{}^b$	$V_{\rm p} \left({\rm cm}^3 {\rm g}^{-1} \right)$	$V_{\rm micro}^{c} (\rm cm^{3} g^{-1})$	$V_{\rm meso}/V_{\rm micro}^{\ \ d}$	$D_{\rm p}^{e} ({\rm nm})$
Ni/MC-550	307.3	66.0	241.3	0.27	0.294	0.112	1.62	4.30
Ni/MC-750	221.9	60.4	161.5	0.37	0.203	0.070	1.90	4.27
Ni/MC-950	177.2	57.0	120.2	0.47	0.165	0.051	2.24	4.40

^{*a*} The BET surface areas are obtained from the adsorption branches in the relative pressure range of 0.05–0.20. ^{*b*} Mesopore surface areas are determined by subtracting the micropore surface areas from the BET surface areas. ^{*c*} Microporous volumes are calculated by the *t*-plot method. ^{*d*} Mesopore volumes are determined by subtracting the micropore volume from the total pore volume. ^{*e*} The pore size distributions are calculated from the desorption branches by the Barrett–Joyner–Halenda (BJH) method.



Fig. 5 Raman spectra and their fitted patterns for (a) Ni/MC-550, (b) Ni/MC-750 and (c) Ni/MC-950.

Table 3 $\,\,\text{H}_2$ adsorption properties and reaction data over Ni/MC-t catalysts

Materials	Ni loading ^a (wt%)	H_2 uptake (µmol g ⁻¹ cat)	Dispersion ^b (%)	$d_{\rm s}{}^c$	$\operatorname{TOF}^{d}(\mathrm{s}^{-1})$
Ni/MC-550	1.49	48.3	3.8	25.6	0.01
Ni/MC-750	0.37	14.9	4.7	20.8	1.44
Ni/MC-950	0.33	11.7	4.2	23.2	0.39

^{*a*} Estimated by ICP-AES. ^{*b*} The Ni dispersion was calculated based on %*D* = 1.17X/Wf (literature⁴⁰). ^{*c*} The average Ni crystallite diameter was calculated by $d_s = 971/\%$ D (literature⁴⁰). ^{*d*} Reaction conditions: 0.01 M 4-NP, 25 µl; 0.01 M NaBH₄, 2.5 ml and duration, 1.25 min. TOF, s⁻¹: (turnover frequency) moles of 4-NP converted per mole surface Ni per second.

estimated by H_2 chemisorption shows a slight deviation from the TEM results.

3.2. Catalytic properties

It is known that 4-aminophenol (4-AP) is very useful and important in many applications including analgesic and antipyretic drugs, photographic developer, corrosion inhibitor and anticorrosion-lubricant, etc.⁴¹ The reduction of 4-NP to 4-AP has been extensively used as a benchmark system to evaluate the catalytic activity of metal NPs. Metal NPs can effectively catalyze the reduction of nitro compounds by acting as an electronic relay system, wherein the electron transfer takes place from donor BH₄⁻ to acceptor nitro groups.^{42,43} As shown in Fig. 6a, the adsorption peak of 4-NP was red-shifted from 317 to 400 nm immediately upon the addition of NaBH₄ solution which corresponds to a color change from light vellow to yellow green, due to the formation of the 4-nitrophenolate ion under alkaline conditions.⁴⁴ In the absence of catalyst, the adsorption peak at 400 nm remained unaltered even for a couple of days. By contrast, addition of a suitable amount of catalyst into the solution caused a decolorization of the 4-nitrophenolate solution, and meanwhile the peak intensity at 400 nm successively decreased with two new adsorption peaks appeared at 235 and 295 nm, suggesting the formation of 4-AP.45 The UV-vis spectra show an isosbestic point at 313 nm (Fig. 6b-d), suggesting that the catalytic reduction of 4-NP gives only 4-AP without a by-product.⁴⁶ Fig. 6b-d illustrates the absorbance vs. reaction time plots towards 4-NP reduction using different Ni/MC-t catalysts. We found that a delay time of 1.25 min at the beginning of the catalytic reduction exists. The short induction period may correlate to



Fig. 6 (a) UV-vis spectra of 4-nitrophenol before and after adding NaBH₄ solution, (b) the reduction of 4-nitrophenol in aqueous solution recorded every 1.25 min using 3.0 mg Ni/MC-550, (b) the reduction of 4-nitrophenol in aqueous solution recorded every 1.25 min using 0.3 mg Ni/MC-750, (c) the reduction of 4-nitrophenol in aqueous solution recorded every 1.25 min using 0.7 mg Ni/MC-950, (e) the relationship between $ln(C_t/C_0)$ and reaction time (t) and (f) the recyclability of the Ni/MC-750.

the coordinatively unsaturated surface Ni atoms, which promote the chemisorption of 4-nitrophenolate ions and thereby accelerate the reaction. The reduction was completely finished within ca. 10 min over 3 mg Ni/MC-550, 0.3 mg Ni/MC-750 and 0.7 mg Ni/MC-950. Considering that the reductant concentration is much higher than that of 4-NP ($C_{\text{NaBN}}/C_{4-\text{NP}} = 100$) in the reaction mixture, the pseudo-first-order rate kinetics with respect to 4-NP concentration could be used to evaluate the catalytic rate. The reaction kinetics can be described as $-\ln(C_t/C_0) = kt$, where k is the rate constant at a given temperature and t is the reaction time. C_0 and C_t are the 4-NP concentration at the beginning and at time t, respectively. As expected, a good linear correlation of $\ln(C_t/C_0)$ vs. reaction time t was obtained (Fig. 6e), whereby the kinetic rate constant *k* was estimated to be 1.51×10^{-3} , 6.26×10^{-3} and 2.40×10^{-3} s⁻¹ for Ni/MC-550, Ni/MC-750 and Ni/MC-950. To compare different catalysts, we calculated the ratio of rate constant K over total weight of nickel catalyst, where K = k/m. Thus the activity factor K was calculated to be 0.5, 20.9 and 3.4 s⁻¹ g⁻¹ for Ni/MC-550, Ni/MC-750 and Ni/MC-950, respectively. It is clear that Ni/MC-750 shows the largest activity factor (in agreement with the comparison of TOF values listed in Table 3), which is about 22 times larger than the previously reported ratio for NiCo₂ alloys $(0.95 \text{ s}^{-1} \text{ g}^{-1})$,⁴⁷ and *ca*. 9 times more than that for the reported Ni NPs (7 nm) in a spherical polyelectrolyte brush nanoreactor (2.38 s⁻¹ g⁻¹).⁴⁸ The best performance of Ni/MC-750 arises from the combined uniform spherical Ni NPs and bottle-neck mesopores with enhanced graphene structure facilitating mass transformation. To explore whether there is leaching during reactions, we performed a filtration to remove the Ni/MC-750 catalyst from the 4-NP solution when the reaction proceeded for 3 min. Following that, the filtrate was continuatively stirred and monitored by UV-vis spectroscopy at regular intervals. It is found that the peak height at 400 nm remains nearly unchanged, suggesting that no leaching occurred. To check the reusability of nickel catalysts, and to avoid any possible saturation effect, when ca. 40% 4-NP was converted, the representative Ni/MC-750 was recovered from the reaction mixture by simple filtration and washing with water, and reused under the same conditions as for the initial cycle. As shown in Fig. 6f, Ni/MC-750 can be successfully recycled and reused in 6 successive reactions with a conversion of 37.0-42.0%. Moreover, TEM analysis of the spent Ni/MC-750 catalyst revealed that the dispersion and size distribution of Ni NPs did not show any obvious change after six runs (Fig. S10, ESI†) compared with the fresh catalyst (Fig. 2b), suggesting the high stability of the Ni/MC-750 catalyst.

4. Conclusions

In summary, novel nickel based mesoporous carbons have been facilely fabricated *via* direct pyrolysis of surfactantdirected CTAB-chitosan-nickel supramolecular aggregates under different temperatures. Construction of an evenly dispersed nickel complex in the precursor composite Ni/CTS-P is the key to realize the homogeneously distributed Ni NPs on the mesoporous carbonaceous framework after pyrolysis, confirmed by various characterization techniques. All nickel based mesoporous carbons are active for the catalytic reduction of 4-NP, but their catalytic performances vary with the morphology of Ni NPs and the textural property of carbonaceous supports created under different pyrolysis temperatures. It is revealed that the Ni/MC-750 catalyst simultaneously possessing uniform spherical Ni NPs (24.5 nm) and bottle-neck mesopores exhibits the largest activity factor of 20.9 s⁻¹ g⁻¹ and outperforms any nickel catalysts reported. Recyclability test demonstrates that Ni/MC-750 is stable and can be recycled. Therefore, it should be noted that the methodology demonstrated in this study may be extended to the preparation of other metal based mesoporous carbons, since CTS-HQ can chelate with many other metal species, such as Fe, Co, Cu, Ru and Pt.

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