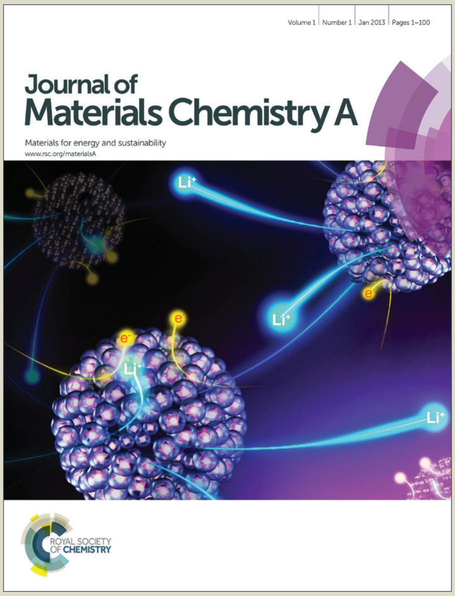
Journal of Materials Chemistry A

Accepted Manuscript



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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Polymer microcapsules loaded with Ag nanocatalyst as active microreactors†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We report on fabrication of a new complex catalytic system composed of silica-supported silver nanoparticles (AgNP) encapsulated inside of polymer microcapsules (MC). Silver nanocatalyst itself was obtained by reduction of silver salt in the presence of SiO_2 particles acting as AgNP carriers, to provide complex Ag/SiO_2 catalyst with Ag surface completely free of capping agents. Ag/SiO_2 particles were enclosed inside the interior of polymer microcapsules. Due to the presence of hydrophobic shell on the MC surface, catalytic reactions become feasible in organic solvent environment. On the other hand, the hydrophilic nature of MC interior forces the water-soluble reactants to concentrate inside the capsules which act as microreactors. On the example of catalytically driven reduction of 4-nitrophenol we demonstrate that encapsulated Ag/SiO_2 particles possess enhanced catalytic activity as compared to catalyst being freely dispersed in reaction medium.

Introduction

Catalysis with nanoparticles (NP) (i.e. nanocatalysis) is usually considered as an intermediate between heterogeneous and homogeneous ones.[1] In the recent past the research interest towards nanocatalytic systems based on metal or metal oxide NP of different size and shape substantially increased.[2-7] The high catalytic activity of nanosized particles is caused by their large surface-to-volume ratio and an existence of easily accessible special binding sites on their surface,[8] and, thus, largely depends on their size and shape.[9] However, the very small size of the nanoparticles significantly complicates their separation and effective recovering after the reaction. Another problem of pristine NP is their low dispersion stability and enhanced tendency to aggregate, which lowers their catalytic efficiency significantly.

To prevent the nanoparticles from aggregation various stabilizing agents, such as charged molecules,[10-13] low molecular weight ligands,[14, 15] polymers,[16-18] dendrimers,[19-21] micelles[22] or microemulsions[23] can be applied, ensuring particles dispersion stability in both polar and non-polar media. Nevertheless, such enhanced stability of NP in reaction media does not solve the problem or even complicates the procedure of their recovering.

The difficulties with the nanocatalyst recovery can be largely overcome by utilization of supported or confined nanocatalyst. Recently, a number of reports have been focused on catalytic systems, where the nanoparticles are attached to the substrate. For instance, SiO_2, Al_2O_3 or other metal oxides were successfully used as supports for immobilisation of different types of NP and their catalytic efficiency was examined.[24-31] One of the drawbacks of such systems is that inorganic oxide particles usually form stable dispersions only in water and in polar medium. Therefore, the method of preparation of easily recoverable metal nanocatalysts, which can be used in non-polar environment, still remains an open question.

Alternative way to ensure nanocatalyst dispersion stability and facility of recovery is encapsulation into hollow structures, e.g. microcapsules (MC). Utilization of hollow structures as nanocatalyst carriers requires that their intrinsic properties, e.g. dispersion stability, recoverability, chemical resistance etc., will meet the requirements for the systems to be used for catalytic purposes. Hollow structures can be prepared via layer-by-layer (LbL) technique, self-assembly, vesicular polymerization or microfluidic fabrication.[32-39] Additionally, the etching of SiO_2 core from corresponding SiO_2/polymer particles also represent the way to obtain hollow structures.[40, 41] This step-wise approach typically involves formation of the polymer shell on the solid core (e.g. layer-by layer deposition of desired material or surface-initiated polymerisation) and followed by the removal of the core.

An example of the application of templating approach for preparation of polymer-confined nanocatalyst was recently reported by Kang and co-workers.[42] The authors exploited sol-gel reaction combined with precipitation polymerisation to produce Ag/air/PMMA hybrid nanorattles with a silver nanocore and solvent-resistant polymer shell. This method, however, is quite complicated due to the multistep procedure. In addition, it requires dissolution of hard template after the formation of the polymer layer which might also lead to contamination of the capsules interior, in particular because of difficulties associated with complete template removal.

Herein, we report a simple and straightforward method to obtain Ag/SiO_2 nanocatalyst encapsulated inside poly(N-isopropylacrylamide) (PNIPAM) microcapsules stabilized with hydrophobic shell. Suggested method intends formation of metal nanocatalyst on the surface of silica particles followed by encapsulation of such composite particles into the polymer capsules interior. The use of silica support allows obtaining of pristine metal nanocatalyst with the surface free of any stabilizing agents. In turn, after enclosing into permeable MC, active species retain accessible to reactants, gaining an additional benefit in their removal from the reaction mixture by simple filtration or centrifugation.

The advantages of our method of nanocatalyst encapsulation are its routine simplicity and "clean" conditions. We demonstrate that using simple one-pot preparation protocol we can produce polymer microcapsules already loaded with the nanocatylyst, avoiding thus the multistep synthetic process and eliminating the requirements of sacrificial material destruction.

Experimental

Materials

Poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO, M_n(PI) = 24300 g/mol, M_n(PEO) = 5830 g/mol, PDI(PI-*b*-PEO) = 1.3), was synthesized according to the previously published protocol.[43] The molecular weight ratio of PI and PEO blocks was tuned to ensure the hydrophilic-lipophilic balance (HLB) value of 4. The monomer, N-isopropylacrylamide (NIPAM, Acros, 97.0%) was re-crystallized from toluene/hexane mixture (1/1 v/v). Other chemicals: N,N-methylenebis(acrylamide) (MBA, Merck, 98.0%), ammonium persulfate (APS, Merck, 98.0%), tetraethyl orthosilicate (TEOS, Aldrich), silver acetate (CH_3COOAg, 99% Aldrich), sodium borohydride ($NaBH_4$, 96% Aldrich), 4-nitrophenol (4-NP, 99%, Aldrich), ammonium hydroxide solution (28% Acros), trimethylpentane (TMP, 99.5%, Aldrich), THF and ethanol (analytical grade, Acros Organics) were used as received.

Synthesis of silica particles

Silica particles (SiO_2) (d_{av}=219 nm, PDI=0.012 as determined by DLS) were prepared by Stöber method[44] by addition of 1 ml of aqueous solution of ammonium hydroxide, 1 ml of TEOS and 0.1 ml of water to 15 ml of ethanol. The reaction mixture was stirred at room temperature for 4 hours. Afterwards particles were separated by centrifugation, washed with ethanol and water and finally dried in vacuum oven at 50 °C overnight to get SiO_2 in dry (powder) state.

Synthesis of Ag/SiO_2 catalyst

To 1.7 mg of SiO_2 powder dispersed in 10 ml of THF 0.25 ml of 6 mM aqueous solution of silver acetate was added and the mixture was stirred at room temperature for 12 hours. Next, 1 ml of 0.01% THF solution of $NaBH_4$ was added and the reaction mixture immediately turned to dark brown, indicating the formation of silver nanoparticles (AgNP). Ag/SiO_2 particles were recovered from the butch solution and purified by repeated centrifugation and re-dispersion in water. The presence of AgNP on the SiO_2 surface was proved by SEM and TEM imaging and UV-Vis measurements.

Encapsulation of Ag/SiO_2 into PNIPAM microcapsules

Ag/SiO_2 composite particles were encapsulated into PNIPAM-based microcapsules interior by adopting previously reported protocol of water-in-oil suspension polymerisation of NIPAM in the presence of BCP surfactant.[43] Briefly, 0.15 g of PI-*b*-PEO was dissolved in 3 mL of trimethylpentane. Separately, 0.15 g of monomer (NIPAM), 0.01 g (5 mol.%) of cross-linker (MBA) and 0.006 g (1 mol.%) of initiator (APS) were mixed with 0.5 mL of aqueous dispersion of Ag/SiO_2 (3.8 mg/ml) to form a water phase. Water and oil phases were mixed in Ultra-Turax mixer (IKA, Germany) at 13500 rpm for 2 minutes and the resulting emulsion was transferred into the glass tube equipped with magnetic stirrer. Temperature of the mixture was rapidly risen to 80°C and the polymerization was carried out for 1 hour. The excess of the surfactant was washed out by 5 times repeated centrifugation and re-dispersion in pure trimethylpentane. Finally microcapsules were dispersed in THF and used for further experiments.

Monitoring of 4-nitrophenol reduction

The kinetics of catalytic reduction of 4-nitrophenol was monitored with UV-Vis spectroscopy. In typical experiment a freshly prepared aqueous solution of sodium borohydride (1.5 M, 0.1 mL) was added to a THF/water (9/1 v/v) solution of 4-nitrophenol (0.125 mM, 3.0 mL). Next, a certain amount of silver-containing catalyst was added to this solution. UV spectra of the mixture were recorded immediately after the addition of the catalyst every 1 minute in the wavelength range 250–500 nm. The evaluation of the reaction kinetics was performed by monitoring the change in intensity of the absorbance peak at 400 nm with time. To eliminate the contribution to the absorbance originated from the presence of silver nanoparticles, the catalyst dispersion with the same concentration of silver was used as a reference in each particular UV-Vis experiment.

Methods

SEM images were obtained with Ultra 55 (Carl Zeiss SMT, Jena, Germany) operated at 3 kV using secondary electron (SE) detector. TEM images were recorded with Libra 200 (Carl Zeiss SMT) operated at 200 kV. UV-Vis measurements were carried out on Perkin-Elmer UV-Vis spectrometer Lambda 800. Dynamic light scattering (DLS) measurements were performed with Zetasizer Nano S (He-Ne-laser 4 mW, 632.8 nm, back scattering, NIBS Technology, Malvern Instruments). TGA experiments were carried out in nitrogen atmosphere using TA Q5000 thermal analyser (TA instruments, USA) at heating rate of 10 K/min.

Results and discussion

In this work we report on fabrication of complex catalytic system composed of silica-supported metal nanocatalyst encapsulated inside the polymer microcapsules (MC(Ag/SiO_2)). First, silver nanoparticles were synthesized on the surface of larger SiO_2 particles. Next, obtained Ag/SiO_2 were encapsulated into the interior of polymer microcapsules as shown in Fig. 1. An application of SiO_2 supports allows to prepare AgNP having their surface completely free of stabilizing layer. This also prevents nanoparticles from undesirable aggregation, ensures their highest surface-to-volume ratio and enhances catalytic activity.[43] Moreover, silica-supported nanocatalyst can be easily recovered by centrifugation and further re-used for catalytic purposes. Encapsulation of Ag/SiO_2 into the interior of hydrophobicaly covered polymer microcapsules provides the possibility to perform catalysis in non-polar organic media in which Ag/SiO_2 particles are poorly dispersible.

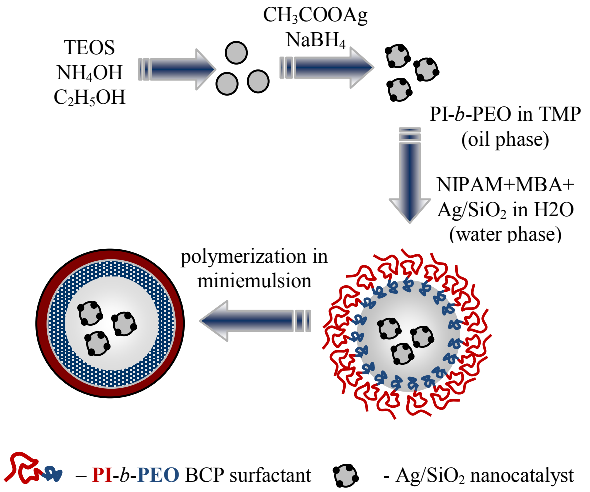

Fig. 1 Schematics of encapsulation of Ag/SiO_2 particles into the microcapsules interior.

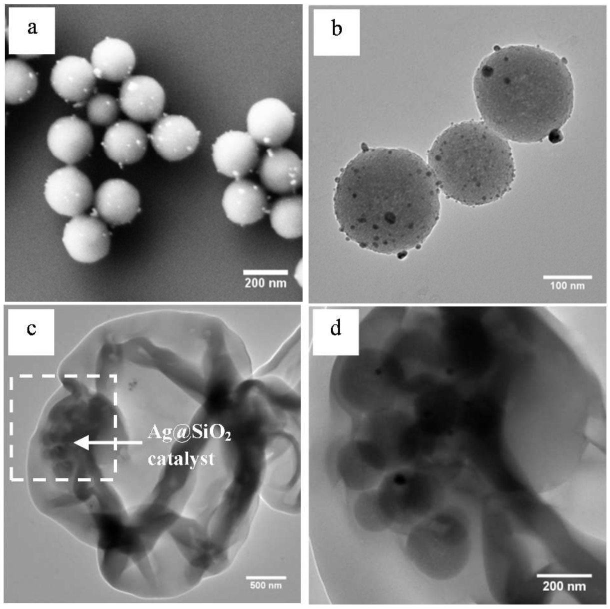

Fig. 2 SEM (a) and TEM (b) images of Ag/SiO_2 particles and (c,d) TEM images of MC filled with Ag/SiO_2 at different magnifications.

Synthesis of Ag/SiO_2 nanocatalyst

SiO_2 particles (d_{av} = 219 nm) were prepared according to Stöber procedure[44] and used as supports for silver nanocatalyst. The size of silica particles was optimized by varying the TEOS/H_2O/NH_4OH ratio in order to make them easy to handle and, in the same time, small enough to be encapsulated into the interior of the microcapsules. Silica-supported silver nanoparticles (Ag/SiO_2) were prepared by borohydride reduction of silver acetate in the presence of SiO_2 particles. The reaction was carried out in THF/water mixture where the minor amount of water (ca. 1.5 vol %) was used to solubilise silver acetate. Such reaction conditions allowed to generate silver nanoparticles predominantly attached to the silica surface (Fig. 2 a,b). The size of the silica-supported AgNP was 19.3 nm (SD =3.8 nm) as determined from the analysis of TEM images, whereas the calculated Ag:SiO_2 ratio and the surface coverage of SiO_2 with silver were 1:15 (w/w) and ~7.3 wt.%, respectively. UV-Vis spectrum of Ag/SiO_2 possess surface plasmon resonance (SPR) absorbance peak of silver with maximum at 410 nm (see Fig. S1, ESI†), typical for silver colloids in the nanometer size range.[46] Notably, prepared in such a way AgNP appear firmly attached to the SiO_2 surface and cannot be leached out neither by repeated washing with water or ethanol nor by intense agitation in ultrasonic bath (Fig. S2, ESI†).

It should be pointed out, that our attempts to prepare Ag/SiO_2 particles in purely THF or aqueous environment were less successful and led to the formation of significant amount of crude silver particulates of over micrometer size, lowering thus fraction of AgNP attached to the silica supports significantly (see Fig. S3, ESI†). We suggest, that the hydrophilic nature and porosity of silica particles[47, 48] promote adsorption of water on their surface and hence, force silver ions to concentrate in their vicinity. Secondly, electrostatic interactions between positively charged Ag ions and negatively charged silica particles oblige the reduction of silver to occur directly on the SiO_2 surface. Such conditions, however, are not maintained when reduction is carried out in pure water where the silver ions are not forced to concentrate near to SiO_2 surface, but appear solubilized uniformly through the whole volume.

Ag/SiO_2 encapsulation

Recently, a simple and straightforward synthetic method towards PNIPAM microcapsules using inverse suspension polymerisation was developed in our group.[43] This method was already proved as an efficient way to produce polymer microcapsules of different size[49] and composition.[50] Hollow polymer structures can be produced in water-in-oil (W/O) inverse miniemulsion composed of monomer-containing water droplets, stabilized with amphiphilic bock copolymer which serves simultaneously as surfactant and shell-forming component. Obtained in such a way MC appear readily dispersible in non-polar organic solvents due to the presence of hydrophobic shell on their surface. The water droplets which act as soft templates during capsule formation, provide a perfect basis for direct encapsulation of "guest" materials (reactive molecules, nanoparticles, etc.) into the interior of MC directly during their synthesis.

In present work we exploited these synthetic advantages in order to directly load MC with Ag/SiO_2 particles. For preparation of miniemulsion, the water dispersion of Ag/SiO_2 particles was mixed with the reactants (i.e. NIPAM, MBA and APS) to form a droplet-forming water phase, whereas the BCP surfactant was dissolved in thrimethylpentane and used as continuous phase. Thus, after emulsification, the hydrophilic Ag/SiO_2 particles together with reactants appeared trapped within the interior of water droplets being stabilized with BCP surfactant. Encapsulation of Ag/SiO_2 particles was accomplished by polymerization of NIPAM in droplets at temperature above LCST of PNIPAM that results in hollow structure morphology. Copolymerization of NIPAM with MBA cross-linker ensures the strength of capsules, whereas an application of PI-*b*-PEO surfactant provides them with the hydrophobic shell.

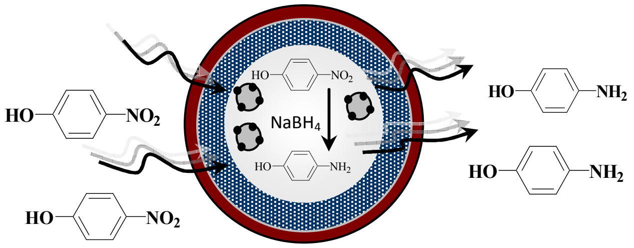

Fig. 3 Schematics of catalytic reduction of 4-nitrophenol inside the microcapsules loaded with Ag/SiO_2.

The success of Ag/SiO_2 encapsulation was proved using TEM imaging (Fig. 2 c,d). From TGA (Fig. S4, ESI†) the amount of encapsulated Ag/SiO_2 particles inside the MC was found to be 15 wt.%, which gives an estimated content of silver nanocatalyst of *ca.* 1 wt.%.

Catalytic activity

Catalytic activity of encapsulated Ag/SiO_2 was studied and compared with the activity of Ag/SiO_2 freely dispersed in reaction medium. As a model reaction for this study catalytically induced reduction of 4-NP was used as shown schematically in Fig. 3. This reaction was chosen due to the instrumental simplicity of its examination. Using UV-Vis spectroscopy it is possible to examine the reaction kinetic by monitoring the intensity of 4-NP absorbance peak (λ_{max} = 400 nm) with reaction time. However, specific character of the investigated system required adjustment of particular experimental conditions. As it was already mentioned, due to the presence of hydrophobic shell on MC they form stable dispersion in organic solvents of low and moderate polarity but aggregate in aqueous environment. On the other hand, in pure aprotic solvents like THF, 4-nitrophenol does not possess any absorption peak in UV-Vis region due to the absence of nitrophenolate ions. To overcome this discrepancy the mixture of THF and water (9/1 v/v) was chosen as the reaction medium to monitor the catalytic processes. In such conditions both Ag/SiO_2 and MC form sufficiently stable dispersions and well pronounced absorbance peak of 4-nitrophenol is observed.

Fig. 4 displays the alteration of the UV-Vis spectra of 4-NP with time during its catalytic reduction carried out in presence of MC(Ag/SiO_2). As it was expected, after addition of $NaBH_4$ the intensity of nitrophenolate peak gradually decreased with reaction time (red arrow in Fig. 4), whereas the peak at 315 nm, attributed to the formation of aminophenol, increased as the reaction proceeded (blue arrow in Fig. 4). Such behaviour is analogous to those being earlier reported on catalytic reduction of 4-nitrophenol in the presence of Pt or Au nanoparticles.[49] Moreover, similar spectrum alteration was also observed when freely dispersed Ag/SiO_2 catalyst particles were used to catalyse the same reaction (Fig. S5, ESI†). Such similarities provide clear evidence that Ag/SiO_2 particles retain the catalytic activity after their confinement into the microcapsules interior and, thus, can be used for catalytic purposes.

The degree of 4-nitrophenol conversion (c/c_0) was directly excerpted from the UV-Vis spectra by measuring the decrease of the peak intensity at 400 nm with time. Fig. 5a shows the depletion of 4-nitrophenol relative concentration versus time determined for different concentration of Ag/SiO_2 catalyst.

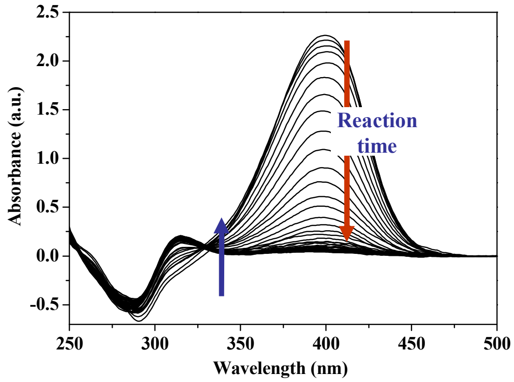

Fig. 4 Successive UV-Vis spectra taken every minute during borohydride reduction of 4-NP catalysed by MC(Ag/SiO_2). Initial concentrations: [4-NP] = 0.125 mM, [$NaBH_4$] = 1.5 M, [Ag] = $0.48\cdot10^{-3}$ mg/ml.

At the concentrations of silver above $0.9\cdot10^{-3}$ mg/ml the full conversion of 4-nitrophenol (more than 99%) was usually accomplished in 60 min. As the common feature for all curves, the initiation period (t_0) was observed as a plateau at the initial stages of the reaction (Fig. 5a).

The appearance of $\boldsymbol{t_0}$ was also detected for the reaction catalysed by other kinds of metal nanoparticles[50] and is usually attributed to substrate-induced surface restructuring, which is necessary to render the metal nanoparticles an active catalyst.[49] It was also observed alike to other studies that the initiation period becomes shorter with an increase of the catalyst concentration in the system. After the initiation period, the reaction proceeds much faster and can be treated as pseudo first-order process (Fig. 5b). The values of the reaction apparent rate constants determined from the linear fit of $\ln(c/c_0)$ for different concentration of Ag/SiO_2 nanocatalyst are summarized in Table 1.

Unforeseen to some extend results were obtained when encapsulated Ag/SiO_2 particles were used as catalyst for the same reaction. First, the activation time substantially decreased and did not exceed 1-2 minutes as compared to 10-15 minutes for freely dispersed Ag/SiO_2 catalyst (Fig. 5c). At higher concentration of encapsulated catalyst the activation time was difficult to detecte, because substantial decrease of 4-nitrophenol concentration was already observed starting from the first minute of measurement. Secondly, unexpectedly high reaction rates were observed when MC(Ag/SiO_2) was used as catalyst (Table 1). At concentrations of Ag in MC above $0.5\cdot10^{-3}$ mg/ml 99% conversion of 4-nitrophenol was achieved already in 10 minutes after addition of catalyst. Nevertheless, the reaction catalysed with MC(Ag/SiO_2) can also be considered as a pseudo-first order process within the catalyst concentration range studied (Fig. 5d). For comparable concentrations of silver, the k values determined for the reaction catalysed with MC(Ag/SiO_2) exceeded 5-10 times of magnitude the corresponding rate constants for catalysis with freely-dispersed Ag/SiO_2. Monitoring of the reaction kinetics at Ag concentration higher than $0.65\cdot10^{-3}$ was hardly possible due to the very fast reaction performance and limitations of detection method. Such significant increase of the apparent rate constant in case of application of MC(Ag/SiO_2) is discussed in terms of possible processes occurring during the performed catalytic reaction.

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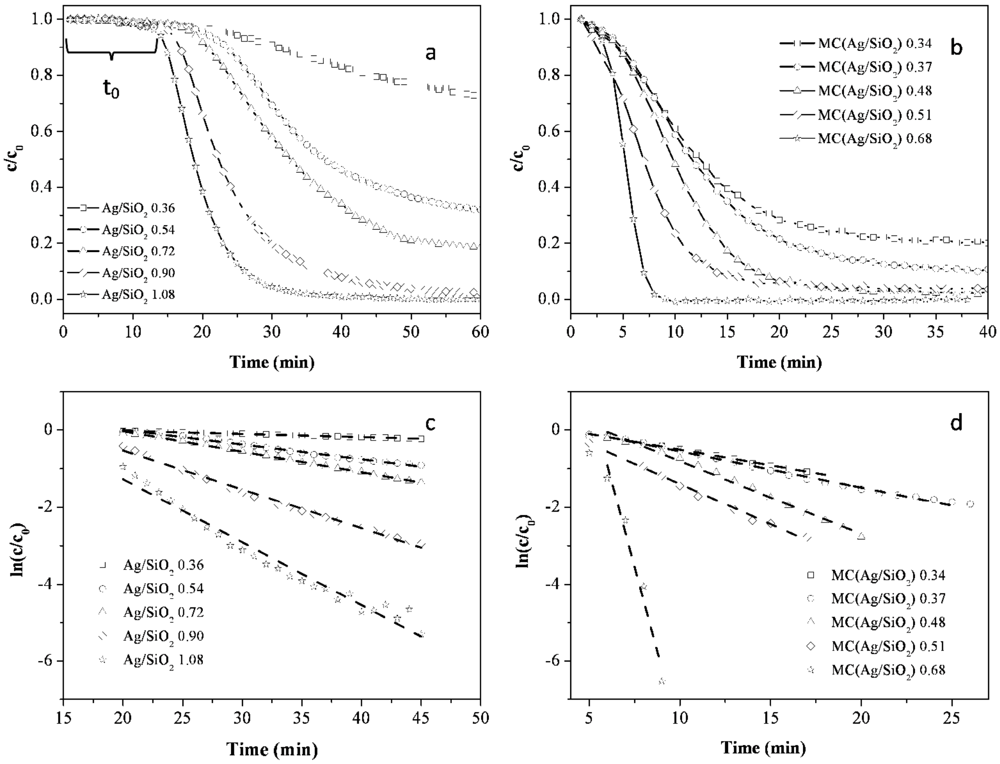

Fig. 5 Plots of c/c_0 (a, c) and $\ln(c/c_0)$ (b, d) versus time for the borohydride reduction of 4-NP catalysed by Ag/SiO_2 (a, b) and $MC(Ag/SiO_2)$ (c, d). Rate constants determined from the linear fits of $\ln(c/c_0)$ (dash lines) and corresponding concentrations of Ag are given in Table 1.

It is well known, that the degree of swelling of PNIPAM-based polymers in water excels their swelling in THF or other organic solvents. On the other hand, the solubility of PNIPAM in certain solvent mixtures can significantly exceed its solubility in pure solvent (the cononsolvency effect).[53] For example, such enhanced swellability of PNIPAM MC in THF/water mixture compare to pure THT was demonstrated in our previous work.[41]

Since the water volume fraction used in this study is less as THF/water cononsolvent ratio for PNIPAM, the MC act as a kind of sponge and selectively absorb water into their interior. Thus, the volume fraction of water inside the microcapsules significantly exceeds the same in surroundings. Due to this fact, sodium borohydride, whose solubility in water at 20° C is almost 400 times higher than in THF, will also concentrate inside the MC. Since the reaction performance depends on concentration of reagents, the local growth of the reactants concentration in the vicinity of catalyst will lead to the consequent increase of the reaction rate. From the additional experiments it was also found that catalytic reduction of 4-nitrophenol in pure water proceeds more than two magnitude faster than in THF, that additionally proves our suggestions concerning the reasons of acceleration of the catalysis in MC. To ascertain possible mechanism of the reaction, the apparent rate constants were plotted as a function of squared concentration of silver nanocatalyst (Fig. 6). For both freely dispersed and encapsulated Ag/SiO_2 particles the rate constants were found to be linearly dependant on squared silver concentration, which, in turn, can be considered as a measure of the surface area of the catalyst. This finding is in agreement with statements of the Langmuir-Hinshelwood mechanism proposed as a model to interpret this reaction.[51]

Table 1 Apparent rate constants of catalytic reduction of 4-nitrophenol[a]

Catalyst	$[Ag/SiO_2]$ mg/ml	$[Ag]\cdot10^3$ mg/ml	$k\cdot10^2$,[b] min^{-1}
Ag/SiO_2 0.36	0.018	0.36	0.82
Ag/SiO_2 0.54	0.027	0.54	3.82
Ag/SiO_2 0.72	0.036	0.72	5.30
Ag/SiO_2 0.90	0.045	0.90	10.08
Ag/SiO_2 1.08	0.054	1.08	16.37
$MC(Ag/SiO_2)$ 0.34	0.016	0.34	8.11
$MC(Ag/SiO_2)$ 0.37	0.018	0.37	9.40
$MC(Ag/SiO_2)$ 0.48	0.022	0.48	18.92
$MC(Ag/SiO_2)$ 0.51	0.024	0.51	20.89
$MC(Ag/SiO_2)$ 0.68	0.032	0.68	36.12

[a] all catalytic reactions were performed in THF/water 10/1 v/v;
[b] k – apparent reaction rate constant at 25°C determined from the lineal fit of $\ln(c/c_0)$ incidence with time

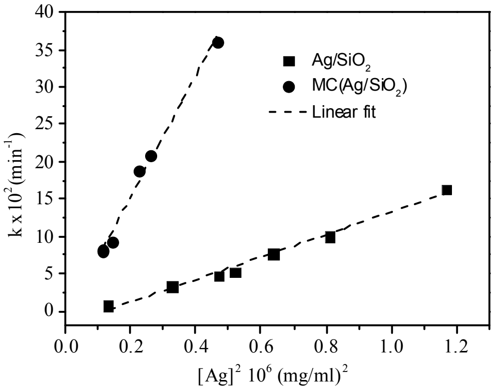

Fig. 6 The apparent rate constants as function of squared silver concentration and corresponding linear fits (dash lines), determined for freely dispersed (squares) and encapsulated (circles) Ag/SiO_2 nanocatalyst.

According to this model borohydride reduction of 4-nitrophenol occurs on the surface of catalyst in two steps. First, borohydride ions react with the surface of the metal catalyst to form surface-hydrogen species. Such species further reduce 4-nitrophenole molecules concurrently adsorbed on the catalyst surface. Since the surface-induced reduction is the rate-determining step, the apparent rate constant should be proportional to the entire surface area of the catalyst accessible for the reactants. From the Fig. 6 it is obvious that catalysis with either freely-dispersed or encapsulated Ag/SiO_2 nanocatalyst perfectly fits to this theory in the whole range of catalyst concentration studied. Considering all aforementioned we suggest that PNIPAM-based microcapsules act not only as hosts for nanocatalyst incorporation, but also serve as microreactors for catalysis. First of all, partial cross-linking of MC walls does not prevent their permeability to water and water-soluble molecules. Second, in THF/water environment hydrophilic nature of PNIPAM causes concentration of water and water-soluble reactants in its vicinity. Finally, the presence of Ag nanocatalyst inside the MC in immediate proximity to the concentrated reactants stimulates the reaction to perform much faster as compared to the catalyst being freely-dispersed in reaction mixture.

To investigate the recyclability and catalytic activity of the MC(Ag/SiO_2), microcapsules were used for several subsequent cycles of the catalytic reaction. Indeed, MC(Ag/SiO_2) remain catalytically active after its recovery and can be re-used in next catalytic cycles of reduction of 4-nitrophenol. After 8 subsequent cycles, the apparent rate constant decreased for ca.10 % as compared to the 1st cycle, which might be attributed to incomplete transfer of the catalyst from centrifugation tube into cuvette (for more details - see Fig. S6 and comments in ESI†).

Temperature dependence of catalytic activity

Employing of PNIPAM polymer induced us to suppose that the thermo-responsive effect of PNIPAM will retranslate onto behaviour of produced MC. It was suggested that with an increase of the reaction temperature above LCST of PNIPAM, the MC should become less penetrable for the reactants and, thus, the total rate of catalysis should be reduced or even completely suppressed. In fact, no suppression of the catalysis was observed in the investigated reaction conditions. Moreover, the catalytic reaction proceeded faster and was accomplished in first several minutes. Similar outcome, i.e. acceleration of the reaction rate with temperature was observed in case of freely-dispersed Ag/SiO_2 nanocatalyst (Fig. 7). Although the relative increase of the reaction rate constant for freely dispersed Ag/SiO_2 nanocatalyst compare to MC(Ag/SiO_2) was found more pronounced (9 and 6 times, respectively), it is rather difficult to speculate about the thermo-control of such reaction.

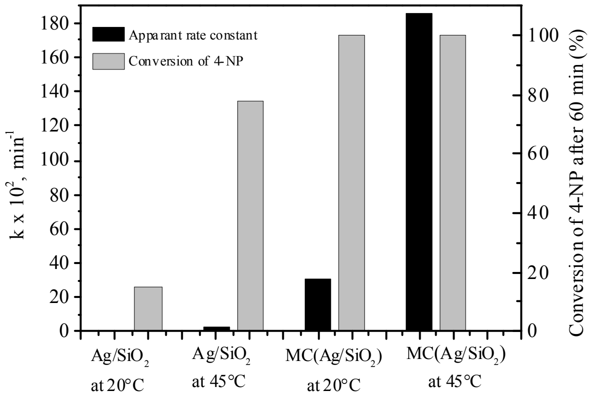

Fig. 7 Temperature dependencies of the apparent rate constant and conversion of 4-NP catalysed by Ag/SiO_2 and MC(Ag/SiO_2).

Obviously, thermo-induced collapse of the microcapsule walls should hinder to some extent diffusion of the reagents to the catalyst, but still it does not prevent the reaction in whole. This becomes explainable, however, taking into account that adsorption constants of nitrophenol and $NaBH_4$ are also temperature-dependent and with an increase of temperature also increase.[51] Thus, an increase of the adsorption constant at higher temperatures would lead also to a corresponding increase of the overall reaction rate constant.

Conclusions

In summary, the composite Ag/SiO_2 guest-host type nanocatalyst has been prepared using templates assisted synthesis of silver nanoparticles. An application of SiO_2 particles during silver reduction allows to obtain SiO_2-supported surfactant-free nanocatalyst. Such composite nanocatalyst was further encapsulated into the interior of PNIPAM based microcapsules, resulting in the catalytically-active system being in the same time easy separable from the reaction mixture applying simple methods, like filtration. Due to the amphiphilic properties of the MC (hydrophilic interior and hydrophobic shell) they form stable dispersion in organic solvents being in the same time able to occlude inorganic nanoparticles in their interior. Prepared in such a way MC(Ag/SiO_2) composite was proved to be an efficient and easy-to-handle catalytic system. On the example of borohydride reduction of 4-nitrophenol it was shown that catalytic activity of encapsulated Ag/SiO_2 substantially exceeds the activity of the same catalyst in freely dispersed state. The apparent reaction rate constants determined for various concentration of MC(Ag/SiO_2) composite nanocatalyst were found superior up to ten times of magnitude compare to freely dispersed Ag/SiO_2.

It is suggested that in case of mixed organic/aqueous environment like THF/water, hydrogel microcapsules containing nanocatalyst act as microreactors. In this case water, which is absorbed by the hydrophilic MC interior, allows the formation of local environment for high concentration of water-soluble reagents. Therefore, the encapsulation of nanocatalyst inside the MC promotes considerable shortening of the reaction activation time and in the same time acceleration of the reaction *in toto*. It was also demonstrated that at the elevating temperature the reaction rate for catalysis with Ag/SiO_2 increases in both cases, i.e. with and without catalyst encapsulation in MC.

In addition to higher performance of proposed catalyst-carrying microreactors, obvious advantages are also the simplicity of their synthesis and easiness of separation from the reaction mixture. The latest feature heavily facilitates the procedure of catalyst purification and recovering. It is therefore envisioned that such versatile catalyst-carrying systems can serve as a useful platform for studying of various heterogeneous catalytic reactions in a confined and controlled manner, while the functional nanocatalyst and nature of polymer microcapsules can be tailored to specific reaction requirements.

Acknowledgements

The authors thank Dr. V. Senkovskyy for providing PI-*b*-PEO block copolymer and Dr. U. Oertel for helpful discussion. We acknowledge DFG (German Research Foundation, SPP 1259 “Intelligente Hydrogele”) and IPF Dresden for financial support.

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† Electronic Supplementary Information (ESI) available: SEM images , TGA data and UV-Vis spectra. See DOI: 10.1039/b000000x/

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Polymer microcapsules loaded with Ag nanocatalyst as active microreactors†

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Silica-supported silver nanoparticles (Ag/SiO_2) were encapsulated inside of the PNIPAM-based microcapsules (MC) and proved as an efficient and easy-to-handle catalytic system. Due to the hydrophilic nature of MC, they act as microreactors in mixed organic/aqueous environment. On the example of borohydride reduction of 4-nitrophenol it was demonstrated that catalytic activity of encapsulated Ag@SiO_2 substantially exceeds the activity of the same catalyst in freely dispersed state.