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Polymer microcapsules loaded with Ag
nanocatalyst as active microreactors†Cite this: *J. Mater. Chem. A*, 2014, 2,
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We report on the fabrication of a new complex catalytic system composed of silica-supported silver nanoparticles (AgNP) encapsulated inside polymer microcapsules (MC)s. The silver nanocatalyst itself was obtained by reduction of silver salt in the presence of SiO₂ particles acting as AgNP carriers, to provide a complex Ag/SiO₂ catalyst with the Ag surface completely free of capping agents. Ag/SiO₂ particles were enclosed inside the interior of polymer microcapsules. Due to the presence of the hydrophobic shell on the MC surface, catalytic reactions become feasible in an organic solvent environment. On the other hand, the hydrophilic nature of the MC interior forces the water-soluble reactants to concentrate inside the capsules which act as microreactors. Based on the example of catalytically driven reduction of 4-nitrophenol we demonstrate that encapsulated Ag/SiO₂ particles possess enhanced catalytic activity as compared to the catalyst being freely dispersed in reaction medium.

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Introduction

Catalysis with nanoparticles (NP)s (*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 NPs of different sizes and shapes is 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 NPs 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} micelles²² or microemulsions²³ can be applied, ensuring particle dispersion stability in both polar and non-polar media. Nevertheless, such enhanced stability of NPs 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 a 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, SiO₂, Al₂O₃ or other metal oxides were successfully used as supports for immobilisation of different types of NPs 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 a non-polar environment, still remains an open question.

An alternative way to ensure nanocatalyst dispersion stability and facilitate recovery is encapsulation into hollow structures, *e.g.* microcapsules (MC)s. Utilization of hollow structures as nanocatalyst carriers requires their intrinsic properties, *e.g.* dispersion stability, recoverability, chemical resistance *etc.*, which 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 the SiO₂ core from the corresponding SiO₂/polymer particles also represents the way to obtain hollow structures.^{40,41} This step-wise approach typically involves the 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 the templating approach for the preparation of a 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 a solvent-resistant polymer shell. This method, however, is quite complicated due to the multistep procedure. In addition,

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it requires dissolution of a 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 the complete template removal.

Herein, we report a simple and straightforward method to obtain an Ag/SiO₂ nanocatalyst encapsulated inside poly(*N*-isopropylacrylamide (PNIPAM) microcapsules stabilized with a hydrophobic shell. The suggested method intends the formation of a metal nanocatalyst on the surface of silica particles followed by encapsulation of such composite particles into the polymer capsule interior. The use of the silica support allows obtaining a pristine metal nanocatalyst with the surface free of any stabilizing agents. In turn, after enclosing into permeable MCs, active species remain accessible to reactants, gaining an additional benefit of 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 a simple one-pot preparation protocol we can produce polymer microcapsules already loaded with the nanocatalyst, avoiding thus the multistep synthetic process and eliminating the requirements of sacrificial material destruction.

Experimental

Materials

Poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO, $M_n(\text{PI}) = 24\,300\text{ g mol}^{-1}$, $M_n(\text{PEO}) = 5830\text{ g mol}^{-1}$, $\text{PDI}(\text{PI-}b\text{-PEO}) = 1.3$), 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*-methylene-bis(acrylamide) (MBA, Merck, 98.0%), ammonium persulfate (APS, Merck, 98.0%), tetraethyl orthosilicate (TEOS, Aldrich), silver acetate (CH₃COOAg, 99% Aldrich), sodium borohydride (NaBH₄, 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 (SiO₂) ($d_{\text{av}} = 219\text{ nm}$, $\text{PDI} = 0.012$ as determined by DLS) were prepared by the Stöber method⁴⁴ 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 a vacuum oven at 50 °C overnight to get SiO₂ in a dry (powder) state.

Synthesis of the Ag/SiO₂ catalyst

To 1.7 mg of SiO₂ 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 NaBH₄ was added and the reaction

mixture immediately turned to dark brown, indicating the formation of silver nanoparticles (AgNP). Ag/SiO₂ particles were recovered from the butch solution and purified by repeated centrifugation and re-dispersion in water. The presence of AgNPs on the SiO₂ surface was proved by SEM and TEM imaging and UV-Vis measurements.

Encapsulation of Ag/SiO₂ into PNIPAM microcapsules

Ag/SiO₂ composite particles were encapsulated into the PNIPAM-based microcapsule interior by adopting the previously reported protocol of water-in-oil suspension polymerisation of NIPAM in the presence of a 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/SiO₂ (3.8 mg ml⁻¹) to form a water phase. Water and oil phases were mixed in an Ultra-Turax mixer (IKA, Germany) at 13 500 rpm for 2 minutes and the resulting emulsion was transferred into the glass tube equipped with a magnetic stirrer. The temperature of the mixture was rapidly increased to 80 °C and the polymerization was carried out for 1 hour. The excess of the surfactant was washed 5 times by 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 by 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 of 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 an Ultra 55 (Carl Zeiss SMT, Jena, Germany) operated at 3 kV using a secondary electron (SE) detector. TEM images were recorded with a Libra 200 (Carl Zeiss SMT) operated at 200 kV. UV-Vis measurements were carried out using a Perkin-Elmer UV-Vis spectrometer Lambda 800. Dynamic light scattering (DLS) measurements were performed with a Zetasizer Nano S (He-Ne-laser 4 mW, 632.8 nm, back scattering, NIBS Technology, Malvern Instruments). TGA experiments were carried out in a nitrogen atmosphere using a TA Q5000 thermal analyser (TA instruments, USA) at a heating rate of 10 K min⁻¹.

Results and discussion

In this work we report on the fabrication of a complex catalytic system composed of a silica-supported metal nanocatalyst encapsulated inside the polymer microcapsules (MC(Ag/SiO₂)). First, silver nanoparticles were synthesized on the surface of larger SiO₂ particles. Next, obtained Ag/SiO₂ were encapsulated into the interior of polymer microcapsules as shown in Fig. 1. An application of SiO₂ supports allows preparation of AgNPs having the surface completely free of the stabilizing layer. This also prevents nanoparticles from undesirable aggregation, ensures the highest surface-to-volume ratio and enhances catalytic activity.⁴⁵ Moreover, the silica-supported nanocatalyst can be easily recovered by centrifugation and further re-used for catalytic purposes. Encapsulation of Ag/SiO₂ into the interior of hydrophobically covered polymer microcapsules provides the possibility to perform catalysis in non-polar organic media in which Ag/SiO₂ particles are poorly dispersible.

Synthesis of the Ag/SiO₂ nanocatalyst

SiO₂ particles ($d_{av} = 219$ nm) were prepared according to the Stöber procedure⁴⁴ and used as supports for the silver nanocatalyst. The size of silica particles was optimized by varying the TEOS/H₂O/NH₄OH 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/SiO₂) were prepared by borohydride reduction of silver acetate in the presence of SiO₂ particles. The reaction was carried out in a THF–water mixture where the minor amount of water (*ca.* 1.5 vol%) was used to solubilise silver acetate. Such reaction conditions allowed generation of silver nanoparticles predominantly attached to the silica surface (Fig. 2a and b). The size of the silica-supported AgNPs was 19.3 nm (SD = 3.8 nm) as determined from the analysis of TEM images, whereas the calculated Ag : SiO₂ ratio and the surface coverage of SiO₂ with silver were 1 : 15 (w/w) and ~7.3 wt%, respectively. The UV-Vis

Fig. 2 SEM (a) and TEM (b) images of Ag/SiO₂ particles and (c and d) TEM images of MCs filled with Ag/SiO₂ at different magnifications.

spectrum of Ag/SiO₂ possesses a 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 AgNPs appear firmly attached to the SiO₂ surface and cannot be leached out neither by repeated washing with water or ethanol nor by intense agitation in an ultrasonic bath (Fig. S2, ESI†).

It should be pointed out that our attempts to prepare Ag/SiO₂ particles in a purely THF or aqueous environment were less successful and led to the formation of a significant amount of crude silver particulates of over a micrometer size, lowering thus fraction of AgNPs 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 SiO₂ 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 the SiO₂ surface, but appear solubilized uniformly through the whole volume.

Ag/SiO₂ 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 sizes⁴⁹ and compositions.⁵⁰ Hollow polymer structures can be produced in water-in-oil (W/O) inverse miniemulsion composed of monomer-containing water droplets, stabilized with an amphiphilic block copolymer which serves both as surfactant and a shell-forming component.

Fig. 1 Schematics of encapsulation of Ag/SiO₂ particles into the microcapsules interior.

Obtained in such a way MCs appear readily dispersible in non-polar organic solvents due to the presence of the 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 MCs directly during their synthesis.

In the present work we exploited these synthetic advantages in order to directly load MCs with Ag/SiO₂ particles. For preparation of miniemulsion, the water dispersion of Ag/SiO₂ 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 trimethylpentane and used as a continuous phase. Thus, after emulsification, the hydrophilic Ag/SiO₂ particles together with reactants appeared trapped within the interior of water droplets being stabilized with a BCP surfactant. Encapsulation of Ag/SiO₂ particles was accomplished by polymerization of NIPAM in droplets at a temperature above LCST of PNIPAM that results in hollow structure morphology. Copolymerization of NIPAM with the MBA cross-linker ensures the strength of capsules, whereas an application of the PI-*b*-PEO surfactant provides them with the hydrophobic shell.

The success of Ag/SiO₂ encapsulation was proved using TEM imaging (Fig. 2c and d). From TGA (Fig. S4, ESI†) the amount of encapsulated Ag/SiO₂ particles inside the MCs was found to be 15 wt%, which gives an estimated content of the silver nanocatalyst of *ca.* 1 wt%.

Catalytic activity

Catalytic activity of encapsulated Ag/SiO₂ was studied and compared with the activity of Ag/SiO₂ 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 kinetics by monitoring the intensity of the 4-NP absorbance peak ($\lambda_{\text{max}} = 400 \text{ nm}$) with reaction time. However, a specific character of the investigated system required adjustment of particular experimental conditions. As has already been mentioned, due to the presence of the hydrophobic shell on MCs they form stable dispersion in organic solvents of low and moderate polarity but aggregate in an aqueous environment. On the other hand, in pure aprotic

solvents like THF, 4-nitrophenol does not possess any absorption peak in the 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/SiO₂ and MCs form sufficiently stable dispersions and a 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 the presence of MC(Ag/SiO₂). As was expected, after addition of NaBH₄ the intensity of the 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 previously reported on catalytic reduction of 4-nitrophenol in the presence of Pt or Au nanoparticles.⁵¹ Moreover, a similar spectrum alteration was also observed when freely dispersed Ag/SiO₂ catalyst particles were used to catalyse the same reaction (Fig. S5, ESI†). Such similarities provide clear evidence that Ag/SiO₂ 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 the 4-nitrophenol relative concentration *versus* time determined for different concentrations of the Ag/SiO₂ catalyst.

At the concentrations of silver above $0.9 \times 10^{-3} \text{ mg ml}^{-1}$ the full conversion of 4-nitrophenol (more than 99%) was usually accomplished in 60 min. As a 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 t_0 was also detected for the reaction catalysed by other kinds of metal nanoparticles⁵² and is usually attributed to substrate-induced surface restructuring, which is necessary to render the metal nanoparticles an active catalyst.⁵¹ It was also observed similar to other studies that the initiation period becomes shorter with an increase of the catalyst

Fig. 3 Schematics of catalytic reduction of 4-nitrophenol inside the microcapsules loaded with Ag/SiO₂.

Fig. 4 Successive UV-Vis spectra taken every minute during borohydride reduction of 4-NP catalysed by MC(Ag/SiO₂). Initial concentrations: [4-NP] = 0.125 mM, [NaBH₄] = 1.5 M, [Ag] = $0.48 \times 10^{-3} \text{ mg ml}^{-1}$.

Fig. 5 Plots of c/c_0 (a and c) and $\ln(c/c_0)$ (b and d) versus time for the borohydride reduction of 4-NP catalysed by Ag/SiO₂ (a and b) and MC(Ag/SiO₂) (c and d). Rate constants determined from the linear fits of $\ln(c/c_0)$ (dashed lines) and the corresponding concentrations of Ag are given in Table 1.

concentration in the system. After the initiation period, the reaction proceeds much faster and can be treated as the 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 concentrations of the Ag/SiO₂ nanocatalyst are summarized in Table 1.

Unforeseen to some extent results were obtained when encapsulated Ag/SiO₂ particles were used as catalysts for the

same reaction. First, the activation time substantially decreased and did not exceed 1–2 minutes as compared to 10–15 minutes for the freely dispersed Ag/SiO₂ catalyst (Fig. 5c). At higher concentration of the encapsulated catalyst the activation time was difficult to detect, because a substantial decrease of the 4-nitrophenol concentration has already been observed starting from the first minute of measurement. Secondly, unexpectedly high reaction rates were observed when MC(Ag/SiO₂) was used as the catalyst (Table 1). At concentrations of Ag in MCs above 0.5×10^{-3} mg ml⁻¹ 99% conversion of 4-nitrophenol was achieved already in 10 minutes after addition of the catalyst. Nevertheless, the reaction catalysed with MC(Ag/SiO₂) 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/SiO₂) exceeded 5–10 times the magnitude of the corresponding rate constants for catalysis with freely-dispersed Ag/SiO₂. Monitoring of the reaction kinetics at the Ag concentration higher than 0.65×10^{-3} was hardly possible due to the very fast reaction performance and limitations of the detection method. Such a significant increase of the apparent rate constant in the case of application of MC(Ag/SiO₂) is discussed in terms of possible processes occurring during the performed catalytic reaction.

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

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

Catalyst	[Ag/SiO ₂] mg ml ⁻¹	[Ag] 10 ³ mg ml ⁻¹	k^b 10 ² 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.

solvent mixtures can significantly exceed its solubility in the pure solvent (the cononsolvency effect).⁵³ For example, such enhanced swellability of PNIPAM MCs in THF–water mixture compare to pure THF was demonstrated in our previous work.⁴³

Since the water volume fraction used in this study is less as the THF–water cononsolvent ratio for PNIPAM, the MCs 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 MCs. Since the reaction performance depends on the concentration of reagents, the local growth of the reactant concentration in the vicinity of the 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 for acceleration of the catalysis in MCs. To ascertain the possible mechanism of the reaction, the apparent rate constants were plotted as a function of squared concentration of the silver nanocatalyst (Fig. 6). For both freely dispersed and encapsulated Ag/SiO₂ particles the rate constants were found to be linearly dependant on the 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

According to this model borohydride reduction of 4-nitrophenol occurs on the surface of the 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-nitrophenol 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 Fig. 6 it is obvious that catalysis with either the freely-dispersed or encapsulated Ag/SiO₂ nanocatalyst perfectly

fits to this theory in the whole range of the 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 a THF–water environment the hydrophilic nature of PNIPAM causes the concentration of water and water-soluble reactants in its vicinity. Finally, the presence of the Ag nanocatalyst inside the MCs in immediate proximity to the concentrated reactants stimulates the reaction to perform much faster as compared to the catalyst being freely-dispersed in the reaction mixture.

To investigate the recyclability and catalytic activity of the MC(Ag/SiO₂), microcapsules were used for several subsequent cycles of the catalytic reaction. Indeed, MC(Ag/SiO₂) 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 the incomplete transfer of the catalyst from a centrifugation tube into a cuvette (for more details – see Fig. S6 and comments in the ESI†).

Temperature dependence of catalytic activity

Employing the PNIPAM polymer induced us to suppose that the thermo-responsive effect of PNIPAM will retranslate onto behaviour of produced MCs. It was suggested that with an increase of the reaction temperature above LCST of PNIPAM, the MCs 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 under the investigated reaction conditions. Moreover, the catalytic reaction proceeded faster and was accomplished in first several minutes. A similar outcome, *i.e.* the acceleration of the reaction rate with temperature was observed in the case of the freely-dispersed Ag/SiO₂ nanocatalyst (Fig. 7). Although the relative increase of the reaction rate constant for the freely dispersed Ag/SiO₂ nanocatalyst

Fig. 6 The apparent rate constants as a function of squared silver concentration and the corresponding linear fits (dashed lines), determined for the freely dispersed (squares) and encapsulated (circles) Ag/SiO₂ nanocatalyst.

Fig. 7 Temperature dependencies of the apparent rate constant and conversion of 4-NPs catalysed by Ag/SiO₂ and MC(Ag/SiO₂).

compared to MC(Ag/SiO₂) was found more pronounced (9 and 6 times, respectively), it is rather difficult to speculate about the thermo-control of such reaction.

Obviously, the 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 as a whole. This becomes explainable, however, taking into account that adsorption constants of nitrophenol and NaBH₄ 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/SiO₂ guest–host type nanocatalyst has been prepared using template assisted synthesis of silver nanoparticles. An application of SiO₂ particles during silver reduction allows us to obtain a SiO₂-supported surfactant-free nanocatalyst. Such a composite nanocatalyst was further encapsulated into the interior of PNIPAM based microcapsules, resulting in the catalytically active system being at the same time easily separable from the reaction mixture by applying simple methods, like filtration. Due to the amphiphilic properties of the MCs (hydrophilic interior and hydrophobic shell) they form a stable dispersion in organic solvents being at the same time able to occlude inorganic nanoparticles in their interior. Prepared in such a way the MC(Ag/SiO₂) composite was proved to be an efficient and easy-to-handle catalytic system. Based on the example of borohydride reduction of 4-nitrophenol it was shown that catalytic activity of encapsulated Ag/SiO₂ substantially exceeds the activity of the same catalyst in a freely dispersed state. The apparent reaction rate constants determined for various concentrations of the MC(Ag/SiO₂) composite nanocatalyst were found superior up to ten times magnitude compare to freely dispersed Ag/SiO₂.

It is suggested that in the case of a mixed organic–aqueous environment like THF–water, hydrogel microcapsules containing the nanocatalyst act as microreactors. In this case water, which is absorbed by the hydrophilic MC interior, allows the formation of a local environment for high concentration of water-soluble reagents. Therefore, the encapsulation of the nanocatalyst inside the MCs promotes considerable shortening of the reaction activation time and at 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/SiO₂ increases in both cases, *i.e.* with and without catalyst encapsulation in MCs.

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 useful platforms for studying various heterogeneous catalytic reactions in a confined and controlled manner, while

the functional nanocatalyst and the nature of polymer microcapsules can be tailored to specific reaction requirements.

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