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Magnetic silica colloids for catalysis

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Abstract

Monodisperse magnetizable colloidal silica particles in a stable dispersion have been functionalized with a homogeneous catalyst: a PCP–pincer Pd-complex. In a proof-of-principle experiment we demonstrate the catalytic activity of the colloids in a C–C bond formation reaction. Advantages of the magnetic silica carriers are the large surface-to-volume ratio and the easy recovery by magnetic separation. After magnetic separation, the catalyst-loaded particles are readily redispersed for further use.

Keywords: Magnetic silica particles; Magnetic separation; Pincer complex; Supported catalyst; Aldol condensation reaction; Maghemite; Silica colloids; Core-shell particles

Colloidal silica is widely used in industrial applications as well as for fundamental research purposes. The preparation of monodisperse silica particles and silica coating of other inorganic colloids are well-documented and the silica particle surface is well suitable for chemical surface modification (see for instance Refs. [1–3]).

Catalysis is an indispensable process in the chemical industry both from an economical as well as environmental point of view. Production of various chemicals ranging from pharmaceuticals to polymers involves the use of transition metal catalysts [4,5]. These catalytic systems are generally divided into two groups: *homogeneous* (catalyst in the same phase as the reactants) and *heterogeneous* (catalyst on a solid support) catalysts. Heterogeneous catalytic systems have the advantage that the catalyst can be recovered after completion of the reaction. On the other hand, a homogeneous catalytic system has a higher reactivity and selectivity. To combine these advantages, homogeneous catalysts are usually immobilized on supports such as mesoporous silica [6–9]. Silica has the advantage that it is inert and hence chemically and thermally stable under most of the conditions at which catalysts are operating, and it can be readily separated from the reaction mixture. Depending on the surface area and pore size of the silica, it can have a restricted approach of the reactant molecules to the catalyst, thereby reducing the reactivity and altering the selectivity. By using colloidal particles (which have a high surface-to-volume ratio) as a support, homogeneous catalysts can be dispersed in a reaction mixture and at the same time be separated from a solution by sedimentation [10,11]. By introducing support particles with induced magnetic properties the separation can be improved and the magnetic support particles can be fixed at the wall of the reaction vessel while the solution is decanted by applying a magnetic field [12]. For efficient recycling of the catalyst, the support particles should be magnetic enough to be collected with a small permanent magnet and easily be redispersed in the reaction medium after removing the magnet so that the catalysis can be continued. Moreover, the support particles must be chemically inert under the conditions at which the catalysis takes place.

Magnetic particles have previously been immobilized onto mesoporous silica structures for catalytic purposes [13]. Single magnetic particles with a silica shell have also been reported on as support particles in catalysis [11,14], but such particles require high fields for efficient magnetic separation from solution, which is a severe drawback.

Here, we report on the preparation of magnetic silica particles (150 nm radius) consisting of monodisperse silica

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cores covered with maghemite nanoparticles and an outer silica shell, grafted with a modified organometallic catalyst based on a PCP-pincer palladium complex [15,16]. This complex is known to catalyze the aldol condensation reaction between benzaldehyde and methyl isocyanoacetate to produce oxazolines [17] (see Scheme 1).

The magnetic silica particles used in this work were prepared according to the scheme in Fig. 1, following a procedure described in more detail elsewhere [18]. Silica cores ($R_{TEM} = 135$ nm, $R_{SLS} = 152$ nm) were prepared by hydrolysis and condensation polymerization of tetraethoxysilane [1] and grafted with a thiol containing silane-coupling agent [3]. Maghemite particles were prepared according to the classic co-precipitation method of Massart et al. [19] and added to the dispersion of thiol-functionalized silica particles, leaving the mixture gently shaken overnight. Excess maghemite was removed by repeated centrifugation. The silica cores covered with maghemite particles were coated with a thin outer silica shell by applying the same seeded-growth synthesis method as for the silica cores, now using the magnetic core-shell particles as seeds. Small aliquots of tetraethoxysilane were added to the reaction mixture while using ultrasonication to prevent aggregation of particles during the silica growth. The silica-coated magnetic core-shell particles were purified by repeated centrifugation and redispersion in ethanol.

The size as well as the internal morphology of the particles was monitored throughout the step-wise preparation using transmission (TEM) and scanning (SEM) electron microscopy (Fig. 2). As a complement, static light scattering (SLS) contrast variation experiments were used for size determination (Fig. 3) [20]. Light scattering measurements are performed directly in dispersion whereas conventional TEM is performed on a substrate with dry particles, which consequently yields an underestimate of the particle size. The intersection point of the angular intensity profiles in Fig. 3 gives the total radius of the particles from $k_m R = 4.4935$ as known from scattering theory of concentric inhomogeneous particles [20]. Additionally, such a well-defined intersection point confirms the presence of non-aggregated particles in dispersion with a low polydispersity. This is valuable information, which cannot always be obtained from TEM due to drying effects. Finally, magnetization measurements were performed on a sample of dried magnetic silica. The absence of hysteresis confirms that the particles are superparamagnetic.

PCP-pincer palladium complexes are known for their catalytic activity in C–C bond formation reactions [17]. A modified version of this complex (**1**, see Fig. 4), which has a triethoxy silane group useful for tethering it to the silica was prepared [21]. This complex was immobilized on to the magnetic silica by a standard process in which a mixture of

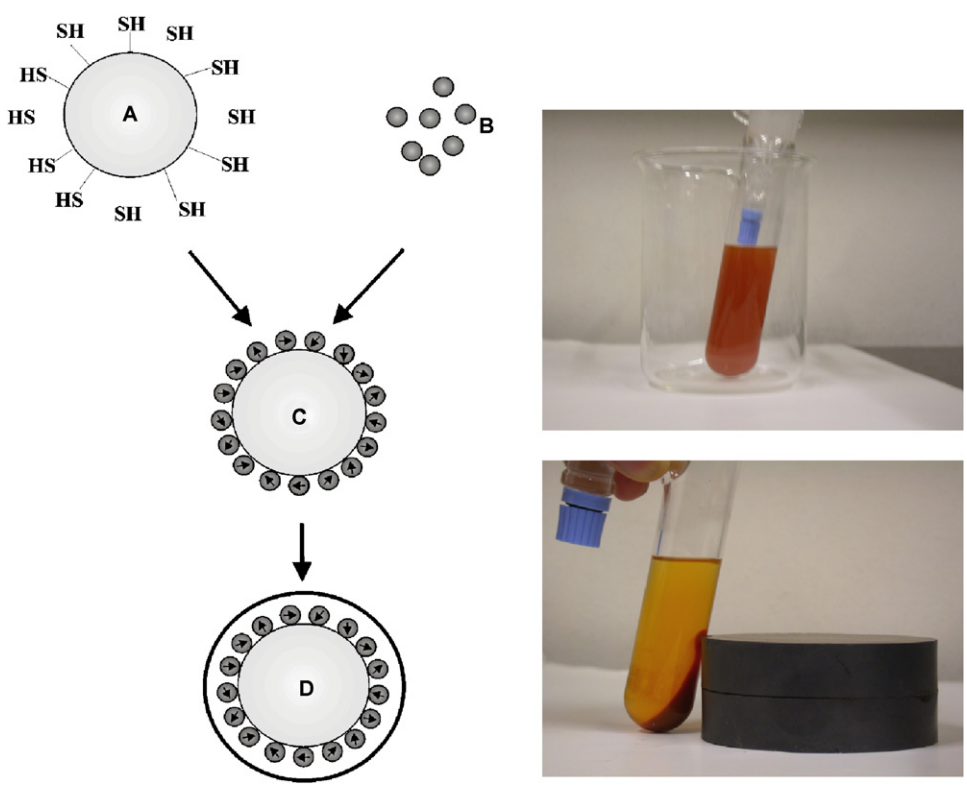


Fig. 1. Left: The stepwise synthesis of magnetic silica: Thiol-functionalized Stöber silica (A) is mixed with maghemite (B) to obtain silica cores with magnetic particles (C) onto which silica can be precipitated to form magnetic core-shell particles with an outer silica shell (D). Right: The particles in dispersion after surface modification with the PCP–Pd complex (top) and collected with a magnet during the purification from unreacted PCP–Pd complex (bottom).

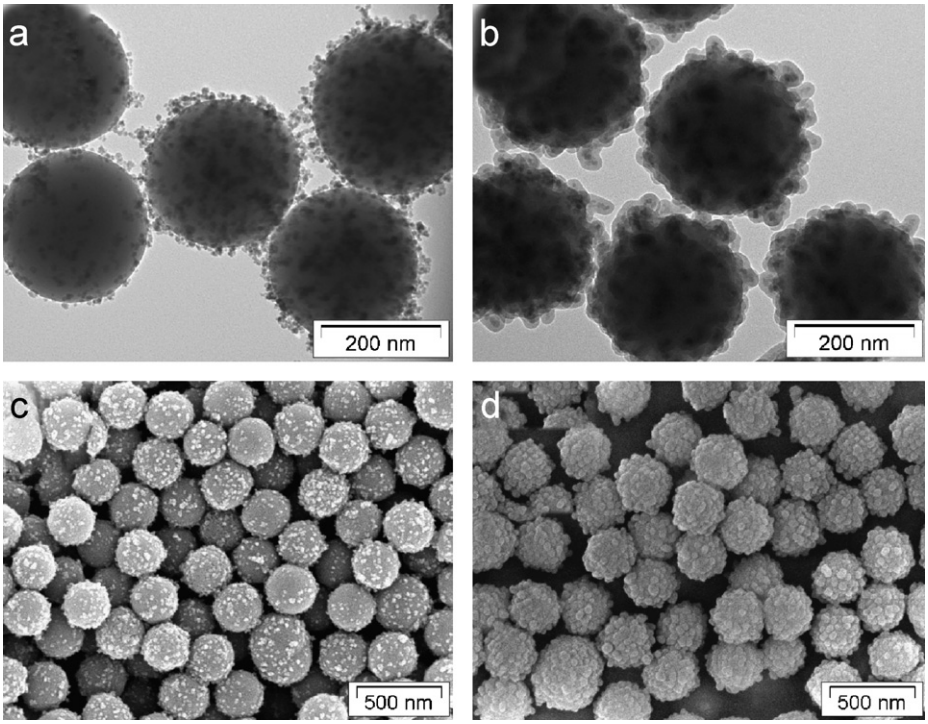


Fig. 2. TEM (top) and SEM (bottom) pictures of maghemite covered silica cores before (a,c) and after (b,d) silica coating.

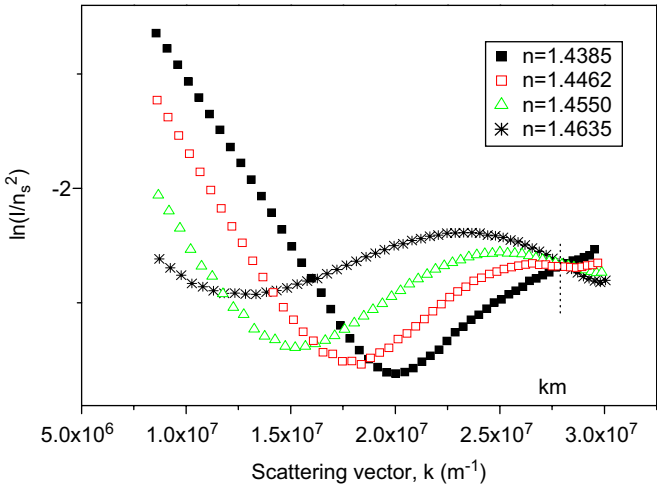


Fig. 3. Results from static light scattering measurements performed on magnetic silica particles, applying optical contrast variation. From the sharp intersection point at $k_m = 2.766 \times 10^7\,m^{-1}$ a total particle radius of 162 nm is obtained in good agreement with the radius obtained from TEM (153 nm). The sharpness of the intersection point and the agreement with the TEM-radius of the particles indicates monodisperse non-aggregated particles.

the magnetic silica and complex **1** was heated at 90 °C in toluene for 20 h. The modified silica was separated from the solution by using a small permanent magnet as shown in Fig. 1. The supernatant was removed and the silica was washed with dichloromethane to remove non-immobilized complex **1**. Every time, the silica was separated with a magnet. The functionalized silica was then suspended in hexane and treated with 1,1,1,3,3,3-hexa-methyldisilazane (HMDS) to cap remaining unreacted surface silanol groups with a trimethylsilyl functionality **3**. The resulting magnetic silica particles, loaded with PCP–Pd complex will be denoted here as MagSi**3**.

Characterization of MagSi**3** was performed by using IR spectroscopy (Diffuse Reflectance, DRIFT), and elemental analysis. IR of the MagSi**3** showed vibrations corresponding to C–H (2982 cm^{-1}) apart from usual silica related vibrations (3366, 2982, 1631, 1447, 1083, 952, and 796 cm^{-1}). With IR, no peaks originating from the catalyst could be detected, since the amount of catalyst is very low compared to the silica content.

From the elemental (ICP) analysis of MagSi**3** it was observed that the palladium content was 0.14%, which corresponds to 0.0135 mmol PCP–pincer Pd-complex **1** per gram MagSi**3**. The molar ratio of phosphorus to palladium was found to be about 2.7. It should be noted that the presence of these elements were analyzed after thoroughly rinsing the magnetic silica particles, which would have removed any free molecules. Based on the palladium content, the surface coverage was estimated to be 1.1 PCP–pincer Pd-complex molecules per nm^2 MagSi**3**. However, this is likely to be an overestimate, since it is assumed that the particles are spherical and that the catalyst molecules form a single monolayer on the particle surface.

Subsequently, the MagSi**3** particles were tested in catalysis. As a test reaction, the aldol condensation reaction between benzaldehyde and methyl isocyanoacetate (Scheme 1) was chosen.

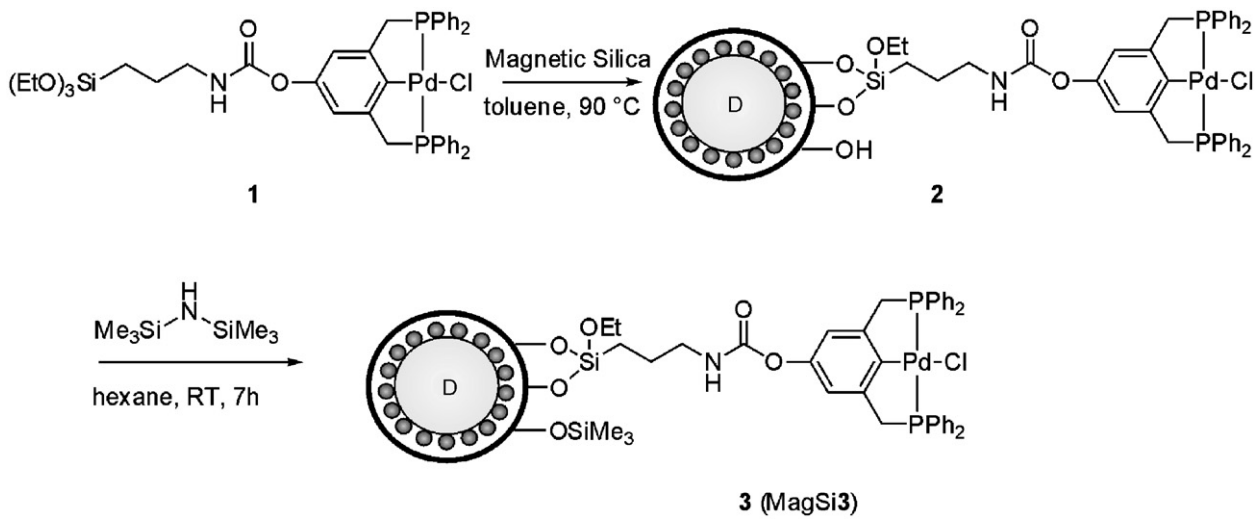
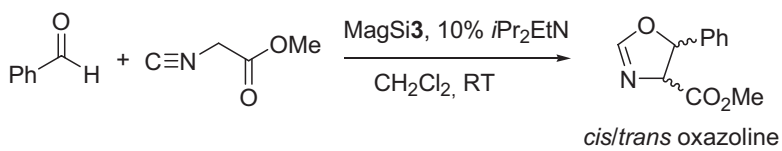


Fig. 4. Scheme of the immobilization of catalytic PCP–pincer Pd-complex (**1**) onto magnetic silica particles (**D**).



Scheme 1. A1dol condensation reaction between benzaldehyde and methyl isocyanoacetate to oxazoline catalysed by magSi**3**.

In this experiment, 1.6 mmol of each benzaldehyde and methyl isocyanoacetate were reacted in the presence of the base *N*,*N*-diisopropylethylamine, $i\mathrm{Pr_2EtN}$ (10 mol%, 0.16 mmol). The amount of MagSi**3** catalyst used was 100 mg, which corresponds to about 1.35 μmol of palladium, and which gives a catalyst concentration of 0.08 mol%. For comparison, a blank reaction was performed using all the above reagents at the same concentration but without the MagSi**3** catalyst. Results of the catalysis and blank reactions are shown in Fig. 5. It is clear that the reaction with MagSi**3** has the higher activity (TOF = $16\,\mathrm{h}^{-1}$ at 40% conversion) over the background reaction. When the silica was sedimented using a magnet, the progress of the reaction decreased to approximately that of the background reaction, whereas the reaction after redispersing the magnetic silica proceeded with the same reaction rate as before removal of the catalyst. These experiments indicate that the observed acceleration is due to the PCP–Pd-based activity and that this is affiliated with the magnetic silica. These results demonstrate the heterogeneous nature of the catalyst. The catalytic activity can be improved by increasing the amount of catalytic particles and/or by decreasing the size of the magnetic silica particles to provide more surface area.

In summary, monodisperse magnetic silica particles have been prepared and grafted with a homogeneous catalyst, in this case a PCP–pincer Pd-complex. In this way, the catalyst can be separated from a reaction mixture in a relatively low magnetic field, by using a small laboratory magnet. Furthermore, we have provided a proof-of-principle of how these catalyst loaded magnetic silica particles can be used in a versatile C–C bond formation reaction. Moreover, after magnetic recovery, the magnetic silica particles with immobilized catalyst can readily be redispersed for further use. The small size of the support particles provides a large surface-to-volume ratio, which makes a large amount of immobilized catalyst available for catalysis per volume magnetic silica.

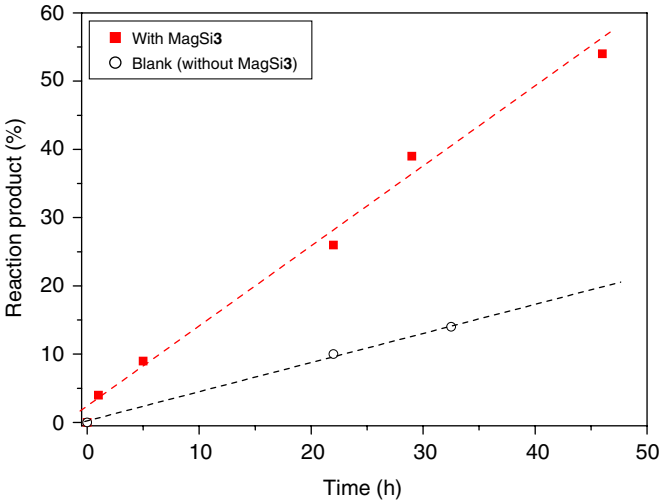


Fig. 5. Kinetic profile of the aldol reaction catalyzed by MagSi**3** and the same reaction without any catalyst present. Note that the dashed lines are no fits but only a guide for the eye.

The results presented here are promising for future work on particle-supported catalysts. The silica chemistry gives the possibility to attach a large variety of catalytic compounds to these magnetic particles, and provides interesting possibilities for use in cascade reactions [12] in which several reaction steps can be catalyzed by immobilizing several different catalysts onto the magnetic silica. In a more detailed study on the catalytic properties, the particles should be employed in catalysis several times and the structure of the PCP–Pd complex should be investigated prior to and after catalysis to ensure the stability of the catalyst.

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References

[1] W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
[2] T. Sugimoto, Fine Particles: Synthesis, Characterization, and Mechanisms of Growth, Dekker, New York, 2000.
[3] A.P. Philipse, A. Vrij, J. Colloid Interface Sci. 128 (1989) 121.
[4] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.
[5] F.R. Hartley, Supported Metal Complexes, Kluwer Academic, Dordrecht, 1985.
[6] J.M. Thomas, R. Raja, J. Organomet. Chem. 689 (2004) 4110.
[7] P. McMorn, G.J. Hutchings, Chem. Soc. Rev. 33 (2004) 108.
[8] D. Brunel, N. Bellocq, P. Sutra, et al., Coord. Chem. Rev. 178–180 (1998) 1085.
[9] J.H. Clark, D.J. Macquarrie, Chem. Commun. (1998) 853.
[10] S.W. Kim, M. Kim, W.Y. Lee, et al., J. Am. Chem. Soc. 124 (2002) 7642.
[11] D.K. Yi, S.S. Lee, J.Y. Ying, Chem. Mater., Chem. Mater. 18 (2006) 2459.
[12] N.T.S. Phan, C.S. Gill, J.V. Nguyen, et al., Angew. Chem. Int. Ed. 45 (2006) 2209.
[13] A.H. Lu, W.C. Li, A. Kiefer, et al., J. Am. Chem. Soc. 126 (2004) 8616.
[14] K. Butter, Iron(oxide) Ferrofluids: synthesis, structure and catalysis, Ph.D. thesis, Utrecht University, 2003.
[15] M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759.
[16] M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750.
[17] J.M. Longmire, X. Zhang, M. Shang, Organometallics 17 (1998) 4374.
[18] E.M. Claesson, A.P. Philipse, Langmuir 21 (2005) 9412.
[19] R. Massart, IEEE Trans. Magn. MAG-17 (1981) 1247.
[20] A.P. Philipse, C. Smits, A. Vrij, J. Colloid Interface Sci. 129 (1989) 335.
[21] N.C. Mehendale, R.J. M. Klein Gebbink, G. van Koten, et al., manuscript in preparation.