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Short Communication

Preparation of high-magnetization Fe_3O_4–NH_2–Pd (0) catalyst for Heck reaction

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ABSTRACT

A magnetically separable Fe_3O_4–NH_2–Pd (0) catalyst was easily synthesized by immobilizing Pd nanoparticles on the surface of magnetic Fe_3O_4–NH_2 microspheres. It was found that the combination of Fe_3O_4 and triethylene tetramine (TETA) could give rise to structurally stable catalytic sites. Furthermore, the high-magnetization Fe_3O_4–NH_2–Pd(0) catalyst can be recovered by magnet and reused for six runs for Heck reaction without significant loss in catalytic activity.

1. Introduction

In modern chemical research, catalysts and catalytic reactions are always attracting considerable attention in fundamental research and industrial applications [1–5]. Conventionally, heterogeneous catalysis is favored over homogeneous catalysis due to its ease of handling and regenerability. But the application of heterogeneous catalysts is limited because of less active site than their homogeneous counterparts. Recently, nanomaterials have emerged as sustainable alternatives to conventional heterogeneous catalysts and catalyst supports [6–9]. The nanomaterials present high specific surface area of the active component, thereby enhance the contact between reactants and catalyst support [10]. Although a higher surface area affords nanomaterials with more active sites, they are easy to agglomerate and hard to be separated. Therefore, it is essential to design an easily recovery and well-dispersed catalysts.

In this regard, magnetic nanoparticles (MNPs) as catalyst supports are very promising due to their large specific surface area and magnetic property [11–19]. It can be easily collected by a magnet for reuse to prevent loss of the catalyst. Recently, much attention has been focused on the surface modification with appropriate capping agents onto the MNP surface to anchor the catalytically active complexes [20–26]. As we know, amines have a strong affinity for general catalysts and can keep the MNPs from aggregating without disturbing their desired properties [27]. Thus, more attention has been focused on amine functionalization procedures to anchor the catalytically active complexes onto the MNP surface. Yi et al. reported on the synthesis of a nanocomposite of Pd nanoclusters supported on silica-coated Fe_2O_3 nanoparticles. The Pd/H_2N–SiO_2/Fe_2O_3 catalyst provides excellent reactivity and reusability in the hydrogenation of nitrobenzene [27]. Guin et al. reported the Pd(0) immobilized on the surface of amine-terminated Fe_3O_4 and $NiFe_2O_4$ nanoparticles. The catalysts can be completely recovered with an external magnetic field, and their catalytic efficiency remains unaltered after 10 repeated cycles [20]. In our previous work [28], a magnetically separable palladium catalyst has been synthesized by immobilizing Pd on the surface of superparamagnetic composite microspheres. It can be conveniently recovered by magnet and reused at least six times. However, an additional amine process is needed after the preparation of MNPs. Therefore, it would be intriguing to synthesize Fe_3O_4–NH_2 nanoparticles in one step.

Described in this communication is a straightforward preparation of Fe_3O_4–NH_2–Pd(0) nanocatalysts with high magnetic sensitivity and the application in Heck reactions. The Fe_3O_4–NH_2 nanoparticles were synthesized through a one-pot solvothermal reaction using $FeCl_3 \cdot 6H_2O$ as a single iron source and triethylene tetramine(TETA) as a ligand. This reaction simplified the procedure of surface amine modification. The TETA on the surface of MNP makes them convenient for coordination with Pd(0). Finally, the catalytic behavior of Fe_3O_4–NH_2–Pd(0) nanoparticles was measured by the Heck reaction.

2. Experimental section

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium acetate (NaAc), ethylene glycol (EG), triethylene tetramine(TETA), $Pd(OAc)_2$, acrylic acid(AA), aryl halides, N,N-dicyclohexylmethylamine,

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dimethylformamide(DMF) and potassium borohydride (KBH_4) were purchased from Sigma-Aldrich and used as received.

2.2. Preparation of amine-functionalized magnetic nanoparticles

The Fe_3O_4–NH_2 nanoparticles were prepared according to Li's method with some modification [29]. A solution of TETA (4.5 g), anhydrous NaAc (2.0 g) and $FeCl_3 \cdot 6H_2O$ (2.5 g) in EG solution (30 mL) was stirred vigorously at 30 °C to give a transparent solution. This solution was then transferred into a teflon autoclave and then kept at 200 °C for 6 h. The magnetic nanoparticles were then rinsed with water and ethanol for several times to effectively remove the solvent and unbound TETA, and then dried under vacuum at ambient temperature. During each rinsing step, the nanoparticles were separated from the supernatant by magnet.

2.3. Preparation of Fe_3O_4–NH_2–Pd (0) magnetic catalyst

0.18 g of as-synthesized Fe_3O_4–NH_2 powder was added to 30 mL of 0.01 g $Pd(OAc)_2$ aqueous solution and stirred for 24 h at 35 °C (S1). And then the powder was reduced by 30 mL of 0.1 M KBH_4 aqueous solution to get a dark black powder (Fe_3O_4–NH_2–Pd (0)) (Scheme 1). The solid catalyst was separated by magnet and was washed several times with ethanol. The Pd content in Fe_3O_4–NH_2–Pd (0) catalyst was determined to be 4.26 wt.% by AAS.

2.4. General procedures for heck reactions and recovery of the supported magnetic catalyst

The novel magnetic supported catalyst (0.5 mol%), acrylic acid (7.5 mmol), aryl halides (5 mmol), N,N-dicyclohexylmethylamine (10 mmol) and DMF(5 mL) were added into a round bottomed flask and stirred at 95–140 °C in atmosphere for 3–14 h. After the reaction mixture was cooled to room temperature, the catalyst was separated by magnet.

3. Results and discussion

3.1. Characterization of Fe_3O_4–NH_2–Pd (0) catalyst

Fe_3O_4–NH_2–Pd (0) catalyst was prepared by ligand-mediated immobilization of Pd (0) nanoparticle on functionalized surfaces of Fe_3O_4–NH_2, as shown in Scheme 1. Fig. 1a shows the TEM micrograph of the Fe_3O_4–NH_2 nanoparticles prepared by solvothermal reduction method. It is observed that the synthesized particles are spherical and nearly monodisperse and with an average diameter of 100 nm. Fig. 1b and c shows the TEM micrographs of Fe_3O_4–NH_2–Pd catalysts before and after reaction, respectively. Molecular simulation (S2) and FTIR (S3) also suggest that the surface of magnetic nanoparticles has been successfully functionalized with amino groups in the synthetic process. As can be seen, the morphology and size of these particles did not change obviously even after several reactions.

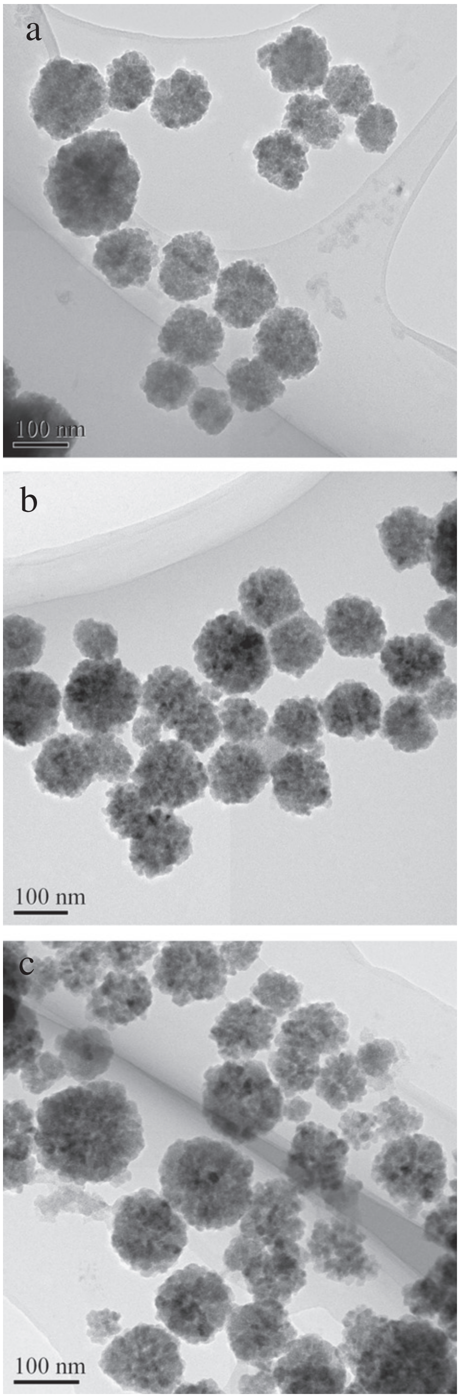
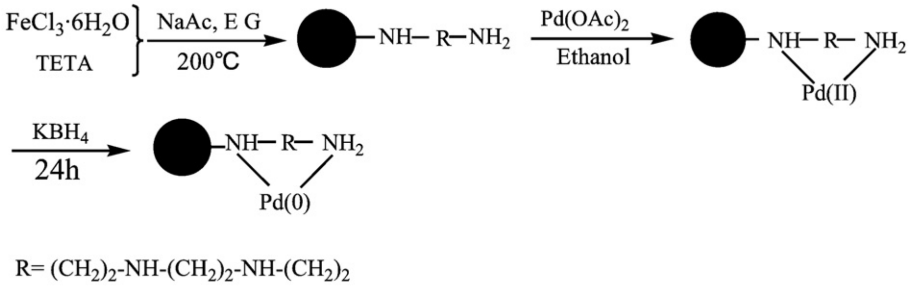


Fig. 1. TEM images of the samples (a) Fe_3O_4–NH_2 (b) Fe_3O_4–NH_2–Pd (II) (c) Fe_3O_4–NH_2–Pd (0).



Scheme 1. Procedure of the preparation of Fe_3O_4–NH_2–Pd (0) catalyst.

The crystalline structures of nanoparticles were determined by XRD. As presented in Fig. 2a, six characteristic diffraction peaks (2θ = 30.1°, 35.3°, 43.0°, 53.4°, 56.9°and 62.5°) corresponded well to the standard for Fe_3O_4 reflections. These peaks are sharp and intense, indicating their well crystallized structure. Each particle is composed of a lot of small Fe_3O_4 nanoparticles with a size around 11.5 nm calculated from the Debye–Scherrer equation, which is comparable with the result in Fig. 2c (around 10 nm). The agglomeration of plenty of small single-crystal particles leads to the formation of bulky hollow nanosphere [30]. As seen from Fig. 2b, the diffraction peaks at 2θ = 39.3°, 45.9° and 67.1° are the characteristic signals of the face centered cubic crystalline phase of Pd. It suggests that Pd nanoparticles successfully deposited onto the $Fe_3O_4–NH_2$ supports and Pd remained highly dispersed on the surface of the $Fe_3O_4–NH_2–Pd$ (0) catalyst after reduction. Other diffraction peaks in Fig. 2b corresponded to the reflections of Fe_3O_4, indicating that the crystalline structure of Fe_3O_4 did not change after the immobilization of organometallic species.

Magnetic properties of the $Fe_3O_4–NH_2–Pd$ (0) complex catalyst were studied by a vibrating sample magnetometer (VSM) at 300 K. The magnetization curves show that the magnetization saturated up to 75 emu/g at an external filed of 15 KOe and the coercivity is almost negligible, indicating this sample the superparamagnetic property (Fig. 3a). These magnetic properties allow a fast separation of the catalyst from the reaction media (Fig. 3b) and the redispersion of the catalysts in solution without severe assembly and/or aggregation in successive reactions (Fig. 3c).

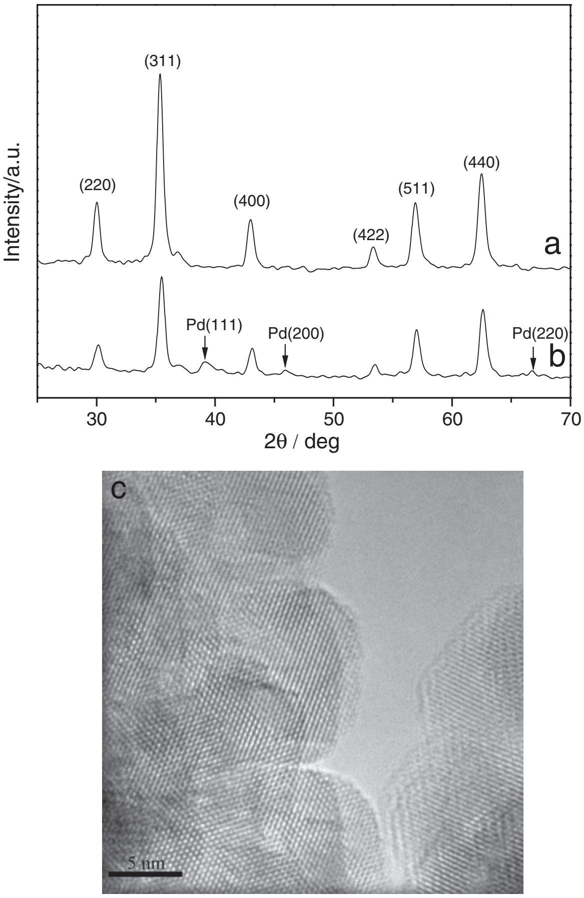


Fig. 2. XRD pattern of $Fe_3O_4–NH_2$ (a) and $Fe_3O_4–NH_2–Pd$ (0) (b) and the HRTEM of $Fe_3O_4–NH_2$ microspheres (c).

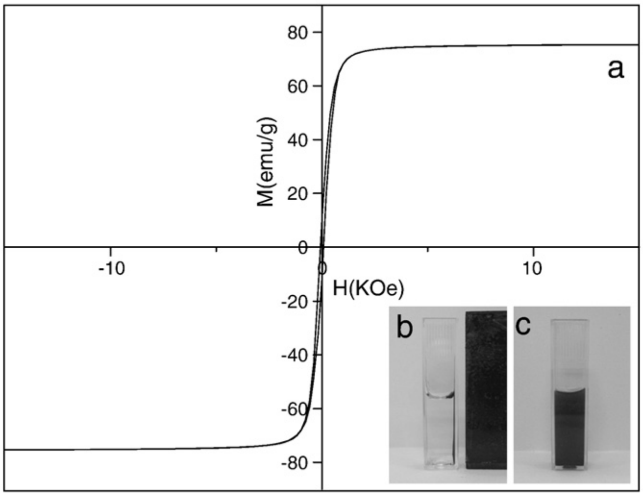


Fig. 3. The magnetization curves of $Fe_3O_4–NH_2–Pd$ (0) measured at 300 K(a). The nanocrystals are drawn from the solution to the sidewall of the vial by an assistant magnet field (b) and also can be easily dispersed in DMF(c).

3.2. Heck reaction catalyzed by $Fe_3O_4–NH_2–Pd$ (0) catalyst

XPS measurements were carried out to confirm that Pd nanoparticle are adsorbed by amino groups of $Fe_3O_4–NH_2$. In Fig. 4, the XPS of a $Fe_3O_4–NH_2–Pd$ (0) sample shows Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies (BE) at 336.4 and 341.5 ev, respectively. According to the literature [31], the binding energy of Pd $3d_{5/2}$ for Pd (0) is 335.1 ev. However, we found that the Pd $3d_{5/2}$ peak shifted to higher values as a result of the presence of the surrounding positively charged ammonium groups of the $Fe_3O_4–NH_2$ nanoparticles. It indicates that there is a good interaction to make Pd more stable on the surface of $Fe_3O_4–NH_2$ nanoparticles. It is also well recognized that amino groups can suppress the agglomeration of Pd nanoclusters, and enhance the catalytic efficiency of Pd nanoparticles [27].

In general, the most important aspect for catalyst was its efficiency and stability. As we know amino groups can enhance the catalytic activity of Pd [31], the TETA on the surface of $Fe_3O_4–NH_2$ provided the ideal environment for better conversions. In order to make Pd more stable on the surface of $Fe_3O_4–NH_2$ nanoparticles, we used the excessive amount of TETA to increase the content of amino group in this experiment and chose the amount of TETA was 4.5 g after a series of optimizations in our experiment. To investigate the catalytic activity of the $Fe_3O_4–NH_2–Pd(0)(40\ m^2/g)$, Heck reaction of cross-coupling of aryl halide with acrylic acid was examined (Scheme 2). For the

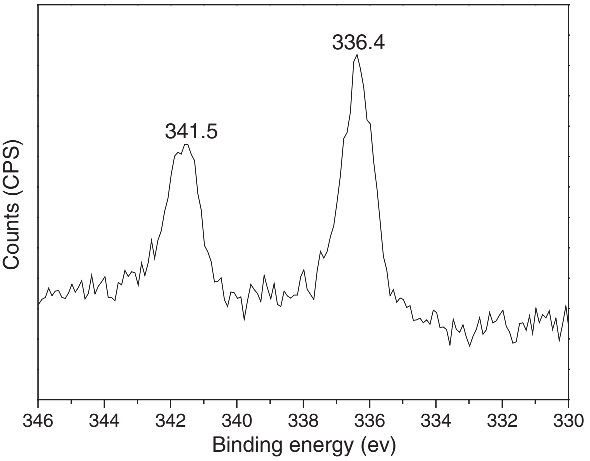
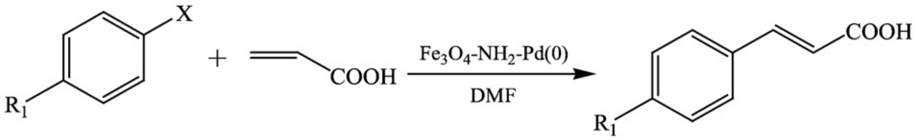


Fig. 4. XPS spectrum of $Fe_3O_4–NH_2–Pd$ (0) catalyst.



Scheme 2. Heck reaction of aryl halide with acrylic acid catalyzed by Fe_3O_4–NH_2–Pd (0) catalyst b.

Heck reaction shown in Table 1, the catalyst showed good catalytic efficiency. The reaction temperature between iodobenzene and vinyl substrate for Heck reaction was low (95 °C) and the yield can reach 97.8%. For bromobenzene, the yield of corresponding product was 12.4% (entry 5) under the same reaction condition. However, when the reaction time was extended to 14 h and the reaction temperature was increased to 140 °C (entry 6), a moderate yield (50.2%) was obtained. It was demonstrated that the reactivity of aryl bromides with electron-withdrawing substituents was higher than that of aryl bromides with electron-donating substituents. Meanwhile, to prove the complete separation of catalyst from the reaction solution, the verification has been done [33] (S4).

Table 1
Heck reactions of various aryl halides and acrylic acid catalyzed by the magnetic catalyst[a].

Entry	R1	X	Time (h)	Temperature(°C)	Yield (%)[b]	TON [32]
1	H	I	3	95	97.8	978
2	CH_3	I	3	95	92.1	921
3	NO_2	I	3	95	97.4	974
4	OCH_3	I	3	95	93.2	932
5	H	Br	3	95	12.4	124
6	H	Br	14	140	50.2	502
7	NO_2	Br	14	140	89.1	891
8	CH_3	Br	14	140	39.4	394

[a] Reaction conditions: aryl halide(5 mmol),acrylic acid (7.5 mmol), N,N-dicyclohexylmethylamine (10 mmol), DMF (5 mL). The supported magnetic catalyst (0.5 mol%).
[b] HPLC yield based aryl halide.

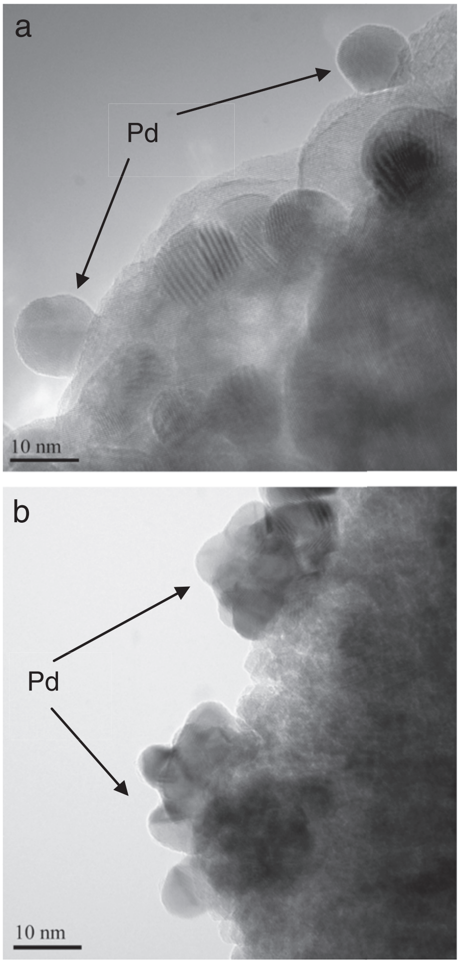


Fig. 5. HRTEM images of the morphology of Pd particles before (a) and after (b) Heck reaction.

Further experiments were performed to verify the stability and recycle of the Fe_3O_4–NH_2–Pd(0) in Heck reactions. We can see from Fig. 5 that the Pd particles dispersed well on the surface of the Fe_3O_4–NH_2 microspheres before the Heck reaction (Fig. 5a). However, the Pd particles agglomerated after the six runs of Heck reaction (Fig. 5b), leading to the yield gradually decreased to about 90% of the initial run after six runs of Heck reaction (Fig. 6). Meanwhile, the AAS result showed that only 0.6 wt.% Pd leached away from the surface of catalyst after six runs of Heck reaction, which indicated the coordination link of Pd (0) with $-NH_2$ ligand is strong. All these results showed that the as-synthesized magnetic catalyst is an excellent potential candidate for reusable and recoverable catalyst.

4. Conclusions

In summary, a high-magnetization (75 emu/g) Fe_3O_4–NH_2–Pd(0) catalyst was prepared by immobilizing Pd(0) nanoparticles on the surface of Fe_3O_4–NH_2 microspheres. The catalyst is recoverable magnetically and could be reused for six runs without significant loss in catalytic activity and selectivity for Heck reaction. Further studies on the effects of Fe_3O_4–NH_2–Pd(0) catalyst on the catalytic activity for other catalyst systems are now in progress.

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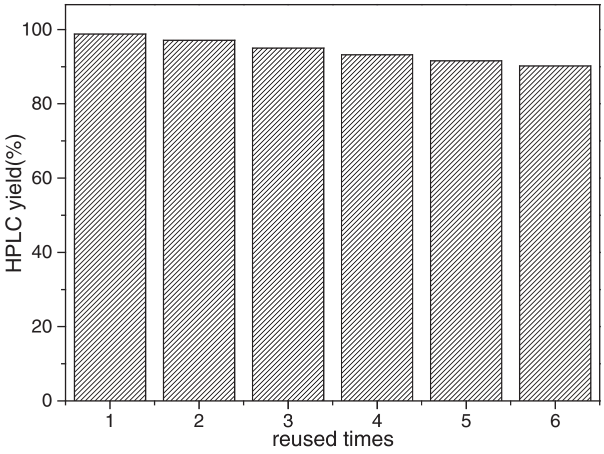

Fig. 6. Reused times of the Fe_3O_4–NH_2–Pd (0) catalyst.

Appendix A. Supplementary Data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.10.015.

References

[1] Y. He, C. Cai, Catalysis Communications 12 (2010) 678–683.
[2] X. Zhang, A. Liu, W. Chen, Organic Letters 10 (2008) 3849–3852.
[3] Y. Gao, C. Chen, H. Gau, J. Bailey, E. Akhadov, D. Williams, H. Wang, Chemistry of Materials 20 (2008) 2839–2844.
[4] T. Mishra, Catalysis Communications 9 (2008) 21–26.
[5] W. Li, J. Liu, C. Yan, Carbon 49 (2011) 3463–3470.
[6] V. Polshettiwar, R.S. Varma, Chemistry A European Journal 15 (2009) 1582–1586.
[7] A. Le Goff, V. Artero, B. Jousselme, P.D. Tran, N. Guillet, R. Métayé, A. Fihri, S. Palacin, M. Fontecave, Science 326 (2009) 1384.
[8] P.A. Berseth, A.G. Harter, R. Zidan, A. Blomqvist, C.M. Araujo, R.H. Scheicher, R. Ahuja, P. Jena, Nano Letters 9 (2009) 1501–1505.
[9] M.N. Nadagouda, V. Polshettiwar, R.S. Varma, Journal of Materials Chemistry 19 (2009) 2026–2031.
[10] V. Polshettiwar, R.S. Varma, Green Chemistry 12 (2010) 743–754.
[11] L. Zhou, C. Gao, W. Xu, Langmuir 26 (2010) 11217–11225.
[12] J.M. Thomas, B.F.G. Johnson, R. Raja, G. Sankar, P.A. Midgley, Accounts of Chemical Research 36 (2003) 20–30.
[13] Y. Zhu, L.P. Stubbs, F. Ho, R. Liu, C.P. Ship, J.A. Maguire, N.S. Hosmane, ChemCatChem 2 (2010) 365–374.
[14] V. Polshettiwar, R.S. Varma, Organic & Biomolecular Chemistry 7 (2009) 37–40.
[15] S. Shylesh, V. Schünemann, W.R. Thiel, Angewandte Chemie International Edition 49 (2010) 3428–3459.
[16] M. Kawamura, K. Sato, Chemical Communications 45 (2006) 4718–4719.
[17] C.W. Lim, I.S. Lee, Nano Today 5 (2010) 412–434.
[18] K. Tanaka, Catalysis Today 154 (2010) 105–112.
[19] V. Polshettiwar, B. Baruwati, R.S. Varma, Green Chemistry 11 (2009) 127–131.
[20] D. Guin, B. Baruwati, S. Manorama, Organic Letters 9 (2007) 1419–1421.
[21] K.S. Lee, M.H. Woo, H.S. Kim, E.Y. Lee, I.S. Lee, Chemical Communications 25 (2009) 3780–3782.
[22] Z. Wang, B. Shen, Z. Aihua, N. He, Chemical Engineering Journal 113 (2005) 27–34.
[23] J. Zhou, R. Zhou, L. Mo, S. Zhao, X. Zheng, Journal of Molecular Catalysis A: Chemical 178 (2002) 289–292.
[24] V. Polshettiwar, Á. Molnár, Tetrahedron 63 (2007) 6949–6976.
[25] L.M. Rossi, I.M. Nangoi, N.J.S. Costa, Inorganic Chemistry 48 (2009) 4640–4642.
[26] Z. Wang, P. Xiao, B. Shen, N. He, Colloids and Surfaces A 276 (2006) 116–121.
[27] D. Yi, S. Lee, J. Ying, Chemistry of Materials 18 (2006) 2459–2461.
[28] D. Yuan, Q. Zhang, J. Dou, Catalysis Communications 11 (2010) 606–610.
[29] L. Wang, J. Bao, L. Wang, F. Zhang, Y. Li, Chemistry A European Journal 12 (2006) 6341–6347.
[30] J. Ge, Y. Hu, M. Biasini, W. Beyermann, Y. Yin, Angewandte Chemie International Edition 46 (2007) 4342–4345.
[31] A.J. Amali, R.K. Rana, Chemical Communications 35 (2008) 4165–4167.
[32] Y. He, C. Cai, Catalysis Communications 12 (2011) 678–683.
[33] A. Lu, W. Schmidt, N. Matoussevitch, H. Bönnemann, B. Spliethoff, B. Tesche, E. Bill, W. Kiefer, F. Schüth, Angewandte Chemie International Edition 43 (2004) 4303–4306.