ChemComm

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COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c3cc43568g

Received 13th May 2013,
Accepted 26th June 2013

DOI: 10.1039/c3cc43568g

www.rsc.org/chemcomm

One-pot synthesis of magnetically recyclable mesoporous silica supported acid–base catalysts for tandem reactions†

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We report one-pot synthesis of magnetically recyclable mesoporous silica catalysts for tandem acid–base reactions. The catalysts could be easily recovered from the reaction mixture using a magnet, and the pore size of the catalysts could be controlled by introducing a swelling agent, resulting in the significant enhancement of the reaction rate.

Magnetic mesoporous nanocomposite materials have attracted tremendous scientific and technological interest because magnetic characteristics can be incorporated into mesoporous structures with large pore volume, high surface area, and easy functionalization capability.[1] Such nanocomposite materials have been extensively applied in various biomedical areas,[2] including separation of biomolecules,[3] magnetically guided targeted delivery,[4] and theragnostics.[5] Magnetic mesoporous nanocomposite materials immobilized with catalytic species have also been extensively investigated as magnetically recyclable catalysts for organic reactions.[6] General synthesis of the magnetic mesoporous materials requires extra work to synthesize and purify the uniform sized magnetic nanoparticles beforehand. Otherwise, the method involves a high temperature process or strong chemical environments to form magnetic species on the surface of the mesoporous materials. Despite their many potential applications, one-step synthesis of the magnetic mesoporous functional materials has been rarely proposed.[7]

Acid–base site-isolated catalysts, which were inspired by enzymes that can effectively perform multistep catalytic reactions through cooperative interactions of isolated catalytically active sites, have been intensively investigated as single-site heterogeneous catalysts.[8] Several silica nanostructured materials have been employed as heterogeneous supports[9] for the site-isolated immobilization of acidic and basic catalytic species,[10] and many research groups have tried to improve the catalytic performance by controlling the morphology[11] and structure of the catalysts.[12] Herein, we report a facile one-pot synthesis of a magnetically recyclable mesoporous silica catalyst for acid–base tandem reactions. We also present results of the effect of pore size on the catalytic activity of the mesoporous materials.

We synthesized magnetic mesoporous silica nanocomposite materials by combining the Massart method[13] for magnetite nanoparticles and the previously reported synthetic procedure for mesoporous acid–base catalysts (the detailed synthetic procedures are described in the ESI†).[14] First, iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate, and cetyltrimethylammonium bromide (CTAB) were dissolved in distilled water. This solution was stirred for 5 min at 70 °C, and 2 M aqueous sodium hydroxide was rapidly added. The color of the solution immediately changed from light yellow to black, indicating the formation of the magnetite nanoparticles upon reaction with hydroxide ions. Without any purification or drying, tetraethyl orthosilicate (TEOS) and a swelling agent, mesitylene, were slowly added to the resulting solution, followed by addition of ethyl acetate. Subsequently, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CESE) dissolved in dichloromethane and [3-(2-aminoethylamino)propyl]trimethoxysilane (AAPS) were added with vigorous stirring, and the resulting mixture was aged for 6 h at 70 °C. Because of the presence of residual hydroxide ions after the magnetite synthesis, addition of extra aqueous sodium hydroxide was not necessary to accelerate the condensation of the silanol groups. The powdery product was retrieved by centrifugation, and was further treated with a mixture of hydrochloric acid and ethanol to remove CTAB and to activate the sulfonic acid groups, thereby producing the final magnetic mesoporous silica nanocomposite with immobilized acidic (sulfonic acid) and basic (diamine) groups.

Transmission electron microscope (TEM) images of the synthesized nanocomposite materials revealed that ~9 nm Fe_3O_4 nanoparticles were enveloped by mesoporous silica shells (Fig. 1). The average pore size and surface area were found to be 5.4 nm and 327 $m^2\ g^{-1}$, respectively, and the material is designated as MMAB

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc43568g

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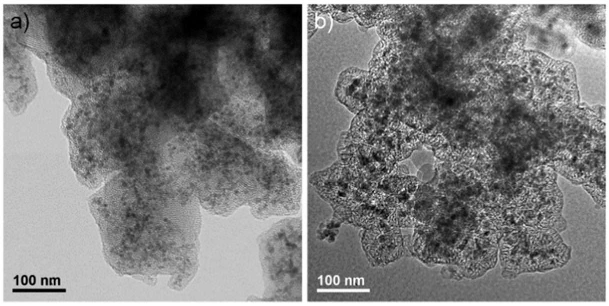


Fig. 1 TEM images of the magnetic mesoporous acid–base catalyst prepared (a) without a swelling agent and (b) with a swelling agent.

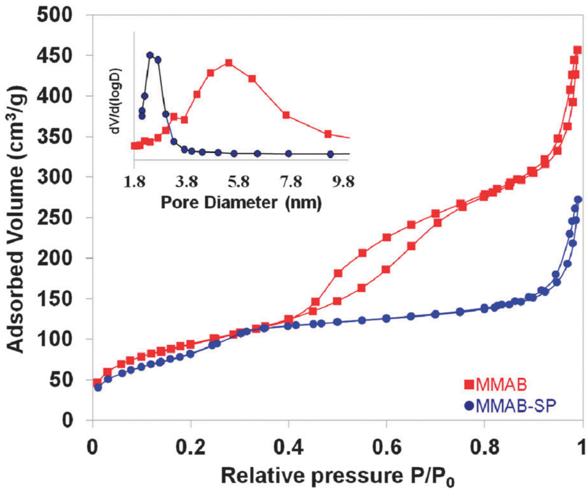
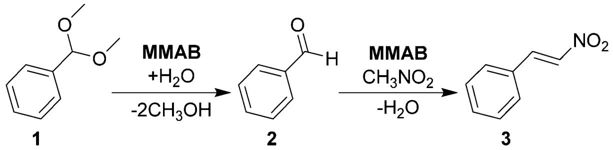


Fig. 2 The N_2 adsorption–desorption isotherms and the corresponding pore size distributions of the catalysts with large pore size (MMAB) and small pore size (MMAB-SP).

(Fig. 2). When we performed the synthesis without using the swelling agent (mesitylene), mesoporous material with a pore size of 2.4 nm and a surface area of 285 $m^2\ g^{-1}$ was generated (designated as MMAB-SP). The X-ray diffraction (XRD) pattern revealed that the embedded iron oxide nanoparticles were magnetite, Fe_3O_4 (Fig. S1, ESI†). The synthesized nanocomposite showed superparamagnetic characteristics with a high saturation magnetization of 78 emu g^{-1} of Fe at 300 K (Fig. S2 and S3, ESI†). This superparamagnetic property is advantageous for the efficient recycling of catalysts because the residual magnetic moment in ferromagnetic materials prevents rapid redispersion.[15] For the catalyst characterization, we performed Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analysis of MMAB (Fig. S4 and S5, ESI†), and we confirmed that the amine and sulfonic acid moieties were properly loaded on the magnetic mesoporous material. Furthermore, we confirmed that both acid and base functions were properly working in the catalysts by monitoring NH_3 and CO_2 temperature programmed desorption (NH_3-TPD, CO_2-TPD) profiles (Fig. S6 and S7, ESI†).

To examine the catalytic activity of MMAB, we performed a one-pot tandem reaction that converts benzaldehyde dimethyl acetal (**1**) to benzaldehyde (**2**) *via* acid-catalyzed deacetalization, followed by conversion of **2** to 1-nitro-2-phenylethylene (**3**) *via* the base-catalyzed Henry reaction (Scheme 1 and Table 1).



Scheme 1 Conversion of benzaldehyde dimethyl acetal (**1**) to 1-nitro-2-phenylethylene (**3**) by MMAB catalysis. Benzaldehyde (**2**) is the intermediate of the tandem reaction.

Table 1 Catalytic deacetalization and Henry reaction using various magnetic mesoporous materials[a]

Entry	Catalyst	Reactant	Product	Yield (%)
1	MMAB	**1**	**2** and **3**	2 (**2**)/96 (**3**)
2	N/A	**1**	—	—
3	MMB	**1**	—	—
4	MMB	**2**	**3**	98
5	MMA	**1**	**2**	93

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), nitromethane (5 mL), catalyst (30 mg), 90 °C, 5 h.

The catalyst showed excellent performance with very high yield and selectivity (entry 1), and as expected, the reaction did not proceed without the catalyst (entry 2). Comparative catalytic reactions were conducted to demonstrate the importance of both the acidic and basic functional groups. When a magnetic mesoporous silica catalyst with only basic groups (MMB) was used, the reaction did not proceed owing to the absence of the acid catalyzed deacetalization reaction that converts benzaldehyde dimethyl acetal to benzaldehyde (entry 3). However, when benzaldehyde was used as a starting material, 1-nitro-2-phenylethylene was produced nearly quantitatively (entry 4). Meanwhile, the catalyst derivatized only with acidic groups (MMA) did transform benzaldehyde dimethyl acetal to benzaldehyde, but could not catalyze the final reaction to form 1-nitro-2-phenylethylene (entry 5).

Lifetime and recyclability of a catalyst are very important for large-scale industrial applications. The MMAB catalyst showed excellent recyclability, maintaining high activity for up to five runs (Table 2). In addition, MMAB could be easily recovered using a magnet after each reaction, and could be reused for subsequent reactions without regeneration or further addition of a catalyst.

Next, we compared the catalytic activities of mesoporous silica catalysts with different pore sizes. We ran the catalytic reactions with the 5.4 nm MMAB and 2.4 nm MMAB-SP under identical reaction conditions, and aliquots were drawn from the reaction mixtures at 15 min intervals. The yield of product **3** in each sample was measured and the results are shown in Fig. 3.

With MMAB, the reaction was completed within 4.5 h, while the reaction with MMAB-SP took more than 7 h for the

Table 2 Magnetic separation and recycling results for the MMAB catalyst in the tandem reaction of 1 to yield 3[a]

Cycle	1st	2nd	3rd	4th	5th
Yield (%)	95	94	93	91	91

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), nitromethane (5 mL), MMAB nanocatalyst (30 mg), 90 °C, 5 h.

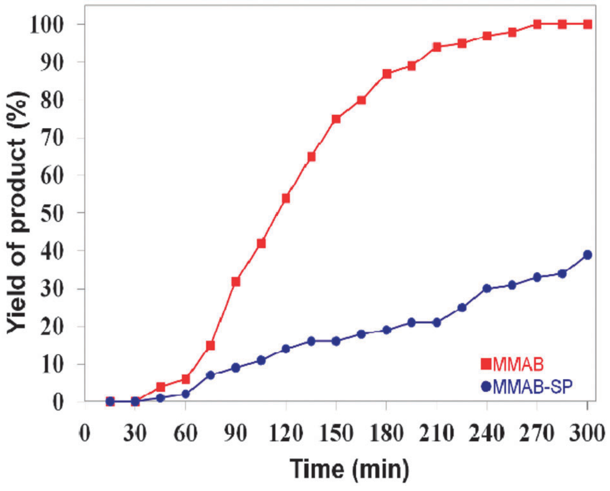


Fig. 3 Time-dependent product yield of the tandem deacetalization–Henry reaction using MMAB and MMAB-SP catalysts. Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), nitromethane (5 mL), MMAB (30 mg) or MMAB-SP (30 mg), 90 °C, 5 h.

completion. This dramatic increase in the reaction rate for the larger pore-sized silica materials can be explained by internal pore diffusion.[16,17] Internal pore diffusivity, which is a function of Knudsen diffusivity, is known to increase as pore sizes increase for diffusion-controlled reactions.[16] Because we synthesized MMAB and MMAB-SP using nearly identical procedures with a similar loading of the catalytic functional groups (Table S1, ESI†), the different catalytic activity can be explained solely by the difference in pore size.

In conclusion, we have successfully synthesized a magnetically separable mesoporous site-isolated acid–base catalyst using a one-pot reaction. The catalyst showed excellent performance with very high yield and selectivity for the conversion of benzaldehyde dimethyl acetal to 1-nitro-2-phenylethylene *via* benzaldehyde using tandem acid-catalyzed deacetalization and base-catalyzed Henry reaction. The catalyst could be easily recovered by using a magnet and dispersed in subsequent reaction mixtures, enabling recycling of the catalyst for up to five uses without losing catalytic activity. Furthermore, comparative studies revealed that the larger-pore-sized materials exhibited higher catalytic activity than the smaller-pore-sized materials. We believe that the current synthetic approach for this magnetic mesoporous acid–base site-isolated catalyst will contribute to the practical applications of tandem catalysts.

We acknowledge financial support from the Research Center Program of Institute for Basic Science (IBS) in Korea.

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