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Amine-bridged periodic mesoporous organosilica nanospheres as an active and reusable solid base-catalyst for water-medium and solvent-free organic reactions

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ABSTRACT

An amine-bridged periodic mesoporous organosilica catalyst in uniform nanospheres (~85 nm) (NH-PMO-NS) was synthesized by surfactant-directed co-condensation between amine-bridged silane and tetraethoxysilane (TEOS). As-prepared NH-PMO-NS contained short and straight mesoporous channels with amine-groups integrally incorporated into silica walls. In water-medium Knoevenagel condensation and solvent-free Henry reactions, this catalyst exhibited much higher activity and selectivity than both the common amine-bridged PMO (NH-PMO-com) with irregular shape synthesized by traditional method and the amine-functionalized MCM-41 in nanospheres (NH-MCM-NS) prepared by grafting amine-groups onto the pore surface. In addition, it displayed comparable catalytic efficiencies with the homogeneous base-catalyst (diethylamine), and could also be easily recovered and used repetitively. Based on the structural characterizations and kinetic studies, the high catalytic activity and selectivity were ascribed to the short and straight mesoporous channels in nanospheres with amine-groups incorporated into silica walls. The accessible basic catalytic sites may facilitate the diffusion and thus, promoted the adsorption of organic reactant molecules, leading to the enhanced activity and selectivity.

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1. Introduction

Since the discovery of M41S [1,2], a great number of efforts have been devoted to designing organic-inorganic hybrid silicas with ordered mesoporous structure due to their wide application potentials in versatile fields, including catalysis, adsorption, separation, etc. [3-6]. Previously, we reported that the organometallic catalysts terminally bonded to the silica supports with ordered mesoporous structure, exhibited higher catalytic efficiencies than those traditional immobilized catalysts owing to the enhanced dispersion of the active sites [7–9]. Recently, we developed a new approach to integrally incorporate organometals into the silica walls, leading to the organometal-bridged periodic mesoporous organosilica (PMO) [10–12], which further improved the catalytic performance owing to the diminished diffusion limit and also improved the durability of catalyst by inhibiting the leaching of metallic active sites [13,14]. Although a great number of metal-based catalysts have been successfully synthesized for organic synthesis, their applications are now gradually limited by the environmental and health considerations. A new pharmaceutical guideline in the United States has dramatically lowered the limits of trace metal impurities (e.g., Ru,

Ir, Rh, and Os) in pharmaceuticals [15]. In fact, the development of the metal-free and environmental friendly organocatalysts was in direct response to these new regulations [16]. Up to now, many amine-based organocatalysts have been reported as alternatives of traditional metal-based systems for a variety of C-C coupling reactions (e.g., Aldol condensation [17], Mannich reaction [18], Michael addition [19], Knoevenagel condensation [20] and Henry reaction [21]). Most studies are focused on homogeneous organocatalysts, but they are difficult to be reused, which inevitably adds cost and even causes the pollution on either the environment or the products [22]. Immobilized organocatalysts could be easily recycled [23], but they usually display lower efficiencies than the corresponding homogeneous analogues [24-27]. Organocatalysts bonded to traditional mesoporous silica supports, including MCM-41, SBA-15 and PMO [28-31] showed significant improvement on the catalytic activity owing to the enhanced dispersion of active sites and the reduced diffusion limit [12,32]. However, the irregular shape and long mesoporous channels might disturb the uniform distribution of active sites and also display steric hindrance for the diffusion of reactant molecules, especially for those with large molecule size, which must be harmful for the catalytic activity and selectivity. Both theoretical and experimental studies predict that the short channels favor the molecule diffusion. Hao et al. reported synthesis of amino-functionalized mesoporous silica in uniform nanospheres (MSN) with amine-groups terminally bonded onto the pore surface

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Scheme 1. Illustration of the preparation of NH-PMO-NSby co-condensation (upper) and NH-MCM-NS by grafting method (bottom).

[33]. However, those pendant amine-groups might still block the pore channels. Herein, we reported a novel amine-bridged periodic mesoporous silica in uniform nanospheres with amine-groups integrally incorporated into silica walls (NH-PMO-NS), which could be used as an active and reusable solid base-catalyst for watermedium Knoevenagel condensation and even solvent-free Henry reactions. It exhibited comparable efficiencies with the diethylamine homogeneous catalyst owing to both the diminished pore blockage by amine-groups and the short pore length, which facilitated the diffusion and adsorption of reactant molecules.

2. Experimental

2.1. Catalyst preparation

The amine-bridged PMO in nanospheres (NH-PMO-NS, where NS refers to nanospheres) was synthesized by surfactant-directed co-condensation as illustrated in Scheme 1 (upper). In a typical run of synthesis, hexadecyltrimethylammnonium bromide (CTAB) (0.89g) was dissolved in 428 mL aqueous solution containing 6.2 mmol NaOH. Then, the desired amounts of tetraethyl silicate (TEOS) and bis [3-(triethoxysilyl)propyl] amine (BTEA) were added. The initial molar ratio in the mother solution is Si:CTAB:NaOH:H₂O = 1:0.23:0.12:0.31:1189, where Si refers to the total amount of silica source. After being stirred for 2 h at 80 °C, the gel solution was aged at 80 °C for 20 h. The white precipitate was filtrated, washed thoroughly with ethanol and deionized water, followed by drying under vacuum at 80 °C for 10 h. Subsequently, the surfactant template was removed by refluxing the solid product twice in 1000 mL ethanol at $80 \,^{\circ}$ C for 24 h and then the product was dried under vacuum at 80 °C overnight. The amine content was adjusted by changing the molar ratio of BTEA to TEOS in the initial solution, leading to NH-PMO-NS-n series samples.

For comparison, the amine-functionalized MCM-41 in nanospheres (NH-MCM-NS) was also synthesized by grafting method as illustrated in Scheme 1 (bottom). Firstly, 0.89 g CTAB was added into 428 mL aqueous solution containing 6.2 mmol NaOH. After all the reagents completely dissolved at 80 °C, 20 mmol TEOS was added dropwise into the solution, followed by stirring for 2 h and aging at 80 °C for 20 h. The precipitate was filtered and dried under vacuum at 80 °C for 10 h. Then, the surfactant template was removed by refluxing the solid product twice in 1000 mL ethanol at 80 °C for 24 h. Then, the solid product was washed thoroughly with ethanol and water, followed by drying at 80 °C under a vacuum overnight, leading to the MCM-41 nanospheres (MCM-NS). Finally, 0.50 g MCM-NS was dispersed in 5.0 mL toluene containing 1.0 mmol BTEA. After being stirred at 70 °C for 24 h, the solid product was recovered by filtration and

washed completely with toluene and ethanol, followed by drying for 10 h at 80 °C under vacuum. Meanwhile, the common aminebridged PMO (NH-PMO-com) was also prepared by traditional surfactant-directed co-condensation method. Briefly, CTAB (0.36 g) was dissolved in H₂O (24 mL) containing concentrated ammonia (28 wt%) (15 g) at 30 °C, followed by adding TEOS (9.2 mmol) and BTEA (0.40 mmol) simultaneously. After being stirred at 30 °C for 0.5 h, the solution was transferred into an autoclave and kept at 100 °C for 15 h. The white precipitate was filtrated and treated according to the procedure used in preparing NH-PMO-NS.

2.2. Characterization

Surface morphologies and mesoporous structures were observed through field emission scan electronic microscopy (FESEM, Hitachi S-4800) and transmission electronic microscopy (TEM, JEOL JEM2011). Small-angle X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/maxr B diffractometer with Cu Ka. N2 adsorption-desorption isotherms were measured at -196°C using a Quantachrome NOVA 4000e analyzer after the samples being degassed at 100 °C for more than 10 h, based on which, the specific surface area (S_{BET}), average pore diameter (D_P) and pore volume (V_P) were calculated by applying multiple-point Brunauer-Emmett-Teller (BET) model and Barrett-Joyner-Halenda (BJH) model on adsorption branches, respectively. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using the KBr method. Solid NMR spectra were recorded on a Bruker DRX-400 NMR spectrometer. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer Pyris Diamond TG analyzer under air atmosphere with a heating ramp of $5 \circ C/min$. The N loading was determined by elemental analysis on a Heraeus CHNS elemental analyzer. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All the binding energy values were calibrated by using $C_{1S} = 284.6 \text{ eV}$ as a reference.

2.3. Activity test

The catalytic performance was evaluated by using Knoevenagel condensation (Reaction 1) and Henry (Reaction 2) reactions (see Schemes 2 and 3) as probes. Reaction 1 was carried out in a 10 mL flask containing a catalyst with desired *N* content, aromatic aldehyde (0.50 mmol), ethyl cyanoacetate (0.60 mmol), H₂O (3.0 mL), and n-decane (100 μ L) as an internal standard. After reaching the maximum conversion, the reaction mixture was extracted with ethyl acetate and followed by analysis on a gas chromatograph (GC, Agilent 1790) equipped with a FID and a JWDB-5 95%



Scheme 2. Chemical equation of the Knoevenagel condensation reaction (Reaction 1).



Scheme 3. Chemical equation of Henry reaction (Reaction 2).

dimethyl-1-(5%)-diphenylpolysiloxane column. The column temperature was programmed from 80 to 250 °C at a ramp of 10 °C/min. N₂ was used as carrier gas. The conversion was calculated based on an aldehyde since the other reactant was excess. Reaction 2 was performed in the similar way by stirring a mixture containing a catalyst with desired *N* content, *p*-nitrobenzaldehyde (0.50 mmol), nitromethane (5.0 mL) and n-decane (100 µL) as an internal standard. After reaction for 24 h under refluxing condition at 90 °C, the solid was removed from the solution using a centrifuge, and the separated liquid was analyzed by GC. The conversion was calculated based on *p*-nitrobenzaldehyde since nitromethane was excess. The reproducibility was checked by repeating each result at least three times and was found to be within acceptable limits (±5%).

To determine the catalyst durability, the catalyst was allowed to centrifuge after each run of reactions, and the clear supernatant liquid was decanted slowly. The catalysts were washed thoroughly with distilled water and ethanol, followed by drying at 80 °C overnight under vacuum condition. Then, the catalysts were reused with fresh charge of reactants for subsequent recycle under the identical reaction conditions.

2.4. Adsorption test

To examine the adsorption behavior, catalyst (50.0 mg) was soaked in water (200 mL) and oscillated at $25 \,^{\circ}\text{C}$ for 12 h, followed by adding aqueous solution (50.0 mL) containing 2.50 mg rhodamine B (RhB). The solution was sampled at given time intervals and the concentration of the left RhB in the solution was determined on an UV-visible spectrophotometer (UV 7504/PC) at the characteristic adsorption wavelength of 523 nm.

3. Results and discussion

3.1. Structural characteristics

The *N*-loadings in different catalysts were determined by elemental analysis and summarized in Table 1. As shown in Fig. 1, the FESEM and HRTEM images revealed that both the NH-PMO-NS-2 and the NH-MCM-NS displayed uniform nanospheres with the average diameter around 85 nm (see the particle size distribution diagrams in Fig. 2). However, the NH-PMO-com showed

Table 1	
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Some structure parameters of different samples.^a

Catalysts	N loading (wt%)	$S_{\text{BET}} \left(m^2 / g \right)$	$D_{\rm P}\left({\rm nm}\right)$	$V_{\rm P}$ (cm ³ /g)
NH-PMO-NS-1	0.33	980	2.7	0.86
NH-PMO-NS-2	0.83	917	2.6	0.97
NH-PMO-NS-3	1.1	776	2.4	0.69
NH-PMO-NS-4	1.6	517	2.1	0.51
NH-PMO-com	0.81	845	2.7	0.87
NH-MCM-NS	0.89	728	2.1	0.70

^a $D_{\rm P}$ and $V_{\rm P}$ were calculated by applying BJH model on the adsorption branches.

irregular shapes with much larger particle size. The HRTEM images further demonstrated that all those samples comprised of straight mesoporous channels with high ordering degree regardless of the different preparation methods.

As shown in Fig. 3a, all the as-prepared samples displayed typical type IV N₂ adsorption-desorption isotherms with H₄-type hysteresis loops indicative of the mesoporous structure. The small-angle XRD patterns in Fig. 3b revealed that all these samples displayed an intense diffraction around $2\theta = 2.2^{\circ}$ of characteristic (100) and two weak peaks at larger 2θ corresponding to (110) and (200) diffractions. These diffraction patterns represent the presence of the ordered 2D *p6mm* hexagonal mesoporous structures [34,35]. With the increase in amine-content from NH-PMO-NS-1 to NH-PMO-NS-4, the principal XRD peak gradually weakened, and the other two small peaks gradually disappeared, indicating the decrease in ordering degree of the mesoporous structure since the addition of a large amount of BTEA molecules might disturb the surfactant self-assembly process [36].

The specific surface area (S_{BET}) , pore volume (V_{P}) and the pore diameter (D_P) were calculated by applying multiple-point Brunauer-Emmett-Teller (BET) model and Barrett-Joyner-Halenda (BJH) model on absorption branches of the N₂ adsorption-desorption isotherms, respectively. As shown in Table 1, the NH-MCM-NS exhibited much lower S_{BET} , D_P and V_P than either the NH-PMO-NS-2 or the NH-PMO-com with the similar N-loadings since the amine-groups in the NH-MCM-NS were terminally bonded onto the pore surface rather than incorporated into the pore walls (see Scheme 1), which might partially block the pore channels. The NH-PMO-NS-2 showed equivalent D_P and V_P to the NH-PMO-com owing to their similar periodic mesoporous structures. The slightly higher S_{BFT} of the NH-PMO-NS-2 than that of the NH-PMO-com could be attributed to the uniform nanospheres in comparison with the large and irregular particles. With the increase of the *N*-loading from the NH-PMO-NS-1 to the NH-PMO-NS-2, no significant change in either S_{BFT} or D_{P} or V_{P} was observed, obviously owing to the incorporation of amine-groups into the silica walls. Further increase in the N-loading caused an abrupt decrease in S_{BET} , D_{P} and V_{P} , evidently due to the damage of the ordered mesoporous structure.

The FTIR spectra in Fig. 4 revealed that the NH-PMO-NS-2, NH-PMO-com and NH-MCM-NS displayed no significant signal at 2937 cm⁻¹, indicating that the CTAB surfactant template had been completely removed [37]. The strong peak around 1640 cm⁻¹ was mainly from the bending vibration of adsorbed H₂O [38]. The absorbance bands around 1080, 795 and 468 cm⁻¹ could be assigned to the vibrations from the Si–O bond while the peak around 953 cm⁻¹ could be attributed to the vibration from the Si–OH groups [39]. In comparison with the pristine MCM-41, the NH-PMO-NS-2, NH-PMO-com and NH-MCM-NS displayed an additional band around 692 cm⁻¹ characteristic of the secondary amine, suggesting that the amine-groups had been successfully anchored to the silica support [40]. The N–H vibration bands around 795 and 1640 cm⁻¹ were overlapped by adsorbed and Si–O vibration bands.

Fig. 5 shows the solid NMR spectra of NH-MCM-NS, NH-PMO-NS-2 and NH-PMO-com. The ²⁹Si CP MAS NMR spectra revealed that all these samples displayed three resonance peaks corresponding to Q^4 (δ =-111 ppm), Q^3 (δ =-102 ppm) and Q^2 (δ =-93 ppm), where Q^n =Si(OSi)_n(OH)_{4-n}, n=2-4, and two other peaks corresponding to T^3 (δ =-67 ppm) and T^2 (δ =-60 ppm), where (T^m =RSi(OSi)_m(OH)_{3-m}, m=1-3) [41,42]. The presence of the Q^n could be attributed to the self-condensations between TEOS. The appearance of T^m peaks confirmed the cross co-condensation between TEOS and BTEA, leading to the incorporation of organic moieties into the silica network. Meanwhile, the ¹³C MAS NMR exhibited three prominent peaks at δ of 6.6, 17, and 47 ppm indicative of three C atoms in



Fig. 1. FESEM (left) and HRTEM (right) images of NH-PMO-NS-2 (a and b), NH-MCM-NS (c and d) and NH-PMO-com (e and f).

the Si–CH₂–CH₂–CH₂–NH–CH₂–CH₂–CH₂–Si group [38]. These results demonstrated that the amine-groups had integrally grafted into the silica network. The incorporation of amine-groups could also be confirmed by TG/DTA analysis.

As shown in Fig. 6, an exothermic peak around 120 °C could be attributed to desorption of adsorbed water or other solvents. No significant exothermic peak and weight loss were found in the range from 130 to 300 °C for all the NH-PMO-NS-2, NH-MCM-NS and NH-PMO-com samples, which further confirmed the complete removal of CTAB surfactant template [30]. The other the weight loss peak found between 300 °C and 700 °C could be attributed to the combustion of amine-groups incorporated into the silica network [40]. The NH-PMO-NS-2 and the NH-MCM-NS exhibited similar weight loss (\sim 10 wt%) at 130 °C, which was much higher than that observed in the NH-PMO-com (\sim 5 wt%), suggesting they adsorbed much more water or other solvents than the NH-PMO-com,



Fig. 2. Particle size distribution diagrams.



Fig. 3. N₂ adsorption-desorption isotherms (a) and low-angle XRD patterns of different samples (b).

possibly owing to higher surface energy of the small nanospheres than that of the large irregular particles. All three samples exhibited a similar weight loss (~9 wt%) between 300 °C and 700 °C since they contained almost the same amount of amine-groups.

The XPS spectra (Fig. 7) revealed that all the NH-PMO-NS-2, NH-MCM-NS and NH-PMO-com samples contained secondary amine groups, corresponding to the binding energy around 399.4 eV in N_{1S} level [43]. In comparison with the BTEA $[(CH_3CH_2O)_3-Si-(CH_2)_3-NH-(CH_2)_3-Si-(CH_3CH_2O)_3]$ and the diethylamine $(CH_3CH_2NHCH_2CH_3)$, no significant shift of the binding energy was observed, suggesting that the amine-bridged silanes were directly integrated into the silica framework without changing the chemical microenvironment of the nitrogen atom.

A key consideration was the location of the amine-groups incorporated into the silica walls of the NH-PMO-NS catalyst. That is to say, were they chemically accessible to the reactant molecules during catalytic reactions? Firstly, the CO₂ temperature programmed desorption (CO₂-TPD) was conducted. As shown in Fig. 8, the NH-PMO-NS-2 organocatalyst before pre-adsorption of CO₂ displayed only two signals around 300 and 525 °C, respectively. This could be attributed to the combustion of the organic residues due to the incomplete hydrolysis of silicon sources and the organic fragments as a part of silica walls in the PMO, leading to the formation of CO₂ exhibited an additional signal around 100 °C indicative of CO₂ desorption from the Bronsted base active sites [33], which demon-



Fig. 4. FTIR spectra of MCM-NS (a), NH-PMO-NS-2 (b), NH-PMO-com (c) and NH-MCM-NS (d).

strated that the amine-groups incorporated into the silica walls were chemically accessible.

Based on the XPS spectra and the elemental analysis, the molar ratio of the surface amine species to the total amine species (*N*%) could be estimated. It is well known that the XPS spectra could estimate the content of surface amine by measuring the peak intensity indicative of nitrogen (I) while the elemental analysis could give the total content of amine (N^{Total}). Taking into account that the NH-MCM-NS displayed 100% surface amine species since all those amine-groups were terminally bonded onto the pore surface rather than incorporated into silica walls, the percentage of exposed amine-groups in the NH-PMO-NS-2 was evaluated as 95% by using the following equation, which further confirmed that nearly all the amine-groups in the NH-PMO-NS organocatalyst were chemically accessible for catalytic reactions.

$$N\% = \frac{I_{\text{NH-PMO-NS-2}} \times N_{\text{NH-MCM-NS}}^{\text{Total}}}{I_{\text{NH-MCM-NS}} \times N_{\text{NH-PMO-NS-2}}^{\text{Total}}}$$

3.2. Catalytic performances

The water-mediated organic reactions should be carefully conducted since they contained three phases. Firstly, the reaction conditions were optimized by testing the effects of various factors (temperature, time, catalyst and water amount) on the reaction conversion and selectivity. As shown in Table 2, the Knoevenagel condensation displayed nearly 100% selectivity toward the target product under different conditions. The benzaldehyde conversion increased gradually with the reaction time. However, it could not reach 100% benzaldehyde conversion even after reaction for a very long period, possibly due to the poor solubility of organic

Table 2	
Effect of reaction conditions on Knoevenagel condensation efficiency. ^a	

Temperature (°C)	Catalyst (mmol)	Water (mL)	Time (h)	Conv. (%)	Select. (%)
40	0.030	3.0	4	79	~100
40	0.045	3.0	4	93	$\sim \! 100$
40	0.055	3.0	4	98	$\sim \! 100$
30	0.045	3.0	4	67	$\sim \! 100$
50	0.045	3.0	4	98	$\sim \! 100$
40	0.045	2.0	4	78	$\sim \! 100$
40	0.045	4.0	4	89	$\sim \! 100$
40	0.045	3.0	3	73	$\sim \! 100$
40	0.045	3.0	5	95	$\sim \! 100$

^a NH-PMO-NS-2 catalyst, 0.50 mmol benzaldehyde, 0.60 mmol ethyl cyanoacetate.



Fig. 5. ²⁹Si MAS NMR (left) and ¹³C MAS NMR (right) spectra of NH-PMO-NS-2 (a and b), NH-PMO-com (c and d) and NH-MCM-NS (e and f).

reactants in water. With catalyst amount increasing from 0.030 to 0.045 mmol, the benzaldehyde conversion increased from 79% to 93%, obviously owing to increased basic sites. Further increase in the catalyst amount displayed no significant promoting effect on the conversion, possibly due to the poor dispersion of the catalyst. Meanwhile, it was also found that the benzaldehyde conversion first increased and then decreased with the increase of water amount, and the optimum water amount was determined as 3.0 mL. The protic water might activate benzaldehyde with weak acidity, which favored the base-catalysis [44]. However, the very large amount of water was harmful for the reaction since the amine active sites in the mesoporous channels were covered by water molecules [45]. Furthermore, the reaction temperature

also exhibited strong influence on the catalytic efficiency, and the reason would be discussed below.

Table 3 summarized the catalytic efficiencies of different catalysts in the water-medium Knoevenagel condensation and solvent-free Henry reactions under the optimized conditions. Considering the NH-PMO-NS series catalysts prepared by the same co-condensation method, one could see that, with the increase of the *N*-loading, the activity first increased from NH-PMO-NS-1 to NH-PMO-NS-2 and then decreased gradually from NH-PMO-NS-2 to NH-PMO-NS-4. Meanwhile, the selectivity in the Henry reactions first increased from the NH-PMO-NS-1 to the NH-PMO-NS-2 and then remained nearly constant from the NH-PMO-NS-2 to the NH-PMO-NS-4. Taking into account that both Knoevenagel



Scheme 4. A plausible catalytic cycle in Knoevenagel reaction.



Scheme 5. A plausible catalytic cycle in Henry reaction.



Fig. 6. TG/DTA curves of different samples.



Fig. 7. XPS spectra of different samples.



Fig. 8. CO_2 -TPD curves of the NH-PMO-NS-2 organocatalyst before (a) and after (b) pre-adsorption of CO_2 .

condensation and Henry reactions involved the cross-coupling of two reactant molecules adsorbed on two neighboring amine active sites (see Schemes 4 and 5), the NH-PMO-NS-1 with very low *N*-loading displayed low activity and selectivity could be mainly attributed to the long distance between two neighboring amine active sites. The NH-PMO-NS-3 and NH-PMO-NS-4 exhibited lower activity than the NH-PMO-NS-2 due to the partial damage of ordered mesoporous structure, leading to the low S_{BET} and narrow D_{P} , which disfavored the diffusion and adsorption of the reactant molecules. Although the NH-PMO-NS-3 and NH-PMO-NS-4 exhibited lower activities, they showed almost the same selectivity as the NH-PMO-NS-2 owing to the enough short distance between two neighboring owing to the enough short distance between two neighboring amine active sites.

It was also found that, with the similar *N*-loading, the NH-PMO-NS-2 exhibited much higher activity and better selectivity than either the NH-PMO-com or the NH-MCM-NS in both Knoevenagel and Henry condensation reactions. The higher activity and selectivity of the NH-PMO-NS-2 could be explored, which was based on the kinetic studies. Firstly, the effect of the reaction temperature (*T*) on the catalytic activity was examined in the Knoevenagel condensation reaction. As shown in Fig. 9a, the liner relationship between catalytic activity and 1/T was obtained for the different catalysts. By using Arrenius Equation ($dC/dt = ke^{-E_a/RT}$), the apparent activation energy (E_a) could be calculated from the line slope. All the NH-PMO-NS-2, NH-PMO-com, NH-MCM-NS and diethylamine showed equivalent E_a values, indicating the similar chemical microenvironments of the active sites, which was consistent with the aforementioned XPS analysis. Meanwhile, the

Table 3

Catalytic efficiencies in	Knoevenagel	condensation	and H	lenry reaction.
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Catalysts	Knoevenagel condensation ^a		Henry reaction ^b	
	Conv. (%)	Select. (%)	Conv. (%)	Select. (%)
NH-PMO-NS-1	89	~100	84	80
NH-PMO-NS-2	93	~ 100	91	87
NH-PMO-NS-3	88	~ 100	88	87
NH-PMO-NS-4	78	~ 100	80	88
NH-PMO-com	83	~ 100	86	79
NH-MCM-NS	85	~ 100	83	82
Diethylamine	98	~ 100	96	84

 $^a\,$ Reaction conditions: a catalyst containing 0.045 mmol N, 0.50 mmol benzaldehyde, 0.60 mmol ethyl cyanoacetate, 3.0 mL H2O, 40 $^\circ$ C, 4 h.

 $^{\rm b}$ Reaction conditions: a catalyst containing 0.047 mmol N, 0.50 mmol p-nitrobenzaldehyde, 5.0 mL nitromethane, 90 $^\circ$ C, 24 h.



Fig. 9. Effect of the reaction temperature on the benzaldehyde conversion within 1 h (a) and dependence of benzaldehyde conversion on the reaction time (b). The inset is the change of $\ln(C_{\text{benzaldehyde}})$ with the reaction time. Reaction conditions: a catalyst containing 0.045 mmol N, 0.50 mmol benzaldehyde, 0.60 mmol ethyl cyanoacetate, 3.0 mL H₂O, reaction temperature = 40 °C.

influence of the benzaldehyde concentration ($C_{\text{benzaldehyde}}$) on the activity of the NH-PMO-NS-2 was investigated, which showed linear relationship between $\ln(C_{\text{benzaldehyde}})$ and the reaction time (see Fig. 9b). The remarkable deviation from the linear relationship could be attributed to the extremely low benzaldehyde concentration. Taking into account that the ethyl cyanoacetate was excess in the present reaction, we could reasonably conclude that the Knoevenagel condensation reaction was first order with respect to the benzaldehyde concentration ($r = kC_{\text{benzaldehyde}}^1$). This meant that the adsorption of the benzaldehyde molecules on the catalyst was not saturated and thus, the adsorption rate played a key role in determining the catalytic activity.

Fig. 10 showed the adsorption behaviors of different catalysts measured by using RhB as a model adsorbent, which could be easily determined by UV spectrometer analysis. Besides the higher adsorption capacity owing to the larger SBET, the NH-PMO-NS-2 also displayed much more rapid adsorption than the NH-PMO-com, which confirmed that the short straight mesoporous channels efficiently diminished the diffusion limit and thus facilitated the adsorption. The NH-MCM-NS displayed the lowest adsorption capacity and the slowest adsorption rate due to the low S_{BFT} and especially, the pore blockage by the amine-groups terminally bonded onto the pore surface rather than incorporated into the silica walls. Obviously, rapid adsorption promoted the reaction, leading to the higher activity of the NH-PMO-NS-2 than that of either the NH-PMO-com or the NH-MCM-NS, which could also account for the higher activity of the NH-PMO-com than that of the NH-MCM-NS. Meanwhile, the higher selectivity of the NH-PMO-NS-2 than that of either the NH-PMO-com



Fig. 10. Adsorption test of different catalysts. Adsorption conditions: 50.0 mg catalyst, 250 mL aqueous solution containing 2.50 mg RhB, adsorption temperature = $25 \degree$ C.

or the NH-MCM-NS in Henry reaction could also be explained based on the adsorption rate. Scheme 3 illustrated a plausible mechanism of Henry reaction. The target product 1-nitro-4-(2-nitrovinyl)benzene was formed through the reaction between *p*-nitrobenzaldehyde and nitromethane anion both adsorbed on the *N* active sites of the amine-catalyst, which mainly occurred inside mesoporous channels. While, the side product 2-nitro-1-(4-nitrophenyl) ethanol was produced by direct attract of the carbonyl group in *p*-nitrobenzaldehyde present freely in the solution with the nitromethane anion adsorbed on the amine-catalyst. So, such reactions mainly occurred at the entrance of mesoporous channels. Since the nitromethane was excess and rapid diffused into the mesoporous channels owing to the smaller molecular size than the *p*-nitrobenzaldehyde, it could easily reach the

Table 4

The water-medium Knoevenagel condensation with different substrates.^a



Fig. 11. Recycling test of the NH-PMO-NS-2 catalyst in Knoevenagel condensation reaction. Reaction conditions are given in Table 2.

adsorption saturation. The rapid diffusion of p-nitrobenzaldehyde molecules inside the mesoporous channels could promote their adsorption on N active site of the amine-catalyst, leading to the cross-coupling reaction between the nitromethane anion and the adsorbed p-nitrobenzaldehyde to form target product. Otherwise, the fraction of the reaction occurring at the mesopore entrance between the free p-nitrobenzaldehyde in the solution and the adsorbed nitromethane anion would increase, corresponding to the decrease in selectivity.

Table 4 shows that the NH-PMO-NS-2 exhibited similar reaction conversions to the homogeneous diethylamine catalyst in other Knoevenagel condensation reactions with various substrates. To make more precise comparison, the turnover frequency (TOF) at an early stage of the reaction was also calculated based on the following equation, taking into account that the Knoevenagel

Substrate 1	Substrate 2	Product	Time (h)	Conv. (%)	$TOF(h^{-1})^{b}$
Сно	$\begin{pmatrix} CN \\ CO_2Et \end{pmatrix}$	$\underset{H}{\overset{NC}{\longrightarrow}} \underset{H}{\overset{CO_2Et}{\longleftarrow}}$	4	93 (98)	4.7 (4.3)
O ₂ N-CHO	$\begin{pmatrix} CN \\ CO_2Et \end{pmatrix}$	$O_2N - H$	1	99 (98)	18.4 (17.6)
Н3СО-СНО	$\begin{pmatrix} CN \\ CO_2Et \end{pmatrix}$	$H_3CO \longrightarrow H$	4	90 (84)	4.5 (4.1)
СНО	$\begin{pmatrix} CN \\ CO_2Et \end{pmatrix}$	$ \begin{array}{c} NC \\ O \\ H \end{array} $ $ \begin{array}{c} O \\ H \end{array} $ $ \begin{array}{c} O \\ O \\ H \end{array} $	1	99 (99)	18.7 (18.0)
СНО	$\begin{pmatrix} CN \\ CO_2Et \end{pmatrix}$	CN CO ₂ Et	4	94 (96)	4.9 (4.9)
СНО	<	\sim H	1	99 (94)	18.3 (17.7)

^a Reaction conditions: the catalyst NH-PMO-NS-2 containing 0.045 mmol of N, 0.50 mmol Substrate 1, 0.60 mmol Substrate 2, 3.0 mL H₂O, reaction temperature = 40 °C. The values in parentheses are obtained by using 0.045 mmol diethylamine as a homogeneous catalyst under the same reaction conditions.

^b TOF values were determined based on conversion of Substrate 1 after reaction for 20 min.



Fig. 12. N₂ sorption isotherm (a), low-angle XRD pattern (b) and HRTEM image (c) of the NH-PMO-NS-2 organocatalyst after being used repetitively for 5 times in Knoevenagel condensation reaction.

condensation reactions exhibited almost 100% selectivity to the target products.

TOF
$$(h^{-1}) = \frac{\text{Conversion } (\%) \times \text{moles of Substrate 1}}{(1/3 \text{ h}) \times \text{moles of amine} \times 95\%}$$

where all the conversions were calculated based on the consumption of Substrate 1 after reaction for 20 min, i.e., 1/3 h. The 95% was used because, according to the aforementioned XPS analysis, only 95% amine groups in the NH-PMO-NS-2 catalyst were chemically accessible. Obviously, the TOF values calculated from the NH-PMO-NS-2 catalyst were similar to those from the homogeneous diethylamine catalyst. These results clearly demonstrated that the NH-PMO-NS-2 catalyst displayed comparable activity with the homogeneous diethylamine catalyst.

To ascertain whether the amine anchored to the silica support or homogeneous amine leached from the support was the real organocatalyst, the following experiments were carried out according to the procedure proposed by Sheldon et al. [46] After reaction for 2 h with the conversion exceeding 60% in the Knoevenagel condensation reaction, the solid NH-PMO-NS-2 catalyst was filtered out, and the liquid solution was allowed to react for another 3 h under identical reaction conditions. No significant change in either the benzaldehyde conversion or the yield of product was observed, indicating that the active phase was not the amine species leached from the NH-PMO-NS-2. Therefore, it is reasonable to conclude that the present catalyst was really heterogeneous in nature.

Besides the high activity and selectivity, the NH-PMO-NS-2 could be easily recycled and used repetitively. As shown in Fig. 11, the NH-PMO-NS-2 catalyst could be used repetitively for

more than five times during Knoevenagel condensation reaction without a significant decrease in activity. According to the elemental analysis, no significant decrease of the *N*-loading in the used NH-PMO-NS-2 catalyst was detected, indicating that the leaching of amine active sites could be neglected. Obviously, the incorporation of amine-groups into the silica walls could effectively stabilize amine-groups against leaching. Meanwhile, the N₂ adsorption–desorption isotherm, low-angle XRD pattern and HRTEM image in Fig. 12 clearly demonstrated that the NH-PMO-NS-2 catalyst still displayed uniform nanospheres and the straight and ordered mesoporous channels were remained after being used repetitively for five times, showing the excellent hydrothermal stability.

4. Conclusions

This work developed a facile approach of surfactant-directed co-condensation for preparing a novel amine-bridged periodic mesoporous organosilica in uniform nanospheres with amine-groups integrally incorporated into the silica walls. This heterogenized organocatalyst exhibited comparable activities and selectivities in various water-medium Knoevenagel condensation reactions and even solvent-free Henry reactions due to the reservation of chemical micro-environment of active sites and the diminished diffusion limit. More importantly, it could be easily recycled and used repetitively. These studies demonstrate the significant potential of its practical applications in organic synthesis.

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