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## Introduction

There has been considerable attention given to one-pot reactions as a favourable synthetic concept for improving overall efficiency and reducing chemical wastes.<sup>1-11</sup> In industrial processes, multi-steps are required to synthesise most fine chemicals, and as a result, purification processes during each reaction step cause the loss of products and production of undesired chemical wastes. One-pot reactions, in which multistep reactions proceed in a single reactor without halfway purification, will enable us to overcome the above mentioned issues. However, difficulties in design of multi-functional

# Synthesis and bifunctional catalysis of metal nanoparticle-loaded periodic mesoporous organosilicas modified with amino groups<sup>†</sup>

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The present article describes the development of a periodic mesoporous organosilica (PMO)-based bifunctional catalyst that includes both oxidative and base catalytic activities. Periodic mesoporous ethylenesilica (PME) was selected as a catalyst support and modified with ethylenediamine through epoxidation of bridging ethylene moieties and the following nucleophilic addition in order to construct base sites. FT-IR measurements for the resulting material, PME-ED, reveal the successful introduction of amino groups into the bridging ethylene moieties. PME-ED can promote Knoevenagel condensation between benzaldehyde and various active methylene compounds as a solid base catalyst. The scope of applicable active methylene compounds in this catalytic system shows the base strength of PME-ED, in which a proton can be abstracted from diethyl malonate ( $pK_a$ : 16.4) but not from benzyl cyanide ( $pK_a$ : 21.9). Moreover, the generation of bifunctional catalytic properties to promote a one-pot tandem reaction consisting of alcohol oxidation and Knoevenagel condensation is realised by loading of Au nanoparticles within PME-ED. This catalyst design methodology can be also extended to developing another bifunctional catalyst that is composed of Pd nanoparticles and PME modified with *N*,*N*-dimethylethylenediamine in order to promote a Tsuji–Trost reaction.

catalysts to promote the multi-step reactions severely circumvent wide practical application of one-pot reaction systems.

Organic-inorganic hybrid materials have recently emerged as platforms for the manipulation of material design. Such materials combine structural functions derived from the inorganic parts and inherent modification possibilities of the organic parts in a single composite. Among those, periodic mesoporous organosilicas (PMOs) have been focus of much attention in the field of adsorbents,12-14 sensors15-17 and heterogeneous catalysts.18-22 Their highly-ordered porous structures and large specific surface areas provide unique adsorption characteristics23,24 and shape- and size-controlled deposition of active species typified by metal nanoparticles.25-27 Moreover, organic moieties covalently embedded within the silicate framework can be readily modified with a variety of functional groups by post-synthetic introduction.<sup>28</sup> Taking these advantages into account, PMO-based solid acid and base catalysts have been developed by introducing the sulfuric acid and amino groups, respectively, into the organic moieties.<sup>29-31</sup> In addition, 2,2'-bipyridyl and phenylene moieties within PMOs have been reported to act as immobilisation sites for various metal complexes.32-36

In this context, we herein report the development of a PMObased bifunctional heterogeneous catalyst containing Au nanoparticles (NPs) and diamine moieties as isolated multiple active sites for a one-pot reaction. For this purpose, periodic

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mesoporous ethylenesilica (PME) was selected as a support material. The diamine moieties were introduced into bridging ethylene moieties within PME through epoxidation reaction and the following nucleophilic addition reaction with ethylenediamine (PME-ED) as shown in Scheme 1. The multiple catalytic performances of Au NPs-loaded PME-ED (Au/PME-ED) were evaluated by a one-pot tandem reaction consisting of alcohol oxidation and Knoevenagel condensation.

### Experimental

#### Materials

1,2-bis(triethoxysilyl)ethene (BTSE) was purchased from Gelest Inc. Pluronic® P-123 and *tert*-butyl hydroperoxide (TBHP) were purchased from Sigma-Aldrich Co. LLC. Hydrochloric acid (35 wt%) and tetrachloroauric(m) acid (HAuCl<sub>4</sub>) was purchased from Kishida Chemical Co., Ltd. Acetonitrile, sodium hydroxide (NaOH), toluene, ethylenediamine, methanol, sodium borohydride (NaBH<sub>4</sub>) and polyvinylpyrrolidone (PVP) were purchased from Nacalai Tesque, Inc.

#### Synthesis of PME

PME was synthesised by a hydrothermal method with BTSE as an organosilica source and P-123 as a structure directing agent (SDA).<sup>30</sup> Typically, to a mixture of ion-exchanged water (33.5 mL), 4 M aqueous HCl solution (22.5 mL) and P-123, BTSE (2.15 g) was added dropwise. The solution was stirred at 313 K for 24 h to give a white precipitate and then aged at 373 K for 24 h without stirring. The resulting white precipitate was separated by filtration, washed with ion-exchanged water and ethanol and dried under vacuum. Finally, the SDA filling the pores was removed from the as-synthesised PME by refluxing in a solution containing 200 mL of ethanol and 5 mL of 4 M aqueous HCl solution for 20 h and the following filtration, washing with ionexchanged water and ethanol and drying under vacuum. This process was repeated twice, yielding PME without SDA.

#### Synthesis of PME-ED

PME modified with ethylenediamine (PME-ED) was synthesised by epoxidation of bridging ethylene moieties within PME and the following nucleophilic addition reaction with ethylenediamine.<sup>30,31,37</sup> Firstly, PME (500 mg) was loaded into a Schlenk flask and degassed at room temperature for 30 min under vacuum. After nitrogen purge, dehydrated acetonitrile (12 mL) and 2 M aqueous NaOH solution (50 mg) were added into the flask and cooled in an ice bath. Then, TBHP (3 mL) was added to the mixture, which was stirred at 273 K for 5 h. The resulting white solid was separated by filtration, washed with acetonitrile



and ethanol and dried under vacuum, yielding an epoxide product (PME-EP).

Subsequently, PME-EP (300 mg) was loaded into a Schlenk flask and degassed under vacuum at room temperature for 30 min and at 393 K for 12 h. After cooling to room temperature and nitrogen purge, dehydrated toluene (15 mL) and ethylenediamine (5 mL) were added into the flask and stirred at 333 K for 12 h. The resulting white solid was separated by filtration, washed with toluene and methanol and dried under vacuum, yielding PME-ED.

#### Synthesis of Au/PME-ED

Au NPs-loaded PME-ED was synthesised by a simple colloidal method.<sup>38</sup> A mixture of 28.23 mM aqueous  $HAuCl_4$  solution (354  $\mu$ L), ion-exchanged water (10 mL) and PVP (23 mg) was stirred in an ice bath. To the solution, 88 mM aqueous NaBH<sub>4</sub> solution (1 mL) was added dropwise, which was stirred at 273 K for 30 min. After that, PME-ED (150 mg) was added into the solution and resulting mixture was stirred at 273 K for 4 h. The thus-obtained solid was separated by filtration, washed with ion-exchanged water and dried under vacuum, yielding Au/PME-ED.

#### General methods

Fourier transform of infrared (FT-IR) spectra were recorded on a JASCO FT-IR 660 Plus apparatus with a resolution of 4 cm<sup>-1</sup> in transmission mode in air. The self-supporting pellet of the sample was loaded in a glass IR cell equipped with CaF<sub>2</sub> windows. Transmission electron microscopy (TEM) observations were carried out using a JEOL JEM-2000FX. Standard  $\theta$ -2 $\theta$  X-ray diffraction (XRD) data were recorded using a Shimadzu X-ray diffractometer XRD-6100 using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). Nitrogen (N<sub>2</sub>) adsorption–desorption isotherms were measured at 77 K using BELSORP-mini (BEL Japan Inc.). All the samples were degassed at 393 K for 12 h prior to data collection.

#### **Knoevenagel condensation reactions**

The reaction was carried out in liquid phase in a 35 mL Schlenk flask. A solution of benzaldehyde (0.5 mmol), active methylene compound (1.0 mmol) and toluene (5 mL) was stirred at 363 K with 20 mg of the catalyst in powder form. The obtained products were analysed by <sup>1</sup>H NMR spectroscopy. The progression of the reaction was monitored by gas chromatography with a Shimadzu GC-14B with a flame ionisation detector equipped with an InertCap®1 capillary column.

#### One-pot tandem alcohol oxidation and Knoevenagel condensation reactions

The reaction was carried out in liquid phase in a 35 mL Schlenk flask. A solution of benzyl alcohol (0.5 mmol),  $K_2CO_3$  (0.5 mmol) and toluene (5 mL) and catalyst (20 mg) were added into the flask.  $O_2$  gas was bubbled through the mixture for 30 min, and the mixture was stirred at 363 K. After 24 h of the reaction, ethyl cyanoacetate (0.5 mmol) was added into the reactor. The obtained products were analysed by <sup>1</sup>H NMR spectroscopy. The progression of the reaction was monitored by gas chromatography with a

Shimadzu GC-14B with a flame ionisation detector equipped with an InertCap®1 capillary column.

## **Results and discussion**

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In Fig. 1 are shown FT-IR spectra of PME, PME-ED and Au/PME-ED. The IR spectrum of pristine PME exhibited peaks at 1578  $cm^{-1}$  and 3038  $cm^{-1}$  attributable to stretching vibrations of C=C bonds and stretching vibrations C=C-H bonds, respectively,<sup>39-41</sup> indicating the formation of an organosilicate material bearing bridging ethylene groups. After functionalisation with ethylenediamine, a new band corresponding to N-H bending vibrations appeared at 1597 cm<sup>-1</sup>.<sup>42</sup> Besides, in a higher wavenumber region, new two peaks were observed at 3300 and 3363 cm<sup>-1</sup>. These peaks can be assigned to N-H symmetric and antisymmetric stretching vibrations, respectively.42 These findings suggest the successful introduction of amino groups by nucleophilic addition of ethylenediamine to epoxide groups. Moreover, in the Au/PME-ED spectrum, a strong band assigned to C=O was observed at 1660  $\text{cm}^{-1}$ . This band should be derived from PVP covering Au NPs.43

To gain an insight into the form of immobilised Au NPs, TEM observations were carried out. The TEM image of Au/PME-ED shown in Fig. 2 displayed fine and highly dispersed Au NPs as well as mesoporous channels of PME-ED. The mean particle size of Au NPs immobilised within PME-ED was determined to be 5.4 nm from this image. In addition, it was found from inductively coupled plasma (ICP) analyses that Au/PME-ED contains 0.5 wt% of Au metal.

Next, detail of the porous structure of Au/PME-ED was investigated by using XRD and N<sub>2</sub> adsorption–desorption measurements. Fig. 3 shows XRD patterns of PME, PME-ED and Au/PME-ED. All the patterns exhibited a clear peak at around  $2\theta$ = 0.9°. These peaks are corresponded to (100) reflection of a hexagonally packed mesoporous structure,<sup>39,44,45</sup> indicating the retaining of long range ordering of the mesoporous structure of PME after functionalisation with ethylenediamine and Au NPs loading. On the other hand, in the higher angle XRD pattern, Au/PME-ED displayed no peaks attributed to Au crystalline



Fig. 2 TEM image of Au/PME-ED.

phases because of very low loading amount of Au NPs.  $N_2$  adsorption-desorption isotherms of PME, PME-ED and Au/ PME-ED are shown in Fig. 4A. All the three isotherms traced a typical type IV curve, indicating the presence of mesoporous structures. These findings are coincident with the results of XRD measurements. In Fig. 4B are shown pore size distribution curves of PME, PME-ED and Au/PME-ED. From these curves, the mean pore diameters of PME, PME-ED and Au/PME-ED were determined to be 7.1, 6.2 and 5.4 nm, respectively. The decrease in the pore diameters along with each treatment would be explained by filling the pores for organic chains and Au NPs. The same trends were observed in BET areas and pore volumes (Table 1).

In order to assess base properties of PME-ED, Knoevenagel condensation reactions were performed. As shown in Fig. 5, the Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate efficiently proceeded on PME-ED at 363 K to give ethyl  $\alpha$ -cyanocinnamate in 90% yield for a 60 min period. By contrast, the pristine PME did not promote the reaction under the same reaction conditions. These findings revealed



Fig. 1 FT-IR spectra of (a) PME, (b) PME-ED and (c) Au/PME-ED.



Fig. 3 XRD patterns of (a) PME, (b) PME-ED and (c) Au/PME-ED.



Fig. 4 (A)  $N_2$  adsorption-desorption isotherms and (B) pore size distributions of (a) PME, (b) PME-ED and (c) Au/PME-ED.

 Table 1
 Textural parameters of PME, PME-ED and Au/PME-ED

Entry	Sample	BET area $[m^2 g^{-1}]$	Mean pore diameter [nm]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]
1	PME	969	7.1	2.48
2	PME-ED	785	6.2	2.03
3	Au/PME-ED	588	5.4	1.48

that PME-ED behaves as an effective heterogeneous base catalyst. In Knoevenagel condensation reactions, the scope of applicable active methylene compounds is known to correspond to base strength of catalysts. As summarised in Table 2, when malononitrile and nitromethane were used as active methylene compounds, the corresponding condensation products were obtained in high yields (see also <sup>1</sup>H NMR data in ESI†). Also, the promotion of the reaction between benzaldehyde and diethyl malonate was observed although the reaction rate was slow. On the contrary, PME-ED did not catalyse the reaction between benzaldehyde and benzyl cyanide. These results indicate that a proton can be abstracted from diethyl malonate ( $pK_a$ : 16.4 in DMSO) but not be abstracted from benzyl cyanide ( $pK_a$ : 21.9 in DMSO) by using PME-ED.<sup>46</sup>

Subsequently, the bifunctionality derived from Au NPs and the basic support, PME-ED, was evaluated for Au/PME-ED by a one-pot tandem reaction consisting of alcohol oxidation and Knoevenagel condensation. The reaction was first carried out at 363 K in the presence of a catalyst, benzyl alcohol and  $K_2CO_3$  in toluene under  $O_2$  atmosphere for 24 h, and then ethyl cyanoacetate was added to promote the second step reaction. The results are summarised in Table 3. Au/PME-ED promoted the one-pot tandem reaction and gave ethyl  $\alpha$ -cyanocinnamate in 89% yield for a 25 h period, while no reaction took place by using PME-ED without Au NPs as a catalyst. Besides, when Au NPs were loaded on pristine PME (Au/PME) and used in the same reaction, benzaldehyde was obtained as a main product. These findings demonstrated that both Au NPs and diamine



Fig. 5 Time course plots for Knoevenagel condensation reaction catalysed by PME and PME-ED.

Table 2 Knoevenagel condensation using various active methylene compounds catalysed by  $PME-ED^a$ 



compound				
$R^1$	$R^2$	Reaction time	Conv. of 1 [%]	Yield of 3 [%]
CN	COOEt	60 min	98	90
CN	CN	10 min	100	97
Н	$NO_2$	24 h	99	92
COOEt	COOEt	24 h	24	20
CN	Ph	24 h	0	0
	CN CN CN H COOEt CN	Active methylene       compound       R <sup>1</sup> R <sup>2</sup> CN     COOEt       CN     CN       H     NO2       COOEt     COOEt       CN     Ph	Active methylenecompoundR1R2Reaction timeR1R2Reaction timeCNCOOEt60 minCNCN10 minHNO224 hCOOEtCOOEt24 hCNPh24 h	Active mentionecompoundConv. of 1 $R^1$ $R^2$ Reaction time $R^1$ $R^2$ Reaction time $R^1$ $R^2$ Reaction time $R^1$ $R^2$ Reaction time $R^1$ $R^2$ $Reaction timeR^1R^2Reaction timeR^1Reaction timeReaction timeR^1$

<sup>a</sup> Reaction conditions: benzaldehyde (0.5 mmol), active methylene compound (1.0 mmol), toluene (5 mL), catalyst (20 mg), 363 K.

moieties are absolutely imperative for promoting the one-pot tandem reaction efficiently and that Au/PME-ED acts as a bifunctional heterogeneous catalyst. Although the oxidation reactivity of the Au/PME-ED catalyst trails somewhat behind by comparison with Ru(OH)<sub>X</sub>/Al<sub>2</sub>O<sub>3</sub> reported by Mizuno *et al.*,<sup>47</sup> it shows coequal basicity. Moreover, the catalyst design methodology developed in this study can be extended to the preparation of another bifunctional catalyst as described below.

In order to survey the versatility of the developed catalyst design methodology, Pd NPs were loaded on PME modified with *N*,*N*-dimethylethylenediamine (see ESI† for the preparation). The obtained catalyst denoted as Pd/PME-DMED was used in a Tsuji–Trost reaction between allyl methyl carbonate and ethyl acetoacetate as a heterogeneous catalyst. The reaction proceeded smoothly on Pd/PME-DMED to afford the corresponding ethyl 2-allylacetoacetate in 44% yield for a 24 h period. By contrast, Pd-loaded PME did not promote the reaction

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Table 3OnepottandemalcoholoxidationandKnoevenagelcondensation using various catalysts<sup>a</sup>



Entry	Catalyst	Conv. [%]	Yield of 2 [%]	Yield of 3 [%]
1	Au/PME-ED	91	1	89
2	PME-ED	0	0	0
3	Au/PME	88	58	19

<sup>*a*</sup> Reaction conditions: benzyl alcohol (0.5 mmol),  $K_2CO_3$  (0.5 mmol), toluene (5 mL), catalyst (20 mg), 363 K,  $O_2$  atmosphere. Ethyl cyanoacetate (0.5 mmol) was added into the reaction vessel after 24 h of the reaction. The total reaction time was 25 h.

efficiently and gave merely 11% of the product. Moreover, no reaction occurred on PME-DMED without Pd NPs. The Tsuji-Trost reaction is a Pd-catalysed allylation of nucleophiles with allylic compounds and well known to be facilitated in the presence of base, in which the activation of nucleophiles takes place *via* proton abstraction by base. These results and fact imply that both Pd NPs and amine moieties within Pd/PME-DMED play important roles in the progression of the Tsuji-Trost reaction, that is, Pd/PME-DMED acts as a bifunctional catalyst.

## Conclusions

In the present study, we have prepared and studied a PMObased bifunctional heterogeneous catalyst containing Au NPs and diamine moieties as isolated multiple active sites. The introduction of diamine moieties into PME was attained by epoxidation of bridging ethylene moieties of PME and the following nucleophilic addition reaction with ethylenediamine. The resulting material, PME-ED, acted as a base catalyst and promoted Knoevenagel condensation reactions between benzaldehyde and active methylene compounds, efficiently. The reaction results using various methylene compounds demonstrated that a proton can be abstracted from diethyl malonate  $(pK_a: 16.4)$  but not be abstracted from benzyl cyanide  $(pK_a: 21.9)$ on PME-ED. Moreover, loading of Au NPs into PME-ED led to the appearance of bifunctionality. A one-pot tandem reaction consisting of alcohol oxidation and Knoevenagel condensation proceeded on the Au/PME-ED catalyst to produce ethyl a-cyanocinnamate from benzyl alcohol and ethyl cyanoacetate via formation of benzaldehyde. Moreover, by using the same catalyst preparation methodology, another bifunctional catalyst consisting of Pd NPs and PME modified with N,N-dimethylethylenediamine was successfully synthesised for a Tsuji-Trost reaction. The observations made in this effort suggest new possibilities to design catalysts for one-pot reactions utilising PMO materials.

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