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Nanocrystalline MgO catalysts for the Henry reaction of benzaldehyde and nitromethane

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ABSTRACT

Nanocrystalline MgO particles of about 3 nm were examined as catalysts for the Henry reaction between benzaldehyde and nitromethane at 273 K. The surface area of nanocrystalline MgO was greater than 600 $m^2\ g^{-1}$ except after thermal treatment in N_2 at 823 K, which reduced the surface area to 359 $m^2\ g^{-1}$. The areal rate of the Henry reaction over nanocrystalline MgO at 273 K was $0.015 \pm 0.002\ \mu mol\ m^{-2}\ s^{-1}$ and was independent of pretreatment temperature over the range of 523–823 K. Addition of (S)-BINOL to nanocrystalline MgO has been reported previously to favor the production of one enantiomer of the Henry reaction. In the current work, negligible enantiomeric excess was observed on (S)-BINOL-modified nanocrystalline MgO catalysts, regardless of the source of nanocrystalline MgO, the MgO activation temperature, the reaction temperature, the sequence of reactant addition or the loading of (S)-BINOL. Adsorption of L-proline onto nanocrystalline MgO catalyst induced a small enantiomeric excess in the Henry reaction products, but the catalytic activity of the catalyst was low.

1. Introduction

The addition of a nitroalkane to a carbonyl compound, namely the Henry (or nitroaldol) reaction, is an important C–C bond formation reaction that produces β-nitroalcohols with up to two adjacent chiral carbons. Reduction of the nitro group in β-nitroalcohols can lead to the formation of aminoalcohols, which occur widely as natural and synthetic products as well as chemical intermediates [1–7]. Developing efficient catalysts that form products with high enantiomeric excess (ee) is of great interest in synthetic organic chemistry and the pharmaceutical industry. Homogeneous catalysts, such as a rare earth BINOL complex [1,2], a dinuclear zinc complex with a chiral semi-azacrown ligand [5,8], a copper acetate–bis(oxazoline) complex [6] and a bifunctional amine-thiourea organocatalyst [3,4], are reported to be effective for chiral Henry reactions. Heterogeneous catalysts for the Henry reaction, whether chiral or achiral, are much less studied. One of the potential advantages of a heterogeneous catalyst is that it can be easily recovered from the reaction medium and hopefully recycled. Choudary et al. reported that nanocrystalline MgO modified with the chiral ligand (S)-BINOL is an effective and reusable catalyst for the Henry reaction with comparable ee to homogeneously-catalyzed systems [9]. However, the nature of the active sites on the modified MgO surfaces is unknown at this time. Since the catalytic properties of MgO materials depend significantly on their preparation methods [9–18], the influences of pretreatment conditions and reaction conditions on the activity and selectivity of the Henry reaction need to be explored.

In this work, the effects of catalyst source, catalyst activation temperature, reaction temperature, ligand loading and chemical addition sequence were explored for the Henry reaction of benzaldehyde and nitromethane over MgO and chirally-modified MgO catalysts.

2. Experimental methods

2.1. Catalyst preparation and characterization

Nanocrystalline MgO was purchased from Strem Chemicals (product name: magnesium oxide nanopowder (high surface area)), designated as nano-MgO-1, and from NanoScale Materials Inc. (product name: NanoActive Magnesium Oxide Plus), designated as nano-MgO-2. The detailed synthesis method used to prepare these two MgO materials can be found elsewhere [15]. The thermal activation of the MgO catalysts was performed by heating 0.5 g of as-received nano-MgO-1 or nano-MgO-2 in 100 $cm^3\ min^{-1}$ flowing N_2 (GT&S, 99.999%) at 5 $K\ min^{-1}$ and holding at various temperatures for 1 h. The modification of MgO by (S)-BINOL (Sigma–Aldrich, 99%) was conducted in the same way as reported by Choudary et al. [9], i.e. (S)-BINOL was simply mixed with the thermally-pretreated MgO catalyst in the solvent THF. In addition, L-proline (Sigma–Aldrich, 99%) modified MgO was also used as a

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catalyst for the Henry reaction. Nano-MgO-2 (0.5 g), which was thermally-treated to 723 K, was magnetically-stirred in a solution of 1.428 g L-proline and 45 mL methanol (Sigma–Aldrich, anhydrous, 99.8%) at room temperature for 1 h. The solid catalyst was then separated by centrifugation, washed with 45 mL THF, and used directly in the Henry reaction. Prior to characterizing the material, L-proline modified nano-MgO-2, it was treated in 100 $cm^3\ min^{-1}$ flowing N_2 for 24 h at room temperature.

The physisorption of N_2 was performed on a Micromeritics ASAP 2020 at 77 K. The BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Hallender) methods were used to calculate the surface area and pore size distribution of the samples, respectively. The XRD (X-ray diffraction) patterns were measured on a Scintag XDS 2000 diffractometer using Cu Kα radiation (λ = 1.54 Å). The samples were scanned in the continuous mode from 4° to 72° at a scan rate of 2° min^{-1}. The IR (infra-red) spectra were recorded in the diffuse reflectance mode on a Bruker Vertex 70 spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory using an MCT detector. The spectra were averaged from 32 scans in the range of 400–4000 cm^{-1} at the resolution of 4 cm^{-1}. The magnesium and nitrogen contents of the nano-MgO-2 loaded with L-proline were determined by ICP analysis and combustion analysis, respectively (Galbraith Laboratories, Knoxville, TN).

The Henry reaction of benzaldehyde and nitromethane was conducted in a 100 mL 3-necked round-bottomed flask that was magnetically-stirred at 800 rpm under N_2 atmosphere. Generally, 0.5 g nano-MgO-1 or nano-MgO-2 catalyst was thermally pretreated and transferred to the reactor under N_2 atmosphere for the Henry reaction with 0.408 mL (4 mmol) of benzaldehyde (Sigma–Aldrich, 99.5%) and 1.074 mL (20 mmol) of nitromethane (Sigma–Aldrich, 99.0%) as reactants and 20 mL tetrahydrofuran (THF, Sigma–Aldrich, anhydrous, 99.9%) as solvent at 273 K unless otherwise indicated. High-performance liquid chromatography (HPLC, e2695 Separations Module equipped with a Waters 2489 UV/Visible Detector at 215 nm) was used to quantify the reactants and products. A CHIRALPAK IB column (4.6 mm I.D., 250 mm L; Chiral Technologies Inc.) operating at 298 K with 1.0 mL min^{-1} n-hexane/2-propanol (95/5, v/v) as mobile phase was used to separate the reactants and products. The samples from the reaction were filtered (0.2 μm) and diluted in mobile phase (sample/mobile phase, 1/10, v/v) before analysis. Since the reaction products (R)-1-phenyl-2-nitroethanol and (S)-1-phenyl-2-nitroethanol are not available commercially, tetramethylguanidine (Acros, 99%) was used as a homogeneous catalyst to react benzaldehyde at various concentrations with nitromethane to produce racemic products [19]. A representative HPLC chromatogram of racemic products is displayed in Fig. 1a. The racemic products were easily resolved and the calibration curves of (R)-1-phenyl-2-nitroethanol and (S)-1-phenyl-2-nitroethanol were based on a mass balance between the converted benzaldehyde and the formation of racemic product. The identification of (R)-1-phenyl-2-nitroethanol versus (S)-1-phenyl-2-nitroethanol was based on an known Henry reaction catalyzed by a copper acetate–bis(oxazoline) complex [6]. In that experiment, 0.267 g $Cu(OAc)_2{\cdot}H_2O$ (Sigma–Aldrich, 99.99%) and 0.0401 mL 2,2-bis((4*S*)-(−)-4-isopropyloxazoline)propane (Sigma–Aldrich, 96%) were first dissolved in 6.822 mL methanol and stirred for 1 h at room temperature before adding 0.101 mL benzaldehyde and 2.923 mL nitromethane and stirring for an additional 24 h. A representative HPLC chromatogram of the enantioselective products of the Henry reaction is shown in Fig. 1b. By comparison to previously reported results [6], the HPLC peaks appearing at 18.8 and 22.2 min are attributed to (R)-1-phenyl-2-nitroethanol and (S)-1-phenyl-2-nitroethanol, respectively. The enantiomeric excess is reported here based on (S)-1-phenyl-2-nitroethanol.

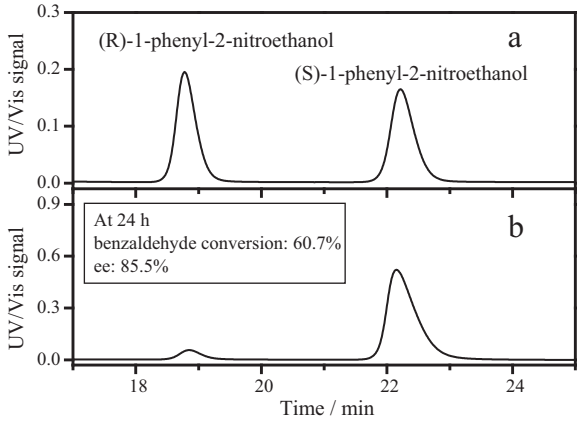

Fig. 1. HPLC chromatograms of (a) racemic Henry reaction products of 0.0102 mL benzaldehyde and 1 mL nitromethane catalyzed by 1 drop of tetramethylguanidine [19] at 273 K for 40 min; (b) enantioselective Henry reaction products at 24 h; reaction conditions: 0.267 g $Cu(OAc)_2{\cdot}H_2O$ and 0.0401 mL 2,2-Bis((4*S*)-(−)-4-isopropyloxazoline)propane as ligand were dissolved in 6.822 mL methanol and stirred for 1 h at room temperature then 0.101 mL benzaldehyde and 2.923 mL nitromethane were added and reacted for 24 h [6].

3. Results and discussion

3.1. Catalyst characterization

X-ray diffraction patterns of the nano MgO materials are presented in Fig. 2. The as-received nano-MgO-1 and nano-MgO-2 samples exhibit two broad peaks at 42.6° and 61.6°, which correspond to the (2 0 0) and (2 2 0) reflections of cubic MgO. The crystallite sizes of the MgO samples were estimated from a line broadening analysis of the XRD patterns in Fig. 2 and the results summarized in Table 1 indicate both samples were 3 nm in crystallite size. Although the crystal structure of the L-proline modified nano-MgO-2 (Fig. 1c) was still cubic MgO, the size of the modified sample increased slightly to 3.4 and 3.6 nm along the (2 0 0) and (2 2 0) directions.

The N_2 adsorption–desorption isotherms of nano-MgO-1 and nano-MgO-2 are provided in Fig. 3a. Both of the samples exhibited type II adsorption isotherms with a small hysteresis loop on the desorption branch. The nano-MgO-1 and nano-MgO-2 had high BET surface areas of 619 $m^2\ g^{-1}$ and 775 $m^2\ g^{-1}$, respectively (Table 1), which is consistent with previously reported results [9,15]. The pore size distributions of nano-MgO-1 and nano-MgO-2 (Fig. 3b) revealed pores in nano-MgO-1 in the range of 2–6 nm with a maximum at ~2.7 nm, whereas nano-MgO-2 had a slightly narrower

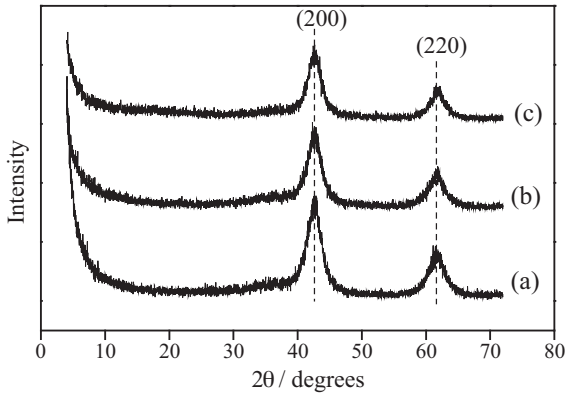

Fig. 2. XRD patterns of (a) nano-MgO-1; (b) nano-MgO-2; and (c) L-proline modified nano-MgO-2.

Table 1
Physical properties of nano MgO catalysts.

Sample	BET ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	$D(2\,0\,0)$[d,e] (nm)	$D(2\,2\,0)$[d,f] (nm)
Nano-MgO-1[a]	619	0.47	3.1	3.0
Nano-MgO-1 (723 K)[b]	635	0.57	–	–
Nano-MgO-1 (823 K)[b]	359	0.59	–	–
Nano-MgO-2[a]	775	0.52	3.3	3.0
L-Proline modified nano-MgO-2[c]	457	0.50	3.4	3.6

[a] Catalysts were degassed at 523 K for 2 h before analysis.
[b] Catalysts were thermal treated at 723 K or 823 K for 1 h under 100 $cm^3\ min^{-1}$ N_2 flowing and then degassed at 523 K for 2 h before analysis.
[c] Catalyst were degassed at room temperature for 2 h before analysis.
[d] The full width at half maximum (FWHM) of the XRD diffraction peaks was calculated by fitting the XRD patterns to pseudo-Voigt functions. Crystallite size was estimated from Debye–Scherrer equation, using silicon as standard to correct the line broadening due to instrument.
[e] Crystallite size along (2 0 0) direction.
[f] Crystallite size along (2 2 0) direction.

pore size distribution in the range of 2–5 nm with a maximum at ~2.5 nm. Although thermally-treating nano-MgO-1 at 723 K for 1 h did not significantly alter its surface area, treatment at 823 K for 1 h decreased the surface area to 359 $m^2\ g^{-1}$, as summarized in Table 1.

Modifying nano-MgO-2 with L-proline decreased its surface area to 457 $m^2\ g^{-1}$ compared to the untreated precursor (775 $m^2\ g^{-1}$). The decrease in surface area is attributed to a substantial loading of L-proline on the nano-MgO-2 surface, which was determined to be 23.9 wt% from elemental analysis and corresponds to a surface coverage of 4.44 μmol m^{-2}. Infrared spectroscopy was also used to characterize nano-MgO-2 and its L-proline modified analogue. As shown in Fig. 4, the as-received nano-MgO-2 exhibited features associated with adsorbed CO_2 [13,20] and H_2O molecules, presumably because of its high basicity. The absorption bands at ~1400 and ~1470 cm^{-1} can be ascribed to the various carbonate species, whereas the band at ~1630 cm^{-1} is attributed to the bending mode of adsorbed H_2O molecules. The hydroxyl stretching region in the range of 2700–3800 cm^{-1} is typical on MgO materials [15,21]. New bands can be observed in Fig. 4b that are assigned to the adsorbed L-proline. The bands at ~1600 and ~1440 cm^{-1} are thus assigned to the asymmetric and symmetric stretches of carboxylate anions [22,23]. The C–H stretches that appeared in the range of 2800–3000 cm^{-1} are also attributed to the adsorbed L-proline moiety on nano-MgO-2.

3.2. Henry reaction

Since IR spectroscopy revealed the presence of CO_2 and H_2O on the surface of MgO, the effect of thermal pretreatment on the rate of the Henry reaction was explored. The nano-MgO-1 catalyst was thermally activated in N_2 at temperatures ranging from 523 to 823 K and transferred to the reactor without exposure to air. The initial reaction rate and the conversion of benzaldehyde at 4 h as a function of pretreatment temperature are presented in Fig. 5. The initial rate of benzaldehyde reaction increased from 0.55 to 0.64 mmol $g^{-1}\ min^{-1}$ by increasing the thermal pretreatment temperature from 523 to 723 K; however, the rate decreased to 0.27 mmol $g^{-1}\ min^{-1}$ after a pretreatment at 823 K. The benzaldehyde conversion after 4 h was about 92% for the lower pretreatment temperatures but decreased to 68% at the catalyst pretreatment temperature of 823 K. The lower reactivity and lower benzaldehyde conversion observed after treating nano-MgO-1 at 823 K is explained by its lower surface area (Table 1). Montero et al. also reported that MgO nano particles prepared solvothermally had surface area of 580 $m^2\ g^{-1}$, which decreased to 140 $m^2\ g^{-1}$ after calcination at 873 K [24]. The reaction rates normalized by surface area of nano-MgO-1 pretreated at 523, 723 and 823 K were quite similar (0.015, 0.017 and 0.013 μmol $m^{-2}\ s^{-1}$, respectively). Although the surface area of nano-MgO-1 decreased significantly after thermal pretreatment at 823 K, the observed rate per exposed surface area was relatively constant over the range of pretreatment temperatures used here. From the results presented in Fig. 5, the optimum catalyst activation temperature was 723 K for the nano-MgO-1 catalyst because of the high surface area of the

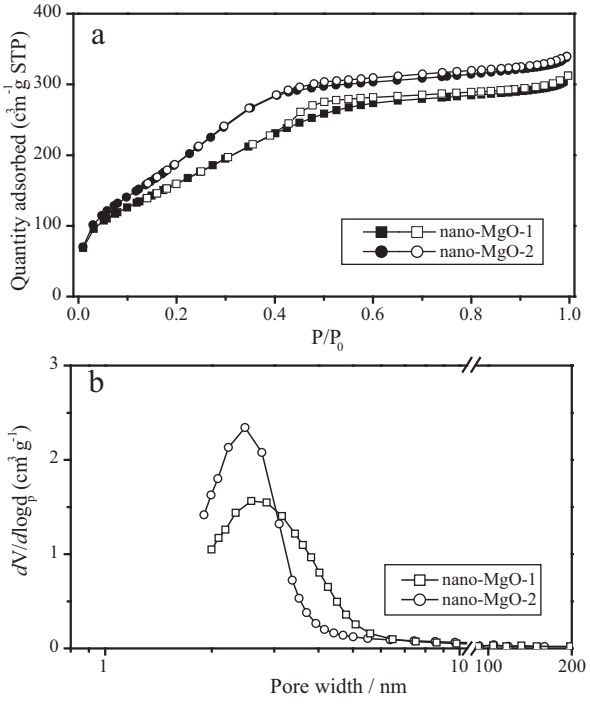

Fig. 3. N_2 adsorption (black symbols) and desorption (white symbols) isotherm (a) and BJH pore size distribution from N_2 adsorption branches (b) of nano MgO catalysts.

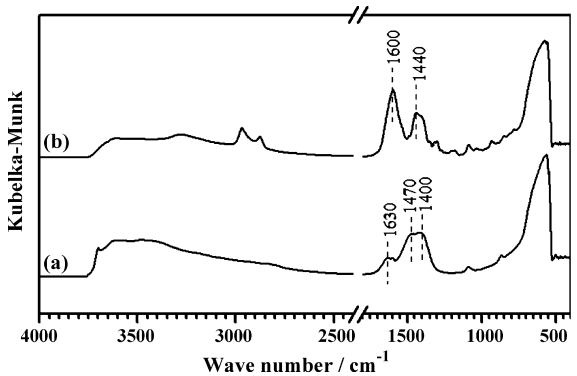

Fig. 4. Diffuse reflectance infrared Fourier transformed spectra (DRIFTS) of (a) nano-MgO-2 and (b) L-proline modified nano-MgO-2.

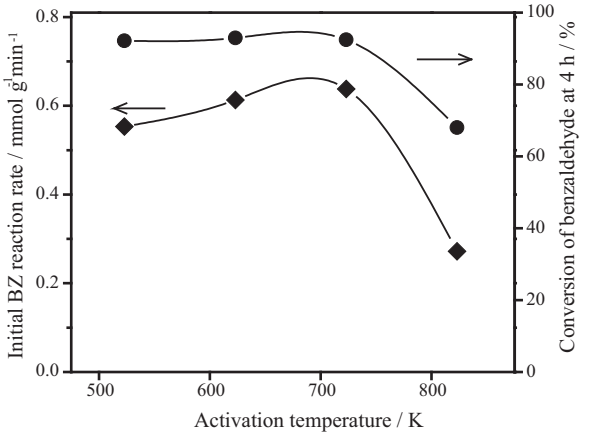

Fig. 5. Effect of activation temperature on nano-MgO-1 catalyst reactivity. Reaction condition: benzaldehyde (8.0 mmol, 0.815 mL); nitromethane (40 mmol, 2.147 mL); THF (40 mL); 0.5 g nano-MgO-1 activated at 523, 623, 723 and 823 K for 1 h (5 K min^{-1}) under 100 cm^3 min^{-1} N_2 flowing; reaction temperature 273 K.

sample. A representative reaction profile is presented in Fig. 6a. It is important to note that only the racemic products, (R)-1-phenyl-2-nitromethanol and (S)-1-phenyl-2-nitroethanol, were observed during the course of the reaction.

Choudary et al. reported that (S)-BINOL modified nano-MgO-2 with high surface area can induce enantioselectivity for Henry reaction [9]. In their paper, (S)-BINOL modified nano-MgO-2 catalyzed the Henry reaction of benzaldehyde and nitromethane with 70% ee after 7 h of reaction at 273 K and 90% ee after 12 h reaction at 195 K. Therefore, we tested (S)-BINOL modified nano MgO for Henry reaction of benzaldehyde and nitromethane and the results are presented in entry 1 of Table 2. The (S)-BINOL/nano-MgO-1 combination had lower initial activity of 0.12 mmol g^{-1} min^{-1}, which is about 16% of the initial activity of nano-MgO-1 without added (S)-BINOL (Fig. 4). The lower initial activity of (S)-BINOL modified nano-MgO-1 is likely due to the adsorption of the ligand, (S)-BINOL, which has a p*Ka* value of 10.28 [25], onto the basic surface of MgO. After 4 h of reaction, benzaldehyde reached 68% conversion in the presence of (S)-BINOL, but the ee of the products was negligible at −1.4%. The low ee observed in entry 1 of Table 2 was not consistent with the prior work of Choudary et al. [9], however, there were some differences in the reaction conditions. Therefore, in entry 2 of Table 2, identical ratios of catalyst, (S)-BINOL and reactants were used and the same catalyst activation temperature of 523 K was used. Again a negligible ee of −0.8% was observed. Entry 3 of Table 2 presents our best attempt to match the source of the MgO, the ratios of the catalyst, (S)-BINOL and reactants, and the activation temperature to those used by Choudary et al. Again, negligible ee was observed after 4 h or 7 h of reaction. The reaction profile of entry 3 of Table 2 is presented in Fig. 6b. In an attempt to explore the influence of other variables in the reaction, entries 4–7 in Table 2 illustrate the effects of the order of addition of reactants, the amount of (S)-BINOL added to the reactor, and the reaction temperature. As expected, altering the sequence of addition of reagents did not affect the rate or the ee. Moreover, addition of up to an order of magnitude more (S)-BINOL did not improve the ee. Although the initial rate at 195 K (entry 7) was two orders of magnitude lower than that at 273 K (entry 3 in Table 2), the observed ee was still negligible, even after 12 h of reaction (6.5% conversion). The reaction profile associated with entry 7 in Table 2 is presented in Fig. 6c. Interestingly, Choudary et al. reported that 100% benzaldehyde conversion and 90% ee were obtained after 12 h of reaction under similar conditions.

Since we were unable to observe any enantiomeric excess by modifying MgO with (S)-BINOL, we attempted a few control experiments that are summarized in Table 3. Entry 10 of Table 3 confirmed that the Henry reaction did not proceed at room temperature

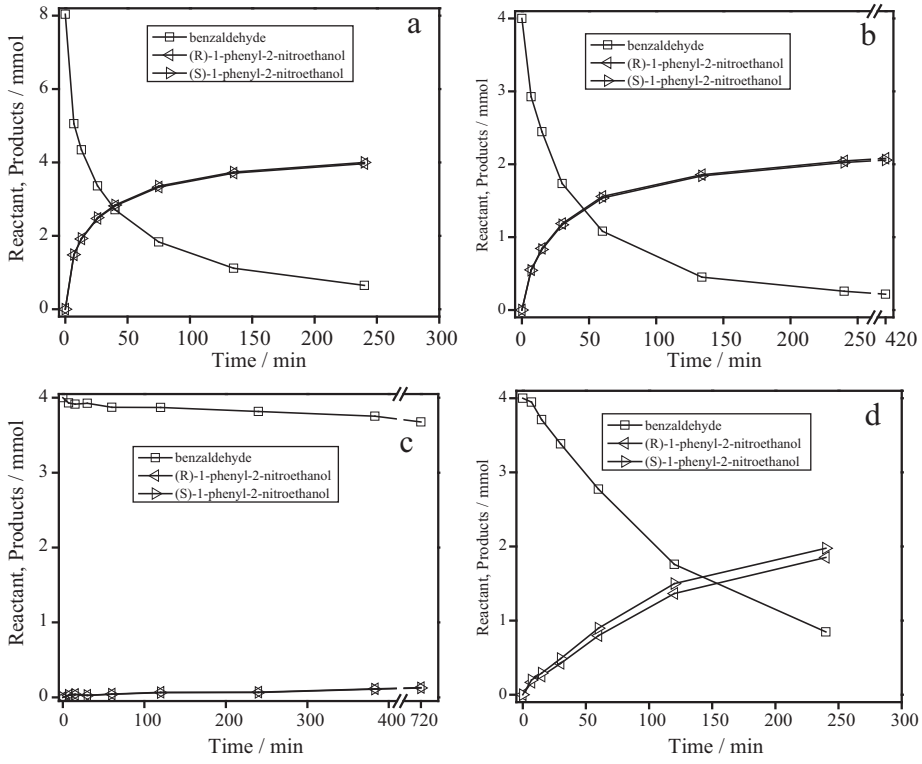

Fig. 6. Reaction profiles of activated nano MgO catalyst for Henry reaction. (a) Nano-MgO-1 (723 K activated), reaction condition same as in Fig. 5; (b) (S)-BINOL modified nano-MgO-2 (523 K activated) catalyst, reaction temperature was 273 K; (c) (S)-BINOL modified nano-MgO-2 (523 K activated) catalyst, reaction temperature was 195 K; (d) L-proline modified nano-MgO-2 (723 K activated) catalyst, reaction temperature was room temperature.

Table 2
Reaction tests of activated nano MgO catalysts for Henry reaction.

Entry	Catalyst precursor[i]	(S)-BINOL (g)	Thermal treatment, T (K)	Reaction, T (K)	Initial benzaldehyde reaction rate (mmol g^{-1} min^{-1})	Benzaldehyde conversion at 4 h (%)	ee at 4 h (%)
1[a,e]	Nano-MgO-1	0.32	723	273	0.12	68	−1.4
2[b,e]	Nano-MgO-1	0.16	523	273	0.25	95	−0.8
3[b,e]	Nano-MgO-2	0.16	523	273	0.23	94	−0.8
						95[c]	−0.5[c]
4[b,f]	Nano-MgO-2	0.16	523	273	0.29	94	−0.6
5[b,f]	Nano-MgO-2	0.8	523	273	0.21	91	−2.3
6[b,g]	Nano-MgO-2	1.6	523	273	0.21	92	−3.5
7[b,e]	Nano-MgO-2	0.16	523	195	0.002	6.5[d]	−2.2[d]
8[b,h]	Nano-MgO-2	–	723	296	0.073	82	3.2
9[b,h]	Nano-MgO-2	–	723	195	–	∼0[d]	20.4[d]

[a] 8 mmol benzaldehyde and 40 mmol nitromethane were used as reactants in 40 mL THF as solvent.
[b] 4 mmol benzaldehyde and 20 mmol nitromethane were used as reactants in 20 mL THF as solvent.
[c] At 7 h.
[d] At 12 h.
[e] Nitromethane and (S)-BINOL were added to THF at reaction temperature and then activated catalyst was added and stirred for 1 h before adding benzaldehyde to initiate reaction [9].
[f] In the mixture of THF, activated catalyst and benzaldehyde at 273 K, (S)-BINOL was added and stirred for 5 min before adding nitromethane to initiate reaction.
[g] Stirring the mixture of THF, (S)-BINOL and activated catalyst at 273 K for 1 h before adding benzaldehyde and nitromethane to initiate the reaction.
[h] L-Proline modified nano-MgO-2 (723 K activated). The activated catalyst was added to THF at reaction temperature and benzaldehyde and nitromethane were then added to initiate the reaction.
[i] 0.5 g catalyst was activated.

without the presence of the MgO catalyst. Since CO_2 is a common poison of base catalysts, we attempted to thermally activate $MgCO_3$ as a catalyst for the Henry reaction. A thermally activated (523 K for 1 h under 100 cm^3 min^{-1} N_2 flowing) commercial $MgCO_3$ (Sigma–Aldrich, ≥40% MgO) was inactive for the Henry reaction after 4 h, as shown in Table 3. To exclude the possibility of leached magnesium cations coordinating with (S)-BINOL and serving as a homogeneous catalyst, magnesium acetate and (S)-BINOL were used in the Henry reaction. As summarized in entry 12 of Table 3, only 2.7% benzaldehyde conversion was observed after 24 h and no ee was observed.

Choudary et al. report that silylation of nano-MgO substantially reduces its activity and eliminated the ee for the Henry reaction in the presence of (S)-BINOL. These results appear to suggest that the hydroxyl groups on the nano MgO contribute significantly to the catalytic activity for the Henry reaction. Apparently, the activation temperature of 523 K is not high enough to remove all of the hydroxyl groups on MgO surface [13,24] and the addition of (S)-BINOL might actually increase the hydroxyl groups on the catalyst surface due to the transfer of protons from (S)-BINOL to Lewis base sites on the catalyst surface. To test the role of hydroxyl groups and control its inventory, the nano-MgO-2 catalyst was hydrated by water vapor for 24 h at room temperature and then activated at 523 K for 1 h before it was tested for Henry reaction. The result summarized entry 13 of Table 3 indicates that the hydrated nano-MgO-2 was poorly active and did not exhibit any ee.

All of our attempts to produce a base catalyst from MgO and (S)-BINOL to promote the Henry reaction with high ee were unsuccessful. As an alternative, L-proline modified nano-MgO-2 was tested in the reaction. L-Proline has a carboxyl group and an amino-group associated with the same chiral center, which makes L-proline a potential catalyst or ligand for asymmetric reactions. Indeed, L-proline [26], L-proline-derived organocatalyst [27] and supported L-proline [28] have been reported to catalyze asymmetric aldol reactions. The acidity of the carboxyl group could lead to high loading of L-proline onto the basic surface of MgO surface, while the basicity of the amino-group and the chiral carbon center of L-proline might lead to activity and enantioselectivity for the Henry reaction.

The results of the Henry reaction on L-proline modified MgO are presented in Table 2 and Fig. 6d. At room temperature, the L-proline modified nano-MgO-2 exhibited moderate reactivity with an initial benzaldehyde reaction rate of 0.073 mmol g^{-1} min^{-1} and little selectivity to (S)-1-phenyl-2-nitroethanol (ee of 3.2%) at 4 h. The ee was improved to 20.4% by lowering the temperature to 195 K, however the reaction rate was so low that the benzaldehyde conversion after 12 h was nearly undetectable. The surface coverage of L-proline on nano-MgO-2 was 4.44 μmol m^{-2}, which is the same as the reported CO_2 adsorption capacity on a synthesized MgO material (4.4 μmol m^{-2}) [29]. Evidently, the surface base sites on MgO were effectively titrated by L-proline. The formation of carboxylate anion as observed by the IR absorption bands (Fig. 4) at 1600 and 1440 cm^{-1} on the L-proline modified nano-MgO-2, suggest that the proton from the carboxyl group of L-proline has been transferred to the basic surface of MgO. Therefore, the activity observed on the L-proline modified nano-MgO-2 is attributed to the amino-

Table 3
Control experiment tests for Henry reaction.

Entry	Catalyst	(S)-BINOL (g)	Reaction, T (K)	Benzaldehyde conversion (%)	ee (%)
10[a,b]	No catalyst	0	296	0 (1 h)	–
11[a,c]	$MgCO_3$	0.16	273	0 (4 h)	–
12[d]	$Mg(CH_3COO)_2{\cdot}4H_2O$	0.189	296	2.7 (24 h)	−0.1 (24 h)
13[a,e]	Hydrated nano-MgO-2	0.16	273	2.6 (4 h)	−0.6 (4 h)

[a] 4 mmol benzaldehyde and 20 mmol nitromethane were used as reactants in 20 mL THF as solvent.
[b] Blank test without catalyst and (S)-BINOL.
[c] 523 K treated 0.5 g $MgCO_3$ was used as catalyst.
[d] In the mixture of 0.0429 g magnesium acetate tetrahydrate (Fisher, 99.2%) and 20 mL methanol, 4 mmol benzaldehyde and 20 mmol nitromethane were added and stirred at room temperature.
[e] Nano-MgO-2 was hydrated in water vapor at room temperature for 24 h, then 0.5 g hydrated nano-MgO-2 catalyst was activated at 523 K and used as catalyst.

group of loaded L-proline rather than the basic sites on the MgO surface.

4. Conclusions

Nanocrystalline MgO is an effective catalyst for the Henry reaction between benzaldehyde and nitromethane. The areal rate of the reaction performed at 273 K was not affected by thermally-treating the samples in N_2 over the range of 523–823 K, although the surface area of the sample treated at the highest temperature was substantially reduced from those treated at lower temperatures. Attempts to produce an enantiomeric excess of chiral product by addition of (S)-BINOL to the reaction mixture were unsuccessful, which contrasts a prior work in the area. The reasons for the differences between the results reported here and those reported earlier are not immediately evident and warrant additional study. Modification of MgO with L-proline revealed some enantiomeric excess in the Henry reaction products formed at low temperature, but the reaction rates were too slow to be interest. The enantiomeric excess of products formed over L-proline modified MgO is likely the result of catalysis by the amino group of the L-proline.

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