RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: RSC Adv., 2015, 5, 42178

Design and application of the recyclable poly (L-proline-*co*-piperidine) catalyst for the synthesis of mesityl oxide from acetone†

Lin Xu,[ab] Jiejun Huang,[bc] Yubing Liu,[a] Yining Wang,[a] Bolian Xu,[a] Kehong Ding,[bc] Yuanhua Ding,[c] Qing Xu,[bc] Lei Yu*[abc] and Yining Fan*[a]

Received 1st April 2015
Accepted 23rd April 2015

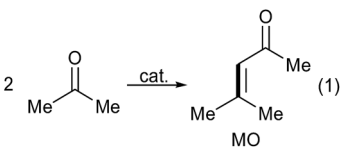
DOI: 10.1039/c5ra05741h

www.rsc.org/advances

Unexpectedly, L-proline/piperidine was found to be a better recyclable catalyst system than L-proline or piperidine alone in the condensation of acetone to prepare mesityl oxide (MO), an important intermediate in the chemical industry. Binding the catalyst system onto polymer resin enhanced the MO selectivity and reduced the catalyst loss. The mechanism of the bi-component catalyst system was also studied through control reactions, as well as by dynamic calculations. The MO selectivity could reach 74.4% and its isolated yield could reach 73.9%, based on the consumed acetone. Although the result does not immediately meet the requirement of industrial production, this study provides a novel organocatalyst system, which might offer a potential alternative to traditional inorganic catalysts that can be used under mild and neutral conditions.

Introduction

Acetone, mostly generated as a by-product during the production of phenol through the oxidation of cumene, is an excess compound in the chemical industry. Therefore, the use of this cheap and abundant material to produce high-value products is highly desirable. Acetone can be converted to mesityl oxide (MO, eqn (1)), an important intermediate in organic synthesis, pharmaceutical chemistry, agricultural chemistry, polymer and materials science[1] and even in natural product syntheses.[2] MO could also be employed to synthesize phorones and isophorones, which are significant compounds in the chemical industry and are also our concern.[3] However, although the condensation of acetone affords a highly atom-economical and concise access to MO, the present methodologies have drawbacks such as the use of one–off metal catalysts, strong alkaline conditions, high catalyst loading, harsh reaction conditions and generation of harmful and corrosive waste.[4] In line with calls for greater environmental protection nowadays, these technologies are facing huge pressure from government policies. Therefore, developing a novel recyclable catalyst that works under neutral and mild conditions and that causes less waste to produce MO from acetone is of great importance for industrial production.



(1)

Still organocatalysts have attracted much attention from chemists because of their availability, cheapness and low-toxicity and due to the option to employ mild reaction conditions and clean procedures.[5] Thus, for the purpose of developing green synthetic methodologies for possible industrial applications,[6,7] we have focused on organocatalysis in recent years.[7] Among our previous studies, many of the organocatalysts were recyclable and these waste-free processes have great potential in industrial production.[7a–d] L-Proline is also a popular organocatalyst and it came to our attention recently because of its ready availability. To date, L-proline has been comprehensively employed in many types of reactions, such as the Mannich reactions,[8] Michael additions,[9] Diels–Alder reactions,[10] and multi-component reactions[11,12] affording powerful and practical tools in organic synthesis owing to the accessible and versatile catalysts, neutral, mild and metal-free conditions and high product yields and selectivities. Moreover, the L-proline-catalyzed condensations of aldehydes and ketones have already been widely applied in organic synthesis,[13] but because L-proline is a very cheap and abundant natural chiral catalyst, people are more inclined to

[a]Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu, 210093, China. E-mail: ynfan@nju.edu.cn; Fax: +86-25-83317761; Tel: +86-25-83594620

[b]Jiangsu Yangnong Chemical Group Co. Ltd., Yangzhou, Jiangsu, 225009, China

[c]Jiangsu Co-innovation Center for Prevention and Control of Important Animal Infectious Diseases and Zoonoses, School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu, 225009, China. E-mail: yulei@yzu.edu.cn; Fax: +86-514-87975244; Tel: +86-136-65295901

† Electronic supplementary information (ESI) available: Experimental details, analysis details, detailed data tables, spectra and calculations procedures. See DOI: 10.1039/c5ra05741h

develop asymmetric synthetic methodologies with it, while the condensation of acetone to produce the simple but important MO has so far been ignored for a long time. During our continuous cooperative research projects with industrial circles,[6c,7g,7j] we began to pay close attention to the condensations of aldehydes and ketones because of their high atom-economy and efficiency in C–C bond formations.[7f] Recently, we investigated the L-proline-catalyzed condensation of acetone to prepare MO. Herein, we wish to report our findings.

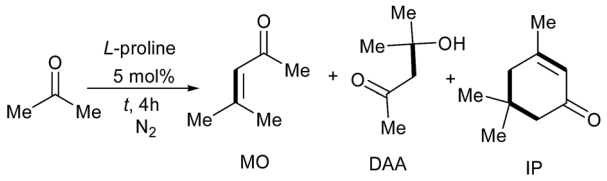
Results and discussions

Initially, we added 300 g of acetone and 30 g of L-proline in an autoclave. After keeping in N_2 at 1.0 MPa for 10 min, the pressure was relieved and the mixture was stirred at 500 rpm and heated at 80 °C for 4 h. Spectrophotography analysis showed that 76.3% of the catalyst L-proline remained after the reaction, while GC analysis showed that the conversion ratio of acetone was 23.3% and that the selectivities of MO and the by-product diacetone alcohol (DAA) and isophorone (IP) were 67.0%, 10.7% and 0.3%, respectively (Table 1, entry 1).[14] To optimize the reaction conditions, a series of different reaction temperatures were then tested (Table 1, entries 2–6). The conversion ratio of acetone did not change much at different temperatures but the selectivities of the products varied. In general, reactions at higher temperature generated more IP but less MO and DAA (Table 1). It was shown that the catalyst L-proline decomposition was accelerated at high reaction temperatures, and less than 20% of L-proline survived above 100 °C (Table 1, entries 3–6). Although L-proline itself was stable even at 250 °C, under this reaction condition, it decomposed to pyrrolidine at temperatures above 100 °C, which was confirmed by GC-MZ.[13] Thus, considering the highest MO selectivity and good acetone conversion, as well as the possibility for catalyst recycling in the future, 90 °C should be considered the best reaction temperature (Table 1, run 2).

We next tried to optimize the reaction conditions by introducing some weak nitrogen-containing organic bases because the condensations of acetone were always performed in alkaline conditions. As illustrated in Table 2, the promoters quinoline (**I**), pyridine (**II**), triethyl amine (**III**), *N*-methyl pyrrolidone (**IV**), *N*,*N*-dimethyl piperazine (**V**), piperidine (**VI**) and *N*-methyl piperidine (**VII**) were tested, and the experimental results showed that piperidine (**VI**) was the best one, affording the highest MO selectivity and a high acetone conversion (Table 2, entry 6 *vs.* entries 1–5 and 7). Interestingly, the promoters **I–VII** do not show any catalytic activity by themselves and using **I–VII** alone afforded a rather low acetone conversion (<6%), as confirmed by the blank reactions summarized in the ESI.†[14] The effects of the catalyst dosage and reaction time were also examined. As shown in the ESI,† neither increased catalyst dosages nor a prolonged reaction time could help to improve the conversion ratio of acetone.[13] Thus, the best reaction conditions should be that as in Table 2, entry 6, while the carbon mass balance of the reaction was calculated to be 99.3% from the detailed analysis and calculations.[14]

The previous investigations showed that most of the catalyst L-proline survived at 90 °C (Table 1, entry 2), and after the reaction, its precipitation was observed as a white crystal, revealing the possibility to recycle and reuse the catalyst. Therefore, at the end of the reaction, the precipitated L-proline was collected by filtration and reused in the next turn. As summarized in Table 3, the L-proline recovery ratios of each turn were generally around 70%, and after a supplement of the lost catalyst and the catalyst promoter piperidine, both the

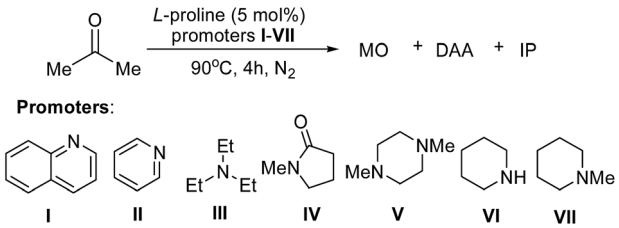
Table 1 Screening of reaction temperature[a]



Run	t/°C	r%[b,c]	X%[d,e]	Selectivity[e]/% MO	DAA	IP
1	80	76.3	23.3	67.0	10.7	0.3
2	90	69.2	26.5	69.4	6.1	1.5
3	100	16.7	27.0	64.0	5.2	13.6
4	110	16.3	27.4	57.0	7.8	20.3
5	130	16.0	26.3	52.2	5.9	28.6
6	150	13.3	26.8	42.7	7.3	32.5

[a] Acetone (300 g, 5.17 mol) and L-proline (30 g, 0.26 mol, 5 mol%) were heated at different temperatures in an autoclave for 4 h under N_2. [b] Recovered ratio of catalyst L-proline. [c] Determined by spectrophotography.[14] [d] Conversion ratio of acetone. [e] Determined by GC with methyl using benzoate as an internal standard.[14]

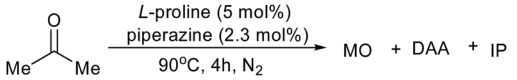
Table 2 Screening of organic bases as catalyst promotors[a]



Entry	Cat. promoter	X%[b,c]	Selectivity[c]/% MO	DAA	IP
1	**I**	32.3	65.3	7.7	1.8
2	**II**	30.0	41.0	6.7	0.9
3	**III**	34.2	65.6	5.2	3.2
4	**IV**	35.0	62.0	5.4	4.0
5	**V**	33.6	63.1	6.3	3.3
6	**VI**	37.9	67.0	8.7	3.3
7	**VII**	38.0	55.5	6.1	2.1

[a] Acetone (300 g, 5.17 mol), L-proline (30 g, 0.26 mol, 5 mol%) and catalyst promoter **I–VII** (10 g) were heated at 90 °C in an autoclave for 4 h under N_2. [b] Conversion ratio of acetone. [c] Determined by GC using methyl benzoate as an internal standard.

Table 3 Recycle of L-proline catalyst[a,14]

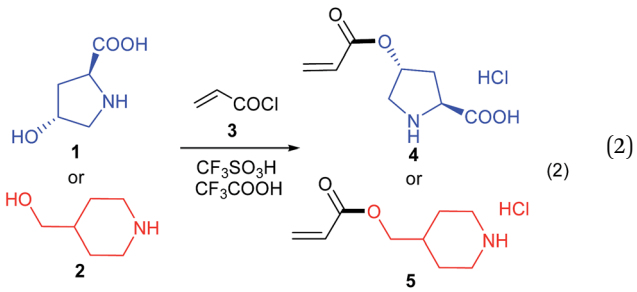


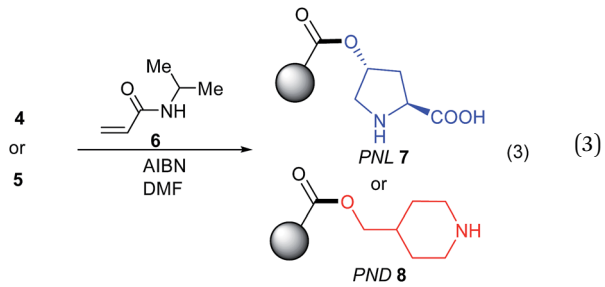
Entry	Recycle no.	r%[b]	X%[c,d]	Selectivity[d]/% MO	DAA	IP
1	0[e]	71.1	38.3	66.1	4.7	6.9
2	1	69.3	34.3	65.9	7.2	4.7
3	2	70.8	35.6	65.7	9.5	5.9
4	3	67.8	33.9	65.5	6.7	6.2

[a] Acetone (30 g, 0.517 mol), L-proline (3 g, 0.026 mol, 5 mol%) and piperidine (1 g, 0.012 mol, 2.3 mol%) were heated at 90 °C in an autoclave for 4 h under N_2. [b] Isolated recovery ratio of catalyst L-proline. [c] Conversion ratio of acetone. [d] Determined by GC using methyl benzoate as an internal standard. [e] First use.

acetone conversion and MO selectivity remained the same without loss in the next turn (Table 3, entries 1–4).

However, although the catalyst L-proline was precipitated after the reaction and could be recollected, the catalyst promoter piperidine dissolved in the solvent and was thus used as a one–off. Moreover, about 30% loss of the catalyst also pushed this technology far away from industrial requirements. Thus, to develop an improved catalyst system that generates less waste and is more suitable for large-scale preparation, we then tried to bind the catalyst and the catalyst promoter onto a polymer resin that could be recycled more efficiently.[6c] As illustrated in eqn (2)–(4), the idea was easily realized using readily accessible materials: *trans*-4-hydroxyl-L-proline **1** and 4-methylolpiperidine **2**.[14] The reactions of **1** or **2** with the accessible acryloyl chloride **3** afforded the monomer **4** or **5** in their hydrochloride form (eqn (2)). The copolymerization of **4** or **5** with the accessible thinner *N*-isopropylacrylamide **6** (ref. 15) gave the material *PNL* **7** or *PND* **8**, respectively, (see eqn (3)). The *PNLD* **9** with both L-proline and piperidine moieties was also accessible through the copolymerization of **4**, **5** and **6**. The catalyst loading on the polymer could be calculated from the peak area of the ^{1}H NMR spectra, as shown in the ESI.†[14]





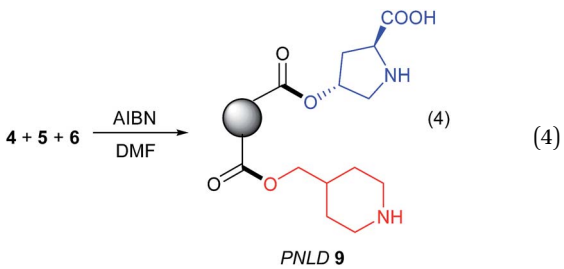
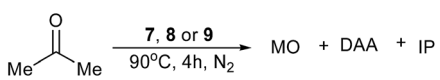


Table 4 Reactions using *PNL* **7**, *PND* **8** and *PNLD* **9**[a]



Entry	Cat.	Cat. promoter	X%[b,c]	Selectivity[c]/% MO	DAA	IP
1	—	*PND*	0.2	—	—	—
2	*PNL*	—	9.7	58.6	10.3	0.3
3	*PNL*	*PND*	13.1	65.4	10.0	0
4	*PNLD*	—	23.1	73.2	4.5	0.3

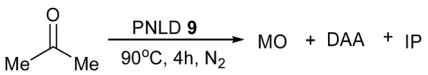
[a] Acetone (3.5 g, 0.060 mol) was heated at 90 °C for 4 h in the presence of *PND* (0.17 g), *PNL* (0.5 g), *PNL* (0.5 g)–*PND* (0.17 g) or *PNLD* (0.67 g). [b] Conversion ratio of acetone. [c] Determined by GC using methyl benzoate as an internal standard.

The catalytic activities of the materials **7**–**9** were then tested through a series of parallel experiments. As shown in Table 4, the polymerized catalyst promoter *PND* **8** did not have any catalytic ability, and only 0.2% of acetone was converted when using it alone (Table 4, entry 1). When *PNL* **7** was employed, about 9.7% of the acetone was converted, affording MO in a 58.6% selectivity (Table 4, entry 2). The conversion of acetone was obviously enhanced when *PNL* **7** and *PND* **8** were employed simultaneously, and the selectivity of MO was also slightly improved to 65.4%, which was the same level as using the homogeneous catalyst (Table 4, entry 3 *vs.* Table 2, entry 6). We were very glad to find that *PNLD* **9**, the easy-to-use polymer resin, containing both L-proline catalyst and piperidine catalyst promoter moieties, had very good activity. Although the conversion ratio of acetone using *PNLD* **9** was lower than the homogeneous catalyst, it gave a higher selectivity of MO, which was an even more important parameter from the point of view of industrial application (Table 4, entry 4 *vs.* Table 2, entry 6). It should be noticed that the catalyst was very practical and a scaled-up reaction using 350 g of acetone afforded 51.2 g of MO

after rectification with 268 g of acetone recycled. Thus, the isolated yield of MO based on the consumed acetone should be 73.9% in the reaction.

The advantages of *PNLD* **9** over homogeneous catalysts are not only limited to the higher MO selectivity, it is also much more convenient to recycle and leads to less wastes. After each turn, up to 85.3% of the catalyst *PNLD* **9** could be recovered (Table 5, entries 1–4). Compared with the results using an homogeneous catalyst, *PNLD* **9** was obviously much more eco-friendly because of the lower waste from the catalyst and the catalyst promoter (Table 5, entries 1–4 *vs.* Table 3, entries 1–4). As the ^{1}H NMR studies indicated that the catalyst L-proline concentration was 1.02 mmol g^{-1}, the highest TON and TOF were accordingly calculated to be 15.8 and 1.1 × 10^{-3} s^{-1}, respectively.[14] Obviously, the TON and TOF of the polymer-supported heterogeneous catalyst *PNLD* **9** were much higher than those of the homogeneous L-proline-piperidine bi-organocatalyst, which were calculated to be 5.0 and 3.5 × 10^{-4} s^{-1}, respectively (Table 2, entry 6).

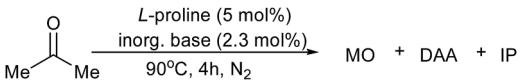
Table 5 Recycling of *PNLD* **9**[a,13]



Entry	Recycle no.	r%[b]	X%[c,d]	Selectivity[d]/% MO	DAA	IP
1	0[e]	85.3	23.1	73.2	4.5	0.3
2	1	84.2	22.4	74.3	3.8	0.1
3	2	83.9	24.1	74.4	4.2	0.1
4	3	83.1	23.8	73.9	3.8	0.2

[a] Acetone (3.5 g, 0.060 mol) was heated at 90 °C for 4 h in the presence of PNLD **9** (0.68 g). [b] Isolated recovery ratio of catalyst PNLD **9**. [c] Conversion ratio of acetone. [d] Determined by GC using methyl benzoate as an internal standard. [e] First use (results in Table 4, entry 4).

Table 6 Control reactions employing inorganic bases as a co-catalyst[a]



Entry	Co-cat.	X%[b,c]	Selectivity[c]/% MO	DAA	IP
1	NaOAc	47.9	52.3	6.9	1.2
2	Na_2CO_3	50.6	50.9	4.1	2.1
3	NaOH	56.8	45.4	4.1	10.9
4	$Ca(OH)_2$	49.6	53.8	4.4	2.3

[a] Acetone (30 g, 5.17 mmol), L-proline (3 g, 0.26 mol, 5 mol%) and 0.12 mmol *co*-catalyst (2.3 mol%) were heated at 90 °C in an autoclave for 4 h under N_2. [b] Conversion ratio of acetone. [c] Determined by GC using methyl benzoate as an internal standard.

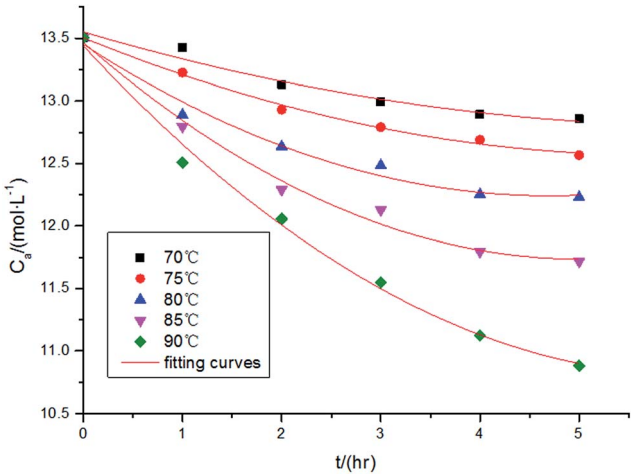


Fig. 1 $C_a \sim t$ curve of the reaction using the *PNLD* catalyst.

The mechanisms of this reaction were our next concern. Since nitrogen-containing organic bases greatly improved the reactions in the presence L-proline but did not have any catalytic activities themselves, we were very interested in the roles they played in the reactions. In order to understand these phenomena more deeply, a series of control reactions using inorganic bases as the alternatives were tested. It was shown that all inorganic bases enhanced the conversion ratio of acetone but reduced MO selectivity obviously (Table 6, entries 1–4 *vs.* Table 2, entries 1–7). The results indicated that the nitrogen-containing organic bases not only play the role as a pH-regulator, but also played some important roles that might cooperate with L-proline and direct the reaction to give MO in a high selectivity under mild and nearly neutral conditions.

To get more hints for mechanism studies, a series of parallel reactions were performed using the heterogeneous catalyst system of *PNLD* under different times and temperatures. The C_a–T curves from 70 °C to 90 °C are drawn in Fig. 1 accordingly and the relationships of $(C_a^{-1}–C_0^{-1}) \times 10^3$ with the reaction

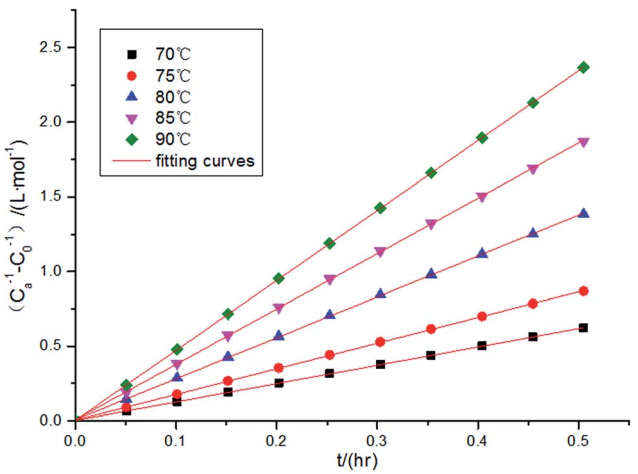


Fig. 2 $(C_a^{-1}–C_0^{-1}) \times 10^3 \sim t$ curve of the reaction using the *PNLD* catalyst.

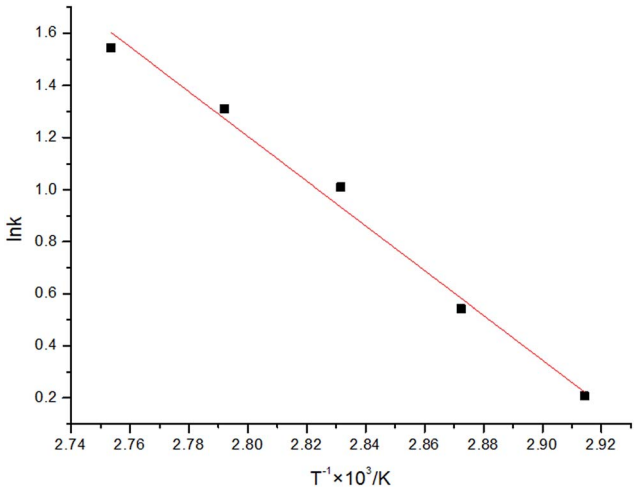
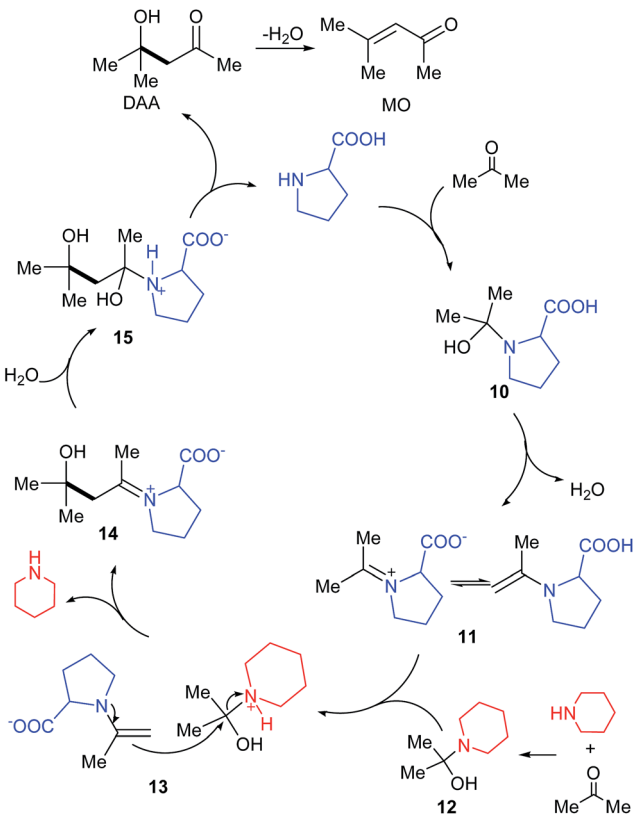


Fig. 3 ln $K \sim 1/T \times 10^3$ curve of the reaction using the *PNLD* catalyst.

times were approximately linear, as illustrated in Fig. 2.[16] All of these phenomena indicated a second order reaction, and its reaction rate constant K at 70–90 °C was calculated from the $(C_a^{-1}–C_0^{-1}) \times 10^3 \sim t$ curve, respectively.[14] The ln $K \sim T^{-1} \times 10^3$ curve was drawn in Fig. 3 accordingly and showed good linearity. Induced from the abovementioned results, the kinetic equation for this reaction should be $(-r_a) = 2.61 \times 10^4 \exp(-71.45/RT)C_a$,[2] and the activation energy was 71.45 kJ mol^{-1}, lower than that of the reactions catalyzed by *PNL* alone (169.17 kJ mol^{-1}), as calculated in the ESI.†[14] Obviously, the addition of piperidine reduced the activation energy and because it was a second order reaction, L-proline and piperidine might react with acetone first to generate two different intermediates, the further reaction of which pushed the whole reaction to proceed forward and to generate the final product MO.

Thus, based on the abovementioned experimental results, as well as on the literature,[13,17] a plausible mechanism is proposed. As a second order reaction, the reaction of acetone with catalyst L-proline generated the intermediate **10**, which afforded **11** through dehydration.[17] Moreover, the reaction of piperidine with another acetone led to intermediate **12**. The reaction of **11** with **12** afforded the ionic pair **13**. Releasing piperidine, intermediate **14** was generated and soon transformed to intermediate **15** through hydration, which then afforded the product DAA and released the catalyst L-proline. Dehydration of DAA gave the final product MO (Scheme 1). Although this mechanism remains to be fully clarified and alternative processes may also exist, Scheme 1 is the most likely mechanism based on the abovementioned experimental findings and the related ref. 13 and 17.



Scheme 1 Plausible mechanisms.

Conclusions

In conclusion, we developed a novel poly(L-proline-*co*-piperidine) catalyst for the synthesis of the high-value and important intermediate MO from acetone. Compared with the reported references,[4] the easily-prepared, mild and neutral polymer resin supported catalyst *PNLD* is recyclable and low-loss in the reaction, thus avoiding the generation of intractable wastes. Thus, this novel catalyst is eco-friendly and has good potential for large-scale preparation. The mechanisms of these unexpected and interesting L-proline/piperidine catalysis procedures were investigated on the basis of a series of control reactions, as well as on dynamic calculations, facilitating the further optimization of this methodology, which is now ongoing in our laboratory. It should be noted that although in this article, the accessible and recyclable polymer resin-supported chiral L-proline catalysts were employed in simple acetone condensation only, they might have much more comprehensive applications in asymmetric synthesis in the future. We are also interested in these ideas and more related works are ongoing in our laboratory for both academic and industrial purposes.

Experimental section

General methods

All the chemicals were purchased and directly used as received without further purification. All the reactions were carried out under nitrogen atmosphere and monitored by gas chromatography (GC) analysis. The detailed analysis method is given in the ESI.†

Procedure for the synthesis of MO catalyzed by the homogeneous L-proline/piperidine system (Table 3)

Acetone (30 g, 0.517 mol), L-proline (3 g, 0.026 mol, 5 mol%) and piperidine (1 g, 0.012 mmol, 2.2 mol%) were added into an

autoclave. After keeping in N_2 at 1.0 MPa for 10 min, the pressure was relieved and the mixture was stirred at 500 rpm and heated at 90 °C for 4 h. The mixture was then cooled to 30 °C using cold water. The oil layer was sent for analysis and the precipitated catalyst L-proline was recycled and reused in the next turn.

Procedure for the synthesis of monomers 4 and 5

trans-4-Hydroxyl-L-proline **1** (16.42 g, 0.125 mol) and CF_3CO_2H (60 mL, solvent) were added into a round-bottom flask equipped with a magnetic stirring bar and a condenser. The mixture was stirred at 0 °C and CF_3SO_3H (2.0 mL) was injected. After 5 min, acryloyl chloride **3** (20.31 mL, 0.250 mol) was added and the mixture was stirred for 2.5 h and cooled by ice water. Then, 200 mL of ether was added and the mixture was filtrated by vacuum and the crystal was washed by ether and dried at room temperature for 12 h to afford 13.2 g of monomer **4** in its hydrochloride form. Reaction at the same scale under similar conditions was also performed to give 14.0 g of monomer **5** in its hydrochloride form.

Procedure for the preparations of *PNL* 7 and *PND* 8

Monomer **4** (0.44 g, 0.002 mol), *N*-isopropylacrylamide **6** (2.06 g, 0.018 mol), AIBN (0.05 g) and DMF (15 mL) were added to a branched 50 mL reaction tube equipped with a magnetic bar. The tube was then charged with N_2 and stirred at 70 °C for 8 h. After cooling to room temperature, the mixture was slowly added to 200 mL of quickly stirred ether and the crude product was isolated by centrifugation. The solid was then dissolved by water and the pH was adjusted to 6–7 with Et_3N and then precipitated with 200 mL ether. The precipitation was dissolved with methanol again and precipitated by ether for purification and then washed with 50 mL of ether. After drying overnight at 50 °C under vacuum, 1.58 g of *PNL* **7** was finally obtained. 1.89 g of *PND* **8** was also synthesized through a similar way in the same reaction scale.

Procedure for the preparation of *PNLD* 9

Monomer **4** (0.33 g, 1.50 mmol), **5** (0.10 g, 0.50 mmol), *N*-isopropylacrylamide **6** (2.06 g, 18 mmol), AIBN (0.05 g) and DMF (15 mL) were added to a branched 50 mL reaction tube equipped with a magnetic bar. The tube was then charged with N_2 and stirred at 70 °C for 8 h. After cooling to room temperature, the mixture was slowly added to 200 mL of quickly stirred ether and the crude product was isolated by centrifugation. The solid was then dissolved by water and the pH was adjusted to 6–7 with Et_3N and then precipitated with 200 mL ether. The precipitation was dissolved with methanol again and precipitated by ether for purification and then washed with 50 mL of ether. After drying overnight at 50 °C under vacuum, 1.45 g of *PNLD* **9** was finally obtained.

Procedure for the *PNLD*-catalyzed condensation and catalyst recycling (Table 5)

Acetone (3.50 g, 0.060 mol) and *PNLD* **9** (0.67 g) were added to a sealed tube charged with N_2 and heated for 4 h. The reaction liquid and the solid phase catalyst were isolated by centrifugation. The yellow transparent liquid was sent for GC analysis, while the solid phase catalyst *PNLD* **9** was washed with acetone and dried at 50 °C under vacuum for 12 h. The recycled catalyst was weighed to obtain the recovery ratio and after supplementation of the lost catalyst, another turn of the reaction was taken.

Procedure for the rectification of MO from the scale-up reaction (350 g acetone)

The scale-up reaction was performed in an autoclave through a similar method mentioned above. When the reaction terminated, the mixture was cooled to room temperature and removed into a 500 mL round-bottom flask. The excess acetone was then distilled and recovered (55.9–58.1 °C/760 mmHg, 268 g). The residue was carefully removed into a 100 mL round-bottom flask equipped with a 1.2 m rectification tower with a circular glass filler for rectification. The fraction at 131.0 °C was collected to give 51.2 g of MO (73.9% isolated yield based on the consumed acetone).

Characterization data of MO

Oil, B. P. 128–130 °C/760 mmHg; IR (film): 2979, 2930, 1712, 1635, 1449, 1365, 1220, 1166, 1019, 963, 818, 621 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.09 (s, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 198.5, 154.9, 124.2, 31.5, 27.5, 20.5; known compound (141-79-7).[1,2,4]

Acknowledgements

We thank NNSFC (21202141, 21173182 and 29503018), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Key Science & Technology Specific Projects of Yangzhou (YZ20122029), the Yangzhou Nature Science Foundation (YZ2014040) and the ZJNSF for Distinguished Young Scholars (R14B020009) for financial support. We thank the analysis centre of Yangzhou University for assistance.

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