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Design and Application of the Recyclable Poly (*L*-Proline-*co*-Piperidine) Catalyst for the Synthesis of Mesityl Oxide from Acetone

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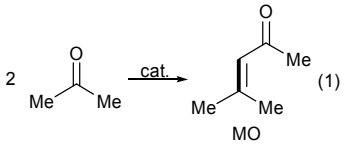
The unexpected *L*-proline/piperidine was found to be a better recyclable catalyst system than *L*-proline or piperidine alone in the condensation of acetone to prepare mesityl oxide (MO), an important intermediate in chemical industry. Binding the catalyst system onto polymer resin enhanced the MO selectivity and reduced the catalyst loss. The mechanism of the bi-component catalyst system was also studied through control reactions as well as the dynamic calculations in this article. The MO selectivity could reach 74.4% and its isolated yield could reach 73.9% based on the consumed acetone. Although the result has some distances to meet the requirement of industrial production immediately, this work provides a novel organocatalyst system, which might be a potential alternative to traditional inorganic catalysts that can be used under mild and neutral conditions.

Introduction

Acetone, mostly generated as the by-product during the production of phenol through the oxidation of cumene, is an excessive compound in chemical industry. Therefore, consumptions of this cheap and abundant material to produce high-value products are highly desirable technologies. Acetone can be converted to mesityl oxide (MO, eq. 1), an important intermediate in organic synthesis, pharmacal chemistry, agriculture chemistry, polymer and material science[1] and even natural product synthesis.[2] MO might be employed to synthesize phorones and isophorones, which are significant compounds in chemical industry and are also our concerns.[3] However, although the condensation of acetone affords a highly atom-economic and concise access to MO, the present methodologies have drawbacks such as the use of one-off metal catalyst, strong alkaline conditions, high catalyst loading, harsh reaction conditions and the accordingly generated harmful and corrosive waste.[4] As the calling of environment protection grows nowadays, these technologies are facing huge pressure from government policies. Therefore, developing novel recyclable catalyst that works under neutral and mild conditions and causes less waste to produce MO from acetone is of great meaning for industrial production.



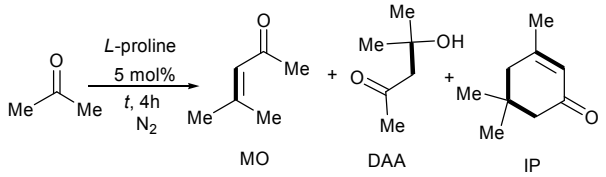
Yet, organocatalysts have attracted much attention of chemists because of their availability, cheapness and low-toxicity and the mild reaction conditions and clean procedures.[5] Thus, for the purpose of developing green synthetic methodologies for possible industrial applications,[6,7] we focused much on organocatalysis in recent years.[7] Among our previous works, 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 into our sight recently because of its ready availability. As yet, *L*-proline has been comprehensively employed in many types of reactions such as the Mannich reactions,[8] Michael additions,[9] Diels-Alder reactions,[10] multi-component reactions,[11] and *et al*,[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. *L*-proline-catalyzed condensations of alderhydes and ketones have already been widely applied in organic synthesis as well,[13] but because *L*-proline is a very cheap and abundant natural chiral catalyst, people are more inclined to develop asymmetric synthetic methodologies with it while the condensation of acetone to produce the simple but important MO is ignored for a long time. During the continuous cooperated research project with the 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 30g of *L*-proline 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 heat at 80 °C for 4 h. Spectrophotography analysis showed that 76.3% of catalyst *L*-proline remained after the reaction while GC analysis showed that the conversion ratio of acetone was 23.3% and 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 products varied. Generally, 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 temperature 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 the temperature 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 future, 90 °C should the best reaction temperature (Table 1, run 2).

Table 1. Screening of reaction temperature.[a]

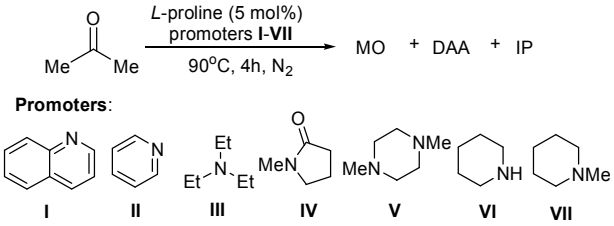


run	*t* /°C	r%[b,c]	X%[d,e]	Selectivity/%[e]		
				MO	DAA	IP
1	80	76.3	23.3	67.0	10.7	0.3
2	90	69.2	26.5	69.4	6.1	1.5
3	100	16.7	27.0	64.0	5.2	13.6
4	110	16.3	27.4	57.0	7.8	20.3
5	130	16.0	26.3	52.2	5.9	28.6
6	150	13.3	26.8	42.7	7.3	32.5

[a] Acetone (300g, 5.17 mol) and *L*-proline (30g, 0.26 mol, 5 mol%) were heated at different temperatures in 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 internal standard.[14]

We next tried to optimize the reaction conditions by introducing some weak nitrogen-contained organic bases because the condensations of acetone were always performed in alkaline conditions. As illustrated in Table 2, 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 high acetone conversion (Table 2, entry 6 VS entries 1-5 and 7). Interestingly, the promoters **I-VII** did not have any catalytic activity by themselves and using **I-VII** alone afforded rather low acetone conversion (< 6%), as confirmed by blank reactions summarized in ESI.[14] The effects of the catalyst dosage and reaction time were also examined. As shown in ESI, neither increased catalyst dosages nor prolonged reaction time could help to improve the conversion ratio of acetone much.[13] Thus, the best reaction conditions should be in Table 2, entry 6, and the carbon mass balance of the reaction was calculated to be 99.3% from the detailed analysis and calculations.[14]

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

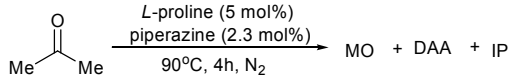


entry	cat. promoter	X%[b,c]	Selectivity/%[c]		
			MO	DAA	IP
1	**I**	32.3	65.3	7.7	1.8
2	**II**	30.0	41.0	6.7	0.9
3	**III**	34.2	65.6	5.2	3.2
4	**IV**	35.0	62.0	5.4	4.0
5	**V**	33.6	63.1	6.3	3.3
6	**VI**	37.9	67.0	8.7	3.3
7	**VII**	38.0	55.5	6.1	2.1

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

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 acetone conversion and MO selectivitie remained without reduction in the next turn (Table 3, entries 1-4).

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

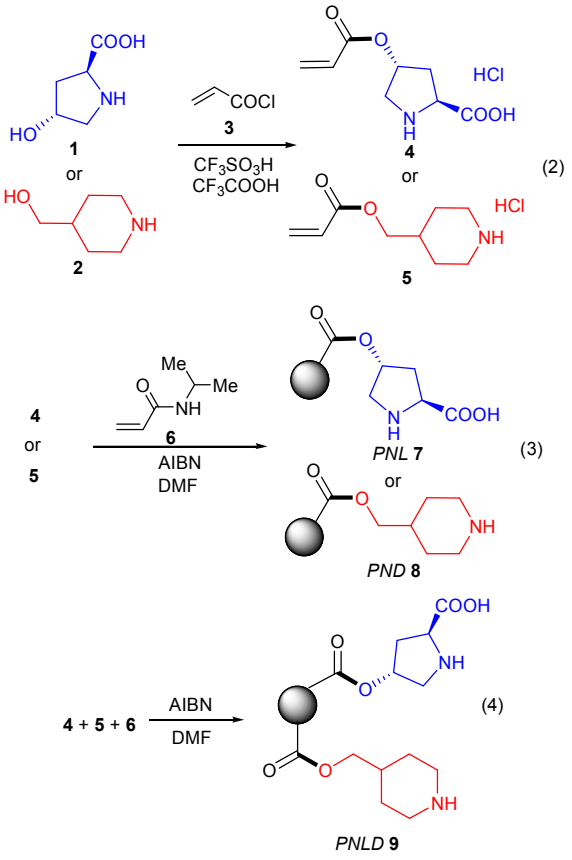


entry	Recycle NO.	r%[b]	X%[c,d]	Selectivity/%[d]		
				MO	DAA	IP
1	0[e]	71.1	38.3	66.1	4.7	6.9
2	1	69.3	34.3	65.9	7.2	4.7
3	2	70.8	35.6	65.7	9.5	5.9
4	3	67.8	33.9	65.5	6.7	6.2

[a] Acetone (30g, 0.517 mol), *L*-proline (3g, 0.026 mol, 5 mol%) and piperidine (1g, 0.012 mol, 2.3 mol%) were heated at 90 °C in 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 internal standard; [e] First use.

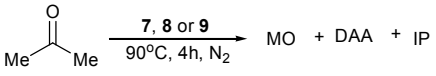
However, although the catalyst *L*-Proline precipitated after the reaction and could be recollected, the catalyst promoter piperidine dissolved in solvent and was one-off. Besides, about 30% loss of the catalyst also pushed this technology far away from the industrial requirement. Thus, to develop an improved catalyst system which generated less waste and was more suitable for large-scale preparation, we then tried to bind the catalyst and the catalyst

promoter onto polymer resin that could be recycled more efficiently.[6c] As illustrated in eq. 2-4, the idea was easily realized using readily accessible material *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 (eq. 2). Copolymerization of **4** or **5** with the accessible thinner N-isopropylacrylamide **6**[15] gave the material *PNL* **7** or *PND* **8** respectively (eq. 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 polymer could be calculated from the peak area of ^{1}H NMR spectra, as shown in ESI.[14]



The catalytic activities of the material **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 acetone was converted, affording MO in 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 %, 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 homogeneous catalyst, it gave 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.

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

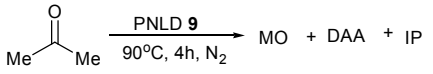


entry	cat.	cat. promoter	X%[b,c]	Selectivity/%[c]		
				MO	DAA	IP
1	-	*PND*	0.2	-	-	-
2	*PNL*	-	9.7	58.6	10.3	0.3
3	*PNL*	*PND*	13.1	65.4	10.0	0
4	*PNLD*	-	23.1	73.2	4.5	0.3

[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 internal standard.

The advantages of *PNLD* **9** over homogeneous catalysts were not only limited to the higher MO selectivity. It was much more convenient to recycle and led to less wastes. After each turn, upto 85.3 % of the catalyst *PNLD* **9** could be recovered (Table 5, entries 1-4). Compared with the results using homogeneous catalyst, the *PNLD* **9** was obviously much more eco-friendly because of the less 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, the highest TON and TOF was 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 that of the homogeneous *L*-proline-piperidine bi-organocatalyst, which were calculated to be 5.0 and 3.5×10^{-4}s correspondingly (Table 2, entry 6).

Table 5. Recycle of *PNLD* **9**.[a,13]



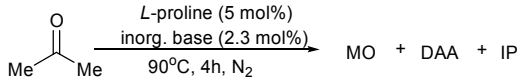
entry	Recycle NO.	r%[b]	X%[c,d]	Selectivity/%[d]		
				MO	DAA	IP
1	0[e]	85.3	23.1	73.2	4.5	0.3
2	1	84.2	22.4	74.3	3.8	0.1
3	2	83.9	24.1	74.4	4.2	0.1
4	3	83.1	23.8	73.9	3.8	0.2

[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 internal standard; [e] First use (results in Table 4, entry 4).

The mechanisms of this reaction were our next concern. Since nitrogen-contained organic bases improved the reactions much in the presence *L*-proline but did not have any catalytic activities by 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 inorganic bases all 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-contained organic bases not only play the role as a pH-

regulator, but also played as some important roles that might cooperate with *L*-proline and direct the reaction to give MO in high selectivity under mild and nearly neutral conditions.

Table 6. Control reactions employing inorganic bases as 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 (30g, 5.17 mmol), L-proline (3g, 0.26mol, 5 mol%) and 0.12 mmol *co*-catalyst (2.3 mol%) were heated at 90 °C in autoclave for 4 h under N_2; [b] Conversion ratio of acetone; [c] Determined by GC using methyl benzoate as internal standard.

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 at 70 °C to 90 °C were drawn in Figure 1 accordingly and the relationships of $(C_a^{-1}-C_0^{-1})\times10^3$ with the reaction times were approximately linear, as illustrated in Figure 2.[16] All of these phenomena indicated a second order reaction and its reaction rate constant K at 70-90 °C were calculated from the $(C_a^{-1}-C_0^{-1})\times10^3$~t curve respectively.[14] The $\ln K \sim T^{-1}\times10^3$ curve was drawn in Figure 3 accordingly and showed good linear. Induced from the above results, the kinetic equation for this reaction should be $(-r_a) = 2.61\times10^4 \exp(-71.45 / RT) C_a^2$ and the activation energy was 71.45 kJ/mol, lower than that of the reactions catalyzed by *PNL* alone (169.17 kJ/mol), as calculated in 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.

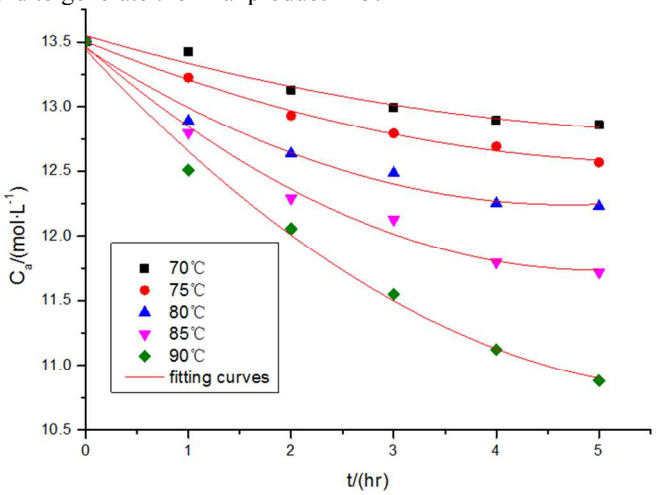


Figure 1. C_a~t curve of the reaction using *PNLD* catalyst.

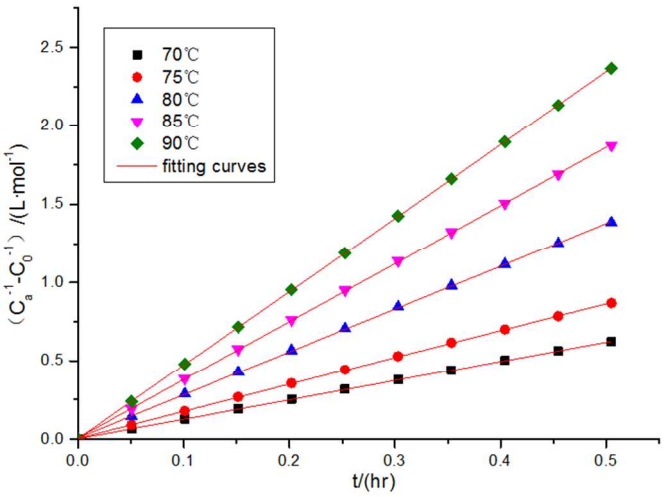


Figure 2. $(C_a^{-1}-C_0^{-1})\times10^3$~t curve of the reaction using *PNLD* catalyst.

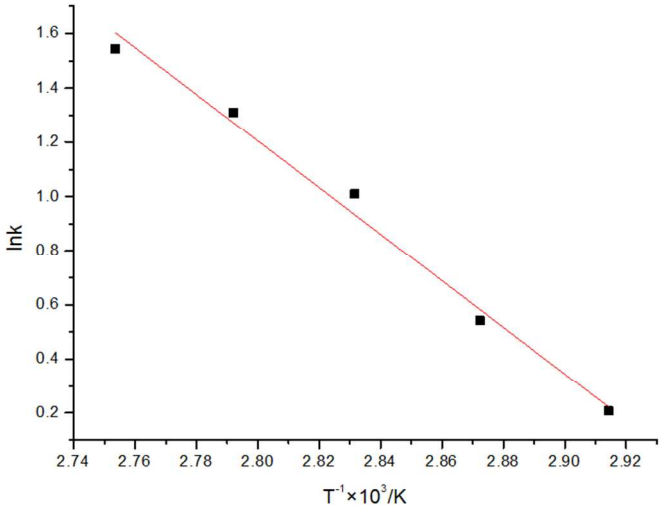
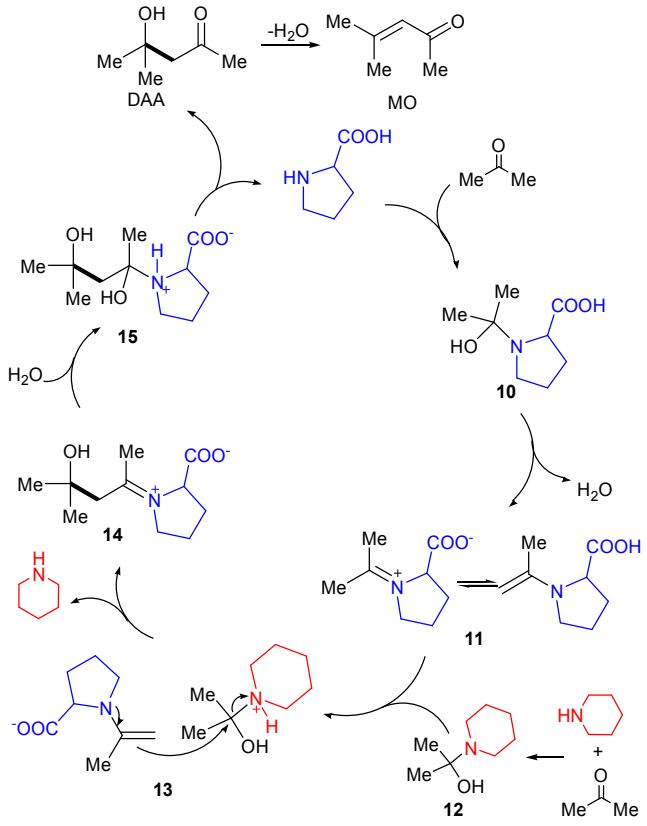


Figure 3. $\ln K \sim 1/T\times10^3$ curve of the reaction using *PNLD* catalyst.

Thus, based on the above experimental results as well as literatures,[13,17] a plausible mechanism was given. As a second order reaction, the reaction of acetone with catalyst *L*-proline generated the intermediate **10**, which afforded **11** through dehydration;[17] Meanwhile, the reaction of piperidine with another acetone led to intermediate **12**. Following 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 should be the most likely mechanism based on the above experimental findings and the related references.[13,17]



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, avoiding the generation of intractable wastes. Thus, this novel catalyst is eco-friendly and has good potential for large-scale preparation. The mechanisms of this unexpected and interesting *L*-proline/piperidine catalysis procedures were supposed on the basis of a series of control reactions as well as the the dynamic calculations, facilitating the further optimization of this methodology, which is now ongoing in our laboratory. It should be noticed 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 future. We are also interested in these ideas and more related works are ongoing in our laboratory for both academic and industrial purpose.

Experimental Section

General methods

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

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

Acetone (30g, 0.517 mol), *L*-proline (3g, 0.026 mol, 5 mol%) and piperidine (1g, 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 heat at 90 ^oC for 4 h. The mixture was then cooled to 30 ^oC by cold water. The oil layer was sent to analysis and the precipitated catalyst *L*-proline was recycled and reusable in the next turn.

Procedure for the synthesis of monomer 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 with a magnetic stirring bar and equipped with a condenser. The mixture was stirred at 0 ^oC 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 the released thermo was 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 in 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 with a magnetic bar. The tube was then charged with N_2 and stirred at 70 ^oC 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 centrifugalization. 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 ^oC under vacuum, 1.58 g of *PNL* **7** was finally obtained. 1.89 g of *PND* **8** was also synthesized through the 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 with a magnetic bar. The tube was then charged with N_2 and stirred at 70 ^oC 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 centrifugalization. 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 ^oC 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 centrifugalization. The yellow transparent liquid was sent to

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 weighted to get the recovery ratio and after a supplement of the lost catalyst, another turn of reaction was taken.

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

The scale-up reaction was performed in an autoclave through the 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 access 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 the 1.2 m rectification tower with 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]

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† Electronic Supplementary Information (ESI) available: Experimental details, analysis details, detailed data tables, spectra and calculations procedures. See DOI: 10.1039/b000000x/

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14 For details, please see experimental section or ESI.

15 The thinner N-isopropylacrylamide **6** was an essential component to adjust the catalyst loadings on the polymer resin and improve the catalyst efficiency by keeping enough spaces between the large steric hindrance catalyst (or catalyst promoter) moieties.

16 C_a was the instant concentration of acetone and C_0 was the initial concentration of acetone (mol/L); r_a was the conversion rate of acetone.

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Table of Contents

Design and Application of the Recyclable Poly (*L*-Proline-*co*-Piperidine) Catalyst for the Synthesis of Mesityl Oxide from Acetone

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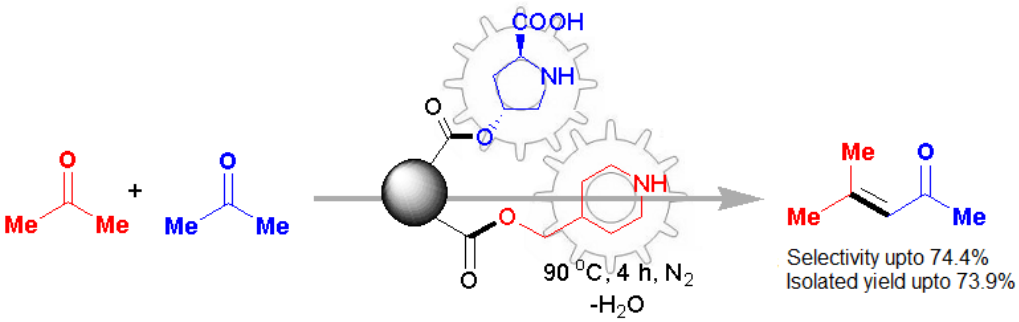

Metal-free ! Solvent-free !
Mild and neutral conditions !
Catalyst recyclable !

The novel poly (*L*-proline-*co*-poperidine) catalyst was developed for the synthesis of the high-value and important industrial intermediate mesityl oxide from acetone. This recyclabe catalyst was more eco-friendly than traditional inorganic bases because of the avoidance of the corrosive solid waste and the neutral and mild reaction conditions. The working mechanism of this interesting *L*-proline/poperidine bi-component catalyst system was also studied through control experiments as well as the dynamic calculations in this article.