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Research paper

Insight into performance of lactam-based Brønsted-acidic catalysts for Prins condensation and their self-separation in water

Yanlong Qi[a,b], Fengchao Cui[a], Janyun He[a], Long Cui[a], Yunqi Li[a], Quanquan Dai[a,*], Chenxi Bai[a,*]

[a] Key Laboratory of Synthetic Rubber, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, # 5625, Renmin Road, 130022, Changchun, PR China
[b] University of Chinese Academy of Sciences, # 19, Yuquan Road, 100049, Beijing, PR China

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ABSTRACT

A series of lactam-based Brønsted-acidic catalysts were prepared for Prins condensation with high efficiency and excellent reusability. We describe detailed investigations on the impact of N-cation from lactam for the reaction and self-separation of catalysts. The experimental data suggested N-cation (organic molecule) played a significant and positive role in the selectivity of Prins condensation, which was confirmed by density functional theory (DFT) calculation with new intermediate. It revealed that N-cation with C=O group can not only stabilize intermediate by sharing electron but also transfer proton between two kind of active centers (N^+ and C^+). Moreover, for self-separation of catalysts, a possible principle was proposed, which can be owed to different solubility of the catalysts at different temperature and partition coefficient of N-cation in oil/water system, both of which resulted from lactam molecules.

1. Introduction

Elastomers have permeated almost every aspect of our lives with almost unlimited tuneable shapes and properties, and become most designable materials of modern world, such as synthetic rubbers [1–4]. Dienes can serve as important polymeric monomers for synthetic rubbers [5–10] which mainly are synthesized via Prins condensation between olefins and aldehydes [11,12]. Recently, many attentions have been paid on this reaction since development of synthetic rubber [13]. In this route, 4, 4-disubstituted 1, 3-dioxanes are indispensable intermediates [14–17] which can be easily converted into dienes with tuneable groups (Scheme 1) [18–22]. Therefore, synthesis of 4, 4-disubstituted 1, 3-dioxanes becomes significant meaningful. However, typical route usually involves aqueous sulfuric acid as catalyst in synthesizing 4, 4-disubstituted 1, 3-dioxanes, [12,23,24] which displays obvious disadvantages with environment and corrosion problems, as well as low selectivity [12,25].

To solve these problems, heteropolyacids (HPAs) [26–29] are employed with high activity, but it is still impeded for harsh separation of catalysts [30]. Inspired by convenient recovery of solid catalysts, HPAs are supported on carriers. [31,32] Unfortunately, it shows lower activity due to decreasing active sites under this condition [33].

To develop an easily recoverable catalyst with high activity, Wang et al. first reported a set of reaction-induced self-separation catalysts for esterification [34,35]. These catalysts were heteropolyacid salts of N-based organic cations containing sulfonic group, which presented feature of thermoregulated phase-transfer catalysts. They showed high activities and excellent self-separation. Yan et al. investigated reactivity of heteropolyacid salts catalysts for transesterifications of trimethylolpropane. The catalysts presented self-separation performance after the reaction with excellent catalytic reusability (eight-run recycling test) [36]. Moreover, heteropolyacid salts of P-based organic cations containing sulfonic group were also confirmed as efficient and facile recoverable catalysts for esterification [26]. Benefit from this idea, heteropolyacid salts containing N-based lactam cations were developed and employed for synthesis of dioxanes, which exhibited high activity and stable reusability with the feature of self-separation [37]. Besides, it implied that the catalysts with lactam showed higher activity than others (including catalyst with sulfonic acid group) presenting excellent capacity of self-separation simultaneously, which was interesting to clarify in-depth.

Unfortunately, it still remains poorly understanding to date, which may be related to the effect of lactam on pathway of Prins

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* Corresponding authors.
E-mail addresses: qqdai@ciac.ac.cn (Q. Dai), baicx@ciac.ac.cn (C. Bai).

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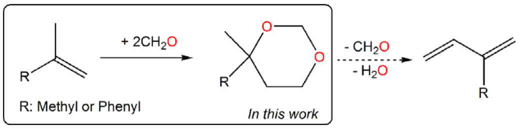


Scheme 1. Synthesis diene-candidates of 4, 4-disubstituted 1, 3-dioxanes.

condensation. Besides, the self-separation principle of lactam-based catalyst is still problematic. Moreover, these works mainly pay attention on synthesis of 4-phenyl-1, 3-dioxanes (not 4, 4-disubstituted 1, 3-dioxanes), which is insignificant for dienes. Therefore, this work focuses on Prins condensation to synthesize 4, 4-disubstituted 1, 3-dioxanes, and clarify the effect of lactam on Prins condensation and catalysts self-separation in water. Combining the experimental data, density functional theory (DFT) calculation is performed to verify the pathway of Prins condensation and effect of lactam on this pathway. Moreover, more quantitative measurements are conducted to demonstrate the self-separation performance of lactam-based catalysts.

2. Experimental

2.1. Materials and chemicals

N-methyl-ε-caprolactam (NMC), 1, 3-dimethyl-pyrimidinone (DP) and α-methylstyrene were supplied by TCI (Shanghai) Development Co., Ltd., and 2-dodecyl-cycloheptanone (DC) by Energy Chemical. 1-Methyl-2-pyrrolidone (NMP), *N*-methyl-polyvinyl pyrrolidone (NMPP) and formaldehyde solution (37 wt.%) came from Guangdong Xilong Chemical Technology Co., Ltd. 12-Phosphomolybdic acid ($H_3PMo_{12}O_{40}$, H_3PMo) and 12-silicotungstic acid ($H_4SiW_{12}O_{40}$, H_4SiW) were purchased from Beijing Chemical Works, and 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, H_3PW) from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without any purification.

2.2. Preparation of catalysts

$[NMC]_4SiW$ was synthesized, in a typical procedure: NMC (12 mmol) was charged in a 250 mL flask, followed by dropwise addition of aqueous solution of H_4SiW (3 mmol) under stirring at ambient temperature, and kept stirring for 12 h. Following by dehydration under reduced pressure, the samples were dried in vacuum at 90 °C for 5 h to obtain final product, affording the catalyst $[NMC]_4SiW$. $[NMC]_3PMo$ and $[NMC]_3PW$ were synthesized as above motioned, except the molar ratios were 12 mmol (NMC) and 4 mmol (H_3PMo or H_3PW), respectively, and $[DP]_2SiW$ was 6 mmol and 3 mmol. The ^1H NMR (DMSO) data for catalysts were as follows:

$[NMC]_3PW$: 1.52 (m, 2H), 1.64 (m, 4H), 2.41 (m, 2H), 2.82 (s, 3H), 3.35 (t, 2H), 7.77 (s, 1H); $[NMC]_3PMo$: 1.53 (m, 2H), 1.64 (m, 4H), 2.41 (m, 2H), 2.82 (s, 3H), 3.35 (t, 2H), 9.13 (s, 1H); $[NMP]_4SiW$: 1.90 (m, 2H), 2.17 (t, 2H), 2.69 (s, 3H), 3.30 (t, 2H), 6.77 (s, 1H); $[NMC]_4SiW$: 1.52 (m, 2H), 1.64 (m, 4H), 2.41 (m, 2H), 2.82 (s, 3H), 3.35 (t, 2H), 6.81 (s, 1H); $[DP]_2SiW$: 1.88 (m, 2H), 2.75 (s, 6H), 3.18 (t, 4H), 7.03 (s, 1H);

2.3. Characterization

Thermal properties of catalysts were examined by Thermal gravimetric analysis (TGA SDT Q600). Acidity was determined on Shimadzu 2550 UV–vis spectrophotometer. X-ray power diffraction patterns were obtained on the Bruker D8 Advance with the Ni-filtered CuKa radiation (λ=0.154 nm). Elemental analysis was performed on a C, N, H elemental analyzer. Partition coefficient of catalysts was measured by GC to investigate distribution in mixture of water/oil system (as Eq. (1) showing).

$$\text{Partition coefficient} = \frac{m(water)}{m(oil)} \tag{1}$$

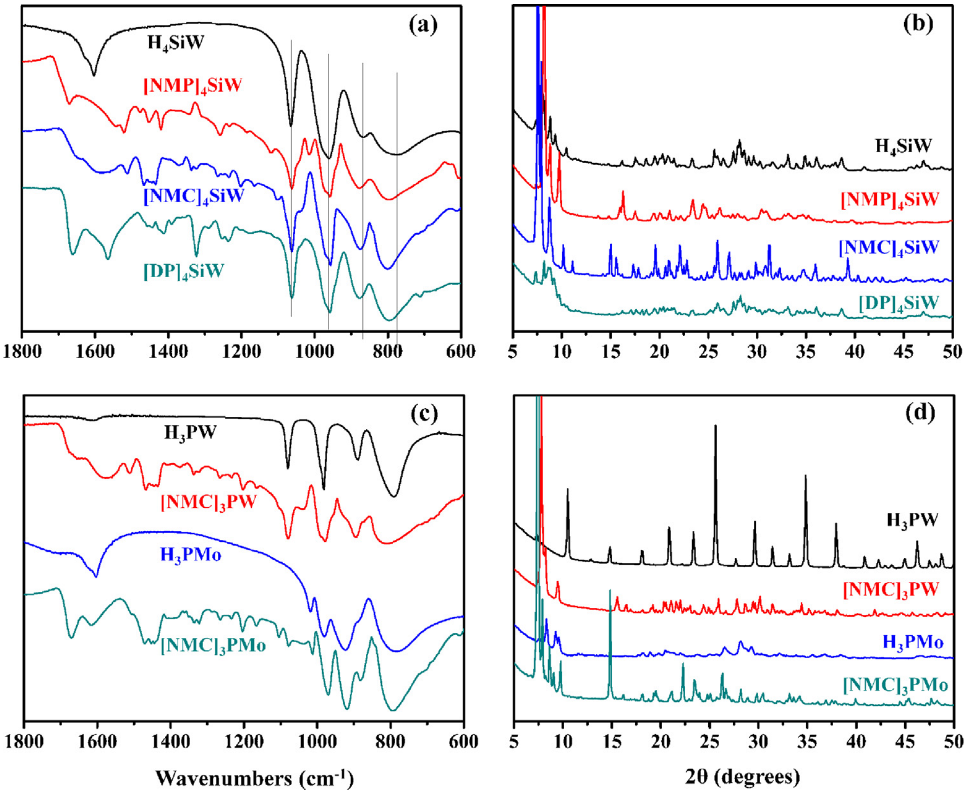


Fig. 1. FT-IR spectra (a), (c) and XRD patterns (b), (d) of catalysts.

Table 1
Elemental analysis for catalysts[a].

Catalysts	C(%)	N(%)	H(%)
$[NMC]_3PW$	7.89(7.73)	1.36(1.29)	1.32(1.29)
$[NMC]_3PMo$	11.70(11.42)	1.83(1.90)	2.11(1.90)
$[NMP]_4SiW$	7.95(7.33)	1.83(1.71)	1.39(1.22)
$[NMC]_4SiW$	9.97(9.92)	1.64(1.65)	1.75(1.65)
$[DP]_2SiW$	4.51(4.59)	1.69(1.78)	1.16(0.89)

[a] Experimental results (theoretical concentrations).

Acidity strength of catalysts (Hammett acidity) were measured based on previous reports (Eq. (2)) [38,39]. H_0 related to strength of acidity, [I] and $[IH^+]$ assigned to the unprotonated and protonated indicator. With consideration of absorption proportional to species concentration, $[I]/[IH^+]$ was calculated based on the absorbance difference corresponding for addition of catalysts in the same condition.

$$H_0 = \mathrm{p}K(\mathrm{I})_{aq} + \log([\mathrm{I}]_s/[\mathrm{IH}^+]_s) \tag{2}$$

4-Aminoazobenzene (AB, 128 mg/L, $pK_a = 2.8$) was employed as basic indicator, for all catalysts, the concentration of $[H^+]$ was fixed at 1.67×10^{-4} mol/L in anhydrous ethanol. And then 0.5 mL of indicator and 2.5 mL of catalysts solution were added in cuvette to get absorbance. Acid concentration (H^+) was measured according to their solubility under reaction condition.

2.4. *Procedure of prins reaction*

In typical procedure, 1.35 g of catalyst was added into a 50 mL round-bottomed flask, followed by addition of 2.36 g of α-methylstyrene and 7.30 g of formalin. Equipped with a reflux condenser, the reaction was performed at 95 °C for 3 h under stirring. After reaction, the catalyst was separated and recycled by decantation, and then washed with ethyl acetate and dried for next run. Reaction product was extracted by the *n*-heptane solution of ethyl acetate (*v*(*n*-heptane)/*v*(ethyl acetate) = 5/1), and analyzed by gas chromatography (Kechuang, GC 9800, Agilent VF–5 ms) with FID detector using *n*-dodecane as internal standard.

2.5. *Computational details*

In this study, Gaussian03 suit of programs were employed for all calculations, and DFT with B3LYP was conducted [40–42]. During optimization procedure, some points were fixed in their position. The nature of these points, which featured with the minima for all real frequencies and just one imaginary frequency for all transition states, was characterized by frequency calculations at the level of B3LYP/6-31G (d, p), the thermal corrections related to Gibbs free energy at 298 K was also obtained in this way. The 6–31G (d, p) basis set was used to optimize geometries in presence of some fixed points, and the results were examined by larger 6–311 + G (2d, 2p) basis set to give more accurate energies. All transition states remained local minima, which were carefully checked by intrinsic reaction coordinate (IRC) calculations. These hybrid organic-HPA catalysts can fully dissociate into polyanion and organic cation under reaction condition [34,35,37], which can owe to the hydrogen bond between the polyanion and organic cation [43–51]. With consideration of Prins reaction activated by protonic acid which derived from N-based cation in this condition, effect of heteropolyanions was ignored during calculations.

Table 2
Effect of acidity on Prins condensation over various catalysts.

Catalysts	H_0	$[H^+]$ (mmol)	Conversion (%)	Selectivity (%)
H_3PW	3.11	1.20	88	66
$[NMC]_3PW$	3.19	0.22	96	83
H_3PMo	3.27	1.20	100	75
$[NMC]_3PMo$	3.31	0.20	98	80
H_4SiW	3.09	1.60	100	80
$[NMP]_4SiW$	3.08	1.10	100	86
$[NMC]_4SiW$	3.08	0.53	99	99
$[DP]_2SiW$	3.06	1.60	100	80

Condition: 90 mmol of formaldehyde, 20 mmol of α-methylstyrene, 0.4 mmol of catalysts, at 95 °C for 3 h.

3. Results and discussion

3.1. *Characterization of catalysts*

All catalysts were solid with different colors. TGA was employed to character their thermal properties. As we all known that the loss under 100 °C should attribute to water, thus starting weight loss temperature (T_s) of catalysts above 100 °C was mainly investigated (Fig. S1). The results implied all catalysts can exist stably during reaction process.

As Fig. 1(a) presents, four characteristic bands in FT-IR spectrum for Keggin structure of neat H_4SiW appeared at 1064, 961, 868 and 775 cm^{-1}, assigned to ν_{as} (Si-O), ν_{as} (W = O), ν_{as} (W-O$_b$-W) and ν_{as} (W-O$_e$-W) [33,37]. For $[NMC]_4SiW$, these feature peaks appeared with shift of 961 cm^{-1} to 957 cm^{-1}, 868 cm^{-1} to 877 cm^{-1} and 775 cm^{-1} to 798 cm^{-1}, which confirmed *N*-cation bonding with heteropolyanion with ionic linkage. Moreover, ^{1}H NMR data of $[NMC]_4SiW$ indicated the NMC structure for the organic moiety. XRD patterns of $[NMC]_4SiW$ and pure H_4SiW were illustrated in Fig. 1(b). The peaks located within $6° \sim 10°$, $15° \sim 22°$, $24° \sim 30°$ and $33° \sim 36°$ attributed to characteristic diffraction peaks of Keggin-type structures. The peaks (*e.g.*, at 2θ of 8.91, 17.65, 19.56, 20.84, 23.41, 33.11, 36.08°) provided a strong proof for $[NMC]_4SiW$ to format Keggin-structure. These all features suggested lactam molecule and HPA kept their own original structures. Moreover, the distinction between $[NMC]_4SiW$ and H_4SiW in XRD demonstrated that the protons of NMC changed the replacement of H_4SiW in crystal lattice, which may explain the variation of T_s in TGA. Moreover, the chemical composition of $[NMC]_4SiW$ was well in accord with theoretical value based on element analysis (as summarized in Table 1).

For the other catalysts, characteristic bands for Keggin structure occurred in both FT-IR and XRD for all catalysts. Combined with the data of ^{1}H NMR, these features suggested that they not only formed Keggin-type structure but also kept original structure. The elemental analysis results of all catalysts were summarized in Table 1. (More detail information was presented in Fig. S2, Tables S1 and S2)

The acidity of catalysts was characterized as the H_0 value (Table S3) and $[H^+]$ concentration (Table S4) summarized in Table 2. Firstly, the result of H_0 indicated that set of H_4SiW catalysts showed strongest relative acidity ($H_0 = 3.09$ for H_4SiW, 3.08 for $[NMP]_4SiW$, 3.08 for $[NMC]_4SiW$, and 3.06 for $[DP]_2SiW$) among these catalysts, while set of H_3PMo catalysts presented weakest relative acidity ($H_0 = 3.31$ for $[NMC]_3PMo$). It was clear that H_0 of H_4SiW was much close to these catalysts with SiW^{4-} heteropoly-anions, indicating their acid strength in same level. Besides, H_0 of catalysts with different heteropoly-anions showed order as $[NMC]_4SiW < [NMC]_3PW < [NMC]_3PMo$, which demonstrated that H_0 was more dependent on the heteropoly-anions. On the other hand, the $[H^+]$ concentration of catalysts with SiW^{4-} exhibited as $[DP]_2SiW > [NMP]_4SiW > [MNC]_4SiW$, and with respect to the catalysts with $[NMC]^+$, it showed as

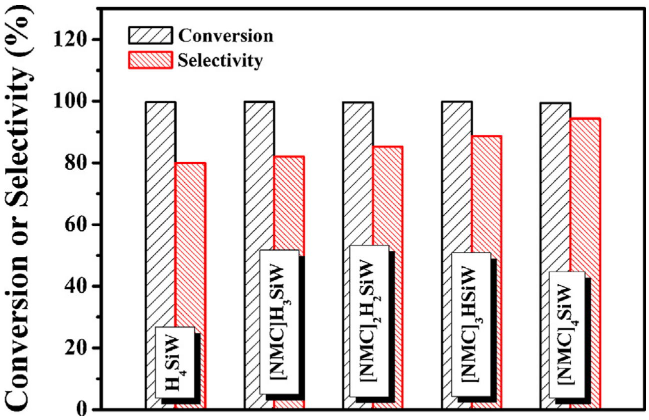


Fig. 2. Effect of NMC on Prins reaction.

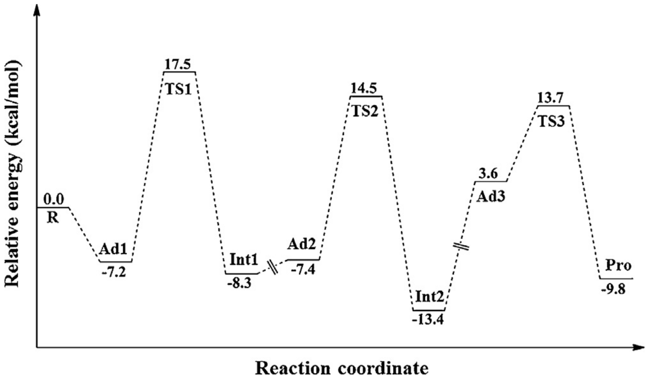


Fig. 3. Computed potential energy profile for optimized model in present condition.

[MNC]$_4$SiW > [MNC]$_3$PW > [MNC]$_3$PMo. Noteworthy, the solubility of [DP]$_2$SiW was much larger than others in 90 mmol solution of formaldehyde. So 0.4 mmol of [DP]$_2$SiW could completely dissolve at reaction condition and supply 1.60 mmol of [H$^+$], as well as H_3PW, H_3PMo and H_4SiW. Moreover, it was evident that cations had distinct effect on [H$^+$] but insignificant on H_0, which can owe to [H$^+$] largely relied on solubility of catalysts but H_0 got close for the catalysts with the same heteropoly-anions. This may suggested that [H$^+$] was up to cation and H_0 to heteropoly- anion, respectively.

3.2. Catalysts reactivity for prins condensation

The catalytic performance for Prins condensation of α-methylstyrene with formaldehyde over catalysts was listed in Table 2 (Table S5). With exception of H_3PW (88% of conversion), the catalysts showed outstanding activity for this reaction with conversion of nearly 100%. The selectivity showed the order as: [NMC]$_4$SiW > [NMP]$_4$SiW > [DP]$_2$SiW ≈ H_4SiW for catalysts with SiW^{4-}, and [NMC]$_4$SiW > [NMC]$_3$PW > [NMC]$_3$PMo for these with [NMC]$^+$. The conversion and selectivity reached as high as 99% and 99% for [NMC]$_4$SiW. Correlation of catalysts acidity (H_0 and [H$^+$]) with reaction results (conversion and selectivity), for the catalysts with same heteropoly-anion, the selectivity presented no relationship with [H$^+$] in the case of closer H_0, which indicated the structure of cations played crucial a role for this condensation process. Moreover, the catalysts with lactam molecules displayed higher activity than pure heteropolyacids (Tables 2 and S5), and exhibited more excellent performance than the catalysts modified by organic molecules without C═O (Table S6). Therefore, the presence of organic molecules certainly affected activity, and if the catalyst was more or less active after modification much depended on organic part with or without lactam molecules in this study. On the other hand, the results of catalysts with [NMC]$^+$ implied that the catalysts with stronger acid strength could improve this condensation to afford products in this study. Moreover, the selectivity of [NMC]$_4$SiW was highest among the set of H_4SiW catalysts, with minimum [H$^+$], which suggested that NMC presented more outstanding performance than other lactam molecules for this reaction. This also can be confirmed by the results of [NMC]$_3$PW and [NMC]$_3$PMo. In summary, the Prins condensation was affected by acidity and structure of catalysts both of which mainly resulted from lactam-based cations. To further clarify effect of the acid strength of catalysts on the reaction, some solid catalysts were applied for and the reaction condition was optimized at 75 °C (Tables 3 and S7). It can be easily concluded that the reactivity (conversion) can be improved with high acidic strength of catalysts. But the selectivity towards desired product was much influenced by the organic molecules.

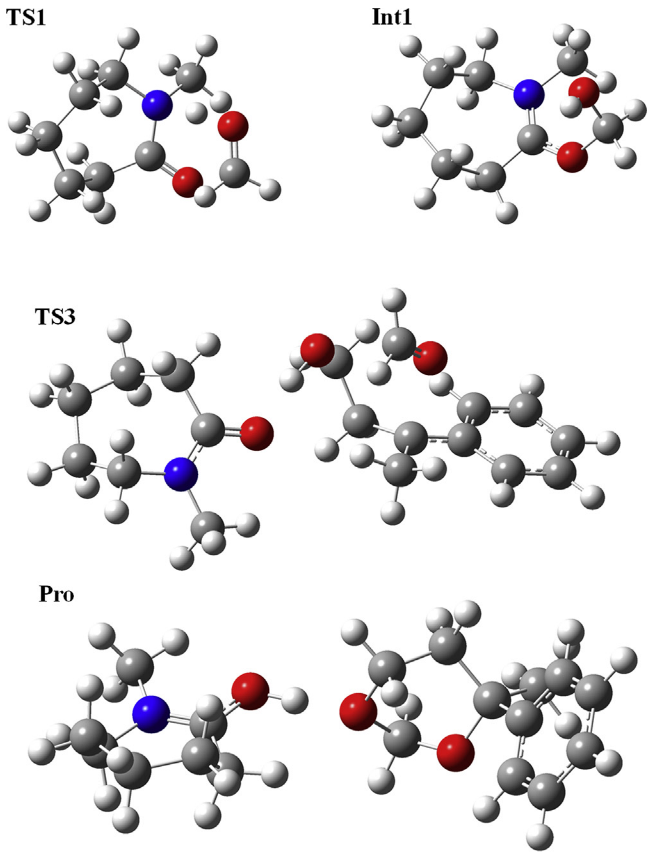


Fig. 4. Optimized structures of the transition states and intermediates.

Table 3
The effect of acid strength of catalysts on Prins reaction.

Catalysts	Temperature (°C)	Conversion (%)	Selectivity (%)
H_3PO_4/SiO_2^{a}	75	45	40
MoP/SiO_2^{a}	75	63	82
H_2SO_4/SiO_2^{a}	75	71	49
SBA-15	75	80	61

Condition: 90 mmol of formaldehyde, 20 mmol of α-methylstyrene, 1.35 g of catalysts, 3 h. ^{a} Obtained by loading 25 wt% of H_2SO_4, H_3PO_4 or solution of $(NH_4)_6Mo_7O_{24}$ and H_3PO_4 on SiO_2 via initial wetness impregnation, SBA-15 from Jilin University.

3.3. Effect of lactam on prins condensation

To deep clarify the effect of NMC on this reaction, catalysts of [NMC]$_{4\text{-}x}$H$_x$SiW were employed, where x was 0, 1, 2, 3, 4.

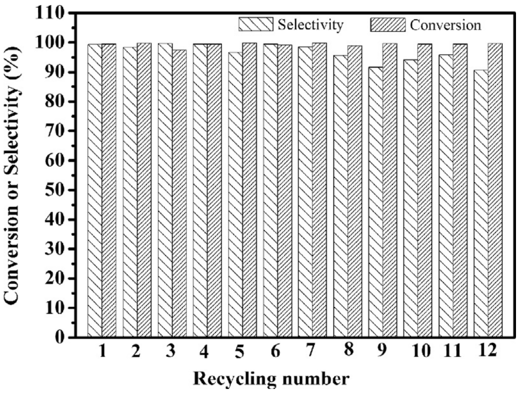
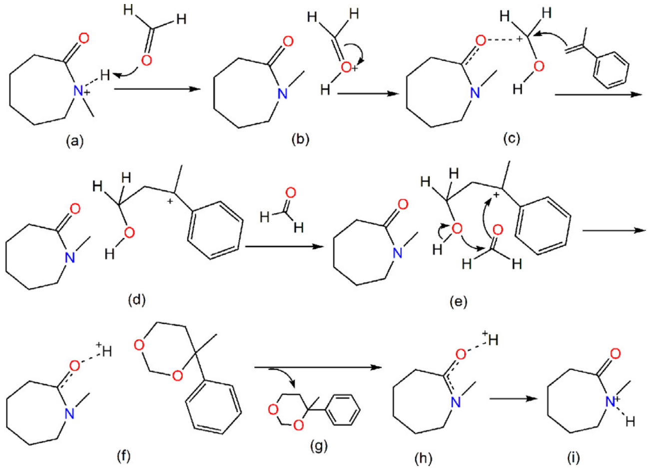


Fig. 5. The recycling of $[NMC]_4SiW$ for cyclization reaction. Reaction conditions: 20 mmol α-methylstyrene, 90 mmol formaldehyde, and 0.4 mmol $[NMC]_4SiW$ at 95 °C for 3 h.

As Fig. 2 presented, the conversion hardly changed (near 100%) but the selectivity continually increased from 80% to 99% with x decreasing from 4 to 0, this verified NMC played a positive role in improving selective activity. But this reaction hardly performed over $[NME]_4SiW$ (Table S6) without C=O group in NME, which was also much lower than that over H_4SiW. Therefore, the outstanding performance of actam-based catalysts for Prins condensation should attribute to the C=O group of organic molecules in catalysts. This was further verified by the result of $[TEA]_4SiW$.

DFT was employed to verify the pathway of Prins reaction in this study as displayed in Fig. 3. The structures of the transition states and intermediates during this process were displayed in Figs. 4 and S3. It suggested lactam played a key role in this process. Firstly, lactam-based catalyst dissociated to produce protonated $[NMC]^+$, together with a formaldehyde molecule formed Ad1. The formaldehyde showed trend of easily obtaining H^+ from catalyst (TS1, Int1) and then integrated with olefin (Ad2, TS2) to form Int2. In this stage, lactam showed property of transfer H^+ and had finished this job with forming as NMC. Following, another formaldehyde molecule approached (Ad3) which involving bonding with olefin and closing ring are simultaneous (TS3). Finally, the desired product was obtained (Pro) involving H^+ returning to NMC in assistance of C=O group. The corresponding catalysis process and the effect of C=O group were displayed in Scheme 2.



Scheme 2. Catalysis process from DFT and effect of C=O group on carbonium stabilization (c) and proton transformation (b), (e)–(i).

In summary, it confirmed that lactam with C=O group showed properties of transferring H^+ between two kind of active center (N^+ and C^+) and stabilization of intermediates by sharing electron. This distinct properties led lactam-based catalyst presenting

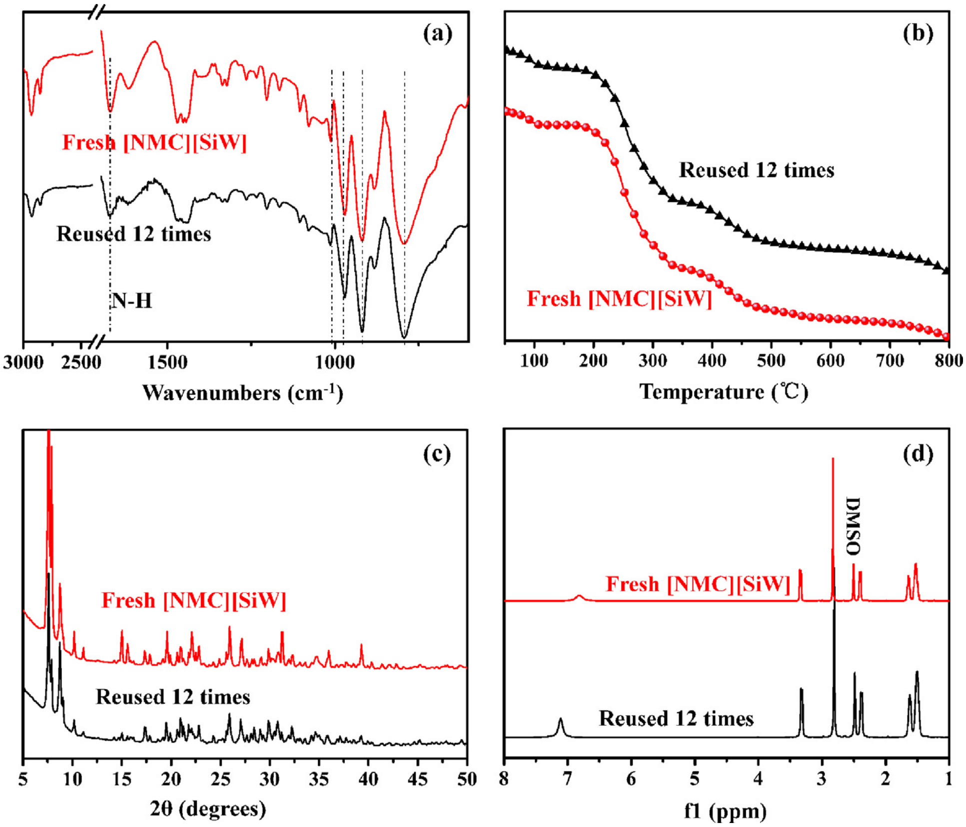
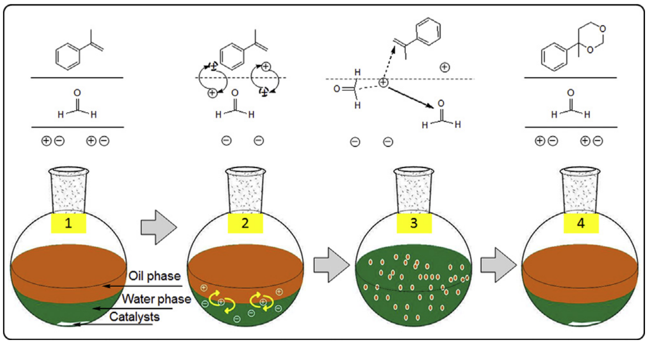


Fig. 6. Characterization of reused $[NMC]_4SiW$: (a) FT-IR, (b) TGA, (c) XRD, (d) ^1H NMR.



Scheme 3. A possible self-separation procedure of $[NMC]_4SiW$ in Prins condensation.

more excellent performance than these catalysts of $[NME]_4SiW$, $[TAE]_4SiW$ and so on, which featured without C=O group.

3.4. *Reusability of $[NMC]_4SiW$ for prins condensation*

Lactam-based Brønsted-acidic catalysts showed feature of self-separation to facilely recycle after reactions. The reusability of the catalyst $[NMC]_4SiW$ was displayed in Fig. 5. It just presented slight decrease in activity after 12 recycling with conversion of α-methylstyrene >100% and selectivity to MPD >91%. The results indicated that $[NMC]_4SiW$ was a robust and reusable catalysts for this reaction. Besides, FT-IR, TGA, XRD and ^1H NMR of recovered catalysts (Fig. 6) suggested that the catalyst structure cannot be destroyed and kept features as the fresh one. So it can be said the catalyst could be reused at least 12 times.

3.5. *Possible self-separation principle*

Some work were performed over $[NMC]_4SiW$ to further understand the performance of catalysts self-separtion. Firstly, the solubility of $[NMC]_4SiW$ at room temperature and reaction temperature was investigated (Table S8), which implied the solubility changed significantly with variation of temperature from 573 mg/100 g at room temperature to 4057 mg/100 g at reaction temperature. This suggested $[NMC]_4SiW$ can dissolve or dissolve out driving by temperature. Moreover, H_4SiW, counterpart of SiW^{4-}, was confirmed with ability to completely dissolve in water, but hardly in α-methylstyrene. This illustrated SiW^{4-} cannot enter into α-methylstyrene. NMC can dissolve in both water and α-methylstyrene, but with a partition coefficient of 3.84 in water/α-methylstyrene system, which implied $[NMC]^+$ mainly dissolving in water phase (Fig. S5).

Based on these views, a possible self-separation principle of $[NMC]_4SiW$ in Prins condensation was proposed. At room temperature, reaction mixture consisted of α-methylstyrene (upper, oil phase), solution of formaldehyde (middle, water phase) and catalyst (bottom, solid phase) as showed in Scheme 3(1). With rising of temperature, the catalyst gradually dissolved in formalin with much water and formed N-cation and heteropoly-anion. The N-cation passed the interface and entered into oil phase under stirring, and the heteropoly-anion was left in water phase (Scheme 3(2)). N-cation may act as surfactant for oil and water phase to form O/W mixture because of its dissolving in both phases (Scheme 3(3)). After reaction, the solubility of catalyst decreased with system cooling, and N-cation in water phase could easily integrate with heteropoly-anion to dissolve out which led concentration of cation in water phase significantly decreasing. The concentration decreasing could drive N-cation in oil phase back water phase in return. Besides, this can remarkable promote driving by partition coefficient of N-cation in water/α-methylstyrene system. Finally majority of N-cation combined with heteropoly-anion and separated out (Scheme 3(4)). Therefore, the self-separation of catalyst can owe to its variation of solubility under different temperatures, as well as partition coefficient in O/W, both of which attributed to lactam molecule.

4. Conclusions

In conclusion, a highly efficient catalyst $[NMC]_4SiW$ was prepared for Prins condensation with conversion of 99% and selectivity of 99%. This kind of catalysts showed feature of self-separation, and can be steadily reused for 12 times. Experimental data suggested N-cation played key role in this reaction, which was confirmed by DFT calculation. It revealed that N-cation with C=O group can not only stabilize intermediate by sharing electron but also transfer proton between two kind of active centers (N^+ and C^+). Moreover, for self-separation of catalysts, a possible principle was proposed. It suggested the self-separation of catalysts was driven by variation of solubility of catalysts at different temperature and partition coefficient of N-cation in oil/water system, both of which resulted from lactam molecules.

Conflicts of interest

None.

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