

Supporting Information

Efficient and recyclable heterogeneous zinc alkyl carboxylate catalyst for the synthesis of N-phenyl carbamate from aniline and dimethylcarbonate

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Contents

I. Materials	S2
II. Preparation of the catalysts	S2
III. Characterization of the catalysts	S3
A. Determination of loadings of alkyl carboxylate and contents of Zn ²⁺	S3
B. Characterization of the catalysts by N ₂ adsorption-desorption technique.....	S4
C. Characterization of the precursor agent and catalysts by NMR.....	S4
D. Characterization of the catalysts by thermogravimetric analysis.....	S4
E. Characterization of the catalysts by FT-IR.....	S4
F. Characterization of the catalysts by ion chromatography analysis.....	S5
IV. Catalyst evaluation and product analysis	S5
A. Turnover frequency (TOF) test.....	S5
B. Integrated reaction and catalyst recycling test.....	S6
C. Product analysis.....	S6
D. Calculation of conversion, selectivity and TOF.....	S6
V. Supporting Scheme, Figures and Tables	S8
VI. References	S12

I. Materials

All chemicals listed below were used as received. Trimethoxysilane (99%), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (AR, Pt \geq 37.5%), tetrahydrofuran (99.9%), acetic acid (99.8%), NaOH (97%), Na_2CO_3 (99.99%), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (99.99%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%), aniline (99.5%), dimethylcarbonate (99%), N-methyl aniline (98%), diphenylurea (98%) and N,N-dimethyl aniline (99%) were all purchased from Shanghai Jingchun Co., Ltd. Zinc formate (98%) and zinc propionate (97%) were purchased from Alfa Aesar China Co., Ltd. Ethyl pent-4-enoate (99%) was provided by Changzhou Xinli Chemical Company. Silica was purchased from Qingdao Meigao Co., Ltd. N_2 (99.99%) was provided by Qinghua Gas Company.

As the target product of the reaction between aniline and dimethylcarbonate, Methyl N-phenyl carbamate (MPC) is not commercially available and was prepared in our laboratory as a standard for analysis. The procedure is as follows: typically 20.0g of the mixture of aniline and dimethylcarbonate (1/20, molar ratio) was charged into a 50 ml of Teflon-lined stainless steel autoclave (a magneton inside) as the reactants and 0.1g of anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ (prepared from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ by drying at 120°C for 3 hours) was added. After 2 hours of reaction at 170°C in oil bath, the reaction mixture was firstly washed thoroughly with deionized water to dissolve $\text{Zn}(\text{CH}_3\text{COO})_2$ and then subjected to distillation under vacuum (2-5 Pa) to remove unreacted dimethylcarbonate, and the rest of the product was recrystallized in n-hexane for three times. Finally white needle-like crystals were obtained. Melting point of the crystals is 47-48°C; IR(KBr) absorption bands: 3330 cm^{-1} (N-H), 2950 cm^{-1} (C-H bond in $-\text{CH}_3$ group), 1710 cm^{-1} , 1240 cm^{-1} and 1070 cm^{-1} (ester group), 1600 cm^{-1} , 1540 cm^{-1} , 1450 cm^{-1} and < 1000 cm^{-1} (benzene ring); ^1H NMR: δ =3.78ppm (strong singlet corresponding to 3H atoms in $-\text{CH}_3$ group); δ =7.07-7.40ppm (nine moderate peaks corresponding to 5H atoms in benzene ring); δ =6.66ppm (one moderate broad singlet corresponding to 1H atom in $-\text{NH}$ group); Results of elemental analysis of the crystals: 63.32% (C), 5.918% (H), 9.068% (N). Theoretical values: 63.56% (C), 6.001% (H), 9.266% (N). It is found that the crystal product is pure MPC with a molecular formula of $\text{C}_8\text{H}_9\text{O}_2\text{N}$.

II. Preparation of the catalysts.

The catalysts were prepared according to the following steps:

1. *Synthesis of the precursor agents.* The precursor agent was synthesized from the reaction between trimethoxysilane and ethyl pent-4-enoate. Typically, a mixture of 0.19 mol of trimethoxysilane, 0.20 mol of ethyl pent-4-enoate and 6.7×10^{-6} mol of H_2PtCl_6 dissolved in 1.0 g of tetrahydrofuran was refluxed for 4 hours. During this period the temperature of the refluxing mixture increased from about 90 °C to 119 °C. After cooled to room temperature, the mixture was distilled under vacuum (2-5 Pa) to give 26.6 g of liquid precursor agent (56.0% yield).

2. *Hydrolysis of the precursor agent.* The precursor agent was mixed with NaOH

aqueous solutions (6.4 M) for hydrolysis. The molar ratio of alkali/precursor agent is 4.1. The hydrolysis was carried out at 60-90 °C under stirring in an open vessel in a fume hood. Water was added from time to time in order to keep the volume of the mixture basically unchanged. The hydrolyzing had been proceeded for 10 hours.

3. *Impregnation of silica followed by calcination.* The hydrolysate solution of precursor agent was filtered to get a clear solution, and then acetic acid was added of to adjust the pH to 9.3. Silica (20-40 mesh, calcined at 300 °C for 6 hours in air) was impregnated by the solution with incipient wetness technique. A series of samples with different loading amounts of precursor agent on silica were prepared by changing the volumes of the solution used and adding different portions of Na₂CO₃ aqueous solution with a pH of 9.3 to afford a constant total volume of the impregnating solution versus a constant mass of silica. After the sample was impregnated for 24 hours and dried at 120 °C for 2 hours, it was transferred into a tubular furnace for calcination at a desired temperature under flowing N₂ atmosphere for a definite period of time.

4. *Ion exchanging with zinc salt solutions.* After the calcined sample was washed thoroughly with deionized water, it was mixed with an aqueous solution of zinc salt. The mixture was stirred at 50-70 °C for an hour. Then the mixture was filtered to remove the solution, and a new batch of the zinc salt solution was mixed with the solid sample for a new run. The operation was repeated three times. Afterwards the solid sample was washed with deionized water thoroughly and dried at 120 °C for 3 hours. Then the catalyst was obtained.

In the procedure described above, the zinc salt used can be selected from zinc acetate, zinc nitrate, zinc formate and zinc propionate with the concentration of Zn²⁺ being 0.38 M. The mass of the zinc salt solution used was 20 times of that of the solid sample.

For the synthesis of the precursor agents, it is worthy to mention that ethylpent-4-enoate can not be replaced by more accessible substituted acrylate, because polymerization occurs preferentially when the latter is employed.¹ In addition, 4-pentenoic acid can not be used instead of ethylpent-4-enoate since carboxyl group can react with the substituted silane.²

Activated carbon (AC) supported zinc acetate was prepared by incipient impregnation method. After impregnating of AC (20-40 mesh, BET surface area = 517.6 m²/g) with aqueous solution of zinc acetate, the sample was dried at 160°C under flowing N₂ stream for 2h, then the catalyst was achieved.

III Characterization of the catalysts

A. Determination of loadings of alkyl carboxylate and contents of Zn²⁺.

The loading amount of alkyl carboxylate species on a catalyst was determined by analysis of carbon element on the sample from which the catalyst was derived after ion-exchanging. The measurement was undertaken on an Elemental Analyzer (vario EL, Elementar Analysensysteme GmbH).

The content of Zn²⁺ as well as Na⁺ on the catalyst was determined by ICP-MS

(inductive coupled plasma emission spectrometer–mass spectrometer, PE/SCIEX Elan 6100 DRC). Before the measurement, the catalyst was washed with HNO₃ aqueous solution (2N) under stirring to dissolve Zn²⁺ as well as Na⁺ into the solution sufficiently. And then the solution was diluted with deionized water to a concentration within the detection range of the instrument.

B. Characterization of the catalysts by N₂ adsorption-desorption technique

Surface areas, pore volumes and average pore diameters of the catalysts were derived from the N₂ adsorption-desorption isotherms recorded on a Quantachrome NOVA 2000E analyzer after the samples were degassed at a definite temperature for 3 hours under vacuum. For most of the catalysts, the degassing temperature is 300 °C; for the catalysts undergone calcination at 180 °C and 240 °C during preparation, the degassing temperature is 180 °C and 240 °C, respectively.

C. Characterization of the precursor agent and catalysts by NMR

¹H and ¹³C NMR spectra of the synthesized precursor agent were recorded at 300 and 75 MHz, respectively in CDCl₃, using a Bruker Avance 300 spectrometer (TMS as an internal standard).

¹H→²⁹Si CP/MAS (cross polarization magic angle spinning) NMR measurements on several catalysts were conducted on a Varian Infinity-plus 400 NMR spectrometer with a commercial double resonance MAS probe at Larmor frequency of 79.47 MHz. The MAS speed was 5 kHz and the cross-polarization contact time was 2.0 ms. A 90° ¹H pulse width of 6.3 μs and a recycle delay of 2 s between scans were applied. The ²⁹Si chemical shifts were determined using a solid external reference Kaolin resonating at -91.5 ppm relative to tetramethylsilane (TMS).

¹H→¹³C CP/MAS NMR spectrum of a typical catalyst was obtained on a Bruker Avance III 500 MHz spectrometer at a frequency of 125.73 MHz, with a 90° ¹H pulse width of 4.5 μs and a contact time of 2 ms, spinning at the magic angle at 5 kHz frequency. The ¹³C chemical shifts were determined using a solid external reference, hexamethylbenzene (HMB). The CH₃ groups of HMB resonate at 17.35 ppm relative to tetramethylsilane (TMS).

D. Characterization of the catalysts by thermogravimetric analysis

In order to assess the thermal stability of the catalyst, thermogravimetric analysis (TGA) was carried out on a catalyst loaded with the most alkyl carboxylate groups. The measurement was carried out on a TA Q600 thermogravimetric analyzer (TA–SDT Q600, USA). The sample (5-10 mg) was placed on a pre-tared 70 μl alumina sample pan and the weight recorded. It was heated over a temperature range 25-800 °C using a linear gradient program at a rate of 15 °C/min under an inert nitrogen flow rate of 30 ml/min. Data were analyzed using Star^e Excellence software.

E. Characterization of the catalysts by FT-IR

Fourier transformed infrared spectroscopy (FT-IR) was used to characterize organic groups on the surface of the catalysts. Since the silica based catalysts are highly

hygroscopic and the powder of the catalysts are difficult to be pressed into self-supported discs with KBr, the infrared spectra of the catalyst powders in fluorolube mulls were studied. The spectra were recorded on a Nicolet Avatar 370 FT-IR spectrometer in the range 4000-400 cm^{-1} at a scan rate of 16 s^{-1} and a resolution of 4 cm^{-1} . The samples were prepared as suspensions of powder catalysts in fluorolube medium and measured between KBr windows at room temperature.

Since the absorption bands of fluorolube and silica are very strong and overlapped below 1350 cm^{-1} ,³ no information concerning grafted organic silicon compounds can be differentiated in this range, so only the spectra above 1350 cm^{-1} are shown in all of the Figures.

F. Characterization of the catalysts by ion chromatography analysis

In order to study the chemical structure of active sites on the surface of the catalysts, ion chromatography method was applied to detect anions of acetate, nitrate, formate and propionate, respectively, possibly leached from typical catalysts undergone ion-exchanging with solutions of zinc acetate, zinc nitrate, zinc formate and zinc propionate, respectively. Before the measurements, the catalysts were subjected to washing with HCl aqueous solutions (1M) under stirring for 1 hour to dissolve the anions sufficiently from the surfaces, and then the solutions were diluted to proper concentrations within the most sensitive detection range of the instrument. All the measurements were carried out on a DIONEX 600 ion chromatograph equipped with an AS-50 (Dionex) autosampler. A 20 μl aliquot of the sample/standard solution was loaded into the eluent-stream. The ions were detected by suppressed conductivity of the eluent using an ASRS-ULTRA self-regenerating suppressor column (Dionex). An AS11-HC analytical column (250 mm \times 4 mm i.d.) was used for separation. Data acquisition, construction of calibration curves and peak integration were achieved with the aid of the Peaknet® Dionex software package.

IV. Catalyst evaluation and product analysis

A. Turnover frequency (TOF) test

10.0 g of the mixture of aniline and dimethylcarbonate (1/20, molar ratio) was charged into a 50 ml stainless steel autoclave (a magneton inside), an appropriate amount of catalyst was introduced simultaneously. Then the autoclave was tightly closed and air in it was replaced by charging–discharging of N_2 repeatedly through a gas inlet tube at ice water temperature. Afterwards the autoclave was heated quickly in silicone oil bath under which a magnetic stirring apparatus was placed. Once the reaction temperature reached 180 $^\circ\text{C}$, stirring started immediately and the temperature was kept constant for 15 minutes. Then the reaction was stopped and the reaction mixture was subjected to analysis by HPLC. Conversion of aniline was kept < 10% in all tests.

Our preliminary experimental results indicate that the performance of the catalyst does not change following the stirring speed when it exceeds 300 r/min, so we fixed the stirring speed at 400 r/min in all tests. In addition, all the solid samples were

formulated to be particles of 20–40 mesh since smaller size did not result in higher activity.

B. Integrated reaction and catalyst recycling test

Integrated reaction with prolonged reaction time was conducted in the same autoclave used in TOF test, but with a Teflon tank attached inside to avoid the catalytic activity of the inner wall. The reusability of the catalyst was tested by repeated evaluation of the catalyst. After one hour of reaction, the reaction mixture was filtered off and the catalyst was reused for a new run. The operations were carried out under protection of N₂.

C. Product analysis

Identification of the products and reactants was done using a LC-MS (Waters 2690-Micromass ZMD) as well as by comparing the retention times to respective standards in LC traces. Quantitative analysis of the liquid reaction mixture was conducted on a LaChrom Elite HPLC instrument (Hitachi) with a UV detector. Mobile phase was the mixture of methanol and water (70/30, volume ratio) with a flow rate of 1 ml/min. The product was monitored at 254 nm. A C18 column was used for separation of the products. Quantification of the components in the product was realized by normalization method based on the peak areas and correction factors of the components on the chromatogram.

Totally five components can be detected in the reaction mixture, i.e., aniline, MPC, N-methyl aniline, diphenylurea and N,N-dimethyl aniline, sequentially eluted from the column and exhibited as discrete peaks on the chromatogram. Since all the five components with high purity are commercially available, molar correction factors were determined from the chromatogram of standard solution with known concentrations of all of these compounds. The composition of the standard solution was as close to that of the reaction mixture as possible. Correction factor of the component was calculated according to equation E1 listed below.

$$f_i = \frac{A_i \times C_i \times f_1}{A_1 \times C_1} \quad (\text{E1})$$

Where f_i is the molar correction factor of component i . A_i is the peak area of component i on the chromatogram and C_i is the molar fraction of component i in the standard solution. A_1 is the peak area of aniline and C_1 is the molar fraction of aniline. f_1 is the molar correction factor of aniline, and we set $f_1=1$.

D. Calculation of conversion, selectivity and TOF

Since dimethylcarbonate is stoichiometrically excessive in the reaction, so only the conversion of aniline was calculated according to equation E2 listed below.

$$Conv = \left(1 - \frac{A_1 f_1}{\sum_i n_i A_i f_i}\right) \times 100\% \quad (\text{E2})$$

Where $Conv$ is the conversion of aniline. A_i is the peak area of component i on the chromatogram and f_i is the molar correction factor of component i . A_1 is the peak area

of aniline and f_i is the molar correction factor of aniline. n_i is the number of aniline molecule incorporated into one molecule of product i .

The selectivity of the product was determined by equation E3 listed below.

$$Sel_i = \left(\frac{n_i A_i f_i}{\sum_i n_i A_i f_i} \right) \times 100\% \quad (E3)$$

Where Sel_i is the selectivity of product i . A_i is the peak area of product i on the chromatogram and f_i is the molar correction factor of product i . n_i is the number of aniline molecule incorporated into one molecule of product i .

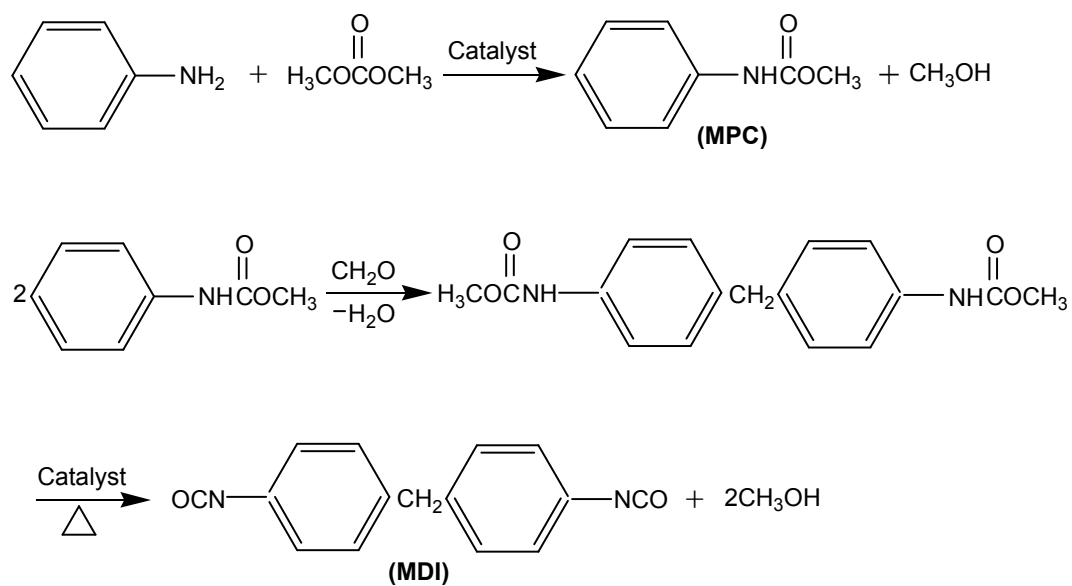
TOF of the target product MPC was calculated according to equation E4 listed below.

$$TOF = \frac{n_A \times Y_{MPC}}{900 \times m_{cat} \times C_{Zn^{2+}}} \quad (E4)$$

Where n_A is the amount of aniline (mol) initially added in the reactants and Y_{MPC} is the yield of MPC which equals conversion of aniline times selectivity of MPC. m_{cat} is the mass of the catalyst and $C_{Zn^{2+}}$ is the content of Zn^{2+} on the catalyst (mol/g). Since the experiment for testing TOF was finished in 15 minutes (900 seconds), so 900 is divided in E4.

Since the numbers of different active sites were not accurately determined, so the TOF calculated according to the above equation is average value on all possible active sites, presuming that Zn^{2+} is the only active center.

V. Supporting Scheme, Figures and Tables



Scheme S1. Reaction equation of methyl N-phenyl carbamate (MPC) synthesis from aniline and dimethylcarbonate and following steps to produce diphenylmethane-4, 4'-diisocyanate (MDI).

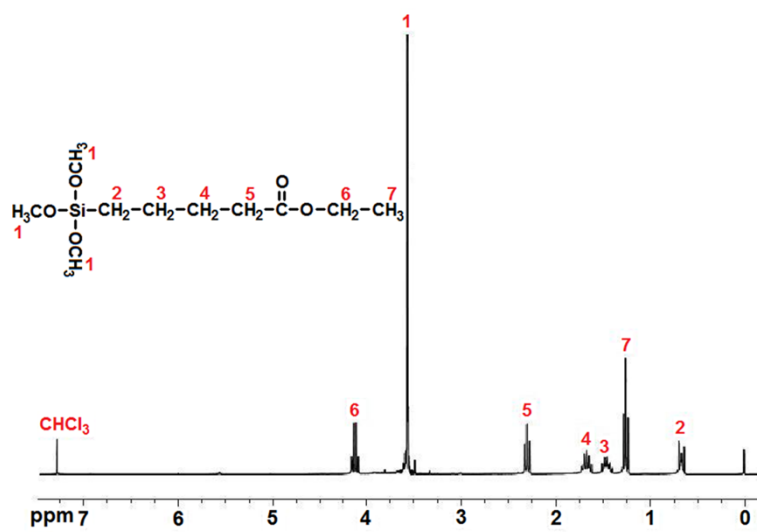


Figure S1. ¹H NMR spectrum of the precursor agent.

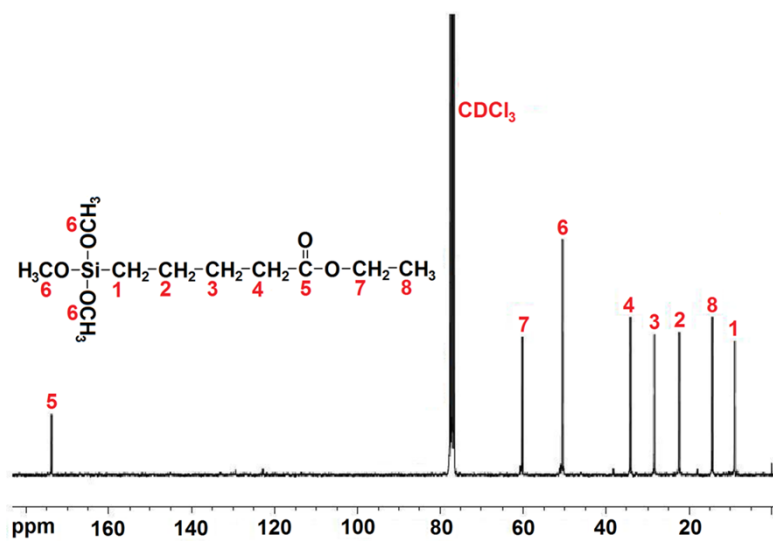


Figure S2. ¹³C NMR spectrum of the precursor agent.

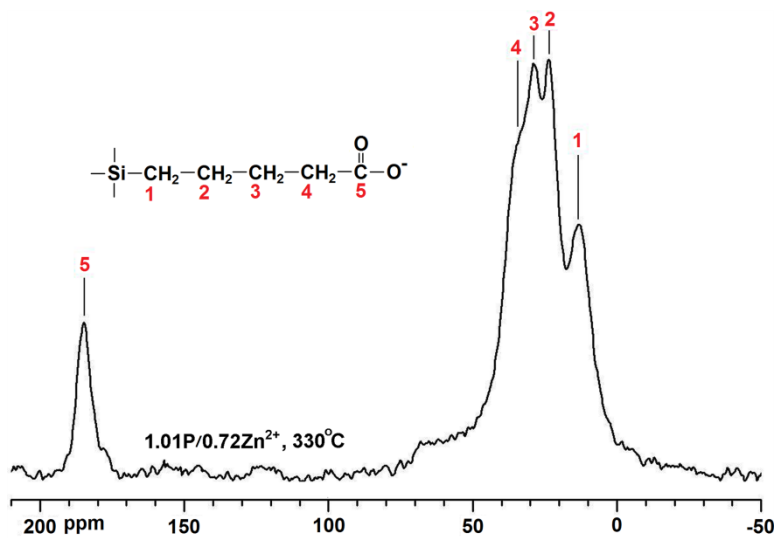


Figure S3. $^1\text{H}\rightarrow^{13}\text{C}$ CP/MAS NMR spectrum of a typical catalyst.

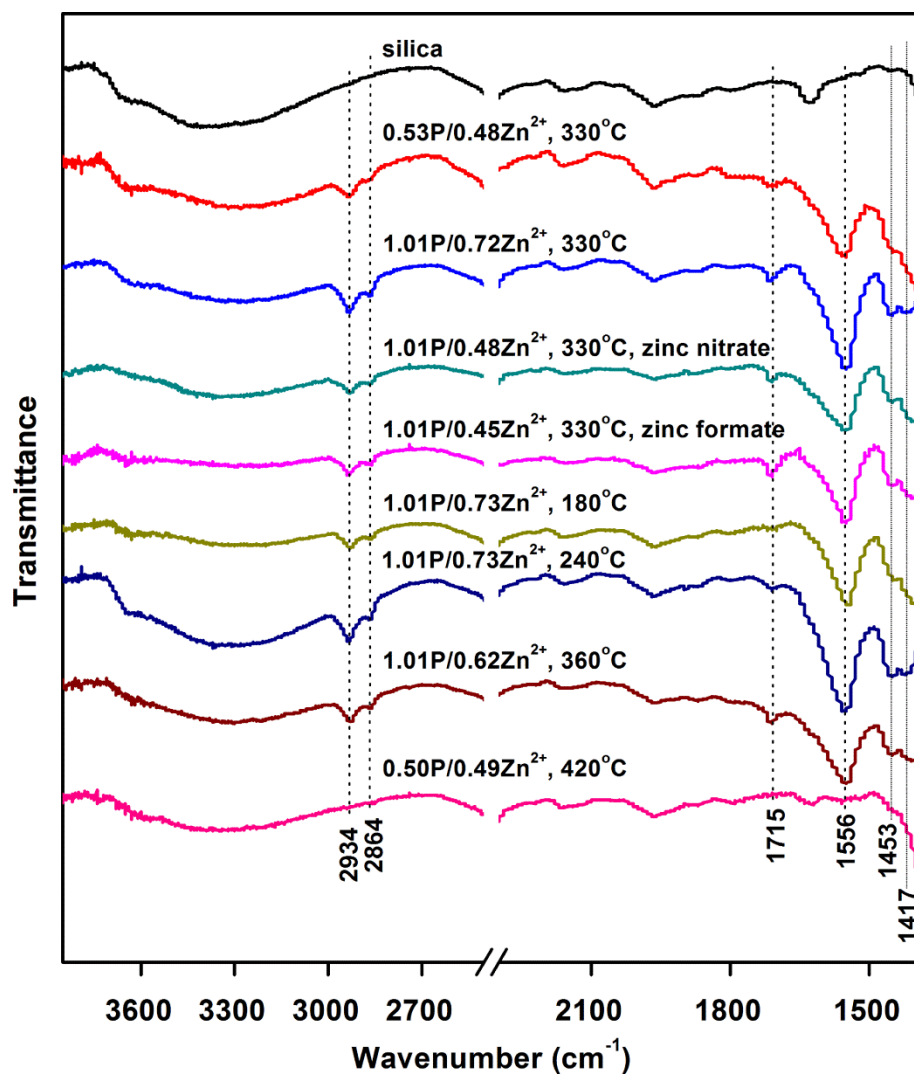


Figure S4. FT-IR spectra of different samples. Loading of carboxylate (mmol/g), content of Zn²⁺ (mmol/g), calcined temperature and zinc salt used for ion-exchanging are labeled (zinc acetate is used if not labeled).

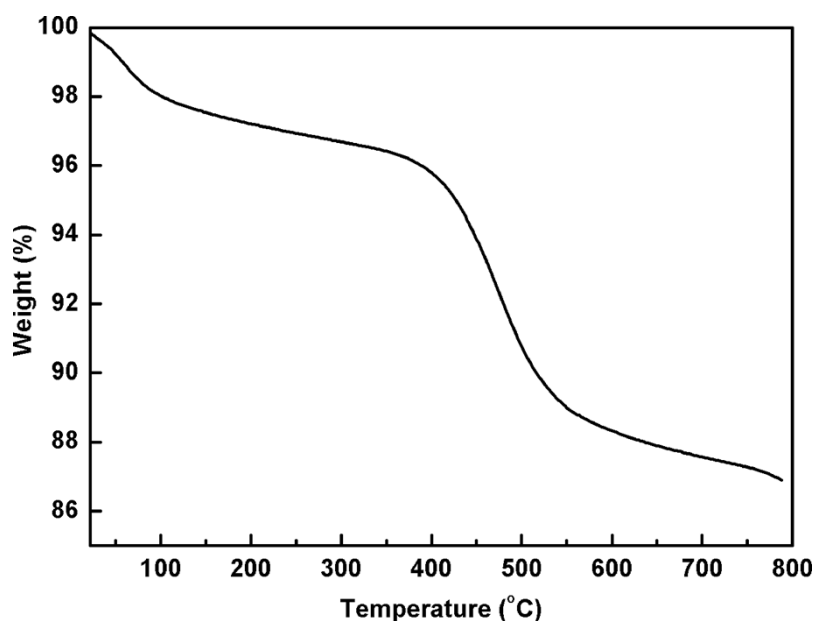


Figure S5. Thermogravimetric analysis curve of 1.25P/0.73Zn²⁺, 330°C catalyst.

Table S1. Physical property of different catalysts.

Catalyst ^a	BET surface area (m ² /g)	Pore size (nm)	Pore volume (ml/g)
Silica	297.7	16.5	1.22
0.53P/0.48Zn ²⁺ , 330°C	222.8	14.7	0.82
1.01P/0.72Zn ²⁺ , 330°C	214.5	12.3	0.66
1.25P/0.73Zn ²⁺ , 330°C	177.3	11.9	0.53
1.01P/0.73Zn ²⁺ , 180°C	196.7	12.0	0.59
1.01P/0.73Zn ²⁺ , 240°C	183.7	12.8	0.59
1.01P/0.62Zn ²⁺ , 360°C			
0.50P/0.49Zn ²⁺ , 420°C			
1.01P/0.48Zn ²⁺ , 330°C ^b	227.0	12.4	0.70
1.01P/0.45Zn ²⁺ , 330°C ^c	217.3	12.3	0.67
1.01P/0.57Zn ²⁺ , 330°C ^d	201.4	12.9	0.65

^a The catalyst is marked in terms of the loading of alkyl carboxylate (mmol/g)/the content of Zn²⁺ (mmol/g), calcined temperature. ^{b, c, d} Exchanged with the solution of zinc nitrate, formate and propionate during preparation, respectively. All the other catalysts underwent ion-exchanging with zinc acetate solution.

Table S2. Zn²⁺, Na⁺ contents and exchange degrees on several typical catalysts.

Catalyst	Zn ²⁺ content (mmol/gcat)	Na ⁺ content (mmol/gcat)	Exchange degree (%)
0.53P/0.48Zn ²⁺ , 330°C	0.48	0.005	99.5
1.01P/0.72Zn ²⁺ , 330°C	0.72	0.008	99.4
1.01P/0.48Zn ²⁺ , 330°C ^a	0.48	0.002	99.8

^a Exchanged with the solution of zinc nitrate during preparation.

Table S3. Results of ion chromatographic analysis on typical catalysts.

Catalyst	Anion detected	Loading of anion (mmol/g)	Anion/Zn ²⁺ (molar ratio)
0.53P/0.48Zn ²⁺ , 330°C	CH ₃ COO ⁻	0.023	1/21
1.01P/0.72Zn ²⁺ , 330°C	CH ₃ COO ⁻	0.011	1/65
1.01P/0.48Zn ²⁺ , 330°C ^a	NO ₃ ⁻	0.00027	1/1778
1.01P/0.45Zn ²⁺ , 330°C ^b	HCOO ⁻	0.0013	1/346
1.01P/0.57Zn ²⁺ , 330°C ^c	CH ₃ CH ₂ COO ⁻	0.0011	1/518

^{a, b, c} Exchanged with the solution of zinc nitrate, formate and propionate during preparation, respectively.

VI. References

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