Supporting Information

On-line attenuated total reflection infrared spectroscopy (ATR-IR): A powerful tool for investigating Methyl cyclopentenone synthesis process

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1 Experimental sections

ESI 1: Procedure for MCP synthesis

Step 1: Synthesis of N.N-dimethyl-5-methylfurfuramide from 2-methylfuran

33.4 g dimethylamine hydrochloride was solved in 15.72 g distilled water, then added 31.17 g formaldehyde. After stirring the mixture for 0.5 h at 50-52 ℃, added 30 g 2-methylfuran, raised the temperature to 60 ℃ for continue reaction (equipped with reflux condenser).

Step 2: Ring opening reaction of N.N-dimethyl-5-methylfurfuramide

60.0 g N.N-dimethyl-5-methylfurfuramide was added into 90 g distilled water, then added 59.64 g 30 % hydrochloric acid dropwise to adjust the pH value of the reaction solution below 1.0. Heating the reaction mixture to 98-100 ℃ and reacted for 6 h.

Step 3: Closed loop reaction of 1-(dimethylamino) hexane-2,5-dione

Cooled the reaction liquid above to 65 ℃, then added 125 g sodium hydroxide to adjust the pH to 12-13. Reacting for 0.5 h at 70-80 ℃, stepped by a quick cooling to 25 ℃, and the organic phase was obtained by static stratification.

Step 4: 2-(dimethylamino)-3-methyl-2-cyclopentene-1-one rearrange to MCP

35.2 g 2-(dimethylamino)-3-methyl-2-cyclopentene-1-one was added to 18 g of distilled water, and then 29.6 g hydrochloric acid was added to the mixture. Heating the mixture to 98-100 ℃ and reacted for 3 h. Then cooled the reaction mixture to 50 ℃ by stages, and finally cooled it to 10 ℃.

ESI 2: Monitoring the synthesis of MCP by ATR-IR

In situ ATR-IR spectra were obtained by inserting the ATR probe into the reaction bottle during the whole synthesis process. The spectrum of the reaction solution before adding 2-Methylfuran was taken as the spectral background when monitoring step 1. The infrared spectrum of water was collected as the spectral background for deduction when monitoring the following synthesis process.

ESI 3: Quantification method for N.N-dimethyl-5-methylfurfuramide

Quantitative univariate model was established for N.N-dimethyl-5-methylfurfuramide by monitoring the intensity of infrared absorption at 1562 cm^{-1} of standard series. The concentration of the standard series were determined by HPLC.

ESI 4: Study on the formation mechanism of the side product generated in Step1

25.7 g dimethylamine hydrochloride was solved in 15.72 g distilled water, then added 31.17 g formaldehyde. After stirring the mixture for 0.5 h at 50-52 ℃, added 30 g 2-methylfuran, raised the temperature to 60 ℃ for continue reaction (equipped with reflux condenser).

2 Supporting Figures

Fig. S1 Infrared absorption spectra of 2-methylfuran (98 %) and N. N-dimethyl-5-methylfurfuramide (99 %) at T = 298.15 K and P = 1 atm.

Fig. S2 Infrared absorption spectrum of pure N.N-dimethyl-5-methylfurfuramide (black curve, T = 298.15 K and P = 1 atm) and N.N-dimethyl-5-methylfurfuramide in simulated reaction solution (red curve, T = 333.15 K and P = 1 atm).

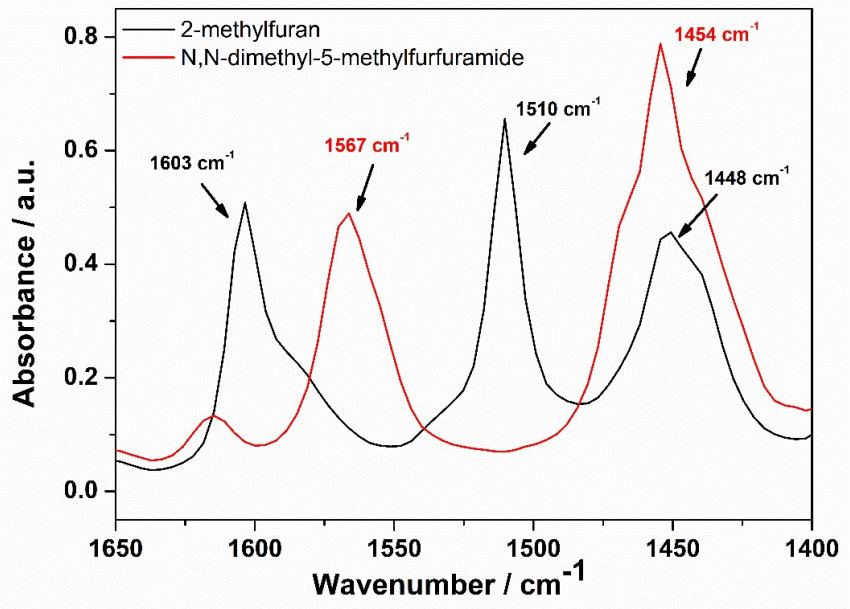
Fig. S3 Quantitative working curve of N.N-dimethyl-5-methylfurfuramide.

Fig. S4 ^{1}H-NMR spectrum of the possible impurities generated during Step 1.

Fig. S5 Second derivative of infrared spectrum collected during the reaction process between pure formaldehyde and 2-methylfuran under same experimental conditions.

Fig. S6 GC-MS spectrum of the reaction solution between (5-methylfuran-2-yl)methanol and 2-methylfuran.

Fig. S7 3D IR spectra of closed-loop reaction (Step 3) of 1-(dimethylamino) hexane-2,5-dione.



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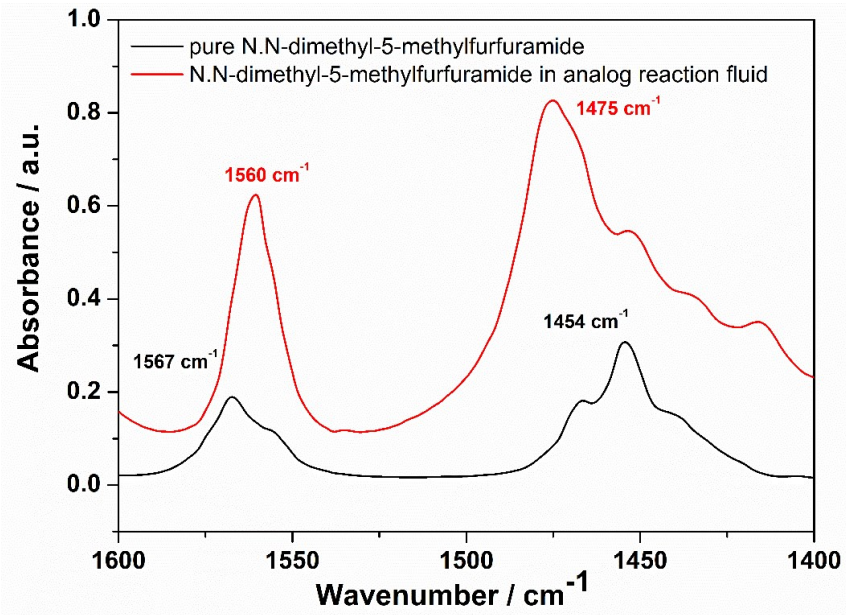

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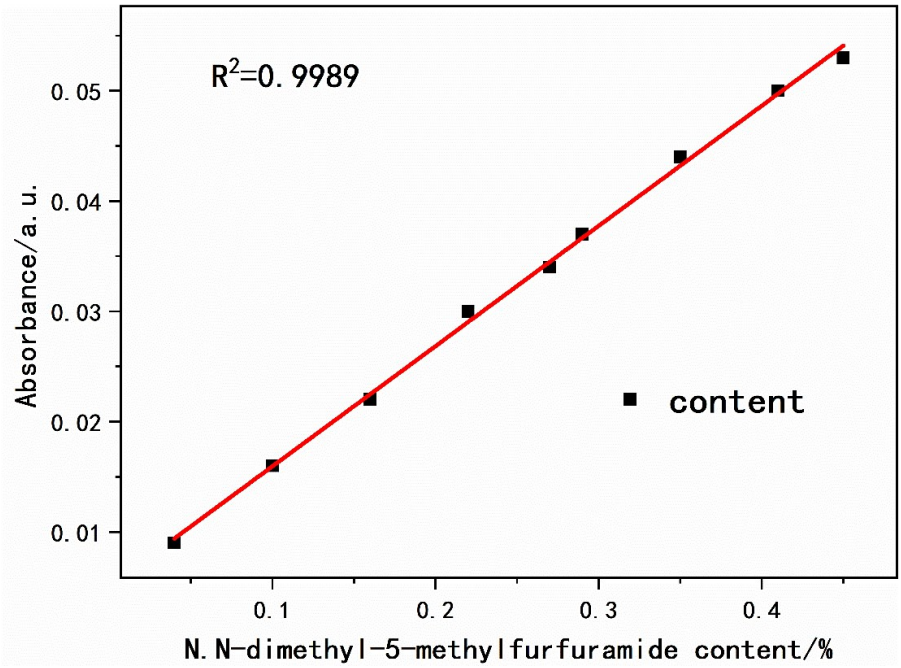


Fig. S3 Quantitative working curve of N.N-dimethyl-5-methylfurfuramide.

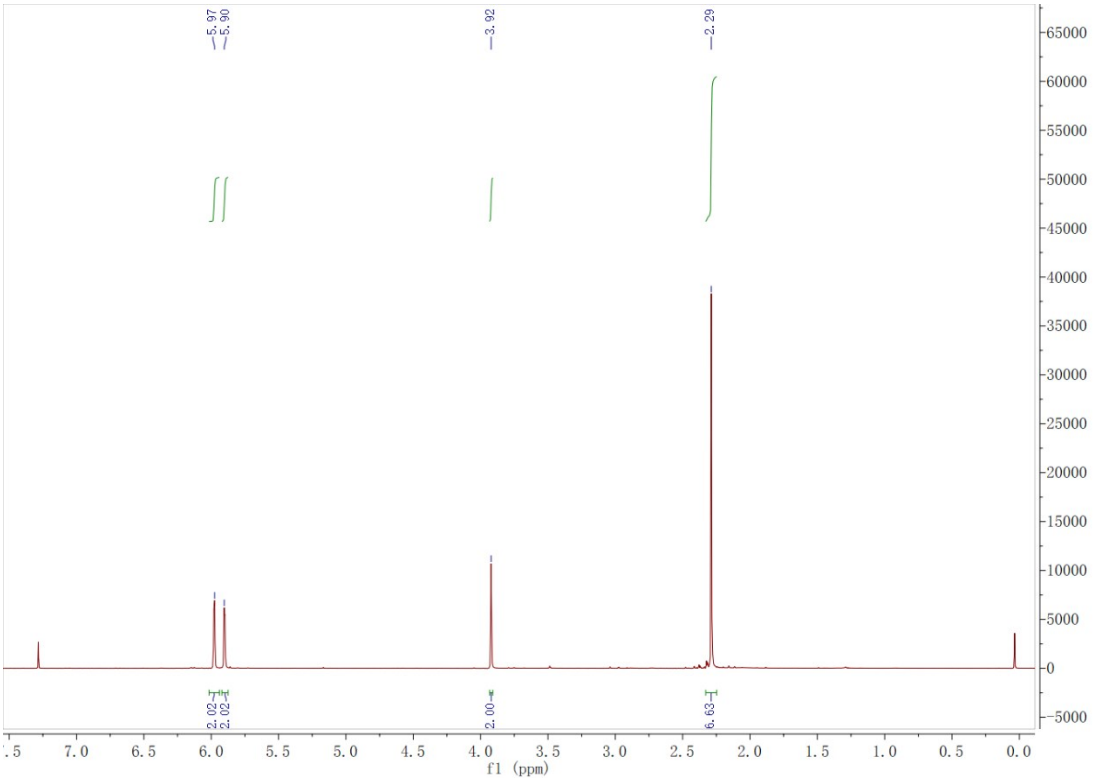


Fig. S4 ^{1}H-NMR spectrum of the possible impurities(bis(5-methylfuran-2-yl)methane) generated in Step 1.

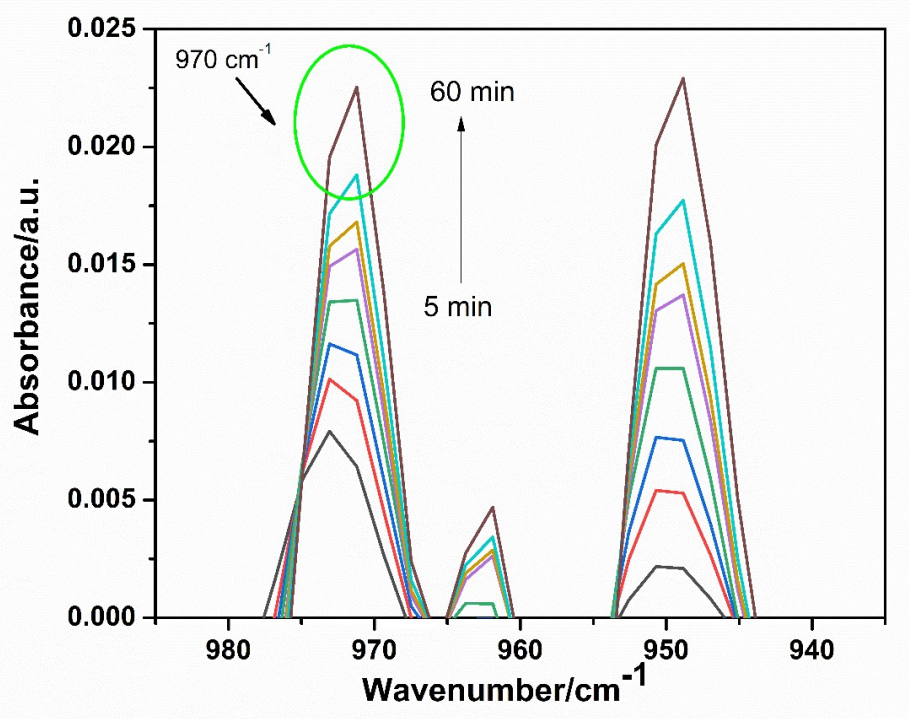


Fig. S5 Second derivative of infrared spectrum collected during the reaction process between pure formaldehyde and 2-methylfuran under same experimental conditions.

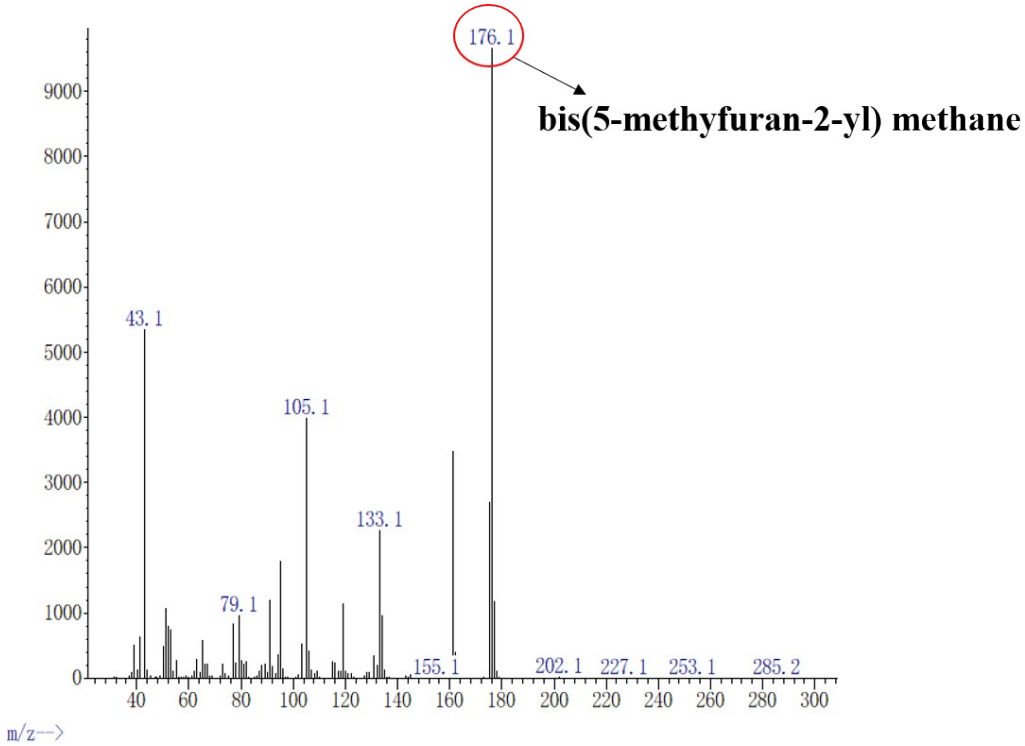
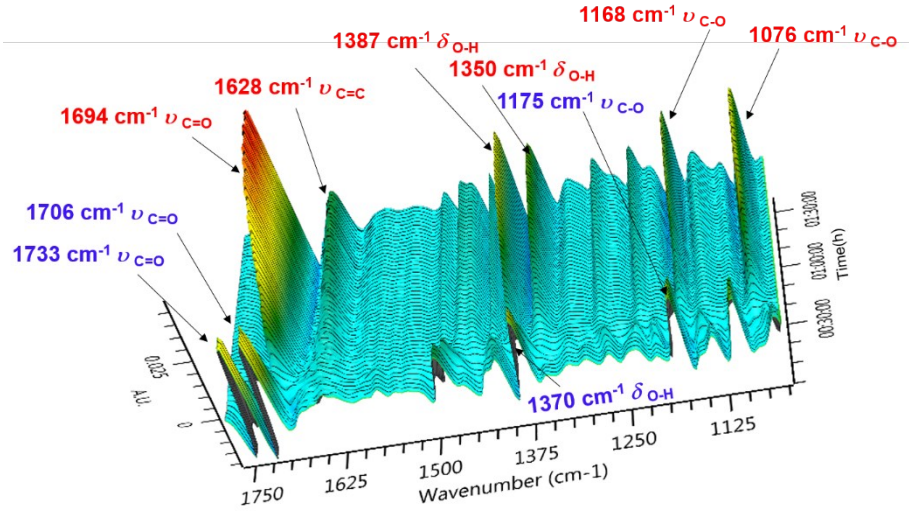


Fig. S6 GC-MS spectrum of the reaction solution between (5-methylfuran-2-yl) methanol and 2-methylfuran.



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