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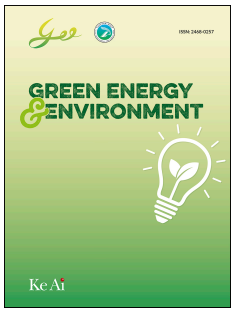

Highly efficient synthesis of 1-methoxy-2-propanol using ionic liquid catalysts in a micro-tubular circulating reactor

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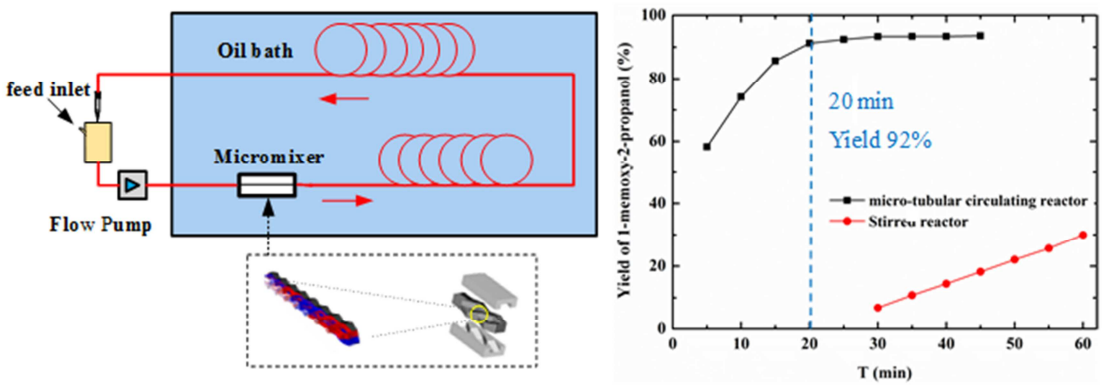

Graphical abstract

Highly efficient synthesis of 1-methoxy-2-propanol using ionic liquid catalysts in a micro-tubular circulating reactor

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Abstract

The catalysis of ionic liquids (ILs) in the traditional stirred reactor suffers from insufficient mass and heat transfer, which always needs a long reaction time and results in a low reaction rate. In this work, highly efficient synthesis of 1-methoxy-2-propanol via the alcoholysis reaction of propylene oxide (PO) with methanol was proposed and achieved by the combination of micro-tubular circulating reactor with the IL $[N_{4444}][Buty]$ catalyst. Compared with the stirred reactor, the rate of alcoholysis reaction in a micro-tubular circulating reactor was found to be significantly improved. The reaction time was remarkably shortened to 20 minutes from 180 minutes as well as the yield of 1-methoxy-2-propanol reached 92%. Moreover, the kinetic study further demonstrated that the main reaction rate to 1-methoxy-2-propanol (K_1) was about 20 times larger than the side reaction rate to byproduct 2-methoxy-1-propanol (K_2) in the temperature range of 363-383 K. Such combination of micro-tubular circulating reactor with IL catalysts is believed to be a class of effective process intensification technique for highly efficient synthesis of 1-methoxy-2-propanol.

Keywords: Ionic liquids, Micro-tubular circulating reactor, Alcoholysis, Propylene oxide, 1-Methoxy-2-propanol,

1. Introduction

As a new type of eco-friendly reaction medium and green solvent, ionic liquids (ILs) have received widespread attention in these years owing to their particular properties such as negligible vapor pressure, wide liquid range, excellent solubility, high catalytic activity and good selectivity [1-3]. The utilization of ILs as catalysts and media have been successfully implemented in various chemical processes [4-6]. For example, Rogers et al. [7] found that chloride based ILs could efficiently dissolve cellulose, and resultant solution contains as high as 25 wt.% cellulose, which indicated that ILs were economical and effective in comparison with traditional methods. Liu et al. [8] found that the isobutane alkylation reaction catalyzed by a composite IL could approach a reaction balance of 20 s at 15 ºC. Therefore, the ILs being as a green medium shows a very attractive prospect for chemical process intensification.

As a type of propylene glycol methyl ether (PGME), 1-methoxy-2-propanol shows a much lower toxicity and influence on the environment [9]. Thus it has been widely used as a versatile solvent for painting, adhesive, printing inks, etc. in the chemical industries [10]. 1-Methoxy-2-propanol is generally produced by the alcoholysis reaction of propylene oxide (PO) with methanol using base catalysts. Nevertheless, the conventional base catalysts such as NaOH and Na_2CO_3 usually facilitated the formation of byproduct 2-methoxy-1-propanol and resulted to low catalytic selectivities for synthesis of 1-methoxy-2-propanol. In our previous work [11], we reported

that a tetrabutylphosphonium IL acted as an efficient catalyst for obtaining PGME with a yield of 93 % at 6 h compared with other kinds of catalysts [9, 12-15]. Despite the IL possessing excellent performance, the least of perfection is that there still needs a long reaction time (6 h) in the conventional stirred reactor for the production of 1-methoxy-2-propanol. Therefore, the challenge remains regarding whether a new intensified process can be developed for highly efficient synthesis of 1-methoxy-2-propanol.

Recently, the development of microreactor technologies has gained widely attention for chemical reaction engineering owing to the requirement of process intensification and production platforms [16, 17]. Compared to the traditional reactors, microreactors offer smaller devices volumes, enhanced mass and heat transfer efficiency, improved yields over shorter periods of time, increased process control, greater safety, and flexible production [18-21]. Therefore, these miniaturized microreactors have good potential to intensify the alcoholysis reaction for efficient synthesis of 1-methoxy-2-propanol, which would result in a greater yield in a shorter time.

In this work, three tetrabutylammonium carboxylate ILs ([N_{4444}][CA]) were designed and synthesized via simple neutralization reactions (Scheme 1). Then, the combination of micro-tubular circulating reactor with [N_{4444}][CA] IL catalysts was studied for highly efficient synthesis of 1-methoxy-2-propanol via the alcoholysis of PO with methanol. The rate of alcoholysis reaction could be significantly improved as well as the reaction time was remarkably shortened to 20 minutes from 180 minutes with a 92% yield of 1-methoxy-2-propanol, verifying the outstanding superiority of micro-tubular circulating reactor. Moreover, the effects of ILs, reaction temperatures, reactant molar ratios, flow rates, and catalyst loadings on the yield of 1-methoxy-2-propanol were

investigated systematically. A kinetic model for this alcoholysis reaction in micro-tubular circulating reactor was further developed for the correlation of experimental data.

2. Experimental

2.1 Materials

Tetrabutylammonium hydroxide (40 wt.% in water), tetrabutylphosphonium bromide (purity ≥ 99%) and propylene oxide (purity ≥ 99 %) were purchased from Aladdin (Shanghai, China). Other reagents such as methanol, acetic acid, propanoic acid, and butyric acid were of analytical grade and used without any further purification.

2.2 Preparation of $[N_{4444}][CA]$ ILs.

$[N_{4444}][Buty]$ was synthesized by the procedure as follows: $[N_{4444}]OH$ aqueous solution was firstly neutralized with equimolar butyric acid by stirring at room temperature for 6 h. Then, the prepared IL $[N_{4444}][Buty]$ was dried under vacuum at 70 °C for 48 h to eliminate traces of residual water prior to use. The synthesis procedure of $[N_{4444}][Ace]$ and $[N_{4444}][Prop]$ was according to the case of $[N_{4444}][Buty]$ [22]. In addtion, $[P_{4444}][Buty]$ was prepared by the procedure in our previous work. [11]. The water content of these carboxylate ILs was determined with a Karl Fisher titration and found to be less than 0.10 wt%.

2.3 Synthesis of 1-methoxy-2-propanol in a micro-tubular circulating reactor.

Scheme 2 shows the schematic overview of the experimental setup. The micro-tubular circulating reactor system (purchased from Dalian Weikai Chemical Co. Ltd.) includes a T-micromixer and a spiral pipeline. The T-micromixer has a 0.3 mm (width) ×0.3 mm (depth)

cross-section channels. The internal diameter and the length of the spiral capillary reactor are 0.93 mm and 3 m, respectively. The T-micromixer and spiral pipeline reactor was immersed in the oil bath with a temperature control of ± 0.1 °C.

In a typical run, PO (0.3 mol), methanol (1.2 mol), and carboxylate IL [N_{4444}][Buty] (22.5 mmol) were charged into a vessel. Then the whole reaction mixture was pumped into the micro-tubular circulating reactor pipeline by a liquid chromatography pump with liquid flowmeter. Running the micro-tubular circulating reactor for a certain time, the sample was then withdrawn and mixed with a quantity of internal standard *n*-propanol (⩾99.9%) to quantify the products by an Agilent 7890A chromatograph equipped with a flame ionization detector (FID). The detailed analysis conditions were described as follows: the injector and detector temperatures were 180 and 250 °C, respectively; the column temperature was increased stepwise to 200 °C, holding at 50 °C for 2 min, increasing to 200 °C at 10 °C min^{-1}, holding at 200 °C for 1 min. Then the conversion and selectivity were calculated according to the area of chromatograph peak using *n*-propanol as an internal standard. After the reaction is completed, the reaction mixture was treated in a rotary evaporator to distill off methanol and 1-methoxy-2-propanol at 80 °C under reduced pressure. Subsequently, the residual mixture was placed in a vacuum oven at 80 °C for 12 h to further remove the residual reactants and products. At last, the carboxylate IL catalyst could be recovered and reused in the next run.

3. Results and Discussion

3.1 [N_{4444}][CA] ILs-catalyzed alcoholysis reaction in micro-tubular circulating reactor

Three [N_{4444}][CA] ILs were used as catalysts for synthesis of 1-methoxy-2-propanol via the

alcoholysis reaction of PO with methanol in a micro-tubular circulating reactor. The results are shown in Figure 1. It was found that these three [N_{4444}][CA] catalysts showed different catalytic activities, and the sequence was [N_{4444}][Buty] > [N_{4444}][Prop] > [N_{4444}][Ace]. Among [N_{4444}][CA] ILs, [N_{4444}][Buty] catalyzed the alcoholysis reaction to have the highest yield of 1-methoxy-2-propanol (92%) at a very short reaction time of 20 minutes in the micro-tubular circulating reactor. This can be explained that owing to the electrondonation of alkyl group, the basicity of carboxylate increases slightly with prolonging the carbon chain length [11, 22]. As a result, [N_{4444}][Buty] shows the stronger basicity than [N_{4444}][Prop] and [N_{4444}][Ace] have, and thus the highest yield of 1-methoxy-2-propanol could be achieved. Furthermore, it is found that the alcoholysis reaction could not take place without the catalyst. When the other basic catalysts such as [P_{4444}][Buty], sodium butyrate, and NaOH were studied for the synthesis of 1-methoxy-2-propanol in the micro-tubular circulating reactor, the results showed that these typical basic catalysts exhibited slow reaction rates and induced relatively low yields at the reaction time varying from 5 to 20 minutes. By contrast, [N_{4444}][Buty] catalyzed the alcoholysis reaction to have a 92% yield at reaction time of 20 minutes, showing the excellent reaction rates and high yield.

Figure 2 shows the comparison of catalytic performance of [N_{4444}][Buty] IL in the micro-tubular circulating reactor and stirred reactor for synthesis of 1-methoxy-2-propanol. The reaction conditions are as follows: PO (0.3 mol), methanol (1.2 mol), catalyst loading (7.5 mol% of PO), and reaction temperature (383 K). It is obvious that the alcoholysis reaction rate was really quickly in the micro-tubular circulating reactor with a circulating flow rate of 10 mL/min. In a very short time (5 min), the yield of 1-methoxy-2-propanol could be significantly enhanced to 59%. Increasing the time

to 20 minutes could further result to a 92% yield of 1-methoxy-2-propanol. Nevertheless, as the reaction time was prolonged to 40 minutes, the yield of 1-methoxy-2-propanol almost kept constant. For comparison, in a 10 mL stirred reactor with a rotate speed of 500 rpm, it must take 180 minutes to approach 92% yield of 1-methoxy-2-propanol under identical conditions, which is consist with the previous reported results [11]. This finding shows that the superiority of micro-tubular circulating reactor could powerfully intensify the alcoholysis reaction efficiency and dramatically decrease the reaction time from 180 to 20 minutes. That is to say, the reaction efficiency in the micro-tubular circulating reactor is nearly 9 times greater than that in the stirred reactor. The miniaturized micro-tubular circulating reactor owning the small void volume usually contributes to the short diffusion paths in the fluid stream, and thereby leads to the rapid mixing of reactants and very effective transport to the active sites of catalyst [23-25]. As a result, a high yield of 1-methoxy-2-propanol can be obtained in the micro- tubular circulating reactor within a short period of time.

3.2 Optimization of reaction conditions

Figure 3 shows the effect of reaction temperature on the 1-methoxy-2-propanol yield in the micro-tubular circulating reactor. It was demonstrated that the yield of 1-methoxy-2-propanol increased accordingly with the increase of reaction temperature. For example, when the temperature was set at 353 K, 1-methoxy-2-propanol was obtained in only 18% yield at 20 minutes. Increasing the temperature to 383 K could further induce a 92% yield of 1-methoxy-2-propanol at 20 minutes. This suggests that high temperature is positive to the 1-methoxy-2-propanol yield in the micro-tubular circulating reactor, whereas the previous finding indicates that the

1-methoxy-2-propanol yield would decrease at the overhigh reaction temperature in the stirred reactor because of the inefficient contact of reactants with the IL catalyst [11]. Considering that the yield of 1-methoxy-2-propanol reached 92% at 20 minutes, the optimized reaction temperature was fixed at 383 K for the synthesis of 1-methoxy-2-propanol in the micro-tubular circulating reactor.

The effect of initial molar ratio of PO to methanol on the 1-methoxy-2-propanol yield was studied in the range of 1:1–1:4. As shown in Figure 4, the amount of methanol was found to be good for the yield of 1-methoxy-2-propanol. It was indicated that as methanol consumption increased with the molar ratio of PO to methanol from 1:1 to 1:4, the 1-methoxy-2-propanol yield improved rapidly from 20% to 61% at 5 minutes. As a result, the molar ratio of 1:4 could obtain the highest 1-methoxy-2-propanol yields in comparison to the other molar ratios. Furthermore, after the reaction time of 20 minutes, the yield of 1-methoxy-2-propanol kept mostly unchangeable, suggesting that the optimal molar ratio for this alcoholysis reaction is 1:4.

Figure 5 shows the effect of circulating flow rate on the 1-methoxy-2-propanol yield at a molar ratio of PO to methanol of 1:4 at 383 K. When the circulating flowrate was changed from 2 to 10 mL/min, the yields of 1-methoxy-2-propanol obviously increased from10% to 58% at the reaction time of 5 minutes. We guess this is because the mixing performance of PO, methanol, and $[N_{4444}][Buty]$ in the micro-tubular circulating reactor became good at a high liquid flow rate. The higher flow rate often reduced transfer resistance [26], and thereby resulted in a fast reaction rate. Therefore, it was demonstrated that the suitable flow rate for this reaction was set to 10 mL/min.

The effect of catalyst loading on the yield of 1-methoxy-2-propanol was studied by setting the catalyst dosage of $[N_{4444}][Buty]$ at 2.5 mol%, 5.0 mol%, 7.5 mol%, and 10 mol% of PO, respectively.

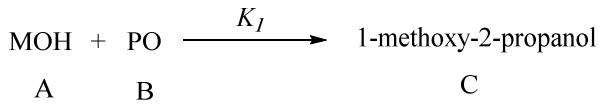
Figure 6 shows that the yield of 1-methoxy-2-propanol increased gradually with the increase of catalyst loading. The increase of catalyst amount provided more basic active sites and resulted to improve the yield of 1-methoxy-2-propanol. However, when the amount of catalyst further increased from 7.5 mol% to 10 mol% of PO, only a slight change was observed in the yield of 1-methoxy-2-propanol. This suggests that the further increase in the amount of catalyst is not very necessary. In this work, 7.5 mol% of PO was taken as the optimal catalyst loading and used in most of the alcoholysis experiments.

3.3 Reusability of [N_{4444}][Buty]

The stability and reusability is of importance for evaluation of a catalyst system. Thus, the reusability of [N_{4444}][Buty] catalyst in the alcoholysis reaction of PO with methanol in the micro-tubular circulating reactor was also investigated. As depicted in Figure 7, the results showed that the yield of 1-methoxy-2-propanol had no obviously change after five times. It was also found that the IR spectra (Figure 8) of reused [N_{4444}][Buty] after five runs were nearly the same as those of a fresh catalyst. Therefore, it was demonstrated that the IL [N_{4444}][Buty] exhibited its good recyclability in the alcoholysis reaction of PO.

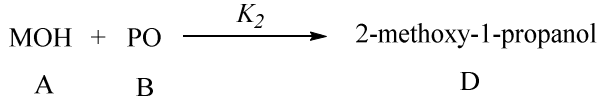
3.4 The Kinetic Model

The study of kinetics for [N_{4444}][Buty] in the alcoholysis reaction of PO with methanol was carried out in the temperature range of 363–383 K with reaction time of 20 minutes, PO/methanol molar ratio of 1:4, catalyst loading of 7.5 mol%, and circulating flow rate of 10 mL/min. The main reaction is expressed as:



(1)

The side reaction is:



(2)

where A, B, C and D are PO, methanol, 1-methoxy-2-propanol, and 2-methoxy-1-propanol, respectively. k_1 and k_2 are the forward reaction rate constant. According to the elementary reaction law [27], the rate equations for alcoholysis reactions (1) and (2) reaction equation are written as:

$$dC_C/\,dt = k_1 C_A^{n_1} C_B^{m_1} \quad (3)$$

$$dC_D/\,dt = k_2 C_A^{n_2} C_B^{m_2} \quad (4)$$

where t is reaction time, C_A, C_B, C_C, and C_D are the molar concentration of methanol, PO, 1-methoxy-2-propanol and 2-methoxy-1-propanol, respectively. n_1 and m_1 are the order of main reaction with respect to methanol and PO, respectively. n_2 and m_2 are the order of side reaction with respect to methanol and PO, respectively. Because the concentration of reactant methanol was much higher than that required for the alcoholysis of PO, the molar concentration of methanol (C_A) in the whole process of the reaction, can be considered as a constant. Let $k_1 C_A^{n_1} = K_1$, $k_2 C_A^{n_2} = K_2$, Eqs. (3) and (4) thus can be further simplified as:

$$dC_C/\,dt = K_1 C_B^{m_1} \quad (5)$$

$$dC_D/\,dt = K_2 C_B^{m_2} \quad (6)$$

A fourth-order Runge-Kutta method was used to integrate the Eqs. (5) and (6). The reaction rate constants (K_1 and K_2) and reaction orders (m_1 and m_2) can be estimated according to experimental data. And these parameter values at different temperatures are summarized in Table 1. In general, it

was indicated that the main reaction rate to 1-methoxy-2-propanol (K_1) was about 20 times larger than the side reaction rate to byproduct 2-methoxy-1-propanol (K_2) in the micro-tubular circulating reactor in the temperature range of 363-383 K. With the increase of temperature, the value of K_1 improved accordingly, implying that the reaction rate for main reaction can be promoted by enhancing the temperature. However, for side reaction, all the K_2 values were very small and it suggests that the side reaction can be effectively suppressed in the micro-tubular circulating reactor. Moreover, increasing the temperature also resulted to reduce the m_1 value. Then it is believed that the concentration of reactant PO has obviously less impact on the reaction rate of main reaction, when the reaction temperature increases gradually.

Moreover, with the reaction rate constants K_1 and K_2 at different temperatures, the activation energies and pre-exponential factors of main reaction (1) and side reaction (2) were calculated based on the Arrhenius law by drawing a linear fit between ln K_i and 1/T.

$$K_i = K_{i,0} e^{-E_{a,i}/RT} \tag{7}$$

Eq. (7) can be rewritten as:

$$\ln K_i = \ln K_{i,0} - E_{a,i}/RT \tag{8}$$

By plotting ln K_i versus 1/T, straight lines were shown in Figure 9. The values of the pre-exponential factor ($K_{1,0}$, $K_{2,0}$) and activation energy ($E_{a,1}$, $E_{a,2}$) were also listed in Table 2. The results indicated that all the correlation coefficients R^2 were above 0.99 and then the kinetic equations (5) and (6) could give a good description of the alcoholysis kinetic behavior. Moreover, the apparent activation energy for main reaction and side reaction were found to be as high as 180 kJ/mol and 176 kJ/mol. Then it was demonstrated that this alcoholysis process was really sensitive to

reaction temperature. This finding is consistent with the results of Luo et al [18]. In addition, the preexponential factors of 1-methoxy-2-propanol generation was near 80 times higher than that of byproduct 2-methoxy-1-propanol, which suggested that the main reaction rate to 1-methoxy-2-propanol was much greater than the side reaction rate. Therefore, it was concluded that increasing temperature could effectively promote the main reaction rate and thereby improve the yield of 1-methoxy-2-propanol in the micro-tubular circulating reactor.

4. Conclusions

In summary, the combination of micro-tubular circulating reactor with the IL $[N_{4444}][Buty]$ catalyst was successfully used for highly efficient synthesis of 1-methoxy-2-propanol via the alcoholysis of PO with methanol in this work. The rate of alcoholysis reaction in the micro-tubular circulating reactor was significantly enhanced in comparison with that in the stirred reactor. The reaction time was remarkably shortened to 20 minutes from 180 minutes as well as the yield of 1-methoxy-2-propanol reached 92%. Furthermore, the kinetic model for this alcoholysis reaction can give a good description of the alcoholysis kinetic behavior in the micro-tubular circulating reactor. The main reaction rate to 1-methoxy-2-propanol was found to be about 20 times greater than the side reaction rate to byproduct 2-methoxy-1-propanol. Based on the results obtained in this work, it is concluded that the micro-tubular circulating reactor system plus the IL $[N_{4444}][Buty]$ catalyst is a class of effective process intensification technique for highly efficient synthesis of 1-methoxy-2-propanol.

Acknowledgments

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Notes

The authors declare no competing financial interest.

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List of Tables, Schemes and Figures

Figure 5. Effect of circulating flow rate on the yield of 1-methoxy-2-propanol. Reaction conditions: PO (0.3 mol), methanol (1.2 mol), reaction temperature (383 K), catalyst loading (7.5 mol% of PO).

Figure 6. Effect of catalyst loading on the yield of 1-methoxy-2-propanol. Reaction conditions: PO (0.3 mol), methanol (1.2 mol), reaction temperature (383 K), circulating flow rate (10 mL/min).

Figure 7. Reusability of $[N_{4444}[Buty]$ for synthesis of 1-methoxy-2-propanol.

Figure 8. IR spectra of $[N_{4444}][Buty]$ after five runs.

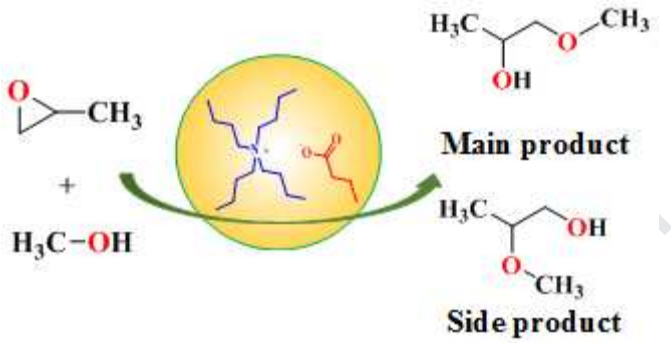
Figure 9. Arrhenius plots for the alcoholysis of PO with methanol.

Table 1. Calculated reaction rate constants and reaction orders at different temperatures.

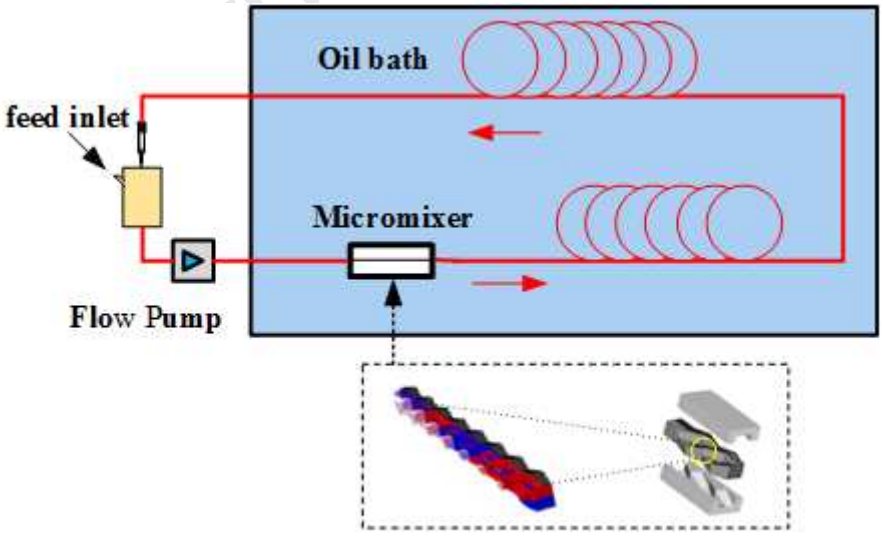
Time (K)	Main reaction (1)		Side reaction (2)	
	K_1 $(mol^{1-m_1}\ L^{m_1-1}\ min^{-1})$	m_1	K_2 $(mol^{1-m_2}\ L^{m_2-1}\ min^{-1})$	m_2
363	0.0218	0.7179	0.0010	0.2811
373	0.1004	0.5510	0.0051	0.5592
383	0.4889	0.5233	0.0209	0.3451

Table 2. Kinetics parameters for reactions.

Reaction	$K_{i,0}$ $(mol^{1-m_1}\ L^{m_1-1}\ min^{-1})$	$E_{a,i}$ (kJ mol^{-1})
Main reaction (1)	1.53×10^{24}	180
Side reaction (2)	1.99×10^{22}	176



Scheme 1



Scheme 2

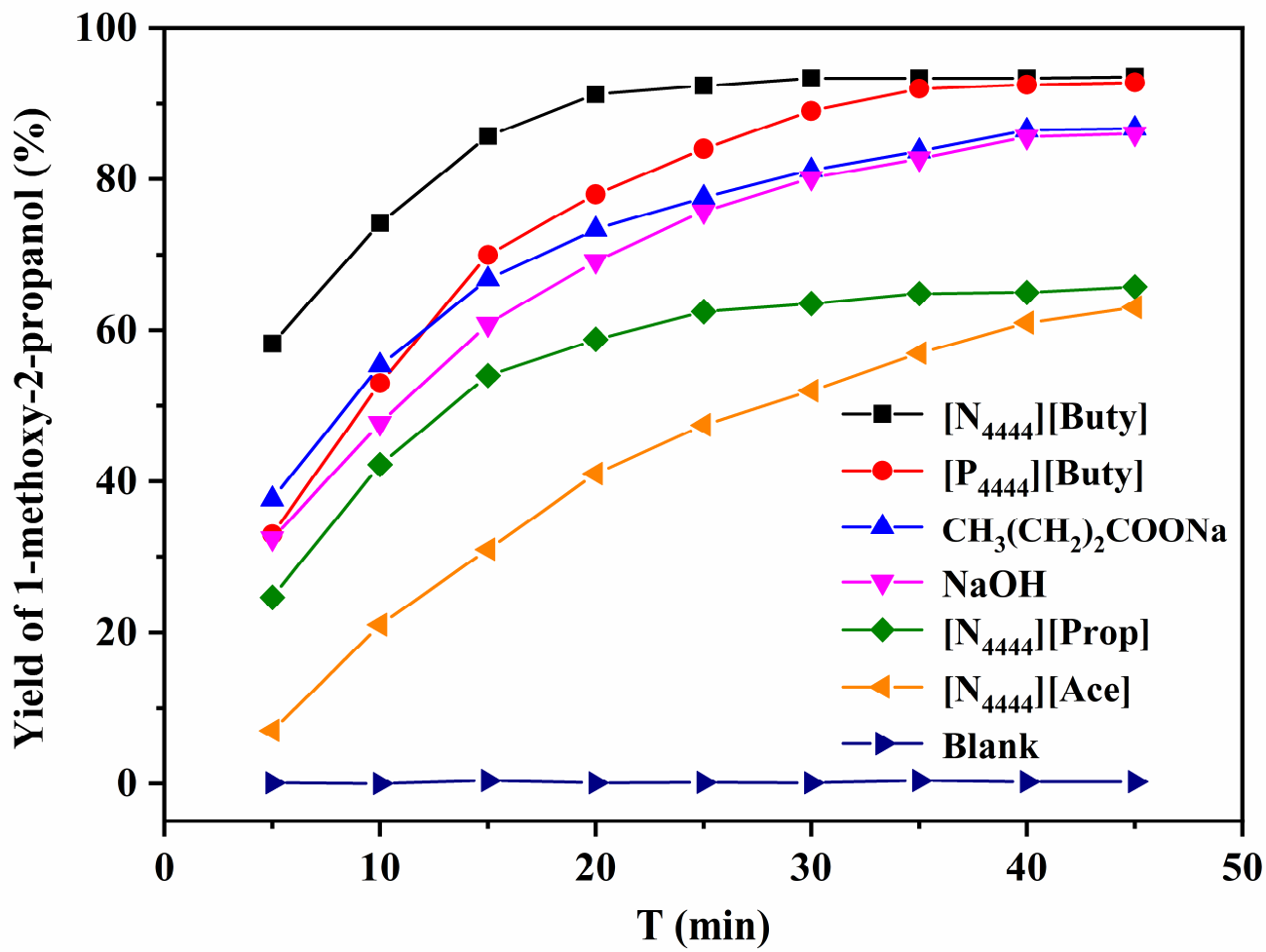


Figure 1

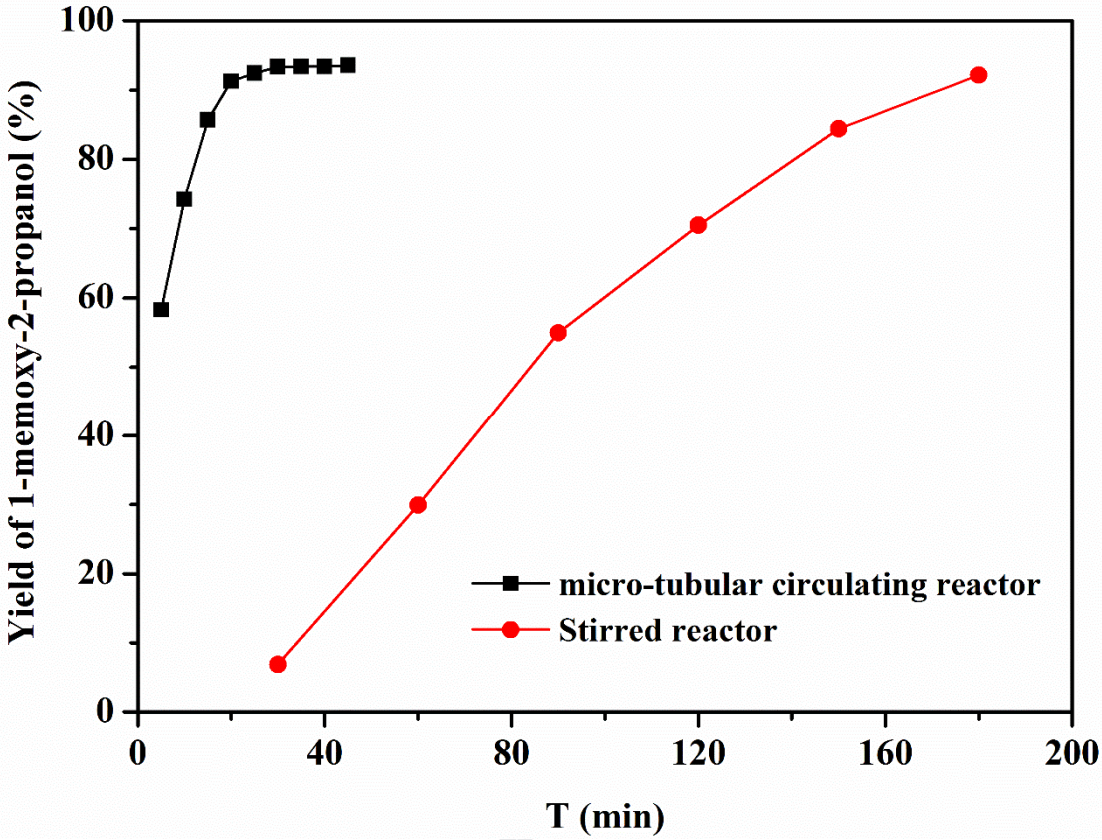


Figure 2

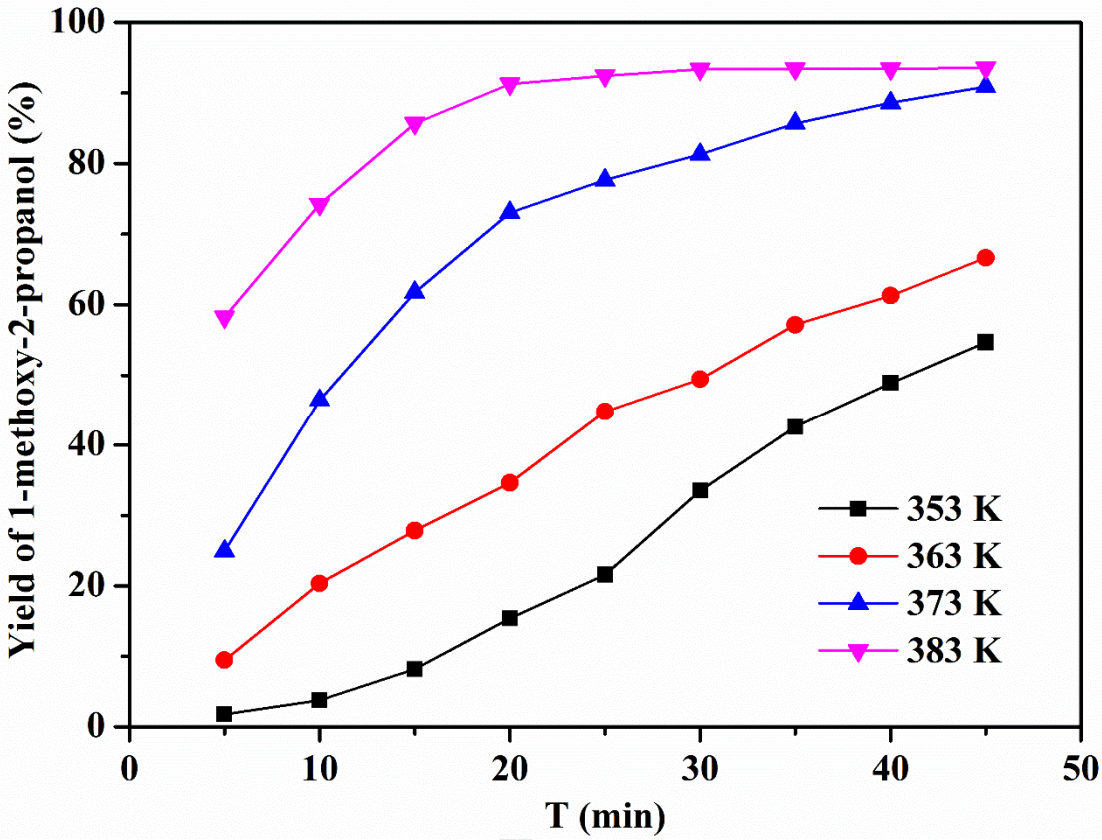


Figure 3

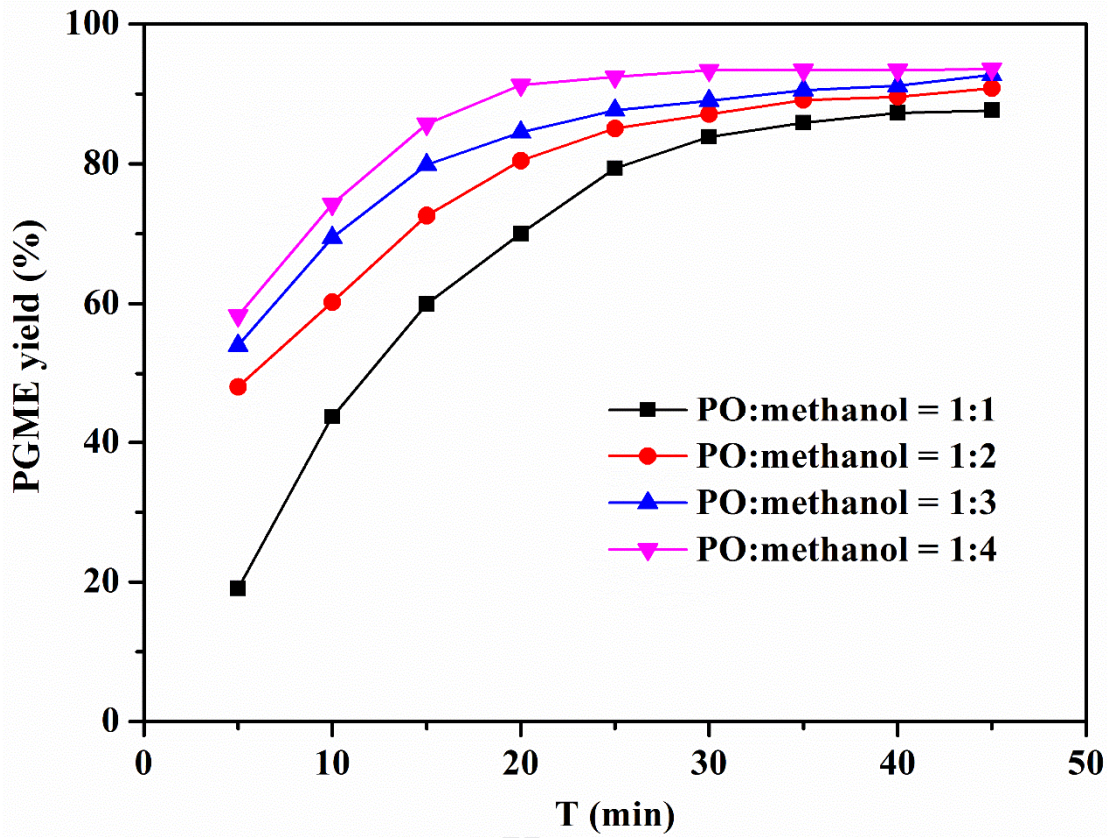


Figure 4

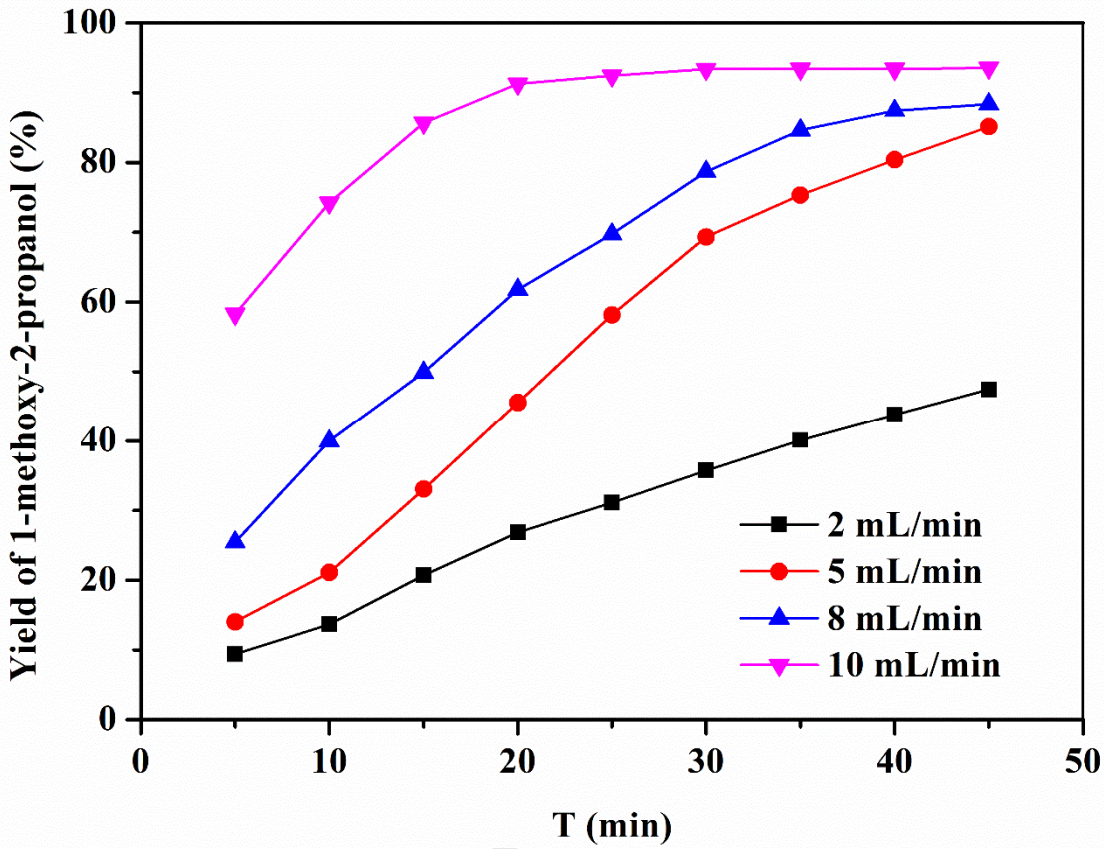


Figure 5

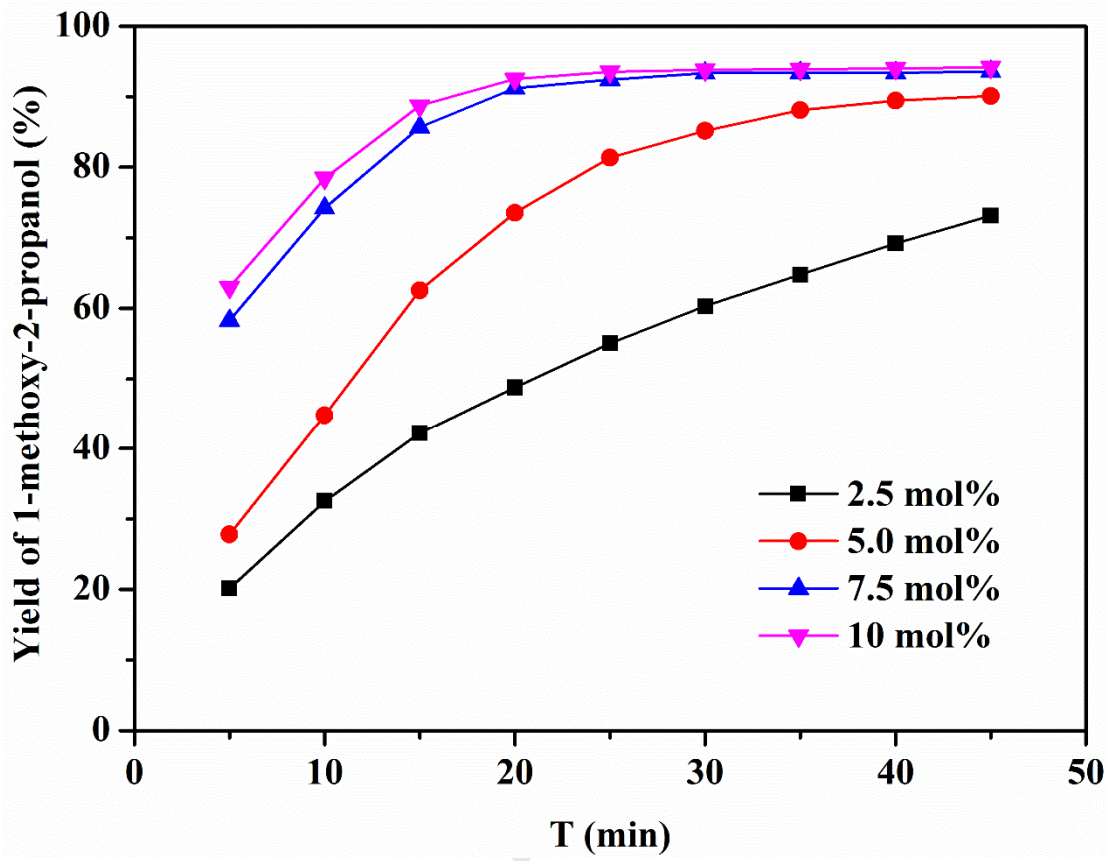


Figure 6

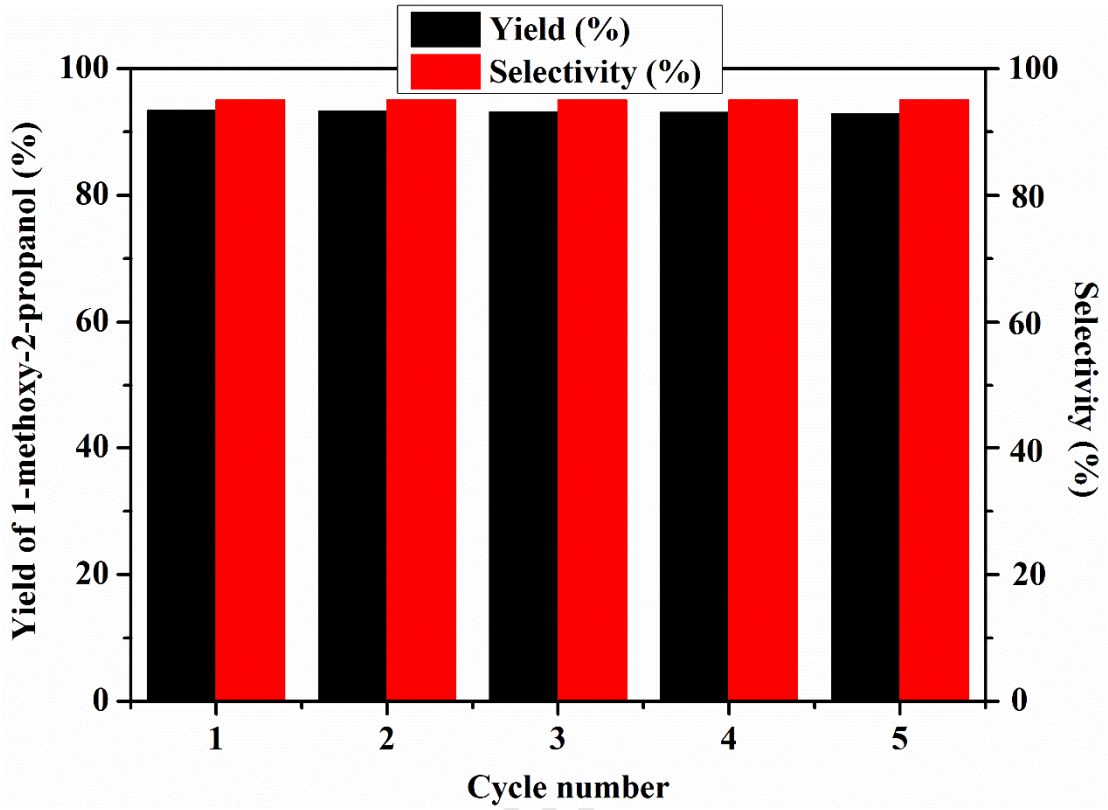


Figure 7

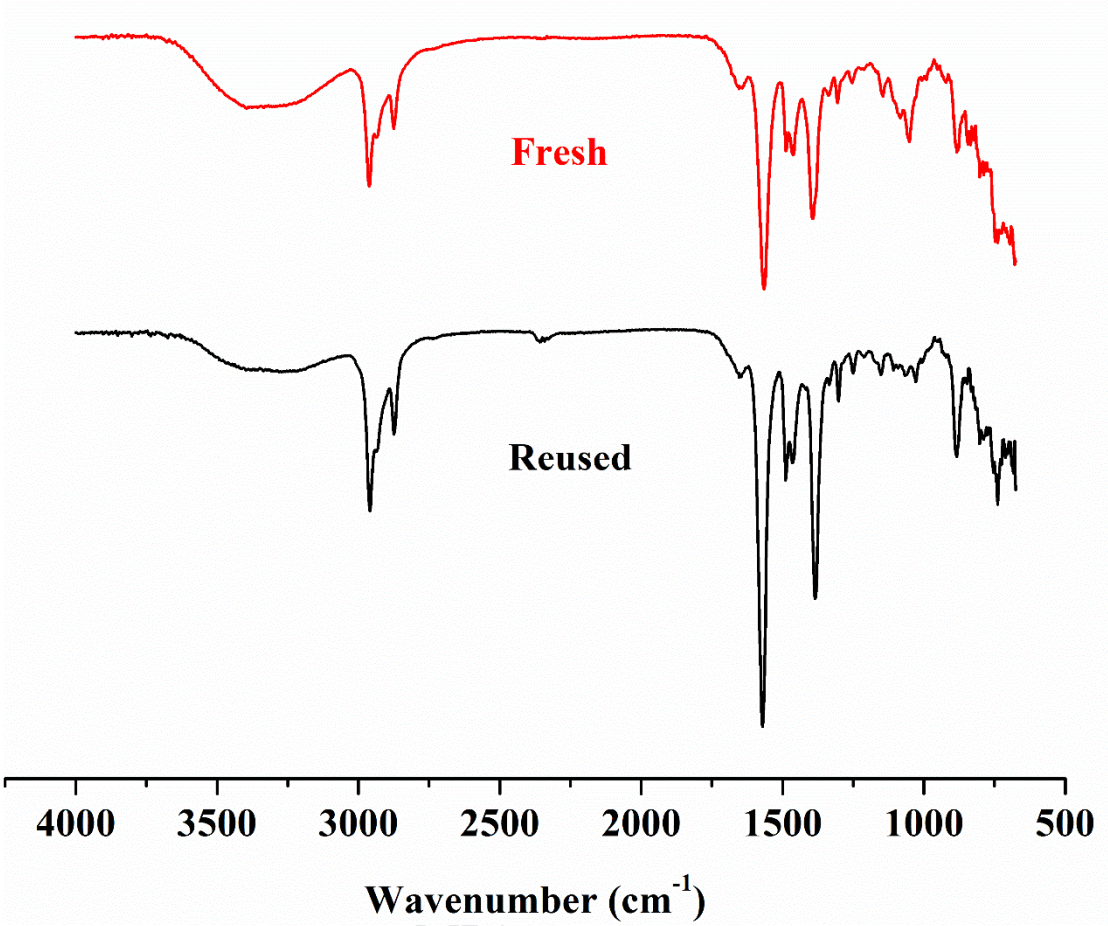


Figure 8

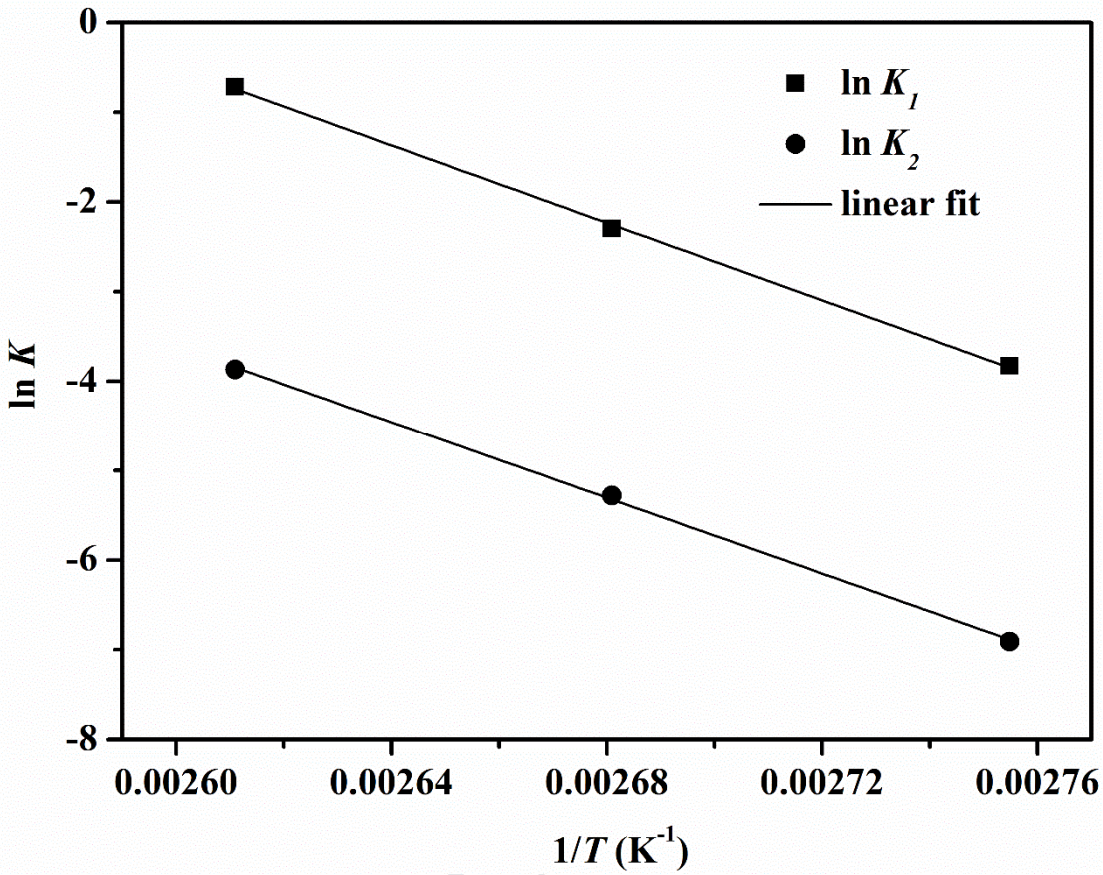


Figure 9