



# Isomerization and Redistribution of 2,5-Dichlorotoluene Catalyzed by $\text{AlCl}_3$ and Isomerization Thermodynamics

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The isomerization and redistribution reactions of 2,5-dichlorotoluene (2,5-DCT) over Lewis acidic  $\text{AlCl}_3$  catalyst were investigated at the reaction temperatures ranging from 392.15 K to 452.15 K. 2,6- (3,5-, 2,4-, 3,4-, and 2,3-) Dichlorotoluenes (DCT) with the yields of *ca.* 5.6%, 9.6%, 16.2%, 3.3%, and 2.3% were formed *via* the isomerization reactions at equilibrium. Chlorobenzene (CB), dichlorobenzene (DCB), and dichloroethylene (DCX) with the yields of *ca.* 0.5%, 19.2%, and 20.4% were formed *via* the redistribution reactions. Valuable chlorinated aromatics, DCT, DCB, and CB, with a high total yield of *ca.* 57% were formed *via* the catalytic isomerization and redistribution of 2,5-DCT. The isomerization thermodynamics analysis revealed that the isomerization reactions were endothermic and the yields of isomers were slightly affected by the reaction temperature.

**Keywords:** 2,5-Dichlorotoluene;  $\text{AlCl}_3$ ; Isomerization; Redistribution; Thermodynamics

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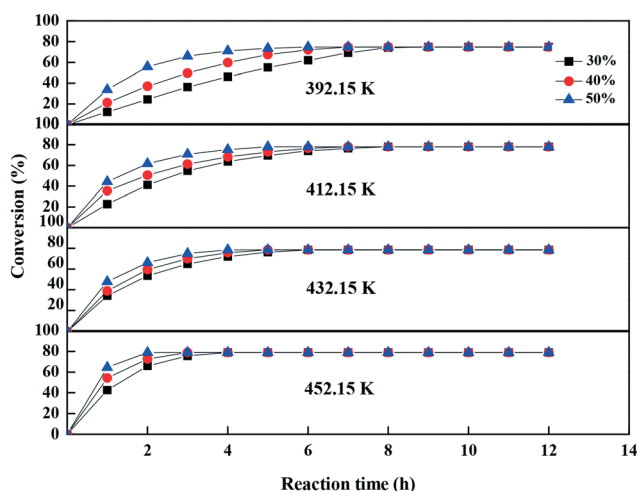
## 1. Introduction

Chlorinated toluene chemicals have abundant applications in the manufacture of pesticides, herbicides, medicines, and dyestuffs.<sup>1–8</sup> Dichlorotoluenes are conventionally produced by the chlorination of toluene with gaseous chlorine under mild reaction condition over metallic iron catalyst in China. Among the dichlorotoluenes, 2,6-dichlorotoluene (2,6-DCT), 2,4-dichlorotoluene (2,4-DCT), 3,4-dichlorotoluene (3,4-DCT), and 2,3-dichlorotoluene (2,3-DCT) are important raw materials in the synthesis of fine chemicals. However, 2,5-dichlorotoluene (2,5-DCT) with the selectivity of *ca.* 30% produced in the toluene chlorination process faces an oversupply problem due to its limited utility compared to its isomers. Although conversion of 2,5-DCT to high-valued isomers has been recently industrialized in the Jiangsu Beyond Chem. Co. Ltd. located at Zhenjiang, China, the process parameters have not been disclosed for the protection of technical secrets.

Isomerization reactions of xylene, dichlorobenzenes, and monochlorotoluene have been investigated over various catalysts, such as Pt/Fe-ZSM-5,<sup>9</sup>  $\text{La}_2\text{O}_3$ - (MgO-) modified HMC-22,<sup>10</sup> HZSM-5,<sup>11</sup> EU-1 zeolite,<sup>12</sup> hierarchical ZSM-5,<sup>13</sup> and  $\text{AlCl}_3$ -LiCl<sup>14,15</sup> catalysts. Interestingly, the Lewis acidic  $\text{AlCl}_3$ -LiCl catalyst exhibited good catalytic activity for the isomerization of 1,4-dichlorobenzene to 1,3-dichlorobenzene.<sup>14,15</sup> For the isomerization of dichlorotoluene, H $\beta$  and H $\beta$ -supported metallic Ag and Cu catalysts effectively catalyzed the isomerization of 2,5-DCT to 2,6-DCT and 2,4-DCT.<sup>16</sup> Although the

isomers of 2,5-DCT are high-value chemicals, the isomerization of 2,5-DCT has rarely been investigated.<sup>16</sup>

Metal chlorides, such as  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{CrCl}_2$ , LiCl,  $\text{SbCl}_5$ , and  $\text{SnCl}_4$ , containing an empty orbital to accept the electrons are conventionally used as the Lewis acidic catalysts for the chlorination,<sup>17–19</sup> isomerization,<sup>14,15,20</sup> dehydration,<sup>21,22</sup> alkylation, and acylation reactions. The Lewis acidic metal chloride catalysts could effectively catalyze the isomerization reactions of monochlorotoluenes and dichlorobenzenes at relatively lower reaction temperatures of 140–200 °C.<sup>14,15</sup> However, H $\beta$  and H $\beta$ -supported metallic Ag and Cu



**Fig. 1** Conversions of 2,5-DCT catalyzed by  $\text{AlCl}_3$  with different catalyst loadings at 392.15–452.15 K.

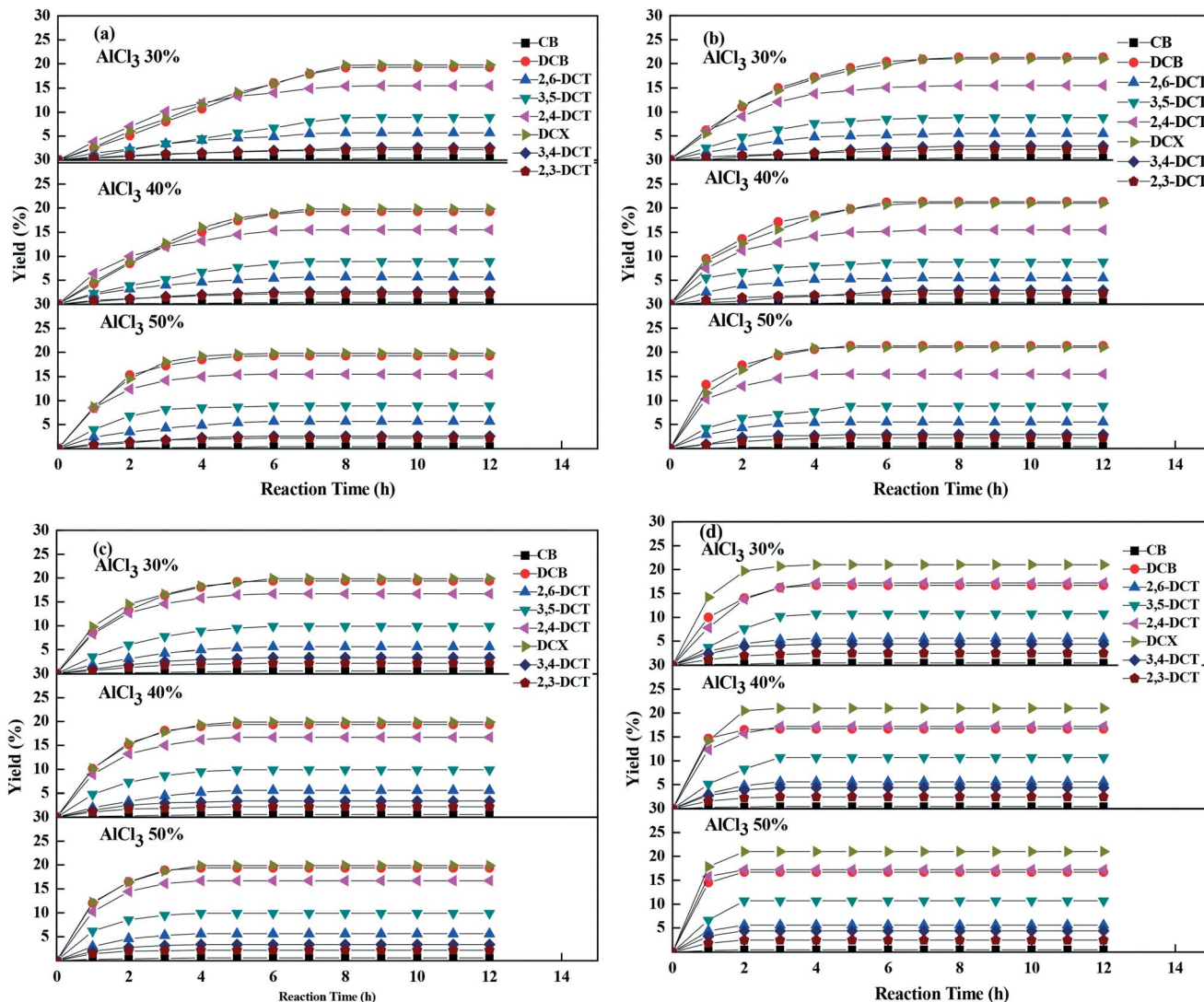
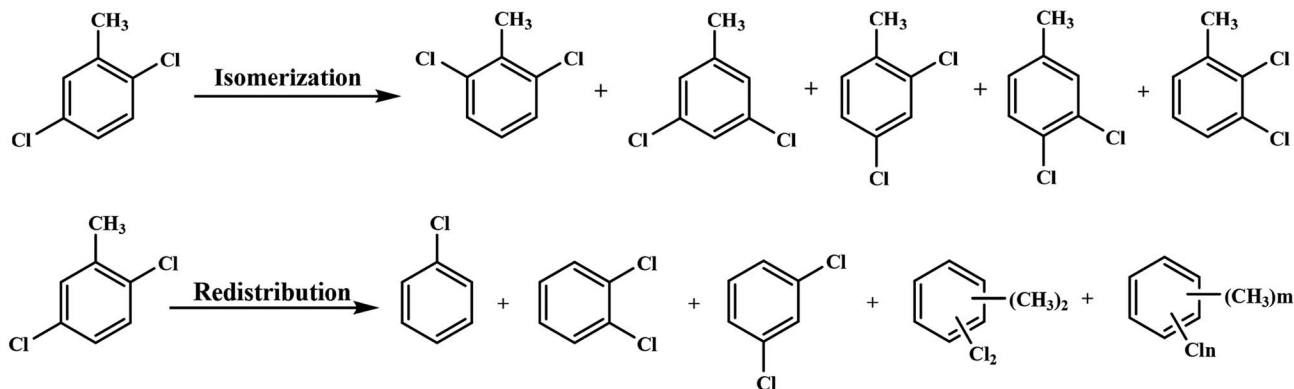


Fig. 2 Product yields in the conversion of 2,5-DCT catalyzed by AlCl<sub>3</sub> catalyst with the catalyst loading of 30%, 40% and 50% at (a) 392.15 K, (b) 412.15 K, (c) 432.15 K, and (d) 452.15 K, respectively.

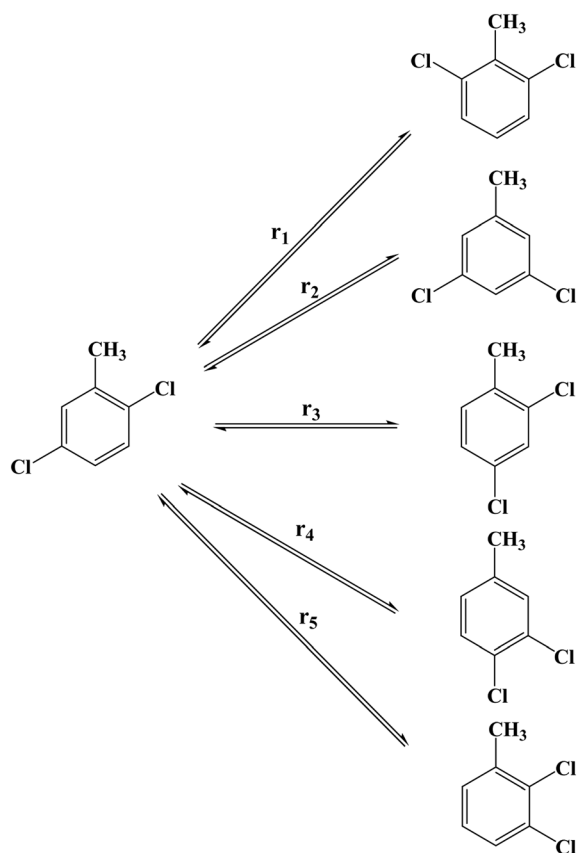
Table 1 Conversions of 2,5-DCT and product yields at equilibrium catalyzed by AlCl<sub>3</sub> at different reaction temperatures with different catalyst loadings<sup>a</sup>.

Reaction temperatures (K)	Catalyst loadings (wt%)	Equilibrium time (h)	Conversions of 2,5-DCT (%)	Product yields (%)								
				CB	DCB	2,6-DCT	3,5-DCT	2,4-DCT	DCX	3,4-DCT	2,3-DCT	Others
392.15	30%	9	74.8	0.4	19.3	5.7	8.9	15.5	19.8	2.6	2.2	0.4
	40%	7										
	50%	6										
412.15	30%	8	77.9	0.4	21.3	5.5	8.8	15.5	21.0	2.9	2.2	0.3
	40%	6										
	50%	5										
432.15	30%	6	78.5	0.6	19.4	5.6	9.9	16.7	19.9	3.4	2.2	0.8
	40%	5										
	50%	4										
452.15	30%	4	78.9	0.5	16.7	5.6	10.7	17.2	21.0	4.4	2.5	0.3
	40%	3										
	50%	2										

<sup>a</sup>The conversions of 2,5-DCT and product yields were the average values of the equilibrium data obtained at different catalyst loadings.



Scheme 1 Reactions in the catalytic conversion of 2,5-DCT over AlCl<sub>3</sub> catalyst.



Scheme 2 Independent isomerization reactions of 2,5-DCT.

catalysts could catalyze the isomerization and redistribution reactions of 2,5-DCT at higher reaction temperatures of 310–350 °C.<sup>16</sup> To the best of our knowledge, the Lewis acidic metal chloride catalysts have not been used for the catalytic isomerization and redistribution of dichlorotoluene. The catalytic activity of Lewis acidic catalyst in the isomerization and redistribution of 2,5-DCT is worth of investigation.

In our present work, AlCl<sub>3</sub> was used as the Lewis acid catalyst for the isomerization and redistribution of 2,5-DCT. The thermodynamics of the isomerization reactions of 2,5-DCT to 2,6-DCT, 3,5-DCT, 2,4-DCT, 3,4-DCT, and 2,3-DCT were analyzed.

## 2. Experimental

### 2.1. Chemicals

2,5-DCT, 2,6-DCT, 3,5-DCT, 2,4-DCT, 3,4-DCT, 2,3-DCT, 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), chlorobenzene (CB), *n*-butanol, and anhydrous AlCl<sub>3</sub> were of agent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Catalytic conversion of 2,5-DCT

Isomerization and redistribution reactions of 2,5-DCT catalyzed by AlCl<sub>3</sub> were carried out in a four-necked round bottom glass flask (250 mL) equipped with a sampling outlet, a thermometer, a reflux condenser, and a mechanical stirrer. 100 mL of 2,5-DCT was added into the flask. When the reaction solution was heated to a given temperature, a given amount of AlCl<sub>3</sub> catalyst was added into the reaction solution. The weight percentages of AlCl<sub>3</sub> catalyst in the reaction mixtures were set at 30%, 40%, and 50%, respectively. At certain time intervals, about 1 mL of sample was taken out. The remained AlCl<sub>3</sub> catalyst in the sample was hydrolyzed with water. The reaction mixture was analyzed on an Agilent GC 7890A gas chromatograph with a KR-ELJB capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. *n*-Butanol (0.20 mL) was used as the internal standard.

## 3. Results and discussion

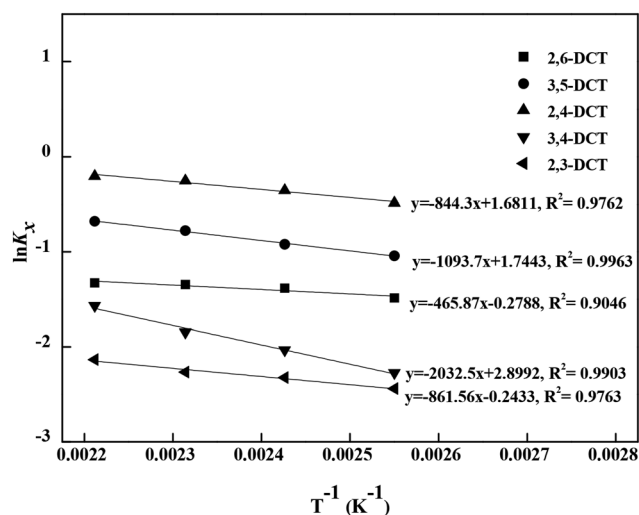
### 3.1. Conversion of 2,5-DCT catalyzed by AlCl<sub>3</sub>

When AlCl<sub>3</sub> was used as the catalyst for the conversion of 2,5-DCT, CB, DCB (including 1,4-DCB and 1,3-DCB), 2,6-DCT, 3,5-DCT, 2,4-DCT, 3,4-DCT, 2,3-DCT, and dichloroethylene (DCX) were detected as the main products (Figures 1,2). The 2,5-DCT conversions and product yields increased with the increase in catalyst loading and reaction temperature in the initial reaction time period. Reaction equilibriums were obtained when the catalyst loading was 50% at 392.15, 412.15, 432.15, and 452.15 K for 6, 5, 4, and 2 h, respectively. High catalyst loading shortened the time required for the reaction to reach equilibrium. The reactions reached equilibrium in 9 h at the reaction temperatures of 392.15–452.15 K and the AlCl<sub>3</sub> catalyst loadings of 30–50%. The 2,5-DCT conversions at equilibrium were *ca.* 74.8%, 77.9%, 78.5%, and 78.9% and the average yields of CB, DCB,

**Table 2** Experimentally determined compositions of reaction mixtures at equilibrium and  $K_x$  values of the isomerization reactions of 2,5-DCT over  $AlCl_3$  catalyst.

Reaction Temperatures (K)	$x_i^a$						$K_x$				
	2,5-DCT	2,6-DCT	3,5-DCT	2,4-DCT	3,4-DCT	2,3-DCT	$K_{x(r1)}$	$K_{x(r2)}$	$K_{x(r3)}$	$K_{x(r4)}$	$K_{x(r5)}$
392.15	0.252	0.057	0.089	0.155	0.026	0.022	0.226	0.353	0.615	0.103	0.087
412.15	0.221	0.055	0.088	0.155	0.029	0.022	0.251	0.398	0.701	0.131	0.098
432.15	0.215	0.056	0.099	0.167	0.034	0.022	0.260	0.460	0.777	0.158	0.104
452.15	0.211	0.056	0.107	0.172	0.044	0.025	0.265	0.508	0.815	0.209	0.118

<sup>a</sup> $x_i$  is the ratios of mole numbers of products to initial mole number of 2,5-DCT.



**Fig. 3** Plots of  $\ln K_x$  versus  $T^{-1}$  at different reaction temperatures of 392.15–452.15 K.

2,6-DCT, 3,5-DCT, 2,4-DCT, DCX, 3,4-DCT and 2,3-DCT were around 0.5%, 19.2%, 5.6%, 9.6%, 16.2%, 20.4%, 3.3%, and 2.3%, respectively (Table 1). At the equilibrium, the total dichlorotoluene yield was ca. 37% with a 2,5-DCT conversion of ca. 78%. The dichlorotoluene yields slightly increased with the increase in reaction temperature.

The conversion of 2,5-DCT included isomerization and redistribution reactions, which are summarized in Scheme 1. 2,6-DCT, 3,5-DCT, 2,4-DCT, 3,4-DCT, and 2,3-DCT were formed *via* the isomerization reactions of 2,5-DCT while CB, DCB, and DCX were formed *via* the redistribution reactions.

### 3.2. Thermodynamics of isomerization reactions

**3.2.1. General aspects.** The thermodynamics of five independent isomerization reactions were analyzed. The isomerization reactions of 2,5-DCT to 2,6-DCT, 3,5-DCT, 2,4-DCT, 3,4-DCT, and 2,3-DCT are denoted as  $r_1$ ,  $r_2$ ,  $r_3$ ,  $r_4$ , and  $r_5$ , respectively (Scheme 2).

According to the second law method (equilibrium constant measurement), for a general chemical reaction in the liquid phase, the true thermodynamic equilibrium constant,  $K_a$ , is defined as the ratio of the activity,  $a_i$ , of product and reactant under equilibrium condition. Verevkin et al<sup>15</sup> suggested that the activity coefficients of monochlorotoluenes (or dichlorobenzenes) are identical. In our present research, the activity coefficients of the dichlorotoluene isomers are considered identical. Therefore, it is suggested that that  $K_a$  can be replaced by  $K_x$ , i.e.  $K_a = K_x$ . The ratios of the mole numbers of the

formed isomers to initial mole number of 2,5-DCT are listed in Table 2. The equilibrium constants for the five independent isomerization reactions were calculated according to the following equation.

$$K_{x(r_i)} = x_i / x_{i(2,5)} \quad (1)$$

where  $x_i$  is the ratio of the mole number of the formed DCT ( $i$ ) to the initial mole number of 2,5-DCT at equilibrium.  $x_{i(2,5)}$  is the ratio of the mole number of the remained 2,5-DCT to the initial mole number of 2,5-DCT at equilibrium. The equilibrium constants,  $K_{x(r_i)}$ , are listed in Table 2.

**3.2.2. Standard thermodynamic functions.** The basic thermodynamic equation for the standard reaction Gibbs free energy is listed as follows.

$$\Delta_{r_i}G_m^0 = \Delta_{r_i}H_m^0 - T \times \Delta_{r_i}S_m^0 \quad (2)$$

where  $\Delta_{r_i}G_m^0$  represents the standard reaction Gibbs function.  $\Delta_{r_i}H_m^0$  and  $\Delta_{r_i}S_m^0$  are the standard reaction enthalpy and the entropy of the isomerization reaction, which are assumed as constant in the reaction temperature range.

$\Delta_{r_i}G_m^0$  is a function of reaction temperature and can be calculated by standard equilibrium constant,  $K_{x(r_i)}$ .

$$\Delta_{r_i}G_m^0 = -RT \times \ln K_{x(r_i)} \quad (3)$$

Substituting  $\Delta_{r_i}G_m^0$  in equation (2) by equation (3), the equation (4) can be obtained.

$$\ln K_{x(r_i)} = -\Delta_{r_i}H_m^0 / (RT) + \Delta_{r_i}S_m^0 / R \quad (4)$$

By plotting  $\ln K_{x(r_i)}$  versus  $1/T$ , the slope is  $-\Delta_{r_i}H_m^0/R$  and the intercept is  $\Delta_{r_i}S_m^0/R$  (Figure 3). Figure 3 shows that the straight lines with the coefficients ( $R^2$ ) of above 0.9046 were obtained, indicating that the experimental data well fitted the equation (4). The standard thermodynamic parameters,  $\Delta_{r_i}H_m^0$ ,  $\Delta_{r_i}S_m^0$ , and  $\Delta_{r_i}G_m^0$  for the reactions 1–5 are listed in Table 3.

All the  $\Delta_{r_i}H_m^0$  values of 2,5-DCT isomerization reactions were positive, indicating that these isomerization reactions are endothermic. The  $\Delta_{r_i}G_m^0$  values were in an order of  $\Delta_{r_5}G_m^0 > \Delta_{r_4}G_m^0 > \Delta_{r_1}G_m^0 > \Delta_{r_2}G_m^0 > \Delta_{r_3}G_m^0$  while the  $K_{x(r_i)}$  values were in a reverse order of

**Table 3** Thermodynamic functions  $\Delta_r H_m^0$ ,  $\Delta_r S_m^0$  and  $\Delta_r G_m^0$  of reactions 1–5.

Reactions	Reaction Temperatures (K)	$K_{x(r)}$	$\Delta_r H_m^0$ /kJ mol <sup>-1</sup>	$\Delta_r S_m^0$ /J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta_r G_m^0$ /kJ mol <sup>-1</sup>
$r_1$	392.15	0.226	3.87	-2.32	4.78
	412.15	0.251			4.83
	432.15	0.260			4.87
	452.15	0.265			4.92
$r_2$	392.15	0.353	9.09	14.50	3.41
	412.15	0.398			3.12
	432.15	0.460			2.83
	452.15	0.508			2.54
$r_3$	392.15	0.615	7.02	13.98	1.54
	412.15	0.701			1.26
	432.15	0.777			0.98
	452.15	0.815			0.70
$r_4$	392.15	0.103	16.90	24.10	7.45
	412.15	0.131			6.88
	432.15	0.158			6.40
	452.15	0.209			5.91
$r_5$	392.15	0.087	7.16	-2.02	7.96
	412.15	0.098			8.00
	432.15	0.104			8.04
	452.15	0.118			8.08

$K_{x(r3)} > K_{x(r2)} > K_{x(r1)} > K_{x(r4)} > K_{x(r5)}$ . The results revealed that the product yields in the isomerization of 2,5-DCT at equilibrium depended on the chemical structures of the DCT isomers. 2,4-DCT was favorably formed. The equilibrium constants slightly increased with the reaction temperature.

## 4. Conclusions

Isomers of 2,5-dichlorotoluene, dichlorobenzene, chlorobenzene, and dichloroxylene were synthesized by the isomerization and redistribution reactions of 2,5-dichlorotoluene over  $AlCl_3$  catalyst. 2,4-Dichlorotoluene was favorably formed with the yield of ca. 16.2% via the isomerization reaction at equilibrium. Dichlorobenzene and dichloroxylene with the yields of 19.2% and 20.4% were formed via the redistribution reaction, respectively. The thermodynamics analysis showed that the isomerization reactions are endothermic and the standard reaction Gibbs free energies are positive. The equilibrium constants changed slightly with temperature.

It is worth noting that the total yield of high-value dichlorotoluene, dichlorobenzene, and monochlorobenzene over  $AlCl_3$  catalyst was ca. 57%, which was 2 times those over  $H\beta$  and  $H\beta$ -supported metallic Ag and Cu catalysts.<sup>16</sup>  $AlCl_3$  catalyst has a potential application for the catalytic conversion of 2,5-dichlorotoluene to high-valued chlorinated aromatics via the isomerization and redistribution reactions.

## Conflict of interest

There are no conflicts to declare.

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