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Short communication

# Intrinsic kinetics of direct oxidative carbonylation of vapour phase methanol to dimethyl carbonate over Cu-based catalysts

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## Abstract

In this paper, the process of direct oxidative carbonylation of vapour phase methanol to dimethyl carbonate (DMC) is investigated. The impregnation method is recommended to prepare the catalyst using $CuCl_2$ as precursor. Activated carbon AC1 is employed as support and heteropolyacid (HPA) as promoter or as the second support. The direct oxidative carbonylation of vapour phase methanol to DMC is a very complex reaction accompanied by by-products. By means of a modified Gauss–Newton method, an intrinsic double-rate kinetic model has been obtained. Residue analysis and variance tests show that the model is adequate. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Dimethyl carbonate; Methanol; Oxidative carbonylation; Catalyst; Kinetics

## 1. Introduction

Dimethyl carbonate (DMC) is a non-irritant, non-toxic chemical. DMC has two carbon centres at which a nucleophile may react: the carbonyl and the methyl group. Thus, DMC is a useful agent for methylation and carbonylation. As a green chemical intermediate, DMC is a safe substitute for dimethyl sulphate and phosgene in many industrial processes [1]. Furthermore, DMC can be characterised overall as a very good blending component and an outstanding oxygenating agent (due to its very high oxygen content, 53 wt.%) for environmental gasoline. The distribution of DMC in gasoline–water two-phase systems is much more favourable than for the C1–C3 light alcohols. Even more recently, automotive emissions testing with DMC within Amoco has indicated that DMC is a more effective oxygenating agent than MTBE. DMC reduced total hydrocarbon and CO emissions more than MTBE at the same weight percentage of oxygen in the fuel [2,3]. Finally, DMC is an excellent solvent in the medium boiling range. So, in recent years, DMC has attracted industrial and academic interest [4–6].

The conventional synthesis of DMC is via the reaction of methanol and phosgene. However, there is increasing interest in replacing the use of toxic phosgene or the intermediates derived therefrom, such as the chloroformic ester, by other processes. These methods result in the production of hydrogen chloride and thereby lead to the undesirable production of chloride-containing by-products. Romano et al. [1] developed a two-step slurry process to make DMC from the oxidative carbonylation of methanol. Cuprous chloride was used as the catalyst. Perrotti [7] described a process in which an alcohol reacted with oxygen and carbon monoxide in solution in the presence of cuprous chloride complexed with an organic base bound to the copper atoms by coordinate bonds to produce dihydrocarbyl carbonates. Homogeneous catalysts are very difficult to separate from the products. This difficult separation, which results in not only the loss of catalyst but, more importantly, product impurity, emphasises the undesirable nature of such homogeneous catalysts. To overcome these determinant factors, Curnutt and Mich [8] developed a gas phase one-step continuous flow process using a carbon-supported cupric chloride catalyst. The gas phase one-step process is more desirable because it is more economical than the liquid phase batch operation. However, such a $CuCl_2$/carbon catalyst suffers deactivation due to the loss of chloride. In order to regenerate the deactivated catalyst, hydrogen chloride must be added to the reactor or a portion of the catalyst must be removed from the reactor and subjected to treatment with HCl. These highly acidic agents introduce an important corrosion problem.

The direct oxidative carbonylation of vapour phase methanol to DMC is a very complex reaction accompanied

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by by-products. So far, a kinetic model has not been reported. In this paper, we prepared $CuCl_2/C$ catalysts [9] and obtained the power-law intrinsic kinetic model. In previous research [10], we elaborately selected a Cl-containing compound which can be added as a constituent to the reactant methanol to cyclically regenerate the deactivated catalyst; after several regeneration cycles, the activity remains unchanged. As the catalyst lifetime approaches completion, the process of regeneration can be carried out immediately. This guarantees that every experimental rate is measured at the same catalytic activity.

## 2. Experimental details

### 2.1. Catalyst preparation

In this study, an appropriate support such as activated charcoal was used. The catalysts were prepared by impregnating supports (crushed to 20–40 mesh, 0.85–1.70 mm) with ethanol solutions of $CuCl_2$ and ammonium phosphomolybdate (heteropolyacid, HPA). They were dried at 105–120°C and calcined in an air flow at 170°C for 10 h.

In order to achieve efficient loading of the catalyst precursor to obtain an excellent catalytic performance, commercial activated charcoal should be free of impurities, such as silica, metal ions, ash and mineral material. It is thus necessary to pre-treat and chemically modify the surface of activated charcoal as follows: (a) by acid–base washing following a standard procedure; the carbon was washed for 24 h with 10 bed volumes of 0.5 M aqueous sodium hydroxide solution, demineralised water until $pH \leq 9$, for 24 h with 10 bed volumes of 0.5 M hydrochloric acid and finally demineralised water until neutral (pH 6); then the carbon was dried overnight at 105–120°C; (b) oxidation for 1 h in boiling 6 M $HNO_3$, followed by extensive washing with distilled water; (c) impregnation activated charcoal oxidised by $HNO_3$ with an ethanol solution of ammonium phosphomolybdate.

### 2.2. Catalytic performance and kinetic experiment

The evaluation tests of the catalysts and the measurement of kinetic data were performed in a U-type tube fixed bed reactor (∅ 18×3), which was immersed fully in an oil-bath. Fig. 1 shows the experimental flow diagram. The loading of the reactor was achieved by filling it (nearly 50 vol.%) with quartz sand. The first and last stages of the reactor were also filled with quartz sand. The apparatus was flushed with nitrogen and then with reactant feedstock. Liquid methanol (analytically pure) was fed to a vaporiser operated at 185°C with an LC pump which allows small amounts of $CH_3OH$ to be added to the system under pressure. Carbon monoxide (99%) and oxygen diluted with an inert gas, such as nitrogen, were fed through gas flow meters individually, and then mixed with evaporated methanol. The entire reaction feed was contacted with the catalytic bed under carbonylation conditions so as to prepare DMC. The molar ratio of the inlet reaction mixture feed gas was: CO, 0.35–0.69; $O_2$, 0.059–0.124; $CH_3OH$, 0.24–0.44. The variation of the concentration of each component is so large that the power exponents have a high confidence level in the reaction kinetics equation. The gas hourly space velocity was about $2000\,h^{-1}$, and the reaction temperature and pressure were (110.0–140.0)±0.5°C and 2.0 MPa, respectively.

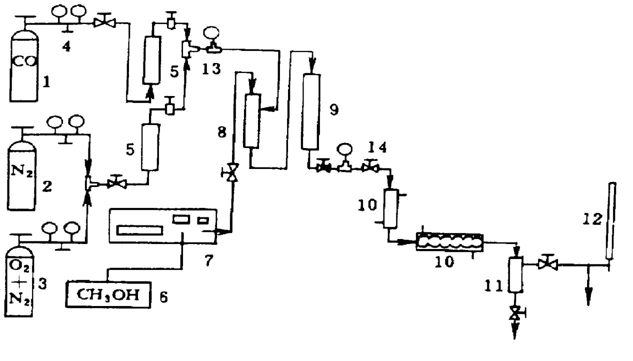

Fig. 1. Experimental flow diagram: 1, CO cylinder, 2, $N_2$ cylinder, 3, $N_2+O_2$ cylinder, 4, reducing valve, 5, mass flow meter, 6, methanol vessel, 7, LC pump, 8, vaporiser, 9, reactor, 10, condenser, 11, separation, 12, soapsuds flow meter, 13, pressure gauge, 14, reducing valve.

After condensation, gas–liquid separation and depressurisation, the reaction products were continuously monitored on-line by a double-column GC-900B (Shanghai, China) with a thermal conductivity detector. The gas phase was analysed by gas chromatography (GC) using a TDX-02 column (80–100 mesh); analysis of liquid samples was carried out by GC using organic 402 monomer columns (60–80 mesh).

The ratio of the height of the catalytic bed to the granular diameter and the ratio of the diameter of the catalytic bed to the granular diameter accord with the demand of a plug flow reactor. During this series of experimental runs, the temperature difference in the axial direction was less than ±0.5°C, and both the internal diffusion and external diffusion resistances were negligible.

Blank runs under catalytic conditions, i.e. with all the reactants present except the catalytic precursor, gave no catalytic product; this shows that the quartz sand and the inner wall of the reactor have no influence on the kinetic test. Extensive and thorough cleaning of the reactor was necessary to ensure the absence of impurities remaining from the preceding experiments.

## 3. Double-rate kinetic model

### 3.1. Experimental data

In order to obtain the reaction rate equation, 22 runs were carried out (Table 1).

Methanol conversion $x_M$, DMC selectivity $S_{DMC}$ and yield $Y_{DMC}$ can be calculated as follows:

Table 1
Experimental data of reaction kinetics[a]

| No. | $T$ (°C) | $N_{T,1}$ (mol min$^{-1}$) | $y_{M,1}$ | $y_{CO,1}$ | $y_{O2,1}$ | $x_M$ | $S_{DMC}$ | $Y_{DMC}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 120 | 0.010083 | 0.4236 | 0.3559 | 0.1058 | 0.1359 | 0.6477 | 0.0880 |
| 2 | 120 | 0.011785 | 0.2765 | 0.4652 | 0.1239 | 0.1770 | 0.5609 | 0.0993 |
| 3 | 120 | 0.010512 | 0.3100 | 0.5559 | 0.0643 | 0.2450 | 0.5843 | 0.1432 |
| 4 | 120 | 0.010968 | 0.2183 | 0.6531 | 0.0617 | 0.2299 | 0.5965 | 0.1372 |
| 5 | 120 | 0.010109 | 0.3175 | 0.4524 | 0.1105 | 0.2028 | 0.5607 | 0.1137 |
| 6 | 120 | 0.010558 | 0.3087 | 0.4738 | 0.1044 | 0.1906 | 0.6015 | 0.1146 |
| 7 | 120 | 0.010874 | 0.2770 | 0.5096 | 0.1025 | 0.2267 | 0.5753 | 0.1304 |
| 8 | 120 | 0.011123 | 0.2464 | 0.5441 | 0.1006 | 0.1982 | 0.5652 | 0.1120 |
| 9 | 110 | 0.011040 | 0.2169 | 0.6551 | 0.0614 | 0.2054 | 0.5363 | 0.1101 |
| 10 | 120 | 0.011022 | 0.2173 | 0.6548 | 0.0614 | 0.2135 | 0.5965 | 0.1274 |
| 11 | 130 | 0.011014 | 0.2174 | 0.6547 | 0.0614 | 0.2459 | 0.5551 | 0.1365 |
| 12 | 140 | 0.011002 | 0.2177 | 0.6545 | 0.0613 | 0.2407 | 0.5894 | 0.1419 |
| 13 | 110 | 0.010478 | 0.3110 | 0.5560 | 0.0638 | 0.2175 | 0.5982 | 0.1301 |
| 14 | 120 | 0.010446 | 0.3120 | 0.5552 | 0.0637 | 0.2431 | 0.6573 | 0.1598 |
| 15 | 130 | 0.010443 | 0.3121 | 0.5552 | 0.0637 | 0.2549 | 0.6505 | 0.1658 |
| 16 | 140 | 0.010428 | 0.1325 | 0.5548 | 0.0637 | 0.2659 | 0.6503 | 0.1729 |
| 17 | 110 | 0.006999 | 0.2822 | 0.5944 | 0.0593 | 0.2144 | 0.6238 | 0.1337 |
| 18 | 120 | 0.006999 | 0.2822 | 0.5944 | 0.0593 | 0.2199 | 0.6316 | 0.1389 |
| 19 | 130 | 0.006999 | 0.2822 | 0.5944 | 0.0593 | 0.2388 | 0.6323 | 0.1510 |
| 20 | 140 | 0.007017 | 0.2822 | 0.5949 | 0.0593 | 0.2575 | 0.6146 | 0.1583 |
| 21 | 120 | 0.010111 | 0.4224 | 0.3567 | 0.1060 | 0.1386 | 0.6545 | 0.0907 |
| 22 | 120 | 0.011756 | 0.2772 | 0.4647 | 0.1238 | 0.1856 | 0.6413 | 0.1190 |

[a] $P$=2.0 Mpa; $W$=1.0416 g; $d_p$=20–40 mesh.

$$x_M = \frac{N_{T,1} y_{M,1} - N_{T2,} y_{M,2}}{\mathrm{N}_{T,1} y_{M,1}} \tag{1}$$

$$S_{DMC} = \frac{y_{DMC,2}}{y_{DMC,2} + y_{DMO,2}} \tag{2}$$

$$y_{DMC} = x_M S_{DMC} = \frac{2y_{DMC,2}}{y_{M,1}(1 + 1.5y_{DMC,2} + 25y_{DMO,2})} \tag{3}$$

### 3.2. Kinetic model

According to the analysis of production, the liquid products include dimethyl carbonate (DMC), dimethyl oxalate (DMO) and water ($H_2O$). The gas sample contains a minor amount of $CO_2$. The following two reaction equations are suggested:

$$CO + \tfrac{1}{2}O_2 + 2CH_3OH \rightarrow (CH_3O)_2CO + H_2O \tag{4}$$

$$2CO + \tfrac{1}{2}O_2 + 2CH_3OH \rightarrow (CH_3COO)_2 + H_2O \tag{5}$$

From an investigation of the thermodynamics of the above two reaction equations [11], their equilibrium constants are very large. So, their reverse reactions can be eliminated, and the power-law intrinsic double-rate kinetic model with 10 parameters can be written as the follows:

$$R_1 = \frac{dN_{DMC}}{dW} = k_{0,1}\,e^{-E_1/RT}\,p_{CO}^{a,1}\,p_{O2}^{b,1}\,p_M^{c,1} \tag{6}$$

$$R_2 = \frac{dN_{DMO}}{dW} = k_{0,2}\,e^{-E_2/RT}\,p_{CO}^{a,2}\,p_{O2}^{b,2}\,p_M^{c,2} \tag{7}$$

From the material balance calculations of the reaction system (see Table 2), this can be given as

$$N_{T,1} = N_T(1 + 1.5y_{DMC} + 2.5y_{DMO})$$

Let

$$1 + 1.5y_{DMC} + 2.5y_{DMO} = B$$

Table 2
Material balance calculations of reaction system

| Components $i$ | $y_{i,1}$ | $N_{i,1}$ (mol min$^{-1}$) | $N_i$ (mol min$^{-1}$) |
|---|---|---|---|
| CO | $y_{CO,1}$ | $N_{T,1}y_{CO,1}$ | $N_{T,1}y_{CO,1}-N_Ty_{DMC}-2N_Ty_{DMO}$ |
| $O_2$ | $y_{O2,1}$ | $N_{T,1}y_{O2,1}$ | $N_{T,1}\ y_{O2,1}-0.5N_Ty_{DMC}-0.5N_Ty_{DMO}$ |
| $CH_3OH$ | $y_{M,1}$ | $N_{T,1}y_{M,1}$ | $N_{T,1}y_{M,1}-2\mathrm{N}_Ty_{DMC}-2N_Ty_{DMO}$ |
| $N_2$ | $y_{N2,1}$ | $N_{T,1}y_{N2,1}$ | $N_{T,1}y_{N2,1}$ |
| DMC | 0 | 0 | $N_Ty_{DMC}$ |
| DMO | 0 | 0 | $N_Ty_{DMO}$ |
| $H_2O$ | 0 | 0 | $N_Ty_{DMC}+N_Ty_{DMO}$ |
| Total | 1 | $N_{T,1}$ | $N_T=N_{T,1}-1.5N_Ty_{DM}-2.5N_Ty_{DMO}$ |

So that

$$R_1=\frac{\mathrm{d}N_{\mathrm{DMC}}}{\mathrm{d}W}=\frac{\mathrm{d}}{\mathrm{d}W}(N_{\mathrm{T}}y_{\mathrm{DMC}})=\frac{\mathrm{d}}{\mathrm{d}W}\left(\frac{N_{\mathrm{T},1}y_{\mathrm{DMC}}}{B}\right),$$
$$R_2=\frac{\mathrm{d}N_{\mathrm{DMO}}}{\mathrm{d}W}=\frac{\mathrm{d}}{\mathrm{d}W}(N_{\mathrm{T}}y_{\mathrm{DMO}})=\frac{\mathrm{d}}{\mathrm{d}W}\left(\frac{N_{\mathrm{T},1}y_{\mathrm{DMO}}}{B}\right) \qquad (8)$$

We can rewrite these relationships as

$$R_1=\frac{N_{\mathrm{T},1}}{B^2\,\mathrm{d}W}\left[B\,\mathrm{d}y_{\mathrm{DMC}}-(1.5\,\mathrm{d}y_{\mathrm{DMC}}+2.5\,\mathrm{d}y_{\mathrm{DMO}})\,y_{\mathrm{DMC}}\right],$$
$$R_2=\frac{N_{\mathrm{T},1}}{B^2\,\mathrm{d}W}\left[B\,\mathrm{d}y_{\mathrm{DMO}}-(1.5\,\mathrm{d}y_{\mathrm{DMC}}+2.5\,\mathrm{d}y_{\mathrm{DMO}})\,y_{\mathrm{DMO}}\right] \qquad (9)$$

The following can be derived:

$$\frac{\mathrm{d}y_{\mathrm{DMC}}}{\mathrm{d}W}=\frac{B^2\left[(1+1.5y_{\mathrm{DMC}})R_1-2.5y_{\mathrm{DMO}}R_2\right]}{N_{\mathrm{T},1}\left[(1+2.5y_{\mathrm{DMO}})(1+1.5y_{\mathrm{DMC}})-3.75y_{\mathrm{DMC}}y_{\mathrm{DMO}}\right]} \qquad (10)$$

$$\frac{\mathrm{d}y_{\mathrm{DMO}}}{\mathrm{d}W}=\frac{B^2\left[(1+2.5y_{\mathrm{DMO}})R_2-1.5y_{\mathrm{DMC}}R_1\right]}{N_{\mathrm{T},1}\left[(1+2.5y_{\mathrm{DMO}})(1+1.5y_{\mathrm{DMC}})-3.75y_{\mathrm{DMC}}y_{\mathrm{DMO}}\right]} \qquad (11)$$

If $W$=0, $y_{\mathrm{DMC}}$=0 and $y_{\mathrm{DMO}}$=0, by integrating Eqs. (8) and (9) from 0 to $W$, the calculated results $y_{\mathrm{DMC,2c}}$ and $y_{\mathrm{DMO,2c}}$ of the outlet concentration and $y_{\mathrm{DMC,2}}$ and $y_{\mathrm{DMO,2}}$ of the reactor can be derived, individually. Defining

$$F=\sum_{i=1}^{22}\left[(y_{\mathrm{DMC,2}}-y_{\mathrm{DMC,2c}})^2+(y_{\mathrm{DMO,2}}-y_{\mathrm{DMO,2c}})^2\right] \qquad (12)$$

as the objective function, by minimising the objective function, we can obtain the parameters of the kinetic model.

### 3.3. Parameter estimation

By means of a modified Gauss–Newton method, we can derive the rate relationships as follows:

$$R_1=0.3674\times10^7\exp\left(\frac{-0.15890\times10^5}{RT}\right)\times p_{\mathrm{M}}^{1.402}\,p_{\mathrm{CO}}^{0.953}\,p_{\mathrm{O2}}^{0.005}\quad(\mathrm{mol\,g^{-1}\,h^{-1}}) \qquad (13)$$

$$R_2=0.1613\times10^5\exp\left(\frac{-0.4038\times10^4}{RT}\right)\times p_{\mathrm{M}}^{0.728}\,p_{\mathrm{CO}}^{1.031}\,p_{\mathrm{O2}}^{0.172}\quad(\mathrm{mol\,g^{-1}\,h^{-1}}) \qquad (14)$$

The experimental data and calculated results of the outlet DMC and DMO concentrations are shown in Table 3. Fig. 2 shows the distribution of residues of Eqs. (13) and (14). Table 3 and Fig. 2 show that the relative residues of most of the experimental runs are below ±15%. Using the correlation coefficients, $\rho^2$ and $F$-test, the confidence level of the parameters obtained can be evaluated. The correlation coefficients $\rho^2$ of Eqs. (13) and (14) are 0.9941 and 0.9940, respectively. They are greater than 0.95. When the confidence limit is 95%, the $F$-test results of Eqs. (13) and (14) are far greater than 10 times $F_{\mathrm{t}}$ ($F_{\mathrm{t}}$=2.81). This indicates that, at the 95% confidence level, the kinetic model obtained is adequate.

Table 3
Comparison of residue calculation of double-rate kinetic model

| No. | $y_{\mathrm{DMC,2}}\times10^2$ | $y_{\mathrm{DMC,2c}}\times10^2$ | $(y_{\mathrm{DMC,2}}-y_{\mathrm{DMC,2c}})/y_{\mathrm{DMC,2}}$ | $y_{\mathrm{DMO,2}}\times10^2$ | $y_{\mathrm{DMO,2c}}\times10^2$ | $(y_{\mathrm{DMO,2}}-y_{\mathrm{DMO,2c}})/y_{\mathrm{DMO,2}}$ |
|---|---|---|---|---|---|---|
| 1 | 0.8946 | 0.9834 | −0.0992 | 0.4864 | 0.5071 | −0.0426 |
| 2 | 0.6341 | 0.6941 | −0.0946 | 0.4964 | 0.5003 | −0.0078 |
| 3 | 1.0086 | 0.9700 | 0.0383 | 0.7175 | 0.5883 | 0.1801 |
| 4 | 0.6762 | 0.6874 | −0.0166 | 0.4574 | 0.5310 | −0.1607 |
| 5 | 0.7815 | 0.8234 | −0.0536 | 0.6124 | 0.5293 | 0.1357 |
| 6 | 0.7913 | 0.8270 | −0.0451 | 0.5243 | 0.5386 | −0.0273 |
| 7 | 0.8341 | 0.7602 | 0.0885 | 0.6156 | 0.5340 | 0.1326 |
| 8 | 0.6652 | 0.6855 | −0.0306 | 0.5118 | 0.5221 | −0.0202 |
| 9 | 0.5846 | 0.6005 | −0.0273 | 0.5055 | 0.5119 | −0.0127 |
| 10 | 0.6877 | 0.6843 | 0.0050 | 0.4651 | 0.5300 | −0.1394 |
| 11 | 0.6921 | 0.7741 | −0.1184 | 0.5547 | 0.5476 | 0.0127 |
| 12 | 0.7607 | 0.8710 | −0.1451 | 0.5298 | 0.5652 | −0.0668 |
| 13 | 0.9017 | 0.8566 | 0.0501 | 0.6057 | 0.5690 | 0.0606 |
| 14 | 1.1407 | 0.9777 | 0.1429 | 0.5948 | 0.5894 | 0.0090 |
| 15 | 1.1560 | 1.1060 | 0.0432 | 0.6210 | 0.6093 | 0.0188 |
| 16 | 1.2465 | 1.2455 | 0.0008 | 0.6704 | 0.6291 | 0.0615 |
| 17 | 0.8370 | 0.7988 | 0.0456 | 0.5047 | 0.5626 | −0.1148 |
| 18 | 0.9103 | 0.9089 | 0.0015 | 0.5308 | 0.5823 | −0.0971 |
| 19 | 1.0867 | 1.0278 | 0.0542 | 0.6319 | 0.6018 | 0.0476 |
| 20 | 1.0573 | 1.1525 | −0.0901 | 0.6629 | 0.6207 | 0.0637 |
| 21 | 0.9064 | 0.9815 | −0.0827 | 0.4786 | 0.5074 | −0.0600 |
| 22 | 0.7965 | 0.6960 | 0.1263 | 0.4455 | 0.5007 | −0.1237 |

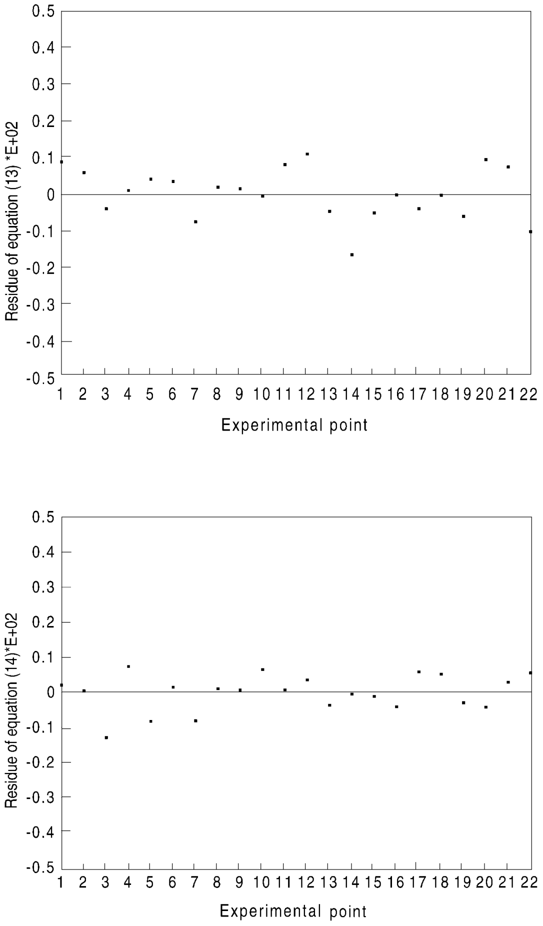

Fig. 2. Residue distribution.

## 4. Conclusions

Contacting oxygen, carbon monoxide and vaporised methanol with $CuCl_2/C$ can produce DMC. In the preparation of the $CuCl_2/C$ catalyst, it is necessary to take into account the support. After chemical modification of the surface of activated charcoal, activated carbon AC1 is used as support and HPA as promoter or as the second support.

Owing to the simple method of regeneration, all the data are measured at the same catalytic activity. The direct oxidative carbonylation of vapour phase methanol to DMC is a very complex reaction accompanied by by-products. By means of a modified Gauss–Newton method, an intrinsic double-rate kinetic model has been obtained. Using residue analysis and variance tests the model is adequate.

## 5. Nomenclature

| | |
|---|---|
| $a,b,c$ | power exponents in kinetic model |
| $B$ | coefficient, $B=1+1.5y_{DMC}+2.5y_{DMO}$ (dimensionless) |
| $E$ | activation energy ($J\,mol^{-1}$) |
| $k_0$ | frequency factor |
| $n$ | runs of experiment |
| $N_T$ | the sum of mole fraction in mixture ($mol\,min^{-1}$) |
| $P$ | total pressure (MPa) |
| $p_i$ | partial pressure of $i$th component (MPa) |
| $R$ | universal gas constant ($J\,mol^{-1}\,K^{-1}$) |
| $R_1$, $R_2$ | reactant rate ($mol\,g^{-1}\,h^{-1}$) |
| $S_{DMC}$ | selectivity for production of DMC |
| $T$ | temperature (K) |
| $W$ | weight of catalyst (g) |
| $x_M$ | methanol conversion (dimensionless) |
| $y_i$ | mole fraction of $i$th component (dimensionless) |
| $Y_{DMC}$ | yield of DMC (dimensionless) |

*Subscript*

| | |
|---|---|
| M, CO, O2, N2, DMC, DMO | methanol, carbon monoxide, oxygen, nitrogen, dimethyl carbonate, dimethyl oxalate |
| 1,2 | inlet and outlet of reactor, or reactant, Eqs. (4) and (5), respectively |
| c | calculated results |

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