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On-line monitoring of the catalytic conversion of methyl formate to methanol and carbon monoxide by gas chromatography

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Abstract

A simple gas chromatographic system has been developed for the rapid, on-line analysis of products produced during the selective decomposition of methyl formate to methanol and carbon monoxide over basic catalysts. The system utilizes a single oven, a thermal conductivity detector, a six-way sampling valve and three packed columns connected by a column-switching device. Complete analysis of the products can be achieved in 0.5 h.

Keywords: Process analysis; Methyl formate; Methanol; Carbon monoxide

1. Introduction

Methyl formate (MF), a useful intermediate of many important chemicals, has been noticed recently [1–7]. As a source or carrier of pure CO, MF has been selectively decomposed to CH₃OH and CO over NaOH-doped MgO [8] and zeolites [9]. Since the reaction mixture possibly consists of H₂, CO, CH₄, CO₂, H₂O, CH₃OH and unreacted MF, a simple procedure, e.g. gas chromatography (GC) with a single column, is hardly effective for their separation and analysis.

In some previous reports [10–15], a cold trap with ice-water or liquid nitrogen or C₂H₅OH–solid CO₂ as the coolant was usually placed at the exit of the reactor. When the reaction mixture passed through it, the noncondensable products (e.g., H₂, CO, CH₄ and CO₂) were analyzed directly by on-line GC, whereas the condensable constituents (e.g., H₂O, CH₃OH and

unreacted MF), were collected, weighed and then analyzed off-line. This approach, capable of providing good identification, suffers from the following disadvantages: (1) Calculation is difficult and complicated. (2) The composition of the product mixture may change during storage and handling. (3) At low conversion levels, which are desirable for kinetic studies, this practice is impractical. (4) This method can also not be used to follow the dynamics of catalyst deactivation or changes in reaction conditions [16].

Our attention has been focused on developing on-line GC, which can be used not only in the laboratory but also in process analysis [17]. In GC, the use of combinations of two or more columns with different packings, either in parallel or in series, is a common approach to solve difficult separation problems [18–20]. As for the evolution of on-line GC, emphasis has been put on the use of multicolumn and column-switching methods [21]. Hachenberg [17] reported some applications of on-

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line GC to the monitoring of catalyst deactivation and the characterisation of catalyst behavior. This method has also been successfully applied to the analysis of Fischer–Tropsch synthesis products [16,22,23].

Due to its convenience, rapidity and accuracy, on-line GC has been widely used. Based on the selection of columns and optimization of analytical conditions, an on-line GC method with a single sampling, to monitor the selective decomposition of MF to CH_3OH and CO, has been established in our study.

2. Experimental

Conditions

1. Reaction system: glass micro catalytic reactor, 6 mm I.D.; carrier gas, Ar; volume rate, 30 ml/min; amount of catalyst, 0.2 g; reaction temperature, 523 K; saturator temperature, 273 K.

2. GC analytical system: Shimadzu GC-9A gas chromatograph; detector, TCD; working current, 70 mA; columns, Porapak-T, 3 m×3 mm, 60–80 mesh; Carbosiev 601, 2 m×3 mm, 80–100 mesh; glass bead, 3 m×3 mm, 60–80 mesh; carrier gas, Ar; volume rate, 34 ml/min; temperatures: column, 413 K; injection and detection, 423 K.

2.1. Reactor

A glass micro catalytic reactor (6 mm I.D.), with 0.2 g of catalyst kept between two quartz fiber plugs (proved to be inert to the present reaction by blank tests of the whole system), was connected to stainless-steel tubings of the flow system by connectors. The reactor was heated by a vertical tube furnace. The reaction temperature (523 K) was controlled and detected by an EA thermocouple placed in close contact with the reactor wall, near the center of the catalyst bed (Fig. 1).

2.2. Gas system

Argon (Ar), as the reaction carrier gas (30 ml/min), was purified by passing it through columns of

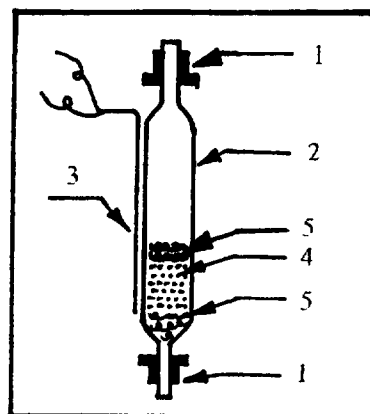


Fig. 1. Reactor. (1) connector; (2) glass reactor; (3) EA thermocouple; (4) catalyst; (5) quartz fiber.

silica gel, molecular sieve 5A, activated charcoal and a 401 deoxidizer. It was then divided into two streams after passing through pressure and flow stabilizers. One of these was directly charged into the catalyst bed during the process of heating and the other was introduced into a bubbler filled with MF liquid at 298 K and then into a saturator thermostated at 273 K to make MF vapor saturated at that temperature (partial pressure of MF, 195 Torr; 1 Torr=133.322 Pa). It was then fed into the reactor during the reaction period (Fig. 2).

2.3. Apparatus and materials

A flow sheet of the experimental device is shown in Fig. 3. A Shimadzu GC-9A gas chromatograph equipped with a thermal conductivity detection (TCD) system (working current, 70 mA) was used for analysis. All the columns were made of stainless-steel tubing with 3 mm I.D.

Materials and chemicals were provided by the following suppliers: Porapak-T (3 m×3 mm, 60–80 mesh; Waters, USA); Carbosiev 601 (2 m×3 mm, 80–100 mesh), glass bead and MF, No. 1 reagent (Factory of Shanghai, China); 401 deoxidizer (mainly consisting of manganese and nickel oxides) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences). Ar was used as carrier gas at a flow-rate of 34 ml/min. Column temperature, 413 K; injection and detection temperature, 423 K.

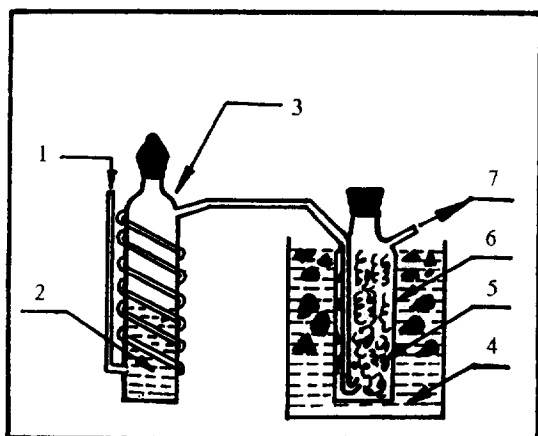


Fig. 2. Bubbler. (1) Ar; (2) MF liquid; (3) glass spiral bubbler; (4) ice-water bath; (5) glass spirals; (6) saturator; (7) mixture of carrier gas and MF vapor.

3. Results and discussion

3.1. Establishment of the analytical method

The behavior of H_2 , N_2 , He and Ar as the carrier gases for gas chromatography has been inspected.

The results showed that N_2 is not suitable for the analysis because the thermal conductivity of N_2 is higher than that of some components but lower than that of the others, and both positive and negative peaks will appear on the chromatogram. Hydrogen is a by-product of MF decomposition in some cases, and is also not suitable as the carrier gas. Although He is better than Ar, Ar was selected as the carrier gas because of its lower price.

In order to establish a satisfactory analytical method, the performances of Porapak-T, Porapak-P, molecular sieve 5A and Carbosiev 601 columns was investigated. Poor separation results showed that a single column could not satisfy the needs of our study. A series-parallel connection of columns was therefore employed in our research work.

A six-way switching valve was installed between the columns to introduce reaction products into different columns at different times during the analytical process (Fig. 4). The reaction mixture was separated into two groups according to their different retention times on a Porapak-T column (column A). One of the groups, called group 1, consists of H_2 , CO, CH_4 and CO_2 which have relatively shorter

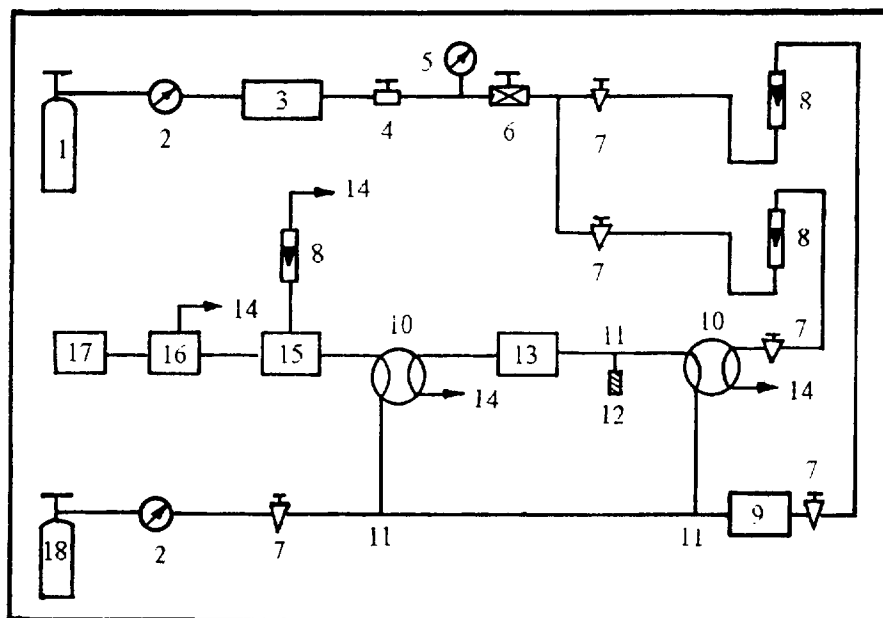


Fig. 3. Experimental setup. (1) Ar steel cylinder; (2) pressure reducing valve; (3) purifier; (4) pressure stabilizing valve; (5) pressure gauge; (6) flow stabilizing valve; (7) needle valve; (8) rotameter; (9) bubbler; (10) four-way valve; (11) three-way stop-cock; (12) septum cap; (13) reactor; (14) to air; (15) heated gas sampling cock; (16) GC-9A; (17) integrator; (18) standard gas steel cylinder.

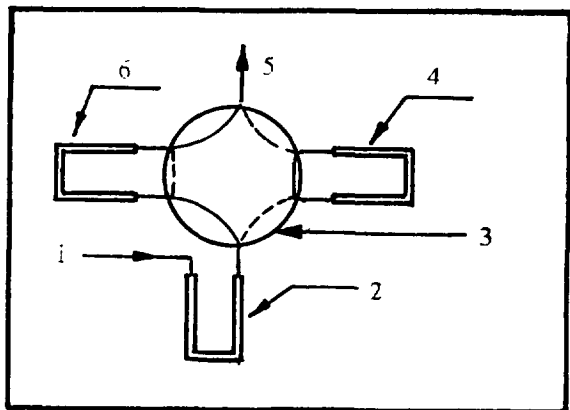


Fig. 4. Connection of columns. (1) reaction mixture; (2) column A; (3) six-way valve; (4) column B; (5) to TCD; (6) column C.

retention times; the other group, called group 2, includes H_2O , CH_3OH and MF which have relatively longer retention times.

A heated gas sampling cock, an accessory of GC-9A, was used for sampling (Fig. 5). The sample passed through column A first and then passed into a Carbosiev 601 column (column B) (Fig. 4 dotted line position). After about 8 min, group 1 has passed completely through the column A. All of its members, except CO_2 , were separated and detected by TCD. However, group 2 was still on column A,

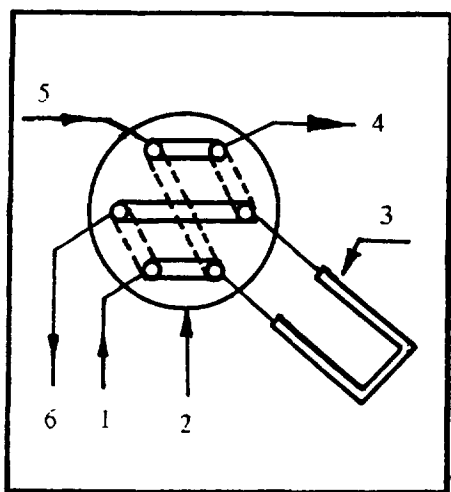


Fig. 5. Heated gas sampling cock. (1) Reaction mixture; (2) six-way valve; (3) sampling tube; (4) to GC columns; (5) GC carrier gas (Ar); (6) to air.

because of its longer retention time, and CO_2 was retained on column B. At this point, the six-way valve was switched immediately to the real line position (Fig. 4) to avoid group 2 members flowing into column B, as they would stay on column B permanently. The group 2 members were then carried out of column A through a glass bead resistance column (column C) and were detected by TCD in 25 min. After analyzing the group 2 members completely, the six-way valve was switched again to the dotted line position (Fig. 4) to carry CO_2 previously retained on column B out to TCD. The reaction mixtures were analyzed by GC directly at time intervals of 40 min, for a period of up to 10 h for each experiment.

Column A was 3 m long packed with 60–80 mesh Porapak-T. Column B was 2 m long packed with 80–100 mesh Carbosiev 601. Column C was 3 m long packed with 60–80 mesh glass beads. The volume rate of carrier gas (Ar) was selected as 34 ml/min, the column temperature was 413 K, the injection and detection temperatures were 423 K and the TCD working current was 70 mA.

3.2. Qualitative and quantitative analyses

Qualitative and quantitative analyses of the products are based on their retention time (t_R) and molar factors (f) respectively.

In every experiment, the molar factor of MF (f_{MF}) was easily obtained by direct sampling and analyzing of the Ar–MF mixture evolving from the bubbler and saturator thermostated at 273 K (Fig. 2). The factor f_{MF} is calculated by Eq. (1):

$$f_{\text{MF}} = P_s / (P \times A_{\text{MF}}) \quad (1)$$

in which P_s represents the saturated vapor pressure of MF at 273 K, P represents the total pressure (which is approximately atmospheric pressure) and A_{MF} represents the peak area of MF.

The molar factors of H_2 , CO , CH_4 and CO_2 were obtained by direct sampling and analyzing of standard gases from the steel cylinder, the molar factors (f) can be calculated from Eq. (2):

$$f_i = X_i / A_i \quad (2)$$

in which X_i and A_i represent the mole fraction and peak area of component i respectively.

In order to simplify the experimental apparatus and process, a simple calculation method for obtaining $f_{\text{H}_2\text{O}}$ and $f_{\text{CH}_3\text{OH}}$ has been developed under selected chromatographic conditions as follows:

Firstly, inject pure MF, H₂O and CH₃OH liquid separately to obtain their volume factors (f_v^0):

$$f_v^0 = \text{sample volume/peak area} \quad (3)$$

then calculate their molar factors (f^0) through Eq. (4):

$$f^0 = f_v^0 \times d/M \quad (4)$$

in which d represents density and M represents the molecular mass.

The relative molar factors of H₂O ($f_{\text{H}_2\text{O}}^r$) and CH₃OH ($f_{\text{CH}_3\text{OH}}^r$) with respect to MF can be easily obtained from Eq. (5) and Eq. (6), respectively:

$$f_{\text{H}_2\text{O}}^r = f_{\text{H}_2\text{O}}^0 / f_{\text{MF}}^0 \quad (5)$$

$$f_{\text{CH}_3\text{OH}}^r = f_{\text{CH}_3\text{OH}}^0 / f_{\text{MF}}^0 \quad (6)$$

The values of $f_{\text{H}_2\text{O}}^r$ and $f_{\text{CH}_3\text{OH}}^r$ are 0.242 and 0.482 respectively.

At the beginning of each catalyst testing experiment, f_{MF} was first determined under that particular experimental condition. Then the $f_{\text{H}_2\text{O}}$ and $f_{\text{CH}_3\text{OH}}$ under corresponding conditions were calculated from Eq. (7) and Eq. (8):

$$f_{\text{H}_2\text{O}} = f_{\text{H}_2\text{O}}^r \times f_{\text{MF}} \quad (7)$$

$$f_{\text{CH}_3\text{OH}} = f_{\text{CH}_3\text{OH}}^r \times f_{\text{MF}} \quad (8)$$

The data listed in Table 1 are averages of 30 repeated analyses and the experimental errors are less than 1.5%.

Table 1

The retention time (t_r) and molar factor (f) of components under selected gas chromatographic conditions

Component	H ₂	CO	CH ₄	H ₂ O	CH ₃ OH	MF	CO ₂
t_r (min)	2.21	3.72	6.47	13.32	15.71	19.34	27.02
f	7.36×10^{-6}	7.93×10^{-5}	1.88×10^{-5}	1.57×10^{-5}	3.13×10^{-5}	6.49×10^{-5}	5.46×10^{-5}

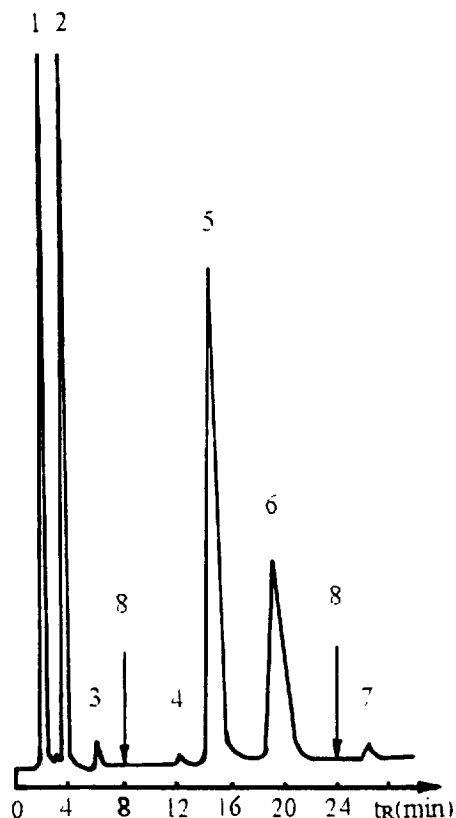


Fig. 6. Gas chromatogram showing the separation of reaction products resulting from the decomposition of MF over a CuO–ZnO–Al₂O₃ catalyst. (1) H₂; (2) CO; (3) CH₄; (4) H₂O; (5) CH₃OH; (6) MF; (7) CO₂; (8) valve switching.

3.3. Example

The above method was used to monitor MF decomposition over more than ten different catalysts. A typical chromatogram is given in Fig. 6.

To test and verify the reliability of this analytical method, we calculated the mass balance of the reaction process. For example, in the decomposition of MF over 0.42 mmol Na⁺/g MgO, only CO, CH₃OH and unreacted MF were detected by TCD

Table 2

The selective decomposition products of MF over 0.42 mmol Na⁺/g MgO catalyst, at the reaction time of 280 min

Input	Contents of the reaction mixture			Relative error	
	X _{MF}	X _{CH₃OH}	X _{CO}	$[X_{MF}^0 - (X_{MF} + X_{CH_3OH})]/X_{MF}^0$	$[X_{MF}^0 - (X_{MF} + X_{CO})]/X_{MF}^0$
2.82×10^{-1}	2.74×10^{-1}	4.55×10^{-3}	4.86×10^{-3}	1.22%	1.11%

during a reaction time of 280 min. Under the above experimental conditions, the mass balance results of the reaction products are shown in Table 2. It is evident that the relative error of mass balance throughout the whole reaction period is satisfactory.

4. Conclusions

Good separation of MF decomposition products over catalysts was achieved by selecting suitable columns, devices and conditions for GC analysis. Mass balance and reproducibility were satisfactory. The present method can be directly used conveniently to monitor processes producing similar reaction products as MF decomposition.

The utilization of retention time differences on different columns is a common practice in multicolumn GC. However, the practice of switching back to a certain column to fetch a left-over component is a good tactic for solving the problem of the overlapping of retention times between columns, and may make the multicolumn practice more powerful in solving difficult analysis problems. The use of relative molar factor for a part of the components can simplify calculation and increase reliability under varying reaction and analysis conditions.

Acknowledgments

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