

Vapor-phase reactions of catechol with dimethyl carbonate. Part I. *O*-Methylation of catechol over alumina

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Received 29 August 1997; received in revised form 19 September 1997; accepted 22 September 1997

Abstract

The reaction of catechol (pyrocatechol) with dimethyl carbonate (DMC) on alumina was studied. The main product was guaiacol, the selectivity for it being ca. 70%. Addition of water to the feed considerably increased the catalytic activity and the yield of guaiacol. The conversion of catechol was 68% at time-on-stream of 1 h at 553 K, though it decreased to 35% at 5 h. Addition of carbon dioxide to the feed considerably decreased the catechol conversion, indicating that the basic sites on alumina are active centers for methylation. It is also demonstrated that DMC is a much more efficient methylating agent than methanol in the methylation of catechol over alumina. © 1998 Elsevier Science B.V.

Keywords: Guaiacol; Dimethyl carbonate; *O*-Methylation; Catechol; Alumina

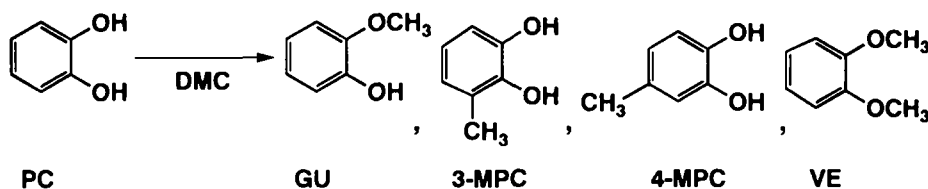
1. Introduction

Guaiacol (*O*-methoxyphenol) is an important synthetic intermediate in the production of fine chemicals, for example, the synthesis of flavorings, fragrances and pharmaceuticals [1]. It is conventionally synthesized by methylation of catechol with dimethyl sulfate using sodium hydroxide as a homogeneous catalyst in liquid phase [2], or with methyl halide in the presence of sodium hydride in tetrahydrofuran at room temperature [3]. These methylating agents are corrosive and toxic. Therefore, special care is necessary in handling them and the materials for the reactors. Furthermore, tedious procedures are required for the disposal of the waste

water. To avoid these disadvantages, vapor-phase methylation with methanol over heterogeneous catalysts has been attempted [4–9]. In the vapor-phase methylation, the reaction leads to different products. It is also required to keep low conversion level to avoid the formation of polymethylated products (see Scheme 1).

Furthermore, the catalyst deactivation is usually observed. Matsuzaki et al. used kaolin as the catalyst, which gave a 78% selectivity for guaiacol at a 35% conversion at 563 K [4]. Renken et al. reported that the selectivity for guaiacol was ca. 50% at the catechol conversion level of 20% at 533 K [5,6]. Fischer et al. claimed exceptionally high selectivities for guaiacol when they used X- or Y-type zeolites as catalysts. They did not give any details such as information on the deactivation [7]. In preliminary experiments, we also carried

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Scheme 1.

out the reaction over NaX and NaY as catalysts to find the very rapid decay of the activity, though their initial activities were high.

It has been demonstrated that a very high selectivity together with a high conversion was attained in the vapor-phase methylation of phenol over Y zeolites when dimethyl carbonate (DMC) was used as a methylating agent [10]. DMC was also used for the methylation of catechol in liquid phase [11]. The catalyst was NaOH/NaI and the reaction was totally *O*-selective, the ratio of guaiacol and veratrole (*O*-dimethoxybenzene) being dependent on the conversion.

This work is concerned with the vapor-phase reaction of catechol with DMC over alumina, aiming at highly selective production of guaiacol.

2. Reaction procedures

The reactions were carried out in a fixed bed continuous down-flow reactor at atmospheric pressure. Some alumina (Surface area: 125 m²/g, 32–60 mesh) was packed in the reactor made of silica tubing (I.D.=10 mm and Length=380 mm) placed in a vertical furnace and calcined in a dry air flow for about 1 h at 673 K. Then nitrogen was passed for about 1 h prior to the reaction. The mixture of catechol and dimethyl carbonate was fed into the reactor by means of a motor driven syringe. The products were collected in a trap in an ice bath and analyzed every hour by a gas chromatograph equipped with a capillary column. Propyl benzene was used as an internal standard for quantitative analysis.

W/F is defined as the weight of the catalyst in gram divided by the sum of the flow rates of the reactants and nitrogen in moles per hour.

3. Results and discussion

3.1. Product distribution

Fig. 1 shows the change in the catechol conversion and yields of the products with time-on-stream in the methylation of catechol with DMC over Al₂O₃ at 553 K. The conversion of catechol was 51% at time-on-stream of 1 h. It sharply decreased to 20% at 4 h. The selectivity did not change with time-on-stream. Guaiacol is the most predominant product, the selectivity for it being ca. 68%. The selectivity values for other products are as follows: 3-methyl catechol:

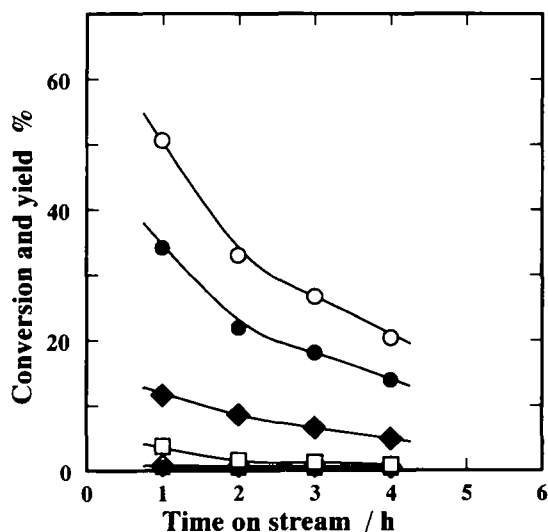


Fig. 1. Product distribution of *O*-methylation of catechol (PC) and dimethyl carbonate (DMC) over Al₂O₃. Reaction conditions: Temperature=553 K, PC partial pressure=10 kPa, PC/DMC=1/2 W/F=9.4 g h mol⁻¹. Conversion of catechol (○). Product yields of guaiacol (●); 3-methyl catechol (◆); 4-methyl catechol (■); polymethylated products (□); veratrole (◇).

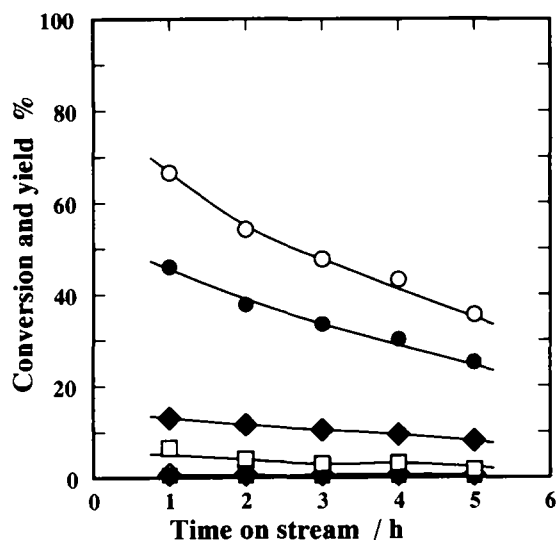


Fig. 2. Product distribution of *O*-methylation of catechol and DMC over Al_2O_3 accompanied with H_2O . Reaction conditions: Temperature=553 K, PC partial pressure=10 kPa, PC/DMC/ H_2O =1/2/0.5, W/F=9.4 g h mol⁻¹. Conversion of catechol (○). Product yields of guaiacol (●); 3-methyl catechol (◆); 4-methyl catechol (■); polymethylated products (□); veratrole (◇).

25%, 4-methyl catechol: 2%, polymethylated products: 5%. The selectivity for the *O*-methylated products based on DMC was about 70% under the reaction conditions.

3.2. Effect of water

Renken et al. reported that the addition of water to the feed decreased the polymethylated side-products and suppressed the rate of the catalyst deactivation in the methylation of catechol with methanol over alumina [5]. Therefore, we examined the effect of water on the catalytic performance in the reaction of catechol with DMC over alumina.

Fig. 2 shows the change in the catechol conversion and the yields of products with time-on-stream in the presence of 5 kPa of water. The reaction conditions are same as those in the run shown in Fig. 1, except for the presence of water. It is clearly seen that the conversion was increased by adding water to the feed. Thus, the initial conversion reached 68%. The conversion decreased with time-on-stream, being 35% at 5 h.

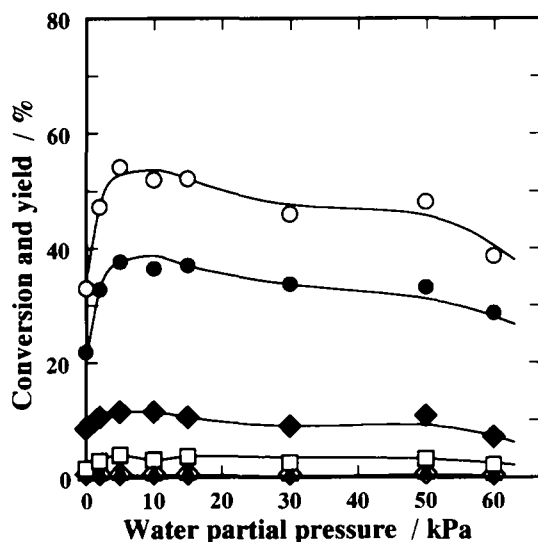


Fig. 3. Variation of product distribution in *O*-methylation of catechol with DMC as a function of water amount over Al_2O_3 . Reaction conditions: Temperature=553 K, PC partial pressure=10 kPa, PC/DMC=1/2, W/F=9.4 g h mol⁻¹. Time-on-stream=2 h. Conversion of catechol (○). Product yields of guaiacol (●); 3-methyl catechol (◆); 4-methyl catechol (▲); polymethylated products (□); veratrole (◇).

The selectivity for each product was not appreciably affected by the addition of water.

Fig. 3 shows the effect of the partial pressure of water on the catechol conversion and the yields of products at 553 K. The data were taken at time-on-stream of 2 h. In the absence of water, the conversion of catechol was 33%. It increased with water partial pressure up to 5 kPa where a maximum conversion (54%) was observed. The conversion gradually decreased upon raising the partial pressure of water. The distribution of products did not change appreciably in the range of the partial pressure of water studied (00–60 kPa).

3.3. Effect of DMC partial pressure on guaiacol yield

Fig. 4 shows the effect of DMC partial pressure on the guaiacol yield in the presence of 10 kPa of water. The catechol partial pressure was kept constant (10 kPa). At DMC partial pressure of 30 kPa, the guaiacol yield was high, about 64% at time-on-stream of 1 h, and rapidly decayed from 3 h of time-on-

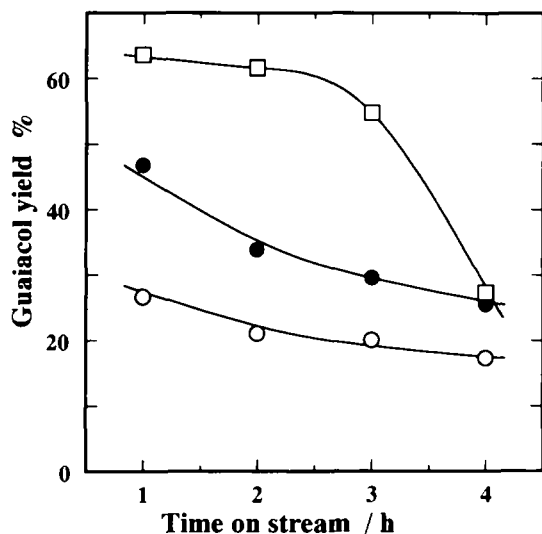


Fig. 4. Effect of DMC partial pressure on *O*-methylation of catechol over Al_2O_3 . Reaction conditions: Temperature—553 K, PC partial pressure—10 kPa, PC/ H_2O —1/1, W/F—9.4 g h mol^{-1} , 10 kPa (○), 20 kPa (●), 30 kPa (□).

stream. The guaiacol yield slowly decreased with time-on-stream at 10 and 20 kPa. It is found that the deactivation became slow with decrease in the DMC partial pressure. The product distribution was independent of DMC partial pressure. Guaiacol selectivity was about 70% at any DMC partial pressure. Thus, the DMC partial pressure of 20 kPa is adapted for the production of guaiacol.

3.4. Effect of reaction temperature

Fig. 5 shows the effect of reaction temperature on the conversion of catechol and the yields of the products in the reaction of catechol (10 kPa) and DMC (20 kPa) in the presence of water (30 kPa). The catechol conversion monotonously increased with increasing reaction temperature. The yield of guaiacol gradually increased from 13 to 34% as the temperature was changed from 523 to 573 K. However, the further increase of reaction temperature to 623 K resulted in only a slight increase of the guaiacol yield (38%). At this temperature, the yield of polymethylated products (such as methylated guaiacol) sharply increased and the decomposition of DMC was appreciable and the selectivity for methylation on DMC bases dropped significantly.

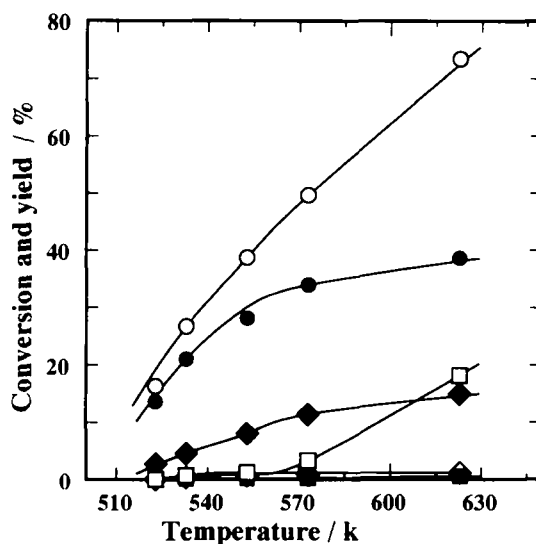


Fig. 5. Variation of product distribution in *O*-methylation of catechol with DMC as a function of reaction temperature over Al_2O_3 . Reaction conditions: PC partial pressure—10 kPa, PC/DMC/ H_2O —1/2/3 W/F—9.4 g h mol^{-1} , Time-on-stream—3 h. Conversion of catechol (○). Product yields of guaiacol (●); 3-methyl catechol (◆); 4-methyl catechol (■); polymethylated products (□); veratrole (◇).

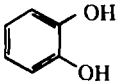
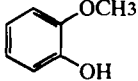
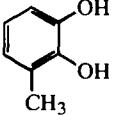
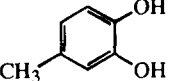
3.5. Comparison of the reactivity of DMC with methanol

The reactions of catechol with methanol and DMC were carried out over alumina and the results are compared in Table 1. A big difference was observed in the conversion of catechol; 41% in the reaction with DMC and 6% with methanol. It is clear that DMC is a much more efficient methylating agent than methanol in the methylation of catechol. The selectivity for guaiacol was higher with DMC (71%) than with methanol (59%). Therefore, the yields of guaiacol was about eight times higher in methylation with DMC (29.1%) than with methanol (3.6%). Instead, the selectivity for the C-methylated products was higher in the methylation with methanol.

3.6. Effect of carbon dioxide on the catalytic activity

Alumina has both acidic and basic functions. In our previous works on the methylation with DMC over zeolites, we suggested that the basic property of

Table 1
Comparison of *O*-methylation of catechol with DMC and methanol

	Conversion %			Selectivity %	
					Polymethylated products
DMC	41	71	22	1	6
MeOH	6	59	32	2	7

Reaction conditions: Catalyst—Al₂O₃, Temperature—553 K, PC. Pressure=10 kPa W/F=9.4 g h mol⁻¹, PC/DMC(MeOH)/H₂O=1/2/1, Time-on-stream—3 h.

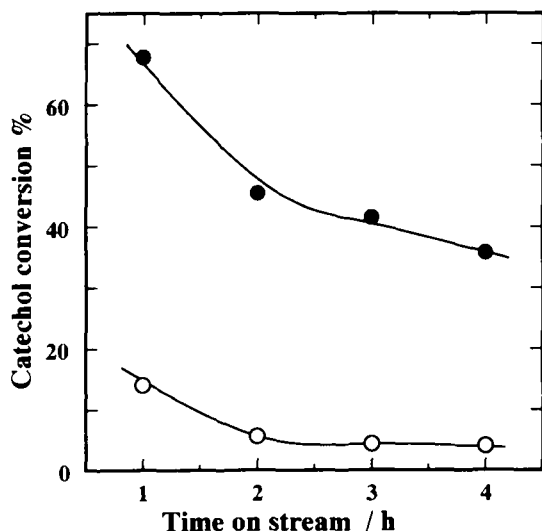


Fig. 6. Effect of carbon dioxide on conversion of catechol over Al₂O₃. Reaction conditions: Temperature—553 K, PC partial pressure=10 kPa PC/DMC/H₂O=1/2/1, CO₂ partial pressure=10 kPa, presence of CO₂ (○), absence of CO₂ (●).

zeolites is essential for the reactions [10,12,13]. To examine the role of basic sites in the methylation of catechol with DMC over alumina, we examined the effect of carbon dioxide, an acidic molecule, on the catalytic activity for the reaction. As shown in Fig. 6, the addition of 10 kPa of carbon dioxide sharply

suppressed the catalytic activity of alumina, indicating that the basic sites are involved in the catalysis. Since carbon dioxide is one of the products in the methylation, the strong adsorption of carbon dioxide on the basic sites may be one of the key factors in the catalyst deactivation.

4. Conclusions

DMC is a much more efficient methylating agent than methanol in the methylation of catechol over alumina. The main product was guaiacol, the selectivity for it being ca. 70%. Addition of water to the feed considerably increased the catalytic activity and the yield of guaiacol. The conversion of catechol was 68% at time-on-stream of 1 h at 553 K, though it decreased to 35% at 5 h.

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