



# Article Vapour-Phase Selective O-Methylation of Catechol with Methanol over Metal Phosphate Catalysts

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**Abstract:** Guaiacol (2-methoxyphenol), an important fine chemical intermediate, is conventionally synthesized by liquid-phase processes with expensive, corrosive and toxic methylating agents such as dimethyl sulphate and dimethyl iodide. Recently, vapour-phase alkylation of catechol (1, 2-dihydroxybenzene) with methanol for the synthesis of guaiacol in the presence of heterogeneous catalysts has received more attention, as the route is economical and environmentally friendly. However, most of the investigated catalysts exhibited unsatisfactory catalytic performance for industrial applications. In this study, five metal phosphates M-P-O (M = La, Ce, Mg, Al, Zn) catalysts were synthesized and tested in the selective *O*-methylation of catechol with methanol. Among these catalysts, cerium phosphate (CP) showed the highest catalytic activity and guaiacol yield. Lanthanum phosphate (MP) and aluminium phosphate (ALP). Zinc phosphate (ZP) was not active in the reaction. Relevant samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), N<sub>2</sub> adsorption-desorption, temperature programmed desorption of NH<sub>3</sub> or CO<sub>2</sub> (NH<sub>3</sub>-TPD, CO<sub>2</sub>-TPD). The suitable acid-base properties contribute to the superior catalytic performance of CP. Long-term stability and regeneration tests were also studied.

Keywords: metal phosphates; catechol; methanol; O-methylation; guaiacol

# 1. Introduction

Guaiacol (2-methoxyphenol) is a significant intermediate in fine chemical production, especially for the synthesis of vanillin (4-hydroxy-3-methoxybenzaldehyde) [1,2]. Traditionally, guaiacol is prepared in liquid-phase by using dimethyl sulphate or alkyl halides as methylating agents and sodium hydroxide as homogeneous catalyst, however the methylating agents are expensive, corrosive, and toxic [3]. Currently, vapour-phase methylation of catechol (1, 2-dihydroxybenzene) with non-toxic methanol or dimethyl carbonate (DMC) has attracted more attention because of its economical and environmentally friendly [4,5]. From the point of practical application, methanol is more suitable as methylating agent than DMC due to its lower cost.

Various heterogeneous catalysts have been investigated in vapour-phase methylation of catechol with methanol, including metal oxides [6,7], sulphates [2], metal phosphates [5,8,9], and supported heteropoly acids [10]. In general, the catalytic performance of these catalysts is greatly affected by the operation conditions, catalyst structures, acid and/or base properties. However, a common problem is that most of the investigated catalysts exhibited unsatisfactory catalytic performance.

Metal phosphates are a family of metal salts with high thermal stability and acidbase properties, which can be used as catalysts directly for oxidative dehydrogenation of



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). isobutane (2-methylpropane) [11] or ethylbenzene [12], hydrolysis [13,14] or decomposition [15,16] of fluoride, vapor-phase O-alkylation of phenol [17], and selective catalytic reduction of NO with NH<sub>3</sub> [18]. Alternatively, metal phosphates can also be used to prepare supported catalysts such as Ru/CePO<sub>4</sub> for the aerobic oxidation of alcohols [19], Pd/AlPO<sub>4</sub> for hydrogenation of naphthalene [20], metal phosphate-supported Au or Pt for CO oxidation [21,22], metal phosphate-supported RuO<sub>x</sub> catalysts for N<sub>2</sub>O decomposition [23].

Zhang and co-workers [9] found that the acid-base properties of aluminium phosphate with lower Ti content were weaker, favouring guaiacol formation and catalytic stability. In addition, the catalytic performance of aluminophosphates could be enhanced by adjusting P/Al ratio [24] or coating microporous aluminophosphate on mesoporous SBA-15 [25], further confirming that suitable acid-base properties were crucial to vapour-phase methylation of catechol with methanol. However, Jafari et al. [5] found that catechol conversion and product distribution depended highly on acidity of Ti or Cs modified lanthanum phosphate. Thus, the reaction mechanism is still controversial.

Previous studies mainly focused on a particular metal phosphate. The objective of the current work is to systematically study the catalytic performance of different metal phosphates M-P-O (M = La, Ce, Mg, Al, Zn) in vapour-phase methylation of catechol with methanol. Among these catalysts, cerous phosphate (CP) is the most active one. Reasons for the observations were elucidated through detailed characterization.

# 2. Results

# 2.1. Basic Physicochemical Properties of Metal Phosphates Samples

XRD patterns of the as-synthesized products are shown in Figure 1. According to the literatures [26–29], the characteristic diffraction peaks are obtained for crystallized CP, LP, MP and ZP samples. ALP show a broad peak between 20° and 30° corresponding to the characteristic of amorphous phase, and two small sharp peaks (around 20°) corresponding to crystalline aluminium phosphate [30]. FT-IR test was carried out to further identify the products.



Figure 1. XRD patterns of different metal phosphate catalysts.

Figure 2 shows the FT-IR spectra of different M-P-O samples. As shown for all metal phosphates, the absorption band at 3430 cm<sup>-1</sup> and 1628 cm<sup>-1</sup> are ascribed to O–H stretching vibration and O–H bending vibration of adsorbed water molecules, respectively [31,32]. The band at ca. 1046 cm<sup>-1</sup> and 615 cm<sup>-1</sup> are attributed to P–O asymmetric stretch vibration and O=P–O bending vibration, and the bands at ca. 538 cm<sup>-1</sup> are due to O–P–O bending

vibration typical for  $PO_4^{3-}$  [32,33]. These observations confirm the formation of metal phosphates, thus supporting the XRD results.



Figure 2. FT-IR spectra of different metal phosphate catalysts.

The morphology of M-P-O samples was investigated with SEM analysis. As shown in Figure 3 and Figure S1, metal phosphates have irregular particles except LP. LP is mainly composed of small cubic column with a length of about 5  $\mu$ m. The particle size distribution of CP and ALP are mainly in range of 1–5  $\mu$ m, while that of ZP is in range of 10–50  $\mu$ m. The average particles sizes of MP are about 2  $\mu$ m. The degree of agglomeration is increased from CP to LP, and further to MP. However, ALP and ZP are highly dispersed.



Figure 3. SEM images of (a) CP, (b) LP, (c) MP, (d) ALP, and (e) ZP.

Table 1 summarizes the textual properties of M-P-O samples obtained by the N<sub>2</sub> adsorption-desorption data. The BET surface areas of catalysts show the sequence of LP > CP > MP > ALP > ZP. As shown in Figure 3, an increase in particle size of ZP may lead to a significant decrease in the BET surface area. The pore volumes of LP and MP are much larger than the others, which is probably owing to secondary pores formed by obvious aggregation.

Catalyst	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)
СР	68	0.09
LP	88	0.20
MP	64	0.35
ALP	29	0.11
ZP	7	0.02

 Table 1. Textural properties of different metal phosphate catalysts.

#### 2.2. Catalytic Performance

The catalytic activity and selectivity for the selective *O*-methylation of catechol had been investigated over the M-P-O catalysts. As presented in Figure 4a, for the CP sample, an initial catechol conversion of 80.3% and falls to 65.3% after 11 h on stream. The catechol conversion observed for the LP catalyst keeps constant at about 40.4% during 11 h on stream. However, the initial catechol conversion on MP (10.5%) and ALP (7.2%) are obvious lower than CP and LP, and deactivation is rather fast. ZP shows almost no conversion of catechol, indicating it is inactive in selective *O*-methylation of catechol. Apparently, the catechol conversion on catalysts follows the sequence of CP > LP > MP > ALP > ZP.



Figure 4. Cont.



**Figure 4.** Effect of time on stream on catechol conversion (**a**) and guaiacol selectivity (**b**) over different metal phosphate catalysts. Reaction conditions: atmospheric pressure;  $T = 270 \degree C$ ; WHSV = 0.4 h<sup>-1</sup>.

The effects of time on stream on the selectivity of guaiacol for each catalyst is shown in Figure 4b. As shown, the initial guaiacol selectivity of CP, LP, MP, and ALP are 92.6%, 88.4%, 85.7%, 97.4%, respectively. However, ZP shows no selectivity. The guaiacol selectivity of CP, LP, and ALP increased slightly with time. After 11 h on stream, the guaiacol selectivity of ALP and CP was as high as 99.3% and 97.8%, respectively. In contrast, the guaiacol selectivity of selectivity of MP decreased with time. The guaiacol selectivity follows the sequence of ALP > CP > LP > MP > ZP.

## 2.3. TPD Characterization

For selective *O*-methylation of catechol and some other alkylation reactions, the catalytic activity is correlated to the acidity and basicity of catalysts [25,32,34].

The acid strength and the amounts of acid sites on M-P-O catalysts were characterized by NH<sub>3</sub>-TPD (Figure 5, Table 2). As shown, M-P-O catalysts show two types of peaks below and above 300 °C, corresponding to NH<sub>3</sub> desorbed from the weak and strong acid sites, respectively [35]. The temperature corresponding to the desorption peak of weak acid sites follows the sequence of ZP < MP < CP < ALP < LP, consistent with the sequence of weak acid strength. The area of NH<sub>3</sub> desorption peak follows the sequence of CP > LP > ALP >MP > ZP, indicating that the amount of weak acid sites of CP is the highest. For strong acid sites, the desorption temperature follows the sequence of CP = ALP < ZP < MP, and the area of NH<sub>3</sub> desorption peak follows the sequence of MP  $\approx$  ZP > ALP > CP. LP have no desorption of NH<sub>3</sub> above 300 °C, indicating the lack of strong acid sites.



**Figure 5.** NH<sub>3</sub>-TPD curves of different metal phosphate catalysts.

Catalyst	Peak Temperature (°C)	Intensity (a.u.)
СР	215	391.24
	426	42.66
LP	233	381.51
	—	—
MP	199	128.91
	525	740.59
ALP	224	351.23
	426	408.90
ZP	179	35.40
	450	734.60

Table 2. Textural properties of different metal phosphate catalysts.

The basicity of the catalysts is evaluated by  $CO_2$ -TPD (Figure 6, Table 3). The strength and the amounts of base sites were related to the temperature and area of  $CO_2$  desorption peak, respectively. Figure 6 shows CP, LP and ALP have obvious peaks corresponding to  $CO_2$  desorption, while MP have very limited desorption of  $CO_2$ . The  $CO_2$  desorption temperature of CP, MP and ALP are very close, and higher than that of LP, indicating LP has relatively weak basicity. On the other hand, ZP shows no  $CO_2$  desorption peak, indicating the absence of base sites on these catalysts. The amounts of base sites of these catalysts follow the sequence of MP < CP < LP < ALP (Table 3). The interpretation of the TPD data will be presented in Section 4.



Figure 6. CO<sub>2</sub>-TPD curves of different metal phosphate catalysts.

Catalyst	Desorption Temperature (°C)	Intensity (a.u.)
СР	150	3.71
LP	94	4.24
MP	147	0.50
ALP	154	5.46
ZP	-	-

Table 3. CO<sub>2</sub>-TPD results of different metal phosphate catalysts.

# 2.4. Catalytic Stability and Catalyst Regeneration

Figure 7 shows the catalytic performance of the most active CP catalyst in two-cycle experiments. In the first cycle, the catechol conversion of CP decreased from 71.7% to 43.3% and gradually stabilized after 72 h on stream (Figure 7a). Then the catalyst was regenerated, and its catechol conversion recovered from 43.3% to 66.5%. The catechol conversion of regenerated CP in the second cycle decreased from 66.5% to 37.8% with the time on stream, consistent with the trend seen in the first cycle.

As shown in Figure 7b, the initial guaiacol selectivity of the regenerated CP was slightly lower than that of fresh CP, but increased with the reaction time, and finally close to the guaiacol selectivity of fresh CP (97.6%).



**Figure 7.** Catechol conversion (**a**) and guaiacol selectivity (**b**) of CP catalyst in cycle experiment, (■) the first cycle, (•) the second cycle.

# 3. Discussion

In this work, metal phosphates were prepared by precipitation method. According to XRD data (Figure 1) and FT-IR spectra (Figure 2), all as-synthesized samples were metal phosphates in nature. Among them, CP, LP, MP and ZP were in crystallized phase, whereas ALP was in amorphous phase. We found that the initial catalytic activities (conversion of catechol) of metal phosphates follow the sequence of CP > LP > MP > ALP > ZP (Figure 4a), while the initial guaiacol selectivity follows the sequence of ALP > CP > LP > MP > ZP (Figure 4b), thus resulting in the initial guaiacol yield follows the sequence of CP (74.4%) > LP (39.4%) > MP (9.0%) > ALP (6.4%) > ZP (0%).

The selective *O*-methylation of catechol with methanol is commonly regarded as an acid-base catalytic reaction for the production of guaiacol [4,9,10,24,25]. Therefore, the different acid-base properties of metal phosphates may have an effect on their catalytic performance. From NH<sub>3</sub>-TPD data (Figure 5), it can be seen that there are two kinds of acid sites in metal phosphates samples, i.e., weak and strong acid sites. Generally, coke deposition easily occurs on strong acid sites [4,9]. The amount of strong acid sites on

MP, ALP, ZP was much higher than CP and LP (Table 2), thus coke rapidly formed and blocked acid sites of MP, ALP and ZP, further causing their low initial activities and quick deactivation in the reaction. Additionally, MP, ALP and ZP samples were black in colour after 11 h reaction, indicating the fast coke formation.

The catalytic activity in *O*-methylation of catechol is correlated with the weak acid properties of metal phosphates [8,24]. The weaker strength and larger amount of the weak acid sites (Figure 5) might be responsible for the higher catechol conversion of CP. However, due to the presence of small amount of strong acid sites on CP, the catechol conversion decreased by 15.0% after 11 h reaction. In contrast, the catechol conversion of LP kept constant because of the absence of strong acid sites.

The weak base sites on the catalyst are beneficial for forming O-methylated products [2,6,24]. By comparing ALP, CP, and MP with similar base strength, it is note-worthy that the guaiacol selectivity is associated with the amount of base sites, i.e., the selectivity increases as the amount of base sites increases (Figure 4b or Figure 6). Though CP and LP possess comparable amounts of base sites, the guaiacol selectivity of CP is higher because of its suitable base strength (Figure 1). ZP shows no guaiacol selectivity, probably due to its strong acid sites and the absence of weak basic sites. From the above results, it can be concluded that the high catalytic activity and selectivity of CP own to its suitable weak acid-base sites. Moreover, it further confirms the acid-base co-operation mechanism in selective *O*-methylation of catechol with methanol [2,9].

The most active CP is compared with other acid and/or basic catalysts. As shown in Figures S2–S4, SAPO-34 and HAP samples exhibits poor catalytic performance, which is related to their high amount of strong acid sites and the presence of strong basic sites (CO<sub>2</sub> desorbed above 250 °C). Similar to the strong acid sites, coke is easily formed on strong basic sites [9]. Besides, the blockage of SAPO-34 pores also results in the decrease of catalytic performance [4]. Therefore, irregular pores created by the agglomeration of CP and MP may be blocked by oligomeric products and coke (Figure 3, Table 1), this is probably another reason for deactivation of CP and MP.

In the cycle experiment (Figure 7), although the catalytic activity of the fresh and regenerated CP both decrease with the time on stream, most of the activity of the used CP can be recovered by regeneration, indicating that coke deposition is the main reason for the loss of catalytic activity of CP. It is noteworthy that the guaiacol selectivity of fresh and regenerated CP keep constant at 97.6% as the reaction proceeded, which was significantly higher than that in the literature [2,5,25]. High guaiacol selectivity facilitates the separation and purification of the products.

#### 4. Materials and Methods

# 4.1. Materials

The chemical reagents used included catechol, methanol, aqueous ammonia, phosphoric acid, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (lanthanum nitrate hydrate), Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (cerium (III) nitrate hexahydrate), Mg(NO<sub>3</sub>)<sub>2</sub> (magnesium nitrate), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (aluminum nitrate nonahydrate), and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (zinc nitrate hexahydrate). All the above reagents of analytical grade were obtained from Adamas and used as received.

#### 4.2. Sample Preparation

Metal phosphates M-P-O (M = La, Ce, Mg, Al, Zn) catalysts were prepared by precipitation method. In a typical synthesis, 8.702 g La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 1000 mL deionized water, then 4.980 g phosphoric acid solution was added dropwise with vigorous stirring. The pH of the gel was adjusted to 8.0 by adding concentrated aqueous ammonia. After stirring continuously at room temperature for 24 h, the product was separated by filtration and washed with water, dried at 100 °C overnight, and calcinated at 400 °C for 4 h. The obtained sample is denoted as LP.

Other metal phosphates M-P-O (M = Ce, Mg, Al, Zn) samples were prepared following the same synthesis method as LP. M-P-O prepared from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O are denoted as CP, MP, ALP, and ZP, respectively.

# 4.3. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer (Rigaku, Tokyo, Japan) with Cu K $\alpha$  radiation, operated at 40 kV and 40 mA.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS5 spectrometer (Thermo Scientific, Baltimore, MD, USA). A sample was mixed with dry KBr and compressed at 10 MPa for 5 min. Measurements were conducted at a resolution of  $0.8 \text{ cm}^{-1}$ , using the spectrum of pure KBr tablet as the background.

Scanning electron microscopy (SEM) experiments were conducted on a Hitachi S-4000 instrument (Hitachi, Tokyo, Japan).

Textural properties were determined with a Micrometrics ASAP 2020 M+C adsorption apparatus (Micromeritics, Norcross, GA, USA) at liquid N<sub>2</sub> temperature (-196 °C), using N<sub>2</sub> as adsorbate. Before measurement, all the samples were degassed at 200 °C for 10 h.

Temperature programmed desorption of NH<sub>3</sub> or CO<sub>2</sub> was performed on a conventional flow apparatus. Prior to adsorption, 0.15 mg sample (40–60 mesh) was pretreated in flowing N<sub>2</sub> (30 mL/min) at 300 °C for 2 h, cooled down to 30 °C. Then the sample was exposed to 30 mL/min of 10% NH<sub>3</sub>/N<sub>2</sub> or 10% CO<sub>2</sub>/N<sub>2</sub> flow for 30 min and swept with N<sub>2</sub> (30 mL/min) to remove physically adsorbed NH<sub>3</sub> or CO<sub>2</sub>. NH<sub>3</sub> or CO<sub>2</sub> desorption was conducted in flowing N<sub>2</sub> (30 mL/min) by raising the temperature at a heating rate of 10 °C/min. TCD or MS ()(Pfeiffer Omnistar, Germany) was used to detect desorbed NH<sub>3</sub> and CO<sub>2</sub>, respectively.

#### 4.4. Catalytic Evaluation

Vapour-phase selective *O*-methylation of catechol with methanol was carried out in a continuous-flow, fixed-bed microreactor under atmospheric pressure. A 1.5 g catalyst (40–60 mesh) was placed in a quartz tube (i.d. = 10 mm), and pretreated in flowing N<sub>2</sub> (50 mL/min) at 400 °C for 2 h. After the catalyst cooled down to 270 °C, the reactant mixture (catechol: methanol = 1:6, molar ratio) was pumped through a piston pump (WHSV of reactant mixture was  $0.4 h^{-1}$ ). The effluent products were condensed using a cold trap, and then analysed via an FLGC9720 gas chromatograph (Fuli, Zhejiang, China) with a flame ionization detector (FID). The catechol conversion was calculated as ([catechol]<sub>in</sub> – [catechol]<sub>out</sub>)/[catechol]<sub>in</sub> × 100%, where [catechol]<sub>in</sub> is the catechol content in the reactant mixture (no reaction occurs), and [catechol]<sub>out</sub> is the catechol content in the effluent products.

Long-term stability and catalyst regeneration tests were conducted, they were measured as function of time on stream at 270 °C. After the first cycle of stability test, the catalyst was regenerated in flowing air (40 mL/min) at 400 °C for 6 h, then cooled down to 270 °C, the reactant mixture was fed again (denoted as the second cycle).

# 5. Conclusions

Different metal phosphates M-P-O (M = La, Ce, Mg, Al, Zn) catalysts were prepared by precipitation method. MP, ALP and ZP with high amount of strong acid sites showed low catalytic activity in the selective *O*-methylation of catechol with methanol. The stable catalytic activity of LP can be ascribed to its absence of strong acid sites. The higher activity of CP can be related to the weaker strength and higher amount of the weak acid sites. In addition, the suitable base strength and larger amount of weak base sites contribute to the higher guaiacol selectivity of CP. Most of the catalytic activity of used CP can be recovered by regeneration. Although here we only studied the selective *O*-methylation of catechol with methanol, we believe that potential uses of metal phosphates can be explored in other alkylation reactions in the future. **Supplementary Materials:** The following are available online at https://www.mdpi.com/article/ 10.3390/catal11050531/s1, Figure S1: SEM images of (a) CP, (b) LP, (c) MP, (d) ALP, and (e) ZP. (a magnification of 2000), Figure S2: Effect of time on stream on catechol conversion (a) and guaiacol selectivity (b) over CP, SAPO-34, HAP catalysts. Reaction conditions: atmospheric pressure; T = 270 °C; WHSV = 0.4 h<sup>-1</sup>, Figure S3: NH<sub>3</sub>-TPD curves of CP, SAPO-34, HAP catalysts, Figure S4: CO<sub>2</sub>-TPD curves of CP, SAPO-34, HAP catalysts.

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