Vapor-phase Hydrolysis of Chlorobenzene Catalyzed by Copper(II) Ion-exchanged Zirconium Phosphate

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Copper(II) ion-exchanged zirconium phosphate (ZP-Cu(II)) effectively catalyzed the vapor-phase hydrolysis of chlorobenzene to phenol at 450 °C under atmospheric pressure. Per-pass conversion of chlorobenzene was between 12 and 18% with selectivity for phenol from 90 to 95 mol %. The catalytic activity was influenced by the content of copper, the ratio of phosphate to zirconium, and the pH at which copper(II) ions were introduced into zirconium phosphate. ZP–Cu(II) catalyst was amorphous and it turned inactive by thermal treatment at above 800 °C, resulting in a crystalline substance. The active site of ZP–Cu(II) for this hydrolysis reaction appears to be the phosphate groups of ZP bearing copper(II) ion. The reaction seems to proceed *via* a Rideal mechanism in which an adsorbed chlorobenzene molecule reacts with water in the vapor phase at the catalyst surface. The desorption of hydrogen chloride was rate controlling.

Ion-exchange properties of zirconium phosphate (ZP) as well as its crystallography have been the subject of a great deal of research in the field of inorganic and nuclear chemistry. On the other hand, little interest have been shown in the catalysis of ZP since Austerweil first tried to employ ZP as a catalyst for the Pechmann condensation of malic acid with phenol into cumarins in 1959.[1–6] Recently, acidic characteristics of ZP have been investigated in detail in connection with its catalysis in dehydration of 2-propanol and isomerization of 1-butene.[7,8]

Since amorphous ZP has a large surface area (100—350 m^2/g) and it is also considerably durable against thermal and chemical treatments, ZP would be expected to show unique catalytic performance in several organic reactions when combined with various transition metal ions or metals through ion exchange or subsequent reduction. The authors have previously reported that the acidic amorphous ZP loaded with a small amount of finely dispersed palladium metal is an efficient bifunctional catalyst for the direct synthesis of isobutyl methyl ketone by the liquid-phase reductive aldol condensation of acetone.[9–11] As another attempt of applying ZP to catalyst, we have examined the vapor-phase hydrolysis of chlorobenzene to phenol over the ZP incorporating copper(II) ions through ion exchange (ZP–Cu(II)).

The Raschig process, an existing commercial technology of phenol synthesis, involves oxychlorination of benzene to yield chlorobenzene and subsequent vapor-phase hydrolysis of the chlorobenzene to phenol:

$$C_6H_6 + 1/2O_2 + HCl \longrightarrow C_6H_5Cl + H_2O, \quad \Delta H = -43\ \text{kcal/mol at 500 K} \tag{1}$$

$$C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl, \quad \Delta H = -0.64\ \text{kcal/mol},\ K_p = 0.877\ \text{at 700 K.} \tag{2}$$

Although silica has been found effective for the second step reaction (Eq. 2),[12–14] calcium hydroxyapatite, often promoted by copper(II) ion, is commercially employed at present.[15] But this "calcium phosphate" catalyst (CP) still has drawbacks such as poor thermal durability and loss of copper at high temperatures (375—450 °C). It is, therefore, interesting to examine the applicability of thermally stable ZP catalyst to this hydrolysis reaction.

The present study concerns itself with a general examination of ZP-Cu(II) catalyst in the hydrolysis of chlorobenzene, its nature, and possible reaction mechanism.

Experimental

Catalyst Preparation. ZP–Cu(II) catalyst was directly prepared by reacting phosphate ion with zirconium salt in the presence of copper(II) ion at a pH around 4.0, because ZP was fully ion-exchangeable even in a state of hydrous gel. This method was preferable to obtain such ZP as contained homogeneously distributed metal cations in it. The standard ZP–Cu(II) catalyst was prepared as follows: 0.6 g of copper(II) chloride ($CuCl_2 \cdot 2H_2O$) was added to an aqueous solution of zirconium dichloride oxide ($ZrOCl_2 \cdot 8H_2O$ 24 g/H_2O 100 ml). Separatly, 8.0 g of sodium hydroxide was added to an aqueous phosphoric acid (85 vol% H_3PO_4 14.8 g/H_2O 100 ml). The former solution was added to the latter under vigorous stirring at room temperature. The ratio of phosphate to zirconium (P/Zr) was 2: 1. The mixture was then allowed to stand for 44 h. A light blue gel was precipitated, leaving a colorless liquid, pH of which was 4.08. The hydrous gel was filtered, washed with water, dried at 110 °C, and finally calcined at 400 °C for 3 h to yield 20 g of ZP–Cu(II) catalyst. The copper content was 1.1% by weight.

Calcium hydroxyapatite was prepared by a known procedure.[16] Copper doping of the calcium hydroxyapatite was carried out after Reichle.[15]

Chlorobenzene Hydrolysis. The reaction was carried out using a fixed-bed flow apparatus under atmospheric pressure. A Pyrex tube reactor (20 mmϕ×400 mm) was placed in a fluidized alumina bath. The catalyst (18—28 mesh) was placed in the middle of the reactor, and the remainder was filled with catalytically inactive porcelain chips. Reaction temperature was measured with a thermocouple inserted in a Pyrex thermowell (7.5 mmϕ) extending longitudinary through the center of the reactor. Both water and chlorobenzene were continuously metered into the reactor by means of microfeeders. The products were withdrawn as oil and aqueous condensates in a receiver held in an ice bath. When the reaction was carried out with a nitrogen flow to dilute the reactants, a trap containing water was connected with the receiver in order to completely recover the produced hydrogen chloride.

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Analytical Methods. The aqueous condensate was separated from the reaction products and extracted with benzene to recover the dissolving phenol. The extract was joined to the oil condensate and the mixture was analyzed by means of gas chromatography using a 3 m Silicone DC-550 column at 80 °C with a flow rate of carrier gas (H_2) 40 ml/min. The hydrogen chloride dissolving in the aqueous condensate was determined by means of alkalimetry. Thus the total per-pass conversion of chlorobenzene (x) was calculated from the amount of hydrogen chloride. The selectivity for phenol was calculated as $100\,m(1-x)/x$ (%), where m denotes the molar ratio of phenol to chlorobenzene in the reaction products that was determined by the above described analysis by gas chromatography.

Copper in catalyst was determined by means of iodometry. A powdered ZP–Cu(II) sample was previously treated with 1 M nitric acid at 80 °C to remove copper(II) ions.

The thermal analysis of catalyst was carried out by use of a differential thermal analyzer. A 20 mg sample was heated in an aerobic atmosphere at the rate of 10 °C/min using α-alumina as a reference.

Results and Discussion

Catalytic Activity. Figure 1 shows the results of the vapor-phase hydrolysis of chlorobenzene over ZP (P/Zr=2.0), standard ZP–Cu(II), CP and CP–Cu(II) (Cu 2.0 wt%). ZP–Cu(II) was very active compared with other catalysts. The rapid decrease in activity with the time on-stream observed for CP and CP–Cu(II) and the slow one for ZP–Cu(II) were both due to the formation of carbonaceous matter on the catalyst surface. The by-product was benzene. Each of the used catalysts nearly recovered its initial activity after it was regenerated with air to burn off the coke at 450 °C for 2 h. CP was considerably active without the aid of copper. But ZP itself was almost inactive, and copper was essential to the catalysis of ZP for this hydrolysis reaction. These facts suggest that the catalytic performance of ZP is quite different from that of CP. Furthermore, the effect of copper seems to be specific to this reaction because other metal ions incorporated into ZP such as Ag(I), Ni(II), Fe(III), and Co(II) were all inactive except Ca(II) which was slightly effective (conversion=4.0%). The influence of copper content of ZP–Cu(II) (P/Zr=2.0) upon the activity is shown in Fig. 2 in more detail. The chlorobenzene conversion rapidly increased with the copper content until around 2.0% by weight (0.6 meq/g catalyst). On the other hand, the selectivity for phenol gradually decreased with the copper contents as a result of increasing catalytic decomposition of chlorobenzene to benzene. The optimum range of the copper content was between

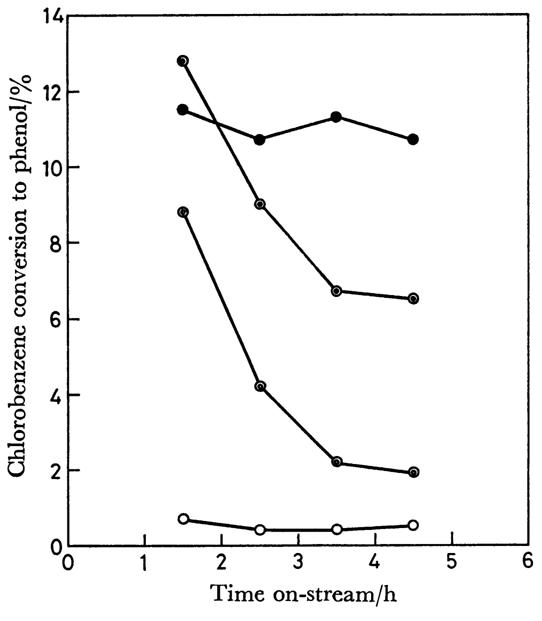

Fig. 1. Vapor-phase hydrolysis of chlorobenzene at 450 °C under atmospheric pressure. H_2O/C_6H_5Cl mole ratio: 3.84, contact time: 1.6 s.
●: ZP–Cu(II), ⊙: CP–Cu(II), ◎: CP, ○: ZP.

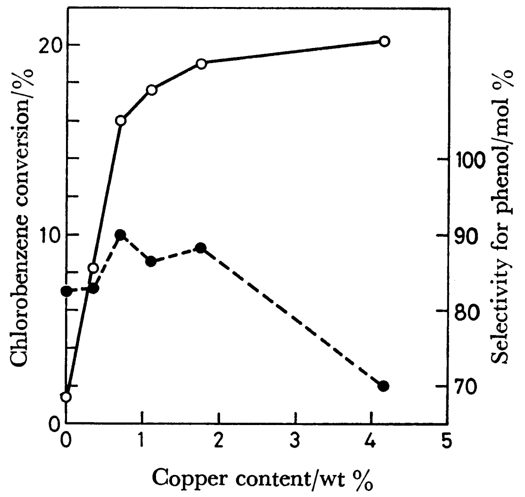

Fig. 2. Effect of copper content of ZP–Cu(II) on initial conversion (○) and selectivity (●). Reaction conditions: 450 °C, 1 atm, H_2O/C_6H_5Cl 3.8, contact time 1.8 s. Data represent the average values during the initial 2.75 on-stream hours.

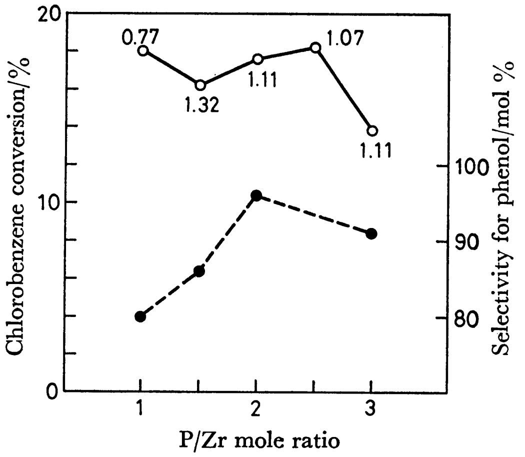

Fig. 3. Effects of P/Zr mole ratio of ZP–Cu(II) on initial conversion (○) and selectivity (●). Reaction conditions: 450 °C, 1 atm, H_2O/C_6H_5Cl 3.8, contact time 1.8 s. Data represent the average values during the initial 2.75 on-stream hours. The figure beside each conversion plot denotes copper content (wt %).

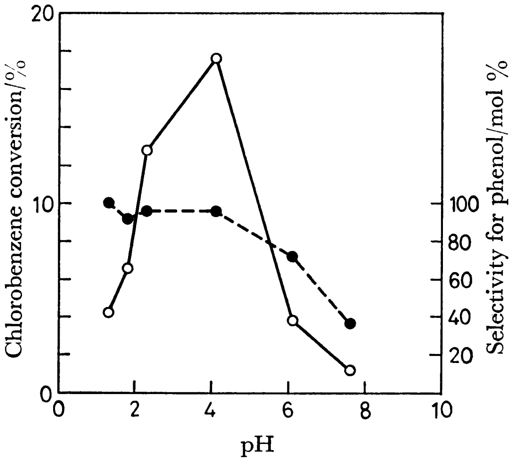

Fig. 4. Effect of pH at catalyst preparation on initial conversion (○) and selectivity (●). Reaction conditions: 450 °C, 1 atm, H_2O/C_6H_5Cl 3.8, contact time 1.8 s. Data represent the average values during the initial 2.75 on-stream hours.

1 and 2 wt % at which the maximum space-time yield of phenol was obtained.

Figure 3 shows the effect of the P/Zr molar ratio in ZP–Cu(II) catalyst. The ratio considerably affected the selectivity for phenol, though the conversion of chlorobenzene was almost unaffected except for a P/Zr ratio 3.0. The optimum P/Zr ratio was 2.0.

Characterization of ZP–Cu(II). The catalyst efficiency remarkably changed with the pH at which ZP–Cu(II) hydrous gel was precipitated (Fig. 4). The most active catalyst was obtained at a pH about 4.0 that was most preferable to introducing copper(II) ion into ZP hydrous gel through ion exchange. At a pH below 4.0 ion exchange became incomplete, while at a pH above 5.3 ineffective copper(II) hydroxide was deposited in ZP hydrous gel. Since not only fresh catalyst but also used one contained no chloride ion, ZP–Cu(II) catalyst appears to hold copper not as liberated copper(II) chloride but as copper(II) ion that is bound to its phosphate groups. In fact, it was experimentally found that both copper(II) chloride and copper(II) phosphate themselves were inactive for this reaction. The ion-exchange capacity of ZP (P/Zr=2.0) was measured 0.7 meq/g for copper(II) ion at a pH 4.0. This corresponded to 2.2 wt % as the copper content. Considering that the activity rapidly increased until around this value of copper content (Fig. 2), the active site of ZP–Cu(II) catalyst seems to be represented by the phosphate groups in ZP bearing a copper(II) ion.

Figure 5 illustrates the thermal change of the standard ZP–Cu(II) catalyst in an aerobic atmosphere, together with a thermogram of ZP (P/Zr=2.0). Although the catalyst was an amorphous solid, it was transformed into an unknown crystalline substance when heated at above around 800 °C, turning completely inactive. The ZP containing no copper was found to change into zirconium pyrophosphate (ZrP_2O_7) at above around 1000 °C.

Activity Maintenance. A continuous catalyst testing was performed by using ZP–Cu(II) (P/Zr=2.0, copper content=2.2 wt %). Although the catalyst was regenerated with air at 430 °C for 33 min every 3.5 h, the conversion of chlorobenzene gradually decreased with the time on-stream. This change in activity is mainly due to the loss of copper in catalyst because the surface area of catalyst was almost unchanged except for its rapid decrease observed during the initial 14 h (Table 1). The selectivity for phenol gradually increased due to the decrease in the copper content of catalyst with reaction time. The copper removed from the catalyst was detected as copper(II) chloride on the reactor wall. Probably, the copper(II) ion bonding to the phosphate groups in ZP reacted with hydrogen chloride to change into copper(II) chloride and vaporized out of the catalyst. Since the vapor pressure of copper(II) chloride is as much as 28 mmHg[††] at 450 °C, the copper(II) chloride thus liberated on the catalyst surface seems to be liable to vaporize.

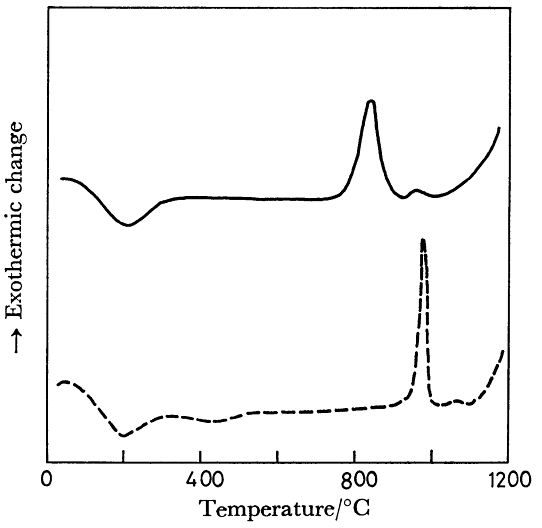

Fig. 5. DTA curves of ZP–Cu(II) (——) and ZP (----).

Table 1. Changes of surface area and copper content of ZP–Cu(II) with time on-stream of reaction

Time on-stream h	BET surface area m^2/g	Copper content wt %
0	169	2.16
14.3	118	1.06
47.5	114	0.39

In order to maintain the activity for longer duration, another catalyst testing with continual supply of copper was undertaken at 450 °C using a stainless steel reactor (28 mm$\phi \times$400 mm). Preheated gaseous reactants had passed at 400 °C through a reactor zone packed with copper metal chips (15 mm in depth) before they reached the catalyst bed (40 mm in depth). The catalyst was regenerated with air at 450 °C for 33 min every 3.5 h, and at the same time the surface of the copper metal chips above the catalyst bed were also

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[††] (1 mmHg≈133.3 Pa).

oxidized. Copper(II) oxide thus formed catalyzed the decomposition of chlorobenzene and a small amount of hydrogen chloride was produced. The hydrogen chloride, in turn, reacted with the surface copper(II) oxide to form copper(II) chloride. The catalyst could be, therefore, continually supplied with the vapor of copper(II) chloride from the zone of copper metal chips. By means of such continual supply of copper, the ZP-Cu(II) catalyst maintained both the conversion and the selectivity at their stationary levels for 600 on-stream hours, except for a slight decrease in the conversion observed during the initial 140 h.

Reaction Mechanism. The kinetic data of the hydrolysis of chlorobenzene were obtained using small particles (18—24 mesh) of the standard ZP-Cu(II) catalyst. The linear velocity of the flow of gaseous reactants was kept above 22 cm/s at the reaction temperature. Under these conditions, the reaction rate was released from the influence of both external and internal mass-transport processes. The total pressure of the reactants was varied by the dilution with nitrogen. Figure 6 shows the changes in the initial reaction rate with the water to chlorobenzene molar ratio and with the total pressure of the reactants. The initial rate at each reaction temperature remained nearly unchanged under varied partial pressures of the reactants and different total pressures. At a reaction temperature as high as 400 to 450 °C, it is unlikely that the adsorption constant for chlorobenzene or for water is large enough to cancel the effect of the total pressure of the reactants on the initial rate. It is, therefore, probable that the desorption of one of the products was rate-controlling. Figure 7 gives the change in the initial rate when one of the products was added to the reactants beforehand. The rate again remained approximately constant with all the amount of hydrogen chloride added. On the other hand, the phenol in the feed clearly lowered the rate. Considering that the equilibrium constant for the over-all reaction is less than unity at 400 to 450 °C, the above kinetic data are well interpreted by assuming that the desorption of hydrogen chloride is rate-controlling. The apparent activation energy was 8.6 kcal/mol at a reaction temperature between 400 and 450 °C.

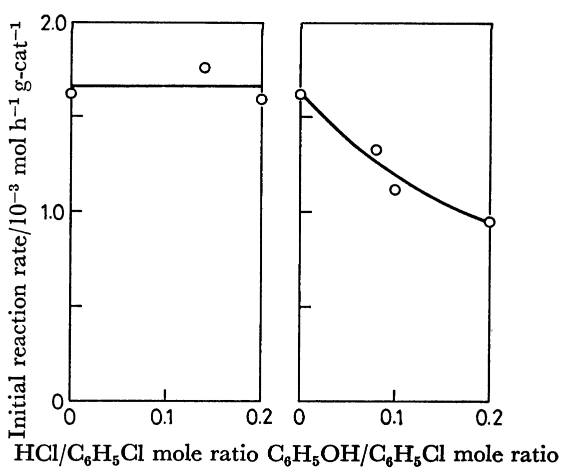


Fig. 7. Effects of hydrogen chloride and phenol on initial reaction rate at 450 °C. Data were obtained between initial 1.0 and 2.0 on-stream hours. Catalyst: regenerated, total pressure: 0.65 atm.

Furthermore, in order to presume the reaction mechanism, it was examined at what stage in the reaction path phenol was formed. Water and chlorobenzene were alternately adsorbed on the catalyst surface and each desorbed product was analyzed (Fig. 8). It was found that phenol was formed only when water was supplied to the catalyst on which chlorobenzene had already been adsorbed, but on the other hand no phenol was detected in the reactor effluent when chlorobenzene was fed to the catalyst on which only water had been adsorbed. This experiment suggests that the reaction proceeded *via* a Rideal mechanism in which adsorbed chlorobenzene reacts with water in the vapor phase.

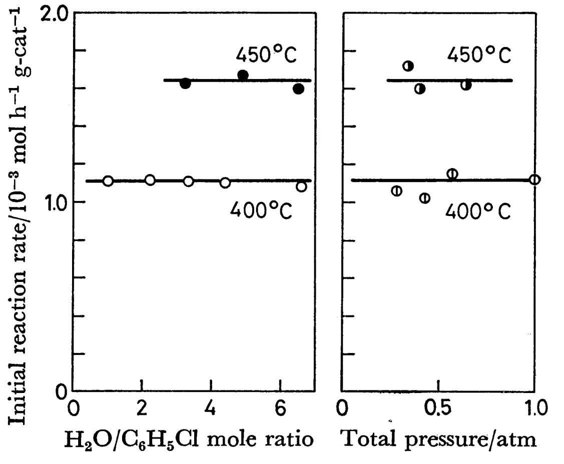


Fig. 6. Effects of mole ratio of reactants and total pressure on initial reaction rate. Data were obtained between initial 1.0 and 2.0 on-stream hours.

○: fresh catalyst, total pressure 1.0 atm; ●: regenerated catalyst, total pressure 0.7 atm; ⦶: fesh catalyst, H_2O/C_6H_5Cl 2.2; ◐: regenerated catalyst, H_2O/C_6H_5Cl 3.2.

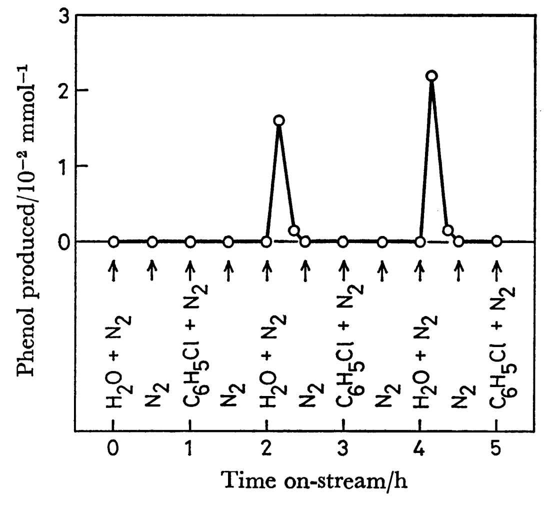
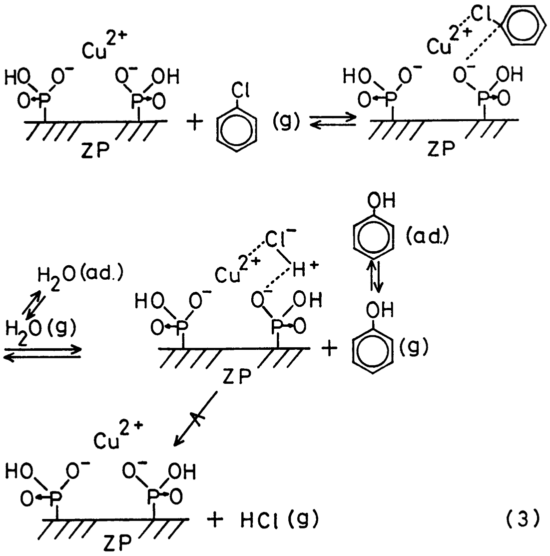


Fig. 8. Phenol formation by alternate feed of water and chlorobenzene at 305 °C.

Catalyst: standard fresh ZP-Cu(II) 2.0 g, H_2O flow rate: 0.0992 mol/h, C_6H_5Cl flow rate: 0.0306 mol/h.

Considering the structure of the active site in ZP-Cu(II) discussed above, the vapor-phase hydrolysis of chlorobenzene over ZP-Cu(II) catalyst appears to proceed as follows:



(3)

A chlorobenzene molecule is first adsorbed on the active site and activated by copper(II) ion and phosphate group. The activated molecule is then hydrolyzed with the water in the vapor phase at the catalyst surface, and finally converted into phenol, leaving adsorbed hydrogen chloride behind. The rate-determining step is the desorption of hydrogen chloride.

Reichle[15] has previously investigated the vapor-phase hydrolysis of chlorobenzene over calcium hydroxyapatite promoted by copper(II) ion and proposed a mechanism of nucleophilic displacement of chlorobenzene by the hydroxide ion of the apatite. The copper(II) ion held in the apatite crystal would activate the formation of a Meisenheimer type complex from chlorobenzene and hydroxide ion. Thus the calcium apatite catalyst works as a nucleophile by itself:

$$2C_6H_5Cl + Ca_{10}(OH)_2(PO_4)_6 \longrightarrow 2C_6H_5OH + Ca_{10}Cl_2(PO_4)_6 \quad (4)$$

$$2H_2O + Ca_{10}Cl_2(PO_4)_6 \longrightarrow 2HCl + Ca_{10}(OH)_2(PO_4)_6 \quad (5)$$

On the other hand, ZP-Cu(II) in the present study catalyzes the reaction presumably in this way that both copper(II) ion and the phosphate group concertedly activate or polarize a chlorobenzene molecule and facilitate a nucleophilic attack of water on the chlorobenzene molecule.

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