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Direct hydroxylation of aromatics over copper–calcium–phosphates in the gas phase

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Dedicated to Prof. F. Trifiró on the occasion of his 65th birthday.

Abstract

A new alternative process for the direct gas phase hydroxylation of aromatics is studied using molecular oxygen (air) or nitrous oxide in the presence of copper containing calcium–phosphate. The activity of Cu–Ca–phosphate catalyst in the reaction of benzene with oxygen, N_2O or the mixture of oxygen–ammonia as oxidants is compared. Beside benzene also alkyl aromatics were used in the same reaction. The preferred reaction is attack on a side chain. We suggest that the oxidation of benzene starts via formation of phenyl radical.

Keywords: Benzene; Phenol; Hydroxylation; Phenyl radical

1. Introduction

Direct hydroxylation of the aromatic ring is a very challenging approach to synthesise phenols. The direct gas phase hydroxylation of aromatics with nitrous oxide over Fe-zeolites is the most studied process [1–3]. Phenol is formed over Fe-ZSM5 catalyst with selectivity 95% and benzene conversion up to 30%. The process Alphox utilizing nitrous oxide and Fe-ZSM5 was designed with connection to adipic acid production plant, where N_2O is produced as waste-greenhouse gas [4]. Except N_2O produced as waste, nitrous oxide is rather an expansive chemical commodity. Considering the quantity of N_2O from an adipic acid plant, only a portion of phenol world-wide produced can be obtained from direct benzene hydroxylation via Alphox. Furthermore, a peculiar problem arising due the pore system of ZSM5 catalyst – for example deactivation by coke deposition – has to be solved [5]. Synthesis of phenol from benzene and N_2O was also reported over non-porous Fe–phosphate catalyst with benzene conversion of 2% and phenol selectivity 85% [6].

However, oxidation of aromatics with molecular oxygen or air is more attractive for application in the large-scale industrial synthesis. The particularity of hydrocarbon oxidation with molecular oxygen is summarised in the book of Arpentinier et al. [7]. Several catalytic systems active in the hydroxylation of benzene with oxygen based on copper catalyst have been published. Liquid and gas phase hydroxylation with in situ produced hydrogen peroxide over Cu, Pd catalyst is object of intensive research. The reaction proceeds in the liquid phase over supported Cu catalyst with O_2 in the presence of H_2 [8] or ascorbic acid with phenol yield up to 1.7% [9,10]. Dihydroxyphenols were found as by-products. Similarly in the gas phase, copper containing catalyst is active with the mixture of O_2–H_2 with an yield of phenol 0.9% [11]. In situ formation of hydrogen peroxide was observed using these catalytic systems. The presence of Cu(II)/Cu(I) redox pair in the reaction mechanism was suggested [11,12]. Molecular oxygen is activated for further reaction by taking an electron from the Cu(I) ion. Hydrogen or ascorbic acid is needed as co-reductant for copper (II) ions [10].

Formation of phenol was reported in vapour phase in the presence of Cu–phosphate or calcium–copper–phosphate from benzene and water, though re-oxidation of copper is

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very probably needed for a true catalytic system [13,14]. The hydroxylation of benzene with oxygen and without the co-reductant over copper containing calcium–phosphate catalyst was studied and very promising results were obtained [15]. It was found that phenol rapidly decomposes at the temperature over 500 °C, so the optimal temperature is around 450 °C [15,16]. A high selectivity is reached if ammonia is present in the reaction mixture. Conversion of benzene decreases with increasing NH_3/C_6H_6 ratio at constant pressure of oxygen. However the selectivity to phenol increases as the total oxidation to CO_2 decreases. The yield of phenol increases with increasing partial pressure of oxygen at constant pressure of ammonia in the reaction mixture, but the production of carbon oxides increases too. Thus, maximal selectivity to phenol is reached with high partial pressure of ammonia and low pressure of oxygen in the reaction mixture. A necessity of water in the reaction mixture was also experimentally proved. At such conditions, a higher yield of phenol is reached only at the start of the reaction and after approximately 3 h the conversion decreases. It was found that nitrous oxide is formed in situ from the catalytic decomposition of ammonia [15].

The effect of the used oxidant is studied in this work. The activity of copper–calcium–phosphate catalysts is compared in the presence of nitrous oxide and oxygen–ammonia mixture. The influence of kinetic parameters on the hydroxylation of benzene with N_2O–H_2O is investigated. A reaction mechanism concerning the existence of phenyl radical is discussed. Moreover, catalysts described in papers [15] and [16] contained more phosphate phases so it is hard to define active centres. New catalysts with a single crystal phase of hydroxyapatite (HAP) were prepared by deposition of copper on calcium diphosphate and calcium hydroxyapatite. The structure of copper active sites is then discussed.

2. Experimental

The reaction was carried out in a stainless steel 75 cm long reactor (1 cm i.d.) using 2 g of phosphate catalyst with particle size 0.3–0.6 mm in a standard run. Some experiments have been done using a glass reactor 15 cm long (1.5 cm i.d.). No effect of steel reactor on conversion and selectivity was found at all. Organic compounds and water were collected in a frozen flask, homogenised with methanol and analysed with GC using a FI detector. Carbon oxides were analysed from off-gases with GC using a TC detector. Reaction products from the conversion of substituted aromatics were identified with a GC-MS equipment (Shimadzu QP5000).

2.1. Catalyst preparation

Copper–calcium–hydroxyphosphate with 43 wt.% of copper was prepared by co-precipitation by simultaneous adding of calcium (100 ml, 1 M) and copper nitrate (300 ml, 1 M) solutions to the solution of ammonium monohydrogen orthophosphate (400 ml, 0.6 M). The precipitate obtained was then dissolved with a solution of nitric acid (160 ml, 2 M). Copper–calcium–phosphate was precipitated from a clear solution by increasing pH to 10 with the aqueous solution of ammonia (1 M). Solutions were prepared by dissolving or diluting of corresponding chemicals (p.a.). Hydroxyphosphates are formed by hydrolysis of orthophosphates obtained during precipitation. Hydrolysis is favoured at higher pH and temperature. The suspension stands for 5 h at 80 °C. During the ageing time pH of the solution was several times adjusted to 10. The portion of copper added to the precipitation remained in the solution in the form of a copper–ammonia complex. The precipitate was then filtered and carefully washed with deionised water to remove dissolved ions. The obtained phosphate was then dried at 110 °C and calcined at 580 °C for 5 h.

Catalysts with the structure of hydroxyapatite – $Ca_{10}(OH)_2(PO_4)_6$ bearing 0.01 and 0.1 wt.% of Cu were prepared by ion exchange. Ion exchange was performed from an ammonia complex of copper by the substitution of coordinated ammonia with surface OH-groups by analogy to silanol groups on SiO_2 described in [17]. The suspension of hydroxyapatite (25 g) calcined previously at 900 °C was stirred in water (100 ml) at pH 9 adjusted with ammonia solution (1 M). The aqueous solution of $[Cu^{2+}(NH_3)_4](NO_3^-)_2$ with a concentration of 0.01 M was then added dropwise to the hydroxyapatite suspension. Diluted solutions of copper were used to avoid precipitation of $Cu(OH)_2$ on the surface of the catalyst resulting in crystalline or para-crystalline CuO. Catalyst with 1 wt.% of Cu was prepared by impregnation of hydroxyapatite from the aqueous solution of copper

Table 1
Effect of the type of oxidant on the hydroxylation of benzene

Oxidant	Reaction mixture					Products	
	C_6H_6 (mmol/h)	NH_3 (mmol/h)	O_2 (mmol/h)	N_2O (mmol/h)	H_2O (mmol/h)	Y_{Phenol} (%)	Y_{Co_2} (%)
NH_3–O_2–H_2O	11.2	13.8	1	0	37.1	1.3	0.1
O_2–H_2O	11.2	0	5.1[a]	0	55.4	3.2	7.1
N_2O–H_2O	11.2	0	0	7.4	55.4	3.1	1.4
N_2O–NH_3–H_2O	11.2	13.8	0	7.4	55.4	0.4	0

Catalyst: Cu–Ca–phosphate (43 wt.% Cu), 2 g, 450 °C, samples collected during 5 h of steady state conditions, balanced with N_2, total molar feed 91.2 mmol/h.

[a] Experiment with air.

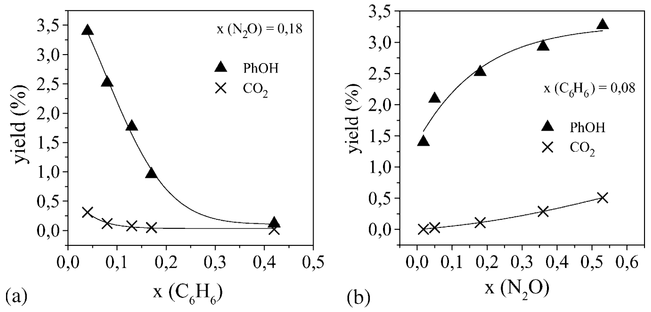

Fig. 1. (a) Effect of benzene concentration at constant concentration of $x(N_2O) = 0.18$, $x(H_2O) = 40.3$, balanced with N_2, total molar flow 136 mmol/h. (b) Effect of nitrous oxide concentration at constant benzene concentration $x(C_6H_6) = 0.08$, $x(H_2O) = 40.3$, balanced with N_2, total molar flow 140 mmol/h – on the yield of phenol and carbon dioxide. Steady state conditions, Cu–Ca–phosphate (43 wt.% Cu), 2 g, 450 °C.

nitrate. The impregnation method was used to develop copper oxide on the surface of the carrier. The catalysts were calcined at temperature 580 °C during 5 h with the heating rate 100 °C/h.

3. Results and discussion

We have found that the hydroxylation of benzene over Cu–Ca–phosphate proceeds not only with NH_3–O_2–H_2O, but also with O_2–H_2O or with N_2O–H_2O mixtures.

If benzene reacts with the O_2–H_2O mixture, the selectivity to phenol is lower than with the mixture NH_3–O_2–H_2O and carbon dioxide is the main product. It follows that ammonia is not implicitly needed for the hydroxylation of benzene, but it suppresses the total oxidation in the presence of oxygen.

The activity of the catalyst is higher using the N_2O–H_2O mixture, as an oxidizing agent than with the mixture NH_3–O_2–H_2O but the selectivity to phenol is lower. If ammonia is used in the presence of nitrous oxide, the activity of the catalyst rapidly decreases (Table 1). We suppose that ammonia adsorbs strongly on Cu sites. Oxygen is able to substitute ammonia in the coordination sphere of copper or in specific sites by oxidizing ammonia. Intensive oxidation of ammonia occurs over copper–calcium–phosphate at 450 °C forming NO and N_2O with an yield around 1%. Depending on the O_2/NH_3 ratio in the mixture NH_3–O_2–H_2O total conversion of oxygen can take place, as it was noticed in the reference [15]. Nitrous oxide is probably not susceptible to such reaction with ammonia adsorbed on Cu and the activity of catalyst decreases.

On the other hand if the fresh catalyst was used, the reaction proceeded also with the mixture of NH_3–H_2O, i.e. without oxidant from the gas phase. In this case the oxygen from the structure of the catalyst was used. During the first 3 h of benzene oxidation with the mixture NH_3–H_2O, the yield of phenol reaches 1% with selectivity over 95% and then continuously decreases with the time on stream.

If benzene reacts with the mixture of NH_3–O_2–H_2O beside phenol also aniline is formed as by-product. No aniline or nitrogen containing aromatic compounds were found with the mixture N_2O–H_2O, but carbon dioxide was formed as by-product beside phenol. Biphenyl and benzofurane were identified in trace amounts. The presence of biphenyl was noticed only at higher concentration of benzene in the reaction mixture. If oxygen or the mixture of NH_3–O_2–H_2O was used, no biphenyl was found among the products.

Using the mixture of C_6H_6–N_2O–H_2O as an oxidant, the yield of phenol depends on the N_2O/C_6H_6 ratio. The yield of phenol increases as the ratio of N_2O/C_6H_6 increases. However, also the total oxidation of benzene to CO_2 increases (Fig. 1a and b).

A similar effect of oxygen and benzene concentration in the reaction system was observed in the experiments where the mixture of C_6H_6–O_2–H_2O was used as an oxidant. In contrary to the hydroxylation of benzene with N_2O, the total oxidation of phenol in the presence of O_2 is more significant than in the experiments with N_2O.

Phenol formed by catalytic hydroxylation of benzene can react in a free volume of the oxidation reactor with oxygen and thus diminish the selectivity of oxidation. The results of the gas phase oxidation of phenol with O_2 in the empty reactor (without a catalyst) have shown that the homo-

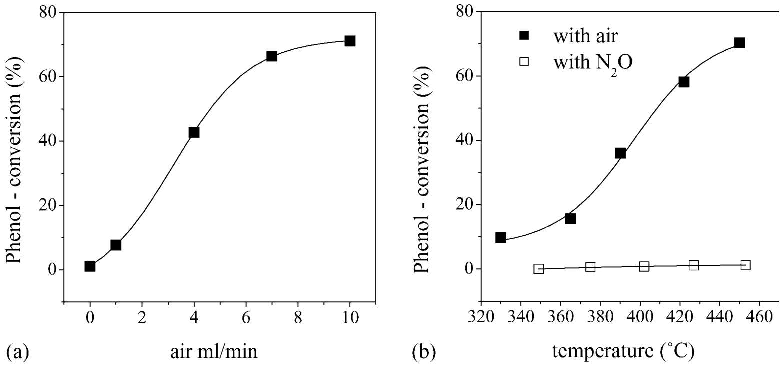

Fig. 2. (a) The effect of air flow at 450 °C and (b) the effect of temperature (air 10 ml/min, N_2O 10 ml/min) on the conversion of phenol in the empty reactor. Phenol 0.349 mmol/h, H_2O 55.4 mmol/h.

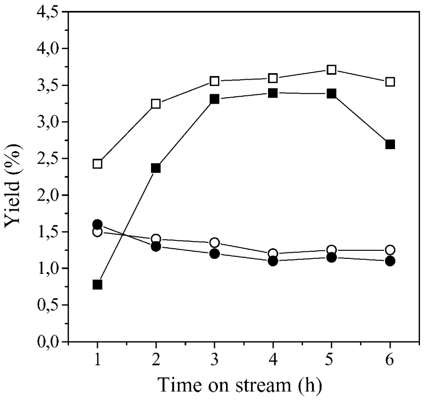

Fig. 3. Effect of phenol in the feed on the yield. Squares: yield of C_6H_5OH; circles: yield of CO_2; hollow symbols: without phenol added; solid symbols: with 0.349 mmol/h of added C_6H_5OH. C_6H_6 11.25 mmol/h, H_2O 55.45 mmol/h, N_2O 7.35 mmol/h, N_2 1.72 mmol/h Cu–Ca–phosphate (43 wt.% Cu), 2 g, 450 °C.

geneous oxidation of phenol depends on the O_2/C_6H_6 ratio and the reaction temperature (Fig. 2). Under the same reaction conditions homogeneous oxidation of benzene does not proceed.

3.1. The effect of phenol

Hydroxylation of benzene over Cu–Ca–phosphate catalyst with the mixture of N_2O–H_2O as an oxidant produces phenol with the overall yield 3.1% during 5 h. Under the same conditions an experiment was done, in which phenol (0.349 mmol/h) was added to the feed to the reactor. A certain amount of phenol was dissolved in water and injected continuously to the reactor. The amount of phenol added to the feed represents about 3% yield of phenol. Thus, a higher yield of phenol, about 6% (than in a standard run) was expected. Surprisingly, in the experiment with added phenol to the feed, the overall yield of phenol was lower, even as in the standard experiment (Fig. 3). The yield of carbon dioxide practically remains on the same value as in the experiment without phenol in the feed. The formation of the same amount of carbon dioxide in these experiments indicates that the added phenol is not decomposed. Phenol added to the feed probably affects the rate of hydroxylation of benzene over phosphate catalyst.

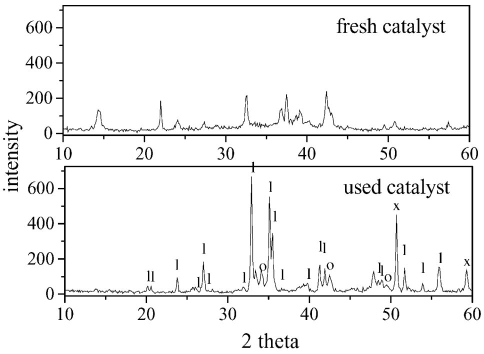

Fig. 4. XRD pattern of fresh catalyst calcined in air at 580 °C and catalyst after reaction with C_6H_6–N_2O–H_2O at 450 °C for 7 h. Cu–Ca–phosphate (43 wt.% Cu), Cu Kα, phase annotation: I – $Cu_2P_2O_7$, ○ – Cu_2O, × – Cu.

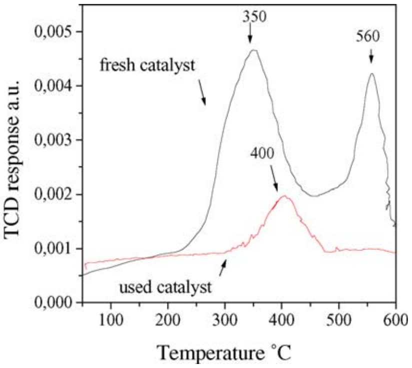

Fig. 5. TPR (H_2 30 ml/min, 10 °C/min) of fresh catalyst calcined in air at 580 °C and catalyst after reaction with C_6H_6–N_2O–H_2O at 450 °C for 7 h. Cu–Ca–phosphate (43 wt.% Cu).

3.2. Catalyst characterisation

The catalyst during the first hours of experiment, undergoes a considerable reconstruction of crystal phases and is partly reduced (Figs. 4 and 5). Prior to the reaction the catalyst was calcined in air at 580 °C. Therefore, the reconstruction of the catalyst is induced rather with the reactants than by temperature itself. Various crystal phases have been found in the catalysts using XRD. The fresh catalyst is mainly composed of crystalline calcium–phosphate and also certain crystal phases assigned most probably to mixed copper–calcium–phosphates. After reconstruction, the overall crystalinity of the catalyst increases. The crystal phase of copper diphosphate ($Cu_2P_2O_7$) is evidently strengthened. Crystalline copper oxide and cuprite (Cu_2O) were found as minor phases. The extent of reduction depends on the content of oxygen or nitrous oxide in the reaction mixture. The reduction peaks at 350 and 560 °C were found in the fresh catalyst, but only one strong peak at 400 °C was found after the catalytic run. This peak is probably a result of deep reconstruction of the catalyst. However, from the relative comparison of an area below the TPR curve we can estimate that most of Cu is

Table 2
Selectivity of phenol formation over phosphate catalysts bearing different Cu species

Catalyst	Cu (wt.%)	Possible Cu species	Y_{PhOH} (%)	S_{PhOH} (%)
OHAp	0	–	0.45	92
Cu/ns-OHAp	0.01	Isolated Cu ions	1.5	88
Cu/ns-OHAp	0.1	Isolated Cu ions	1.5	88
Cu/ns-OHAp	1	Cu-clusters	1.7	69
Cu–Ca–phospate	43	$Cu_2P_2O_7$	3.26	65

Catalyst: 2 g, mol.%: C_6H_6 (12.3), H_2O (60.8), N_2O (8.1), N_2 (18.8); 0.4393 g $(C_6H_6)/g_{CAT}\,h^{-1}$, 450 °C.

Table 3
Products of toluene conversion with various oxidation mixtures over Cu–Ca–phosphate

Oxidizing agent	Ba (g)	Y (Ba) (%)	Cres (g)	Y (Cres) (%)	PhOH (g)	Y (PhOH) (%)	R
N_2O–H_2O	0.0033	0.4	0.0011	0.1	0.0016	0.2	4.4
O_2–H_2O	0.1277	14.4	0.0179	2.0	0.0184	2.1	8.1
NH_3–O_2–H_2O	0.0484	5.5	0.0039	0.4	0.0075	0.8	14.5

Catalyst: Cu–Ca–phosphate (43 wt.%), 2 g, 450 °C, steady state conditions, toluene 9.61 mmol/h, N_2O 7.35 mmol/h, H_2O 55.45 mmol/h, O_2 5.14 mmol/h, NH_3 13.83. Ba – benzaldehyde, Cres – *o,m,p*-cresols, PhOH – phenol, *Y* – yield, *R* – molar ratio between products of methyl group oxidation (Ba + PhOH) and aromatic ring hydroxylation (Cres).

reduced in the used catalyst. The catalyst bearing 43 wt.% of copper undergoes deep reconstruction and contains various crystal phases. The catalyst with defined structure was prepared by deposition of copper on the surface of hydroxyapatite. With respect to loading of copper, the existence of different copper species is expected. Formation of well dispersed, isolated Cu ions is favoured below 1 wt.% of Cu loaded from the solution of copper–ammonium complex by ion exchange. Clusters of copper oxide are developed by impregnation from the solution of copper nitrate especially at higher loading of copper. Considering this we have found out that if the catalyst contains isolated Cu ions, oxidation of benzene with the mixture of N_2O–H_2O produces phenol with a selectivity as high as 88%. If also CuO is present on the catalyst, the selectivity of oxidation decreases to 69–65% (Table 2).

3.3. Hydroxylation of alkyl aromatics

At the same conditions as benzene also toluene, ethylbenzene and cumene were oxidized over copper–calcium–phosphate (43 wt.% Cu) using N_2O–H_2O as an oxidant. Toluene was converted to benzaldehyde and cresols. The main reaction of ethylbenzene oxidation was dehydrogenation which led to styrene. 3-Ethyl-phenol was formed in less extent. Oxidation of cumene produces α-methyl styrene as the product of its dehydrogenation. It was observed that a ratio between oxidation of the methyl group of toluene and hydroxylation of aromatic nucleus depends on the type of oxidizing agent. The ratio (*R*) is set as mol of benzaldehyde and phenol to mol of cresols formed during 1 h of oxidation (Table 3). As is evident from results in Table 3 all tested oxidizing agents preferably oxidize the methyl group than the aromatic nucleus. Hydroxylation of the aromatic ring is relatively higher using the mixture of N_2O–H_2O as oxidizing agent while oxidation of methyl group to benzaldehyde is prevailing with the mixture of NH_3–O_2–H_2O. The highest conversion of toluene was reached with the mixture of O_2–H_2O.

3.4. Reaction mechanism

The gas phase hydroxylation of benzene and alkyl aromatics proceeds over mixed Cu–Ca–phosphates with O_2, N_2O and the mixture of NH_3–O_2 as the oxidizing agents. The yield and selectivity of phenol formation depends on the conditions and the type of oxidizing agent used. High selectivity is reached if ammonia is present in the reaction mixture. Strong adsorption of phenol on Cu sites of the catalyst is probably responsible for a low reaction rate in the presence of phenol in the feed. The preferred reaction during oxidation of alkyl aromatics over Cu–Ca–phosphate catalyst with all studied oxidants is attack on a side chain. When the mixture of N_2O–H_2O was used for the oxidation of benzene or toluene, biphenyl or biphenyl methane were found as by products. It was observed that formation of biphenyl depends on the partial pressure of benzene in the reaction mixture. It is generally known that biphenyl is the product of recombination of phenyl radicals. It suggests that the oxidation of benzene starts most probably with formation of the phenyl radical. The phenyl radical is then converted to phenol. Since oxygen is an effective scavenger for phenyl radicals the formation of biphenyl was not noticed in experiments in the presence of ammonia and air. It supports also observation that in the presence of oxygen phenol is the only product of transformation of the phenyl radical [18].

4. Conclusions

Phenol is produced in the gas phase oxidation of benzene with oxygen or nitrogen oxide over Cu–Ca–phosphate catalyst. The selectivity and activity depends on the composition of the oxidation mixture. The highest activity is reached if ammonia is present in the mixture of O_2–H_2O. The highest yield of phenol is reached using the mixture of N_2O–H_2O over Cu–Ca–phosphate (43 wt.% Cu) at 450 °C. The yield of phenol increases with the concentration of nitrous oxide and decreases with concentration of benzene in the gas phase. The presence of phenol has a negative effect on the reaction rate. The selectivity of phenol formation depends on the catalyst preparation. Formation of phenol is favoured over the catalyst prepared by ion exchange, while total oxidation proceeds over Cu impregnated calcium–phosphate catalyst. Dehydrogenation is the main reaction of ethylbenzene and cumene under tested conditions. Oxidation of toluene with O_2–H_2O over Cu–Ca–phosphates gives cresols with ca. 2% yield, beside phenol (2%) and benzaldehyde (14%). Hydrogen abstraction and formation of phenyl radical is probably the rate limiting step of phenol formation. The molecular mechanism of formation of phenyl radicals and OH group addition will be described in the next paper.

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