DIRECT HYDROXYLATION OF BENZENE TO PPHENOL

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Abstract

Direct synthesis of phenol from benzene, which could replace the multistage cumene process, is an object of intensive research. We have studied the gas phase conversion of benzene to phenol over bimetallic hydroxyphosphates comprising calcium and copper. We have found that nitrous oxide, produced in-situ from the catalytic oxidation of ammonia with air, enables selective hydroxylation of benzene. A reaction mechanism was proposed comprising nitrous oxide formation and phenyl radical reaction. Beside benzene also toluene, ethylbenzene and cumene were employed in this catalytic system and the products were identified.

Keywords: hydroxylation, benzene, phenol, copper-calcium phosphate

Introduction

Several catalytic systems for the direct benzene hydroxylation to phenol in the gas phase have been designed. Benzene is selectively converted to phenol with hydrogen peroxide over Cu-Pd/SiO$_2$ [1,2] or Pt-VO$_x$/SiO$_2$ [3]. Hydrogen peroxide is formed in-situ from a mixture of O$_2$ and H$_2$ in the presence of a catalyst and subsequently decomposed to hydroxyl radicals. More likely applicable is the process utilizing waste nitrous oxide as a selective oxidant. Nitrous oxide decomposes leaving so called active oxygen inside the pore system of ZSM 5 zeolites [4,5]. Benzene reacts directly with active oxygen forming phenol. The direct hydroxylation of benzene over calcium-copper phosphate was first reported by Matsuda and Kato [6]. We have examined this potential way for the direct hydroxylation of benzene with a mixture of ammonia and air. An optimal catalyst composition and reaction conditions were determined [7]. In this work, we have examined the influence of reaction mixture composition on the selectivity and product distribution employing benzene and substituted aromatics.

Experimental

The hydroxylation reaction was carried out in a 75 cm long stainless steel reactor with an internal diameter of 10 mm. The catalyst bed consisted of 2g of catalyst with a particle size of 0,3-0,6 mm placed on a stainless steel net. Benzene, water or an aqueous solution of ammonia were fed by linear dozers to the reactor. The flow of gases was regulated by mass flow controllers. The reaction products were led to a cold trap. The condensed products were taken in desired time intervals, homogenised with methanol and analysed by a gas chromatograph equipped with

a flame ionisation detector. Carbon oxides in the off-gases were analysed with infrared flow analysers. A sample from the off-gas was withdrawn to the gas tight syringe for more precise determination and analysed by GC equipped with a thermal conductivity detector.

The structure of phosphate catalysts was identified using an X-Ray Diffractometer ($CoK\alpha,\ 2\theta \in <10,60>°$). The content of phosphorus and calcium in the catalyst was determined by a titration method. Copper was determined using an UV-VIS spectrometer.

Catalyst preparation

The hydroxyapatite (Hap) with the stoichiometric formula $Ca_{10}(OH)_2(PO_4)_6$ was prepared by the precipitation method. This precipitation took place in a mixed thermostated bottle. The bottle was separated from outer atmosphere by water plug to prevent absorption of carbon dioxide. A calcium nitrate solution was added in stoichiometric amount drop-wise to the solution containing 0,1 mol/l of phosphate anion and adjusted to pH equal 9 with an ammonia solution. The temperature was kept at 80°C during the precipitation and the next five hours during ageing time. The solution over the precipitate was several times substituted by a fresh solution to remove an excess of hydrogen cations and facilitate hydrolysis. The precipitate was separated, dried and calcined at 900°C. The material obtained had a structure of slightly calcium deficient non-stoichiometric hydroxyapatite (ns-Hap) proven by XRD.

Copper calcium hydroxyphosphates were co-precipitated by simultaneous adding of defined volumes of calcium and copper nitrate solutions to the solution of phosphate anion. The structure and composition of the obtained precipitate was governed by the con-

centration of source solutions, rate of precipitation, temperature, pH and ageing time. The precipitate was filtered and carefully washed with deionised water to remove dissolved ions. The obtained phosphate was then dried at 110°C and calcined at 550°C for 5 hours.

Cu-Ca phosphates with a structure of ns-Hap bearing 0,01 and 0,1 wt% of Cu were prepared by ion exchange on hydroxyapatite. Ion exchange was performed from an ammonia complex of copper. The suspension of hydroxyapatite calcined previously at 900°C was stirred in water at pH 9. The aqueous solution of $[Cu^{2+}(NH_3)_4]$ with a concentration of 0,01 mol/dm^3 was then added drop-wise to the hydroxyapatite suspension. A special attention was paid not to exceed 0,001 mol/dm^3 of Cu in the solution over hydroxyapatite to avoid precipitation of $Cu(OH)_2$ resulting in crystalline or para-crystalline CuO. The catalyst with 1 wt.% of Cu was prepared by impregnation of hydroxyapatite. The impregnation method was used to develop copper oxide on the surface of the carrier.

Results and discussion

Influence of the catalyst structure

A dependence was found between copper content and activity of catalysts prepared by co-precipitation. Two optimal compositions were found with 22 wt.% and 43 wt.% of Cu. Powder diffraction analyses showed that the fresh catalysts with 22 wt.% of Cu was predominantly amorphous, but crystal phases were developed under reaction conditions. The catalyst with 43 wt.% of Cu was composed of the hydroxyapatite phase $Ca_{10}(OH)_2(PO_4)_6$ and copper pyrophosphate $Cu_2P_2O_7$ (Fig.2). Under the flow of benzene, ammonia, air and water vapour at 450°C the pyrophosphate phase was strengthened and cuprite (Cu_2O) was developed. To relieve the structure of the active centre, a group of

catalysts with Cu deposited on hydroxyapatite by ion exchange and impregnation was prepared. Hydroxyapatite has a good stability, hydroxyl groups susceptible to chemical interaction and relatively weakly bound – exchangeable calcium cations.

Cu-hydroxyapatite catalysts with a Cu content from 0,01 wt.% to 1 wt.% do not undergo a noticeable reconstruction of their crystalline phase under reaction conditions. The activity of the tested catalysts during six hours of time on stream is compared in Table 1.

Calcium hydroxyapatite has no activity in the presence of an ammonia – air mixture. However, in the presence of nitrous oxide, phenol is formed in a low yield. Phenol is produced with higher selectivity over the catalyst prepared by ion exchange than by impregnation. Presence of CuO on the surface of the hydroxyapatite probably facilitates total oxidation. We cannot exclude the presence of CuO on the catalysts prepared by co-precipitation. Co-precipitated catalysts have highest activity.
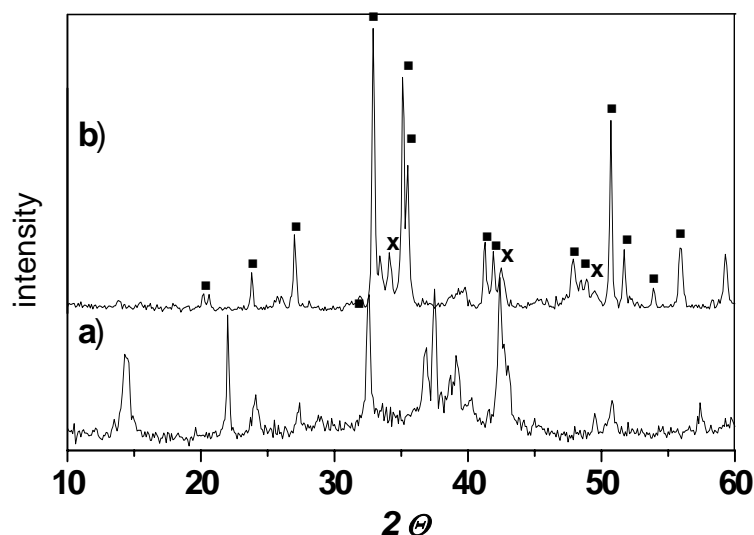

Fig. 1: XRD: Cu-Ca phosphate (43 wt.% Cu) a) fresh catalyst, b) used catalyst – NH_3, O_2, H_2O, 450°C; square: $Cu_2P_2O_7$, cross: Cu_2O

Table 1: Hydroxylation of benzene over hydroxyphosphate catalysts

Catalyst	Most abundant M^{2+} species	wt.%	$NH_3 – O_2 – H_2O$		$N_2O - H_2O$	
			Y_{PhOH} %	S_{PhOH} %	Y_{PhOH} %	S_{PhOH} %
OHAp	-	0	0,05	100	0,45	92
Cu / OHAp	Isolated Cu ions	0,01	0,3	96	1,5	88
Cu / OHAp	CuO	1	0,39	95	1,7	69
Cu-Ca phosp.	Cu phosphate	22	1,1	97	3,0	66
Cu-Ca phosp.	Cu phosphate	43	1,3	96	3,26	65
Pd-Ca phosp.	Pd phosphate	1	0,4	96	3,0	67

Y_{PhOH} -phenol yield, S_{PhOH} – selectivity of benzene conversion to phenol. Reaction conditions benzene: 570 $mg/h/g_{kat}$, mol ratio: (C_6H_6:O_2:NH_3:H_2O = 1:0,5:1,2:3,3), (C_6H_6:N_2O:H_2O =1:2,4:4,7), 450°C, 6 hours time on stream

Palladium is also active in the benzene hydroxylation. Pd-Ca phosphate prepared by co-precipitation has a comparable activity as Cu-Ca phosphate with a similar copper content (but different structure) in the presence of ammonia and oxygen. In the presence of

N_2O, palladium produces more phenol than copper calcium phosphate (with a similar structure, but a different content of modifying metal) based on the content of copper bound in the catalyst.
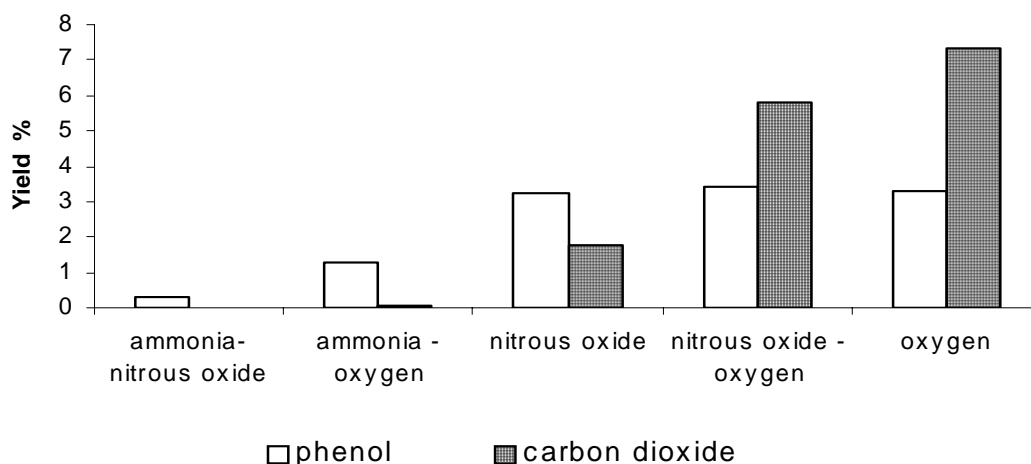
Fig. 2.: Yield of phenol and carbon dioxide over Cu-Ca phosphate (43 w.% Cu) in the presence and in the absence of ammonia. Reaction conditions: benzene: 570 mg/h/g_{kat}, mol ratio: (C_6H_6:NH_3: N_2O:H_2O = 1:0,5:1:3,3), (C_6H_6:O_2:NH_3:H_2O = 1:0,5:1,2:3,3), (C_6H_6:N_2O:H_2O = 1:1:3,3), (C_6H_6:O_2:N_2O:H_2O = 1:0,25:0,5:3,3) (C_6H_6:O_2:H_2O = 1:0,5:3,3), 450°C

Influence of reaction mixture

Applying different reaction mixtures, distinct by-products were found. In the presence of an ammonia-air mixture, aniline and carbon dioxide are formed beside phenol. The total oxidation is suppressed by employing molecular oxygen in the ammonia oxidation pathway. Ammonia probably deactivates copper oxide by adsorption on it. Under optimal conditions, the conversion of oxygen reaches 100%. Biphenyl, benzofuran and carbon dioxide are formed as by-products if nitrous oxide is used as an oxidant. If ammonia is added to this system the yield of phenol is low. Carbon dioxide is the main product of benzene oxidation over Cu-Ca catalysts if oxygen (air) and nitrous oxide or oxygen are used.

The role of water

Phenol is formed over copper calcium phosphate catalysts only in the presence of water. If water is excluded from the reaction mixture conversion of benzene decreases and carbon dioxide is the main product. The presence of water is crucial with the mixture of ammonia and air as well as with nitrous oxide. The dependence between phenol yield and concentration of water exhibits saturation level (Fig. 3). At a low concentration of water, the phenol yield strongly increases with water content in the reaction mixture.
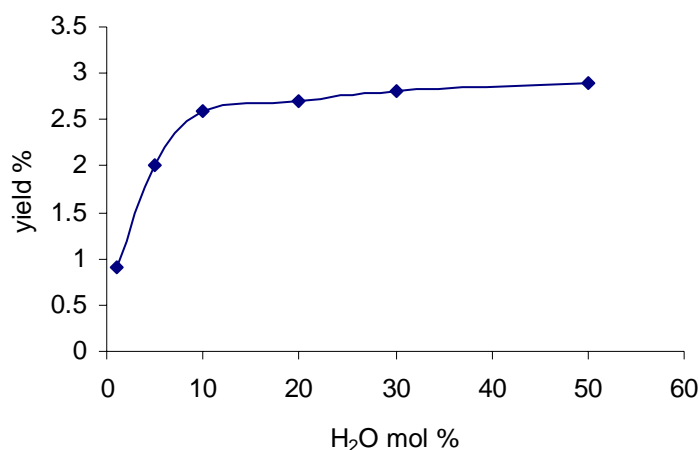

Fig. 3. Influence of water content on the yield of phenol. over Cu-Ca phosphate (43 w.% Cu). Reaction conditions: benzene: 570 mg/h/g_{cat}, t=450°C

Above the saturation level, only a weak relationship is found. Water has probably more functions. A certain partial pressure is necessary to prevent the catalyst from loosing its constitutional water. Water facilitates phenol desorption by stripping it from the surface. Moreover, we cannot exclude water from the reaction mechanism of benzene hydroxylation.

Hydroxylation of substituted aromatics

Toluene, ethylbenzene and cumene were employed at the same conditions as benzene using nitrous oxide as an oxidant over copper calcium phosphate (43 wt.% Cu). Products and by-products are summarised in Table 2. Phenol is the main product only if benzene is applied. Abstraction of hydrogen from the side chain competes with aromatic ring hydroxylation.

Table 2.: Products of conversion of benzene and substituted aromatics

Reactant	Products	By products
Benzene	Phenol	Biphenyl, Benzofuran
Toluene	Benzaldehyde, Cresols	Xylene, Diphenylmetane
Ethylbenzene	Styrene	Acetophenone, 3-ethyl-phenol
Cumene	1-propenylbenzene, Phenol	Acetophenone, Cinnamon aldehyde

Reaction mechanism

Ammonia is oxidised with air in the presence of catalysts to nitrous oxide, nitrogen oxide and nitrogen. If the catalyst is active with a mixture of air and ammonia, its activity is enhanced in the presence of nitrous oxide. Based on this a reaction mechanism was proposed, concerning in-situ formation of nitrous oxide in the first step [7]:

$$2\ NH_3 + 2\ O_2 \rightarrow\ N_2O + 3\ H_2O \tag{1}$$

Nitrous oxide decomposes on the catalyst in the next step allowing selective oxidation of benzene:

$$N_2O + (\ ) \rightarrow (O) + N_2 \tag{2}$$

$$C_6H_6 + (O) \rightarrow (C_6H_5OH) \tag{3}$$

$$(C_6H_5OH) \rightarrow C_6H_5OH + (\ ) \tag{4}$$

This part of the mechanism does not answer the question in which way the hydroxyl group is developed on the aromatic ring. Biphenyl and biphenyl methane are formed as by-products when benzene or toluene reacts with N_2O (Table 2). We can conclude that phenyl radical is formed as an intermediate to biphenyl. Oxygen is an effective scavenger for phenyl radicals. Thus formation of biphenyl was not noticed in the presence of ammonia and air. In the presence of oxygen and the phenyl radical, phenol is the only product detected [8].

Kinetic isotope effect

We have arranged the experiment with hexadeuterobenzene to find out if the phenyl radical is an intermediate in the mechanism of phenol formation. An equimolar mixture of benzene and D6 benzene was used with nitrous oxide and water over Cu-Ca phosphate (43 wt.% Cu). The rate of phenol formation from benzene and hexadeuteroben-
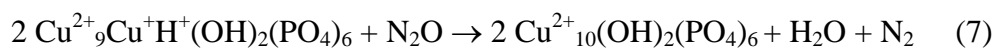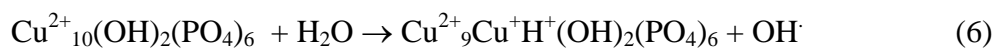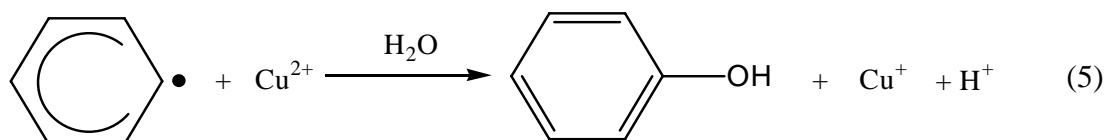
zene was then compared. Phenol from benzene was formed predominantly. The ratio between the rate of phenol formation from benzene and D6 benzene was determined as high as 30 000. The kinetic isotope effect gave us the evidence of C-H bond breaking in the rate-limiting step.

Evidence of hydroxyl radical

The phenyl radical can be formed from thermal decomposition of benzene at 450°C, but the yield of phenol in the absence of the catalyst is negligible. If substituted aromatics are converted over the Cu-Ca phosphate catalyst, a hydrogen abstraction competes with aromatic ring hydroxylation (Table 2). Hydrogen abstraction beside aromatic ring hydroxylation is a characteristic reaction of the electrophilic hydroxyl radical at elevated temperature in the gas phase [9]. Formation of the hydroxyl radical over phosphate catalyst is possible according to reactions (6) and (7).

Phenyl radical hydroxylation in the presence of Cu^{2+} and water, as described in reaction (5), was reported in the liquid phase [10].

$$Cu^{2+}_{10}(OH)_2(PO_4)_6 + H_2O \rightarrow Cu^{2+}_9Cu^+H^+(OH)_2(PO_4)_6 + OH^{\cdot} \qquad (6)$$

$$2\,Cu^{2+}_9Cu^+H^+(OH)_2(PO_4)_6 + N_2O \rightarrow 2\,Cu^{2+}_{10}(OH)_2(PO_4)_6 + H_2O + N_2 \qquad (7)$$

Conclusions

Calcium copper phosphates show a promising catalytic activity in the benzene hydroxylation to phenol. Active sites probably consist of copper phosphate surrounded by calcium hydroxyapatite. An optimal composition of these two phases is necessary for high activity of the catalysts. Surface copper oxide has a detrimental effect on the selectivity. A high selectivity is reached, if ammonia and air are used as oxidant. Nitrous oxide is formed in-situ in catalytic oxidation of ammonia. Under reaction conditions the $OH^{\cdot}$ radical is formed on the catalyst. The hydroxyl radical attacks benzene forming the phenyl radical and water. The phenyl radical is converted to phenol in the next step concerning the redox Cu^{2+}/Cu^+ pair, or by chain reaction with oxygen.

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