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Direct gas phase hydroxylation of benzene over phosphate catalysts

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Abstract

The gas phase hydroxylation of aromatics is studied over Cu-modified phosphate catalysts. Benzene is converted to phenol in the presence of oxygen and ammonia at 450 °C. The same catalysts are active for benzene hydroxylation using nitrous oxide as the oxidant. Catalysts with different copper loading are tested and the effect of the structure of copper species on the yield of phenol is compared. The effect of used oxidants, water as well as possible reaction mechanism is discussed.

Keywords: Benzene; Hydroxylation; Phenol; Phosphate catalysts

1. Introduction

Direct synthesis of phenol from benzene is an object of intensive research. Several catalytic systems have been designed with the attempt to take advantages of heterogeneous catalysts and the gas phase conversion of benzene to phenol (Table 1). Benzene is selectively converted to phenol with a mixture of O_2 and H_2 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 the catalyst and subsequently decomposed to hydroxyl radicals. Using of oxygen–hydrogen mixture in a large-scale synthesis is not preferred, so a process utilising nitrous oxide as the selective oxidant is more likely applicable. Nitrous oxide decomposes leaving so-called active oxygen inside the pore system of ZSM 5 zeolites [4,5]. Benzene reacts directly with the active oxygen forming phenol. The drawback of this catalytic system is that the production capacity of phenol depends on a source of waste nitrous oxide like the adipic acid plant.

An attractive catalytic system for the hydroxylation of benzene should use oxygen, preferably air as the cheap and available oxidant. We have studied a conversion of benzene to phenol over various phosphates as the catalysts. We have found that phosphate catalysts containing one metal atom from the IIA group and one transient metal in the structure show a promising catalytic effect. Air can be used as the oxidant in the presence of ammonia in the reaction mixture. Nitrous oxide is formed in situ and benzene is then converted to phenol with high selectivity forming aniline, CO_2, biphenyl or benzofurane as by-products. Phosphate catalysts have the advantage of active site location accessible to large molecules, high stability, low cost and simple preparation process.

2. Experimental

Calcium orthophosphates containing any other metal in the structure were prepared by co-precipitation from aqueous solutions of corresponding nitrates or chlorides and ammonium mono-hydrogen orthophosphate at pH 9–10 according to [7]. The precipitate was filtered and carefully washed with deionised water to remove dissolved ions. The obtained phosphate was then dried at 100 °C and calcined at 550 °C for 5 h. Ion exchange of Cu on hydroxyapatite was performed from an ammonia complex of copper. The ammonia complex of copper was prepared from a copper nitrate solution adding a sufficient amount of aqueous solution of ammonia. The suspension of hydroxyapatite calcined previously at 900 °C was stirred in water at pH = 9 adjusted with an ammonia solution. 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. It is generally assumed that isolated surface Cu species are formed at low surface concentration of copper, if

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Table 1
Catalytic systems active in benzene hydroxylation in the gas phase

Catalyst	Oxidant	Temperature (°C)	References
$Cu–Pd/SiO_2$	O_2–H_2/in situ generated H_2O_2	150–200	[1,2]
$Pt–VO_x/SiO_2$	O_2–H_2/in situ generated H_2O_2	140	[3]
Fe, Al, Ga ZSM-5	N_2O/α-O	300–350	[4,5]
Pd, Cu hydroxyapatite	N_2O	450	[6,7]
Cu–Ca hydroxyphosphate	O_2–NH_3/in situ generated N_2O	450	[7]

precipitation of $Cu(OH)_2$ is preserved. Special attention was paid not to exceed 0.001 mol/dm^3 of Cu in the solution over hydroxyapatite. The equilibrium of ion exchange was established within 1 h [8]. Testing of the catalyst was performed in a fixed bed steel reactor at 450 °C under atmospheric pressure. Condensable products were collected in a glass bottle cooled at 0 °C, homogenised with methanol and analysed by GC. Carbon oxides were analysed by GC and nitrogen oxides with a quadruple mass spectrometer from an effluent gas after the separation of condensable products.

3. Results and discussion

3.1. Effect of catalyst structure

All the modified calcium phosphate catalysts carried around 44 wt.% of modifying metal, and were a solid solutions composed of crystalline calcium hydroxyapatite, crystalline or amorphous hydrogen phosphates, orthophosphates and diphosphates of the modifying metal. The conversion of benzene to phenol was studied with air–ammonia aqueous solution and with nitrous oxide–water mixture. Samples collected during 5 h after 2 h of equilibration period were analysed and the results are compared in Fig. 1.

Copper modified calcium phosphate, was found the most active catalysts among phosphates containing other metals (Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Zr, Mo, Ag, Ba, Hg) with the mixture of oxygen–ammonia. When the mixture of N_2O–H_2O was used as the oxidant, the same catalyst was active for hydroxylation of benzene. Using nitrous oxide also palladium–calcium phosphate showed notable activity (Fig. 1). According to this comparison, copper modified calcium phosphates were further studied. Monometallic calcium hydroxyapatite is less active for hydroxylation of benzene in the presence of ammonia–air. However, in the presence of nitrous oxide, hydroxylation of benzene proceeds even over pure calcium hydroxyapatite (Table 2). Calcium hydroxyapatite was chosen as support for copper catalyst prepared by ion exchange. When this type of catalyst contains also Cu ions, the yield of phenol increases up to four times, most probably by the redox properties of copper. The structure of copper species on hydroxyapatite changes from isolated ions to copper oxide by increasing the surface loading of copper. The activity of catalysts prepared by ion exchange with 0.01 and 1 wt.% of Cu is compared in Table 2. Considering the reaction in the presence of nitrous oxide, we can find that the yield of phenol is similar but the selectivity increases with decreasing copper loading. This can be explained by decreasing the amount of copper

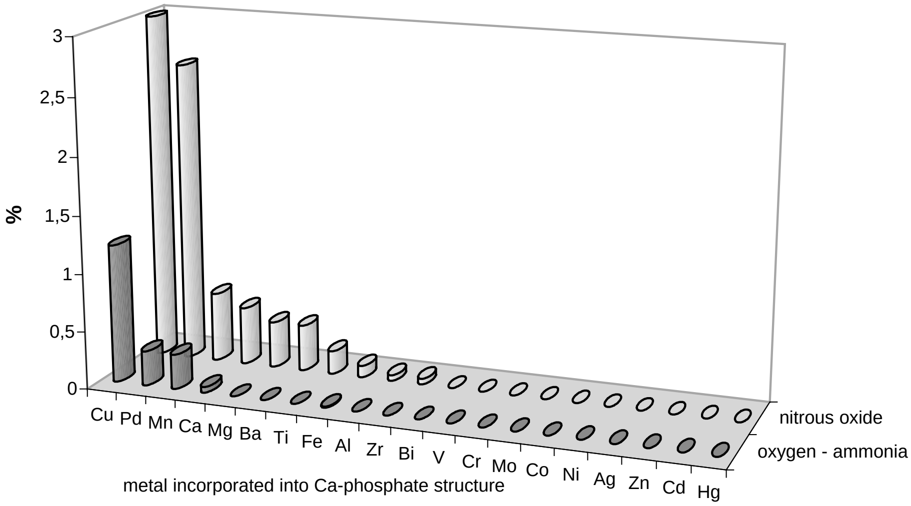


Fig. 1. Yield of phenol over calcium phosphate catalysts modified with another metal cation. Reaction conditions: 450 °C; 2 g of the catalyst; catalyst loading: 570 mg/h g_{KAT} of benzene; feed composition (mol%)—first row: C_6H_6: 13; NH_3: 15.9; H_2O: 42.8; O_2: 5.9; N_2: 22.3—second row: C_6H_6: 12.3; H_2O: 60.8; N_2O: 26.9.

Table 2
Hydroxylation of benzene with the mixture of oxygen and ammonia or with nitrous oxide as oxidant over calcium and copper hydroxyphosphate catalysts

Catalyst	Most abundant Cu species	Cu (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 phospates	Incorporated Cu phosphate	47	1.3	96	3.26	65

Y_{PhOH}: phenol yield; S_{PhOH}: selectivity of benzene conversion to phenol. Reaction conditions: 450 °C; benzene: 570 mg/h g_{KAT}; feed composition (mol%): C_6H_6: 13; NH_3: 15.9; H_2O: 42.8; O_2: 5.9; N_2: 22.3; or C_6H_6: 12.3; H_2O: 60.8; N_2O: 26.9.

oxide on the catalyst surface. Total oxidation of benzene over CuO is a well-known process. The copper ions active in the hydroxylation of benzene should have a structure of isolated copper ions distributed on the phosphate surface or the copper ions incorporated in the phosphate structure as it is seen from the results summarised in Table 2.

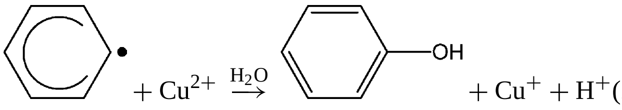
Using distinct reaction mixtures different by-products were found. When the mixture of ammonia–oxygen–water was used, aniline and carbon-dioxide were found as by-products. If nitrous oxide was employed as oxidant, carbon-dioxide was the main by-product. Biphenyl was found only in trace amounts.

3.2. *Influence of ammonia, water, nitrous oxide and oxygen*

The presence of ammonia suppresses total oxidation of benzene by employing molecular oxygen in the ammonia oxidation pathway (Fig. 2). Under given conditions in the presence of ammonia a total conversion of oxygen is observed. The product of ammonia oxidation are N_2O and NO which are produced in the concentration under 1 mol%. If nitrous oxide was employed as oxidant, the activity of the catalyst increased. Based on this observation a two-step reaction mechanism was proposed concerning the formation of nitrous oxide in situ [7]. However, the hydroxylation proceeds, although not selectively also with oxygen in the absence of ammonia (Fig. 2). The drop of selectivity observed in the presence of nitrous oxide as oxidant could be explained by formation of molecular oxygen from catalytically decomposed N_2O at higher pressures of nitrous oxide:

$$2N_2O \rightarrow 2N_2 + O_2 \tag{1}$$

The obtained experimental data suggest reduction and oxidation mechanism proposed for the oxidation of benzene in the liquid phase [8]. A phenyl radical can be formed in the presence of suitable metal catalyst. The formed phenyl radical reacts with water, producing phenol and reduced Cu^+ and H^+ ions on the catalyst. The reduced form of catalyst is re-oxidised by nitrous oxide or oxygen:



(2)

$$\begin{aligned}&{Cu_{10}}^{2+}(OH)_2(PO_4)_6 + H_2O\\ &\quad\rightarrow {Cu_9}^{2+}Cu^+H^+(OH)_2(PO_4)_6 + OH^-\end{aligned} \tag{3}$$

$$\begin{aligned}&2{Cu_9}^{2+}Cu^+H^+(OH)_2(PO_4)_6 + N_2O\\ &\quad\rightarrow {Cu_{10}}^{2+}(OH)_2(PO_4)_6 + H_2O\end{aligned} \tag{4}$$

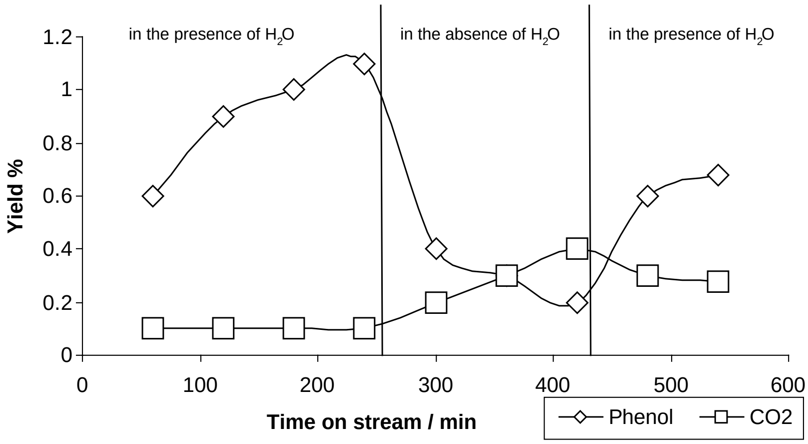


Fig. 2. Activity and selectivity of Cu–Ca phosphate (44 wt.% Cu) in the presence and in the absence of water. Reaction conditions: 450 °C; 2 g of the catalyst; catalyst loading: 570 mg/h g_{KAT} of benzene; feed composition (mol%): C_6H_6: 13; NH_3: 15.9; H_2O: 42.8; O_2: 5.9; N_2: 22.3 or C_6H_6: 14.1; NH_3: 16; O_2: 5.9; N_2: 64.

The fact that water takes part in the supposed reaction mechanism is supported by the necessity of water vapour in the reaction mixture. The hydroxylation of benzene with the mixture of O_2/NH_3 proceeds over hydrated surface of the catalysts. If water is excluded from the reaction system the activity and the selectivity of the catalyst decreases (Fig. 2). The activity is within few hours partially restored by adding water. The same behaviour was observed using a mixture of air–ammonia or nitrous oxide as the oxidant. This fact could be also explained by the ability of hydroxyapatite to convert to oxyapatite by its constitutional water. Dehydration of hydroxyapatite is a reversible process, which leads to an oxygen vacancy (⌈) in the apatite structure. Temperature and partial pressure of water vapour influence dehydration reaction [9,10]:

$$2OH^- \leftrightarrow H_2O(g) + O^{2-} + \lceil \qquad (5)$$

The vacancy could be filled with oxygen from the gas phase forming radical oxygen species. Although, structural changes of the catalyst have not been proven in situ, the mechanism of benzene oxidation over hydroxyapatite types of catalysts is very likely to occur under our reaction conditions.

4. Summary

Direct hydroxylation of benzene in the gas phase proceeds over copper–calcium hydroxyphosphates using either molecular oxygen (air) or nitrous oxide. The presence of ammonia suppresses total oxidation of benzene during oxidation with molecular oxygen and phenol is produced with high selectivity. Surface copper(II) oxide has the detrimental effect on the selectivity. Isolated Cu ions and Cu-phosphate enhance selective oxidation to phenol over hydroxyapatite catalyst. The reaction mechanism involving active oxygen species from decomposition of nitrous oxide formed in situ, as well as the possibility of the phenyl radical reaction should be considered in a further study of this catalytic system.

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