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Direct synthesis of phenol from benzene over hydroxyapatite catalysts

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Abstract

The direct synthesis of phenol from benzene in the gas phase was studied over hydroxyapatite catalysts. The reaction was carried out in a fixed-bed reactor at atmospheric pressure and reaction temperature of 450°C in the presence of ammonia. A high selectivity (about 97%) of phenol formation at about 3.5% conversion of benzene was achieved over catalysts containing Ca and Cu ions in the cation part of hydroxyapatite. Besides phenol as the main reaction product, aniline is also formed. The reaction mechanism involves formation of N_2O from NH_3 in the first step of reaction. Benzene is oxidized by active oxygen species which are formed on the catalyst by decomposition of N_2O. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Benzene; Phenol; Hydroxyapatite catalysts; Oxidation

1. Introduction

Hydroxylation of aromatics is an important process of organic synthesis. Industrial preparation of phenol from benzene is realized mainly by the multistage cumene process which produces acetone as the co-product.

A very attractive way for the synthesis of phenol is the direct hydroxylation of benzene in both the liquid or gas phase. Recently, many papers and patents devoted to this reaction appeared in the literature. The direct hydroxylation of aromatics to phenol proceeds with molecular oxygen and is catalyzed by Cu(II) salts in the presence of sulfuric acid in acetonitrile or ascorbic acid [1,2]. Solid palladium catalyzes the oxidation of benzene to phenol with hydrogen peroxide [3,4], oxygen [5,6] or a mixture of hydrogen and oxygen [7]. A very high selectivity of benzene oxidation to phenol is obtained with nitrous oxide in the gas phase over Fe-ZSM-5 catalyst [8–12]. At 330°C and 25% conversion of benzene, the selectivity to phenol formation is more than 99%.

In our laboratories we have studied the direct oxidation of benzene to phenol with nitrous oxides as the oxidizing reagent produced in situ. Mixed hydroxyapatite catalysts composed of calcium and other transition metals were found to be active for this reaction system. Actually, both oxygen and ammonia are fed simultaneously over the catalyst and the produced nitrous oxides subsequently attack benzene.

In this paper, we describe the preparation and testing of the hydroxyapatite catalysts, and propose the mechanism of this reaction.

2. Experimental

The oxidation reaction of benzene to phenol was carried out at atmospheric pressure in a fixed-bed

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reactor made from stainless steel with 10 mm internal diameter and 750 mm length. The reactor containing 2 g of the solid catalyst (particle size 0.6–1.0 mm) was electrically heated and the temperature in the catalyst bed measured with a thermocouple. Benzene and water or aqueous ammonia solutions were pumped into the reactor with linear dosers. The flow of nitrogen or air was followed by mass flowmeters. The reaction products were collected during 5 h in a flask containing 4 ml of distillated water. After finishing the reaction nitrogen flowed through the reactor for 15 min to strip organic compounds from the catalyst and the walls of the reactor.

In the experiments focused on the study of the reaction mechanism, the outlet gases were analyzed continuously by the mass spectrometer Quadrex 200 connected to the reactor.

2.1. Catalysts preparation

Analytical grade reagents 0.6 M $(NH_4)_2HPO_4$ and 1 M $Ca(NO_3)_2$ were used to prepare the precipitate, according to the method similar to Jarcho et al. [13]. Aqueous solution of $Ca(NO_3)_2$ was dropped into the stirred aqueous solution of $(NH_4)_2HPO_4$. The formed precipitate was dissolved with 2 M HNO_3 and the obtained clear solution was dropped slowly into the stirred solution of NH_4OH. The obtained suspension was heated at 80°C for 5 h, then filtered, three times, washed with deionized water and dried at 110°C for 5 h. The precipitate was calcinated at 500°C for 6 h with the temperature gradient 100°C/h. The catalysts prepared by this procedure were modified with Cu(II) by ion exchange or impregnation. The same mixed catalysts were prepared by direct precipitation from nitrate solutions of appropriate metals.

2.2. Catalyst characterization

The temperature programmed reduction of catalyst (50 mg) was performed in pure hydrogen in a conventional apparatus with a thermal conductivity detector. The rate of heating the catalyst sample from 30°C up to 650°C was 10°C/min. Then, isothermal conditions were kept until the reduction of the catalyst was finished. The flow rate of hydrogen was 30 cm^3/min.

The specific surface area of supports was measured at -196°C using the Pulse Chemisorb 2700 apparatus (Micromeritics) with nitrogen as an adsorbing gas.

XRD analysis of the catalyst powder was measured under following conditions: Cu Kα, $2\Theta \in \langle 10, 55 \rangle$°C, 40 kV and 25 mA using an X-ray powder diffractometer.

2.3. Analysis

The content of phenol and aniline in the reaction product was determined by gas chromatography using the method of absolute calibration. The liquid reaction product was diluted with methanol in a 50 ml volumetric flask and then analyzed. This analysis was carried out on a Shimadzu GC 17 chromatograph fitted with an FID. The glass column (4 mm i.d., 100 cm length) was packed with 5% Carbovax and 5% SE 30 on Chromatone NAW DMCD impregnated with 1% KOH and programmed from 150 to 200°C at 10°C/min. Nitrogen (35 ml/min) was used as a carrier gas. The injector and oven temperatures were 230 and 250°, respectively.

The products were identified by the combination of GC/MS analysis (GC–MS QP 500 Shimadzu, column 50 m × 0.2 mm × 0.33 μm HP-1).

3. Results and discussion

3.1. Effect of hydroxyapatite catalyst

The reaction of benzene with ammonium hydroxide in the presence of air was carried out over hydroxyapatite catalysts at 450° and atmospheric pressure. In a fixed-bed reactor hydroxyapatite catalysts containing Sr, Co, Fe, Zn, Ca, Mn and Cu metals were tested. Hydroxyapatites containing Sr, Co, Fe and Zn gave phenol and aniline only in trace amounts. The results are summarized in Table 1 show that all hydroxyapatite type catalysts which contain the combination of metals Ca, Cu, Mn in their cation part are catalytically active. The catalysts containing only one metal as a cation are catalytically inactive for the transformation of benzene to phenol. The activity of the hydroxyapatite catalysts influences also the ratio of metals. As can be seen in Fig. 1, in Ca and Cu containing bimetal-

Table 1
Reaction of benzene with ammonium hydroxide in the presence of air[a]

Catalyst composition (wt.%)	X_{Ph} (%)[b]	X_A (%)[c]
4.06 (Ca), 13.98 (Cu), 21.05 (Mn)	1.30	0.12
3.55 (Ca), 14.16 (Cu), 20.84 (Mn)	1.20	0.08
17.01 (Ca), 11.43 (Cu)	0.40	0
16.89 (Ca), 7.73 (Cu), 6.34 (Mn)	1.50	0.27
6.03 (Ca), 23.60 (Cu), 14.19 (Mn)	0.81	0.08
38.40 (Cu), 2.60 (Mn)	1.29	0.34
21.15 (Ca), 27.09 (Cu)	0.65	0.11
27.18 (Ca), 15.32 (Cu)	0.34	0.05
21.78 (Ca), 18.23 (Cu)	0.37	0.06
26.23 (Ca), 15.95 (Cu)	0.26	0.06
25.1 (Ca)	0	0
28.3 (Cu)	0	0

[a] Reaction conditions: 450°C; flow of benzene 1.0 ml/h; ammonium hydroxide (26 wt.%) 1.0 ml/h; air 10 ml/min.

[b] X_{Ph}: conversion of benzene to phenol.

[c] X_A: conversion of benzene to aniline.

lic hydroxyapatite catalysts, the highest activity was achieved at the ratio of Ca/Cu=0.33.

In the presence of ammonium hydroxide beside phenol also aniline was formed as a product in very low yield. However, both products phenol and aniline are produced with a selectivity higher than 96%. The presence of trace amounts of biphenyl, diphenyl ether, benzofuran, dibenzofuran and dibenzo-1,4-dioxime in the reaction mixture was detected by the GS/MS method.

3.2. Effect of temperature

The results in Fig. 2 show that the conversion of benzene to phenol and also to aniline increases almost linearly with temperature in the range 350–450°C. At reaction temperatures above 500°C formation of carbon oxides and organic by-products rapidly increases.

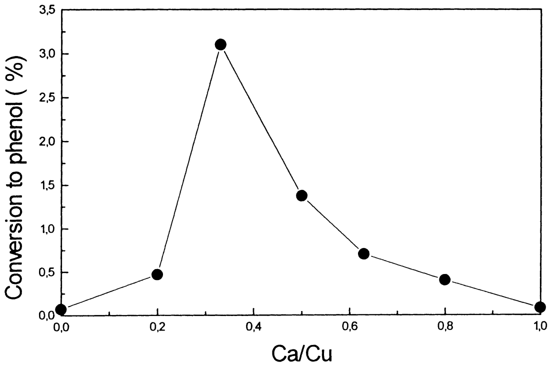

Fig. 1. Influence of the Ca/Cu ratio in the bimetallic catalyst on the phenol formation.

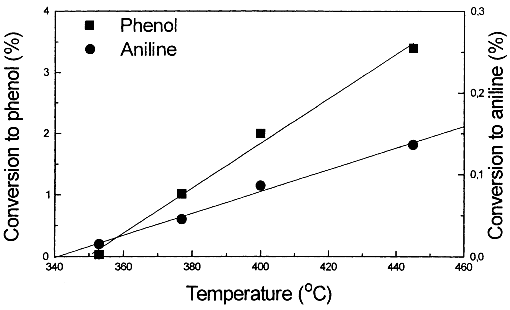

Fig. 2. Effect of temperature on the conversion of benzene to phenol and aniline. Catalyst composition (%): 5.4 (Ca), 11.9 (Cu) and 22.4 (Mn); flow of benzene 1.0 ml/h; ammonium hydroxide 1.0 ml/h; air 10 ml/min.

3.3. Effect of ammonia

Experimentally it was proved that the transformation of benzene to phenol over hydroxyapatite catalyst requires ammonia in the reaction system. As it is shown in Fig. 3, in the absence of ammonia conversion of benzene to phenol is on a level of error of its detection. This fact is probably caused by the rest of ammonia which is adsorbed on the catalyst or walls of the reactor in previous experiments.

However, with increasing concentration of ammonia not only the yield of phenol but also that of aniline

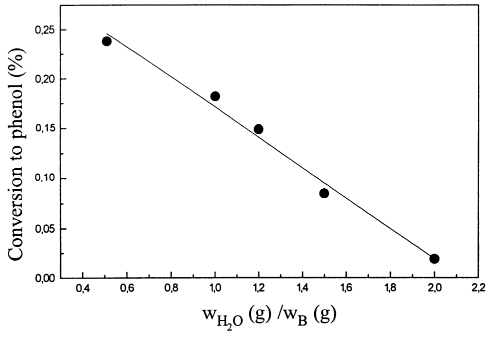

Fig. 3. Effect of the weight ratio of water to benzene on the conversion of benzene to phenol at 450°C. Catalyst composition (%): 6.3 (Ca), 5.2 (Cu) and 10.4 (Mn); flow of benzene 1.0 ml/h; air 10 ml/min; water 1.0 ml/h.

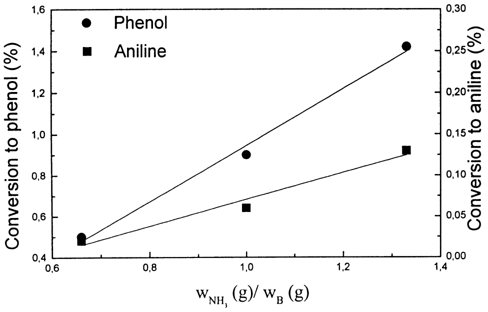

Fig. 4. Effect of the weight ratio of aqueous ammonia solution (26 wt.%) to benzene on the conversion of benzene to phenol and aniline. Catalyst composition: see Fig. 3; flow of benzene 1.0 ml/h; air 10 ml/min; solution of ammonia 1.0 ml/h.

increases (Fig. 4). At the same reaction conditions the influence of water on the reaction is practically unimportant, however, ammonia has a positive effect on the reaction also at high concentrations of water.

3.4. Effect of the mode of catalyst preparation

The hydroxyapatite catalysts containing Ca and Cu were prepared by three different methods. The catalyst KA 086 was prepared by dropping NH_4OH into the aqueous solution of $Ca(NO_3)_2$, $Cu(NO_3)_2$, $(NH_4)_2HPO_4$ and HNO_3. The catalyst KA 087 was synthesized by simultaneous mixing of the NH_4OH drops with the drops of the aqueous solution of $Ca(NO_3)_2$, $Cu(NO_3)_2$, $(NH_4)_2HPO_4$ and HNO_3. The catalyst KA 091 was prepared by dropping the aqueous solution of $Ca(NO_3)_2$, $Cu(NO_3)_2$, $(NH_4)_2HPO_4$ and HNO_3 into the NH_4OH solution. The catalysts designated Hap 10 and KA 088 were prepared by dropping the aqueous solution of $Ca(NO_3)_2$, $(NH_4)_2HPO_4$and HNO_3 into the NH_4OH solution. Fig. 5 shows that all prepared hydroxyapatite catalysts are crystalline but the mode of the catalyst preparation influences their crystallinity. The comparison of interplanar distances for catalysts Hap10 and KA 088 with the standard table values [14] showed that these catalysts are pure calcium hydroxyapatites. They were modified with Cu(II) ions by ion exchange or impregnation. It was found out that the hydroxyapatite structure after ion exchange remains the same, however, new crystalline phases are formed in the catalyst prepared by impregnation. When we compare the catalytic activity of the catalyst prepared by precipitation (KA 091), impregnation or ion exchange we can see (Table 2), that the most active is the catalyst prepared by impregnation which contains new crystalline phases.

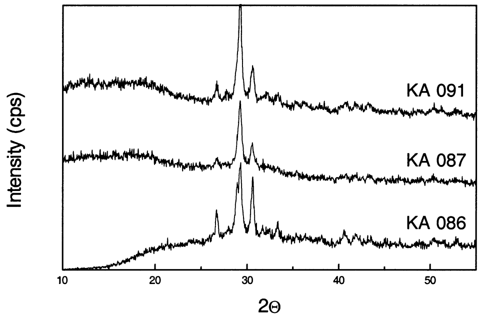

Fig. 5. XRD patterns of the catalysts prepared.

Table 2
Activity of hydroxyapatite catalysts prepared by impregnation, ion exchange and precipitation[a]

Catalyst	X_{Ph} (%)	X_A (%)
KA 091-precipitation	0.4309	0.0183
KA 093-ion exchange	0.4357	0.0430
KA 094-impregnation	0.6523	0.1057

[a] Reaction conditions: 450°C; flow of benzene 1.0 ml/h; ammonium hydroxide (26 wt.%) 1.0 ml/h; air 5 ml/min.

3.5. Lifetime of the catalyst

The changes of the catalyst activity and its crystallinity were investigated after 20 h of time-on-stream. It was found out (Fig. 6) that in the tested interval the activity of the catalyst gradually decreases but

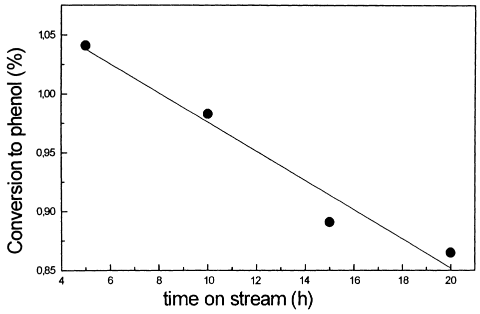

Fig. 6. Lifetime of the KA 093 catalyst.

surprisingly after 20 h of time-on-stream the catalyst was more crystalline than before the reaction. The crystalline phases were more significant and also new phases were formed. This is probably caused by the short time of the catalyst calcination before its use.

3.6. Reaction mechanism

The experiments performed in the reactor with continuous analysis of the outlet gases by on-line mass spectrometry show, that under reaction conditions, in the absence of benzene, ammonia is oxidized to nitrous oxides (Fig. 7). Formation of nitrogen by decomposition of NH_3 was registered too. The experiments without catalyst verified that nitrous oxides are formed also in this case, but NO in a much smaller concentration. This is probably caused by the catalytic action of the walls of the stainless steel reactor.

The above mentioned results suggest, that the primary reaction step is oxidation of ammonia to nitrous oxides and nitrogen (reactions (1)–(4)).

$$4NH_3+5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

$$4NH_3+4O_2 \rightarrow 2N_2O + 6H_2O \qquad (2)$$

$$4NH_3+3O_2 \rightarrow 2N_2+6H_2O \qquad (3)$$

$$4NH_3+6NO \rightarrow 5N_2+6H_2O \qquad (4)$$

Hydroxyapatite catalyst influences the course of these reactions what indicates a higher concentration of nitrous oxides in the presence of the catalyst. Nitrogen oxide is not participating in the benzene oxidation, because none aromatic nitro- or nitroso-compounds were detected in the reaction mixture. In the next step the hydroxyapatite catalyst participates in the formation of reactive oxygen species by the reaction with N_2O (reaction (5)). The empty parentheses represent the active centres of the catalyst.

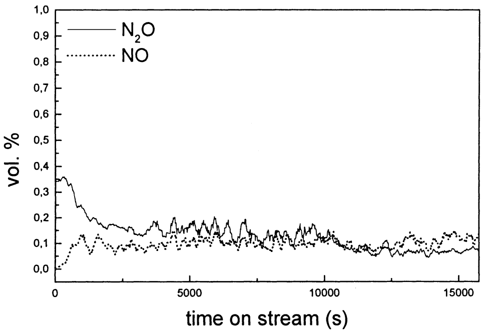

Fig. 7. Formation of N_2O and NO by oxidation of NH_3 with oxygen over the KA 091 hydroxyapatite catalyst.

$$N_2O + (\ ) \rightarrow (O)+N_2 \qquad (5)$$

Participation of hydroxyapatite catalyst in the formation of reactive oxygen species by the reaction with N_2O was proved in experiments where diluted (with nitrogen) N_2O was used as the reactant. Under similar reaction conditions benzene was oxidized to phenol over active hydroxyapatite catalysts. It seems that the direct attack of benzene proceeds by oxygen species adsorbed on the catalyst surface (reactions (6) and (7)).

$$C_6H_6+(O) \rightarrow (C_6H_5OH) \qquad (6)$$

$$(C_6H_5OH) \rightarrow C_6H_5OH + (\ ) \qquad (7)$$

The water present in the reaction system helps to strip the formed phenol from the catalyst, thus protecting its subsequent oxidation or decomposition on the catalyst.

Aniline which in all experiments accompanies phenol formation is a product of the consecutive reaction of phenol with ammonia (reaction (8)). The properties of hydroxyapatite catalysts probably influence also this reaction.

$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2+H_2O \qquad (8)$$

The proposed mechanism of benzene oxidation in the presence of ammonia has common features with the oxidation of benzene with N_2O over Fe-ZSM-5 catalyst [9–12].

4. Conclusions

The oxidation of benzene to phenol proceeds over hydroxyapatite catalysts in the presence of air and ammonia. Almost 97% selectivity of phenol formation was achieved at about 3–4% conversion of benzene. Beside phenol always aniline is formed in a less amount. In the reaction mixture trace amounts of biphenyl, diphenyl ether, benzofuran, dibenzofuran and benzo-1,4-dioxime were also detected.

It was found out that the catalysts which contain Ca and Cu or Mn in their cation part are active for hydroxylation of benzene. The catalysts containing only one metal as a cation possess no catalytic activity for the transformation of benzene to phenol.

The mechanism of benzene oxidation involves N_2O which is formed in the first step by catalytic oxidation of ammonia. Decomposition of N_2O on the active sites of hydroxyapatite catalyst leads to the formation of active oxygen species which directly oxidize benzene molecules to phenol.

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