



Gas phase hydroxylation of benzene with air–ammonia mixture over copper-based phosphate catalysts



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ABSTRACT

The direct gas phase hydroxylation of benzene to phenol over copper-based phosphate catalysts has been studied. Nitrous oxide and air–ammonia mixtures were used as oxidizing agents. It has been found that nitrous oxide can be replaced by air–ammonia mixture without significant deterioration of the phenol yield. Nanostructured Ca–Cu phosphate catalysts with a dominant mixed pyrophosphate structure, prepared in the presence of suitable surfactants were found highly active and selective. Using surfactant-modified phosphate catalysts with sponge-like structure above 95% selectivity and about 6.5% and 4.2% phenol yields were achieved at the benzene WHSV 1 h^{-1} and under not optimized reaction conditions using N_2O and air–ammonia mixture as oxidizing agents, respectively. These catalysts, compared with unmodified ones, were found to be much more resistant toward deactivation caused by the chemical reduction of catalytically active copper phase during the catalytic test. The activity of the spongy Ca–Cu phosphate catalyst after 37 h on stream decreased only by about 25%. In contrast, over similar unmodified Ca–Cu phosphate catalyst the phenol yield already after 8 h on stream drops to about one third of the initial value.

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1. Introduction

Benzene as a raw material is widely used in many industrial processes, including phenol production. More than 90% of the world's phenol production is based on the cumene route that implies alkylation of benzene, oxidation of cumene by a free-radical mechanism and cleavage of the formed hydroperoxide catalyzed by a mineral acid [1]. Despite its great success, the cumene process has some disadvantages such as high environmental impact, the use of corrosive catalyst, the production of an explosive intermediate and a co-production of acetone. Therefore, the success of this process significantly depends on the marketability of the by-product acetone and on the ratio between the demands for phenol vs. acetone [2]. Other processes of industrial manufacture of phenol, as the Dow process [3,4] involving toluene oxidation to benzoic acid and its

decarboxylation using a copper salt catalyst to phenol, represent only a minor contribution to the commercial phenol production.

Several studies have been published during the past two decades on the synthesis of phenol via one-step oxidation of benzene. Direct hydroxylation of the aromatic ring is a challenging reaction to synthesize phenol, due to the formation of over-oxygenated by-products. The synthesis of phenol by direct hydroxylation of benzene was extensively studied using different oxidants, such as N_2O , O_2 , H_2O_2 as well as the $\text{H}_2\text{--O}_2$ mixture [5–8].

Using hydrogen peroxide to oxidize benzene, the self-decomposition and the price of hydrogen peroxide is the most common limiting factor. However, using vanadium oxide supported on mesoporous SBA-16 [9] or metal doped heteropolyacids [10], hydrogen peroxide-based systems reach high selectivities.

An attractive catalytic system for the hydroxylation of benzene should use oxygen, preferably air as a cheap and available oxidant. Several catalytic systems, active in the hydroxylation of benzene with O_2 [11], often use a co-reducing agent apart from the oxygen [12]. It is well known, that copper-based phosphate catalysts, depending on its nanostructure can alter their catalytic properties [13]. For the direct hydroxylation of benzene the role of the

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oxidation state of copper and finding of the phase responsible for the catalytic activity [14–16] are other important keys for understanding the mechanism of the catalytic hydroxylation of benzene.

One of the most widely studied catalytic systems for the gas phase hydroxylation of aromatics with N_2O uses Fe-zeolite catalysts [17,18]. Fe/ZSM-5 is reported to be highly active and stable in DeNO_x systems designed to decompose N_2O [19]. Over similar catalysts phenol is formed with a selectivity exceeding 90% [20]. One of the major problems of these systems was their rapid deactivation (either published or observed in practice). Similarly, a very rapid deactivation was reported also over AlPO catalysts [21]. Another drawback of catalytic systems using N_2O as oxidant is their dependence on the source of waste nitrous oxide, usually obtained from adipic acid plants [22].

In the present work we focused attention on the preparation copper-based phosphate catalysts for gas-phase oxidation of benzene, using nitrous oxide and an air–ammonia mixture as oxidizing agents. The oxidation state and the structure of the copper-based domains and their influence on catalytic properties are mainly discussed.

2. Experimental

2.1. Catalysts preparation and characterization

As a basis of comparison, copper–calcium–phosphate with 43% of copper (relative to the overall amount of cations) was prepared by precipitation of the calcium and copper nitrate solutions (1.00 M) with a 0.60 M ammonium monohydrate orthophosphate solution at ambient temperature. The hydrogen phosphate solution was added drop wise to the metal nitrate solution while stirring vigorously. The precipitate was stirred for 3 h, then filtered and excessively washed with deionized water to extract the relics of the precursors, until pH 7. The catalysts with 5% copper content were prepared using a similar procedure.

Iron–calcium–phosphate was prepared accordingly, replacing copper nitrate with an equimolar amount of ferric nitrate monohydrate. Mixed Cu–Fe–Ca phosphate catalysts were prepared as well, by replacing 50 mol% of copper nitrate by ferric nitrate. A Pd–Cu–Ca phosphate catalyst was prepared by introducing palladium by wet impregnation from a 1.00 M Pd(acac)₂ solution in toluene onto a pre-prepared Cu–Ca phosphate sample (43% Cu). The overall palladium content of the resulting material, calculated as metallic palladium, was 1.5 wt%.

To prepare phosphate catalysts with sponge-like structure, various structure-directing agents were added to the solution of metal nitrates in an amount of 10 wt% relative to the precipitate (calculated as metal pyrophosphates) prior to the precipitation by ammonium hydrogen phosphate. Stearyl amine polyethylene glycol ether with 7 ethoxy units (SAPEG7), Pluronic P-123, dodecylbenzene sulphonate-Na (DBS), as well as active carbon FW285 (Evonik) were tested as structure-directing agents.

Silica-modified catalysts were prepared by two methods: (i) by precipitating the metal ion-exchanged silicas with an ammonium hydrogen phosphate solution (denoted as Cu-IE), and (ii) by adding pre-hydrolyzed tetraethyl orthosilicate (TEOS) to the metal nitrate solutions in a ratio 1:1. The former set was prepared by stirring overnight a 1 wt% suspension of silica Aerosil® 200 (Degussa, declared BET-surface area 200 m² g⁻¹) with an equimolar amount of copper nitrate in aqueous solution. The silica was then filtered, washed with deionized water until neutrality to sodium sulphide and re-suspended in 10% aqueous solution of ammonium monohydrate orthophosphate. The suspension was stirred overnight, filtered, washed excessively, dried at 180 °C and calcined. The latter set was prepared by pre-hydrolyzing 5 wt% of TEOS in a 0.05 N

Table 1

Summary of the prepared mixed Ca–Cu phosphate catalysts. Metal contents are given as per cents relative to overall cation content.

Denotation	Cu content/%	Modifier
Parent	43	No
5Cu-p	5	No
Cu-Fe-p	21.5	21.5% Fe
Pd-Cu-p	43	2% Pd
SAPEG7-p	43	SAPEG7
P123-p	43	Pluronic P123
DBS-p	43	DBS
FW285-p	43	Active carbon FW285
TEOS-p	43	TEOS
Cu-IE	<1	Silica ion-exchanged by Cu

aqueous solution of hydrochloric acid, at the temperature of 50 °C for 3 h, while stirring vigorously. The resulting solution was used to dissolve the metal nitrates, and was precipitated by ammonium hydrogen phosphate as described above. The precipitate was stirred at 80 °C for 24 h, filtered, washed until neutrality, and dried. All the catalysts were calcined prior to catalytic tests at 600 °C in air flow during 5 h, with a heating rate of 100 K h⁻¹. The prepared catalysts are summarized in Table 1.

The catalysts were characterized by powder X-ray diffraction using a Stadi Stoe apparatus in Bragg–Brentano geometry and a Bruker D8 DISCOVER diffractometer in a parallel beam geometry with parabolic Goebel mirror in the primary beam; the diffraction patterns were recorded in grazing incidence set-up with the angle of incidence $\alpha = 6^\circ$. Temperature programmed reduction and BET-measurements were carried out using a Micromeritics Pulse Chemisorb 2700 apparatus. SEM measurements were carried out using a JEOL JSM-7500F microscope; XPS were measured using a Thermo Scientific K-Alpha XPS system with an Al K α X-ray source at 6 mA, 12 kV.

2.2. Catalytic tests

The experiments were carried out in a fixed-bed glass reactor at the temperature of 450 °C, using 1 g of catalyst. The catalysts prior to testing were pelletized and crushed to the grain size of 0.2–0.3 mm. The temperature was controlled by a thermocouple in the axis of the catalytic bed. The gaseous oxidizing agent (air or N_2O) with the flow rate of 70 ml min⁻¹, was saturated by benzene (1.0 g h⁻¹) before entering the reactor. In experiments where air–ammonia mixture was used as an oxidizing agent, aqueous ammonia solution (with the ammonia concentration of 25%) was added by a syringe pump (2.0 g h⁻¹) to the reactant stream. In some experiments, only water was injected instead of ammonia solution. The reaction products were collected in an ice-cooled flask, homogenized with methanol and analyzed by GC, equipped with FID for the detection of organic products, and TCD for the analysis of CO₂ in the gaseous products. To verify the composition of reaction products a Shimadzu QP-500 GC–MS was used.

3. Results

3.1. Catalysts characterization

3.1.1. XRD-characterization

The parent Ca–Cu phosphate represents a mixed phase system (Fig. 1). As being a co-precipitate, one can expect various separated phosphates of copper and calcium, and bimetallic phosphates. The calcination temperature of the precipitate, 600 °C, presages the dominance of pyrophosphates over orthophosphates or hydrogen phosphates in the resulting material [23–25]. Hydroxyapatites, if formed, can retain their structure above the calcination

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