



Effect of steaming on the catalytic performance of ZSM-5 zeolite in the selective oxidation of phenol by nitrous oxide



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ABSTRACT

Gas-phase oxidation of phenol to dihydroxybenzenes (DHB) with nitrous oxide was performed over a set of ZSM-5 zeolites steamed at different temperatures in the range from 550 to 750 °C. The best of the catalysts demonstrated 70% N₂O conversion and a more than 90% selectivity for DHB. However, significant differences were observed in DHB isomer distribution and catalyst deactivation due to changes in the acidity of the zeolites. The steaming procedure reduces the concentration of Bronsted acid sites, thus allowing a decrease in coke loading. Simultaneously, a substantial decline in the molar ratio of hydroquinone to catechol in the reaction products was observed, mainly due to the increased selectivity to the ortho isomer – catechol. These results can be used to control the selectivity for different DHB isomers in the title reaction by varying steaming severity.

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1. Introduction

Dihydroxybenzenes (DHB) are important intermediates and products of organic chemistry, which can be further processed to produce dyes, polymers, and pharmaceuticals. Hydroquinone (HQ) and catechol (CH), the two most widely used isomers, are produced simultaneously by liquid-phase oxidation of phenol with hydrogen peroxide catalyzed by strong inorganic acids, Fenton's reagent [1], and crystalline titanium silicates TS-1 and TS-2 [2–4]. Depending on the catalyst selection, the ratio of CH to HQ in the reaction products can vary from three to one [2–6]. Disadvantages of all these processes are the formation of a significant amount of tar and the so-called non-selective decomposition of hydrogen peroxide to water and molecular oxygen, resulting in a significant increase in the cost of DHB. In these processes, the selectivity of phenol conversion to DHB is 80–90%, and that of hydrogen peroxide is no more than 50–70%. Various supported metal oxides and organic and inorganic metal complexes have been tested as catalysts in the liquid-phase oxidation by H₂O₂ [7–11]. The third isomer, resorcinol (RS), is obtained mainly by alkaline melting of the intermediate m-isomers of aromatic derivatives (e.g., 1,3-benzene disulfoacid) or by a multi-step process similar to the cumene process [12,13].

Although hydrogen peroxide is an environmentally friendly oxidant with a high content of active oxygen, the development of selective processes using molecular oxygen is of greater practical interest. Numerous attempts to carry out gas-phase synthesis of DHB by direct oxidation of phenol with molecular oxygen were unsuccessful due to very low selectivity for DHB. This forces to seek new opportunities for the synthesis of DHB from phenol. One of such opportunities is the use of alternative oxidants, which would make it possible to carry out the reaction in the gas phase and with greater selectivity. Nitrous oxide is a promising candidate among the known oxidants used for gas-phase reactions (ozone, nitric oxide). N₂O has been successfully used in selective oxidation processes, in particular, in benzene oxidation to phenol [14–19]. Recently, a new method has been developed to produce DHB by gas-phase oxidation of phenol with N₂O over FeZSM-5 zeolites. Although gas-phase processes offer some advantages over liquid-phase oxidation with hydrogen peroxide (ease of separation and the possibility of catalyst regeneration in continuous flow mode), this method of DHB synthesis also has its drawbacks. These include coking, which reduces the catalyst activity with time of reaction, and difficulties in predicting and controlling the isomeric composition of the resulting mixture of DHB. Gas-phase oxidation of phenol with N₂O yields a mixture of DHB isomers, as does phenol oxidation with hydrogen peroxide.

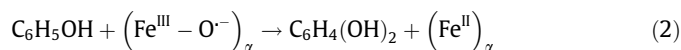
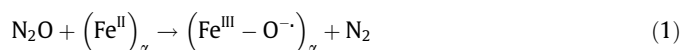
Approaches to improving the stability of zeolite catalysts for benzene oxidation have also proven suitable for improving the stability of catalysts for phenol oxidation [20]. These approaches

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include the selection of reaction conditions (use of a large excess of the oxidized substrate and high reaction temperature to facilitate desorption of high-boiling products, i.e., DHB, from the zeolite surface) and optimization of the chemical composition of the catalyst. In a previous study [21], we investigated the kinetics of the reaction and its optimal conditions in terms of the yield of DHB and stable operation of the zeolite catalyst. The optimal conditions were found to be a temperature range of 450–500 °C and a phenol/N₂O molar ratio of 30:3. Under these conditions, the average productivity of DHB reaches 3.0 mmol/g h with preferential formation of HQ and CH without significant deactivation of the catalyst for 12-h onstream. In addition, the reaction products contain 6–7 mol% RS, and its fraction is found to be independent of the reaction conditions. It was also noted [21,22] that this reaction provided a higher ratio of the para isomer to the ortho isomer in the mixture of DHB as compared to the existing methods of simultaneous synthesis of HQ and CH using H₂O₂. For example, in the liquid-phase hydroxylation of phenol with H₂O₂ over TS-1, this ratio does not exceed 1 [5,6], in contrast to the gas-phase process involving N₂O, where it is 1.2 (averaged over a time-on-stream of 10 h). In this connection, it is necessary to determine whether the relatively high content of HQ in the mixture of DHB is a general characteristic of this process or it is a specific feature of the particular catalyst whose properties have been investigated in previous studies. In addition, it is necessary to elucidate the factors that affect the HQ/CH ratio and the fraction of RS. The issue of the regioselectivity of oxidation on zeolites using N₂O has also been addressed in the literature, in particular, for the oxidation of toluene and halogen derivatives of benzene [23]. It has been shown that in the case of toluene oxidation, a reduction in the reaction temperature and contact time of the feed stream with the catalyst leads to an increase in the fraction of the para isomer. Possibilities of modifying the zeolite to change the regioselectivity of the reaction have not been examined. As for phenol oxidation, it has been shown [21,22] (using relatively stable catalyst-ZSM-5 zeolite with an alumina binder) that the isomeric composition of DHB changes during the reaction as the catalyst is partly deactivated due to coke formation. It is generally accepted that the formation of coke deposits in zeolites of various types is due to the presence of acid sites [24–26]. In this connection, the issue of establishing the relationship between the acid properties of zeolites, coke formation, and the distribution of isomers in the reaction products is of both fundamental and practical interest. However, this issue should not be considered separately from the already known methods of regulating the catalytic activity of zeolites in the title reaction by changing the concentration of the active sites.

The activity of ZSM-5 zeolites in the gas-phase oxidation of phenol with N₂O is assumed to be associated with the participation of α -sites in the reaction, by analogy with benzene oxidation. These sites are complexes of reduced iron (Fe^{II}) formed during high-temperature activation of zeolites. Iron may be present as an impurity in zeolites or added intentionally [27–29]. Among the various forms of iron, only α -sites catalyze the decomposition (according to Eq. (1)) of nitrous oxide with the formation of a special form of active oxygen atoms, so-called α -oxygen, which is responsible for the direct hydroxylation of the aromatic compound, in this case, phenol (Eq. (2)):



Chemical and thermal treatments of zeolites that produce a sufficient concentration of α -sites inevitably lead to the formation of acid sites (both Bronsted and Lewis active sites, BASs and LASs)

or surface defect sites in the zeolite structure and can also lead to partial amorphization of zeolites [29,30]. In our case, acid sites may be responsible for side reactions: condensation and oxidative condensation of phenol and DHB and isomerization of the resulting DHB. It is a priori unknown how the activity, selectivity, and stability of a catalyst are influenced by the conditions of formation of α -sites in the catalyst. Moreover, it is unclear how these conditions affect the ratio of the DHB isomers in the reaction products.

It is known that steaming of zeolites is one of the most effective and widely used methods of producing α -sites and controlling their number in zeolites [29]. In addition, steaming can be used to control the number of acid sites of different types (the ratio of BASs to LASs) in zeolite catalysts [24–26,31,32]. Changing the steaming temperature has the most significant effect on the concentration of both α -sites and acid sites in zeolite catalysts. In this work, the effect of steaming temperature on the acidity and catalytic properties of ZSM-5 zeolites in the oxidation of phenol with nitrous oxide was investigated. The aim of the work was to increase the catalytic activity and the total selectivity for DHB in this reaction, as well as to explore the possibility of controlling the regioselectivity of the process.

2. Experimental

2.1. Catalysts

We investigated a series of zeolite samples obtained from the same parent ZSM-5 zeolite. This zeolite was used in our previous study [21] as the basis for obtaining catalysts formed with alumina binder. Its chemical composition in the H-form (Si/Al = 40) comprises 0.9 wt% Al, 0.01 wt% Na, and 0.03 wt% Fe (ICP (inductively coupled plasma) spectroscopy data). This composition is specifically designed to provide small Fe concentration, which allows the reaction to be carried out at a high temperature to ensure efficient desorption of such highboilers as DHB from the catalyst surface. It can be assumed that, as for the related oxidation reaction of benzene [33,34], desorption of the reaction products is the rate-determining step. Under this condition, an excess concentration of iron and, hence, α -sites may lead to overoxidation of the non-desorbed DHB. The zeolite was first calcined in dry air at 500 °C for 4 h and then steamed (50% H₂O and the rest He, 60 ml/min, amount of catalyst – 2 cc, heating rate – 5 grad/min) for 2 h at different temperatures from 550 to 750 °C with an interval of 50° for different samples. After steaming, all samples were cooled to room temperature in pure He. As a result, we obtained a series of ZS-x zeolites, where x is the steaming temperature. For example, the notation ZS-600 in Table 1 indicates that the parent zeolite Z-500 was activated by steaming at a temperature of 600 °C. The chemical composition of the samples remained unchanged under all treatments.

2.2. Characterization of catalysts

Textural parameters of the zeolites (micropore volume, V_{μ} ; total pore volume, V_{Σ} ; mesopore volume (pores with diameters of 17–50 Å), V_{meso} ; Brunauer–Emmett–Teller (BET) adsorption method surface area, A_{BET} , and external surface area of the zeolites, A_{ext} , were determined by low-temperature nitrogen adsorption at 77 K after vacuum treatment at 270 °C during 10 h. The obtained data (Table 1) allow us to compare the contents of the zeolite phase in the samples and to evaluate the relative degree of crystallinity, calculated from micropore volume (γ_{ads}), with respect to the selected standard Z-500, where the $\gamma_{\text{ads}} = 100 * (V_{\mu} \text{ of ZS-x}) / (V_{\mu} \text{ of Z-500})$. The structure, high crystallinity (γ_{XRD}), and the absence of foreign phases were confirmed by X-ray powder diffraction

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