



Oxidation of phenol to dihydroxybenzenes by nitrous oxide

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ABSTRACT

Gas phase oxidation of phenol by nitrous oxide for preparation of dihydroxybenzenes (DHB) is of significant interest. However, due to experimental difficulties caused by the high boiling points of DHB (240–285 °C), no detailed investigation of this reaction has been conducted until now. In the present work, the reaction was studied for the first time using a catalytic setup specially designed for operation with high-boiling compounds.

FeZSM-5 zeolites were shown to be efficient catalysts for the title reaction. An unusual isomeric distribution of DHB depending on reaction conditions was found. Formation of resorcinol, in addition to hydroquinone and catechol, is a particular feature of the reaction. Although the fraction of resorcinol averaged over 12 h time-on-stream is not high (6–9 mol.%), in the initial period of reaction it may comprise over 70% of the total amount of DHB.

A comparison with the current liquid-phase processes of phenol oxidation by H₂O₂ shows that the oxidation by N₂O may open a new promising way for alternative production of DHB in the gas phase.

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1. Introduction

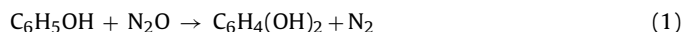
Dihydroxybenzenes (hydroquinone, resorcinol, and catechol) are important intermediates used in chemical, agrochemical, pharmaceutical and food industries. Present-day processes of their production are quite imperfect. Catechol (CH) and hydroquinone (HQ) are usually produced simultaneously by liquid phase oxidation (hydroxylation) of phenol with hydrogen peroxide. The strong acids HClO₄ and H₃PO₄ (Rhodia process), Fenton's reagent of Fe²⁺/Co²⁺ (Brichima process) or TS-1 zeolite (Enichem process) are used as catalysts for this reaction [1]. In all cases, intense tar formation and H₂O₂ decomposition take place. The total dihydroxybenzenes (DHB) selectivity based on phenol is 80–90%, and that based on H₂O₂ is 50–70%.

The synthesis of resorcinol (RS) is usually conducted via an intermediate preparation of some aromatic *m*-isomers, viz. 1,3-benzenedisulfonic acid, which is then subjected to alkali fusion to form the desired product.

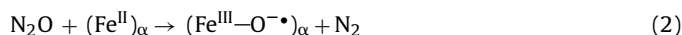
Currently, the oxidation of phenol to DHB is extensively studied in many laboratories to find more effective ways for implementation of this difficult reaction. Various metals, metal oxides, organic and inorganic metal complexes have been tested as catalysts using

H₂O₂ oxidant in the liquid phase [2–7]. However, the progress seems to be rather modest.

The transfer of a reaction into the gas phase can provide some important technological advantages related, in particular, to continuous operation of the process, catalyst separation, and catalyst regeneration. In particular, the latter operation can be conveniently done in the same reactor by burning out carbonaceous deposits from the catalyst surface. Therefore, it would be of significant interest to develop a gas-phase process of phenol oxidation. Previous attempts to carry out this reaction in the gas phase using dioxygen proved unsuccessful because of the very low selectivity of DHB. One may expect that the use of nitrous oxide can give a more favorable prospect for this transformation:



Indeed, the related reaction of benzene oxidation to phenol by N₂O over FeZSM-5 zeolites proceeds with a very high selectivity [8–16]. The efficiency of these catalysts is due to the presence of α-sites, which are formed from admixed or specially introduced iron in the process of high-temperature zeolite activation [10,17–19]. The α-sites consist of reduced Fe^{II} complexes located in the micropore space of the zeolite matrix. A remarkable feature of α-sites is that they are inert to dioxygen, but are readily oxidized by nitrous oxide to generate a very reactive anion radical species of α-oxygen [8,11,17,20–22]:



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Table 1
Characteristics of FeZSM-5 samples.

Samples	C_{α} (site/g)	Texture parameters			
		V_{μ} (cm ³ /g)	V_{Σ} (cm ³ /g)	A_{BET} (m ² /g)	A_{ext} (m ² /g)
1. Parent FeZSM-5 (500 °C, dry air)	0.5×10^{17}	0.165	0.275	443	75
2. Parent FeZSM-5 (steamed at 650 °C)	6.5×10^{17}	0.160	0.265	430	68
3. FeZSM-5/Al ₂ O ₃ (500 °C, dry air)	0.5×10^{17}	0.100	0.390	390	155
4. FeZSM-5/Al ₂ O ₃ (steamed at 650 °C)	2.7×10^{17}	0.085	0.400	345	144
5. FeZSM-5/Al ₂ O ₃ (steamed at 750 °C)	1.7×10^{17}	0.080	0.350	335	138

A number of studies have shown that α -oxygen is involved in the hydroxylation of benzene. Especially convincing results were obtained by Uranov et al. [23] and Chernyavsky et al. [24], who showed that the rate of benzene oxidation increased linearly by about 2 orders of magnitude with increasing the concentration of α -sites.

As for the oxidation of phenol, this reaction has not previously been studied in detail. It was first mentioned in [25] with reference to patent [26]. The patent is mainly focused on the oxidation of benzene, suggesting also some examples with other aromatic compounds, including phenol. Costine et al. [27] tested phenol in line with some other aromatic molecules to elucidate the effect of a substituent nature on their reactivity toward N₂O. In both cases, the oxidation of phenol provided DHB products comprising only HQ and CH with a total selectivity of 92–98%. The latter values are certainly overestimated since the selectivities were calculated without taking coke into account, which, as we will see below, may have a significant effect on the results. Ivanov et al. [28] investigated the oxidation of phenol in its mixture with benzene. The authors showed that benzene significantly improved stability and selectivity of the reaction. However, they could use only minor concentrations of phenol in the feed (4.6%) to prevent plugging of the setup gas lines by condensing DHB products. Therefore, productivity of the reaction was very low.

The lack of detailed studies on phenol oxidation by N₂O is due to significant experimental difficulties caused by the high boiling points of DHB. In conventional catalytic setups, the temperature of the gas lines usually does not exceed 180 °C. Since the boiling points of CH, RS, and HQ are 240, 281 and 285 °C, respectively, this temperature is not high enough to prevent their condensation. It leads to an increasing resistance to the feed flow with time-on-stream, and ultimately to the failure of the run. This problem is discussed in [28].

In the present work, the oxidation of phenol by N₂O was studied for the first time using a catalytic setup specially designed for operation with high-boiling compounds. The temperature of the analytical part of the setup can be maintained at up to 330 °C. The obtained results revealed high catalytic potential of FeZSM-5 zeolites, which open a new promising way for preparation of DHB.

2. Experimental

2.1. Catalysts

A parent FeZSM-5 zeolite was prepared according to [29]. Its chemical composition in H-form comprises 0.9 wt.% Al, 0.01 wt.% Na, and 0.03 wt.% Fe (ICP data). This composition was specially designed to provide a small Fe concentration, which would allow one to conduct reaction at a rather high temperature thus ensuring an efficient desorption of DHB from the catalyst surface. Under this condition, an excess concentration of iron and consequently that of α -sites may lead to overoxidation of the products. Texture parameters of the zeolite (micropore volume, V_{μ} ; total pore volume, V_{Σ} ; BET surface area, A_{BET} ; and external surface area, A_{ext}) obtained with the low-temperature N₂ adsorption are typical of the

MFI structure (Table 1). High crystallinity of the zeolite as well as the absence of foreign phases are evidenced by XRD data collected both before and after its activation (Fig. SM. 1 in supplementary material section).

The parent FeZSM-5 zeolite (sample 1, Table 1) was used for preparation of formed catalysts. For that, the zeolite was mixed with boehmite peptized by dilute HNO₃ (65 wt.% FeZSM-5 and 35 wt.% of the boehmite). Afterwards, the material was extruded using a die of 3 mm diameter, dried at 383 K and calcined in dry air at 773 K (sample 3, Table 1). A calculated composition of the formed and calcined catalyst corresponds to 70 wt.% of the zeolite and 30 wt.% of Al₂O₃ binder. Activation of the catalyst was done by steaming in a He flow containing 50 mol.% H₂O at two different temperatures: one sample at 650 °C and the other one at 750 °C (samples 4 and 5 in Table 1). Further in the text, the activated samples will be referred to as FeZSM-5 (650 °C), FeZSM-5/Al₂O₃ (650 °C) and FeZSM-5/Al₂O₃ (750 °C), accordingly.

From texture parameters presented in Table 1 one can see that both the forming procedure and the steam activation of the formed samples lead to a decrease of V_{μ} . In the case of formed catalysts, it probably resulted from a partial sealing of micropores by a binder. Since α -sites locate precisely in the micropore space [8,13,30–32], it resulted in a drop of the α -site concentration (C_{α}): from 6.5×10^{17} site/g for the parent zeolite to 2.7×10^{17} and 1.7×10^{17} site/g for the formed samples (Table 1).

The value of C_{α} was calculated from the N₂ amount evolved at the N₂O decomposition at 230 °C. At this temperature the reaction proceeds stoichiometrically according to Eq. (2). Additionally, the isotopic exchange of α -oxygen ¹⁶O $_{\alpha}$ with dioxygen ¹⁸O₂ was conducted at 100 °C, providing similar results. In more detail, procedures for measuring the concentration of α -sites are given elsewhere [31,33].

2.2. Flow setup

Catalytic experiments were performed in an automated flow setup having a high-temperature switching valves with rotors made of “polyamide/PTFE/carbon” composite, which operating temperature is 150–330 °C (Valco Instrument Co., Inc.). Analytical part of the setup was accommodated in a ventilated thermal box at 290 °C. This temperature prevents condensation of the reaction products and provides a reliable on-line GC analysis. A picture of the setup and a typical on-line chromatographic pattern are presented in Figs. SM. 2 and SM. 3 of the supplementary material section.

To conduct catalytic runs, 1 g of a catalyst (0.5–1.0 mm particles) was placed into a quartz reactor with the inner diameter 7 mm. Before testing, the catalyst was treated in flowing air at 550 °C. Nitrous oxide and helium were fed by flow mass controllers (MKS Instruments); phenol of C.P. grade was fed by a high-performance syringe pump 500 D (ISCO) capable of keeping phenol in a liquid state at 60 °C.

The reaction mixture was automatically sampled and analyzed each 16 min. Analysis of N₂O and N₂ was performed at room temperature using a packed column filled with Porapak Q and TCD. For a more accurate CO_x measurement, carbon oxides were first

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