Oxidation of phenol to dihydroxybenzenes by nitrous oxide

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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⁺ (Birchim 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:

\[ C_6H₅OH + N₂O \rightarrow C₆H₄(OH)₂ + N₂ \]  \hspace{1cm} (1)

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 Fe⁴⁺ 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]:

\[ N₂O + (Fe^{III})ₐ \rightarrow (Fe^{III}O−•)ₐ + N₂ \]  \hspace{1cm} (2)

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