

# New Way of Hydroquinone and Catechol Synthesis using Nitrous Oxide as Oxidant

D. P. Ivanov, V. I. Sobolev, L. V. Pirutko, G. I. Panov\*

Borekov Institute of Catalysis, Pr. Lavrentieva 5, Novosibirsk 630090, Russia  
Fax: (+7)-3832-344687, e-mail: panov@catalysis.nsk.su

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Dedicated to R. A. Sheldon on the occasion of his 60th birthday.

**Abstract:** The synthesis of dihydroxybenzenes (DHB) *via* the gas-phase oxidation of phenol with nitrous oxide in the presence of benzene was studied. Addition of benzene to the feed mixture greatly improves the selectivity and catalytic stability of the Fe-containing ZSM-5 zeolite, that was previously considered to be a main obstacle to the development of a new process. Reaction conditions strongly affect the distribution of the DHB isomers: the ratio of hydroquinone to catechol may vary from 1.4 to 10, with the resorcinol fraction being nearly constant and comprising 3–5%. Some 40 h experiments on the

oxidation of a phenol-benzene mixture demonstrated the high efficiency of the formed FeZSM-5 catalyst. With a good stability, the catalyst provides 97% phenol selectivity referred to DHB and 85–90% N<sub>2</sub>O selectivity referred to the sum of DHBs and phenol. A new process for hydroquinone and catechol synthesis based on the neat oxidation of benzene with recycling of the phenol as an intermediate product is suggested.

**Keywords:** benzene oxidation; dihydroxybenzenes; iron; nitrous oxide; phenol oxidation; zeolite

## Introduction

Dihydroxybenzenes (hydroquinone, catechol, resorcinol) are among the most important intermediates of organic synthesis. The existing methods of their preparation are far from being perfect. They often use aggressive reagents and form large amount of wastes resulting, according to Sheldon's environmental strategy, in a high E factor.<sup>[1]</sup> Hydroquinone and catechol, which are the main subject of this work, are mainly produced jointly *via* phenol oxidation with hydrogen peroxide. Different catalysts are used in different versions of the process: strong acids (HClO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>), Fenton reagent (Fe<sup>+++</sup> and Co<sup>++</sup>), or zeolite TS-1 of titanosilicate composition. The Enichem process involving the TS-1 catalyst has some advantages as compared with the acid and radical processes. It provides higher selectivity, greater hydroquinone to catechol ratio, and smaller tar amounts.<sup>[2,3]</sup> However, it still has some disadvantages, such as the presence of solvent, deactivation of the catalyst, and the need for its regeneration, which is quite a difficult task for a liquid-phase process. In addition, hydrogen peroxide is a rather expensive oxidant, and its thermal instability imposes considerable limits on the reaction conditions.

It would be of great importance to develop a gas-phase process for phenol oxidation to dihydroxybenzenes,

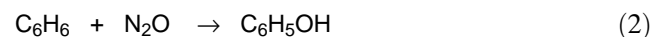
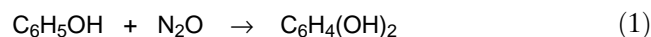
with nitrous oxide used as oxidant. In recent years, nitrous oxide has attracted great attention as a mono-oxygen donor, and proved to be especially effective in the direct oxidation of benzene to phenol.<sup>[4]</sup> The best catalysts for this reaction are Fe-containing ZSM-5 zeolites, which provide nearly 100% selectivity. On this basis, a new technology for phenol production was developed and successfully tested in a pilot plant.<sup>[5]</sup> The remarkable catalytic performance of zeolites is related to the so-called  $\alpha$ -sites, which form at a high activation temperature from the admixed or intentionally added iron.<sup>[6]</sup> According to Mössbauer spectroscopy,  $\alpha$ -sites are reduced iron atoms capable of the reversible redox transition  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  in the presence of N<sub>2</sub>O.<sup>[7]</sup> This transition generates a new oxygen species of surface oxygen ( $\alpha$ -oxygen) that very selectively oxidizes benzene to phenol.<sup>[8,9]</sup>

Attempts to extend this approach to the oxidation of benzene derivatives (phenol, toluene, xylene, benzonitrile, aniline, styrene, etc.) were less successful.<sup>[10–15]</sup> No detailed study was published in the literature on the oxidation of phenol and there are only two papers<sup>[10,15]</sup> providing very brief information on the subject. Tírel et al.<sup>[15]</sup> using HZSM-5 zeolite at 400 °C, obtained 5% phenol conversion with 87% dihydroxybenzenes (DHB) selectivity. Panov et al.<sup>[10]</sup> reported a significantly higher activity of FeZSM-5 catalyst (11.5% conversion, 92% selectivity at 350 °C) but emphasized

a heavy deactivation problem as being the main obstacle to the development of the gas-phase DHB process.

A high benzene excess in the feed mixture was shown to be an effective means for decreasing coke formation at the benzene to phenol oxidation.<sup>[16,17]</sup> In this case, benzene acts not only as the starting reagent but also as a component providing a several-fold increase in the heat capacity of the reaction mixture. This decreases the probability of uncontrollable overheating, suppresses side reactions and improves the catalyst stability. However, this approach is much less convenient for the oxidation of phenol since a large phenol excess in the feed assumes its multiple recirculation, which is much more difficult to do as compared with benzene.

The idea of this work is to examine the feasibility of phenol oxidation to dihydroxybenzenes in an excess of benzene rather than phenol. With such a reaction mixture, oxidation of both phenol to DHB and benzene to phenol should concurrently take place:



As we will see further, this approach provides very promising results.

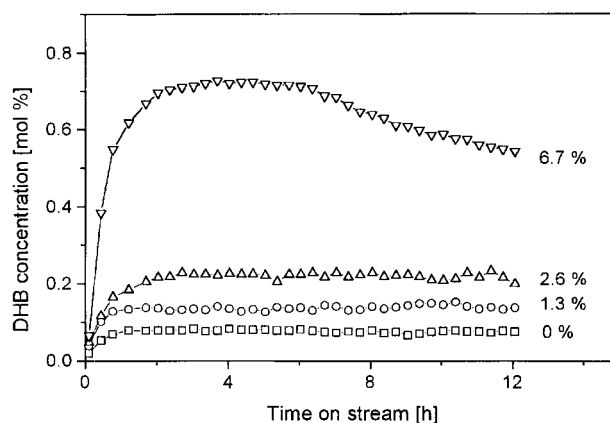
## Results and Discussion

### Effect of Phenol Concentration in the Feed Mixture

To reveal the effect of feed phenol concentration on DHB productivity, we carried out a set of experiments on the oxidation of various phenol-benzene mixtures over the FeZSM-5 zeolite ( $C_{\text{Fe}} = 0.02$  wt %). Experiments were conducted for 12 h at 450 °C with the feed mixture comprising 50 mol %  $\text{C}_6\text{H}_6$ , 5 mol %  $\text{N}_2\text{O}$  and a variable concentration of phenol (0.0–6.7 mol %), helium being the balance. Figure 1 shows changes of

the summed DHB concentration in the reaction products depending on phenol concentration in the feed (here and later benzoquinone is also included in the DHB). One may see that a minor amount of dihydroxybenzenes forms even at feeding neat benzene. Phenol addition to the feed greatly increases DHB concentration in the products.

Quantitative results of these experiments averaged over 12 h are listed in Table 1. One may see that increase of the feed phenol increases the DHB concentration nearly by an order of magnitude. At a phenol concentration of 6.7%, DHB productivity reaches quite a high value of 1.8 mmol/g · h. The phenol concentration in the feed has no systematic effect on nitrous oxide conversion, which comprises 70–80%. Therewith, the concentration of the deep oxidation products,  $\text{CO}_x$ , increases several times, although in all cases it remains insignificant. Due to the limited temperature of our thermal box (180 °C), a further increase of the feed phenol concentration results in plugging of the gas lines and breaking down of the experiment. In the subsequent discussion we shall use the feed mixture close to the following standard composition: 5 mol % phenol, 20 mol % benzene, 2.5 mol % nitrous oxide, helium the balance.



**Figure 1.** Effect of phenol in the feed phenol-benzene mixture on DHB concentration. Figures at the curves show phenol concentration (mol %) in the feed. Reaction conditions:  $\text{C}_6\text{H}_6$  50%,  $\text{N}_2\text{O}$  5%,  $\text{C}_6\text{H}_5\text{OH}$  0–6.7%, temperature 450 °C, contact time 1 s.

**Table 1.** Effect of phenol concentration in the feed phenol-benzene mixture on DHB productivity.<sup>[a]</sup>

Exp. no.	Phenol concentration in the feed [mol %]	$\text{N}_2\text{O}$ conversion [%]	Outlet concentration [mol %]		DHB productivity [mmol/g · h]
			DHB	$\text{CO}_x$	
1	0	81	0.08	0.068	0.23
2	1.3	71	0.15	0.12	0.43
3	2.6	69	0.21	0.11	0.62
4	6.7	76	0.63	0.18	1.83

<sup>[a]</sup> Reaction conditions:  $\text{N}_2\text{O}$  5 mol %; benzene 50 mol %; phenol 0–6.7 mol %; temperature 450 °C; contact time 1 s.

**Table 2.** Effect of temperature on the oxidation of benzene-phenol mixture. (Reaction conditions: C<sub>6</sub>H<sub>6</sub> 20.2 ± 0.2 mol %, C<sub>6</sub>H<sub>5</sub>OH 4.6 ± 0.2 mol %, N<sub>2</sub>O 2.4 ± 0.1 mol %; contact time 1.0 s, temperature 400–475 °C).

Exp. no.	T [°C]	Product concentration [mol %]			C <sub>coke</sub> [wt %]	Conversion [%]			N <sub>2</sub> O selectivity [%]			Phenol selectivity [%]			Benzene selectivity [%]			Productivity [mmol/g·h]
		N <sub>2</sub>	CO <sub>x</sub>	DHB		PhOH	N <sub>2</sub> O	PhOH	PhH	DHB	CO <sub>x</sub>	Coke	PhOH	DHB	CO <sub>x</sub>	PhOH	Coke	
1	400	0.64	0.03	0.07	4.9	27	1.6	2.3	15.6	7.0	1.8	93	7.0	96.7	3.3	0.20	1.4	
2	425	1.25	0.08	0.13	5.6	52	3.3	4.7	12.4	9.9	1.2	91	9.0	97.8	2.2	0.38	2.8	
3	450	1.92	0.14	0.19	5.6	77	4.4	7.0	10.8	11.1	0.9	89	11	98.4	1.6	0.56	4.2	
4	475	2.30	0.40	0.30	5.8	98	8.1	6.8	13.6	27.3	1.3	82	18	97.1	2.9	0.88	4.0	
5 <sup>[a]</sup>	450	1.82	0.05	0.02	1.65	72	–	7.9	1.3	5.5	1.2	–	–	98.9	1.1	0.06	4.6	

<sup>[a]</sup> No phenol was added to the feed in this experiment.

## Effect of Reaction Temperature

Averaged values of product concentrations (N<sub>2</sub>, CO<sub>x</sub>, DHB, PhOH) obtained in 12-h runs with the standard feed mixture at various temperatures are listed in Table 2. In spite of the high accuracy of the reaction mixture analysis provided by our experimental technique, it is difficult to calculate precise reaction parameters for the oxidation of a phenol-benzene mixture. This is caused by the concurrent occurrence of two interrelated reactions (1) and (2), which hampers evaluation of the contribution of each reaction to the amounts of the resulting products. In addition, the situation is complicated by the impossibility to estimate precisely the increment of phenol concentration in the reaction, ΔC<sub>PhOH</sub>, since the small value of the latter is calculated as the difference of large values (Eq. 3):

$$\Delta C_{\text{PhOH}} = C_{\text{PhOH}}^{\text{in}} - C_{\text{PhOH}}^{\text{out}} \quad (3)$$

A complete, though somewhat approximate, description of the process can be done under the assumption that each product forms only due to one reaction.

We may correlate products and reactions by comparing the results of experiments no. 3 and no. 5 in Table 2. These experiments were conducted under similar conditions, except that in experiment no. 3 4.8 mol % phenol was added to the feed mixture, while in experiment no. 5 no phenol was added. One may see that the DHB and CO<sub>x</sub> concentrations are much higher in the experiment with phenol as compared to the experiment without phenol. Thus, formation of these products may be referred completely to the phenol oxidation (reaction 1). At the same time, the amount of coke accumulated over the catalyst in these experiments differs only slightly (6.1 wt % vs. 5.2 wt %), so the entire coke may be referred to benzene oxidation (reaction 2). Under these assumptions, with the known DHB and CO<sub>x</sub> amounts, one may determine the phenol conversion and selectivities of phenol transformation to each of these products.

Similarly, with the known nitrous oxide conversion, one may estimate selectivities of N<sub>2</sub>O referred to DHB, CO<sub>x</sub> and coke. In calculations related to coke, for simplicity we assumed the chemical composition of coke to be identical to that of phenol, i.e., 77 wt % carbon, 6 wt % hydrogen and 17 wt % oxygen. Considering a relatively small coke amount, some inaccuracy in its chemical composition would not affect noticeably the results of our analysis. N<sub>2</sub>O selectivity referred to phenol is calculated from the balance, which further allows the estimation of benzene conversion into phenol.

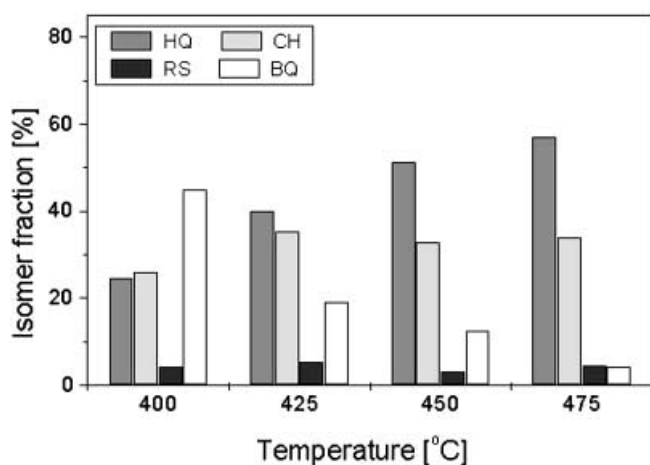
Table 2 presents experimental data (conversions, selectivities and productivities) calculated under the

above assumptions. One may see that elevation of the reaction temperature from 400 to 475 °C leads to a considerable increase in conversions of nitrous oxide (27% → 98%), phenol (1.6% → 8.1%), and benzene (2.3% → 7.0%). The temperature effect on selectivities is more complicated. N<sub>2</sub>O selectivity referred to DHB depends on temperature only slightly and comprises 11–15%; the selectivity referred to phenol decreases from 75.6% at 400–450 °C to 57.8% at 475 °C, which relates to a sharp increase in CO<sub>x</sub> formation at the latter temperature. N<sub>2</sub>O consumption for coke formation is insignificant, S<sub>N<sub>2</sub>O→coke</sub> = 1.2–1.8%.

The feed phenol mainly transforms into DHB. With increasing temperature, the value of S<sub>PhOH→DHB</sub> decreases from 93% at 400 °C to 82% at 475 °C, which is compensated by increasing of phenol selectivity referred to deep oxidation products, S<sub>PhOH→CO<sub>x</sub></sub>, from 7.0 to 18%.

Benzene selectivity referred to phenol varies little with the temperature and remains high in all cases (97–98%). Benzene selectivity referred to coke varies from 1.6 to 3.3%.

DHB productivity increases from 0.2 to 0.9 mmol/g·h, and phenol productivity increases from 1.4 to 4.0 mmol/g·h as the reaction temperature elevates. It also leads to changes of the DHB isomers distribution (Figure 2), which are especially strong with hydroquinone (HQ) and benzoquinone (BQ). With increasing temperature, the HQ fraction increases monotonously from 25% to 57%, while the BQ fraction decreases from 45% to 4.5%. The resorcinol fraction is small and practically constant (3.5–5%). The catechol fraction also changes slightly and comprises 26% at 400 °C and 35% at all other temperatures.



**Figure 2.** Effect of reaction temperature on DHB isomers distribution. (For reaction conditions see Table 2.)

### Effect of Contact Time

The effect of contact time on the oxidation of phenol-benzene mixture was studied at 450 °C. The contact time was varied from 0.5 to 2 s *via* changing the velocity of the feed mixture. Table 3 lists the concentrations of products at the reaction outlet, amount of coke, as well as all other reaction parameters obtained by calculation. One may see that increasing contact time increases conversion of all initial reactants: N<sub>2</sub>O, phenol and benzene.

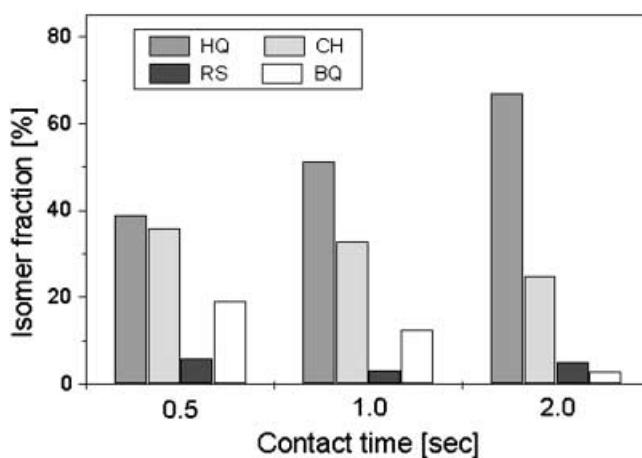
Let us consider changes of selectivities related to nitrous oxide and phenol. The selectivity of nitrous oxide referred to DHB remains constant for all contact times (~11 mol %). N<sub>2</sub>O selectivities referred to other products change dramatically at contact time 2 s. These changes are caused by sharp intensification of the deep oxidation, indicated by *ca.* two-fold increase in CO<sub>x</sub> selectivities based on both N<sub>2</sub>O (11% → 23.4%) and phenol (11% → 19%). At contact time 2 s, selectivity of benzene to phenol oxidation slightly decreases (98.7% → 96.1%) due to increased coke formation.

Although concentrations of both DHB and phenol in the outlet mixture increase with increasing the contact time, reaction productivity referred to these products decreases.

The contact time affects significantly the distribution of DHB isomers, similar to the case with reaction temperature. In Figure 3, one may see that, as the contact time increases, the benzoquinone fraction decreases (19% → 1.2%) and the hydroquinone fraction increases (39% → 67%). Fractions of resorcinol and catechol change to a less extent.

### Hydroquinone and Benzoquinone

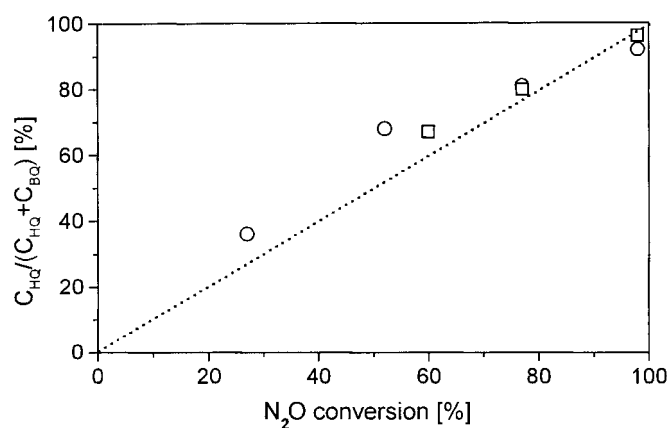
The above results show that experimental conditions have a profound effect on the HQ and BQ fractions in



**Figure 3.** Effect of contact time on DHB isomers distribution. (For reaction conditions see Table 3.)

**Table 3.** Effect of contact time. (Reaction conditions:  $C_6H_6$  19.5 ± 1 mol %,  $C_6H_5OH$  4.6 ± 0.2 mol %,  $N_2O$  2.2 ± 0.2 mol %; contact time 0.5–2 s, temperature 450 °C).

Exp. no.	Contact time [s]	Product concentration [mol %]			$C_{\text{coke}}$ [wt %]	Conversion [mol %]			N <sub>2</sub> O selectivity [mol %]						Phenol selectivity [mol %]		Benzene selectivity [%]		Productivity [mmol/g·h]	
		PhOH				N <sub>2</sub> O	PhOH	PhH	DHB	CO <sub>x</sub>	Coke	PhOH	CO <sub>x</sub>	DHB	CO <sub>x</sub>	PhOH	Coke	Pr <sub>DHB</sub>	Pr <sub>PhOH</sub>	
		N <sub>2</sub>	CO <sub>x</sub>	DHB																
1	0.5	1.42	0.10	0.14	6.8	60	3.4	5.0	11.4	0.6	77	89	11	98.7	1.3	0.82	6.5			
2	1.0	1.92	0.14	0.19	6.1	77	4.4	7.0	10.8	0.9	77.2	89	11	98.4	1.6	0.56	4.2			
3	2.0	2.06	0.30	0.21	7.2	98	5.7	6.9	10.6	1.8	64.2	81	19	96.1	3.9	0.31	2.2			



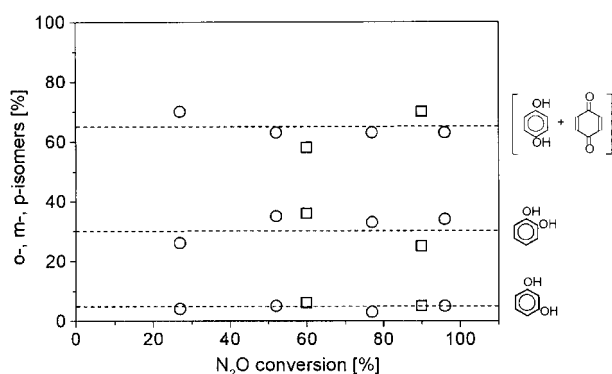
**Figure 4.** Hydroquinone fraction as a function of N<sub>2</sub>O conversion in experiments at various temperatures (circles) and various contact times (squares).

the reaction products. For example, in the experiment at 400 °C (Figure 2) the BQ fraction is much higher than that of HQ. In contrast with that, in some other experiments shown in Figures 2 and 3, mainly HQ is present, while the BQ fraction is small.

Analysis of the results shows that the ratio between HQ and BQ depends on the N<sub>2</sub>O concentration at the reactor outlet or, in another words, on its conversion. In experiments with minimal N<sub>2</sub>O conversion (high outlet concentration), the benzoquinone fraction is maximum. At N<sub>2</sub>O conversion close to 100%, which is achieved by increasing either the temperature or the contact time, BQ virtually does not form. This conclusion is illustrated in Figure 4, showing the ratio of hydroquinone concentration to the total concentration of hydroquinone and benzoquinone vs. N<sub>2</sub>O conversion. This dependence includes the results obtained with variation of both the temperature (circles, Table 2) and the contact time (squares, Table 3). At high nitrous oxide conversions the hydroquinone fraction approaches 100%, while at low conversions it seems to approach zero. To explain this surprising phenomenon one should assume an easy equilibrium between HQ and BQ. However, the mechanism of this interconversion is presently not clear.

### Distribution of DHB Isomers

Distribution of DHB isomers is an important characteristic of the reaction not only in terms of the mechanism, but also in terms of practical value. Figure 5 shows the fractions of *ortho*-, *meta*-, and *para*-isomers of DHB vs. N<sub>2</sub>O conversion. (The *para*-fraction is referred to the sum of HQ and BQ.) One may see that the isomer distribution is approximately constant for all 12-h experiments performed at various temperatures and contact times. This distribution has the following averaged values: (HQ + BQ)–65%, CH–31%, RS–4%. However, note that this distribution is not univer-



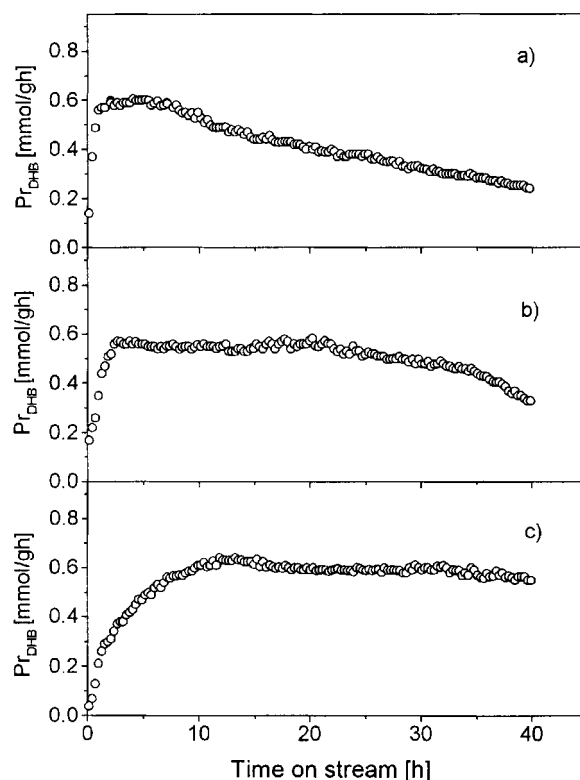
**Figure 5.** DHB isomers distribution in experiments at various temperatures (circles) and various contact times (squares).

sal. It changes significantly with changing the composition of phenol-benzene mixture and also, as we shall see further, with changing the catalyst. Moreover, a considerable change of DHB composition may occur with the progress of a single experiment.

Nevertheless, the above isomer distribution is typical for the FeZSM-5 zeolite under study and has some distinctions as compared to the liquid-phase phenol oxidation with  $\text{H}_2\text{O}_2$ . The formation of resorcinol in our case, even in small amount, is a remarkable phenomenon. Due to the induction effect, the OH group activates the *o*- and *p*-positions in the aromatic ring and deactivates the *m*-position. Therefore, in the case of  $\text{H}_2\text{O}_2$  oxidation, only CH and HQ form, with no attack to the *m*-position. In the case of  $\text{N}_2\text{O}$  oxidation, resorcinol formation is additional evidence for a very high reactivity of  $\alpha$ -oxygen generated on the FeZSM-5 surface.<sup>[4,18]</sup>

The high HQ:CH ratio is another feature of phenol oxidation with nitrous oxide. In the above experiments with the FeZSM-5 zeolite, this ratio, on the average, is 2.1 and differs considerably from the statistical distribution. On phenol oxidation with  $\text{H}_2\text{O}_2$  over TS-1 zeolite, the HQ:CH ratio may vary from 0.8 to 2 depending on the reaction conditions.<sup>[3]</sup> Despite many mechanistic studies on phenol oxidation over TS-1, the factors affecting the isomer distribution are still a matter of discussion. They may relate to different steric limitations for the diffusion of *o*- and *p*-isomers inside the zeolite crystals, as well as to some occurrence of the reaction on the external surface of zeolite.

Oxidation with nitrous oxide proceeds exactly inside the ZSM-5 micropore space. This was convincingly shown by studies on the mechanism of benzene oxidation.<sup>[14,19,20]</sup> Therefore, steric restrictions within the micropores should be a very important factor affecting the distribution of *o*- and *p*-isomers at phenol oxidation with nitrous oxide.



**Figure 6.** Time dependence of DHB productivity for 40-h runs with FeZSM-5 zeolite (a), formed catalyst FC-I (b), and formed catalyst FC-II (c).

### Long-Term Experiments

One may see from Figure 1 that in some of the 12-h experiments on the oxidation of phenol-benzene mixtures a rather stable activity of the FeZSM-5 zeolite in DHB formation was observed. But to estimate the practical prospects, long-term runs are needed. With this aim we conducted three 40-h runs, with their results presented in Table 4 and Figure 6. Different catalysts were used. Run no. 1 was performed with the same FeZSM-5 zeolite, which was used for all preceding experiments, runs no. 2 and no. 3 were conducted with the formed zeolite catalysts prepared using an alumina binder.

Catalysts stabilities may be estimated from the changes of DHB productivities vs. time on stream in Figure 6. One may see that general form of the dependencies is similar in all cases: the  $\text{Pr}_{\text{DHB}}$  value increases at the initial period, reaches its maximum and then decreases as the catalyst is deactivated by coke. The reason for the low initial activity is not quite clear. This may be caused by both the reaction products adsorption on the catalyst surface and their consumption for coke formation, which may intensively occur at the initial period of reaction. Deactivation rate differs considerably with the catalyst. Over the FeZSM-5 zeolite  $\text{Pr}_{\text{DHB}}$

**Table 4.** Long-term experiments. (Reaction conditions: C<sub>6</sub>H<sub>6</sub> 19 ± 0.5 mol %, C<sub>6</sub>H<sub>5</sub>OH 4.6 ± 0.2 mol %, N<sub>2</sub>O 2.3 ± 0.1 mol %.)

Run no.	Catalyst	T [°C]	Contact time [s]	N <sub>2</sub> O Conversion [mol %]	C <sub>coke</sub> [wt %]	N <sub>2</sub> O selectivity [mol %]			Phenol selectivity [mol %]			Benzene selectivity [mol %]			DHB distribution			Productivity [mmol/g·h]			
						DHB	CO <sub>x</sub>	Coke	DHB	CO <sub>x</sub>	Coke	PhOH	PhOH	Coke	o (%)	m (%)	p (%)	HQ:CH	Pr <sub>DHB</sub>	Pr <sub>PhOH</sub>	
1	FeZSM-5	450	1	60	3.5	6.0	15.8	10.5	13.5	1.0	76	89	11	98	2.0	37	3	60	2.0	0.42	3.5
2	FC-I	450	1	70	4.5	—	—	13.0	18.0	—	—	89	11	—	41	4	55	1.4	0.50	—	—
3	FC-II	475	2	97	8.9	9.1	10.4	15.0	10.5	0.5	74	97	3	99.3	0.7	27	4	69	2.6	0.55	2.5

decreases approximately linearly with the time on stream, decreasing 2 times for 40 h.

The formed catalysts exhibit much higher stability. FC-I catalyst, after reaching the maximum productivity, retains the activity constant for *ca.* 20–25 h and then shows an accelerating deactivation rate. FC-II catalyst is the most stable one. After reaching the maximum, the Pr<sub>DHB</sub> value remains practically constant for the further time on stream.

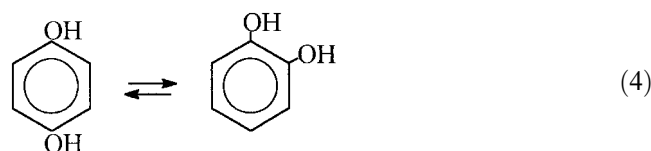
Quantitative parameters of the long-term experiments averaged over 40 h are listed in Table 4. One may see that the best results are obtained with the FC-II catalyst. In this experiment, conversions of both benzene and phenol are about 9%, and conversion of N<sub>2</sub>O approaches 100%. The total N<sub>2</sub>O selectivity referred to DHB and phenol (S<sub>N<sub>2</sub>O→DHB</sub> + S<sub>N<sub>2</sub>O→PhOH</sub>) comprises 89% (15% and 74%, respectively), and only 11% N<sub>2</sub>O is consumed for the deep oxidation products (10.5%) and coke (0.5%).

Benzene and phenol selectivities referred to the selective oxidation products are close to 100%.

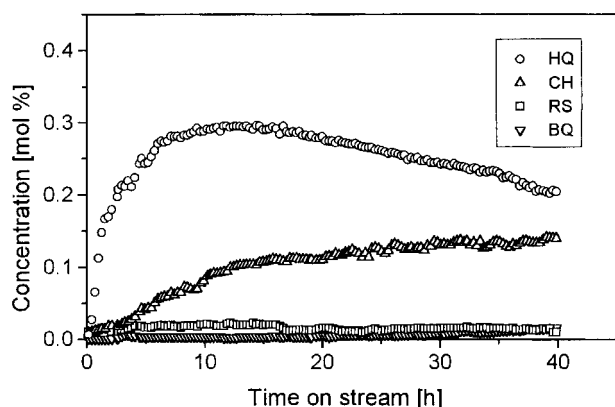
Note a low coke amount over FC-II catalyst (10.4 wt %). Assuming that all coke amount forms from benzene, it means that S<sub>PhH→coke</sub> = 0.7%. Assuming that all coke forms from phenol, it means that S<sub>PhOH→coke</sub> = ~3%, which also is a rather small value.

The total productivity of FC-II catalyst referred to the target products is 3.05 mmol/g·h, with 0.55 mmol/g·h related to DHB and 2.5 mmol/g·h related to phenol.

Table 4 shows the averaged results on distribution of *o*-, *m*-, and *p*-isomers of DHB. This distribution depends on the catalyst used, which is especially clearly seen from the HQ:CH ratio. In the case of FC-II catalyst, this ratio is very high and, on the average, equals 2.6. Figure 7 shows changes of isomer concentrations for the experiment with FC-II catalyst. RS and BQ concentrations remain very low for the whole experiment. HQ and CH concentrations vary dramatically, so that the HQ:CH ratio gradually decreases from 10–12 at the beginning of the experiment to 1.6 at the end. The reason of such behavior remains unclear. One may assume that the HQ:CH value of *ca.* 10 corresponds to the “true” original distribution of the isomers provided by phenol hydroxylation inside micropore space of the zeolite. With increasing time on stream, as coke accumulates at the external zeolite surface, this ratio gradually decreases due to coke’s ability to catalyze the reaction of DHB isomerization:



Naturally, this hypothesis requires experimental support.



**Figure 7.** Concentrations of DHBs vs. time on stream over FC-II catalyst. (For reaction conditions see Table 4.)

### Comparison with Phenol Oxidation by Hydrogen Peroxide

In Table 5, experimental results over FC-II catalysts are compared with the process parameters of HQ and CH production *via* phenol oxidation by  $\text{H}_2\text{O}_2$ .<sup>[2]</sup> Results obtained with nitrous oxide seem rather promising, especially regarding high phenol selectivity and small coke amount. In addition, the cost of  $\text{N}_2\text{O}$  produced by the oxidation of ammonia is several times lower than that of  $\text{H}_2\text{O}_2$ .<sup>[21]</sup> Low DHB yield referred to  $\text{N}_2\text{O}$  (15% as compared to 50–70% for  $\text{H}_2\text{O}_2$ ) is only seemingly a disadvantage, since the remaining  $\text{N}_2\text{O}$  fraction is consumed mainly for the useful reaction, i.e., benzene to phenol oxidation, so that total  $\text{N}_2\text{O}$  yield referred to the sum of DHB and phenol is 89%. Besides, the DHB yield may be increased through increasing the phenol fraction in the feed.

When comparing the technologies of HQ and CH preparation, one should keep in mind that in the case with  $\text{N}_2\text{O}$  the DHBs may be prepared directly from benzene, as shown in Figure 8, rather than from phenol, as in the case with  $\text{H}_2\text{O}_2$ .

In this scheme, benzene and nitrous oxide are the only starting reagents, with the fraction of resulting phenol being recirculated as an intermediate product. Considering this approach in the experiment with FC-II catalyst (Table 4), *ca.* 25% phenol should return to the

front end of the scheme for the oxidation to DHB, while the other 75% should be used as a final product. As a result, the starting benzene will be converted into the mixture of phenol and DHB with the DHB concentration at about 20%.

### Conclusion

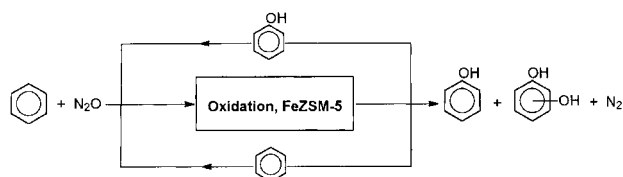
Oxidation of phenol-benzene mixtures by nitrous oxide opens a way for the development of a new gas-phase process for hydroquinone (HQ) and catechol (CH) synthesis. Significant catalyst stability can be achieved for this reaction. One of the samples tested in the present work (FC-II) provided nearly constant activity for several tens of hours with the average dihydroxybenzenes (DHB) and phenol productivities of 0.55 mmol/g·h and 2.5 mmol/g·h, respectively. DHB productivity may be increased by increasing the phenol fraction in the feed mixture.

### Experimental Section

#### Catalyst

Main experiments on oxidation of phenol-benzene mixtures were performed with ZSM-5 zeolite (CBV-8014, Zeolyst Inc.), the characteristics of which are shown in Table 6. The zeolite is a high-crystalline material of MFI structure (XRD data), with the admixed iron concentration of 0.02 wt % (ICP OES technique). Texture parameters of the sample (micropore volume, BET and external surface areas) were determined using low-temperature nitrogen adsorption.

To provide an elevated  $\alpha$ -sites concentration, the zeolite was activated *via* steam treatment at 700 °C for 2 h in a helium flow



**Figure 8.** The process scheme for joint production of dihydroxybenzenes and phenol.

**Table 5.** Comparison of hydroquinone and catechol synthesis via phenol oxidation with  $\text{H}_2\text{O}_2$  and  $\text{N}_2\text{O}$ .

Process parameters	$\text{H}_2\text{O}_2$ oxidation <sup>[2]</sup>			$\text{N}_2\text{O}$ oxidation
	Rhone Poulenc ( $\text{HClO}_4$ , $\text{H}_3\text{PO}_4$ )	Brichima ( $\text{Fe}^{++}/\text{Co}^{++}$ )	Enichem (TS-1)	
Phenol conversion [%]	5	10	25	9
$\text{H}_2\text{O}_2$ ( $\text{N}_2\text{O}$ ) yield [%]	70	50	70	15 (89)
Phenol selectivity [%]	90	80	90	95
HQ:CH ratio	1:1.4	1:2.3	1:1	2.6:1
Tars [%]	10	20	12	< 5 (coke)



**Table 6.** Characteristics of FeZSM-5 zeolite.

Structure	Chemical composition (wt %)			Texture parameters			$C_{\alpha}$ ( $\alpha$ -site/g)
	Al	Fe	Na	$V_{\mu}$ [cm <sup>3</sup> /g]	$A_{\text{BET}}$ [m <sup>2</sup> /g]	$A_{\text{ext}}$ [m <sup>2</sup> /g]	
MFI	0.9	0.02	0.03	0.160	430	70	$5.5 \cdot 10^{17}$

having 50 mol % H<sub>2</sub>O. The  $\alpha$ -sites concentration of the activated sample, measured by N<sub>2</sub>O decomposition and oxygen isotopic exchange, is  $5.5 \cdot 10^{17}$  site/g.

Procedures for measuring the zeolite characteristics are described in more detail elsewhere.<sup>[22]</sup>

### Catalytic Studies

**Flow setup:** Catalytic experiments were carried out with an automated flow setup provided with on-line chromatographic analysis of the gas phase. 2 ccm (~1.1 g) of the 0.5–1.0 mm catalyst particles were placed into a quartz reactor with an inner diameter of 7 mm. Before testing, the catalyst was treated in flowing air at 550 °C. Gases were fed by the flow mass controllers (MKS Instruments), the liquid phenol-benzene mixture of the given composition was fed using a high-performance syringe pump 500 D (ISCO).

The reaction mixture was automatically sampled and analyzed each 19 min. The light gases (N<sub>2</sub>, N<sub>2</sub>O, CO, CO<sub>2</sub>) were analyzed at room temperature with a packed column filled with Poropak Q, using a TCD. For a more accurate measurement of low CO<sub>x</sub> concentrations, carbon oxides were hydrogenated over a nickel catalyst and then analyzed as methane using FID. Analysis of organic components was performed at the programmed temperature elevation from 180 to 280 °C with a capillary column DB-1701 (J&W Scientific) using FID.

From the chemical composition of the inlet and outlet reaction mixtures, conversions of the starting reagents (N<sub>2</sub>O, phenol, benzene) were calculated as well as their selectivities referred to the target (DHB, phenol) and side reaction products (CO<sub>x</sub>, coke).

Performing experiments with high-boiling organic compounds is a very difficult task because of their easy condensation resulting in plugging of the gas lines of a setup. To some extent this relates to phenol, but especially to DHBs. For example, the melting point of hydroquinone is 170 °C, while its boiling point is 285 °C. To prevent DHB condensation, the gas lines of our setup are placed inside a ventilated thermal box kept at 180 °C. After each experiment, the gas lines were washed with liquid acetone. This procedure provides reliable and well reproducible results.

**Regeneration and coke amount:** The catalyst deactivates due to coke formation in the course of reaction. After the reaction completion, coke was carefully burned out to determine its amount and to regenerate the catalyst for the next experiment. Before regeneration, the catalyst was blown off at 450 °C in flowing helium for 30 min. The carbonic deposits, not removed from the surface under these conditions, were considered as coke. Coke burning out was performed in flowing helium with 2 mol % N<sub>2</sub>O, at gradual temperature elevation from 450 to 550 °C. The regeneration was monitored

by the CO<sub>x</sub> concentration in the gas phase. Coke amount was calculated from the total amount of CO and CO<sub>2</sub> produced. Some control experiments with the coke measurements by the TGA technique showed well-consistent results. Regeneration of the catalyst provides complete restoration of its activity.

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