

Oxidative Coupling and Hydroxylation of Phenol over Transition Metal and Acidic Zeolites: Insights into Catalyst Function

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Abstract Reaction of phenol with hydrogen peroxide over H-MFI, Fe-MFI, H-BEA, Fe-BEA and TS-1 zeolite catalysts was investigated. Over H-BEA, biphenyl product was observed. It is suggested, that the larger pore size of H-BEA facilitates coupling of two phenol molecules. Two distinct reaction mechanisms are proposed for acid and redox catalysts.

Keywords Catalysis · Zeolites · Phenol · Hydroxylation · Redox · Pore size

1 Introduction

The use of biomass combustion for power generation is regarded as an attractive greenhouse gas reduction strategy. Such processes revolve around the pyrolysis of lignocellulose that results in the formation of bio-oils. Other processes include the blending of biomass with coal; a practical and attractive approach to increase the renewable energy input in traditional coal power plants [1, 2]. However as a consequence of co-combustion with coal, numerous types of VOCs can be formed, including aromatic hydrocarbons [3, 4]. The aromatic hydrocarbons are present in wood smoke that is a product of biomass combustion [5, 6]. The toxicity of the aromatic hydrocarbons, especially phenol, is known to cause symptoms like muscle weakness, convulsions and coma if introduced to humans through skin absorption, inhalation and vapour inhalation

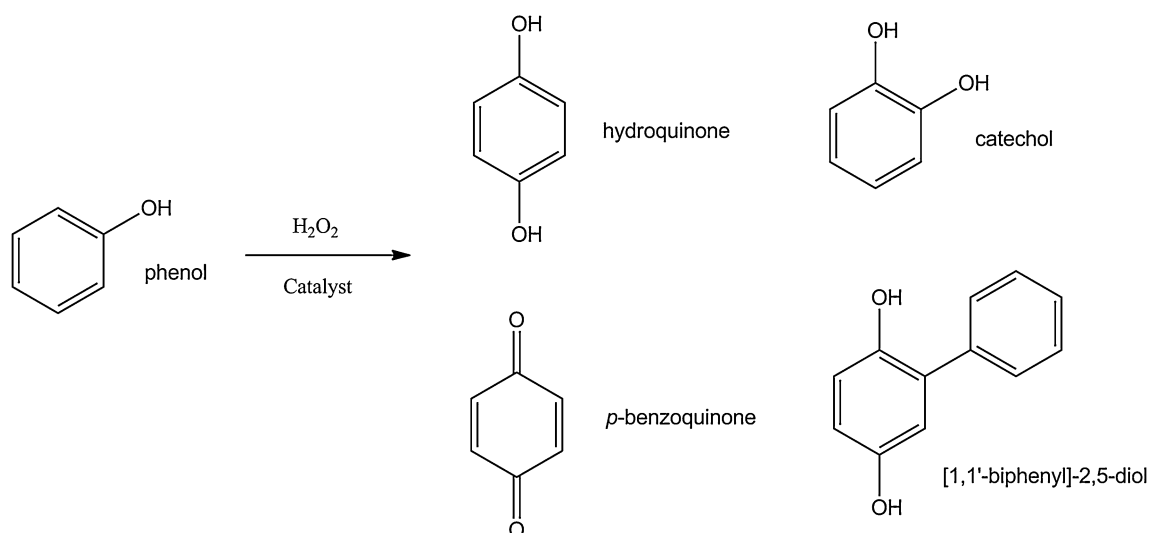
[7] and thus removal and conversion of phenols to valuable products is highly desirable.

Apart from its toxicity, phenol creates significant problems through its reaction with other species present as VOC's in the flue gases streams of combustors. These reactions can lead to oligomerization [8, 9], resulting in significant and undesirable flue gas treatment challenges. One potentially viable treatment strategy involves the upgrading of phenol through a hydroxylation reaction, using hydrogen peroxide, in order to produce *p*-benzoquinone and catechol (Scheme 1). These products are used as valuable precursors for rubber manufacture [10] and as fine chemicals in perfumes and pharmaceuticals [11].

Hydrogen peroxide (H₂O₂) treatment has emerged as a viable approach for treatment of aromatic compounds found in aqueous waste streams. Its use, in general, does not lead to the formation of undesirable by-products and it is an ecologically 'clean' and non-toxic chemical [12]. Studies of the hydroxylation of phenol by hydrogen peroxide catalyzed by protonic FAU zeolites has been undertaken [13] and other studies indicate that a catalyzed process over porous materials is possible, provided that the catalyst pore sizes are sufficiently large. For zeolites, catalysts with too small a pore size are not active, due to the large pore diameter required to accommodate the reaction [14, 15].

It has been argued that the catalytic reaction of phenol with H₂O₂ does not proceed through an electrophilic aromatic substitution reaction with a hydroxonium cation (which would be generated from hydrogen peroxide at the surface of the acid catalyst). Instead, it is generally considered that the catalytic process occurs via a redox mechanism involving hydroquinone/*p*-benzoquinone [16, 17]. The goal of this research is to compare and contrast the catalytic performance of zeolite catalysts in terms of their pore size, redox properties, and acidity.

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Scheme 1 Hydroxylation of phenol and the observed products

2 Method

2.1 Catalyst Preparation

The zeolite catalysts studied here (MFI and BEA) have a three dimensional pore system that is rather similar (consisting of intersecting straight and sinusoidal channels) and mainly vary in the pore diameter. Thus structural dependency of the catalytic reaction is restricted to pore size to be able to pinpoint the origin of the different reactivities.

H-MFI and H-BEA were prepared by calcining $\text{NH}_4\text{-MFI}$ (Zeolyst, Si/Al = 15) and $\text{NH}_4\text{-BEA}$ (Zeolyst, Si/Al = 12.5) respectively, at 500 °C in air at a rate of 5 °C/min. This was held for 2 h before cooling to 300 °C. Fe-MFI and Fe-BEA was prepared by ion-exchange. In separate procedures, commercial $\text{NH}_4\text{-MFI}$ (Zeolyst, Si/Al = 15) and $\text{NH}_4\text{-BEA}$ (Zeolyst, Si/Al = 12.5) were impregnated with an aqueous solution of 0.01 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and maintained at a pH of 8 by dropwise addition of ammonium hydroxide. The procedure was repeated three times. Following the transition metal exchange procedure, the catalysts were vacuum filtered and dried at 115 °C overnight. The catalysts were then calcined at 500 °C at a rate of 5 °C/min. This was held for 2 h before cooling to 300 °C, before adding to the reaction mixture. TS-1 (Zeolyst Si/Ti = 72) was activated by heating to 500 °C in air at a rate of 5 °C/min. This was held for 2 h before cooling to 300 °C, before adding the catalyst to the reaction mixture.

2.2 Characterization

Surface area measurements were made by N_2 adsorption/desorption by using a Micrometrics Gemini II 2370 surface

area analyzer. The samples were pre-treated in vacuum at a pressure of 1.2×10^{-3} mbar at 115 °C for 24 h.

Temperature programmed desorption (TPD) measurements were conducted in a compact, stainless steel apparatus equipped with a turbo pump. The desorption cell was connected through a leak valve to an independently pumped, Pfeiffer Prisma quadrupole mass spectrometer. The catalyst samples of known mass were introduced into the desorption cell, evacuated and activated at 500 °C at 5 °C/min, followed by cooling to 115 °C in order to adsorb probe molecules for acid site quantification. Adsorption was performed at 115 °C in order to minimize multilayer adsorption of the adsorbates. For acid site quantification, ammonia was adsorbed on the catalyst at 1 mbar pressure. Loaded catalysts were cooled to 30 °C and followed by controlled desorption of the probe from 30 to 500 °C with a heating rate of 5 °C/min.

Inductively coupled plasma-optical emissions spectrometry (ICP-OES) was performed on the Fe-MFI catalysts in order to know more accurately the actual Fe loading. A Varian Radial 715-ES series ICP-OES was used for the elemental analysis. Samples were digested with acid in a microwave, using an yttrium-based internal standard for quantification.

2.3 Reaction

Experiments were carried out in a 10 mL stirred glass reactor equipped with a condenser and a magnetic stirrer. Blank tests were conducted with H_2O_2 and phenol in the absence of catalysts.

The reaction was performed at 100 °C with continuous stirring and at atmospheric pressure. The reaction mixture

Table 1 Summary of catalyst properties Langmuir surface area, total pore volume and acid concentration

Catalyst	Langmuir surface area (m ² /g)	Total pore volume (mL/g)	Acid concentration ^b (mmol/g)
TS-1	563	0.20	0.046
H-MFI	451	0.28	1.450
Fe-MFI (0.61 wt%) ^a	442	0.22	0.918
Fe-MFI (1.56 wt%) ^a	426	0.21	1.088
Fe-MFI (2.14 wt%) ^a	373	0.21	0.910
Fe-MFI (2.78 wt%) ^a	355	0.18	0.810
H-BEA	731	0.41	1.209
Fe-BEA	710	0.40	0.850

^a Fe content determined by ICP-OES^b Acid concentration determined by NH₃-TPD

contained 4.7 g of phenol and 0.45 g of H₂O₂ (30 wt% aqueous solution). Toluene (140 mg) was added as an internal standard. Catalyst (140 mg) was added to the reaction mixture while hot, in order to minimize moisture adsorption from the atmosphere.

The reaction components were quantified and identified using gas chromatography mass spectrometry (GC/MS). The GC used for the analysis was an Agilent 6890 equipped with an Agilent 5973 mass selective detector (MSD), and a 30 m Restek Rtx-200ms column with a crossbond trifluoropropylmethyl polysiloxane stationary phase. Separation was carried out using a temperature program that commences at 45 °C, held for 5 min, heated to 115 °C at a rate of 10 °C/min and held for 3 min. This was then followed by heating up to 285 °C at a rate of 10 °C/min and held for 3 min. The detector was turned off at time periods of 0.01–3.30 min and 4.40–8.00 min in order to avoid saturating the detector with signal from the solvent peak.

3 Results

The results of the Langmuir surface areas, pore volumes and acid site concentrations are summarized in Table 1.

In the blank reaction using only H₂O₂ and in the absence of any catalyst, trace amounts of *p*-benzoquinone and catechol were detected, with a higher selectivity towards *p*-benzoquinone. Using H₂O₂, it is generally recognized that a phenolate anion is formed, which facilitates resonant stabilization to hydroxylate phenol at the *para* and *ortho* positions. The general mechanistic pathway for phenol interaction with H₂O₂ is shown in Scheme 2 [18].

The catalysts studied in the investigation effectively catalyzed the phenol hydroxylation reaction, and all catalysts converted phenol to *p*-benzoquinone, catechol and

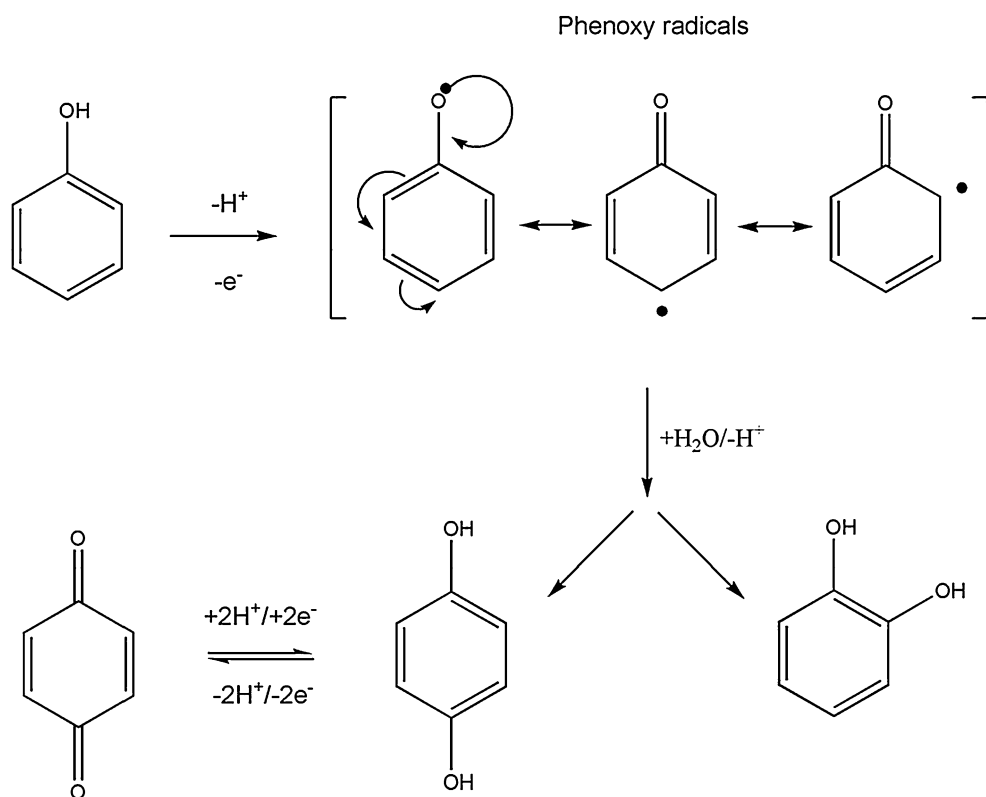
hydroquinone. Over H-BEA however, an additional reaction pathway is evident, leading to the formation of [1,1'-biphenyl]-2,5'-diol in addition to the hydroxylation products. The catalytic activity of H-MFI, Fe-MFI and TS-1 is consistent with the results reported in other studies [19–21]. The results for the catalytic activity and product selectivity of the catalysts examined are summarized in Table 2.

In order to demonstrate that the catalytic activity is not significantly affected by mass transport, Fe-MFI of varying iron loading was prepared. With increasing iron loading on the MFI structure, the Langmuir surface area and the total pore volume decreases slightly. Results showed that 2.14 wt% Fe-MFI had the highest conversion compared to the other Fe-MFI samples. 2.14 wt% Fe-MFI exhibited reduced surface area and total pore volume, thus the catalytic activity is mainly determined by the number of redox sites and not mass transport limitations.

4 Discussion

For TS-1 (a non-acidic catalyst), its redox properties (and structure) are relevant and have a significant influence on its catalytic activity. The catalytic activity of TS-1 manifests its properties from the tetrahedral titanium present in the TS-1 structure. The titanium in the TS-1 structure is able to transition between oxidation states and can form titanyl species on the surface [22]. The presence of tetrahedrally coordinated titanium species in TS-1 facilitates redox reactions occurring in TS-1, and in turn it is likely to result in the formation of radicals from H₂O₂. The radical formation is key for the TS-1 catalyst because as shown by the TPD experiments, TS-1 possesses the lowest acid concentration in comparison to the other catalysts used, yet exhibits the highest phenol conversion. Similar catalytic activity is observed in other titanium impregnated catalysts [23, 24], which can generate electron holes that oxidize water to create hydroxyl radicals. The hydroxyl radicals then react with the phenol (in the phenoxy radical state) which generates the products *p*-benzoquinone, catechol, and hydroquinone in a direct route. The surface of TS-1 also provides chemoselective control of product formation which results in the formation of hydroquinone and catechol, with very little *p*-benzoquinone being produced.

H-MFI exhibited higher concentration of acid sites and in the group of Fe-MFI catalysts the 1.56 wt% loading possessed the highest acid site concentration. The addition of Fe results in ion exchange with the protonic acid sites. Fe on the other hand introduces some Lewis acidity as well as the redox function. With the 2.14 wt% loading, an optimal balance of the acid sites generated by the Fe atoms, the acidic protons and redox sites gives rise to a higher phenol conversion compared to the other Fe-MFI zeolites.



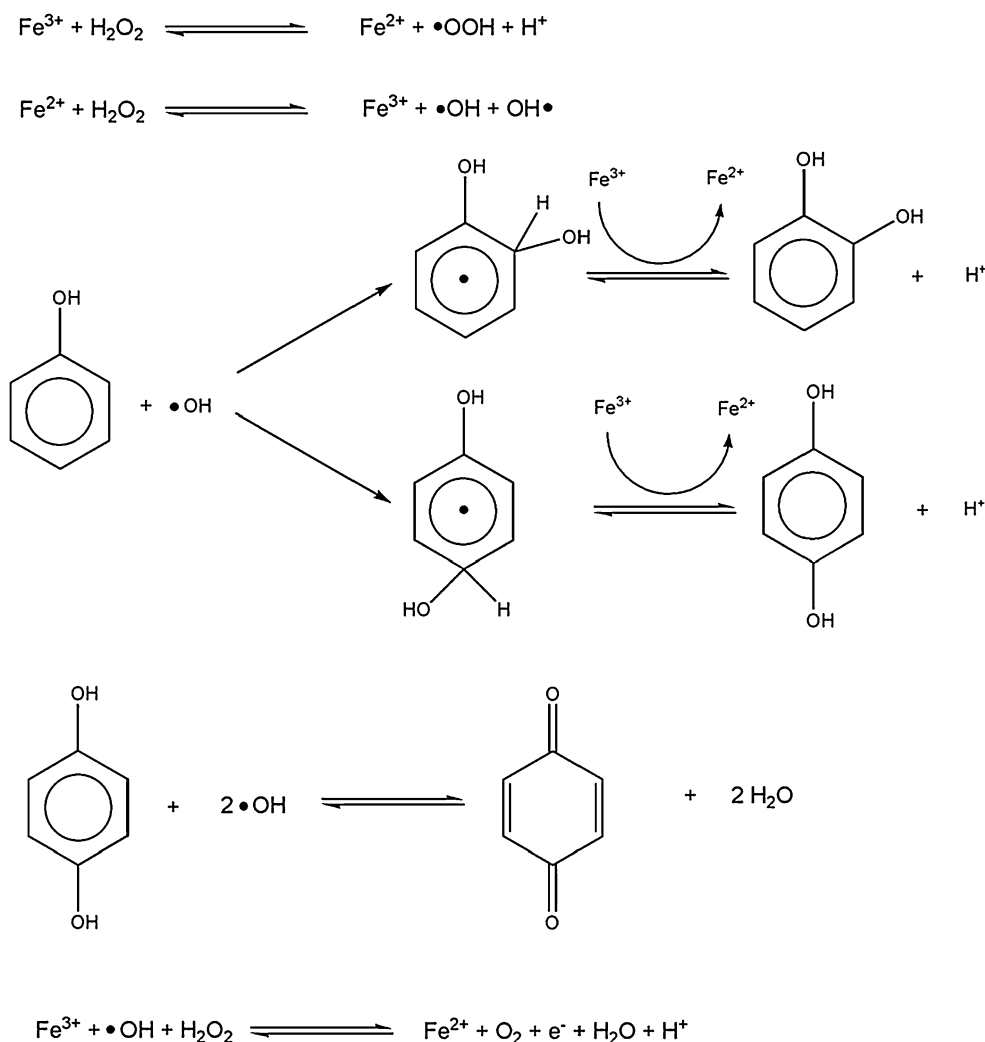
Scheme 2 Non-catalysed phenol oxidation reaction and major product formation mechanism [18]

Table 2 Summary of phenol conversion and product selectivity after 6 h

	Phenol conversion after 6 h (%)	Product selectivity (%)			
		<i>p</i> -benzoquinone	Catechol	hydroquinone	[1,1'-biphenyl]-2,5'-diol
No catalyst	5	80	20	0	0
TS-1	30	5	45	50	0
H-MFI	2	100	0	0	0
Fe-MFI (0.61 wt%)	8	100	0	0	0
Fe-MFI (1.56 wt%)	8	91	8	0	0
Fe-MFI (2.14 wt%)	20	38	35	27	0
Fe-MFI (2.78 wt%)	10	35	34	31	0
H-BEA	23	3	62	28	7
Fe-BEA	8	34	33	33	0

At 2.14 and 2.78 wt% loading, the acidic protons are replaced with the Lewis acidic Fe cations which result in reduction in the acid site concentration. We observed an increased selectivity towards catechol and hydroquinone. The acid site concentration does not appear to have a simple relationship with the catalytic activity. However, it the data suggests that the nature and concentration of acid sites do have an influence on the product selectivity as H-MFI and 0.56 wt% Fe-MFI formed only *p*-benzoquinone. Further addition of Fe atoms reduces the selectivity towards *p*-benzoquinone, forming catechol and

hydroquinone. A possible explanation is an acid catalyzed conversion of catechol and hydroquinone to benzoquinone or a direct route via stabilization of the phenoxy radical. This is consistent with the data found for 2.14 and 2.78 wt% Fe-MFI, as well as TS-1 catalyst. For H-BEA, the acid sites are suggested to catalyse the formation of the condensed product, because the pore size in BEA is larger which enables the condensation reaction. This also suggests that the redox properties of the catalysts have more influence on the conversion than the acidity.



Scheme 3 Phenol hydroxylation reaction pathway involving H_2O_2 and $\text{Fe}^{3+}/\text{Fe}^{2+}$ (fenton reaction) [25, 26]

It has been suggested that the catalytic decomposition of hydrogen peroxide, in the presence of Fe^{2+} ions (Fenton reaction), takes place through a redox mechanism [25, 26]. A representative pathway is shown in Scheme 3. The oxidation potential of iron is not high enough to generate similar electron holes in titanium dioxide. For iron catalysts to be effective, it has been found that iron in a tetrahedral coordination on a support results in more effective active sites [27, 28]. The reactivity for both the Fe-MFI and Fe-BEA suggest that the iron coordination on the respective zeolite surfaces creates a sufficient concentration of Fe^{2+} species that enables a redox reaction between the zeolite and hydrogen peroxide. In both the Fe-MFI and Fe-BEA catalysts, the selectivity of *p*-benzoquinone, catechol, and hydroquinone are virtually equal, suggesting that the Fe provides little chemoselective control of product selectivity.

It is important to note that in many studies focusing on the hydroxylation of phenol using H_2O_2 as an oxidant, *p*-benzoquinone, catechol, and hydroquinone are the only

products to form. However in the present study, we observe an additional product [1,1'-biphenyl]-2,5'-diol formed in during the reaction catalyzed by H-BEA (Scheme 1). Although Atoguchi and colleagues observed similar conversion levels and product selectivity as the present study, in their work only catechol, and hydroquinone were reported as major products [20]. It is likely that they had produced the additional [1,1'-biphenyl]-2,5'-diol product, but was not observed in their study as they had used a biphenyl internal standard, which is expected to have very similar retention time to [1,1'-biphenyl]-2,5'-diol on the GC column and thus could have been missed in the analysis. H-BEA differs from the H-MFI, Fe-MFI and TS-1 catalysts in that its effective average pore diameter is significantly larger than those of the other zeolites studied. It also possesses significant mesoporosity and has accessible surface acid sites in these mesopores.

Oxidative coupling of phenols has been thoroughly investigated using biological catalysts, observing biphenyl

and triphenyl compounds in many cases [29, 30], and even high molecular weight products formed from polymerization [31]. The coupling of phenol moieties would suggest that polymerization is more likely to occur in biological system than over heterogeneous catalysts due to a combination of the enzyme activity and the lack of space restriction. In some studies, functional groups were added to phenol which facilitates the selective coupling to occur [32, 33].

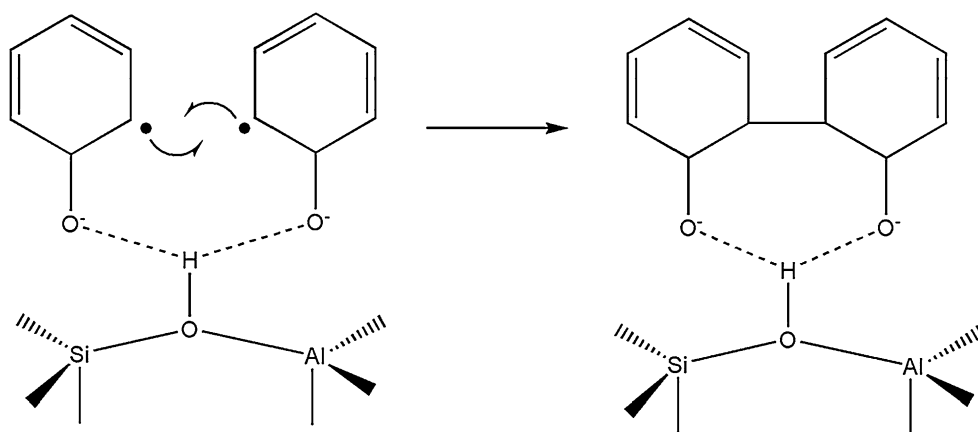
The larger pore size of H-BEA in combination with the high acid concentration generated from the surface protons, enables two molecules of phenol to diffuse inside its pores and coordinate two molecules of phenoxy radicals to a single proton on the H-BEA surface in a hydride formation. The proximity of the two molecules of phenoxy radicals enables coupling at the *ortho* positions of the molecules. The high product selectivity towards catechol would suggest that the phenoxy intermediate is more susceptible to reaction from the *ortho* positions of the molecules. As a result of the coupling, one of the hydroxyl groups is removed and transferred to the adjacent phenoxy intermediate, leading to a formation of a diol in the *para* position in one of the phenoxy molecules. This results in the formation of [1,1'-biphenyl]-2,5'-diol, which is small enough to diffuse out of the pores. The significance of this coupling reaction is that it occurs in mild and solventless conditions. This holds great scientific interest as it demonstrates the potential of forming other useful products in addition to the commonly observed catechol, hydroquinone and benzoquinone. Biphenyl compounds are for example useful precursor materials for valsartan: a drug used in the treatment for Alzheimer's disease.

The pore sizes for all the zeolites investigated in this study are of sufficient diameter to accommodate at least a single ringed aromatic compound, and a biphenyl compound in the case of reaction over H-BEA. The acidic protons from H-BEA stabilize the phenoxy radicals, as shown in Scheme 4. This facilitates their reaction, which results in the formation of the condensed product. The

catalyst pores restricts further polymerization to occur between the individual phenoxy radicals. Since hydroxylated products and benzoquinone are also formed over acidic H-BEA, a biphenyl compound is a possible intermediate for the acid catalyzed reaction. Despite the high acid concentration of H-MFI, the pores of acidic H-MFI are not sufficiently large enough to enable the formation of the condensed product, and result in very low selectivity for the formation of the biphenyl species. H-MFI possesses a pore diameter of 5.5 Å, while a phenol molecule has a kinetic diameter of 2.5 Å [34]. The diffusion in and out of the pores would be restricted to single file diffusion of phenol and benzoquinone. H-BEA possesses a pore diameter of 7.8 Å which allows at least two molecules of phenol to diffuse, form a transition state and accommodate diffusion of a single molecule of the biphenyl compound to diffuse out of the catalyst pores. Thus, for the acid catalyzed reaction, the reaction intermediate is too bulky to be accommodated in the MFI structure but can accommodate a single hydroxylated species (or phenyl radical) which can further react to benzoquinone. Over TS-1 (again an MFI structure), a smaller intermediate is formed with the redox active site but the reaction stops at the hydroquinone/catechol level, because of the lack of acid sites.

Reaction using Fe-BEA is less effective than H-BEA, as demonstrated by its reduced acid concentration and catalytic activity. Fe-BEA is unable to catalyze the formation of biphenyl compounds. This is intriguing, considering that Fe-BEA possess similar pore size with H-BEA. This would indicate that along with the pore size being a factor for [1,1'-biphenyl]-2,5'-diol formation, the nature of the catalyst surface is also important. While Fe ions on the zeolite surface are able to facilitate a redox reaction with hydrogen peroxide that lead to phenol hydroxylation, it is unable to stabilize phenoxy radicals sufficiently for the coupling reaction to occur. Over Fe modified MFI, similar to TS-1, an intermediate species of smaller kinetic diameter is formed that restricts to the formation of product species.

Scheme 4 Phenoxy radicals stabilized on H-BEA surface



Comparing the redox catalysts Fe-MFI, Fe-BEA, and TS-1 with the acid catalysts H-MFI and H-BEA, it is clear that the reaction proceeds through different catalytic pathways. Reaction over the redox catalysts results in the formation of a large quantity of hydroxyl radicals through hydrogen peroxide generation and decomposition reactions thus increasing the likelihood of phenol interacting with the radicals. Over the acid catalysts, the acid sites function by stabilizing (most likely condensed) phenoxy radicals that are formed through resonance stabilization, enhancing their reactivity with hydroxyl radicals or potentially via a consecutive reaction of catechol/hydroquinone to form benzoquinone. Deactivation of the MFI catalyst could also have an influence on catalyst activity, resulting from stronger acid sites over the H-MFI [20, 35]. H-MFI has been found to exhibit significant coking by phenol oxidation products [36].

5 Conclusions

The present study reports on the oxidation of phenol using H_2O_2 using heterogeneous catalysts under mild conditions and in the absence of solvent. The primary products from the heterogeneous acid catalysis of the hydroxylation of phenol by hydrogen peroxide are *p*-benzoquinone and catechol. Using H-BEA as catalysts and under the same reaction conditions, additional products hydroquinone and [1,1'-biphenyl]-2,5-diol, were observed, in addition to the hydroxylated product. The formation of [1,1'-biphenyl]-2,5-diol indicates that selective aromatic coupling is possible without further oligomerization. Fe-BEA was apparently less active than H-BEA, and did not result in the formation of [1,1'-biphenyl]-2,5-diol.

The redox catalysts and the acid catalysts proceed through differing mechanistic pathways. It is suggested that the pathway over redox catalysts are reliant on hydroxyl radical formation from hydrogen peroxide reaction, while the acid pathway relies on the stabilization of phenoxy intermediates. For the acid catalysts, the condensation reaction requires a more open pore structure to allow for intermediates and transition states to form.

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