

# Hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub> over Fe<sup>2+</sup> and/or Co<sup>2+</sup> ion-exchanged NaY catalyst in the fixed-bed flow reactor

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## Abstract

The catalysts, Fe-NaY, Co-NaY and Fe-Co-NaY, were prepared by ion-exchange of NaY through the wet method, and characterized. Their catalytic performance was evaluated for the hydroxylation of phenol between 30 and 90 °C. The Fe-Co-NaY catalyst showed higher activity than either Fe-NaY or Co-NaY catalysts. The optimum temperature was found to be 70 °C. The reaction conditions, phenol/H<sub>2</sub>O<sub>2</sub>, water/phenol and WHSV, were found to remarkably influence the activity of the catalysts. Under the optimum reaction conditions, 21.8% phenol conversion was obtained with 44.8% selectivity to catechol, and 16.5% to hydroquinone. Based on the high phenol conversion over Fe-Co-NaY compared to Fe-NaY and Co-NaY catalysts, it was suggested that well-dispersed Fe with optimum loading was the requirement for high phenol conversion and products selectivity. The long-run catalytic test for 44 h confirmed the absence of leaching of metal ion from the pores of Fe-Co-NaY catalyst. The reaction was carried out in a fixed-bed flow reactor, which could be a convenient solution to the problem of the batch type reactor in industrial applications.

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## 1. Introduction

Hydroxylation of phenol with clean oxidants like H<sub>2</sub>O<sub>2</sub> is a research topic of high industrial importance. The reaction has been carried out over metal oxides [1–3], metal complex oxides [4,5], zeolite-encapsulated metal complexes [6] and hydrotalcite-like compounds [7,8]. Very recently, some novel catalysts, such as metal modified mesoporous materials [9–11], copper hydroxyphosphate [12] and copper Keggin-type heteropoly compounds [13] have also been applied to this reaction extensively. The use of TS-1 for hydroxylation and its commercialization by Enichem workers [14–16] illustrates an important advancement in this area. Following this, various microporous metallosilicates [17] such as TS-2 [18], Ti-β [19], TAPO-5,

TAPO-11 [20], Ti-ZSM-48 [21], VS-2 [22] and Cu-AlPO<sub>4</sub>-5 [23] have also been examined for the reaction. However, owing to the complicated synthesis and high cost of these transition metal framework-substituted zeolites, their large-scale practical utilization can be feasible, only if the catalyst can be separated conveniently from the solid–liquid reaction medium and recycled. Further, most of the previous studies were carried out in the batch reactor, and few researchers [24,25] have recently investigated into catalytic activities in the fixed-bed flow reactor that can resolve the catalyst separation problem.

The metal ion-exchange in zeolites has been used as an important technique to fine-tuning of pore size, acidity and also the catalytic activity and selectivity of zeolites. By this technique the homogenous metal ion catalysed reactions can be conveniently heterogenized by planting such catalytically active metal ions as the charge compensating ions on the zeolite channel surface. In addition, an advantage is also obtained by running the reaction in the zeolite micro pores, since there could be molecular

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pre-activation via electronic confinement effect [26]. Such diversified topics in zeolite catalysis have generated interest in us to heterogenize hydroxylation of phenol with the Fenton's reagent, which has been hitherto carried out homogeneously in aqueous medium. The transition metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  [27,28] with  $\text{H}_2\text{O}_2$  have been employed for this reaction.

It is therefore, reasonable to suppose that such transition metal ion-exchanged zeolites can be convenient heterogeneous catalysts for phenol hydroxylation, if the zeolite pore size is large enough to allow the reaction to occur inside. Indeed, in a batch reactor we have recently observed high catalytic performance of  $\text{Cu}^{2+}$  ion-exchanged zeolites in phenol hydroxylation with  $\text{H}_2\text{O}_2$  [29], and among the zeolites studied  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  ion-exchanged Na $\beta$  zeolites exhibited high activity at room temperature [30]. In continuation of this work, we report in the present study the catalytic activity, selectivity and stability of the mono- and bi-metal ion-exchanged zeolites, Fe-NaY, Co-NaY and Fe-Co-NaY, for the hydroxylation of phenol in an atmospheric fixed-bed flow reactor, and also the influence of reaction conditions on the catalytic performance.

## 2. Experimental

Fe-NaY was obtained by the ion-exchange of NaY pellets (zeobuilder Co.,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  4.5, binder 30 wt.%, average diameter 3 mm, and length 3 mm) with 0.01 M aqueous solution of  $\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  (Aldrich, G.R.) with the liquid/solid weight ratio of 2.5 by stirring for 5 h at 70 °C. The suspension was filtered, and the residue was washed with water, dried at 120 °C for 8 h, and calcined at 450 °C for 5 h in air. Fe-Co-NaY was prepared by subjecting Fe-NaY to  $\text{Co}^{2+}$ -exchange with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich, G.R.) by the same procedure. To obtain Co-NaY,  $\text{Co}^{2+}$ -exchange was carried out by treating NaY with the aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at the liquid/solid weight ratio of 2.5 at 70 °C for 5 h. TS-1 sample (Si/Ti=71) was synthesized using tetraethyl orthosilicate (TEOS, Showa Chemical), titanium isopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , Sigma-Aldrich), tetrapropyl-ammonium hydroxide (TPAOH, Sigma-Aldrich), isopropyl alcohol (IPA, Sigma-Aldrich) and water. The molar composition of the gel was 1:0.014:0.2:22.2 (TEOS:Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>:TPAOH:IPA:water). The gel was transferred to a teflon-lined autoclave and treated at 180 °C for 4 days. The product was recovered by filtration, dried at 100 °C overnight, and calcined in air at 550 °C for 8 h.

UV-vis-DRS were recorded on a Shimadzu UV-2501PC, spectrometer. The iron and cobalt contents in the solid catalysts was estimated by an inductively coupled plasma (ICP) spectrometer (J.Y. Ultima C, Jobin Yvon). BET surface area was measured from  $\text{N}_2$  adsorption isotherms using a Micromeritics model ASAP 2400 instrument. The metal content and BET surface area of catalysts are shown in Table 1. A slight difference in the iron and cobalt contents for Fe-Co-NaY from Fe-NaY and Co-NaY catalysts was noted. All the catalysts have high surface areas, above 400  $\text{m}^2 \text{g}^{-1}$ .

The catalytic test for phenol hydroxylation with  $\text{H}_2\text{O}_2$  was carried out in an atmospheric fixed-bed up-flow teflon microreactor with an inner diameter of 6 mm. Phenol, dissolved in

Table 1  
Fe and Co content and BET surface area of the catalysts

Catalyst	Fe content (wt.%)	Co content (wt.%)	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )
NaY	–	–	467
Fe-NaY	2.1	–	401
Co-NaY	–	2.4	467
Fe-Co-NaY	1.9	1.8	449
TS-1	–	–	407
Fe-Co-NaY (used)	1.9	1.8	–

water, and 50 wt.% aqueous solution of  $\text{H}_2\text{O}_2$  were injected separately by a high-pressure pump into the teflon reactor. The catalyst (2.0 g) in the form of extrudates (average diameter 3 mm and length 3 mm) was kept at the center of the reactor. The typical reaction conditions were as follows: reaction temperature 70 °C, atmospheric pressure, weight hourly space velocity (WHSV) based on phenol  $4.0 \text{h}^{-1}$ , bulk density as stacked =  $0.59 \text{g}_{\text{cat}} \text{cm}^{-3}$ , and the molar ratio of phenol to  $\text{H}_2\text{O}_2$  3:1 in the liquid feed. The products were sampled periodically per hour. Both the reactants and products were analyzed by a high-performance liquid chromatograph (HPLC, Shimadzu, LC-10ADVP, equipped with an RP, C18 column) with a UV-vis detector (ICI, LC1200) using 4-fluorophenol as the external standard. Besides the target products, catechol (CAT) and hydroquinone (HQ), benzoquinone isomers (BQ), by-products (BPs) such as maleic acid, acrylic acid, acetic acid, and oligomerization products were also detected.

The conversion and selectivity were calculated as follows.  $X_{\text{PhOH}} (\%) = 100 \times ([\text{PhOH}]_i - [\text{PhOH}]_f) / [\text{PhOH}]_i$ , where  $X_{\text{PhOH}}$  is the conversion of phenol;  $[\text{PhOH}]_i$ , the molar concentration of phenol before reaction; and  $[\text{PhOH}]_f$  is the molar concentration of phenol after sampling. Product selectivity (%) =  $100 \times [\text{product}]_f / ([\text{CAT}]_f + [\text{HQ}]_f + [\text{BQ}]_f + [\text{BPs}]_f)$ , where  $[\text{product}]_f$  is the molar concentration of catechol, hydroquinone, benzoquinone and the by-products, after the reaction.  $\text{CAT}/\text{HQ} = [\text{CAT}]_f / [\text{HQ}]_f$ .  $\text{H}_2\text{O}_{2\text{eff}} (\%) = 100 \times ([\text{CAT}]_f + [\text{HQ}]_f + 2[\text{BQ}]_f) / [\text{H}_2\text{O}_2]_{\text{add}}$ , where  $\text{H}_2\text{O}_{2\text{eff}}$  is the effective conversion of  $\text{H}_2\text{O}_2$ ; and  $[\text{H}_2\text{O}_2]_{\text{add}}$  is the molar concentration of  $\text{H}_2\text{O}_2$  in the reaction mixture.

## 3. Results and discussion

### 3.1. Catalytic activity of Fe-NaY, Co-NaY, Fe, Co-NaY and TS-1

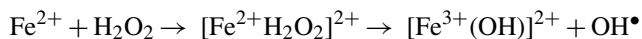
The catalytic activity of NaY, Fe-NaY, Co-NaY, Fe-Co-NaY and TS-1 for hydroxylation of phenol with  $\text{H}_2\text{O}_2$  was carried out at 70 °C. The  $\text{PhOH}/\text{H}_2\text{O}_2$  molar ratio and WHSV were set at 3 and  $4 \text{h}^{-1}$ , respectively. The phenol conversion,  $X_{\text{PhOH}}$ , effective  $\text{H}_2\text{O}_2$  conversion,  $\text{H}_2\text{O}_{2\text{eff}}$ , and the products selectivity are presented in Table 2. The catalytic hydroxylation of phenol required generation of  $\text{OH}^\bullet$  radicals by the decomposition of  $\text{H}_2\text{O}_2$ . The decomposition was to be initiated by transition metal ions. As the NaY catalyst was devoid of any transition metal ions, it was inactive in hydroxylation. The Co-NaY was the

Table 2  
Catalytic activity in the hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub>

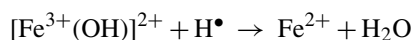
Catalyst	X <sub>PhOH</sub> (%)	Selectivity (%)				CAT/HQ	H <sub>2</sub> O <sub>2</sub> eff (%)
		CAT	HQ	BQ	BPs		
NaY	0.3	0.0	0.0	0.0	100.0	0.0	0
Co-NaY	0.7	0.0	14.7	25.1	60.2	0.0	1.4
Fe-NaY	19.7	39.5	16.9	17.0	26.6	2.3	53.4
Fe-Co-NaY	21.8	44.8	16.5	12.6	26.1	2.7	56.6
TS-1	7.4	15.9	66.9	6.4	10.8	0.2	21.2

Reaction conditions: reaction temperature = 70 °C, PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio = 3, WHSV = 4 h<sup>-1</sup>, water/PhOH weight ratio = 4.5, TOS = 4 h.

least active one among the transition metal loaded catalysts; the conversion was only 0.7%. Hence, Co<sup>2+</sup> might not coordinate to H<sub>2</sub>O<sub>2</sub> strongly enough to decompose it. As Co<sup>2+</sup> contains seven electrons in the 3d sub-shell, the weak field H<sub>2</sub>O<sub>2</sub> ligand cannot make strong coordination. In other words the Co<sup>2+</sup>·H<sub>2</sub>O<sub>2(x)</sub> complex might be highly labile. The same conclusion could also be drawn for phenol, as it is also a weak field type ligand. The Fe-NaY catalyst was intermediate in activity between Co-NaY and Fe-Co-NaY catalysts. Fe<sup>2+</sup> with 3d<sup>6</sup> electron configuration could more strongly coordinate with H<sub>2</sub>O<sub>2</sub>, as it could easily lose an electron to become Fe<sup>3+</sup> with d<sup>5</sup> (half-filled sub-shell) electron configuration. This process could release OH• radical as shown below.



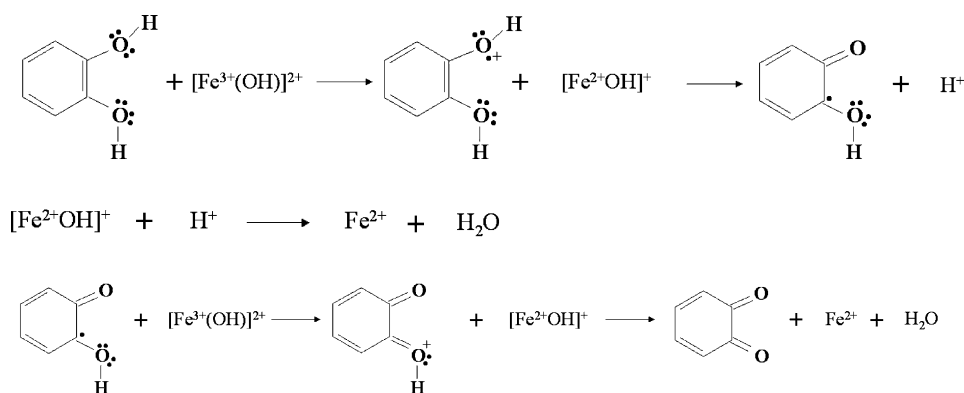
Therefore, the formation of more stable Fe<sup>3+</sup> state could be the driving force for stronger coordination of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup>. This phenomenon, which could be called “the rest effect”, might be the cause for its high activity compared to Co-NaY catalyst. When the OH• radical reacts with phenol, a H• radical will be released, which can convert [Fe<sup>3+</sup>(OH)]<sup>2+</sup> back into Fe<sup>2+</sup>, as shown below.



The Fe-Co-NaY catalyst showed higher conversion than either Fe-NaY or Co-NaY catalyst, though it contained less amount of cobalt and iron than the corresponding Co-NaY and Fe-NaY catalysts. The concept of synergism between Co and Fe inside the zeolite pore cannot be brought into consideration, as

they cannot interact either through space or through intervening Si–O–Al bridges. But the tendency of Co to form labile complexes with phenol or H<sub>2</sub>O<sub>2</sub> might make a small contribution to the activity enhancement, as it could take in and transport both H<sub>2</sub>O<sub>2</sub> and phenol from outside to the more active Fe<sup>2+</sup> sites in the zeolite pore. The medium pore, TS-1, was found to be less active than both Fe-NaY and Fe-Co-NaY catalysts. As there was no much driving force to bring in H<sub>2</sub>O<sub>2</sub> into the TS-1 pore, in contrast to the case of Fe-NaY or Fe-Co-NaY catalysts, the observed activity was low. Again, titanium in TS-1 might not be as readily available as Fe in Fe-NaY or Fe-Co-NaY catalyst for coordination with H<sub>2</sub>O<sub>2</sub>. The coordination of H<sub>2</sub>O<sub>2</sub> with Ti might also require distortion in the tetrahedral coordination around Ti. All these factors were to contribute unfavorably in the hydroxylation of phenol thus giving lower conversion. H<sub>2</sub>O<sub>2</sub>eff also followed the same trend as X<sub>PhOH</sub>. The desired products were only CAT and HQ, but BQ and other BPs (the degraded form of phenol and/or products) were also formed. The selectivity to CAT and HQ over Fe-NaY and Fe-Co-NaY alone are discussed below, as these catalysts were more active than others. The selectivity to CAT over Fe-Co-NaY was higher than that over Fe-NaY, but those of HQ and BPs over both the catalysts were nearly equal. BQ was obtained more selectively over Fe-NaY than over Fe-Co-NaY. The increase in the selectivity to BQ, 4.4%, over Fe-NaY compared to over Fe-Co-NaY matches well with the decrease in the selectivity, 5.3%, of CAT over Fe-NaY compared to over Fe-Co-NaY. Hence, the product BQ, 1,2-isomer, might have largely originated from CAT, as detailed in the following reaction scheme (Scheme 1). The formation of BQ, 1,4-isomer, from HQ could be similarly explained.

The high phenol conversion and high selectivity to CAT depict Fe-Co-NaY as the more selective and active catalyst. The difference between Fe-NaY and Fe-Co-NaY was the amount of metal loading; the former contained more Fe<sup>2+</sup> than the latter. Hence, the high activity of Fe-Co-NaY in spite of its low Fe loading might be due to high dispersion of Fe, increasing the active sites to take part in the reaction. The difference in the selectivity to CAT between Fe-NaY and Fe-Co-NaY was attributed to the difference in the loading of Fe. Although CAT is more susceptible to oxidation than phenol, under the present reaction conditions the concentration of the latter was higher than



Scheme 1. Benzoquinone formation.

the former. Hence, at any instant, particularly at low conversion (<50%), phenol was to be more attacked by  $\text{OH}^\bullet$  than CAT. Therefore, CAT might be mainly oxidized by  $[\text{Fe}^{3+}(\text{OH})]^{2+}$  as detailed in the above reaction scheme. Hence, the concentration of  $[\text{Fe}^{3+}(\text{OH})]^{2+}$  in the zeolite pore is the deciding factor in leading to the difference in the selectivity to CAT between Fe-NaY and Fe-Co-NaY. Since Fe-NaY might have higher concentration of  $\text{Fe}^{3+}$  than Fe-Co-NaY during the reaction, the probability of oxidation of CAT to BQ might be higher over the former than over the latter catalyst. Although the difference in Fe loading between the catalysts was only 0.2%, this small difference was found to have the significant impact on the phenol conversion and products selectivity. The selectivity to the products observed over TS-1 once again confirmed the foregoing discussions. As  $\text{H}_2\text{O}_2$  might weakly coordinate to Ti in the framework due to the tetrahedral framework environment of the latter, the concentration of  $\text{OH}^\bullet$  might be less. In support of our view the selectivity to BQ was much lower than over Fe-NaY and Fe-Co-NaY catalysts;  $\text{OH}^\bullet$  could freely escape from the coordination sphere of Ti. Since the simultaneous coordination of both phenol and  $\text{H}_2\text{O}_2$  to framework Ti was hardly occurs, the ortho-hydroxylation of phenol to CAT became a difficult process. Only the reaction between free  $\text{OH}^\bullet$  and free phenol could yield CAT. But this probability might also be applicable to HQ.

The effect of iron content of Fe-Co-NaY on the phenol conversion was studied to find the optimal level. The results are illustrated in Fig. 1. A linear dependence of phenol conversion on the iron content was noticed up to about 1% loading. Only slight increase in the conversion was observed when the loading was increased from 1.4 to 1.9%. Hence, below 1% loading the ions could be of counter-ions type, but above this loading they might form small oligonuclear clusters and even larger  $\text{Fe}_2\text{O}_3$  particles. Absorbances between 300 and 450 nm and above 450 nm in the DRS UV spectra furnish evidence for established such species (Fig. 2) [31,32]. Similarly, the presence of CoO clusters in the catalyst was also established based on the broad absorbance maximum between 400 and 500 nm in the DRS-UV spectra of

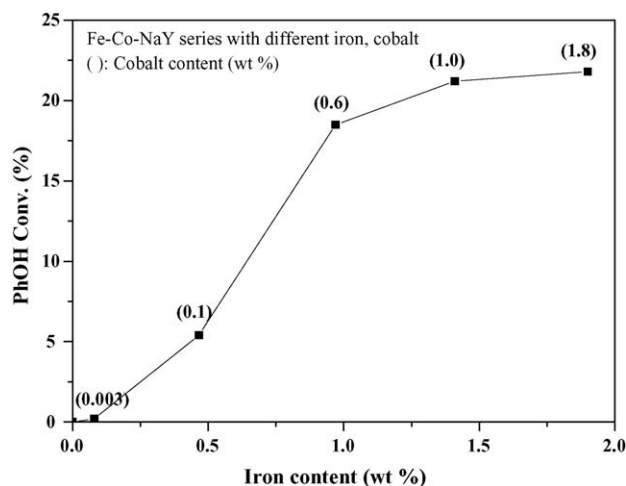


Fig. 1. Phenol conversion over Fe-Co-NaY with different iron and cobalt loadings (reaction conditions:  $\text{PhOH}/\text{H}_2\text{O}_2$  molar ratio=3,  $\text{WHSV}=4\text{ h}^{-1}$ , water/PhOH weight ratio=4.5).

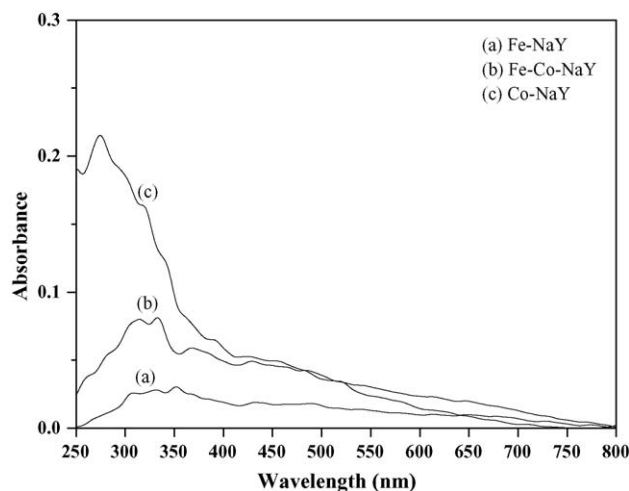


Fig. 2. UV-vis-DRS spectra over used Fe-NaY, Co-NaY and Fe-Co-NaY.

Co-NaY and Fe-Co-NaY catalysts [33]. If these clusters were present out of the zeolite pore, the phenol conversion might be nearly equal to that over about 1% Fe loaded Fe-Co-NaY, with a small increment. On the other hand, if these clusters were present inside pore, there might be large decrease in the conversion compared to 1% Fe loading. But the observed conversions were close to that of 1.4% Fe loading. Hence, the clusters were to be present mainly outside the pores. In addition, the ICP analysis of Fe and Co for the fresh and used catalysts showed the same values (Table 1) for both the fresh and used catalysts suggesting the absence of the active metal leaching from the zeolite pore.

From the foregoing discussion, it was established that for obtaining high conversion the active sites must be well dispersed, the  $\text{OH}^\bullet$  radicals must be free, and the zeolite pore should be less polar with less amount of counter ion to enhance the para selectivity.

### 3.2. Effect of time on stream

The effect of the time on stream on the phenol conversion over Fe-Co-NaY was studied at 30, 50, 60, 70 and 90 °C with  $\text{WHSV}$  of  $4\text{ h}^{-1}$ . The results are illustrated in Fig. 3. At 30 °C the conversion was less than 2%. Slight increase in the conversion was observed at 50 °C. The reaction reached the steady state after 2 h. At 60 °C a three-fold increase in the conversion was observed. These observations clearly indicated that the reaction might be activation energy demanding, although it should be low. At 70 °C a significant increase in conversion was observed compared to that at 60 °C. But at 90 °C the conversion was not higher enough to consider. Based on this observation, 70 °C was selected to be the optimum one. Absence of linear increase in conversion above 70 °C was ascribed to thermal decomposition of  $\text{H}_2\text{O}_2$ .

### 3.3. Effect of $\text{PhOH}/\text{H}_2\text{O}_2$ molar ratio

The effect of the  $\text{PhOH}/\text{H}_2\text{O}_2$  molar ratios on the phenol conversion,  $\text{H}_2\text{O}_2$  conversion and products selectivity was studied

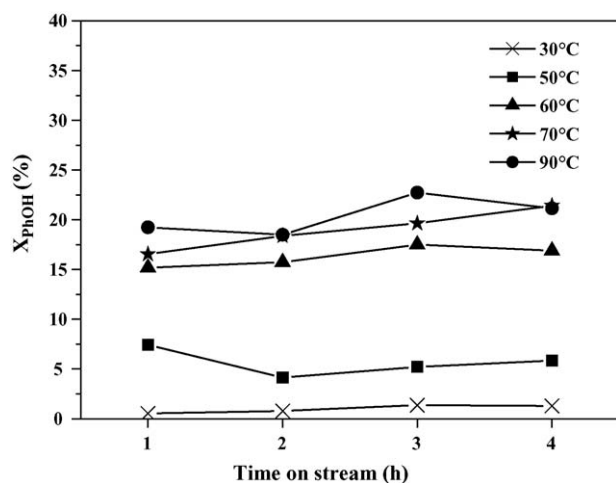


Fig. 3. Effect of reaction temperature on the conversion of phenol over Fe-Co-NaY at different reaction time on stream (reaction conditions: PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio = 3, WHSV = 5 h<sup>-1</sup>, water/PhOH weight ratio = 4.5).

over Fe-Co-NaY at 70 °C with WHSV of 4 h<sup>-1</sup>. The effect was examined for 4 h, and the results are presented in Table 3. The phenol conversion decreased with increase in the PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio. The coordination of H<sub>2</sub>O<sub>2</sub> on the metal, and its subsequent decomposition to OH• radical were the necessary steps in this reaction as described above. At the molar ratio of 1, H<sub>2</sub>O<sub>2</sub> could freely coordinate to metal and decompose to form OH• radical. Hence, high phenol conversion was attained. At the molar ratio of 3, low amount of H<sub>2</sub>O<sub>2</sub> must compete with excess phenol for coordination, and hence formation of OH• radicals might be significantly reduced. Thus, the conversion decreased.

Because of high concentration of OH• radicals at the PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio of 1, the effective conversion of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>eff, was low. Hence, the primary products, namely CAT and HQ, were further oxidized by excess OH• radicals to form more BPs. Hence, the selectivity to the by-products was high. But at the molar ratio of 3, the H<sub>2</sub>O<sub>2</sub>eff increased, as the formation of OH• radicals might be significantly reduced due to the prevention of adsorption of H<sub>2</sub>O<sub>2</sub> on the metal by excess phenol. Hence, such low concentration of radicals could favorably gives primary products rather than the side products. Hence, the selectivity to byproduct was low at the molar ratio of 3. The variation of selectivity with PhOH/H<sub>2</sub>O<sub>2</sub> molar ratios could be similarly explained as follows. Based on the above competitive coordination, the variation of selectivity to CAT and HQ could

Table 3  
Effect of PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio on the catalytic activity of Fe-Co-NaY

PhOH/ H <sub>2</sub> O <sub>2</sub>	X <sub>PhOH</sub> (%)	Selectivity (%)				CAT/HQ	H <sub>2</sub> O <sub>2</sub> eff (%)
		CAT	HQ	BQ	BPs		
1	45.5	32.5	27.0	2.3	38.2	1.2	29.2
2	29.3	39.5	24.9	1.5	34.1	1.6	39.6
3	21.8	44.8	16.5	12.6	26.1	2.7	56.6

Reaction conditions: reaction temperature = 70 °C, WHSV = 4 h<sup>-1</sup>, water/PhOH weight ratio = 4.5, TOS = 4 h.

be unraveled for different molar ratios. At the molar ratio of 1, the OH• radicals formed in the coordination sphere of the metal ions could react with phenol present in the same coordination sphere to form principally CAT. Moreover, the ortho positions of the coordinated phenol were to be close to the freshly formed OH• radical compared to the para position. If phenol was not in the same coordination sphere, the OH• radical could diffuse out of the sphere and react with phenol either at the ortho or para positions. But selectivity to CAT was slightly higher than that to HQ, and so, there might be sufficient amount of phenol in the metal ion coordination sphere close to the coordinated H<sub>2</sub>O<sub>2</sub> to react at the ortho positions. In addition, the free OH• radical could react with free phenol at the ortho or para positions, but here also the ortho substitution could dominate to give high selectivity to CAT.

The selectivity to CAT increased with increase in the PhOH/H<sub>2</sub>O<sub>2</sub> molar ratios. At the molar ratio of 3, because of excess phenol, only small amount of H<sub>2</sub>O<sub>2</sub> could compete with phenol for coordination to metal. This possibility, therefore, compelled more phenol to coordinate adjacently to coordinated H<sub>2</sub>O<sub>2</sub> thus facilitating mainly the ortho substitution. The selectivity to HQ decreased with increase in the molar ratios. As discussed in the preceding paragraph, the possibility of free OH• radicals escaping the coordination sphere might be less likely due to more coordinated phenols close to it. So, the selectivity to HQ was low at the molar ratio 3. Hence, this study clearly established competitive adsorption of both phenol and H<sub>2</sub>O<sub>2</sub> on the coordination sphere of metal ions. The large pore size of Y zeolite might not reserve any constrain on the reactants for the said coordination facility.

### 3.4. Effect of WHSV

Table 4 shows the effect of WHSV on the catalytic activity of Fe-Co-NaY. A nearly steady phenol conversion and H<sub>2</sub>O<sub>2</sub>eff were observed until the WHSV of 10 h<sup>-1</sup> was reached. The WHSV between 4 and 6 h<sup>-1</sup> was employed for further studies. Only at the WHSV of 15 h<sup>-1</sup>, the conversion decreased dramatically to a very low level of 3.3% with the increased selectivity to BQ and BPs. At this WHSV the reactants might better pass through the voids rather than through zeolite pores. A similar phenomenon was also observed by previous workers in

Table 4  
Effect of WHSV on the catalytic activity of Fe-Co-NaY

WHSV (h <sup>-1</sup> )	X <sub>PhOH</sub> (%)	Selectivity (%)				CAT/HQ	H <sub>2</sub> O <sub>2</sub> eff (%)
		CAT	HQ	BQ	BPs		
1.3	20.9	41.2	16.3	14.5	28.0	2.5	54.2
2.5	22.5	42.2	13.7	15.8	28.3	3.1	59.1
4.0	21.8	44.8	16.5	12.6	26.1	2.7	56.6
6.0	21.3	46.5	17.2	11.1	25.2	2.7	54.9
8.0	21.3	44.1	14.7	16.6	24.6	3.0	58.8
10.0	21.5	40.5	13.9	19.6	26.0	2.9	60.4
15.0	3.3	20.6	3.0	36.3	40.1	6.9	9.5

Reaction conditions: reaction temperature = 70 °C, phenol/H<sub>2</sub>O<sub>2</sub> molar ratio = 3, water/PhOH weight ratio = 4.5, TOS = 4 h.

Table 5  
Effect of water/PhOH weight ratio on the catalytic activity of Fe-Co-NaY

Water/ PhOH	$X_{\text{PhOH}}$ (%)	Selectivity (%)				CAT/HQ	$\text{H}_2\text{O}_{2\text{eff}}$ (%)
		CAT	HQ	BQ	BPs		
1	4.1	28.9	7.0	53.5	10.6	4.1	17.6
3	14.6	35.9	18.1	28.4	17.6	2.0	48.5
4.5	21.8	44.8	16.5	12.6	26.1	2.7	56.6
6	20.8	42.0	19.8	14.4	23.8	2.1	56.5
10	18.1	28.8	28.1	16.9	26.2	1.1	49.3
60	0.17	0	0	0	100	0	0

Reaction conditions: reaction temperature = 70 °C, PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio = 3, WHSV = 4 h<sup>-1</sup>, TOS = 4 h.

batch reactors over various catalysts [29,34,35]. Namely, at the early reaction stage, a fast over-oxidation of HQ in the reaction medium causing the formation of BQ and other deep oxidation of BPs occurred to give very low amount of desired CAT and HQ products. Tendulkar et al. [24] carried out the hydroxylation of phenol over titanium-based zeolite using a pilot-scale fixed-bed reactor system at 80 °C with 1.5 h<sup>-1</sup> of WHSV, which was much lower than that of this work.

### 3.5. Effect of water/PhOH weight ratio

Since water was used as the solvent in the reaction, its amount in the reaction medium was thought to be a very important parameter in view of practical utilization. Table 5 shows the influence of weight ratio of water to phenol on the phenol conversion. At the low amount of water, the conversion increased with the increase in the water/PhOH ratio, but at a high water content the phenol conversion decreased. With the very dilute reactants mixture (water/PhOH = 60) the conversion was negligible. The maximum phenol conversion of 21–22% was observed at the water/PhOH = 4.5 and 6. A similar trend was also observed for the effective H<sub>2</sub>O<sub>2</sub> conversion. The selectivity to BQ changed irregularly with increase in the water/PhOH ratio: it decreased with increasing water/PhOH ratio from 1 to 4.5 and increased slightly with increasing ratio from 6 to 10, but at the water/PhOH ratio of 60 it became zero. The selectivity to BPs increased gradually with the increase in water/PhOH ratio. The water content changed the CAT/HQ ratio too; when the water/PhOH ratio increased, the CAT/HQ ratio decreased. This result proved that the proper weight ratio, for example, water/PhOH = 4.5–6, was to be maintained for the high phenol conversion and comparatively low selectivity to BQ and BPs.

The above observation proved clearly that at the high water/PhOH ratios a preferential coordination of water to metal ions thus preventing the coordination of the reactants. At the small molar ratios the primary products were very well accessible to OH• radicals for further oxidation to give high selectivity to BPs. But at the higher ratios, the concentration of OH• radicals decreased; hence, their oxidation of the primary products should hardly occur. Similarly the change of CAT/HQ ratio with water/phenol ratios could also be understood as follows. The lower ratio of CAT/HQ at the higher water/PhOH ratio might be due to prevention of phenol coordination to metal by water. As

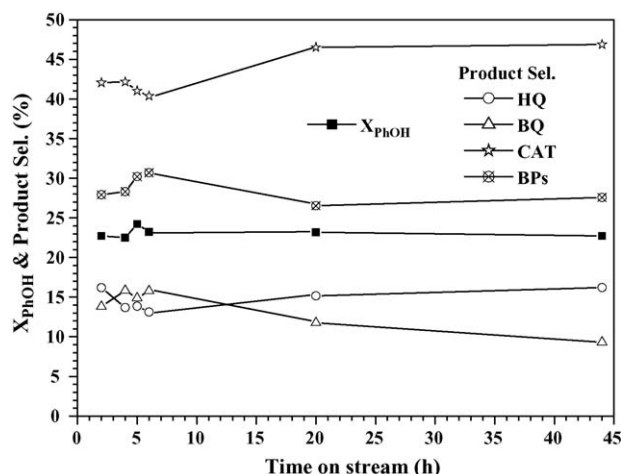


Fig. 4. Long-run catalytic test on the activity, selectivity and stability of Fe-Co-NaY (reaction conditions: reaction temperature = 70 °C, PhOH/H<sub>2</sub>O<sub>2</sub> molar ratio = 3, WHSV = 2.5 h<sup>-1</sup>, water/PhOH weight ratio = 4.5).

discussed above, only metal coordinated phenol could enhance the CAT yield. The free phenol could be attacked by OH• radicals at all positions, thus reducing the CAT selectivity and so also the CAT/HQ ratio.

### 3.6. Long-run test

Fig. 4 shows the results of the long-run catalytic test at WHSV 2.5 h<sup>-1</sup> for Fe-Co-NaY. As coordination of H<sub>2</sub>O<sub>2</sub> and phenol to metal was suggested in this reaction, it was of interest to know whether such coordination could leach out the metal ion from the zeolite pore. But the conversion remained steady for 44 h. Hence, the catalyst was expected to retain the entire amount of Fe<sup>2+</sup> and Co<sup>2+</sup> without leaching. ICP analysis, as discussed above, also confirmed this observation. The phenol conversion remained the same in the range of 22–23% with selectivity to BQ 9–12%, BPs 26–27%, HQ 15–16% and CAT 46–47% from 20 to 44 h time on stream. Therefore, the mechanism of the reaction and the sequence of the reaction remained unaltered, and the effective diffusivity of the reactants and products should be maintained throughout the reaction period.

## 4. Conclusions

The Fe-Co-NaY catalyst prepared by ion-exchange of NaY zeolite was very active for phenol hydroxylation with H<sub>2</sub>O<sub>2</sub> in water. It was much more active than TS-1. Both the conversion and selectivity could be altered conveniently by adjusting the reaction parameters such as temperature, feed ratio, weight hourly space velocity and water content. Over the Fe-Co-NaY catalyst the maximum phenol conversion of 21.8%, effective conversion of H<sub>2</sub>O<sub>2</sub> 56.6%, and selectivity to CAT and HQ 44.8 and 16.5%, respectively, were obtained. Although the Fe and Co contents of Fe-Co-NaY were slightly lower than the respective amount in the Fe-NaY and Co-NaY catalysts, the former was more active than the latter catalysts. Well-dispersed metal ions, particularly Fe<sup>3+</sup> that could avoid molecular crowding around

the metal coordination sphere, were suggested to favorably control the conversion. The long-run catalytic test confirmed the absence of the catalyst deactivation. Hence, there might not be leaching out of either Fe or Co from the pore by either phenol or its products during the reaction. Therefore, Fe-Co-NaY could be a convenient active catalyst for phenol hydroxylation in the designed fixed-bed reactor.

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