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Room-temperature heterogeneous hydroxylation of phenol with hydrogen peroxide over Fe^{2+}, Co^{2+} ion-exchanged Naβ zeolite

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Ion-exchanged Naβ zeolite with Fe^{2+} and Co^{2+} cations shows high catalytic activity at room temperature in phenol hydroxylation with H_2O_2, where the conversion of phenol is *ca.* 21% and the selectivity of benzoquinone is below 3% at a molar ratio of phenol to H_2O_2 of 3 in the starting aqueous reaction medium.

The dihydroxybenzenes, such as catechol (CAT) and hydroquinone (HQ), are high value chemicals. They are widely used as photography chemicals, antioxidants and polymerization inhibitors, and also used in pesticides, flavoring agents and medicines. The most desirable method for producing dihydroxybenzenes is the direct hydroxylation of phenol with hydrogen peroxide (H_2O_2), an environmentally-friendly catalytic process. Homogeneous catalysts[1,2] such as mineral acids, metal ions and metal complexes are difficult to be separated and recovered from the reaction mixture, which prevents their practical utilization. Therefore, numerous heterogeneous catalysts such as metal oxides,[3,4] supported metal complexes,[5] metallosilicalites,[6–12] hydrotalcite-like compounds,[13] metal-bearing mesoporous materials,[14] metal hydroxylphosphates[15] and heteropoly compounds[16] have been attracting research interest recently. Among them, titanosilicalites have proved to be the most important catalysts for commercial production of dihydroxybenzenes.[6–10] However, most of the above catalysts either are high cost and complicated to prepare or show unsatisfied catalytic activity. Moreover, to our knowledge, no heterogeneous catalysts have been found to exhibit high activity in phenol hydroxylation at room temperature.

In contrast with the extensive studies on transition metal framework-substituted zeolites for phenol hydroxylation,[6–12] ion-exchanged zeolites have not been paid much attention. The fact that the well-known oxidative Fenton's reagents are low-valence transition metal ions such as Fe^{2+} and Cu^{2+},[17,18] together with the simplicity of the synthesis of ion-exchanged zeolites, prompted us to investigate the activity of transition metal ion-exchanged zeolites in phenol hydroxylation with H_2O_2. Here we initiate our investigation on the Fe^{2+}, Co^{2+} ion-exchanged Naβ zeolite catalyst, observing that the catalyst is very active even at room temperature in phenol hydroxylation in aqueous medium.

FeNaβ was prepared by the ion exchange of Naβ (PQ, SiO_2/Al_2O_3 = 25) with a 0.005 M aqueous solution of $FeSO_4\cdot 7H_2O$ (Aldrich, A.C.S. reagent) at 25 °C for 8 h with the liquid/solid weight ratio being 100, followed by filtration, washing with water until the filtrate became free from metal ions, drying at 100 °C for 8 h and calcination at 450 °C for 5 h in air. CoNaβ and FeCoNaβ were prepared from Naβ and FeNaβ, respectively, *via* ion exchange with a 0.005 M aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ (Aldrich, A.C.S. reagent) at the same reaction conditions as those for FeNaβ. ICP-AES analysis shows a very similar iron or cobalt concentration level in the three catalysts, *i.e.*, 1.15 wt% of Fe in FeNaβ, 1.14 wt% of Co in CoNaβ, and 1.12 wt% of Fe and 1.26 wt% of Co in FeCoNaβ.

Phenol hydroxylation with H_2O_2 was carried out in a 100 ml three-necked round-bottom flask equipped with a magnetic stirrer, a reflux condenser and a temperature controllable oil-bath. 2.0 g Phenol (Kumho P&B Chem., Inc.) was dissolved in 60 ml water and 0.2 g catalyst was added. After the reaction temperature reached a desired value (20–70 °C), 0.48 ml of H_2O_2 aqueous solution (50 wt%, DC Chem. Co., Ltd) was charged dropwise into the reaction system using a syringe pump at the beginning of the reaction. To avoid any photocatalytic effect on the reaction, the reactor was wrapped in aluminum foil during the reaction. The reaction mixture was sampled periodically and filtered to remove catalyst particles, followed by HPLC (Shimadzu, LC-10ADVP, equipped with a PR, C18 column) analysis using 4-fluorophenol as the external standard, and UV/Vis as the detector (wavelength = 265 nm, ICI, LC1200). Besides the target products, CAT and HQ, 1,4-benzoquinone (BQ) and by-products (BPs), including maleic acid, acrylic acid, acetic acid and oligomerization products, were also detected.

Table 1 compares the catalytic performance of the employed catalysts at 30 °C. No products are detected without catalyst. Naβ alone gives only a small amount of BPs, indicating that the zeolite itself without transition metal is not active for the reaction. Over FeCoNaβ, the conversion of phenol and the effective conversion of H_2O_2 increase with the reaction time while the selectivity of BQ and the molar ratio of CAT to HQ decrease, which is in good agreement with previous results over TS-1 catalysts.[6,7] It is proposed that at early stages of the reaction a fast over-oxidation of HQ by the large concentration of H_2O_2 could cause the formation of BQ in a large amount. The subsequent disappearance of BQ could arise from the decomposition of BQ into deep oxidation or degradation BPs, and/or the oxidation of H_2O_2 by BQ with the formation of HQ and oxygen.[19] Moreover, phenol conversion attains constant values around 21% after 2 h of reaction, and the BQ selectivity drops to a very low level of <4%, with CAT/HQ being 2.9 after 4 h of reaction. On the other hand, no further reaction can be observed in the absence of catalyst for 48 h after filtering FeCoNaβ from the sample of 0.5 h of reaction, as shown in Table 1, confirming the non-leaching of metal ions from the ion-exchanged zeolite during the reaction. In addition, FeNaβ is found to be very active with the same phenol conversion at 21.4% as FeCoNaβ at 3 h of reaction, however, higher selectivities of BQ (18.7 *vs.* 7.0%) and BPs (32.7 *vs.* 26.9%) are found over FeNaβ than those over FeCoNaβ, even if CoNaβ itself is inactive. This observation indicates that cobalt could act as an effective catalytic promoter in FeCoNaβ for the hydroxylation of phenol into dihydroxybenzenes while inhibiting the formation of the undesirable BQ and BPs. Compared with TS-2[7] in Table 1, FeCoNaβ is found to exhibit much higher conversion of phenol (21.3 *vs.* 9.3%) and effective conversion of H_2O_2 (48.2 *vs.* 35.4%), as well as much lower BQ selectivity (2.7 *vs.* 57.2%). Furthermore, the activity of FeCoNaβ at 30 °C is comparable to that of TS-1 at a high temperature of 57 °C, as shown in Table 1, except that a much lower CAT/HQ ratio (1.2) is observed over TS-1 than that (2.9) over FeCoNaβ. Although the BPs have not been measured over TS-1[6] and TS-2,[7] it has been revealed that titanosilicalite catalysts also generate

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Table 1 Activities of various ion-exchanged zeolite catalysts in phenol hydroxylation with H_2O_2 at a reaction temperature of 30 °C

Catalyst	Reaction time (h)	X_{phenol}[a] (%)	$X_{H_2O_2}$[b] (%)	Product selectivity (%) CAT	HQ	BQ	BPs	CAT/HQ[c]
No catalyst	5	0	0	—	—	—	—	—
Naβ	5	0.4	0	0	0	0	100	—
FeCoNaβ	0.17	0.5	0	0	0	0	100	—
	0.34	1.4	3.9	0	0	46.9	53.1	—
	0.5	3.5	12.3	0	0	58.0	42.0	—
	0.5 + 48[d]	3.8	12.9	0	0	57.2	42.8	—
	1	17.9	52.6	35.9	7.1	27.4	29.5	5.1
	2	21.9	56.8	47.3	15.0	11.8	25.0	3.2
	3	21.4	51.4	49.4	16.7	7.0	26.9	3.0
	4	20.4	47.1	51.6	17.6	3.9	27.0	2.9
	5	21.3	48.2	52.1	18.0	2.7	27.2	2.9
FeNaβ	3	21.4	55.2	41.5	7.1	18.7	32.7	5.9
CoNaβ	3	0.5	0	0	0	0	100	—
TS-2[e]	24	9.3	35.4	34.3	8.5	57.2	?	4.0
TS-1[f]	6	19.8	55	55	45	0	?	1.2

[a] Phenol conversion = 100 × (phenol before reaction (moles) phenol after reaction (moles))/phenol before reaction (moles). [b] Effective conversion of H_2O_2 = 100 × products (moles, HQ + CAT + 2BQ)/total H_2O_2 (moles) added. [c] Molar ratio of CAT to HQ. [d] Analyzed after an additional 48 h when the sample of 0.5 h of reaction time was filtered from catalyst particles. [e] From ref. 7, reaction temperature 37 °C, phenol/H_2O_2 (molar ratio) = 3, phenol/catalyst (weight ratio) = 9.4, acetone as a solvent. [f] From ref. 6, reaction temperature 57 °C, phenol/H_2O_2 (molar ratio) = 3, phenol/catalyst (weight ratio) = 10, acetone as a solvent.

considerable deep oxidative tarry by-products.[10]

Fig. 1 compares the conversion of phenol over FeCoNaβ at various reaction temperatures. It is found that FeCoNaβ is very active in the reaction temperature range 20–70 °C. As expected, raising the reaction temperature accelerates the reaction. For example, phenol conversion reaches a plateau value of *ca.* 21% after 4 h at 20 °C; by contrast, only 10 min is needed at 70 °C. On the other hand, a maximum conversion of phenol at *ca.* 24%, and then a slight decrease of conversion could be observed at 0.17–1 h at above 50 °C. This could possibly be ascribed to the more rapid formation of a significant amount of tar products,[4] or the easier decomposition of H_2O_2 in a non-productive manner at higher reaction temperatures. This phenomenon is not found at room reaction temperature. At all reaction temperatures in Fig. 1, both conversion and selectivity reach a steady state within 5 h; when the phenol conversion is *ca.* 20%, the selectivity of BQ is $<3\%$, the selectivity of BPs is *ca.* 27% and the effective conversion of H_2O_2 is *ca.* 50%. In other words, the reactivity of phenol hydroxylation is very insensitive to reaction temperature at 5 h due to the high reaction rate even at 20 °C. This result is very different from that found for many other catalysts,[4–7,13–16] for which the optimal reaction temperature has been found to be 60–90 °C with the reaction being very sensitive to the reaction temperature even at longer reaction times. Indeed, titanosilicalite catalysts have been demonstrated to achieve steady activity after 6 h at 57 °C with acetone as the solvent, the reaction rate of which is even lower than that of FeCoNaβ at 20 °C in this work.[6]

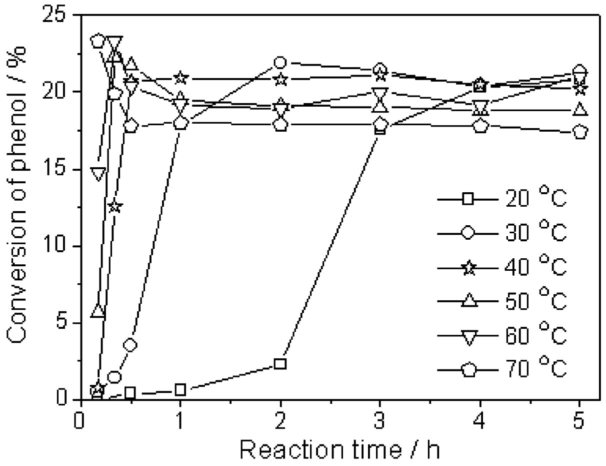

Fig. 1 Effect of reaction temperature on phenol conversion over the FeCoNaβ catalyst in phenol hydroxylation with H_2O_2.

Overall, the results discussed above demonstrate that the FeCoNaβ catalyst is very active and selective for dihydroxybenzenes in phenol hydroxylation with H_2O_2 in aqueous reaction medium at room temperature. Metal ions exchanged into supercages and/or channels of β zeolite are supposed to act as active centers for the reaction. The results described herein are believed to be very important for industrial production of dihydroxybenzenes. Further studies on the reaction mechanism and the promoter role of cobalt are being undertaken.

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