# Direct hydroxylation of benzene to phenol using $H_2O_2$ as an oxidant over Fe- or Cu-containing zeolite catalysts

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The conversion of benzene to oxygen-containing aromatic compounds, such as phenol, is one of the most active topics in applied and fundamental catalytic research. Meanwhile, C-H bond of benzene is very stable like methane so that it is extremely difficult to oxidant under mild conditions. In industry, as a crucial bulk commodity chemical, phenol is in most cases produced by a three-step cumene process. However, this process has drawbacks such as high pollution, high-energy consumption, and relatively low selectivity toward phenol. To address these issues, a direct one-step benzene oxidation approach has been highly desired.[1]

In this paper, Fe- and Cu-containing AEI (SSZ-39), CHA (SSZ-13) and MFI (ZSM-5) zeolite catalysts were prepared by ion-exchange method. The reaction of direct hydroxylation of benzene to phenol using $H_2O_2$ as oxidant was carried out with 50 mg catalyst, 5 mmol benzene, 10 mmol $H_2O_2$ and 10 ml acetonitrile at 60 $^oC$ with stirring for 6 h.

Table 1 Chemical composition of the catalysts

| Catalyst | Si/Al[a] | Si/M[b] | M(wt.%)[b] |
|---|---|---|---|
| [Al]AEI | 8.9 | -- | -- |
| [Fe, Al]AEI | 8.9 | 89 | 0.9 |
| [Cu, Al]AEI | 8.8 | 80 | 1.1 |
| [Al]CHA | 5.0 | -- | -- |
| [Fe, Al]CHA | 4.9 | 45 | 1.5 |
| [Cu, Al]CHA | 5.0 | 39 | 2.0 |
| [Al]MFI | 25 | -- | -- |
| [Fe, Al]MFI | 25 | 51 | 1.7 |
| [Cu, Al]MFI | 24 | 73 | 1.3 |

*[a] measured by ICP-AES; [b] M represents Fe or Cu*

The chemical composition of catalysts was shown in Table 1. Fig. 1 shows the benzene conversion and the phenol yield. [Al]AEI, [Al]CHA and [Al]MFI showed very low benzene conversion, while after loading Fe and Cu on zeolites, the performance was greatly improved. Cu-containing zeolite catalysts show higher benzene conversion than Fe-containing catalysts, while Fe-containing catalysts achieved higher phenol selectivity than Cu-containing catalysts.

The $H_2O_2$ conversion and efficiency of the reaction are shown in Fig. 2. [Al]AEI, [Al]CHA and [Al]MFI present very low $H_2O_2$ conversion due to the low activity. When Cu-containing zeolites used as catalysts, numerous by-products that produce to tar, resulting in non-efficient consumption of $H_2O_2$.

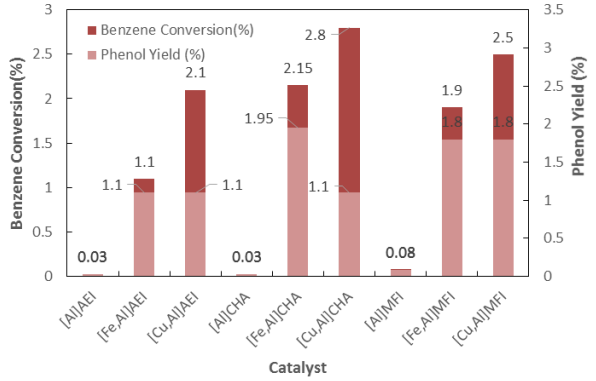


Fig.1 The benzene conversion and phenol yield of Fe- and Cu-containing zeolite catalysts in the reaction of direct hydroxylation of benzene to phenol using $H_2O_2$ as an oxidant.

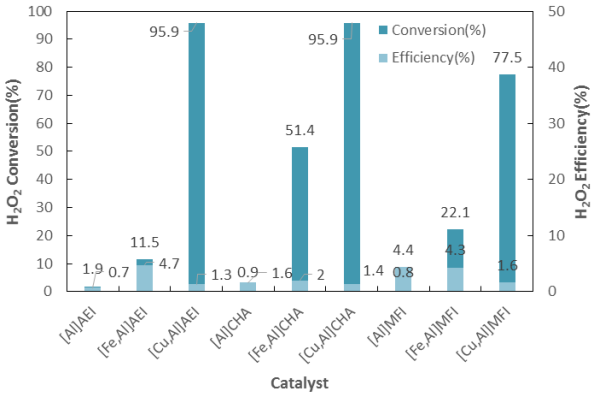


Fig. 2 $H_2O_2$ conversion and efficiency of Fe- and Cu-containing zeolite catalysts in the reaction of direct hydroxylation of benzene to phenol using $H_2O_2$ as an oxidant.

Different topology zeolites present the same result that Cu-containing zeolites get relatively high benzene conversion, Fe-containing zeolites achieved relatively higher selectivity. The interesting phenomenon would provide a new clue to improve the performance of direct hydroxylation of benzene to phenol.

## REFERENCES

[1] J.H. Yang, G. Sun, D. Ma, ect., Energy Environ. Sci., 6(2013), 793–798