Theoretical suggestion of selective benzene hydroxylation in aquaeous solution by Keggin-type polyoxometalate

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Owing to the high toxicity of benzene and its derivatives, it is necessary to develop catalysts that decompose them in aqueous solution. Previously, Ru-oxyl complex catalyzing the oxidative cracking of benzene have been reported,[1] but there is a serious problem that Ru–oxyl species decomposes organic aromatic ligands itself and/or other Ru–oxyl complexes. Herein we focused on the benzene hydroxylation by Ru-substituted Keggin-type polyoxometalate $[Ru(O)XW_{12}O_{39}]^{n-}$, namely **Ru^{V}OX**, (X = heteroatoms such as Al, Ga, Si, Ge, P, As and S) having robustness in aqueous solution and the oxidative-tolerant ligand. Since **Ru^{V}OX** also can catalyze water oxidation,[2] leading to the decreasing the selectively of benzene hydroxylation in aqueous solution, we considered both reaction paths.

We found that the energy level of the unoccupied π* orbital in Ru^{V}=O acting as the frontier orbital in benzene hydroxylation reaction is stabilized by heteroatoms substitution (Figure (a) and (b)), leading to the decreasing of the activation energy for benzene hydroxylation reaction but not water oxidation. This stabilization is not “electron push-pull effect” but “geometrical push-pull effect” due to the depending on the bond distance between Ru and O_i (Ru–O_i) changed by the bond distance between heteroatoms and O_i. In addition, we confirmed the reaction rate ration between benzene hydroxylation and water oxidation reactions (r_B/r_W) and found a good liner correlation (R^2 = 0.98) between $\log(r_B/r_W)$ and distance in Ru–O_i (Figure (c)). Our results demonstrated that **Ru^{V}OS** is the candidate of the selective benzene hydroxylation catalyst in aqueous solutions.[3]

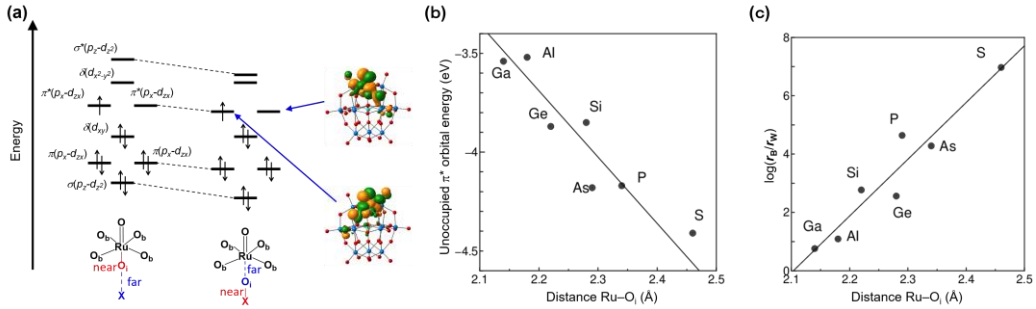

Figure. (a)Schematic orbital energy levels in Ru^{V}=O species and π* orbitals. Distance in Ru–O_i versus (b) energies of unoccupied π* orbitals (R^2 = 0.88) and (c) $\log(r_B/r_W)$ values (R^2 = 0.98).

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