

Study on one-pot oxidation of benzene to phenol by tungstate-based polyoxometalates photocatalysts

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(タングステン系ヘテロポリ酸光触媒によるベンゼンからフェノールへの一段合成反応に関する研究)

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論 文 内 容 の 要 旨

Thesis Summary

This thesis focuses on the photocatalytic benzene oxidation to phenol, which is one of the most important but challenging chemical reaction. The polyoxometalate including $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Na}_4\text{W}_{10}\text{O}_{32}$ showed high activity for benzene oxidation to phenol under typical reaction condition. The application of supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ for heterogenous photocatalytic benzene oxidation to phenol was also investigated. The photocatalytic benzene oxidation to phenol by semiconductor-based photocatalysts was discussed as well.

In Chapter 2, the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can utilized as a photocatalysts for efficient oxidation of benzene to phenol in an aqueous acetonitrile solution. Due to the unique catalytic reaction mechanism, the oxidation process has been significantly adjusted by the reaction conditions, especially by adding acetonitrile as co-solvent. By adding 50% acetonitrile into the solvent, the phenol overoxidation significantly suppressed due to the inhibited precomplexation between catalysts and phenol molecular. On the other hand, benzene showed different reaction mechanism which still can be oxidized in this reaction condition. Hence, benzene can be oxidized but phenol can not be oxidized in our reaction system, resulting a unnormal but high phenol yield and selectivity.

In Chapter 3, we change the organic cation of decatungstate to inorganic cation (Na^+), achieved high phenol yield and selectivity in an aqueous solution. Acetic acid as co-solvent involved in the oxidation process, which increased the phenol formation. This behavior is significantly different with that of TiO_2 , which showed no activity by adding acetic acid as co-solvent. The totally different reaction mechanism with TiO_2 leading to the high phenol formation (phenol yield, 24%; phenol selectivity, 81%) in this reaction system.

In chapter 4, we tried to support $\text{H}_3\text{PW}_{12}\text{O}_{40}$ into mesoporous silica by a direct method and impregnate method. The textural and structure have been fully characterized and proved that the higher stability of the sample prepared by the direct method. However, the leaching of active species into the aqueous solution is inevitable even the direct method can improve the stability of the supported sample. We found that the leaching species for homogenous photocatalytic reaction is dominant in the reaction. The heterogenous reaction by the supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ showed low reaction rate for benzene oxidation in aqueous solution. The low reaction rate may be due to the suppressed reoxidation of photocatalysts in the redox cycle.

In chapter 5, we investigated several typical type of semiconductor photocatalysts for selective oxidation of benzene to phenol. The band structure and active species were considered for the different reaction mechanism. Low phenol selectivity due to the unselective of the holes and radicals generated from semiconductor-based photocatalysts such as TiO_2 and ZnWO_4 . Pt loaded WO_3 showed much higher phenol yield compared with commercial WO_3 .

In a word, oxidation of absorbed benzene molecular on the surface of semiconductor photocatalysts will promote benzene oxidation to CO_2 by holes. The indirectly oxidation of benzene with OH radical is more promising for efficient oxidation of benzene to phenol. Hence, WO_3 and some other suitable photocatalysts is highly desired to be developed and modified for efficient benzene oxidation to phenol in the future.