

1. テーマ

<ベンゼンのヒドロキシル化反応に対する修飾ヘテロポリ酸塩を利用した触媒設計>

2. 研究メンバー

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4. 研究の概要

Using selectively site-substituted vanadium(V) Keggin and Dawson heteropolytungstates (HPA), the catalytic activities for hydroxylation of benzene in the presence of 30 % aqueous H_2O_2 were examined at room temperature under atmospheric pressure in a two liquid phase, aqueous and organic process. In particular, potassium salts of di- and tri-vanadium(V) substituted Keggin HPAs, α -1,2- $PW_{10}V_2$ and α -1,2,3- PW_9V_3 , showed 0.81 and 8.69 catalytic turnovers for phenol production with excellent selectivity, respectively, for 48 h reaction under the conditions: 0.1 mmol catalyst, 1 mL (11.3 mmol) benzene, 2 mL of acetonitrile and 2 mL of 30 % H_2O_2 . The activity of tri-substituted, PW_9V_3 , HPA was initially high, but it maximized after 48 h and its structure completely decomposed, whereas that of di-substituted, $PW_{10}V_2$, HPA gradually increased and exceeded that of the PW_9V_3 after 120 h. The polyoxoanion structure of the $PW_{10}V_2$ was maintained even after 576 h. Their activities and stabilities as catalysts were compared with those of vanadium(V)-substituted Dawson HPAs (α - $P_2W_{17}V$ and α -1,2,3- $P_2W_{15}V_3$), vanadium(V)-containing isopolyanions (IPA; VW_5 and V_{10}), the Milas reagent (V_2O_5 and aqueous H_2O_2), and the picolinate-vanadium(V) oxo peroxo complex.

Keywords: hydroxylation, benzene, vanadium(V)-substituted polyoxoanions, Keggin-type, Dawson-type, heteropolytungstate, catalyst precursor

<発表論文>

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