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Organometallic-polyoxometalate hybrid based on V-Schiff base and phosphovanadomolybdate as a highly effective heterogenous catalyst for hydroxylation of benzene

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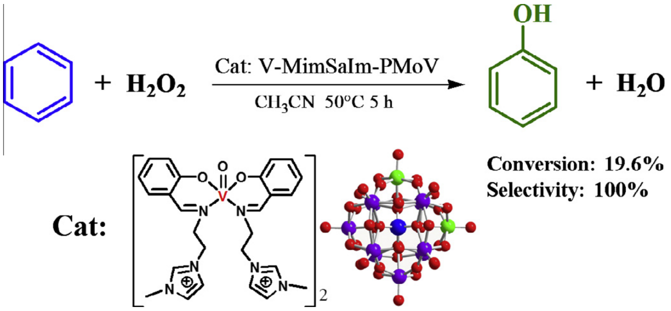
HIGHLIGHTS

- A novel organometallic-polyoxometalate hybrid is prepared.
- The hybrid catalyst leads to the heterogeneous hydroxylation of benzene with H_2O_2.
- The hybrid catalyst gives high conversion and selectivity.
- The catalyst can be easily recovered and reused.

GRAPHICAL ABSTRACT

A new organometallic-polyoxometalate hybrid is synthesized and proved to be a highly efficient and steadily reused heterogeneous catalyst for hydroxylation of benzene with H_2O_2.



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ABSTRACT

A novel organometallic-polyoxometalate hybrid has been prepared by anion-exchange of V Schiff base functionalized ionic liquid with V-containing Keggin-type polyoxometalate. The hybrid solid with two types of catalytic active V components demonstrates remarkable capability for heterogeneous hydroxylation of benzene with excellent phenol yield 19.6% and 100% selectivity. After reaction, the catalyst can be simply recovered by filtration and reused at least 4 times without the change of catalyst structure. The synergistic effect between metal Schiff base complex and polyoxometalate plays an important role in the promotion of catalytic activity.

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1. Introduction

As an important chemical intermediate, phenol is mainly produced by the three-step cumene process with low atom utilization, high energy consumption and environmental pollution [1]. So far, many potential attempts have been made for direct hydroxylation of benzene to phenol using clean oxidants, such as O_2 [2], H_2O_2 [3,4], and N_2O [5], as well as the H_2—O_2 system with the Pd-based composite membrane reactors [6,7]. Liquid phase hydroxylation of benzene to phenol with H_2O_2 has been investigated as an environmentally friendly process. For which, various transition metal catalysts (Cu, Mn, V, Mo, and Fe) have been developed [8], and vanadium-based catalyst systems are promising for

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hydroxylation of benzene because of their intrinsic ability towards the hydrocarbon oxidation [9–11].

Polyometalates (POMs) are a class of discrete anionic metal–oxygen clusters with structural diversity. Because of the rich redox chemistry, POMs have been widely used as the catalysts for organic oxidations [12,13]. Among which, V-containing POMs have been proved to be very effective for the hydroxylation of benzene with H_2O_2 [14,15]. On the other hand, transition metal Schiff base complexes are another important class of redox catalysts because of that the metal–organic framework is suitable for the construction of a highly functionalized coordination site, which may provide an opportunity to further enhance catalytic activity [16,17]. Particularly, some of metal Schiff base complexes have shown very interesting catalytic properties in direct hydroxylation of benzene [18,19]. Despite the versatile applications of POMs and metal Schiff bases in various catalytic reactions, hydroxylation selectivity from benzene to phenol and the recyclability of catalysts has always been a challenge. Recently, bifunctional or trifunctional catalysts that show enhanced catalytic activity and reusability by using two or three catalytic groups have attracted much attention [20]. A topic interest in this context is the combination of POMs with metal–organic moieties for efficient catalytic applications [21], and many noble metal complex-POM hybrid compounds have been prepared and used as catalysts for organic transformations [22,23]. For example, Neumann reported a series of organometallic-POM hybrid compounds, such as M-salen- [24], Pt(II) phenanthroline-crown ether- [25], platinum(II) bipyridinium-POM [26], and demonstrated that by this combination the electronic and catalytic properties of the two compounds in catalysts could be modified, leading to improved reactivity or synergistic effects. For hydroxylation of benzene with H_2O_2, Chen [27] have shown that hybrid compounds of Schiff base (Cu, Fe, Co) with molybdovanadophoric were efficient catalysts for hydroxylation of benzene in the presence of PPh_3 additives. Therefore, the above researches demonstrate that the combination of POMs with metal–organic moieties has a promoting effect on the improvement of the reactivity of the hybrid compounds for catalytic applications.

Task specific ionic liquids (TSILs), in which functional groups are covalently tethered to the cation or anion (or both) of the ILs, have increased attention over the last few years as it is possible to form any specific composition depending upon user's need of the desired physical, chemical and catalytic properties [28,29]. An interesting example of TSILs is focused on the incorporation of organometallic groups into a branch appended to the cation of ILs [30,31]. Further, POM-anions have been used as counteranions for TSILs redox catalysts [32,33]. Accordingly, we think that it is rational to prepare a composite catalyst by pairing POM-anions with metal–organic moieties-containing IL cations such that the catalyst contains two metal centers in a composite structure. The resulting composite may be a novel heterogeneous catalyst for hydroxylation of benzene.

Herein, we present a new catalytic active organometallic-POM hybrid whereby a V Schiff base complex with distal IL "handle" is attached to a V-containing Keggin type POM, via an anion exchange interaction according to Scheme 1. They were used as a heterogeneous solid catalyst in the hydroxylation of benzene, showing a better catalytic activity than the Schiff base metal complex or V-containing POM along.

2. Experimental section

2.1. Materials and methods

All chemicals were of analytical grade and used as received. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–400 cm^{-1} region. ^1H NMR spectra were measured with a Bruker DPX 300 spectrometer at ambient temperature in using TMS as internal reference. Elemental analyses (C, H and N) were performed on a CHN elemental analyzer (FlashEA 1112). TG analysis was carried out with a STA409 instrument in N_2 atmosphere at a heating rate of 10 °C/min. XRD patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu/Kα radiation source at 40 kV and 20 mA, from 5° to 80° with a scan rate of 4°/min. SEM image was performed on a HITACHI S-4800 field-emission scanning electron microscope. ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at X-band. The measurements were done at 163 K in a frozen solution provided by a liquid/gas nitrogen temperature regulation system controlled by a thermocouple located at the bottom of the microwave cavity within a Dewar insert.

2.2. Catalyst preparation

2.2.1. Synthesis of $H_5PMo_{10}V_2O_{40}$

$H_5PMo_{10}V_2O_{40}$ abbreviated as PMoV was prepared according to our previous literature [14].

2.2.2. Synthesis of [3-aminoethyl-1-vinylimidazolium]Br (MimAM)

N-methylimidazole (9.4 g, 0.1 mol) and 2-bromoethylamine hydrobromide (20.5 g, 0.1 mol) were dissolved in 50 mL absolute ethanol at 80 °C for 48 h under nitrogen atmosphere with reflux and stirring. On completion, solvent was removed by distillation, and the residue was washed with ethyl acetate for 3 times to afford the IL precursor MimAM·HBr. KOH was added into the aqueous solution of the above solid for neutralization, followed by the evaporation under vacuum. Methanol (20 mL) and $CHCl_3$ (2 mL) were added into the resulting mixture with the appearance of precipitated salts. After filtration, the filtrate was evaporated to give the MimAM product as yellow oil. ^1H NMR (300 MHz, D_2O, TMS) δ (ppm) = 3.47 (m, 2H, —CH_2), 4.58 (m, 2H, —CH_2), 5.40 (dd, 1H, —CH), 5.81 (dd, 1H, —CH), 7.13 (m, 1H, —CH), 7.66 (s, 1H, —CH), 7.81 (s, 1H, —CH), 9.18 (s, 1H, —CH).

2.2.3. Preparation of V Schiff base-phosphovanadomolybdate hybrid (V-MimSaIm-PMoV)

MimAM (10 mmol) and salicylaldehyde (10 mmol) were dissolved in 30 mL absolute ethanol at 80 °C for 24 h under reflux and stirring. On completion, solvent was removed by distillation, then the residue was washed with ethyl acetate and acetone and dried at 50 °C for 12 h to afford precursor MimSaIm. ^1H NMR (300 MHz, D_2O, TMS) for VMCA δ (ppm) = 1.23 (t, 3H), 3.66 (t, 1H), 4.15 (t, 2H), 4.62 (t, 2H), 6.90 (q, 1H), 7.44 (m, 1H), 7.65 (d, 2H), 8.52 (t, 2H), 9.10 (d, 1H). A stirred solution of MimSaIm (6 mmol) in dry methanol (50 mL) was treated with $VO(acac)_2$ (3 mmol) dissolved in dry methanol (20 mL) and the resulting reaction mixture was refluxed for 2 h. On completion, solvent was removed by distillation, then the residue was washed with ethyl acetate and dried at 50 °C for 12 h to afford V Schiff base complex (V-MimSaIm).

V-MimSaIm-PMoV was prepared by reacting the ethanol solution of V-MimSaIm (2 mmol) and $H_5PMo_{10}V_2O_{40}$ (1 mmol) at room temperature for 24 h. Yellow precipitate formed was filtered and washed with water 3 times, followed by drying in a vacuum to give the final product V-MimSaIm-PMoV. V-MimSaIm-PMo was prepared based on the same method.

2.3. Catalyst test

Benzene (0.78 g, 10 mmol), acetonitrile (6 mL), and catalyst V-MimSaIm-PMoV (0.1 g, × mmol) were added to a 25 mL flask reactor. Aqueous H_2O_2 (30 wt.%, 30 mmol) was drop-wise added

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