



Highly efficient transformation of alcohol to carbonyl compounds under a hybrid bifunctional catalyst originated from metalloporphyrins and hydrotalcite



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ARTICLE INFO

Article history:

Received 4 October 2015
Revised 24 November 2015
Accepted 25 November 2015
Available online 18 January 2016

Keywords:

Bifunctional catalyst
Alcohol oxidation
Metalloporphyrin
Hydrotalcite
Synergistic effect

ABSTRACT

The development of a highly active and selective catalytic system that is economical, environmentally benign, and easily recoverable is highly desirable. Bifunctional hybrid catalysts originated from metalloporphyrins (MTSPP; M = Co, Fe, and Mn), and hydrotalcite have been synthesized, characterized, and investigated in the aerobic oxidation of alcohols in the presence of isobutyraldehyde. The designed catalysts exhibited excellent activity, broad applicable scope, and good stability in the oxidation. The effect of surface basicity on the catalytic performance has been studied in detail. The research results showed that as well as protecting the metalloporphyrin molecule, the surface basicity of hydrotalcite also contributed to improving the catalytic activity and the selectivity of aldehyde, and a synergistic effect was observed in the catalytic system. A proposed mechanism for the reaction involving the formation of high-valence cobalt-oxo porphyrin intermediate was postulated based on catalytic results and Hammett and $H_2^{18}O$ experiments.

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1. Introduction

Selective oxidation of alcohols to carbonyl compounds, especially from primary alcohols to aldehydes using molecular oxygen, is one of the most challenging transformations in the synthesis of fine chemicals, for the low cost and environmentally friendly nature of oxygen compared with the stoichiometric oxidant [1,2]. However, it is difficult to control this reaction because of overoxidation or side reactions under conventional severe reaction conditions, such as a high pressure of oxygen or a high reaction temperature. Thus, it is desired to search for milder reaction conditions to suppress these reactions in order to develop an efficient oxidation method.

The utilization of efficient catalysts (heterogeneous or homogeneous) may provide a highly desirable approach. Obviously, heterogeneous catalysts in the liquid phase will offer several advantages over homogeneous ones, such as ease of recovery and recycling, atom utility, and enhanced stability in the oxidation reactions. For the purpose, a range of heterogeneous catalysts based on Cu [3–6], Ni [7], Co [8,9], Mn [10], active carbon [11], polymers [12], noble metals [13–23], etc. have been extensively utilized in alcohol oxidation. Among these, the noble metals

always exhibited the most efficient performance. However, a large excess of homogeneous base additives has always been employed in the reactions. The base in alcohol oxidation has been verified to be beneficial to the catalytic transformation and the selectivity of aldehyde [10,24–28]. Therefore, to avoid the use of a soluble base, some common solid bases, such as MgO, Mg(OH)₂, and hydrotalcite, have been widely applied as supports, such as Pd(II) acetate–pyridine complex/hydrotalcite [29], Ru/hydrotalcites [30], Pt_xAu_y-starch/hydrotalcites [31], Au–Pd nanoalloys supported on MgAl mixed metal oxides [32], and Au nanoparticles supported on NiAl layered double hydroxides (LDHs) [33]. It has been demonstrated that the Au/LDH catalysts can be more active in the absence of base additives than other commonly used gold catalysts such as Au/TiO₂, Au/CeO₂, and Au/Al₂O₃, suggesting synergy between AuNPs and basic sites of the LDHs [34,35]. However, from the viewpoint of economy and sustainable chemistry, it is especially important to develop economical catalysts for selective oxidation, because noble metal catalysts are expensive and scarce. In addition, most of these catalysts are only applicable to a very limited range of substrates under base-free conditions. For example, Wang et al. [36] have reported Au nanoparticles supported on LDH catalysts, but the conversion of aliphatic alcohols and the selectivity of the corresponding carbonyl compounds were low.

Metalloporphyrins, as model catalysts of cytochrome P-450, have been widely used as catalysts for the oxidation of various

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substrates, including alcohols [37–40]. For example, Woo and co-authors reported the aerobic homogeneous oxidation of benzyl alcohol with oxotitanium porphyrin (TTP)Ti=O, which gave benzaldehyde in a modest yield (48%) after 94 h [41]. Kato et al. reported heterogeneous aerobic oxidation of benzyl alcohol using $[\text{Ru}_2^{\text{III}}(\text{H}_2\text{TCPP})\text{BF}_4]$, in which high selectivity of benzaldehyde (95%) was obtained after 24 h with a low turnover number (TON) [42]. Some other metalloporphyrins have also been used as catalysts in alcohol oxidation by molecular oxygen in the presence of isobutyraldehyde (IBA), and Ru(TPP)Cl showed excellent activity and selectivity for oxidation of various alcohols only when benzotrifluoride was used as the solvent [43]. A similar example was found in a reaction catalyzed by Ru(TPFPP)(CO), where tetrabutylammonium hydroxide and the solvent bromotrichloromethane were needed [44]. In addition, the method was not efficient for alcohol substrates containing heteroatoms and some aliphatic alcohols containing phenyl. The same drawback was also found in the metallodeuteroporphyrins-catalyzed system reported by Sun et al. [45]. Liu and co-workers have reported that (TSPP)Rh (III) could catalyze the selective oxidation of various alcohols with a buffer solution, but the TOF of the reaction was only 80 h^{-1} in the case of benzyl alcohol [40].

In addition, these noble metal catalysts were costly, seriously minimizing their potential for commercial applications. Although some non-noble metals, such as Co, Mn, Fe, and Cu, have been introduced into the metalloporphyrin-catalyzed system [43,46], the catalytic activities and selectivities of benzaldehyde were rather low or the scope was limited. Another common drawback for these metalloporphyrin catalytic systems for the oxidation of alcohol is that they were all homogenous and the active sites were always deactivated by aggregation of porphyrin rings by π - π interaction as the reaction proceeded. Therefore, the porphyrin molecule should be supported to be a heterogeneous catalyst to prolong its lifetime and avoid some inherent drawbacks in homogeneous reaction systems.

LDHs having a hydroxalcalite-like structure are composed of positively charged trioctahedral hydroxide layers with interlayer anions, represented by the general formula $[\text{M}(\text{II})_{(1-x)}\text{M}(\text{III})_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$ [47,48]. The particular property of LDHs that their properties can be fine-tuned because of the adjustability of the cations and anions in the brucite layer and interlayer [49,50] should provide a new method of designing multifunctional catalysts possessing both basicity and redox functionality. It has been demonstrated that LDH meets the requirement for an inorganic support for immobilizing anionic metal complexes and may provide an alternative to homogeneous metal complexes [51,52].

On the basis of this analysis, we envisioned that if the metalloporphyrin molecule with substituted anionic groups was intercalated into the interlayers of LDHs, a multifunctional catalyst should be produced. The intercalated material will possess some positive functions, including (I) a high capacity for catalytic oxidation of alcohol based on metalloporphyrin, (II) basic sites on the surface that may act as a co-catalyst in alcohol oxidation, and (III) conversion of the metalloporphyrin to the heterogeneous catalyst, which can increase the durability of the complex in reactions. The new material would afford us an efficient, heterogeneous, inexpensive, and recyclable catalyst for the selective oxidation of alcohols.

Our group has been investigating metalloporphyrins as a biomimetic catalyst, and modified hydroxalcalites and intercalated materials as efficient catalysts in the selective oxidation of many substrates [38,53–55]. The design and develop of multifunctional and economical catalysts for oxidation are significantly important in the industrial and academic fields. Therefore, our ongoing interest has been drawn to synergistic catalysis between the metalloporphyrin catalyst and a second functional site for the high

selectivity of objective products. With this knowledge and background, in the present study, tetra(4-sulfonatophenyl)porphyrinato-metal anions (MTSPP, M = Co, Fe, and Mn) intercalated into ZnAl hydroxalcalites have been prepared as heterogeneous bifunctional catalysts for the aerobic oxidation of alcohol in the presence of IBA. The structures of these hybrids have been characterized, and the substrate scope has been studied. Also, the synergistic effect between metalloporphyrin molecules and hydroxalcalite and the reaction mechanism have been discussed.

2. Experimental

2.1. Preparation of MTSPP-Zn_xAl-LDHs

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.67 g, 0.0056–0.014 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.05 g, 0.0028 mol) was dissolved in 50 mL of deionized water. The aqueous solution was slowly added with mechanical stirring to 10 mL of distilled water at 25 °C with sodium MTSPP (M = Co, Fe, Mn, 1.54×10^{-3} mol), synthesized according to Refs. [56,57]; pH 8.5 was maintained by the continuous addition of 0.1 mol/L NaOH. The resulting suspension was stirred for 24 h at 80 °C. The product was filtered, washed with distilled water at 80 °C, and finally dried at room temperature.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns of the as-synthesized samples were obtained using a Rigaku D/max 2500 PC X-ray diffractometer with $\text{Cu K}\alpha$ (1.5402 Å) radiation at 10 min^{-1} . Diffuse reflectance ultraviolet and visible spectra (DR UV-vis) were recorded in a Perkin-Elmer Lambda 35 spectrophotometer, using BaSO_4 as a reference. For the scanning electron microscopy (SEM) of the samples, a JEOL JSM-6360LA scanning electron microscope was used. The compositions of samples were analyzed by inductively coupled plasma analysis (ICP) using a Varian Vista-AX device. The basic properties were determined by titration with 0.01 M benzoic acid solution in toluene using 0.15 g of vacuum-dried solid sample suspended in 2 mL of phenolphthalein indicator solution [58].

2.3. Catalytic oxidation of alcohol

Liquid-phase catalytic oxidation of benzyl alcohol was carried out in a 25 mL two-neck flask with reflux condenser and magnetically stirred autoclave heated in an oil bath under atmospheric pressure. Dioxygen was bubbled (10 mL/min) through a solution of acetonitrile (ACN, 8 mL), benzyl alcohol (108 mg, 1 mmol), IBA (216 mg, 3 mmol), and catalyst (1.9×10^{-6} mmol, calculated on the intercalated metalloporphyrin) at 60 °C. The product samples were drawn at regular time intervals and analyzed with a gas chromatograph (Shimadzu GC-2010AF) having a Chromopak capillary column and FID detector. The products were further confirmed using GC-MS (Shimadzu GCMS-2010). The conversions of the reactions were calculated with no allowance for the background. After the reaction, the resulting mixture was cooled and the catalyst was separated by centrifugation and washed with solvent. After drying in vacuum, the recycled catalyst can be reused in the next run under the same conditions. The conversion, yield of benzaldehyde, and selectivity presented here are based on the GC calculations using chlorobenzene as the internal standard reference compound.

2.4. ^{18}O -labeled H_2^{18}O experiments

Through a mixture of benzyl alcohol (11 mg, 0.1 mmol), CoTSPP-Zn₂Al-LDH (1.0×10^{-6} mmol), IBA (21 mg, 0.3 mmol),

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