

Tungstated zirconia catalyzed bromination of phenol red under nearly neutral solution

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Abstract

The performance of tungstated zirconia catalysts prepared by co-precipitation (WZ) and impregnation (W/m-ZrO₂) techniques in phenol red bromination reaction was tested. Both types of catalysts showed excellent activity in this reaction in aqueous solution. The activity of WZ increases as the W loading decreases and the most active 0.6WZ catalyst contained highly dispersed WO_x of low surface density on zirconia. The W/m-ZrO₂ catalysts showed even higher activity in this reaction but maximum performance is observed for 1.3W/m-ZrO₂ instead. The active site for the redox reaction is probably the monomer or dimer of WO_x with a single oxo group whereas low surface density of WO_x provides enough space on zirconia for the adsorption of phenol red without blocking the redox sites.

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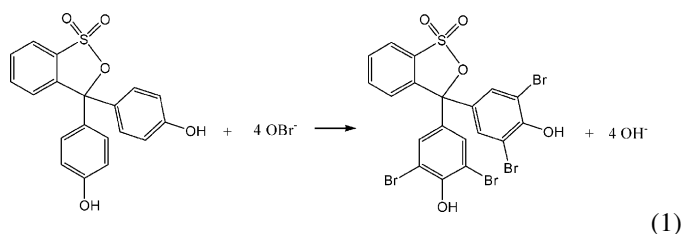
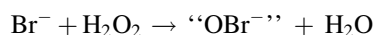
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1. Introduction

Bromination of aromatic compounds is a class of reactions of both laboratory and industrial importance. Often, bromination of aromatic substrates is performed with elemental bromine which is difficult to handle. The substitution reaction, with the formation of hydrobromic acid as a by-product, would reduce the atom efficiency by 50%. Also the generated hydrobromic acid must be neutralized before it can be discharged. In order to overcome these problems, an environmentally friendly process may involve oxidation of a bromide anion using a suitable oxidant such as hydrogen peroxide under nearly neutral solution. This concept has been inspired by the enzymes, vanadium dependent bromoperoxidases (VBPO). VBPO can be found in most marine organisms and has been used for the synthesis of halogenated compounds which may play the role of chemical defense [1]. It catalyzes the oxidation of a halide (i.e. Cl⁻, Br⁻, or I⁻) by hydrogen peroxide which is then used for the subsequent halogenation reactions. Many of these halogenated compounds have been used widely in pharmaceutical research due to their biological activities. However, the direct use of haloperoxidase in large-

scale synthesis may not be practical since high cost is involved in the cultivation, extraction and purification of this enzyme from its source. An alternative approach is to find a biomimetic halogenation catalyst instead.

Bromination of phenol red is often used as the test reaction for these biomimetic catalysts since it is facile and can be followed easily by UV–visible absorption technique. A proposed reaction pathway through the formation of “OBr⁻” intermediate is outlined in scheme (1) [1]:



It has been suggested that there exist an equilibrium mixture of bromine intermediates in aqueous solution such as HOBr, Br₃⁺, Br₂, and even Br species coordinated to the catalyst.

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Oxo-peroxy species of early transition metals have been employed as biomimetic catalyst for such reaction. A recent example is a penta-coordinated oxo-peroxy vanadium (V) complex catalyzing the bromination of phenol red [2]. However, for homogeneous catalyst, high concentrations of metal relative to reactants are often needed. The separation cost is a further disadvantage.

Recently, Sels et al. [3–6] have prepared a series of tungstate ion (WO_4^{2-}) exchanged layered double hydroxides (LDH) and they showed the highest activity so far in phenol red bromination reaction at nearly neutral pH condition. Previous studies involving homogeneous catalysts in solution required strong acidic condition for promising results. However, tungstate ion may leach from LDH over long term. It is also known that the LDH structure would dehydroxylate or form new compound with various surface anions at high temperature. In addition, being basic in nature, LDH is not very stable in acidic medium [7]. Stucky and co-workers on the other hand have functionalized mesoporous silica MCM-48 with tungsten and molybdenum [8]. The resulting surface metal-oxo species showed catalytic peroxide activation. However, their bromination activities are apparently rather low and no details on catalysis are given. It seems that silica is a poor support for tungstate to generate the necessary surface acidic and redox species for the catalysis.

Tungstated zirconia, WO_x/ZrO_2 , is a versatile catalyst in that it can catalyze both acid and redox type of reactions. So far, this class of catalyst is only well-known for the study of acid-catalyzed reaction such as the isomerization of *o*-xylene and *n*-alkane [9,10]. However, Lewis acid can also promote oxidation reaction by coordinating with a peroxy species and enhancing dramatically the electrophilicity of these oxidizing reagents toward their reaction with weakly nucleophilic substrates such as bromide. Tungstated zirconia is known to have Lewis acid sites on their surfaces [10].

Normally, loadings higher than full monolayer coverage of WO_x on zirconia are required for maximum acidic catalytic performance such as in isomerization [10]. For biomimetic bromoperoxidation reaction, the active center seems to be monomeric or dimeric species. Now, highly dispersed WO_x surface sites are required for the efficient oxidation of Br^- before electrophilic substitution into the hydrocarbon structure occurs. In this paper, we shall report the catalytic properties of tungstated zirconia in the bromination of phenol red. We report the preparation (co-precipitation and impregnation), characterization (XPS, EXAFS, EPR, IR), and catalytic bromination reaction of phenol red over tungstated zirconia catalysts. Very high turn-over frequency is obtained for catalysts with highly dispersed WO_x on the surface.

2. Experimental

In our study, two kinds of tungstated zirconia catalysts were used: the catalysts prepared by co-precipitation technique were denoted as WZ, whereas those prepared by impregnation technique were denoted as W/m-ZrO₂. It should be noted that mesoporous zirconia (m-ZrO₂) was used for the latter method.

The preparation procedure for WZ and W/m-ZrO₂ are outlined below.

WZ catalyst was prepared by the method previously reported by us [10]. Briefly, the hydroxide precursor of WZ was obtained by co-precipitation technique from a solution of zirconyl nitrate hydrate, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, by adding dropwise a solution containing NH_4OH and ammonium metatungstate hydrate ($\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$. After hydrothermal reaction and separation, the precursor was calcined in static air for 3 h at 600 or 800 °C (for 13.7WZ). The resulting catalyst is denoted as *x*WZ, where *x* is the weight percent of tungsten in WZ.

Hexadecyl trimethyl ammonium bromide (C_{16}TAB) was used as the template for the synthesis of mesoporous zirconium oxide (designated as m-ZrO₂). Mesoporous zirconia was prepared according to the method outlined in reference [11], and has been well characterized [12]. *x*W/m-ZrO₂ (*x* denotes weight percent of W) was prepared by impregnating ($\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$ on mesoporous zirconia and calcined at 630 °C for 4 h.

Elemental composition was analyzed with a simultaneous ICP-AES allied analytical system (Jarrel-Ash, Model ICAP 9000). X-ray diffraction (XRD) analysis was done with powdered samples on Philips Expert instrument. Nitrogen adsorption-desorption data were obtained at −196 °C on a Micromeritics ASAP 2000 apparatus and were analyzed for BET surface area and pore size distribution. Ultraviolet–visible (UV–vis) absorption spectra were taken on a Hitachi U-3010 spectrophotometer. Infrared (IR) spectra were recorded on a Nicolet Magna-IR 550 spectrometer. A Bruker EMX EPR spectrometer (X-band) was employed to measure the electron paramagnetic resonance (EPR) spectra of the sample.

The study on X-ray photoelectron spectroscopy (XPS) was carried out on a VG Scientific ESCALAB 250 XPS instrument with an incident X-ray energy of 1486.8 eV (Al K α). The binding energy (BE) of C 1s peak (284.8 eV) in the spectrum is used as the internal reference for energy calibration. Data analysis involved smoothing, non-linear Shirley-type background subtraction and curve-fitting using mixed Gaussian–Lorentzian functions.

W-L_{III}-edge extended X-ray absorption fine structure (EXAFS) study was performed at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The electron storage ring was operated at about 1.5 GeV with a ring current of about 200 mA. All the experiments were done at room temperature. The resulting EXAFS data were analyzed with standard FEFF6 program. Special scanning procedure was employed for the highly dispersed 0.6WZ catalyst. It was done in the fluorescence mode and each scan took twice as long as the other catalysts. Six such scans were average to give a better spectrum.

Bromination of phenol red to bromophenol blue was carried out at room temperature and monitored using UV–vis spectroscopy. The solvent used was either water or a mixture of water, methanol and tetrahydrofuran where the volume ratio of $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{C}_4\text{H}_8\text{O}$ is 4:3:2 [4]. The solid catalyst was removed before each measurement. The reaction conditions for the catalysis are listed in the table of catalytic results.

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