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# A $FeCl_3$-based ionic liquid for the oxidation of anthracene to anthraquinone

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ABSTRACT

*N*-butylpyridinium bromide ferric trichloride (NBPBFTC), a $FeCl_3$-based ionic liquid, was prepared by a two-step method. NBPBFTC significantly catalyzed the oxidation of anthracene to anthraquinone (AQ) using aqueous hydrogen peroxide (AHPO) as the oxidant. The optimal conditions were determined to be 50 °C, 45 min, 100 mg NBPBFTC, and 1 mL AHPO for the oxidation of 50 mg anthracene. Under the conditions, AQ was obtained in a yield of 99.5%. NBPBFTC can be reused at least 3 times without substantial decrease in activity. With the intense π–π interaction between anthracene and pyridine-based cation in NBPBFTC, anthracene is soluble in the reaction system. Meanwhile, the iron-based anion and AHPO form a Fenton-like reagent to produce HOO· and HO·, which attack 9-position in anthracene to induce anthracene oxidation to AQ.

## 1. Introduction

Anthraquinone (AQ) is one of important fine chemicals and chemical intermediates. It is often used to produce the anthraquinone dye [1] and hydrogen peroxide [2] and to enhance the Kraft process for paper production [3]. Anthracene, as a main component in coal tar, is usually subject to oxidation to yield AQ in industry [3–5]. In general, gas-phase oxidation method involves high temperatures and heavy metal-based catalysts, while liquid-phase one requires strong acids, e.g., concentrated sulfuric acid and dichromic acid [4,5].

Ionic liquids (ILs) have been paid increasing attention due to their negligible vapor pressure, thermal stability, excellent solubility, and design ability by appropriate modifications of cationic or anionic structures [6–9]. The $FeCl_3$-based ILs not only have the above unique properties, but also exhibit a strong response to an additional magnetic field [10–13]. These properties contribute a lot to the potential application of the iron-based ILs in catalytic reactions [14], solvent effects [15], and separation processes [16]. Three kinds of $FeCl_3$-based ILs were used to dissolve coal direct liquefaction residues to obtain asphaltene fractions [17]. Among them, an IL with pyridine-based cation is the most effective, implying that the IL can effectively dissolve aromatics. Besides, $FeCl_3$-based ILs have been employed as an effective medium and catalyst in benzene alkylation [18], isobutene oligomerization [19], and Friedel–Crafts sulfonylation of some aromatics [20]. More interestingly, $FeCl_3$-based ILs along with aqueous hydrogen peroxide (AHPO) could greatly facilitate oxidative desulfurization of liquid fuels [21–24] due to their good dissolubility and high catalytic activity for oxidation.

In the present investigation, *N*-butylpyridinium bromide ferric trichloride (NBPBFTC) was prepared as a $FeCl_3$-based IL and used in the oxidation of anthracene to AQ using AHPO as the oxidant.

## 2. Experimental

### 2.1. NBPBFTC synthesis

NBPBFTC was synthesized by a two-step method according to Scheme 1 [25]. The intermediate IL *N*-butylpyridinium bromide (NBPB) was prepared by the quaternization reaction of pyridine with 1-butyl bromide at 70 °C in cyclohexane in a round flask with a reflux condenser and magnetic stirrer for 48 h. The resulting crude product was purified by repetitious recrystallization and dried in a vacuum oven. Then NBPBFTC was synthesized by mixing equimolar amounts of the purified NBPB and $FeCl_3 \cdot 6H_2O$ at 50 °C in a dry flask with a mechanical stirrer for 24 h. The coarse product was washed several times with diethyl ether and deionized water, and then dried in a vacuum oven to obtain a dark red solid, *i.e.*, NBPBFTC, at room temperature.

### 2.2. Characterizations of NBPB and NBPBFTC

Fourier transformed infrared (FTIR) spectra of the two ILs were recorded on a Nicolet Magna IR-560 FTIR spectrometer by collecting 50 scans at a resolution of 4 $cm^{-1}$ in reflectance mode with a measuring region of 4000–400 $cm^{-1}$. Raman analysis was carried out using a Bruker Senterra Raman spectrometer with a 532 nm laser source at a resolution of 1.5 $cm^{-1}$ with a measuring region of 200–450 $cm^{-1}$. $^1H$-nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker AV-400 NMR spectrometer with tetramethylsilane as the external standard.

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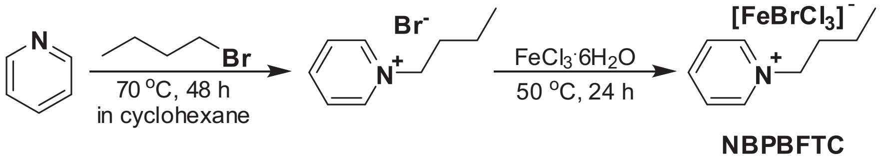

**Scheme 1.** Procedure for NBPBFTC preparation.

Ultimate analysis was performed using a Leco CHN-2000 elemental determinator. The magnetic measurements were conducted on a Quantum Design MPMS-XL-7 magnetometer at 27 °C. The melting point was measured with a Beijing Keyi XT5 melting point determinator.

### *2.3. Anthracene oxidation to AQ*

About 50 mg anthracene, 5 mL $CH_3CN$, and prescribed amounts of NBPBFTC and AHPO were put into a glass tube reactor. Then the mixture was stirred at a designed temperature in a KEM PRS Start-up Kit parallel synthesizer. After reaction for an indicated period of time (15–75 min), the reaction mixture was extracted with dichloromethane (DCM). The extract was analyzed with an Agilent 7890/5975 gas chromatograph/mass spectrometer (GC/MS) equipped with a capillary column coated with HP-5 (cross-link 5% PH ME siloxane, 60 m length, 0.25 mm inner diameter, 0.25 μm film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode. Pure anthracene and AQ were adopted as external standards for quantitative analysis. The yield of AQ was calculated by dividing the molar mass of AQ by the total molar mass of anthracene (including converted and residual one), while the selectivity of AQ was determined by dividing the molar mass of AQ by the converted molar mass of anthracene.

## 3. Results and discussion

### *3.1. Characterizations of NBPB and NBPBFTC*

The contents of carbon, hydrogen, and nitrogen in NBPB are 50.84%, 8.90%, and 6.61%, respectively, which are approximately equal to the theoretical elemental analysis of the IL. The high purity of NBPB synthesized was further evidenced by FTIR (Fig. S1) and $^1H$ NMR (Fig. S2) analyses. FTIR spectrum of NBPBFTC is similar to that of NBPB except for lacking the strong absorbance of –OH caused by the strong hygroscopicity of NBPB, as shown in Fig. S1. The fact indicates that the cation of NBPB does not participate in the complexation reaction during the formation of NBPBFTC. In the Raman spectrum of NBPBFTC (Fig. S3), the bands around 225, 246, 268, 333, and 351 $cm^{-1}$ correspond to the stretch vibration of $[FeClBr_3]^-$, $[FeBrCl_3]^-$, $[FeBr_2Cl_2]^-$, $[FeCl_4]^-$, and $[Fe_2Br_2Cl_5]^-$, respectively [25]. The result suggests that free $Fe^{3+}$, $Br^-$, and $Cl^-$ could be combined to generate different anions in the production of NBPBFTC.

NBPBFTC exhibits the reversible melting and solidifying behaviors. At room temperature, NBPBFTC is a dark red crystal, while it begins to melt around 44 °C and become a fluid with a high viscosity at 50 °C, as displayed in Fig. 1. It turns into a solid when cooling the reaction system to room temperature. Such a temperature-responsive behavior may facilitate NBPBFTC recycle after the reaction by spontaneous phase separation.

As depicted in Fig. 2, the magnetization of NBPBFTC shows a nearly linear field dependence over the applied magnetic field range of −20–20 kOe, which is in accordance with a typical paramagnetic behavior. From the slopes of the fitted line, the magnetic susceptibility of NBPBFTC is determined to be 41.7 memu· $g^{-1}$, which is similar to a reported value for similar Fe(III)-based ILs [26]. Despite the fact that the strong response to an additional magnetic field would be helpful for the recycle of the Fe(III)-based ILs, how to conveniently separate Fe(III)-based ILs from the reaction system needs further investigation [27].

### *3.2. Effects of reaction conditions onanthracene oxidation to AQ*

In the presence of NBPBFTC, the decomposition of $H_2O_2$ in AHPO is too rapid to control the oxidation. So, $CH_3CN$ was added to the reaction system as a dispersant to control the oxidation. As shown in Table 1, under the same conditions except catalyst, AQ selectivity is 100% over either NBPBFTC or $FeCl_3 \cdot 6H_2O$ or without catalyst, but AQ yields are quite different over NBPBFTC (99.3%), $FeCl_3 \cdot 6H_2O$ (21.3%), and without catalyst (1.8%). Both the yield and selectivity of AQ from anthracene oxidation over $FeBr_3$ decrease compared to those over NBPBFTC due to the formation of the by-product 9,10-dibromoanthracene over $FeBr_3$.The best result was obtained over $[(CH_3CH_2CH_2CH_2)_4NH_4]_6[BW_{11}Mn(H_2O)O_{39}]$ in previous publications [28–31], but compared to the expensive catalyst, higher temperature (80 °C), and much longer time (24 h), NBPBFTC should be more appropriate for catalyzing anthracene oxidation to AQ using AHPO as the oxidant.

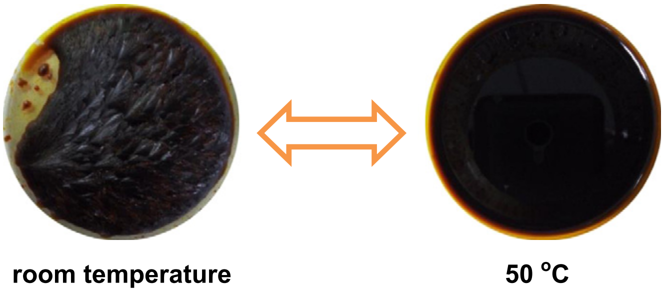

**Fig. 1.** Reversible melting and solidifying behaviors of NBPBFTC.

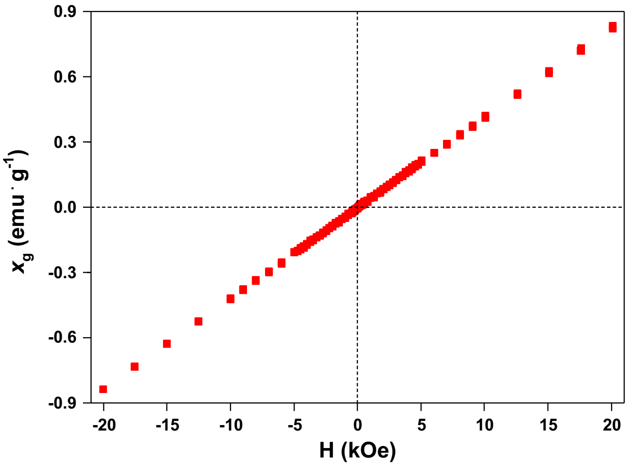

**Fig. 2.** Magnetization of NBPBFTC as a function of applied magnetic field at 27 °C.