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Production of NMSBA from the oxidation of NMST with oxygen catalyzed by $H_3PW_{12}O_{40}$/Co/Mn/Br homogeneous catalytic system

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HIGHLIGHTS

- Catalytic oxidation of NMST to NMSBA with oxygen is studied for the first time.
- Best homogeneous catalytic system is determined.
- Effects of temperature, concentration, oxygen partial pressure are investigated.
- The activation energy and the reaction orders are estimated.

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ABSTRACT

2-Nitro-4-methylsulfonylbenzoic acid (NMSBA) is usually manufactured from the partial oxidation of 2-nitro-4-methylsulfonyltoluene (NMST) by nitric acid under the catalysis of vanadium pentoxide. This paper reports a novel method for the production of NMSBA from the oxidation of NMST by oxygen catalyzed with a homogeneous catalyst system consisting of $H_3PW_{12}O_{40}$/Co(II)/Mn(II)/Br. The experiments prove that this catalytic system realizes the oxidation of NMST to NMSBA. The optimal phosphotungstic acid concentration is 2500 ppm. The optimum Co(II) concentration is 148 ppm. The highest NMSBA yield is obtained with a Mn/Co ratio of 2.1. The best Br concentration is 1163 ppm. Temperature has a strong effect on the reaction rates. Oxygen partial pressure influences the NMST conversion and NMSBA yield greatly. The kinetic parameters, such as activation energy and reaction orders, have been estimated.

1. Introduction

2-Nitro-4-methylsulfonyl benzoic acid (NMSBA) is an important chemicals used widely in dyes, medicine, pesticide and mesotrione production. Because mesotrione is considered to be an environment friendly herbicide, it has been found wider and wider application internationally with the expansion of the corn acreage. Therefore, the production of NMSBA becomes more and more important. Many methods have been tried to produce NMSBA.

Wehrenberg [1] found that NMSBA might be produced from the reaction between 2-nitro-4-nitrobenzoic acid and sodium methanesulfinate catalyzed by ultraviolet and cuprous chloride. Michaely et al. [2] reported that NMSBA could be manufactured from the hydrolysis of 2-nitro-4-methylsulfonyl benzonitrile in sulfuric acid solution at room temperature. NMSBA [3,4] may also be formed by the hydrolysis of the ester of 2-nitro-4-methylsulfonyl benzoic acid that was produced by the oxidation of the ester of 2-nitro-4-methylthiobenzoic acid with hydrogen peroxide. However, the oxidation of 2-nitro-4-methylsulfonyltoluene (NMST) to NMSBA has attracted much attention.

It is very difficult to oxidize NMST to NMSBA because there exists two strong electron-withdrawing groups, $-NO_2$ and $-SO_2$-CH_3, on the benzene ring of NMST. Many methods have been tried to realize the oxidation of NMST to NMSBA. Jary and Legras [5,6] put forward that NMST could be oxidized to NMSBA by hydrogen peroxide in sulfuric acid solution. The method [7] oxidizing NMST to NMSBA (Eq. (1)) in sulfuric acid solution with nitric acid under the catalysis of vanadium pentoxide is the only commercial technology for the production of NMSBA. But this technology suffers from some problems, such as, giving off NO_x pollutants, discharging waste water containing nitric acid and sulfuric acid, and producing multinitro-compounds.

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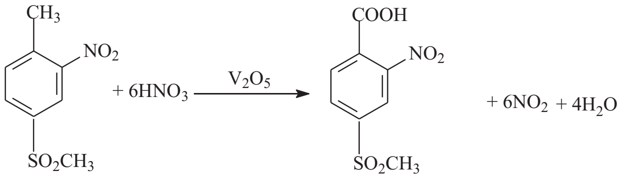
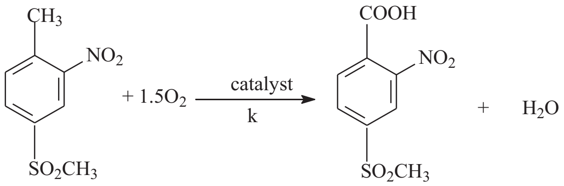


(1)

It is attractive to oxidize NMST to NMSBA with oxygen because it is a cheap and green oxidant (Eq. (2)). The key to the oxidation of NMST to NMSBA by oxygen is to develop an efficient catalyst because of its low oxidizing capability. Jacobson [8] put forward to oxidize NMST to NMSBA by air in acetic acid under the catalysis of cobalt(II) acetate with acetaldehyde as an accelerant. However, this technology has not been put into commercial application yet due to the low catalytic activity of the catalyst.



(2)

It is well known that heteropoly acids (HPAs) are an immense class of oxygen bridged metal cluster anions of mainly tungsten and molybdenum. They exhibit very strong Brønsted acidity approaching to superacid region, fairly high stability, and a structure with high proton mobility. Phosphotungstic acid ($H_3PW_{12}O_{40}$) with a Hammett acidity H_0 of -13.2, which is much stronger than 100% sulfuric acid ($H_0 = -11.9$) [9–12], is a catalyst with a bright promise in the future because of its high acidity, redox properties and pseudo-liquid behavior. Sachdeva and Pant [13] realized the deep desulfurization of diesel via peroxide oxidation using phosphotungstic acid as phase transfer catalyst. Costa et al. [14] used phosphotungstic acid as a catalyst for the liquid-phase isomerization of styrene oxide into phenylacetaldehyde. Kooti and Afshari [15] reported that phosphotungstic acid supported on magnetic nanoparticles could be used as an efficient reusable catalyst for the epoxidation of alkenes. It is well known that manganese and cobalt acetates are important catalysts [16] in oxidation. Bromine often acts as a promoter, initiating hydrogen abstraction from the hydrocarbon and generating bromide [17]. Therefore, the authors put forward to making up a homogeneous catalyst consisting of phosphotungstic acid, Co, Mn and Br to speed up the oxidation of NMST to NMSBA. This paper reports the study on the oxidation of NMST to NMSBA in acetic acid by oxygen catalyzed by such $H_3PW_{12}O_{40}$/Co/Mn/Br homogeneous catalytic system.

2. Experimental section

2.1. Materials

Cobalt(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, tetrabromoethane, $H_3PW_{12}O_4$ and KH_2PO_4 were obtained from Guoyao Co., Ltd. Glacial acetic acid (HAc) and acetonitrile were bought from Lingfeng Co., Ltd. 2-Nitro-4-methylsulfonyltoluene (NMST) and 2-nitro-4-methylsulfonylbenzoic acid (NMSBA) were purchased from Energy Chemicals Co., Ltd. All chemicals were analytical grade without further purification.

2.2. Analytical methods

The analysis of NMST and NMSBA was accomplished by a HPLC with a C18 stainless steel column in the liquid phase. The mobile phase for HPLC analysis was a mixture of acetonitrile and 0.03 mol l^{-1} KH_2PO_4 aqueous solutions. The mobile phase flowed for 4 min with an acetonitrile/KH_2PO_4 ratio of 3:17 (volume) and then the ratio changed to 2:3. The flow rate of the mobile phase was 1.0 ml min^{-1}. According to the analysis of the liquid composition from the reaction system by HPLC, only NMST and NMSBA were detected. Hence other intermediate products from the oxidation of NMST in this catalytic oxidation system could be neglected. NMST and NMSBA were detected by a UV detector at 234 nm. The calibration curves of these components were obtained using standard solutions. Least-squares fits to the data yield standard equations shown in Table 1. A stands for area and C means the concentration with unit of 10^{-6} g ml^{-1}.

The conversion of NMST was calculated as follow:

$$\eta_{\mathrm{NMST}}(\%) = \frac{C^0_{\mathrm{NMST}} - C^t_{\mathrm{NMST}}}{C^0_{\mathrm{NMST}}} \times 100 \tag{3}$$

where η_{NMST} stands for the conversion of NMST, C^0_{NMST} for the initial NMST concentration and C^t_{NMST} for the NMST concentration (kg l^{-1}) at t time in the solution.

The yield of NMSBA was obtained in terms of the following equation:

$$Y_{\mathrm{NMSBA}}(\%) = \frac{C^t_{\mathrm{NMSBA}}}{\frac{M_{\mathrm{NMSBA}}}{M_{\mathrm{NMST}}} C^0_{\mathrm{NMST}}} \times 100 \tag{4}$$

where Y_{NMSBA} is the yield of NMSBA, M_{NMST} and M_{NMSBA} are the molecular weights of NMST and NMSBA, C^t_{NMSBA} is the NMSBA concentration (kg l^{-1}) at t time in the solution.

2.3. Experimental setup and procedure

The experiments for the catalytic oxidation of NMST to NMSBA were performed in the experimental setup shown in Fig. 1. The reactor was a titanium autoclave of 1000 ml. The system was also equipped with a condenser, a gas–liquid separator and a liquid recycle tank to ensure complete condensation and recycling of the evaporated compounds. A cooling coil was installed inside the reactor to remove the reaction heat. The deviation of the reaction temperature was within ±0.2 °C. The fluctuation of the reactor pressure was controlled below 0.02 bar.

The experiments were carried out in the following steps. Firstly, the reactor was charged with mixtures of proposed amount of HAc, NMST, cobalt(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, $H_3PW_{12}O_4$, and tetrabromoethane. The tetrabromoethane may decompose to produce bromide in acetic acid. Secondly, chromatography-grade N_2 was introduced into the autoclave to raise the pressure in the reactor to 3.0 MPa and the stirring was started. The agitation speed was maintained at 300 rpm. Thirdly, the reactor was heated by an electric heating jacket. Fourthly, the reaction started when air was introduced into the reactor as soon as the temperature reached to the scheduled values. The air flow rate was maintained at 0.5 l min^{-1}. Liquid

Table 1
Standard equations.

Sample	Equation	R^2
NMSBA	$C_{\mathrm{NMSBA}} = 13.2985A_{\mathrm{NMSBA}} + 1.2504$	0.99953
NMST	$C_{\mathrm{NMST}} = 7.6311A_{\mathrm{NMST}} + 2.4907$	0.99981