Carbon nanotubes as catalyst for the aerobic oxidation of cumene to cumene hydroperoxide

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ABSTRACT

The effective oxidation reaction system using the commercial carbon nanotubes (CNTs) as catalysts for the liquid aerobic oxidation of cumene to cumene hydroperoxide (CHP) under low temperature is reported in this paper. Several reaction parameters, including the temperature, catalyst content, oxygen flow rate and reaction time were carefully studied. Under optimal conditions, cumene conversion of 24.1% with CHP selectivity of 88.4%, close to that of metal catalyst, was obtained. Cumene oxidation catalyzed by CNTs was proved a radical-involved reaction, and the outstanding catalytic performance was attributed to CHP decomposition catalyzed by CNTs to produce free radicals. Oxygenated functional groups on the surface of catalyst showed a negative effect on cumene oxidation due to the localization of electrons after the introducing of defects and oxygenated functional groups. CNTs as catalysts also showed desirable recyclability after five cycling tests. This study not only provides an applicable method for selective oxidation of cumene to CHP, but also gives some useful information on catalytic role of CNTs-catalyzed liquid-phase oxidation reactions of aromatic hydrocarbons.

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1. Introduction

Liquid-phase oxidation of hydrocarbons with air or molecular oxygen to high value-added oxygen-containing compounds such as peroxides, alcohols, ketones and carboxylic acids is a significant and efficient petro-chemical industrial process [1]. Liquid aerobic oxidation of cumene to cumene hydroperoxide (CHP) is one of such reactions. CHP is an important intermediate in the three-step cumene-phenol process which starts with the alkylation of benzene with propylene to produce cumene, continues with the oxidation of cumene to CHP, and ultimately produces phenol and acetone by the decomposition of CHP in acid medium [2]. Today, more than 90% of the phenol in the world is produced by this route. In the conventional cumene oxidation process, air was used as oxidant and CHP was used as initiator under high temperature and pressure, and alkaline solution was used to instantaneously neutralize the acids produced [3]. Except low efficiency, there are still some drawbacks such as poor safety, difficult catalyst recycling, and negative environmental impact. With the increased awareness of green chemistry and the development of phenol chemical industry, much attention has been paid on the research of new catalyst system. A lot of common-used transition metal catalysts, such as Cu(I)/Cu(II),

Co(II)/(III) and Mn(II)/(III), whether as oxides [4,5], complexes [6,7], or supported catalysts [8] have been typically investigated in the oxidation process experimentally. However, none of these catalysts have been applied in industry. Consequently, it is necessary to develop more efficient, environment-friendly, easily-separated and easily-industrialized catalysts in cumene oxidation process.

Among the many attempts to find feasible catalysts for cumene oxidation, it is particularly interesting to note that nano-sized carbon materials have attracted much attention, owing to their physicochemical and mechanical property, such as high surface areas, outstanding electron conductivity, corrosion resistance, and thermal stability [9–11]. In addition, from an environmental point of view, carbon materials enable a clean disposal by combustion after a certain life-time, making them attractive alternatives to conventional metal oxide catalysts for a more sustainable petro-chemical production process. Recently, carbon nanotubes have been directly applied as catalysts in the oxidative dehydrogenation (ODH) reactions of alkanes to corresponding alkenes [12–14], catalytic wet air oxidation (CWAO) [15–17], and oxidation of aldehydes [18] and so on. Their excellent catalytic performance has been thought to be relevant to their microstructure and surface functionalities. For example, in the most prominent and high-industrial-relevance ODH reaction, the widely-accepted reaction mechanism is that rich-in-electron diketone-like carbonyl ($\rangle$C=O) groups on the surface of carbon materials are active sites [14]. However, S. Yang found easily-broken carboxylic acid groups on the

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surface of CNTs played an important role in CWAO of phenol [15]. Meanwhile, basis surface was also thought to be responsible for improved catalytic performance in CWAO [16,17]. More recently, carbon materials were found to be active for the direct liquid-phase aerobic oxidation of aromatic hydrocarbon. In our previous work, we proved that pristine carbon nanotubes could directly catalyze the aerobic oxidation of cyclohexane to adipic acid and ethylbenzene to acetophenone, and the surface defects and oxygen functionalities had a negative effect on the activity [19,20]. Jing-He Yang etc. also proved that metal-free graphene-based catalyst was effective for one-step oxidation of benzene to phenol with hydrogen peroxide as the oxidant [21]. However, up to now, it is rarely reported that nanostructured carbon as catalyst for selective oxidation reaction of cumene, and the basic knowledge about carbon catalysis remains limited.

Herein, by using cost-cheap commercial carbon nanotubes as catalyst and oxygen as oxidant, we explored their catalytic activity in the aerobic oxidation of cumene without solvent at atmospheric pressure. The influence of catalyst surface oxygen-containing functional groups on catalytic performance was also discussed. The high reaction activity of cumene oxidation and the recyclability of carbon catalyst make this reaction system attractive for potential industrial application.

2. Experimental

2.1. Preparation of catalysts

The commercial carbon nanotubes (denoted as CNTs, $S_{BET} = 85.3\,m^2\,g^{-1}$, $d = 30$–$50\,nm$) were purchased from Shenzhen Nanotech Port Co. Ltd (NTP). They were stirred to purify in hydrochloric acid or heated to reflux in $9\,mol/L$ HNO_3 for 0.5, 2 and 4 h to introduce oxygen functional groups, then washed with deionized water until pH reached 6–7, and dried in air at 383 K overnight. The obtained materials were denoted as CNTs-HNO$_3$-0.5, CNTs-HNO$_3$-2, and CNTs-HNO$_3$-4, respectively. In addition, CNTs-HNO$_3$-2 samples were subjected to heat treatment in a horizontal tubular quartz furnace with 4 cm inner diameter under argon atmosphere at 873 K or 1173 K for 2 h and then cooled under argon, denoted as CNTs-HNO$_3$-2-873 and CNTs-HNO$_3$-2-1173, respectively [22,23].

2.2. Characterizations

Brunauer-Emmett-Teller (BET) specific surface areas were measured by N_2 adsorption at liquid N_2 temperature in an ASAP 2010 analyzer. Raman spectra were obtained in a LabRAM Aramis micro-Raman spectrometer with an excitation wave-length at 532 nm with $2\,\mu m$ spot size. TEM (transmission electron microscopy) and HRTEM (high resolution transmission electron microscopy) images were obtained with a FEI Tecnai G2 12 microscope operated at 100 kV and a JEOL JEM2010 microscope operated at 200 kV. Specimens for TEM and HRTEM were prepared by ultrasonically suspending the sample in acetone and depositing a drop of the suspension onto a grid. X-ray photoelectron spectroscopy (XPS) analysis was performed in a Kratos Axis ultra (DLD) spectrometer equipped with an Al Kα X-ray source in ultrahigh vacuum (UHV) ($<10^{-10}$ Torr). The binding energies (± 0.2 eV) were referenced to the C1s peak at 284.6 eV. The surfaces of samples were cleaned by heat treatment at 373 K in UHV prior to the measurements.

2.3. Catalytic tests

The liquid oxidation reactions were carried out in a three-necked flask (20 mL), supplied with a magnetic stirrer, reflux condenser and the oil bath. Cumene (10 mL) and catalyst were put into the flask, sonicated for 5 min, and then heated to preconcerted temperature followed by the bubbling of oxygen at a constant flow rate. The main product of cumene oxidation is CHP, the by-products are acetophenone (AP) and 2-benzyl-2-propanol (BP), as shown in Scheme 1. The CHP concentration was determined according to the iodometric method [24]. After the reduction of generated CHP to BP *via* triphenylphosphine reaction [25], the other products in the liquid phase were detected by gas chromatography (an Agilent GC-6820) equipped with a $30\,m \times 0.25\,mm \times 0.25\,\mu m$ HP-5 capillary column and a flame ionization detector (detector temperature 553 K, injector temperature 553 K, and oven temperature 413 K) using toluene as external standard. Cumene conversion (X) and products selectivity (S) were calculated using the following equations (I)–(IV).

$$X = \frac{n_{i,cumene} - n_{f,cumene}}{n_{i,cumene}} \times 100\% \tag{I}$$

$$S_{CHP} = \frac{n_{f,CHP} - n_{i,CHP}}{n_{f,CHP} - n_{i,CHP} + n_{f,BP} + n_{f,AP}} \times 100\% \tag{II}$$

$$S_{BP} = \frac{n_{f,BP}}{n_{f,CHP} - n_{i,BP} + n_{f,BP} + n_{f,AP}} \times 100\% \tag{III}$$

$$S_{AP} = \frac{n_{f,AP}}{n_{f,CHP} - n_{i,CHP} + n_{f,BP} + n_{f,AP}} \times 100\% \tag{IV}$$

where $n_{i,m}$ and $n_{f,m}$, respectively, mean the moles of m in initial reactant and final product.

The thermolysis tests of CHP were conducted according to Ref. [26]. 8 mL acetonitrile and 0.1 g catalyst were added in a flask, sonicated for 5 min and then placed in an oil bath at 353 K. After flushing with N_2 for 5 min, CHP (2 g) was added and the reaction was conducted in a closed system. The unreacted CHP was tested by aforementioned iodometric method.

3. Results and discussion

3.1. The optimization of reaction conditions

Cumene liquid-phase oxidation reaction was operated at atmospheric pressure with oxygen as oxidant with carbon nanotubes as catalyst and no solvent was added. In order to optimize the reaction parameters and provide a basis for further mechanism research, the effects of reaction conditions, including catalyst amount, reaction temperature, oxygen flow rate and reaction time on the catalytic performance were investigated in detail.

The effect of catalyst amount on the catalytic activity of cumene under 353 K was shown in Fig. 1A. The flow rate of O_2 was controlled at $10\,cm^3/min$. In the absence of catalyst, the autoxidation rate of cumene is very slow ($X = 2.7\%$, 8 h). After the addition of 50 mg CNTs, the conversion of cumene increased to 17.8% with an outstanding selectivity of 90.8% to CHP. With the increase of CNTs content, the conversion of cumene also increased. On the contrary, too much catalyst leads to decline in selectivity to CHP. With 200 mg CNTs, the 35.0% conversion of cumene was obtained, whereas the selectivity to CHP obviously decreased to 76.2%. This indicates that CNTs play an important role in cumene oxidation. To get an acceptable selectivity to CHP, 100 mg CNTs under reaction condition was chosen.

The effect of reaction temperature on the catalytic performance of cumene was shown in Fig. 1B. It revealed that cumene oxidation could be well carried out under a rather low temperature as 343 K. The conversion of cumene increased significantly with the reaction temperature increasing. Under 353 K, the selectivity to CHP remained stable value of 88.4%. When the temperature reached 373 K, the selectivity to CHP dropped dramatically possibly due to the accelerated decomposition of CHP. Thus, the reaction