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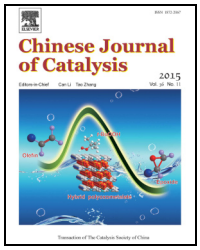

Article

Highly selective production of phenol from benzene over mesoporous silica-supported chromium catalyst: Role of response surface methodology in optimization of operating variables

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ABSTRACT

A Cr/SBA-16 catalyst was prepared using $Cr(NO_3)_3$ as a precursor and mesoporous silica SBA-16 as a support via a simple impregnation method. The catalyst was characterized using wide-angle X-ray diffraction (XRD), low-angle XRD, N_2 adsorption-desorption, transmission electron microscopy, and ultraviolet-visible spectroscopy. The catalyst activity was investigated in the direct hydroxylation of benzene to phenol using H_2O_2 as the oxidant. Various operating variables, namely reaction temperature, reaction time, amount of H_2O_2, and catalyst dosage, were optimized using central composite design combined with response surface methodology (RSM). The results showed that the correlation between the independent parameters and phenol yield was represented by a second-order polynomial model. The high correlation coefficient (R^2), i.e., 0.985, showed that the data predicted using RSM were in good agreement with the experimental results. The optimization results also showed that high selectivity for phenol was achieved at the optimized values of the operating variables: reaction temperature 324 K, reaction time 8 h, H_2O_2 content 3.28 mL, and catalyst dosage 0.09 g. This study showed that RSM was a reliable method for optimizing process variables for benzene hydroxylation to phenol.

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1. Introduction

Phenol is an important chemical intermediate in the manufacture of many petrochemicals, agrochemicals, polymers, and plastics [1,2]. Global production of phenol is mainly performed using the well-known cumene process, but it has disadvantages such as low yields and high energy expenditure, especially in the distillation steps. Moreover, the utility of this process depends on the market demand for the by-product acetone [3]. Because of the commercial importance of producing phenol without any by-products, there is therefore much interest in direct oxidation of benzene to phenol as an alternative route, using various oxidants such as N_2O [4,5], O_2 [6], and H_2O_2 [7]. The use of molecular oxygen is limited, because it leads to destruction of the aromatic ring, therefore the selectivity for phenol decreases. Although N_2O performs well in benzene hydroxylation, deactivation of the catalyst by heavy coke formation is a problem [8]. H_2O_2 is increasingly being used as the oxidant, because it is a green oxidant and the process is simple. Recently, much research has focused on the incorporation of transition metals such as Fe, V, Cu, and Co into various supports to improve the catalytic performance in benzene hydroxylation to phenol [9]. Song et al. [10] reported that a catalyst consisting of VO_2 supported on multiwalled carbon nanotubes gave 23.7%

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benzene conversion and a phenol selectivity of 93.5%. In another study, Fe_3O_4 supported on CMK-3 gave 18% benzene conversion with a phenol selectivity of 92% [11]. It has been reported that V supported on mesoporous carbon nitride (V/*mp*-C_3N_4) gave a phenol yield of 18% with 95.9% phenol selectivity. The catalytic activity of V/*mp*-C_3N_4 is attributed to the high benzene-activation capability of *mp*-C_3N_4 and dispersion of V species [12]. A 21% benzene conversion and 94% phenol selectivity were obtained over CuO/MCM-41 in the hydroxylation of benzene to phenol with H_2O_2 as the oxidant [13]. Kharat et al. [14] used Keggin-type V-substituted molybdophosphoric acid supported on amine-functionalized SBA-15; they achieved 20% benzene conversion and a phenol selectivity of 95%. In a similar study, vanadium oxides supported on mesoporous silica MCM-41 functionalized with 3-aminopropyltrimethoxysilane gave 58.6% benzene conversion and 18.5% phenol selectivity [15].

In recent years, mesoporous silica materials have been successfully used as catalyst supports because of their large uniform pore sizes, large pore volumes, and high surface areas [16–18]. These materials have various structures; SBA-16 has three-dimensional connected channels (cage like) and a cubic structure. These characteristics lead to high mass transfer of reactants. Moreover, its small input of pores prevents metal particle aggregation [19]. A review of the literature on SBA-16-supported metal shows that its activity is appropriate for direct hydroxylation of benzene. Zhu et al. [20] investigated the catalytic hydroxylation of benzene to phenol over VO_x/SBA-16 prepared using an impregnation method; they achieved 13.8% benzene conversion and 97.5% selectivity for phenol. More recently, Co-doped SBA-16, prepared using an evaporation-induced self-assembly method, gave a phenol yield of 28.8% and a phenol selectivity of 96.6% [21]. Cr compounds have also been used for benzene hydroxylation to phenol because of their high initial activities. However, only a few studies in which supported Cr was used as the active catalyst in this reaction have been reported; for example, Cr incorporated into an SAPO-37 framework, and H_2O_2 as the oxidant, gave a benzene conversion of 6% in acetonitrile at 353 K [22]. A phenol yield of 10.3% and a phenol selectivity of 98.4% were obtained over Cr-substituted large-pore zeolite-β [23]. Tagawa et al. [24] investigated the catalytic hydroxylation of benzene to phenol over $K_2Cr_2O_7$ supported on SiO_2, using H_2O_2 as the oxidant; 1.4% benzene conversion was obtained in acetonitrile at room temperature. In another study, Pinnavaia et al. [25] prepared a Cr-substituted MCM-41 catalyst for the hydroxylation of benzene to phenol, and obtained approximately 100% phenol selectivity.

Although some catalysts with adequate performance have been reported, from the industrial perspective, it is essential to explore and prepare new catalysts with high selectivities that can be prepared using simple methods. Benzene oxidation to phenol is a competitive process, because phenol is more active toward oxidation than benzene is, therefore achieving high phenol selectivity without any by-products is still a challenge.

In addition to developing suitable catalyst preparation processes, optimization of the operating variables plays a key role in achieving a good catalytic performance. The published literature shows that parameters such as the amount of H_2O_2, reaction temperature, reaction time, and catalyst dosage have significant effects on the catalytic performance. Previous studies were performed using traditional one-factor-at-a-time approaches to optimize the operating parameters for good catalytic activity [26–31]. Such experimental methods are time consuming and costly, especially if a large number of operating variables need to be considered simultaneously. These methods do not consider interactions among the process variables and result in poor optimum conditions. Statistical techniques such as response surface methodology (RSM), which is a more accurate method, can be used for optimization of a fixed process. RSM is a mixture of mathematical and statistical techniques and can evaluate the effects of process variables and their interactions on response variables [32–34]. We used RSM to statistically optimize the operating parameters in benzene hydroxylation using a minimum number of experiments. To the best of our knowledge, no previous study aimed at the optimization of benzene hydroxylation using RSM has been conducted. Central composite design (CCD) is the most commonly used method for the RSM technique.

In the present study, a Cr/SBA-16 catalyst was synthesized using a simple impregnation method and tested in the hydroxylation of benzene to phenol. X-ray diffraction (XRD), ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), and the Brunauer-Emmett-Teller (BET) method were used for catalyst characterization. The effects of four operating factors, namely the amount of H_2O_2, reaction temperature, reaction time, and catalyst dosage, and their interactions, on the catalytic performance were investigated using CCD coupled with RSM. The yield and phenol selectivity under the optimized conditions were determined. The results showed that Cr supported on mesoporous silica is an effective catalyst for the direct hydroxylation of benzene to phenol using H_2O_2 as the oxidant.

2. Experimental

2.1. Catalyst preparation

Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, M_w = 13600), sodium silicate solution (SiO_2 26%, Na_2O 8%) as a silica source, HNO_3 (65%), $Cr(NO_3)_3{\cdot}9H_2O$, acetonitrile, benzene, H_2O_2 (30%), and toluene were purchased from the Merck Company.

Mesoporous silica SBA-16 with minor modifications was prepared using the method described in the literature [35]. Pluronic F127 (14.1 g) was dissolved in HNO_3 (65%, 144 mL) and deionized water (900 mL). The solution was stirred at 303 K. Sodium silicate solution (62.4 g) was added and the reaction mixture was stirred at 300 r/min for 3 h at 343 K. The product was kept at 373 K for 24 h. The surfactant was extracted using ethanol and HCl (2 mol/L), and the obtained solid was calcined at 823 K for 5 h.

The catalyst was prepared via an impregnation method as follows. SBA-16 (1 g) was dipped in a solution obtained by dissolving $Cr(NO_3)_3{\cdot}9H_2O$ (0.92 g) in water (50 mL). The solvent

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