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Preparation and characterization of Mesopoous VO_x/SBA-16 and their application for the direct catalytic hydroxylation of benzene to phenol

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ABSTRACT

Vanadium oxide supported on mesoporous SBA-16 (VO_x/SBA-16) catalysts have been prepared by the impregnation method and characterized by small-angle XRD, wide-angle XRD, TEM, N_2-physisorption, DRUV–vis, Raman spectrum and H_2-TPR. The VO_x/SBA-16 catalysts retained the cubic cage-like pore structure of SBA-16. The dispersion and the nature of the vanadium species depend strongly on the V amount. At V loading of less than 3.6 wt%, isolated tetrahedral VO_4 is the main existence species that is highly dispersed in the pores of the support SBA-16. With the increase in V loading, the aggregation of isolated tetrahedral VO_4 species occurred to form polymerized VO_4 units. When the V loading was above 5.5 wt%, nanostructured V_2O_5 crystallites were formed besides aggregation of polymerized VO_4 units. VO_x/SBA-16 with 7.3 wt% V showed excellent activity for the hydroxylation of benzene. The effect of reaction time, temperature and the amount of catalyst was investigated over VO_x/SBA-16 (7.3 wt%) catalyst. The highest phenol yield and turnover number were 13.8% and 32.4, respectively, which were attributed to the formation of highly dispersed VO_4 species and polymerized VO_4 units. The TON and yield of phenol also increase in the presence of the V_2O_5 crystallites but its selectivity decreases.

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1. Introduction

Phenol is an important chemical material, which is the major source of phenol resins, fibers, caprolactam, adipic acid, dyestuffs and medicine [1,2]. The worldwide production of phenol is mostly obtained by a well-known three-step process called the cumene process, which produces acetone as a byproduct in equimolar amount and restricts the industrial production of phenol [3]. Accordingly, the direct hydroxylation of benzene to phenol has attracted much attention in terms of an environment-friendly green process and economic efficiency. Studies on direct oxidation of benzene to phenol with various oxidants, such as nitrous oxide [4,5], hydrogen peroxide [6–9], molecular oxygen [10,11] or a mixture of oxygen and hydrogen [12] have been reported. The direct hydroxylation of benzene with hydrogen peroxide as oxidant is widely attempted as a green process at the mild conditions [7–9,13], which would be one of the most useful processes in the future [14]. However, it is a challenge to the higher yield and selectivity of phenol in the process of hydroxylation of benzene, since phenol is more reactive toward oxidation than benzene itself, substantial formation of over-oxygenated byproducts (benzoquinone, catechol, hydroquinone and tars) also occurs [15].

Compounds of vanadium, due to their highly feasible reactivity and remarkable stability, have been utilized as efficient catalysts for a variety of oxidation reactions, especially for the hydroxylation of alkanes and aromatic compounds [15–26]. There were several reports about the benzene to phenol reaction over vanadium-containing catalysts, such as VO_x species anchored on amorphous siliceous microporous mixed oxides and MCM catalysts [15,16], VO_x species supported on SBA-15 [10] and clay [18], vanadium-substituted polyoxometalates [19–23] and phosphomolybdates [24] and sodium metavanadate [25]. Lemke et al. have used vanadium supported on mesoporous siliceous structures of MCM-type, silica of Aerosol® 300-type and amorphous siliceous microporous mixed oxides as catalysts for the direct oxidation of benzene to phenol. Best results of hydroxylation of benzene were obtained on a low vanadium-containing VO_x/SiO_2 catalyst. However, the selectivity of phenol was below 60% when the conversion of benzene was higher than 10% [15]. Lee et al. reported catalytic hydroxylation of benzene over vanadium-containing molecular sieves (MCM-41, MCM-48, BEA and MFI). V-MCM-41 showed the highest activity where the selectivity of phenol was 93%, but the conversion of benzene was only 1.39% [26]. Vanadium-substituted polyoxometalates (polyoxomolybdates [20–22], polyoxotungstates [23]) and phosphomolybdates [24] catalysts on benzene hydroxyla-

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tion with hydrogen peroxide have been well investigated. These catalysts showed a high stability and gave a steady performance by being reused in oxidation recycle in which the phenol yield was up to 10% with phenol selectivity about 85%. However, from the synthetic viewpoint, selectivity site-substituted vanadium (V) polyoxometalates have been very difficult to prepare.

Previous studies have shown that the catalytic performance of supported vanadia catalysts crucially depends on the structure and distribution of the surface vanadium oxide species [16,26–32]. To a certain extent, the effect of the different supports on the dispersed surface vanadium oxide species is important. Mesoporous materials as catalyst support has been attracted much attention since the development of the M41S family [33,34] because of their large surface area, uniform pore size, big pore volume and well-ordered structure. In the family of mesoporous materials, SBA-15 and SBA-16 materials exhibit thicker pore walls and higher hydrothermal stability than M41S [35]. In particular, SBA-16 which has three-dimensional channel and cubic (*Im3m*) cage structured mesoporous silica structure [36,37] can be more favorable for mass transfer kinetics than the unidirectional pore system of other hexagonal mesoporous phases. Studies of vanadium supported on SBA-15 have been extensively reported for applications in the literature [10,29,38–40]. However, relatively few papers have been published on SBA-16 as support [41]. Recently, researchers have paid more attention to SBA-16 and its application in catalysis based on its structure character [42–47].

In this paper, a series of VO_x/SBA-16 catalysts were prepared by impregnation method for the first time, and their catalytic performance was tested for the benzene hydroxylation. The vanadium species and its dispersion on the surface of VO_x/SBA-16 catalysts were discussed. The relationship between vanadium species and catalytic activity was also investigated.

2. Experimental

2.1. Catalyst preparation

2.1.1. SBA-16 support synthesis

The SBA-16 silica was prepared under acidic condition, using Pluronic F127 as a structure-directing agent and TEOS as the silica source [35]. The molar composition of the reaction mixture was 1 TEOS: 7.14×10^{-3} F127: 3×10^{-2} HCl: 2.8 H_2O: 21.74-43.48 EtOH, and the homogeneous solution was stirred vigorously for 1 h at 70 °C. After ageing overnight at 50 °C, the product was dried in air at 80 °C. Finally, the product was calcined under ambient atmosphere at 550 °C with a heating rate of 1 °C min^{-1} and an isothermal period of 4 h.

2.1.2. VO_x/SBA-16 by impregnation

VO_x/SBA-16 catalysts with different V loading were prepared as follows: an amount of aqueous solution of NH_4VO_3 (0.010 $molL^{-1}$) at the appropriate contents was placed in vessel of a vacuum rotary evaporator [15]. 1 g of support SBA-16 was added, and the slurry was briefly evacuated to remove residual air from the pores. Afterwards, water was evaporated at 55 °C. The solid was dried at 80 °C for 12 h and calcined at 400 °C with a heating rate of 1 °C min^{-1} in air for 4 h, a light yellow powder was obtained.

2.2. Catalyst characterization

Small-angle X-ray diffraction (SAXRD) measurements were carried out on a Rigaku D/Max-2400X X-ray diffractometer Cu Kα (λ = 1.5406 Å) radiation (40 kV and 200 mA).

Wide-angle X-ray diffraction measurements (WAXRD) were performed on a Rigaku D/Max-IIIB Cu Kα (λ = 1.5406 Å) radiation (40 kV and 20 mA) and Ni filter. The patterns were collected from $10 < 2\theta < 60$.

The nitrogen physisorption experiments were performed at −196 °C on a Quantachrome Autosorb-1 automated gas adsorption system. The sample was outgassed at 300 °C for 4 h before the measurement. The pore size distribution was calculated from the desorption branch of the isotherm using the BJH method.

Transmission electron microscopy (TEM) measurements were taken on a FEI Tecnai G2 S-Twin electron microscope operating at 200 kV. High resolution transmission electron microscopy (HRTEM) measurements were carried out using a FEI Tecnai F30 electron microscope operating at 300 kV.

The diffuse reflectance ultraviolet–visible (DRUV–vis) spectroscopy were recorded on a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere attachment (ISR-2200). $BaSO_4$ was the reference material. The sample was heated at 300 °C for 0.5 h before test.

The Raman spectrum studies were carried out using a HR800 (JY) spectrometer with a Ar^+ ion laser (458 nm). The laser was operated at a power level of 20 mW measured at the sample using a power meter (Coherent).

Temperature-programmed reduction with hydrogen (H_2-TPR) of the catalysts was measured in a conventional self-made apparatus equipped with thermal conductivity detector (TCD). 30 mg of the catalyst (40–60 mesh) was mounted in a quartz tube and calcined in He flow (20 mL min^{-1}) at 300 °C for 1 h with the aim to remove the physisorbed substances while 10 mg V_2O_5 was used as a comparison test. The sample was reduced with a 5% H_2/N_2 mixture (20 cm^3 min^{-1}) by being heated to 650 °C at a rate of 10 °C min^{-1}.

2.3. Catalytic evaluation

Hydroxylation of benzene with 30% aq. H_2O_2 was run in a 30 mL double layer glass reactor equipped with a reflux condenser, a magnetic stirrer and a superthermostat. The standard condition was as follows: 6.0–20 mg of catalyst, 0.30 mL (3.36 mmol) of benzene and 5 mL of CH_3CN were added. After the mixture was heated to the desired temperature (50–70 °C), 0.8–1.5 mL (7.83–17.62 mmol) of 30% aq. H_2O_2 was added, and reaction was carried out under these conditions for 1–8 h.

The liquid products were analyzed by gas chromatograph (SP-2100 China, FID detector) with an OV-1 capillary column (30 m × 0.25 mm × 0.33 μm). Phenol, benzoquinone, catechol, and hydroquinone in the products were further identified by GC–MS (Agilent 6890/5973N). The quantitative analysis of the mixture was determined by the calibration curves, using toluene as the internal standard.

3. Results and discussion

3.1. Pore structure of catalysts

Fig. 1 shows the small-angle X-ray diffraction (SAXRD) patterns of VO_x/SBA-16 catalysts with different amounts of V loading. All the patterns were similar to each other and showed a very strong (1 1 0) reflection (0.97° 2θ) of the cubic (*Im3m*) structure with a lattice constant of a_0 = 12.8 nm [42], which indicated that the uniform pore structure of SBA-16 was well retained and the vanadium species may be highly dispersed on the surface of SBA-16 mesoporous silicas. In addition, it is obviously observed that the patterns of VO_x/SBA-16 composites showed a decrease in peak intensity with increasing vanadia loading. This is probably due to the difference on the scattering contrasts of the pores and the walls and the formation of nanostructured VO_x species inside the pores of SBA-16 [48,49]. For these SBA-16 samples (2 0 0) and (2 1 1) reflections,

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