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Selective oxidation of benzyl alcohol through eco-friendly processes using mesoporous V-MCM-41, Fe-MCM-41 and Co-MCM-41 materials

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ABSTRACT

MCM-41 nanostructured materials modified with Vanadium, Iron and Cobalt were synthesized by a hydrothermal method. The catalysts were characterized by XRD, UV–Vis-DR, ICP-OES and N_2 adsorption. All the catalysts showed good structural order and high specific areas; however the lowest value in these parameters, corresponding to the Co-M(60) sample, could be due to the higher presence of oxide species determined by UV–Vis-DR. These mesoporous metalosilicates were evaluated in the liquid phase oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) using H_2O_2 as oxidant. Results showed that V-M(60) had better catalytic performance than Fe-M(60) and Co-M(60) exhibiting high TON (1100 mol/mol V), selectivity to BzH (95%) and 31.7% yield at 7 h under optimized reaction conditions. The main reason for the enhanced catalytic performance was attributed to the well dispersion of vanadium species in the framework which could be considered as the active sites for the benzyl alcohol oxidation reaction. At the same time, the catalyst could be recovered and effectively reused during three cycles without a significant loss in its activity and selectivity.

1. Introduction

The selective oxidation of alcohols into the corresponding carbonyl compounds plays a vital role in the organic synthesis since the corresponding aldehyde; ketone or carboxylic derivatives serve as important and versatile intermediates for the synthesis of various chemicals, vitamins, drugs and fragrances [1–10]. Benzaldehyde (BzH) is a typical product of benzyl alcohol (BzOH) oxidation and a chief raw material in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives. It is also widely used as an intermediate for the manufacturing of odorants, drugs, dyestuffs and agrochemicals [11–13]. It is traditionally produced by hydrolysis of benzal chloride and by oxidation of toluene [14,15]. However, BzH produced from hydrolysis of benzal chloride has often some unfavorable aspects such as containing traces of chlorine impurities and generating copious waste. The oxidation of toluene is usually carried out in organic solvents which are environmentally undesirable [16]. The most common methods of oxidation use stoichiometric amounts of inorganic oxygen donors such as manganese or chromium for this transformation [17–20]. However, these oxidants are corrosive, expensive, they have low atom efficiency and they generate big amounts of heavy-metal waste [21,22]. The increasing demand for environment-conscious chemical processes and the need of chlorine-free BzH have impelled many researchers to investigate green technologies [23–36]. Several studies have been reported on the catalytic oxidation of BzOH to BzH with different catalysts and oxidants. Supported noble metal catalysts such as Pd/SiO_2 [37], Au/SBA-15 [38], $Au\text{-}Pd/TiO_2$ [39] and Ag/SBA-15 [40] have been used in the aerobic oxidation of BzOH to BzH. Unfortunately, high costs generally limit the large scale use of noble metal based catalysts. In addition, copper and gold nanoparticules supported on $\gamma\text{-}Al_2O_3$ [41], CoMgAl hydrotalcites [42] and vanadium phosphate [43] were also evaluated as catalysts using *tert*-butyl hydro peroxide. On the other hand, hydrogen peroxide is an environmentally friendly oxidant for liquid phase oxidations because it provides high content of active oxygen species and water is the only byproduct. Many efforts have been devoted to the selective oxidation of benzyl alcohol by H_2O_2 employing different solid catalysts. Cang et al. have achieved high turnover numbers TON (125.8) using imidaziolium-$FeCl_3$ ionic liquid immobilized onto SBA-15 and H_2O_2 as oxidant in a H_2O_2/BzOH molar ratio of 4/1 [44]. Jia et al. reported a conversion of benzyl alcohol and a selectivity to benzaldehyde about 53% and 86% respectively on alkali treated ZSM-5 with H_2O_2 [45]. Epiclhlorydrin-modified Fe_3O_4 microspheres were employed by Xiago et al. obtaining a conversion of benzyl alcohol of 34.7% and 93% of selectivity to benzaldehyde [46].

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MCM-41 is a member of the M41S family with particular characteristics such as large pore volume, uniform distribution in pore size and high specific surface area. These characteristics make them interesting materials to be employed specially in oxidation reactions that involve large molecules and required high selectivity. Nevertheless, some modification of the pure siliceous material (Si-M) is necessary due to its lack of catalytic activity. Recent research has indicated that Si-M modified with transition metals could be potentially used as an effective heterogeneous catalyst with custom properties in eco-compatible processes. Particularly, it is of great interest to develop catalysts based on available transition metals commonly used by living beings such as iron, cobalt, molybdenum [47] which are not environmental hazardous. The incorporation of metallic ions such as Ti, V, Fe and Co in the network structure of molecular sieves has showed good results for the liquid phase oxidation of organic molecules. Thus, Ti-MCM-41 has been used to catalyze the oxidation of various organic compounds e.g. allylic alcohols, olefins and terpenes with H_2O_2 [48–50]. V- MCM-41 has also been well studied in the oxidation of cyclic compounds, olefins and bulkier olefins with H_2O_2 as oxidant [51–54]. In addition, Fe-MCM-41 and Co-MCM-41 have been shown to be active in the oxidation of styrene, cyclohexene and ethyl benzene [55–57]. However, few studies have reported the use of mesoporous materials modified with transition metals in the selective oxidation of benzyl alcohol to benzaldehyde. Trakarnpruk reported a benzyl alcohol conversion of about 78% and a selectivity to benzaldehyde of 67% using Mn- and Co-substituted polyoxotungstates on MCM-41 and a molar ratio H_2O_2/BzOH 3/1 in a Parr reactor [58].

In this work, a series of MCM modified with Co, V and Fe have been prepared by a hydrothermal method. These materials were then characterized and used to catalyze the oxidation of BzOH employing H_2O_2 as oxidant. The effect of the concentration of H_2O_2 on the catalytic performance has been investigated. Special attention was paid to the reaction product selectivity as a function of the concentration of H_2O_2, and the catalytic behavior was related to the metal species observed by UV–Vis-DR.

2. Experimental

2.1. Catalyst synthesis

The mesoporous metalosilicates were prepared by hydrothermal synthesis using cetyltrimethylammonium bromide (CTAB) dissolved in ethanol as a template, tetraethoxisilane (TEOS) as a Si source and VO$(SO_4)\cdot H_2O$, $Fe(NO_3)_3\cdot 9H_2O$ or $Co(NO_3)_2\cdot 6H_2O$ as metal sources. Tetraethylammonium hydroxide 20 wt% aqueous solution (TEAOH) was added in order to adjust the gel pH to 11. The catalysts were synthesized from gel of molar composition Si/M = 60 (where M indicates V, Fe or Co), TEAOH/Si = 0.30, CTAB/Si = 0.30, H_2O/Si = 60. In a typical synthesis, TEOS and the metal source were stirred for 30 min, the CTAB solution and 70% of the TEAOH were added and the stirring continued for 3 h. Finally, the remaining TEAOH and the water were further added dropwise to the milky solution which was then heated at 80 °C for 30 min to remove the ethanol used in the solution and produced in the hydrolysis of TEOS. This gel was transferred into a Teflon-lined stainless-steel autoclave and kept in an oven at 100 °C for 4 days under autogenous pressure. Mesoporous silicate (Si-M) was prepared by the same method but without the addition of a metal source [59].

The final solids were then filtered, washed with distilled water and dried at 60 °C overnight. To remove the template, the samples were heated (heating rate of 2 °C min^{-1}) under N_2 flow up to 500 °C maintaining this temperature for 6 h and subsequently calcined at 500 °C under air flow for 6 h. The obtained materials were named M-M(60) where the first M indicates the metal (V, Fe or Co) and 60 is the Si/M ratio used in the synthesis gel.

2.2. Physicochemical characterization

The metal content in the obtained solids was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) after digestion of the solids using a VISTA-MPX CCP Simultaneous ICP-OES Varian. XRD patterns were obtained in a PANalytical ŹPert PRO diffractometer. The UV–vis Diffuse Reflectance (UV–Vis DR) spectra were obtained in a Jasco V650 spectrometer. The specific surfaces were measured using a Micromeritics Pulse Chemisorb 2700. Samples were previously dried using a N_2 flux for 3 h at 350 °C. The specific surface was determined by the Brunauer-Emmett-Teller (BET) method. A Micromeritic ChemiSorb 2720 was used when Temperature-Programmed Reduction (TPR) experiments were necessary. For this, the samples were heated from 298 to 900 °C at a rate of 10 °C min^{-1} in the presence of 5% H_2/N_2 gas mixture (20 mL/min STP), and the reduction reaction was monitored by the H_2 consumption with a built-in thermal conductivity detector (TCD).

2.3. Catalytic activity

Benzyl alcohol (BzOH) oxidation reactions with H_2O_2 were carried out in a glass reactor with a magnetic stirrer and a reflux condenser, immersed in a thermally controlled bath at 70 °C for 7 h. In a typical reaction, benzyl alcohol (Fluka > 95%) (9.11 mmol), was stirred with hydrogen peroxide (H_2O_2, Riedel de Haën, 35 wt.% in water) (2.28 mmol), using acetonitrile (AcN, Sintorgan, 99.5%) (91.15 mmol) as solvent and M-M(60) as catalyst (100 mg). Reaction progress was followed taking samples at different times by a lateral tabulation without opening the reactor. Liquid samples were immediately filtered and analyzed by gas chromatography equipped with FID detector (HP-1 capillary column) and identified by comparison with known standards. The percentage of each component in the reaction mixture was calculated by using the method of area normalization employing response factors. The BzOH conversion was defined as the ratio of converted species to the initial moles, Eq. (1). Taking into account that BzOH was found in excess in comparison to H_2O_2, the BzOH conversion was also calculated as a percentage of the maximum possible conversion (mol% of max.), that is the maximum amount of the oxygenated products that could be obtained if all H_2O_2 was consumed, Eq. (2). The total conversion of H_2O_2 was measured by iodometric titration, while selectivity to products, yield and turnover numbers (TON) were calculated according to Eqs. (3)–(5):

$$\text{Conversion BzOH}(\%) = \frac{\text{total moles of product}}{\text{initial moles BzOH}} \times 100 \quad (1)$$

$$\text{Conversion BzOH}(\text{mol\%of max.}) = \frac{\text{total moles of product}}{\text{initial moles BzOH}\times\frac{\text{initial moles } H_2O_2}{\text{initial moles BzOH}}} \times 100 \quad (2)$$

$$\text{Selectivity}_i(\%) = \frac{\text{moles of product}_i}{\text{total moles of product}} \times 100 \quad (3)$$

$$\text{Yield}_i(\%) = \text{Conversion BzOH}(\%) \times \text{Selectivity}_i \quad (4)$$

$$\text{TON} = \frac{\text{moles of BzOH converted}}{\text{moles of metal in the catalyst}} \times 100 \quad (5)$$

3. Results and discussion

3.1. Catalyst characterization

Physicochemical parameters and XRD patterns of the pure Si-M and metal modified M-M(60) samples by direct incorporation of the metal source in the synthesis gel are shown in Table 1 and Fig. 1. As it can be observed, for pure Si-M, the sample exhibited a strong peak at