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Research Paper

Highly dispersed cobalt nanoparticles supported on a mesoporous Al$_2$O$_3$: An efficient and recyclable catalyst for aerobic oxidation of alcohols in aqueous media

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A B S T R A C T

In this paper the catalytic performance of a Co/Al$_2$O$_3$ nanocatalyst is investigated on aerobic oxidation of alcohols in a water media at reflux condition. The catalyst was synthesized via a co-precipitation method and characterized by XRD, BET surface area, atomic absorption spectroscopy, SEM, TEM and EDS analysis. The catalyst exhibited a high efficiency on the oxidation of various alcohols into their corresponding carbonyl compounds at relatively short reaction time. Also the results exhibit a consistant activity after several consecutive runs of reaction and regeneration that demonstrates the stability and recyclability of the Co/Al$_2$O$_3$ nanocatalyst.

1. Introduction

The selective oxidation of alcohols into aldehydes and ketones plays a key role in synthesis of organic materials, so, a lot of catalytic systems employing different oxidants have been developed for these reactions [1–3]. Aerobic oxidation of alcohols using inexpensive and non-toxic air or O$_2$ as the exclusive terminal oxidant has continued to achieve much attention in recent years. Moreover, such catalytic systems are industrially attractive alternatives for sustainable alcohol oxidation [4,5].

Various catalytic systems including metal ions and metal nanoparticles such as nanogold, ruthenium, copper, cobalt, palladium and vanadium have been investigated as catalysts for aerobic oxidation of alcohols [6–23]. However, many of these catalytic systems are performed in aromatics or halogenated hydrocarbon solvents. Therefore, introduction of an efficient catalyst for these reactions with an acceptable reactivity in green solvents like water is indispensable.

Metallic nanoparticles supported on different metal oxides play a significant role in nanoscience and nanotechnology. They have many applications such as inoptics, electronics, sensors and heterogeneous catalysis [24]. From the perspective of heterogeneous catalysis, the metallic supported nanoparticles can provide an optimal architecture for bifunctional catalytic systems [25]. In these catalysts, the nanoparticles on the catalyst surface contribute as an active site for the reaction, and the support act as a substrate to stabilize the whole structure and provide a high surface area for the reaction. Preparation of a catalyst with an appropriate interaction between support and nanoparticles can either tailor active sites with an enhanced electronic states for the reaction, and optimized size of nanoparticles [26].

The performance of different alumina-supported cobalt catalysts were investigated in the literature [27–32]. A particular aspect of these catalysts is their partial reduction in the catalytic reaction condition and the possibility of cobalt ions to insert in the aluminum oxides lattice to form a spinel structure that results in an exceptional reducibility and catalysit activity [33].

In this paper, in continuation of our research on the performance of Cu-, Au- and bimetal-nanocatalysts on aerobic oxidation reactions [34–38], we investigated the preparation, characterization

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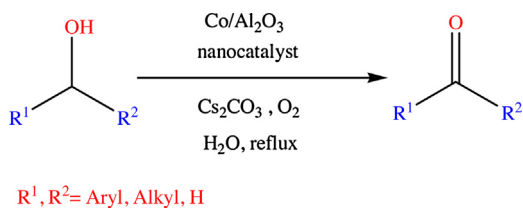
Scheme 1. Aerobic oxidation of alcohols on Co/Al_2O_3 nanocatalyst.

and application of a highly dispersed cobalt nanocatalyst supported on a mesoporous Al_2O_3 structure, as an efficient recyclable catalyst for the aerobic oxidation of alcohols in water under reflux condition (Scheme 1).

2. Experimental

2.1. General

Chemicals were purchased from Merck chemical companies. Products were characterized by comparison of their spectroscopic data (^{1}HNMR, ^{13}CNMR and IR) and physical properties with those reported in the literature. All yields refer to isolated products.

2.2. Catalyst preparation

The 10.0 wt% Co supported on Al_2O_3 support were synthesized by a co-precipitation method. An aqueous solution of 0.5 M NaOH was added drop-wise into a mixture of 0.5 M $Co(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ solution under vigorous stirring at 50 °C. The resulted solution was aged at pH of 9.0 for 1 h at the same temperature, then filtered and washed with plenty of warm deionized water to remove the interfering ions. The precipitatnt was dried overnight at 100 °C and calcined in air at 450 °C for 4 h. Also, a batch of Al_2O_3 substrate without Co was prepared by the same method for the supplementary analysis.

2.3. Catalyst characterization

The specific surface area of the catalyst was analyzed by N_2 adsorption-desorption using BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The samples were purged with N_2 gas for 3 h at 300 °C using VacPrep 061 degas system (Micrometrics).

The XRD analysis was performed using an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-Kα monochromatized radiation source and a Ni filter in the range 2θ = 5–100°, in order to study the structure and crystallinity of the catalysts. The average crystallite size of the sample was determined based on Scherrer equation. A flame atomic absorption spectrophotometer (GBC 906AA) was used to determine the cobalt content of the catalyst.

Scanning electron microscopy (SEM) was performed by a JEOL JSM-6500F instrument, equipped with an EDS analytical system, in order to study the morphology of the prepared catalysts and the presence of different components of the catalyst. Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2100 (200 kV) microscope with an EDS analytical system. The powdered samples were ultrasonically dispersed in ethanol and the obtained suspensions were deposited on to a thin carbon film supported on a copper micro-grid. For each catalyst, about 200 cobalt nanoparticles were measured in order to determine average particle size and its distribution.

2.4. General procedure

A heterogonous mixture of alcohol (1 mmol), Cs_2CO_3 (0.5 mmol) and Co/Al_2O_3 nanocatalyst (0.05 g) in water was stirred under oxygen atmosphere in a slurry reactor connected to an O_2 tube for atmosphere control at total reflux condition for an appropriate time. After reaction completion, catalyst was recovered by filtration, then washed with hot ethanol (2×5 mL), and dried for consecutive reaction runs. The filtrate was quenched with 2 M HCl aqueous solution, extracted with EtOAc three times and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel obtained the pure products.

2.5. Kinetic experiment

A set of experiment was carried out to evaluate the kinetic order of the first and second alcohol's oxidation. To perform this part of research, the oxidation of 2-phenylethylealcohol (0.1 mmol mL^{-1}) and 2-propanol (0.1 mmol mL^{-1}) were separately investigated. In this case, after the reaction was initiated, 0.1 mL of the reaction mixture (10 mL) was removed at 5-min intervals, and diluted with double-distilled water up to 1 mL. Subsequently, 0.5 μL of this analytical sample was injected into the gas chromatography-flame ionization detector (GC-FID). The concentration of alcohol in the analytical sample, was determined by a GC-FID method calibrated in the range of 0.02–0.1 mmol mL^{-1}. However, the dilution factor was considered and the remaining concentration of alcohol was obtained at each interval.

2.6. Gas chromatography analysis

A gas chromatograph (Varian GC CP3800) with a split/splitless injection system and a flame ionization detector was used for separation and determination of 2-phenylethylealcohol and 2-propanol in aqua matrixes. Ultra-pure Nitrogen (99.999%, Fajr Co., Iran) was used as the carrier gas (5 mL min^{-1}). The injection port was held at 120 and 230 °C for 2-propanol and 2-phenylethylealcohol, respectively. Separation was carried out on a Wax column, 30 m × 0.32 mm capillary column with a 0.5 μm stationary film thickness. The oven temperature was programmed as follows: for 2-propanol; initial 60 °C (held 1 min), from 80 to 130 °C at the rate of 10 °C min^{-1}, and for 2-phenylethylealcohol; initial 90 °C (held 1 min), from 90 to 230 at the rate of 20 °C min^{-1}, and held at this temperature. The total time for one GC run was 10 min for 2-propanol and 15 min for 2- phenylethylealcohol. The FID temperature was maintained at

300 °C, hydrogen gas was generated by the hydrogen generator (OPGU–2200s, Shimadzu) for FID and was used at a flow of 30 mL min^{-1}. The flow of zero air (99.999, Sabalan Co, Tehran, Iran) was 300 mL min^{-1} and the split ratio was selected as 1:10. In this condition, the retention time was approximately 6 and 11 min for 2-propanol and 2-phenylethylalchol, respectively.

3. Results and discussion

3.1. Catalyst characterization results

The XRD pattern of Co/Al_2O_3 catalyst are shown in Fig. 1. The catalyst shows diffraction peaks at 2θ = 37.60, 45.79, 66.76 and 85.02°, which are corresponded to (110), (111), (211) and (300) planes of γ-Al_2O_3 (code No. 01-1303). Also, the diffraction peaks at 19.04, 31.35, 36.94, 44.92, 59.51, 65.41 and 77.56° are attributed to (111), (220), (311), (400), (511), (440) and (533) planes of cubic Co_3O_4 (code No. 01-074-1657), respectively. Moreover, the presence of a distinc peak at 94.38° which is corresponded to (731) plane of $CoAl_2O_4$ (code No. 03-0896) demonstrates the incorporation of Co