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Preparation of CoOx/magenium silicate for the liquid oxidation of benzyl alcohol

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ABSTRACT

CoO_x/magenium silicate catalysts are obtained though precipitation and calcination method. The prepared solids were analyzed by XRD, BET, EDS... Cobalt(II) ions supported-magnesium silicate catalysts expressed as effective catalysts for selective oxidation of benzyl alcohol using tert-butyl hydroperoxide as an oxidizing agent. The experimental results showed very high selectivity to the benzaldehyde product at benzyl alcohol conversion of 18-25%.

Introduction

The oxidation reaction of alcohols to aldehydes using catalysts is an important step in the laboratory as well as in the industry [1,2]. Benzaldehyde is one of the consequential intermediates to synthesize many fine organic compounds. In trandition, benzaldehyde is mainly made by two practical methods: benzyl chloride hydrolysis and toluene oxidation [2,3]. However, these methods have many drawbacks such as contaminating chlorides and low selectivity towards benzaldehyde. Therefore, the catalytic oxidation of benzyl alcohol is a good choice to surpass these obstacles [4-6]. Typical catalysts are widely used for the oxidation of benzyl alcohol consisting of transition metal oxides loaded on the carriers as Au-Au-Pd/ceria-zirconia [5], Pd/SBA-15 [6], CoO_x/MnO_x [7]... Magnesium silicate, a soft white clay mineral known as sepiolite, has the theoretical unit cell formula of $(Si_{12}Mg_8O_{30})(OH_2)_4.8H_2O$ [8]. Sepiolite is usually consisted of nanofibers and has large surface area and good sorptive property. Hence, sepiolite is subjected to be a good carrier for loading of metal oxides in the heterogeneous catalysis [4,7,8]. In the present work, CoOx particles were distributed on sepiolite to be a promising catalyst candidate for the oxidation of benzyl alcohol. The liquid- phase reaction were performed in the solvent-free conditions according to the green chemistry principles.

Experimental

Preparation and characterization

CoOx/seopiolite catalysts were prepared by the precipitation of cobalt nitrate in basic environment [8]. In experiment, cobalt(II)nitrare (Sigmal-Aldrich, 99%) and sepiolite (Sigmal-Aldrich, 98%) were mixed in a 250 mL flask containing 100 mL of distilled water and then precipitated by the addition of NaOH 0.05 M solution under constant stirring for 2 hrs at room temperature. The samples were then separated by filtration and dried at 70°C overnight. The obtained solids were ground and calcinated at 410°C in air for 4 hrs, and naturally cooled to room temperature.

X-ray diffraction (XRD) patterns were examined on a D8 Advance-Bruker instruments using CuK_α radiation (λ = 1.59 Å). Nitrogen physisorption was measured at -196°C on an Autochem II 2920 (USA). Energy-dispersive spectroscopy (EDS) data were obtained on a Varian Vista Ax X-ray energy dispersive spectroscope.

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Oxidation of benzyl alcohol

The solvent-free oxidation of benzyl alcohol was taken place under atmospheric pressure. A typical run for the oxidation benzyl alcohol was as follow: CoOx/sepiolite (0.2 g) was charged into a three-necked flask contaminating 3 mL of benzyl alcohol with a reflux condenser under stirring. The mixture was heated to the targeted temperature and then *tert*-butyl hydrogen peroxide (TBHP, 70%) was added into the flask. At the end of the reaction, the mixture was cooled down to ambient and then the catalyst was filtered out. The obtained filtrate was quantitatively determined by a GC-MS (HP-6890).

Results and Discussion

Characterization of CoO_x/sepiolites

Figure 1 represents the XRD pattern of sepiolite and x wt.% Co/sepiolite (x = 3, 5, 7) samples. It can be easily seen that the peak at 2θ = 7.3 - 7.5° is firmly characteristics for sepiolite phase. The diffraction lines appearing at 2θ = 31.2 36.8; 44.8; 59.2 and 65.1, are corresponding to (220), (311), (400), (511) and (440) crystal plans of Co_3O_4, respectively [5,7-9]. Thus, these results substantiate the presence of Co_3O_4 particles on sepiolite carrier [4,7,10].

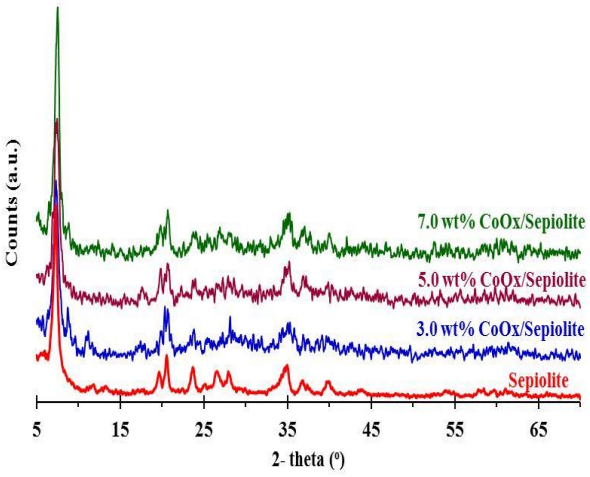

Figure 1: XRD patterns for sepiolite and cobalt oxide/sepiolite samples

The changes in surface areas and pore volumes between sepiolite and CoO_x loaded-catalysts were investigated by the nitrogen physical adsorption/desorption technique. The results are shown that the BET surface area of CoOx/sepiolite sample gives a higher value of 189.2 m^2/g, as compared to 166.2 m^2/g for sepiolite parent. In this case, during the precipitation of Co(II) ions on the sepiolite surface in light basic media accompanied by washing steps, the impurities in the sepiolite were easily dissolved and leached out of the pore-like structural system, thus making sepiolite channels and tunnels cleaner. Therefore, the cleaner pores have enhanced specific surface area of the catalysts. The surface area is one of the factors that control the activity of the catalysts [7,10,11].

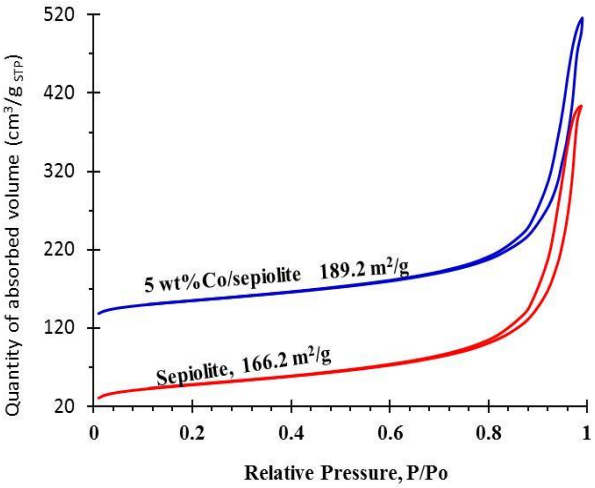

Figure 2: Nitrogen absorption-desorption isotherms of sepiolite and cobalt oxide/sepiolite samples

The elemental composition of a representative sample (5 wt.% CoOx/sepiolite) analyzed by EDS technique was displayed in Fig. 3. Interestingly, this EDS spectrum shows the strong signals of Si, Mg, Al, O, which are belonging to the sepiolite composition. Besides, the peak of Co clearly appears at 6.84 and 7.45 eV.

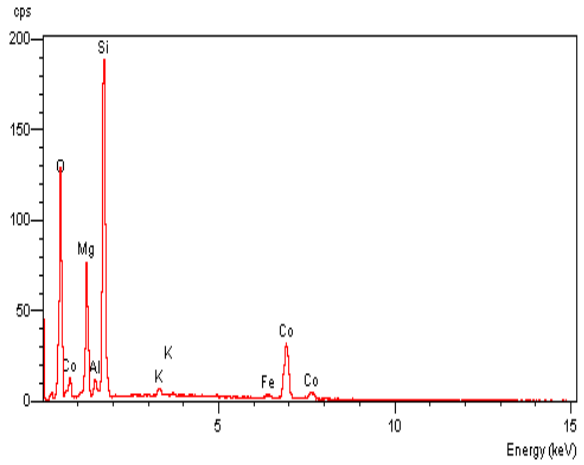

Figure 3: EDS spectrum of 5.0 wt.% CoOx/sepiolite

Oxidation of benzyl alcohol over CoO_x/sepiolites

CoOx/magnesium silicate (MgSiO) samples were tested for benzyl alcohol oxidayion under selected conditions using TBHP as an oxidant. The product mixture is composed of benzaldehyde, benzoic acid and ester... In order to investigate the role of cobalt ions in the oxidation of benzyl alcohol, a reaction series has been carried out using *x* wt.% CoOx/magnesium silicates (x = 0, 3, 5, 7) as heterogeneous catalysts. Figure 4 displays an observable variation in catalytic acitivty of the catalysts with the amount of CoOx-loadings.

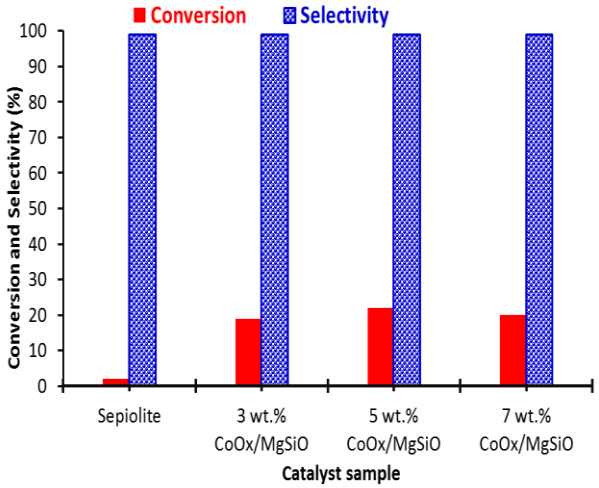

Figure 4: Catalytic activity of CoOx/sepiolite (MgSiO) in the oxidation of benzyl alcohol (0.2 g of catalyst, BzOH : TBHP = 1 : 1.5, 60°C, 4 hrs).

It can be seen that sepiolite shows a negligible activity in the oxidation of benzyl alcohol, but the benzyl alcohol conversion significantly improves as CoOx dispersed on sepiolite (Fig. 4). This indicates an important role of CoOx component in the oxidation of benzyl alcohol with TBHB. As compared with previeous results [4,8-10], sepiolite-loaded CoOx system is more active than MnOx, CuO, NiO-supported catalysts under the same oxidation conditions. Furthermore, CoOx/sepiolite is selective production for benzaldehyde product with a high selectivity degree (Fig. 4) due to a high dispersions of tiny CoOx particles in on the sepiolite open channels. Moreover, Figure 4 expresses that the conversion of benzyl alcohol reaches a maximium value at 5.0 wt.% CoOx/sepiolite. In detail, colbat was loaded on sepiolite from 3–5 wt.%, the benzyl alcohol conversion gradually increases, but then the decreases over 7.0 wt.% CoOx/magnesium silicate. This observation was interpreted by the agglomerate of cobalt oxide particles [6,8,10]. The formation of larger particles of CoOx would remarkably reduce the contacting probability between active cobalt ion sites and reactants, and therefore prevent benzyl alcohol from conversion into the corresponding aldehyde [3,5,10]. Therefore, 5.0 wt.% CoOx/sepiolite sample was selected for the next survey.

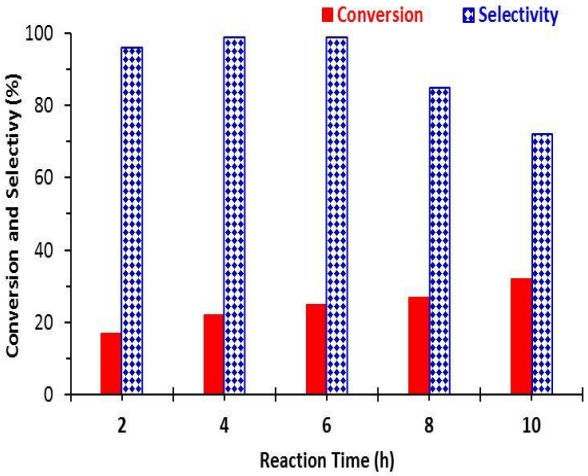

Figure 5: Reaction time versus benzyl alcohol conversion and benzaldehyde selectivity in the oxidation of benzyl alcohol over 5 wt.% CoOx/sepiolite sample (60°C, BzOH : TBHP = 1 : 1.5)

Effect of reaction time on the catalytic activity over 5.0 wt.% CoOx/sepiolite is shown in Figure 5. It could be seen that the conversion of benzyl alcohol augments continuously until 32% as time was kept from 2 to 10 hrs. However, the selectivity towards benzaldehyde declines significantly from 99% at 6 hrs to 72% after 10 hrs, due to the occurrence of deep oxidation of benzaldehyde to benzoic acid and benzoate under reported conditions [5,11,12].

Conclusions

Cobalt oxide supported magnesium silicate catalysts were prepared by the precipitation method. Under preparation, external surface area of CoOx/sepiolites was higher than that of sepiolite parent. Cobalt oxide particles were highly dispersed on the channels of sepiolite aand served as an active component for the oxidation of benzyl alcohol to benzaldehyde. Evaluation of catalytic activity revealed that the CoOx/magnesium silicate exhibited a good ability to conversion of benzyl alcohol into benzaldehyde. The catalytic activity and product selectivity depend on the cobalt loading amounts and reaction time. The conversion of benzyl alcohol over 5.0 wt.% CoOx/sepiolite catalyst at 60°C for 4 hrs is about 22% while the selectivity to benzaldehyde remains about 90-98%.

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