



Photocatalytic Oxidation of 2-Butanol over $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ Spinel Catalyst

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Abstract

The catalyst $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ was prepared by co precipitation methods in different ratios (40: 60, 50: 50, 60: 40,70:30) for the mixed oxides respectively, these ratios were calcinated at 550 °C for 4hours and characterized by using powder X-Ray Diffraction, Fourier transform Infrared spectroscopy. These catalytic activity were investigated in photo oxidation of 2-butanol by using 0.2g.of $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ in different times (0, 15,30,45,60 and 75 min). The result showed that the best ratio gives high activity was 40:60 at 25 °C. The resultant 2-butanone was measured spectrophotometrically at λ maximum=285nm and estimate this concentration depending on the calibration curve of 2-butanone.

Keywords: Cobalt Oxide, Photooxidation of 2-butanol.

Introduction

The heterogeneous photocatalysis reactions is an effective method ,that it was used to production of the Future fuel-hydrogen [1,2], removal of the environmental pollutants[3,4] and oxidation of alcohols to corresponding carbonyl compounds by using the irradiation light with catalyst [5,6]. The energy of UV or visible light is to be sufficient to induce and excite the semiconductor material to produce electron/hole (e^-/h^+) pair, and assist to oxidation of pollutants and splitting of water to produce hydrogen [7].

To increasing the efficiency of semiconductor in photocatalytic system, can be supported over material has a high surface area, which improves of its surface area and resistivity of thermal influence, such sintering effect, these supporter usually be a ceramic oxides such as CaO and Al_2O_3 [8]. Co_3O_4 has a spinel structure in which there are two oxidation state 2+ and 3+, the divalent occupy the octahedral sites and the trivalent occupy the octahedral sites in the structure of AB_2O_4 spinel $(\text{CoO})_T(\text{Co}_2\text{O}_3)_O$ [9,10].

Many of semiconductors oxides are the most efficiency and suitability in the photocatalysis reactions for oxidation of different aromatic and aliphatic alcohols and

production of hydrogen [11, 13], and removal of toxic organic compounds [14, 15]. The aim of this work is to prepare $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ catalyst in different ratios and use in photo oxidation of 2-butanol and choose the best condition for the photocatalytic reaction.

Experimental

Preparation of Catalyst

The co precipitation method was used to prepare the spinel catalyst $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ in different ratios to obtained of their bicarbonates in basic media by using sodium bicarbonate with heating to 60-70 °C for 1.5 hrs.And then left the mixture with stirring after complete the precipitated process, and heating at 60-70 °C for further period .After that dried the precipitate and calcinated at 550 °C for 4 hours

Fourier Transform Infrared Spectroscopy (FT-IR)

The surface of catalyst ratios were studied by using Fourier Transform Infrared Spectroscopy (FTIR), Perkin Elminer Spectrophotometer Company. FT-IR spectra were recorded in the range from 4000-400 cm^{-1} ; the sample was mixed with KBr and

compressed to form a KBr disk, to be ready to examination.

X-ray Diffraction Technique

The catalyst was investigated by using X-ray diffraction analysis via using the instrument (XRD6000, Shimadzu, Japan), with CuK α radiation ($\lambda=1.542 \text{ \AA}$, 40 KV, 30 mA), in the range of 2θ equal to 10-80 degrees.

Photocatalytic Oxidation of 2-butanol

The prepared catalyst was used to photo oxidation of 2-butanol (purity 99 % supplied from BDH company) in different time (0, 15,30,45,60 and 75) min at 25° by suspended of 0.2g. Of catalyst in (30) mL of alcohol (0.01 molar) in each experiments separately. All experiments were done by using a homemade photo cell as in Figure 1.

The low pressure mercury lamp (150) watt (type TQ150 Z2 supplied by Karl Kolb company) which intensity equal to $(0.93 \cdot 10^{-7})$ Einstein $L^{-1}Sec^{-1}$ was used as a UV-light source to irradiate the reaction mixture [16, 17]. 2 cm^3 of reaction sample were withdrawn periodically after 30 min, and separate the solid catalyst by centrifuging the reaction sample to obtained for the supernatant liquid, then measuring the absorbance at ($\lambda=285 \text{ nm}$) by using UV-visible spectrophotometer (UV-1650 PC supplied from Shimadzu company). The concentration of 2-butanone yield is pursued depending on the calibration curve of 2-butanone, which was obtained by plotting of absorbance of different concentration of 2-butanone (0.0005, 0.001, 0.005, 0.01 molar) against the absorbance at $\lambda_{max.} = 285 \text{ nm}$ as in Figure 2.

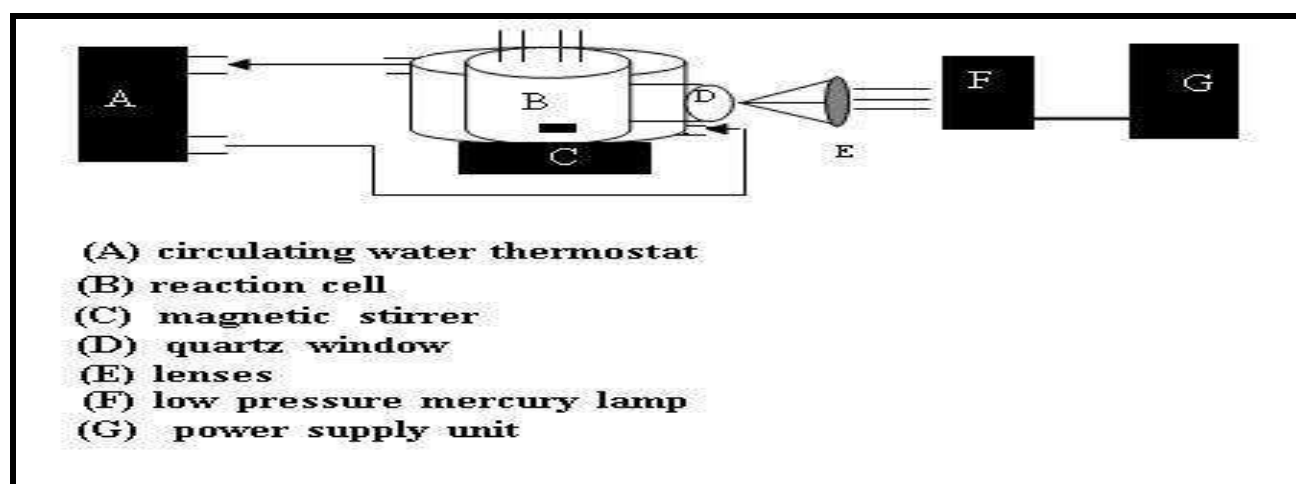


Figure1: The photocatalytic oxidation reaction system

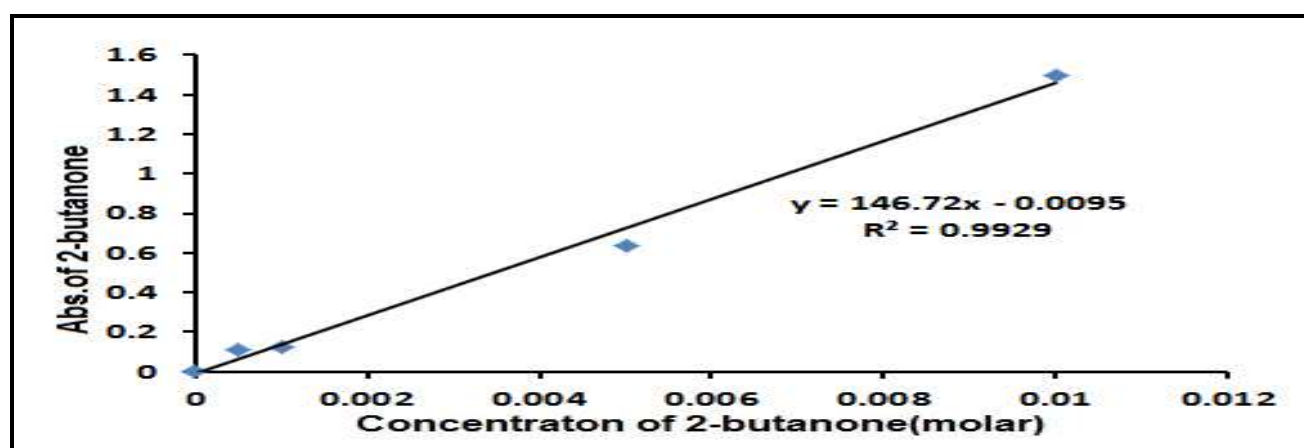


Fig.2: The calibration curve of 2-butanone

Results and Discussion

Fourier Transform infrared Spectroscopy (FT-IR)

The infrared spectrum of catalyst is shown in Figures 3. The appearance of vibrational band at $557-580 \text{ cm}^{-1}$ due to $Co^{III}-O$ bond in the

octahedral sites, the band at $600-660$ due to $Co^{II}-O$ in tetrahedral sites [18]. Vibrational band at $523-567$ due to Al_2O_3 [19]. The band at the stretching vibrational band in the position of 1650 and $3350-3470 \text{ cm}^{-1}$ for the surface hydroxyl group and adsorbed water [20].

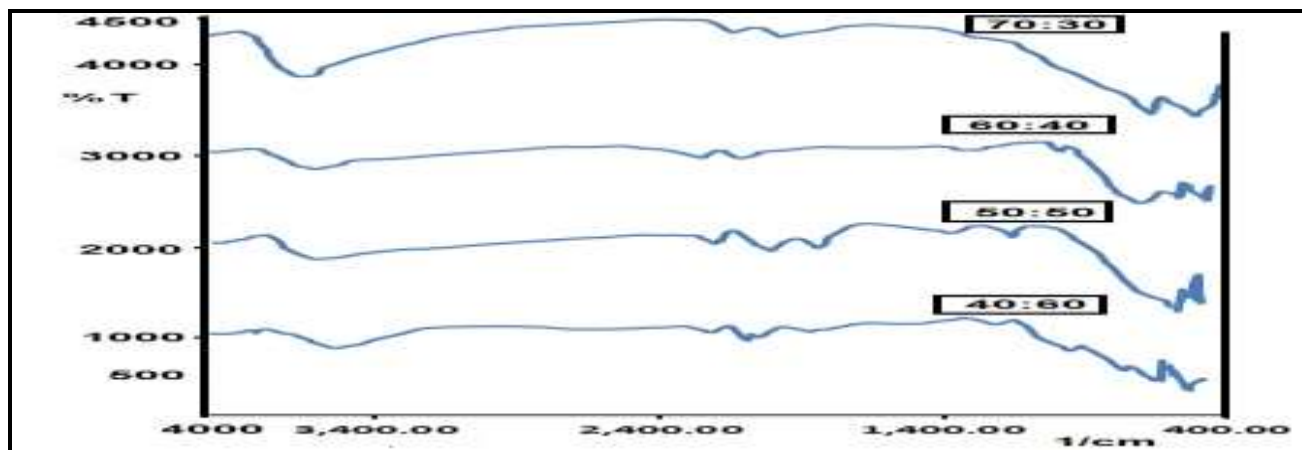


Fig.3: FT-IR spectrum of different ratios of $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ Catalyst

X-Rays Diffraction

From the comparison between XRD data for supporting cobalt oxide on aluminium oxide with the Joint Committee on Powder Diffraction Standards (JCPDS), can be seen that the diffraction angles and main peaks of these oxides were obtained for desired

catalyst, and observed some deviation in these positions and intensities, this deviation is due to the interaction between oxides in the prepared catalysts. Aluminum oxide diffraction peaks are less intense because they are less crystallized and tend to be amorphously [21] as shown in Table 1 and Figure4.

Table 1: XRD diffraction angles and relative intensities of the prepared different ratios of $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ catalyst

Diffraction angle	Relative Intensity I ^o	Oxide
29.32	37	Co_3O_4
31.29	11	Co_3O_4
32.95	64	Al_2O_3
35.9	11	Al_2O_3
36.43	100	Co_3O_4
36.92	12	Al_2O_3
38.83	16	Al_2O_3
44.79	22	Co_3O_4
51.83	14	Al_2O_3
56.8	09	Al_2O_3
59.01	22	Co_3O_4

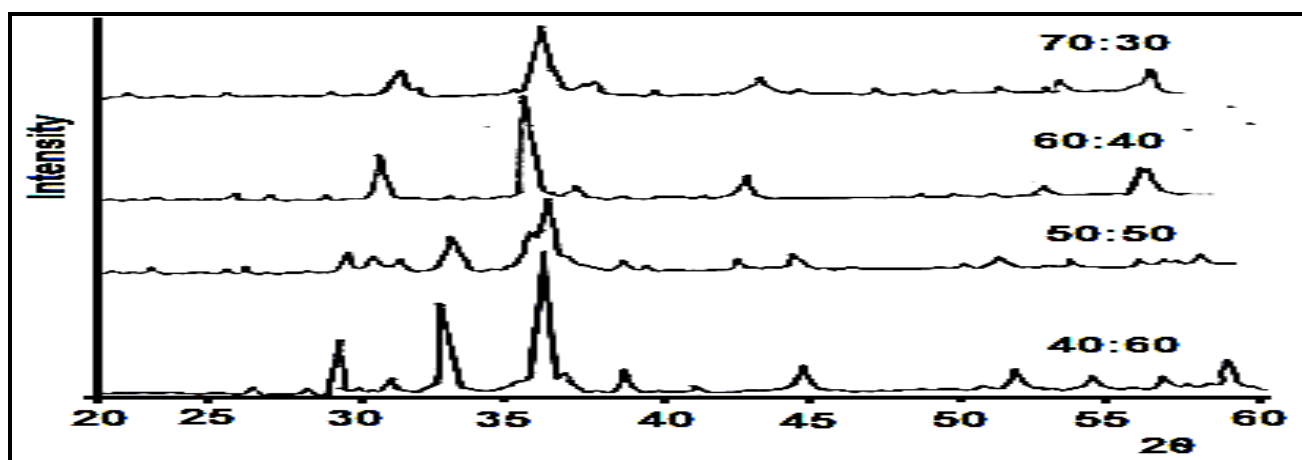


Fig.4: X-ray diffraction patterns of different ratios of $\text{Co}_3\text{O}_4\text{-Al}_2\text{O}_3$ catalyst

Photo-oxidation of 2-butanol

The results of photocatalytic oxidation of 2-butanol by using 0.2 g of catalyst showed

that the best ratio of the prepared catalyst was 40:60, which gives a high 2-butanone yield as in Fig.5.

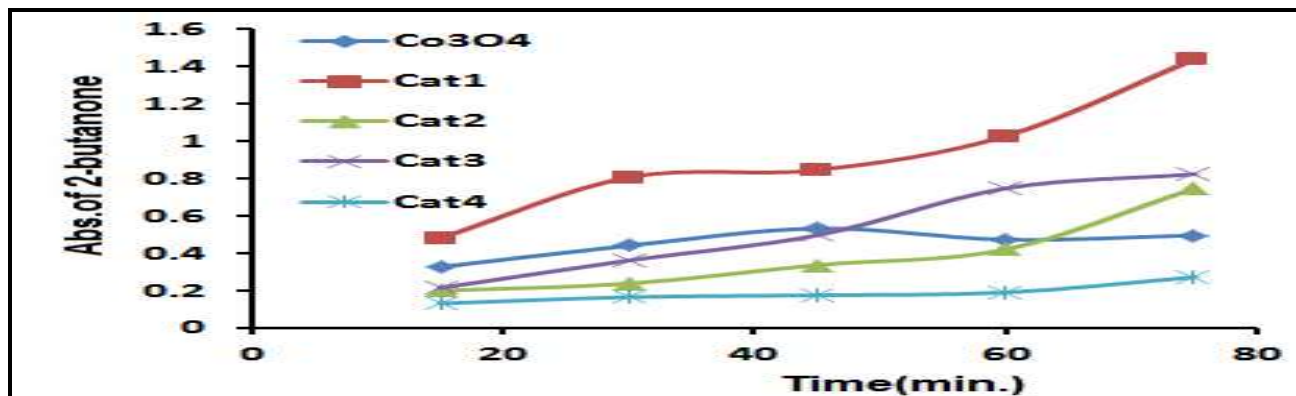
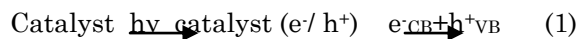


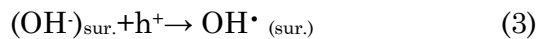
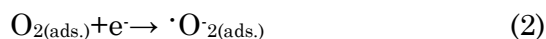
Fig.5:2-butanone absorbance by using different ratios of Co₃O₄-Al₂O₃ Catalyst at different time (min.)

Suggested Mechanism of the Photocatalytic Oxidation of 2-butanone Over the Prepared Catalyst

The semiconductor absorbs the light and produce (e⁻, h⁺) as follow [22]:



The adsorbed oxygen (O₂) ads. On the catalyst surface trapped the photogenerated electron and the hydroxyl group of the surface (OH)_{sur.} trapped the photo hole [23]:



Hydroxyl radical plays a main role in the reactions on the surface of the photocatalyst [24, 25]

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