

Surface Characterization and Catalytic Activity for Alumina-Supported Cobalt Acetate

Somia M. Abad-Elwahad^{1,*}, Ali F. Bukhzam², Gamal A. H. Mekhemer³

¹Chemistry Department, Faculty of Science, El-Marj University, Benghazi, Libya

²Chemistry Department, Faculty of Science University, Benghazi, Libya

³Chemistry Department, Faculty of science Minia University, El-Minia, Egypt

Abstract Supported cobalt oxide samples were prepared by wet impregnation, using alumina gel and alumina as support materials and aqueous cobalt acetate tetrahydrate as the impregnating solution. Prior to application, the support materials were ground to $\leq 200 \mu\text{m}$. The impregnation solution was prepared by dissolving a calculated amount of the precursors CoA of the required loads 3, 5, 10 and 15 wt % CoOx in the final supported oxide materials in a suitable volume of distilled water (25 cc/g support). The catalysts characterized by different technique like X-ray diffractometry, Ex-situ fourier transform infrared spectroscopy. XRD and Ex-situ FTIR spectroscopic analyses of the supported catalysts were performed to get more information about the cobalt oxides loading up to 15 wt% exist as high intensity were results cobalt acetate suggested three bands indicated to formation of the cobalt (II) oxide. The catalytic activity results on the decomposition of Hydrogen peroxide on cobalt acetate suggested that the activity increased with increasing loading levels. Up to however we observe the following descending on catalytic activity order: $\text{CoAlO}_A > \text{CoAl}_A$.

Keywords Characterization, Cobalt oxide and the catalytic activity results on the decomposition of Hydrogen peroxide

1. Introduction

There are two types of chemical interactions may occur depending on the nature of the transition metal oxide and also the preparation conditions, one leading to the formation of a 'surface' metal aluminate spinel form and the other to the segregation of stable oxides [1, 2]. The chemical and textural properties of the support influence the catalytic activity and selectivity of Cobalt nitrate and cobalt acetate catalysts via their modification on the reducibility and dispersion of cobalt or the formation of well fined phases. The synthesis of highly dispersed Cobalt acetate and cobalt nitrate catalysts requires strong interactions between the support and the Cobalt acetate and cobalt nitrate as precursor, but in turn such strong interactions generally lower the reducibility of such precursors [3, 4].

Accordingly metal oxides used in the field of heterogeneous catalysis, both as catalysts and as supports for the so-called monolayer-type catalysts. In such applications the performance is determined by parameters like bulk metal oxide, surface area, the surface oxide structure and surface acidity [5, 6-8]. Also metal oxides must have high stabilities as well as high surface areas under conditions of their use both as catalysts and as support

materials [9, 10]. Metal oxides containing transition metal ions are versatile materials which have received much attention in both science and engineering technology. They provide several technical applications, such as chemical sensors, heterogeneous catalysts and ion conductors. Among these materials, metal oxides having the spinel-type AB_2O_4 structure are often utilized as model systems due to their structural features which facilitate tailoring of relevant properties [11]. Cobalt oxide is one of the versatile materials among the transition metal oxides.

Besides cobalt oxide supported on alumina catalysts are quite promising, among metal oxide supported catalysts, for the catalytic combustion of the volatile organic compounds (VOCs) [12]. A variety of supports are used to prepare supported cobalt oxide catalysts depending on the properties required; however the bulk of the literature is concerned with high surface area oxide supports [13].

Also cobalt oxides, both unsupported and supported on different oxide support materials (including alumina), have proven their high catalytic activity in the field of air pollution control of CO [14-16] and organic pollutants from effluent streams. It has been found that the obtained system has a high catalytic activity in some oxidation reactions, carried out in an aqueous and in a gaseous phase [17]. These changes could be normally accompanied by possible changes in surface and catalytic activity of the doped catalytic systems. Other physicochemical properties, such as thermal stability and oxidation state of solid catalysts could be modified by the doping process [18]. Supported

* Corresponding author:

somiakajo@yahoo.com (Somia M. Abad-Elwahad)

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metal oxides frequently have better catalytic properties than the pure oxide components. In particular, it has been found that mixed oxides can develop very strong surface acidity even when the pure oxide components do not show [4, 19-23].

2. Experimental

2.1. Materials

Thcobalt(II)acetate tetrahydrate (CoA), $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$, MERCK, used as a precursor for supported and unsupported CoOX catalysts aluminium hydroxide $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, dry gel was purchased from SURECHEM Products LTD (SCP, England), used as supplied and high surface area of γ -alumina was obtained by calcinations of alumina gel (SCP) at 870 K for 3 h, in static atmosphere of air. Hydrogen peroxide H_2O_2 : ARJHDTM Guangdong Guanghua Chemical Factory CO., Ltd. Shantou, Guangdong, 515021. China, used as probe molecules to investigate the catalytic properties of the catalysts. Bi-distilled water: was employed, whenever water was needed.

2.2. Techniques

2.2.1. XRD

XRD is a technique used for the identification of the bulk structure of macro-crystalline materials, which is used on measurement of structure-sensitive high energy X-ray radiation. X-ray powder diffractograms were recorded, using Ni-filtered $\text{CuK}\alpha$ - radiation ($\lambda = 1.54056 \text{ \AA}$); on a JSX – 60 PA Jeol X-ray spectrometer. The generator at 35 Kv and 20 mA, and the diffractometer at 2θ diverging and receiving slits and at a scan rate of 20 mm/min . The sample ground to a particle size less than 44μ and packed into the wall of a sample holder, and then mounted in a horizontal position. Diffraction patterns (I/I_0 vis. d-spacing (\AA)) derived from the powder diffractograms were matched with relevant ASTM-standard patterns. Crystallite sizing (Dhkl) was carried out using the line broadening technique in conjunction with Scherrer's formula:

$$D_{hkl} = 0.9 \lambda / B_{hkl} \cdot \cos\theta \quad (1)$$

Where, B_{hkl} is the width at half peak maximum in radians, λ is the incident wavelength ($\lambda = 1.54051 \text{ \AA}$) and θ is the diffraction angle.

2.2.2. Ex-situ FT-IR Spectra

Ex-situ FT-IR spectra of supports, unsupported and supported catalysts were taken at frequency range $4000\text{--}400 \text{ cm}^{-1}$. This was done at a resolution of 4 cm^{-1} using a model Genesis-II FT-IR Mattson Fourier-transform infrared spectrometer (USA) and an online PC with win first Lite (V 1.02) software for spectra acquisition and handling. The spectra were taken for thin ($>20 \text{ mg/cm}$) lightly loaded ($< 1\text{-Wt.}\%$) wafer of KBr-supported test samples. About

1–2 mg of the catalyst as a fine powder was mixed well with spectroscopy pure KBr powder and was finally grinded in agate mortar.

2.2.3. Catalytic Decomposition of Hydrogen Peroxide

The catalytic activity was determined in solution. H_2O_2 decomposition was used to calculate the catalytic alumina supported cobalt oxide catalysts. The reaction was carried out at room temperatures to explore the catalytic activity of test catalysts towards H_2O_2 decomposition.

3. Results and Discussion

3.1. XRD

XRD diffractograms of pure alumina and alumina supported cobalt oxide prepared from cobalt acetate at different loading levels are shown in Figs.1 and 2, respectively. The diffraction pattern exhibited by 3CoAlA (Fig.1) which exhibit a weak peaks for cobalt oxide (Co_3O_4) of a size ($D = 12.3 \pm 1 \text{ nm}$, Table 2). These peaks grow stronger in the pattern of 15CoAlA, thus indicating formation of more Co_3O_4 and/or CoAl_2O_4 particles of larger size ($D = 22.1 \pm 1 \text{ nm}$, Table 2). It is obvious that Co_3O_4 and/or CoAl_2O_4 particles established in these catalysts. Diffractograms obtained for CoAlOA catalysts prepared from crystalline oxide (xCoAlOA series) at different loading levels are displayed in Fig.2. XRD patterns of these catalysts reflected the same structure of xCoAlA. The difference is the high crystalline of these catalysts more than xCoAlA. The particle sizes of these catalysts increase with increasing the loading levels up to 15 wt % of CoOx. Also, the particle size of Co_3O_4 and/or CoAl_2O_4 in these catalysts are lower than the Co_3O_4 and/or CoAl_2O_4 in the catalyst prepared from crystalline alumina.

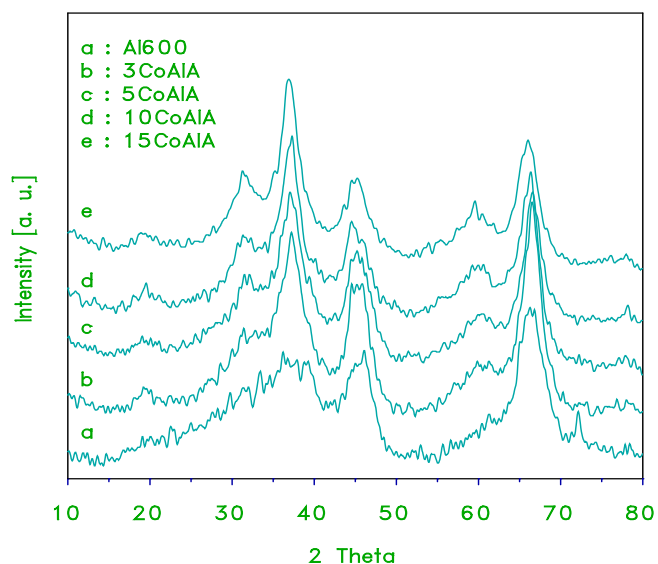


Figure 1. XRD patterns obtained for alumina and the indicated set of alumina-supported cobalt oxide (xCoAlA) catalysts prepared from cobalt acetate and alumina gel used as a support

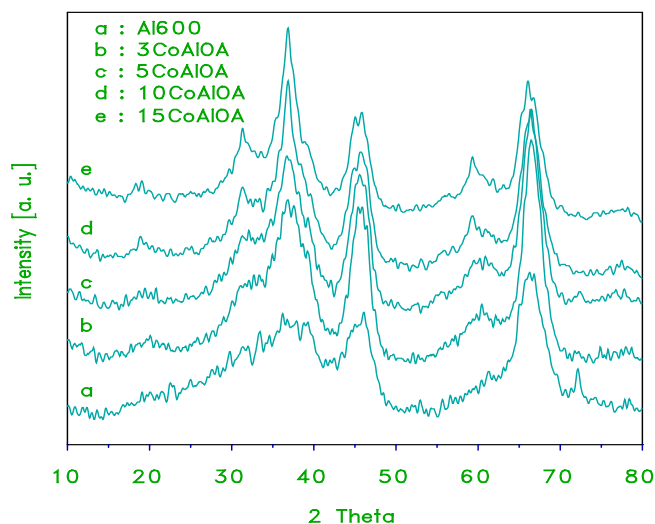


Figure 2. XRD patterns obtained for alumina and the indicated set of alumina-supported cobalt oxide ($x\text{CoAlOA}$) catalysts prepared from cobalt acetate and crystalline alumina used as a support

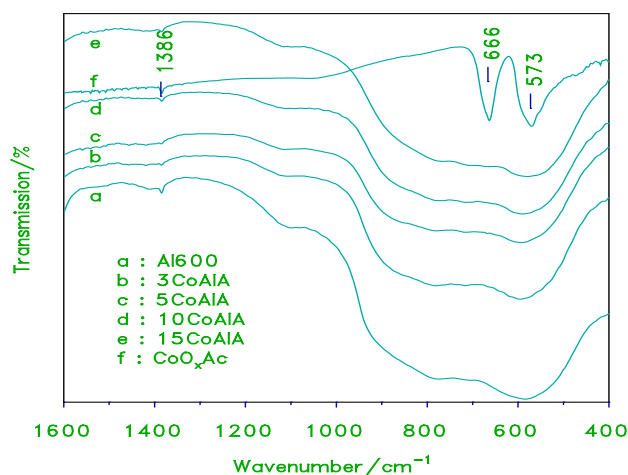


Figure 3. FT-IR transmission spectra obtained for cobalt oxide, crystalline alumina and the indicated set of alumina supported cobalt oxide prepared from acetate $x\text{CoAlA}$ catalysts

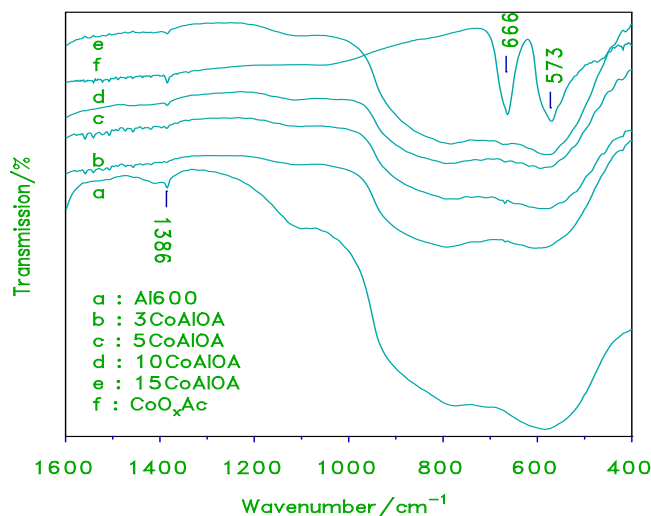


Figure 4. FT-IR transmission spectra obtained for cobalt oxide, crystalline alumina and the indicated set of alumina supported cobalt oxide prepared from acetate $x\text{CoAlOA}$ catalysts

3.2. Ex-situ FTIR Spectra Cobalt Oxide Catalyst

The IR spectra of alumina supported cobalt oxide prepared from cobalt acetate used as a precursor $x\text{CoAlA}$ and $x\text{CoAlOA}$ catalysts are shown in Figs.3 and 4. The spectrum of cobalt oxide prepared from decomposition of cobalt acetate at 870 K for 3 h (Fig.3), displays two strong bands at 666, 573 and another weak band at 470 cm^{-1} . These bands are characteristic to Co_3O_4 and/or CoAl_2O_4 [10, 20]. IR spectra of alumina supported cobalt oxide prepared from cobalt acetate display similar three bands, the intensities of these vibration bands increase with increasing the loading level of cobalt oxide due to the increase in the crystallinity of Co_3O_4 .

3.3. Catalytic Activity

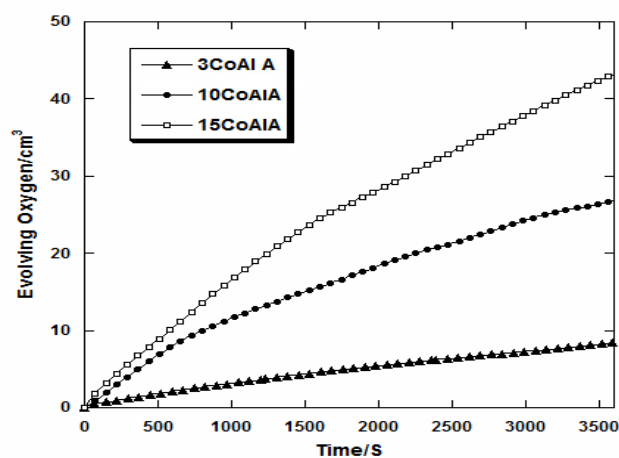


Figure 5. VO_2 -t plots constructed for H_2O_2 decomposition at RT on the indicated alumina supported cobalt oxide catalysts

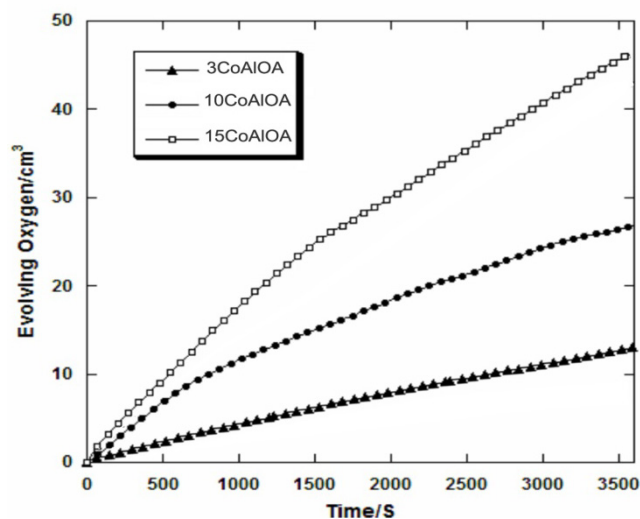


Figure 6. VO_2 -t plots constructed for H_2O_2 decomposition at RT on the indicated alumina supported cobalt oxide catalysts

The catalytic decomposition of H_2O_2 was studied at RT over pure and alumina supported cobalt oxide catalysts prepared from cobalt acetate at different loading level ($x\text{CoAlA}$ and $x\text{CoAlOA}$). Figs.5 and 6 show the decomposition of H_2O_2 on $x\text{CoAlA}$ and $x\text{CoAlOA}$ catalysts,

respectively. Fig.5 display increasing the activity of the catalysts towards decomposition of H_2O_2 at RT with increasing the loading level of cobalt oxide on alumina. Zero-order kinetics were observed at low loading level (3CoAlA) and First-order kinetics were observed at high loading level (10 and 15 CoAlA). Inspection of Fig.6 revealed that the activity is increased with increasing the loading level similar to CoAlA catalysts. The activity of xCoAlOA is higher than the activity of xCoAlA is due to the formation of active sites Co_3O_4 on xCoAlOA more than on xCoAlA. These results are agreement with the results obtained from XRD of the supported cobalt oxide catalysts, which shows a sharp increase in intensities of the XRD patterns of Co_3O_4 phase.

The observed significant increase in the catalytic activity of xCoAlOA catalysts than xCoAlA is due to the higher formation of crystalline Co_3O_4 phase on xCoAlOA catalysts than on xCoAlA.

4. Conclusions

XRD and IR results of cobalt oxide show the formation of crystalline Co_3O_4 and/or $CoAl_2O_4$ increasing the loading level of cobalt oxide (up to 15 wt%).

The above presented and discussed results may help drawing the following conclusions:

- 1 – The activity of all samples increase with increasing the loading level of cobalt oxides.
- 2 – The low loading levels catalysts display zero-order kinetics but higher loading levels catalysts show first-order kinetics.
- 3 – The higher activity of the catalysts is due to the formation of active sites Co_3O_4 . In contrast, the lower activity of catalysts is due to the formation of cobalt aluminate (higher loading level).

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