Effects of Calcination Temperatures on The Catalytic Activities of Alumina Supported Cobalt and Chromium Catalysts

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Research Article

Effects of Calcination Temperatures on The Catalytic Activities of Alumina Supported Cobalt and Chromium Catalysts

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Abstract

Catalysts properties are important for catalytic reactions. The interaction between support and metal in a catalyst is resulted from catalyst preparation. In this study, gamma-alumina (Al_2O_3) supported cobalt (Co) and chromium (Cr) catalysts were prepared by impregnation method and calcined at two different temperatures, they are 400 °C for 4 hours and 800 °C for 4 hours. The resulted catalysts contained 10 wt.% of metal and denoted as Co/Al_2O_3(400), Co/$Al_2O_3$3(800), Cr/Al_2O_3(400), and Cr/Al_2O_3(800) catalysts. The surface and state of the catalysts were examined by using x-ray diffraction (XRD), x-ray photoelectron spectrometer (XPS) and transmission electron microscopy (TEM). The XRD result reveals that strong interaction between Co and Al_2O_3 due to a formation of higher cobalt oxide. The XRD result further indicates aggregation and strong support metal interaction between Co and Al_2O_3 during calcination. On the other hand, TEM result showed that large Co particle was observed on Al_2O_3. The Cr/Al_2O_3 catalysts were characterized by using XPS. The XPS results showed that Cr/Al_2O_3(800) catalyst was dominated by Cr^{6+} species at binding energy 579.04 eV, indicating high dispersion of Cr on Al_2O_3. Moreover, Cr metal particle was not observed on XRD and TEM image. All the characterization results provide information that the impregnated metal on Al_2O_3 showed different properties. Co metal particle tends to be more oxidized and formed large particle, however it was not observed on Cr metal particle.

Keywords: Impregnation; Cobalt Catalyst; Chromium Catalyst; Methane Oxidation

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1. Introduction

Heterogeneous catalyst plays an important role in catalytic reaction of chemical industries.

A catalyst contains two or more important compositions; they are a metal, a promoter, and a support. The metal is usually dispersed on a support to obtain a high surface area of an active metal. The catalytic property of the metal mainly depends on the interaction between metal and support. Therefore, metal-support interaction is important for the final catalysts properties. Some supports such as alumina (Al_2O_3),

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silica (SiO_2) and titania (TiO_2) have been reported to exhibit strong metal-support interaction and low reducibility of metal [1-2]. As a consequence of these, the catalytic activity of the catalysts must be low. Catalysts treatment such as reduction and calcination temperatures somehow indirectly affected the catalysts properties through their metal-support interactions, crystallite sizes and oxidation states of the metals [3-5].

Among the various support, alumina is widely used and attracted much attention as catalyst support due to its high surface area, thermal resistance and stability at high temperature [6]. Alumina with transition metal such as cobalt (Co) and chromium (Cr) is widely applied to different industrially reactions, including methane oxidation and carbon monoxide hydrogenation [7-9]. In a high temperature catalytic reaction, a strong metal-support interaction may leads to the formation of a large metal particle. It is a known fact that the presence of a large metal particle on a support surface may serve as an inactive phase [10], therefore, it is necessary to make the metal particle as small as possible that leads to the high dispersion of active phase. Khangale *et al.* [11] studied the effect of activation with carbon monoxide (CO) for $Co/\gamma\text{-}Al_2O_3$ catalyst, they found that CO can activates $Co/\gamma\text{-}Al_2O_3$ catalyst at low temperature and improves catalyst reduction which is produced a higher number of active sites in the catalyst, hence increased the catalytic activity. Goodman [12] studied the catalytically active Au on TiO_2, he found that strong metal-support interaction leads to the suppression of hydrogen (H_2) and carbon monoxide (CO) chemisorptions for various metal and for active Au/TiO_2 catalyst CO chemisorptions is enhanced due to electron transfer from TiO_2 to Au. Catalytic properties of alumina supported ruthenium (Ru), platinum (Pt), and cobalt (Co) nanoparticles was also investigated by Rekkab-Hammoumraoui and Choukchou-Braham [13], they concluded that the support, the noble and the non-noble metals can be active for oxidation of cyclohexane and they found that Ru and Pt are in metallic form whereas Co is in the oxides form.

Based on the view of the above reasons, the purpose of this study is to investigate the effect of calcination temperatures on the characterization and catalytic activity of alumina supported cobalt and chromium catalysts. The prepared catalysts were characterized by using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) apparatus. The catalytic activity of the catalysts was tested in methane oxidation reaction.

2. Materials and Methods

2.1. Catalyst Preparation

The catalysts preparation is described as follows. Four series of alumina supported cobalt and chromium catalysts were prepared by impregnation method. Gamma-alumina ($\gamma\text{-}Al_2O_3$) was used as support. Two series of alumina supported cobalt (Co/Al_2O_3) catalysts were prepared using required amount of cobalt nitrate ($Co(NO_3)_2.6H_2O$, Merck) which was dissolved in aquadest and impregnated into Al_2O_3 powder. The solution was stirred and dried-up on a hot plate at 80 °C in order to remove the water. The resulted solid was kept in an oven at 80 °C for 12 h. The loading of the Co was 10 wt.%. To observe the effect of calcination temperatures, the solid was calcined in mixture of argon (Ar) and oxygen (O_2) at two different temperatures, 400 °C and 800 °C, for 4 h. The final catalysts were denoted as $Co/Al_2O_3(400)$ and $Co/Al_2O_3(800)$ catalysts. The same procedure of preparation and calcination as described above was also used to prepare alumina supported chromium (Cr/Al_2O_3) catalyst, where $Cr(NO_3)_3.9H_2O$ (Merck) was used as the source of Cr metal. The final catalysts were denoted as $Cr/Al_2O_3(400)$ and $Cr/Al_2O_3(800)$ catalysts.

2.2 Catalyst Characterization

The XRD patterns have been recorded on Rigaku RINT-2500KS instrument by using Cu Kα radiation source (λ = 1.54439 Å) and scintillation counter detector at room temperature. The JCPDS data files were used to identify the XRD phases in the catalysts. The XPS measurements were made on Shimadzu PHI-5800 spectrometer using Al Kα (h = 1486.0 eV) radiation as the excitation source. Before the measurements, the samples were kept in a vacuum overnight. The XPS analysis was done at room temperature and at pressure $1x10^{-8}$ Pa. The binding energies measured with accuracy of ± 0.1 eV and uses C 1s at 284.5 eV as standard. The TEM were conducted with a JEM-200CX (200 kV) apparatus. The catalysts were kept in a vacuum overnight before the measurements.

2.3 Catalyst Test

The catalytic activities of $Co/Al_2O_3(800)$ and $Cr/Al_2O_3(800)$ catalysts were tested on methane oxidation reaction. The reactant gases consisted of methane (CH_4), oxygen (O_2) and argon (Ar) with total flow rate closed to 26 ml/min. The reaction temperature ranged from 200 °C to 480 °C. A micro-reactor contained 0.25 grams catalyst was externally heated by a furnace. The products were detected using a thermal conductivity detector (TCD). Analysis of the products gases hardly detected any formation of carbon monoxide. The products of this reaction were carbon dioxide and water. The overall methane oxidation reaction is represented by Equation (1).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

The methane conversion was calculated from the peak areas obtained from the gas chromatograms. The methane conversion is defined by Equation (2).

$$XCH_4 = \frac{(amount\ of\ CH_4\ in - amount\ of\ CH_4\ out)}{(amount\ of\ CH_4\ in)} \qquad (2)$$

The concentration of each component is defined by Equation (3).

$$Concentration = Area \times Response\ factor \times amount\ of\ component \qquad (3)$$

3. Results and Discussion

The XRD measurements were recorded for Co/Al_2O_3 catalysts subjected to calcination at 400 °C and 800 °C. The 2θ data was collected by using a continuous scan mode ranged from 10° to 70°. Figure 1 shows the XRD patterns of Co/Al_2O_3(400) and Co/Al_2O_3(800) catalysts. As can be seen in Figure 1, the XRD patterns confirmed the existence of Al_2O_3, $CoAl_2O_4$, CoO, and Co_3O_4 phase. The XRD pattern for Co/Al_2O_3(800) catalyst is a little bit shifted to the right, this could be due to different phases on alumina and the transition of the phases as the calcination temperature increases. Based on the literature, on Co/Al_2O_3 catalyst, the peaks of Al_2O_3 are at values of 46.1° and 66.5°, while the peaks relate to Co metal should appeared at 2θ values of 43.8°, 51.5° and 75.6°, and the other cobalt oxides crystal planes are appeared at 2θ values of 36.5°, 42.5° and 60° [14-15]. The chemical structure and structural phases for Co_3O_4 and $CoAl_2O_4$ are difficult to identify on both catalysts because Co_3O_4 and $CoAl_2O_4$ phase has almost identical diffraction peak position [16]. No peaks for Co metal were detected in XRD patterns, it might be due to the overlap with diffraction peaks of Al_2O_3 [15]. On the other hand, the diffraction peak at 61.8° in both catalysts was due to CoO phase.

The main difference between the XRD patterns for both catalysts is the formation of CoO phase which is clearly detected in Co/Al_2O_3 (800) catalyst at 2θ value of 42.7°. This result indicates the existence of Co_3O_4 phase in the surface of Co/Al_2O_3(400) catalyst, however the peak was not observed on the catalyst surface. Further calcination at high temperature increases the metal-support interaction and leads to the formation of CoO phase. It seems that CoO phase is formed during the calcination at high temperature (> 400 °C). In Co/Al_2O_3 catalyst system, Co_3O_4 phase is a thermodynamically stable under the ambient

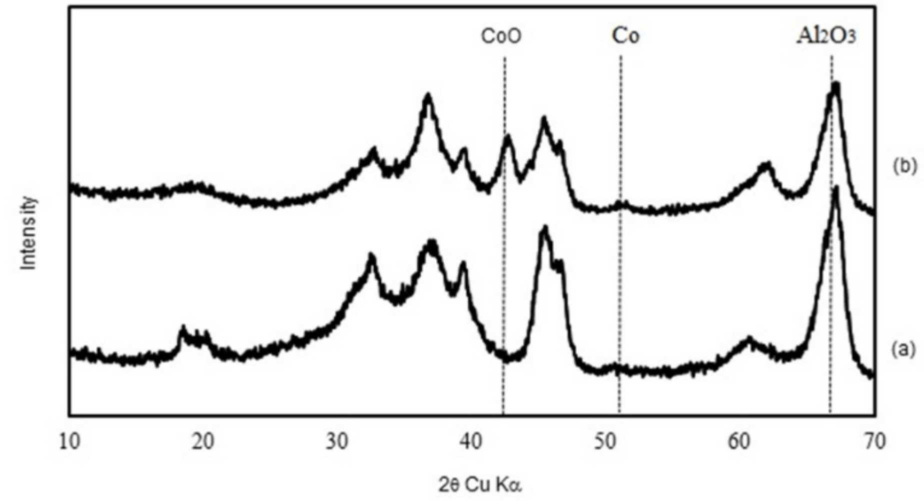

Figure 1. XRD patterns for (a) Co/Al_2O_3(400) and (b) Co/Al_2O_3(800) catalyst

temperature and the formation of CoO phase can be expressed as follows [16].

$$Co_3O_4 \rightarrow 3CoO + \frac{1}{2}O_2 \tag{4}$$

Our results agreed well with Ji *et al*. [16], they found that when metal-support interaction is small, the catalyst is dominated by Co_3O_4 phase, on the other hand, CoO and $CoAl_2O_4$ phases are predominant on the catalyst surface when metal-support interaction increase.

The XPS measurements were only done for Cr/Al_2O_3(400) and Cr/Al_2O_3(800) catalysts, since a significant fraction of Cr is present as a small Cr_2O_3 particle that is detected by the XPS but is not by the XRD. Figure 2 displays XPS spectra for Cr/Al_2O_3 catalysts. The XPS was conducted on curve-fitting area of Cr in range of 550 – 595 eV. The Cr 2p3/2 XPS peaks at binding energy values of 577.2 eV and 579.8 eV are assigned to Cr^{3+} and Cr^{6+} species, respectively, as given by Rahman *et al*. [17]. The Cr/Al_2O_3(400) and Cr/Al_2O_3(800) catalysts were found to behave differently in calcination at 400 °C and 800 °C treatments. The XPS results showed that the Cr/Al_2O_3(400) catalyst has a predominantly Cr^{3+} species on the surface of support, whereas Cr^{6+} species was not observed a characterized by the Cr 2p3/2 signals at 577.0 eV and 580.0 eV, respectively. It might be due to very small formation of CrO_3 species. However, an interesting change was observed in the surface composition of the states of Cr after calcination at 800 °C for 4 h. The differences in calcination temperatures between these catalysts seem affect to the general oxidation states behaviour. Two broad peaks were visible at binding energies 576.8 eV and 579.04 eV which is assigned to the Cr^{3+} and Cr^{6+} species, respectively. The formation of Cr^{6+} species on Cr/Al_2O_3(800) catalyst could be due to a thermally activated process, since it was not found on 400 °C calcined catalyst. The hydroxyl groups and the structure of alumina might affect the formation of Cr^{6+} species. The calcination treatment at high temperature caused significant amount of Cr^{6+} species which suggest to better Cr dispersion [18]. However, these binding energies are shifted and lower compared to the binding energies obtained for

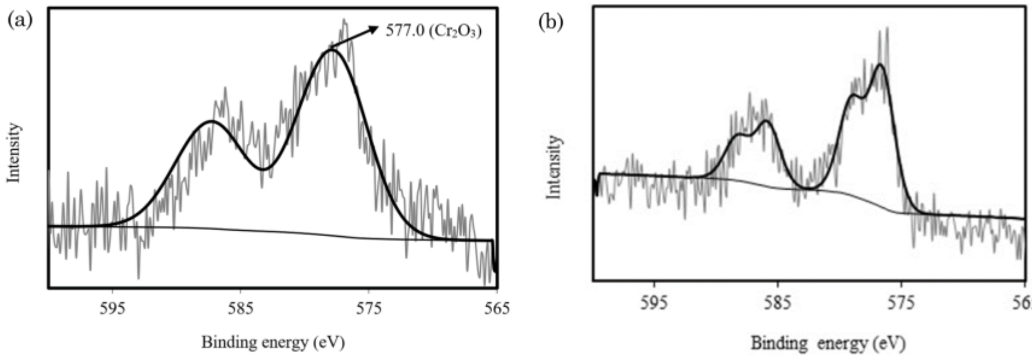

Figure 2. XPS spectra Cr 2p3/2 core level for a) Cr/Al_2O_3(400) and b) Cr/Al_2O_3(800) catalyst

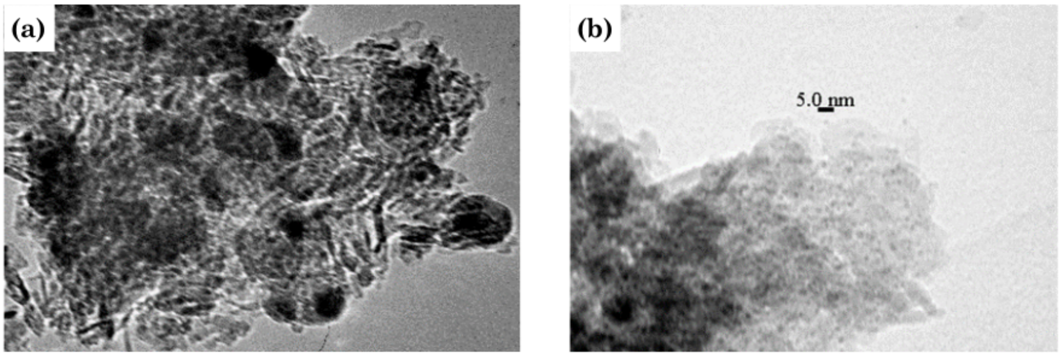

Figure 3. TEM images for (a) Co/Al_2O_3(800) and (b) Cr/Al_2O_3(800) catalyst

Cr/Al_2O_3(400) catalyst as shown in Figure 2. The TEM images of Co/Al_2O_3(800) and Cr/Al_2O_3(800) catalysts are shown in Figure 3. TEM image of Co/Al_2O_3(800) catalyst showed large particles, it might due to agglomeration of Co particles during the calcination treatment, whereas TEM image of Cr/Al_2O_3(800) catalyst showed a very small black dot particles that might assigned to the highly dispersed Cr particles.

Figure 4 shows the comparison of Co/Al_2O_3(800) and Cr/Al_2O_3(800) catalysts over methane oxidation reaction. Both catalysts were active for methane oxidation and the catalysts started their catalytic activities at temperature higher than 250 °C. The results showed that the catalytic activities for both catalysts increase with the increasing of temperatures. However, the catalytic activity of Cr/Al_2O_3(800) is relatively higher than Co/Al_2O_3(800) catalyst. It has been well-known that Cr^{6+} species is active for methane oxidation reaction as reported by Park and Ledford [19]. They studied Cr/Al_2O_3 catalysts with different Cr loading and tested the catalytic activities over methane oxidation and found that the rich Cr^{6+} species catalyst gave the highest activity. Kuznetsova *et al.* [20] also studied the Cr catalysts for hydrocarbons destruction. They found that during the calcination treatments, the surface of alumina changes remarkably. The hydroxyl groups on the surface of alumina are responsible for the adsorptions of Cr from aqueous solution. High calcination temperatures may remove the hydroxyl groups on alumina hence increase the possibility for Cr adsorption onto alumina and increase the thermal stability of Cr^{6+} species. Therefore, at high calcination temperature, Cr^{6+} species is dominant species due to its thermal stability and active towards the reactions of hydrocarbons oxidation.

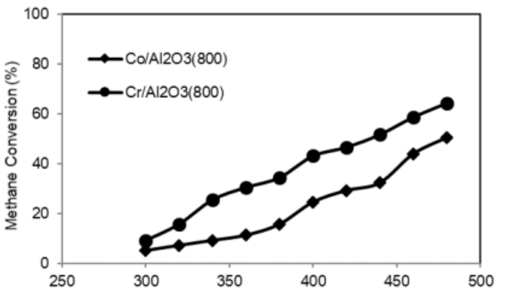

Figure 4. Methane conversion as a function of reaction temperature over Co/Al_2O_3(800) and Cr/Al_2O_3(800) catalyst

4. Conclusions

A series of alumina supported cobalt and chromium catalysts were prepared and calcined at different calcination temperatures (400 °C and 800 °C). The XRD results showed that Co/Al_2O_3(800) catalyst was aggregated during calcination treatment and resulted CoO phase on the catalyst surface. The presence of CoO phase indicates higher metal-support interaction. On the other hand, XPS result for Cr/Al_2O_3(800) catalyst showed the Cr^{6+} species is dominant on the catalyst surface. High calcination temperature may remove the hydroxyl groups on alumina, Co particle may form an aggregation on alumina, and however Cr particle may adsorb and dispersed onto alumina. Both catalyst were active for methane oxidation and Cr/Al_2O_3(800) catalyst showed the higher activity than Co/Al_2O_3(800) catalyst due to the presence of Cr^{6+} species.

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