Effects of Cobalt and Chromium Loadings to The Catalytic Activities of Supported Metal Catalysts in Methane Oxidation

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Abstract

A series of alumina supported cobalt and chromium catalysts with different metal loadings were prepared by impregnation method. Six types of alumina supported cobalt and chromium catalysts contained 5 wt%, 10 wt%, and 15 wt% loadings were produced and tested in methane oxidation. The catalysts were characterized by using x-ray diffraction (XRD) and carbon monoxide chemisorption (CO chemisorption). The XRD results do not confirmed any features of cobalt and chromium metal. The metal sizes for both catalysts were larger in high loading as shown by CO chemisorption results. Methane conversion results showed that the conversion increases with increasing the metal loading, however supported chromium catalysts were higher in activities compared to supported cobalt catalysts. Thermal stability tests on 15 wt% Co/Al and 15 wt% Cr/Al catalyst showed that supported chromium catalyst is more stable and maintain the particle size due to its strong interaction with support, while supported cobalt catalyst decrease in methane conversion due to deactivation of the catalyst. Copyright © 2020 BCREC Group. All rights reserved

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

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1. Introduction

Catalytic hydrocarbon at low temperature has attracted a great attention due to the use of hydrocarbon as an alternative energy source. Hydrocarbon such as methane is a promising alternative fuels, since in the combustion reaction it will produce lower particulate matters and emissions [1-2]. In order to reduce the amount of unwanted products from oxidation or combustion reaction, usually a catalyst is used in a catalytic reaction. Noble metal catalysts, such as: platinum (Pt), palladium (Pd), and ruthenium (Ru), have been known as an active metal for carbon-hydrogen bond activation. However, these noble metals are expensive, therefore, a catalyst from transition metal has become attractive as an alternative metal in a catalyst due to their price and catalytic property [3-4].

Among the various metals, transition metal, such as: cobalt, cerium, vanadium, and chromium, has been reported as an active metal in hy-
drocarbon reaction. Cobalt and chromium-based catalysts have been used in many applications of industrial processes, they are also active for dehydrogenation and oxidation reaction. Lucre’dio et al. [5] studied the cobalt catalysts promoted with cerium and lanthanum applied to partial oxidation of methane reaction. They found that the cobalt concentration and cobalt species formation could be affected by the thermal treatment in air. Also for the promoted catalysts, the thermal treatment could have favored the migration of lanthanum and cerium cations to the surface of catalyst. Yasuda et al. [6] have reported that in the gas-phase oxidation of methacrolein to methacrylic acid over acid-modified chromium/silica catalyst, the formation of interface between chromium and 12-Tungstophosphoric acid particles on silica provides the active site for methacrylic acid formation and on the other hand, the Brønsted acids increase the electrophilicity of carbonyl carbon in methacrolein. The other research on chromium-based catalyst was investigated by Troiani et al. [7] showed that the chromium catalysts were effective as oxidizing and reducing agents and accomplishes the conversion of sulfur dioxide to sulfur trioxide.

On the other hand, the type of the support is important for the catalytic activity and durability [8-9]. Alumina, silica, and titania is widely known as a catalyst support. Fakeeha et al. [10] studied the suitability of titania and magnesium as support for methane decomposition catalyst using iron as an active material. They found that titanium supported iron catalyst exhibited less activity, however, a better performance was presented by the iron catalysts supported on magnesia.

Transition metal on a support shows enhanced catalytic activity for catalytic reaction due to the metal-support interaction [11-14]. Such metal-support interaction has been investigated by Najafishirtari et al. [15], they used Au-based catalyst from colloidal dumbbell-like nanostructures and they found that the reducibility of the nano sized oxide support was different for each samples. They also concluded that the morphological difference on the metal-support affected the catalytic activity. The metal-support interaction may alter the catalyst properties due to its strong or low interaction. The metal-support interaction is strongly depend on few factors, such as catalyst preparation method, thermal treatment (calcination, reduction, or drying), and metal content in the catalyst [16-18].

In hydrocarbon combustion, catalyst may deactivate through the thermal aging and poisoning. Thermal aging and poisoning may cover the active site of catalyst thus decrease the catalytic activity. On the other hand, water formation in the oxidation reaction may inhibits the reaction through the rapid adsorption of water species on the active site of catalyst [19]. In our previous study, we examined the effects of calcination temperatures on the interaction between alumina and metal (cobalt and chromium) catalyst. We observed that cobalt metal was aggregated during calcination at high temperature, on the other hand, chromium dispersed onto alumina. These differences in metal-support interaction showed different catalytic properties. Chromium showed higher catalytic activities than cobalt catalyst [20]. In the present study, we prepared a series of alumina supported cobalt and chromium catalysts to observe the effect of metal loadings and thermal stability to the catalytic activity in methane oxidation reaction.

2. Materials and Methods

2.1 Catalyst Preparation

A series of alumina supported cobalt and chromium catalysts containing 5-15 wt% metal on alumina were synthesized by impregnation method. Alumina supported cobalt catalyst (Co/Al₂O₃) was prepared as follows. A required amount of cobalt nitrate (Co(NO₃)₂·6H₂O, Merck) was added into distilled water and impregnated into gamma-alumina (γ-Al₂O₃). The solution was continuously stirred at room temperature for 10 min and then dried-up on a hot plate at 80 °C. After impregnation, the sample was dried in an oven at 80 °C for 12 h and finally calcined in a mixture of argon (Ar) and oxygen (O₂) at 400 °C for 4 h. The obtained catalysts were denoted as 5 wt% Co/Al₂O₃, 10 wt% Co/Al₂O₃, and 15 wt% Co/Al₂O₃ catalyst. Three series of alumina supported chromium catalysts (Cr/Al₂O₃) were also prepared in the same manner and chromium nitrate (Cr(NO₃)₂·9H₂O, Merck) was used as source of metal precursor. The final Cr/Al₂O₃ catalysts were denoted as 5 wt% Cr/Al₂O₃, 10 wt% Cr/Al₂O₃, and 15 wt% Cr/Al₂O₃ catalyst.

2.2 Catalyst Characterization

X-ray diffraction (XRD) of these catalysts particles was recorded on Rigaku RINT-2500KS instrument (Cu-Kα, λ = 1.54439 Å). The JCPDS data was used to confirm the phases in XRD results.
The cobalt and chromium metal particle size was obtained by using CO chemisorption apparatus (BELCAT-JAPAN). The catalyst was treated by flowing helium (He) gas to remove the impurities and finally reduced in flow of hydrogen (H₂). The decrease in peak area of CO detected by thermal conductivity detector (TCD) was used to calculate the amount of CO adsorbed on catalyst.

2.3 Catalyst Test

The activity of the catalysts in methane oxidation was carried out in a glass tube micro-reactor charged with 0.25 g of catalyst. The reactant gases were argon (Ar), oxygen (O₂), and methane (CH₄). The total flow of reactant gases was closed to 24 ml/min. The catalyst was loaded onto the micro-reactor and catalytic reaction was tested with flowing the reactant gases at 200 °C until 500 °C. The products were analyzed on-line every 20 min using gas chromatograph with thermal conductivity detector (TCD). The stability of optimum catalyst activity (time on stream) was tested at 500 °C for 5 h.

The only products were carbon dioxide (CO₂) and water (H₂O), no formation of carbon monoxide (CO) was detected during the experiment. The methane conversion was calculated using the following formula:

\[
%CH₄ = \frac{(CH₄)_{in} - (CH₄)_{out}}{(CH₄)_{in}} \times 100\%
\]

3. Results and Discussion

3.1 Catalytic Activity

The catalytic activities for the catalysts were evaluated towards methane oxidation.

The catalytic behavior of Co/Al and Cr/Al catalysts was evaluated in the temperature 200 °C until 500 °C. As can be seen in Figure 1 and 2, the methane conversion of Co/Al and Cr/Al catalyst increased with metal loading and reaction temperature. Result presented in Figure 1 shows 10 wt% Co/Al and 15 wt% Co/Al catalyst started their complete methane oxidation at 260 °C and gradually increase with the increasing of temperature. On the other hand, 5 wt% Co/Al catalyst is not active for methane oxidation at temperature below 400 °C. It appears that at low cobalt loading (5 wt% Co/Al catalyst), only small amount of cobalt metal is available for the reaction thus the catalytic activity is low. The presence of small amount of cobalt active site was suggested by slight increase in methane conversion. On the other hand, the cobalt metal is highly dispersed at higher cobalt loading hence more cobalt active site is available for the reaction. Consequently, methane conversion increase significantly. The reasons for the low availability of cobalt active site at low loadings are not yet understood, however, it may be associated with possibility of cobalt metal forming a solid solution with the alumina support [21-22]. The highest activity was obtained over 15 wt% Co/Al catalyst and the temperature needed to reach 37% methane conversion was as low as 500 °C. The descending order of activity for Co/Al catalysts was as follows: 15 wt% Co/Al > 10 wt% Co/Al > 5 wt% Co/Al.

The catalytic performances of Cr/Al catalysts in methane oxidation are presented in Figure 2. Similar to the Co/Al catalysts, the methane conversion for Cr/Al catalysts increased with the increasing of chromium loading and reaction temperature. As can be
seen in the Figure 2, 5 wt% Cr/Al catalyst is inactive at temperature below 350 °C. Methane conversion was lower than 10% for 5 wt% Cr/Al catalyst, while 10 wt% Cr/Al catalyst exhibit a slightly improved conversion and finally reaching 31% conversion at 500 °C. On 15 wt% Cr loading, a significant improvement is observed. Methane starts to react at 200 °C and the maximum conversion was 69% at 500 °C. A comparison of catalyst activities over Co/Al catalysts with Cr/Al catalysts, the maximum conversion was reached by 15 wt% Cr/Al catalyst equal to 69% at 500 °C, whereas the maximum conversion for 15 wt% Co/Al catalyst at that temperature was 37% as shown in Figure 1 and 2.

The catalytic activity of chromium-based catalyst is not surprising higher than other transition metals, since the chromium-based catalyst is commonly used as an additive or second metal in methane oxidation [23-25]. The differences in activity for both catalysts can be related to the differences of metal particle size and also due to their interaction with the support [26-27]. Oxide support such as alumina provide an important ability, that is the ability of dispersing metal, hence resulting a smaller crystallite size and high activity.

3.2 Characterization of the Catalysts

The XRD patterns shown in Figure 3 for 15 wt% Co/Al and 15 wt% Cr/Al catalyst did not reveal the presence of cobalt and chromium metal suggesting high dispersion of these metals. High dispersion of metal on alumina suggests that a stronger interaction may exists between metal and support. The XRD for all calcined catalysts were dominated by alumina hence the presence of cobalt and chromium metal could not be confirmed. As shown in Figure 1 and 2, with an increase in metal loading, the presence of surface metal species increase and the methane conversion gradually increases, though not detected by XRD. These results are agreed well with the results described by other researchers [8,28].

The CO chemisorption results in Table 1 shows cobalt metal size increased from 1.3 nm for 5 wt% Co/Al catalyst to about 2.5 nm for 10 wt% Co/Al catalyst and to about 3.2 nm for 15 wt% Co/Al catalyst. The cobalt metal size increased with increasing cobalt loading. This is similar for Cr/Al catalysts, the chromium metal size increased from 1.09 nm to 1.6 nm and to 2.1 nm for 5 wt% Cr/Al, 10 wt% Cr/Al, and 15 wt% Cr/Al, respectively. This suggests that with an increase in loading the metal size also increase [28]. However, Co/Al catalysts metal sizes were larger than those observed for Cr/Al catalysts.

With an increase in loading the metal crystallite size and the number of surface metal sites increase. The larger number of surface active sites formed with increasing metal loading were able to convert more methane [28]. Thus the metal crystallite size inversely related to the conversion for the supported catalysts containing high cobalt and

![Figure 3. XRD patterns for (a) 15 wt.% Co/Al catalyst; (b) 15 wt.% Cr/Al Catalyst; • Al₂O₃.](image)

### Table 1. Particle size of Co/Al and Cr/Al catalysts before and after reaction.

| wt%  | Co/Al catalyst Before reaction (nm) | Co/Al catalyst After 5 h reaction (nm) | Cr/Al catalyst Before reaction (nm) | Cr/Al catalyst After 5 h reaction (nm) |
|------|-----------------------------------|--------------------------------------|-----------------------------------|--------------------------------------|
| 5    | 1.3                               | -                                    | 1.09                              | -                                    |
| 10   | 2.5                               | -                                    | 1.6                               | -                                    |
| 15   | 3.2                               | 4.5                                  | 2.1                               | 2.2                                  |

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chromium loadings. Interaction between cobalt and alumina was also studied by Das and Deo [28], they found that the cobalt metal crystallite size increased with the increasing cobalt loading and the formation of cobalt metal could not be confirmed by the XRD. These results are agreed well with our results. Based on our results, higher activities of Cr/Al catalysts can be related with smaller metal particle sizes and distribution of chromium on alumina. The influence of metal particle size in methane conversion was also reported by some researchers [29-30]. Chromium is known as the most efficient catalyst in oxidation, other catalysts displayed comparable or even lower activity compared with alumina-supported chromium catalyst [31].

3.3 Catalyst Stability Test

A catalyst thermal stability in methane oxidation is important, since the catalyst is expected operation at high temperatures [32]. However, at high temperature, thermal aging may cause crystal growth and loss of catalytic active surface. In this experiment we tested the optimum catalyst loading under the flow of reactant gas to observe catalyst stability and conversion versus time can be seen in Figure 4. Conversion at 500 °C for 15 wt% Cr/Al catalyst is rather stable after 5 h on stream compared to 15 wt% Co/Al catalyst. This is could be related to the thermal stability of chromium species (Cr(III) and Cr(VI)) on alumina. Finely dispersed chromium species on alumina form Cr(III) species which is reported to retain high activity and tolerance to thermal aging [33-34]. When the interaction is relatively strong, chromium particle is hard to migrate and this may lead to less agglomeration, thus maintain the catalytic activity. As shown in Table 1, CO chemisorption after 5 h reaction showed that 15 wt% Cr/Al catalyst has 2.2 nm which is almost the same before reaction, however metal size for 15 wt% Co/Al catalyst increased from 3.2 nm to 4.5 nm.

Smaller particles can penetrate the pores of alumina which could results in high dispersion. The gradually decrease in methane conversion for 15 wt% Co/Al catalyst is attributed to the deactivation of catalyst and agglomeration of cobalt particles. It is has been known that carbonaceous deposit may occur during the transformation of hydrocarbon compounds at high temperature leads to deactivation of a catalyst [35-37]. On the other hand, deactivation could also have been due to the migration of alumina onto cobalt particle hence cover the active sites of cobalt metal, thus lower methane conversion resulted by a few remaining active cobalt sites. The mechanisms of oxide’s migration onto metal is not fully understood. Fu et al. [38] described the metal encapsulation on titanium oxide (TiO2). This encapsulation process requires electron transfer from oxide to the metal and migration of oxide layer driven by a minimization of the surface energy. Weak interaction may lead to migration of particles and possibly result in formation of larger agglomerates.

Other study suggests that deactivation may due to water presence as an oxidation product [39]. Water presence may affect the catalytic activity, resulting inhibiton of the methane oxidation. The interaction between alumina and cobalt is not strong enough to maintain their interaction, hence water may facilitate the formation of surface hydroxyl groups on alumina which cover or block the active site of cobalt [39-40]. Larger particles cannot easily penetrate the pores of alumina and this have tendency to agglomerate leads to the deactivation. It appears that the interaction of cobalt on alumina is different from the interaction of chromium on alumina. Cobalt-based catalyst on alumina support may favour larger particle size and as a result decrease the activity. A stronger interaction exits between chromium and alumina since Cr/Al possessed higher catalytic activities.

4. Conclusions

Alumina supported cobalt and chromium catalysts have been prepared by impregnation method. The catalysts loading were 5 wt%, 10 wt%, and 15 wt% for each catalyst. The CO chemisorption results showed the metal particle sizes increases with the increasing of metal loadings. Chromium catalysts possessed
smaller particle sizes and showed higher activities compared to cobalt catalysts. Thermal stability tested on the 15 wt% loading of catalysts showed that chromium catalyst is more stable after 5 h reaction, it may be due to strong interaction between chromium and alumina, which leads to the formation of small particle and high stability of Cr(III) species which tolerance to thermal aging. While, methane conversion for 15 wt% loading of cobalt catalyst gradually decreases, cobalt has weaker interaction with alumina than chromium, lead to migration of metal particles and agglomeration which results in a decrease activity.

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