Ammonium hydroxide addition and its influence on the catalytic activities of Pt-based catalysts for methane oxidation

Mardwita M[1,*], and *M. Djoni* Bustan[2]

[1]Chemical Engineering Department, Faculty of Engineering, Muhammadiyah University of Palembang, 30252 Palembang, , Indonesia
[2]Chemical Engineering Department, Faculty of Engineering Universitas Sriwijaya , 30662 Indralaya , Indonesia

Abstract. A series of binary chromium-platinum catalysts were prepared and the catalytic activity was tested in methane oxidation. The effects of aqueous ammonium hydroxide addition into binary catalyst chromium-platinum catalysts were investigated. All the catalysts were prepared by impregnation method. The reactant gases were consisted of methane-oxygen-argon. The reaction was conducted at an atmospheric pressure and the temperature was ranged from 573 to 773 K. The products were analyzed using thermal conductivity detector. Under this experiment conditions, the only products were carbon dioxide and water. The catalysts were characterized using carbon monoxide chemisorptions and x-ray photoelectron spectrometer. The catalytic activity results showed that the catalyst with the addition of aqueous ammonium hydroxide has smaller platinum metal particle size and its catalytic activity is the highest compared to the other catalysts. X-ray photoelectron spectrometer recorded higher intensities and clear peaks on high pH catalysts indicating a change of interaction between chromium and platinum on alumina. However, active state of chromium was not observed on catalyst surface.

1 Introduction

Methane oxidation or methane combustion is a method to reduce methane gas from exhaust gas engine. On the other hand, methane oxidation process may generate some energy [1, 2]. Catalysts play an important role in catalytic reaction, including in oxidation. Noble metal catalysts, such as platinum (Pt) and palladium (Pd), are well-known because of its reactivity, stability, resistance to poison and thermal [3-5]. However, these noble metal catalysts are expensive, therefore it is impossible to use only noble metal in a catalyst system [6]. An in-expensive and low loading of noble metal catalysts poses high catalytic activity is needed, hence another metal from transition metal are usually added as an additive or as a second metal in noble metal catalysts. Transition metals, such as manganese (Mn), cobalt (Co), iron (Fe), nickel (Ni), copper (Cu), and chromium (Cr), has been widely used as an additive in a catalyst system [7-9]. Binary catalyst systems, such as chromium-copper-titanium (Cr-Cu-Ti) oxide catalyst has been reported as a catalyst that has more sulphur resistance compared to platinum-palladium (Pt-Pd) catalyst in combustion reaction [10]. Another bimetallic catalyst such as $La_{3.5}Ru_{4.0}O_{13}$, Pt-Sn, Pt-Ce has been reported to show high catalytic performance [11, 12] and its effect to the catalytic performance of Pt catalyst has been investigated [8]. Among the other transition metal oxide catalyst, supported chromium metal oxide has been found as the most active catalyst in methane combustion [13, 14]. Kuznetsova et al has been studied on the

chromium for hydrocarbon destruction and concluded that the Cr(IV) cations as the main active component [14] and showed the relation between support basicity and the formation of Cr(IV). Though, the mechanism of activated C-H bond on the surface of catalyst is not well-understood yet [15].

To obtain an effective and reactive catalyst in low temperature, the preparation of catalyst plays an important role. The concentration of additive metals, reducing and oxidizing conditions, the pH solutions will affect to the performance of catalyst. It must be considered that the interaction between main metal and additive occurs during the preparation is an important thing. As best of our reviews, there are no studies on catalytic activity of platinum and chromium by the addition of aqueous ammonium hydroxide (NH_4OH). Therefore, in this study we investigated the catalytic performance of platinum and chromium catalysts and also the effect of ammonium hydroxide addition during the catalyst preparation.

2 Experiment details

2.1 Catalyst preparation

A supported platinum (Pt/Al_2O_3) catalyst was prepared by impregnation method. Gamma-alumina (γ-Al_2O_3) was used as the support. Required amount of H_2PtCl_6 solution, as the source of Pt metal, was impregnated into γ-Al_2O_3, the solution was left unstirred at room

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* Corresponding author: wiwitdiita@gmail.com

temperature then it was stirred slowly. The water was removed by stirring and dried-up on a hotplate at 383 K, the resulted solid was kept overnight in an oven at 333 K, finally was calcined in air at 673 K for 3 hours. The loading of Pt was 2.0 wt.% and the catalyst was denoted as $2.0Pt/Al_2O_3$.

The same procedure as described above was also applied to prepare supported chromium (Cr/Al_2O_3) catalyst in loading of 6.0 wt.%, 2.0 wt.%, and 0.5 wt.% Cr. An aqueous solution of chromium nitrate ($Cr(NO_3)_3$) was used as the source of Cr metal. Final catalysts were denoted as $6.0Cr/Al_2O_3$, $2.0Cr/Al_2O_3$, and $0.5Cr/Al_2O_3$.

Three samples of binary Cr-Pt catalysts containing 6.0 wt.% Cr, 2.0 wt.% Cr, and 0.5 wt.% Cr were prepared. The loading of Pt metal was kept constant at 2.0 wt.%. These catalysts were prepared by stepwise-impregnation method. First, binary $Cr/Pt/Al_2O_3$ catalyst was prepared by impregnating aqueous solution of $Cr(NO_3)_3$ into $2.0Pt/Al_2O_3$ catalyst. The pH solution was 4. The catalyst was prepared using the same drying and calcining process as described in preparation of $2.0Pt/Al_2O_3$ catalyst. The resulted catalysts were denoted as $6.0 \, Cr \, /2.0 \, Pt/ \, Al_2O_3$, $2.0 \, Cr \, /2.0 \, Pt \, / \, Al_2O_3$, $0.5Cr/2.0Pt/Al_2O_3$ catalyst.

Catalysts with addition of ammonium hydroxide (NH_4OH) were prepared using the same preparation method for $Cr/Pt/Al_2O_3$ catalyst described above. The aqueous solution of $Cr(NO_3)_3$ was added into $2.0Pt/Al_2O_3$ catalyst and the pH of solution was adjusted to ca. 10 by the addition of NH_4OH drop by drop during the preparation. The other catalyst was prepared by adjusting the pH to ca. 11. All the catalysts contained 6.0 wt.% loading of Cr and 2.0 wt.% loading of Pt. The catalysts were denoted as $6.0Cr/2.0Pt/Al_2O_3$ (pH 10) and $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalyst.

2.2 Catalyst test

Before catalytic reaction, the catalyst was pretreated by calcinations in a stream of air at 773 K for 1 hour to remove impurities and to activate the metal sites, and then the catalyst was cooled into room temperature. The methane oxidation was carried out at atmospheric pressure. The micro-reactor used in this experiment was made of Pyrex glass. The reactor contained quartz wool onto which 0.25 grams catalyst was added and externally heated by a furnace. The total flow rate was closed to 26 ml/min and the fed gases consisting of methane (CH_4), oxygen (O_2), and argon (Ar) with volumetric composition 1%:5%:20% was introduced into the reactor. The reaction temperature was ranged from 573 K to 773 k and measured by a thermocouple inserted in the catalyst bed. All the products, except water were analyzed by a thermal conductivity detector (TCD). The only products were carbon dioxide (CO_2) and water (H_2O). Carbon monoxide (CO) was not detected under this experimental conditions and the conversion was calculated based on the hydrocarbon consumptions.

2.3 Catalysts characterization

The Pt particle size in catalysts was determined using CO chemisorptions apparatus on a BEL-CAT (BEL JAPAN INC). The catalyst in weight of 0.05 grams was loaded into U-tube reactor. In the apparatus, the catalyst was treated by flowing helium (He) gas at 323 K to remove impurities. Then, the temperature was increased to 573 K in flow of hydrogen (H_2) and reduced for 1 hour, finally cooled to 323 K in He flow. CO/He gas was purged into the reactor and TCD will detect the effluent gas. The decrease in peak area of CO due to its adsorption on the catalyst was used to calculate the amounts of CO adsorbed on the catalyst's surface.

X-ray photoelectron spectrometer (XPS) Shimadzu, ESCA-3400 apparatus using Mg Kα (1253.6 eV) radiation was conducted on stepwise impregnated catalyst $Cr/Pt/Al_2O_3$ to analyze the catalyst's morphology and metal state. The XPS was measured in calcined catalysts. Powder sample of catalyst was poured on the double sticky carbon on the sample's place. This sample was kept in vacuum for one day before analysis. The binding energies of catalysts were measured with accuracy of ± 0.1 eV and used C 1s at 284.3 eV as standard.

3 Results and discussion

In order to find the optimal composition of catalyst, the content of Cr loading was investigated on 0.5 wt.%, 2.0 wt.%, and 6.0 wt.%. Figure 1 shows comparison of methane oxidation over $0.5Cr/Al_2O_3$, $2.0Cr/Al_2O_3$, and $6.0Cr/Al_2O_3$ catalyst. The results showed that $0.5Cr/Al_2O_3$ catalyst has no catalytic activity under this reaction condition, meanwhile $6.0Cr/Al_2O_3$ catalyst shows the highest conversion, however a very small amount of CO was detected in products, indicates that supported Cr catalyst leads to the reaction of partial oxidation.

In binary Cr/Pt catalyst, the alumina was chosen as the support because it forms the support-metal-interaction with the Pt metal, this can give another advantages such as to prevent the Pt to form PtO metal during the catalytic reaction. The catalytic activities of Pt/Al_2O_3 and $Cr/Pt/Al_2O_3$ catalysts are shown in figure 2. It is observed that all the catalysts started the complete methane oxidation at 673 K except for $0.5Cr/Al_2O_3$ catalyst which started the catalytic activity at 723 K. Though $6.0Cr/2.0Pt/Al_2O_3$ and $2.0Cr/2.0Pt/Al_2O_3$ catalyst started at the same temperature, their conversions are far different. Besides that, we found that the addition of 2.0 wt.% Cr into supported Pt does not increase the activity so much, even the catalytic activity just little bit higher than $2.0Pt/Al_2O_3$ catalyst. The catalytic activity of $0.5Cr/2.0Pt/Al_2O_3$ and $2.0Cr/2.0Pt/Al_2O_3$ catalyst was mainly due to the Pt metal, as it has been well-known that Pt metal is an active catalyst than transition metal oxide catalyst. Complete methane oxidation which was conducted on $0.5Cr/Al_2O_3$ catalyst shows no catalytic activity, suggests that no active phase was resulted by the

calcinations process on $0.5Cr/Al_2O_3$ catalyst due to its low concentration. The catalyst just existed as un-active phase, when this deposited onto $2.0Pt/Al_2O_3$ catalyst, this un-active phase covered the active site of Pt hence reduces in the catalytic performance. While in $2.0Cr/2.0Pt/Al_2O_3$ catalyst, low aggregation of Cr and Pt, exhibit some activity. Interestingly, the catalytic activity increase dramatically when 6.0 wt.% Cr was deposited onto $2.0Pt/Al_2O_3$ catalyst, it seems high aggregation and interaction between these two metals was occurred during the catalyst preparation. The activities of catalysts decrease as follows: $6.0Cr/2.0Pt/Al_2O_3$ > $2.0Cr/2.0Pt/Al_2O_3$ > $0.5Cr/2.0Pt/Al_2O_3$.
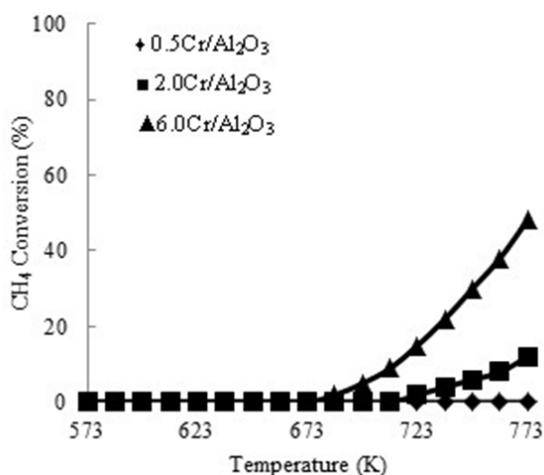

Fig. 1. Methane conversion as a function of temperature for various loading Cr/Al_2O_3 catalysts.

The catalytic activity of physical mixture catalyst ($6.0Cr/Al_2O_3$ + $2.0Pt/Al_2O_3$) showed lower catalytic activity compared to binary $6.0Cr/2.0Pt/Al_2O_3$ catalyst. This strongly suggests that on binary Cr-Pt catalyst, the Pt and Cr metal existed in interaction than existed separately. More than 50% conversion of methane was given by $6.0Cr/2.0Pt/Al_2O_3$ catalyst at 723 K, while at the same temperature the physical mixture catalyst gave 30% conversions. The results are summarized in figure 3.

The $6.0Cr/2.0Pt/Al_2O_3$ (pH 4) catalyst was prepared by stepwise impregnation method and followed the general manner. On the other hand, $6.0Cr/2.0Pt/Al_2O_3$ (pH 10) and $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalysts were prepared by adjusting the pH of impregnated solution with addition of NH_4OH.

Figure 4 shows all the catalysts started their catalytic activities at 623 K and increase with the increases of temperatures. However, the catalytic activities of basic catalysts are relatively higher than acid catalyst. The $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) showed the highest conversions among the others. It could be concluded that the catalyst prepared in basic solution is easier to oxidize the reactant gas than the acid catalyst.

Some authors have investigated the adsorption of bases on Al_2O_3 surface, they concluded that due to the addition of a base, hydroxyl groups on Al_2O_3 surface are removed and replaced by the base groups. This condition

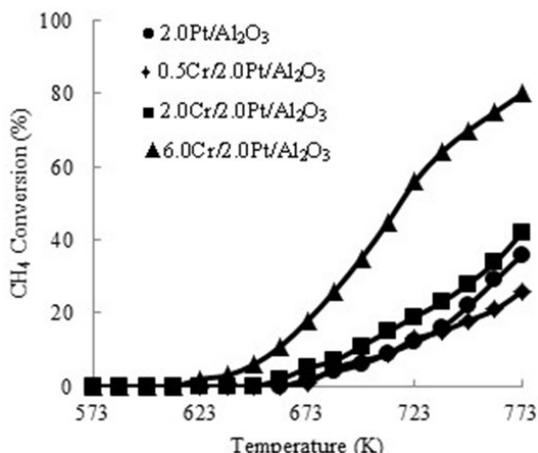may decrease the ability of metal to adsorb on the surface of Al_2O_3 [16-17].

Fig. 2. Methane conversion as a function of temperature for $Cr/Pt/Al_2O_3$ catalysts.

In our experiment, it cannot be calculated the amount of Cr adsorbed on the surface of alumina or electronically adsorbed on the surface of Pt. Based on the catalytic activity results, it can be assumed that during the catalyst preparation, NH_3 cation is adsorbed on the surface of alumina and also interacted with the chromium nitrate. It is expected that the formation of chromium ionic is higher in the presence of NH_4OH, thus increase the interaction between Pt and Cr in catalyst. This interaction gave a synergistic effect that increases the catalytic activity.
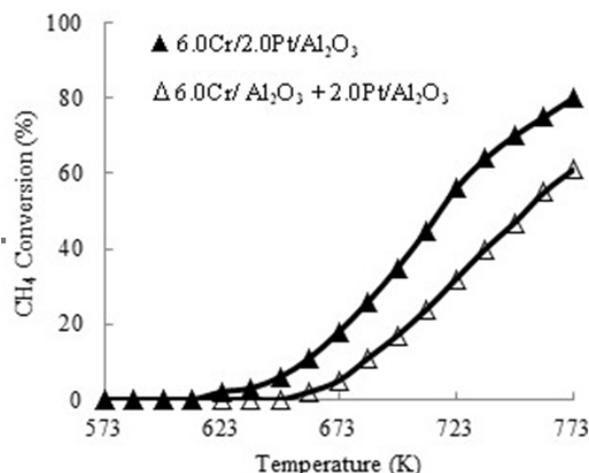

Fig. 3. Comparison of methane conversion over $6.0Cr/Al_2O_3$ + $2.0Pt/Al_2O_3$ catalyst and $6.0Cr/2.0Pt/Al_2O_3$ catalyst.

The Pt particle sizes are shown in table 1. The Pt particle sizes calculated by CO chemisorptions are 2.2, 1.8, and 1.5 nm for $6.0Cr/2.0Pt/Al_2O_3$ (pH 4), $6.0Cr/2.0Pt/Al_2O_3$ (pH 10), and $6.0Cr/2.0Pt/Al_2O_3$ (pH 11), respectively. Somehow, the Pt particle size is smaller in high pH than in low pH, suggests that the addition of NH_4OH also change the Pt dispersion on support.
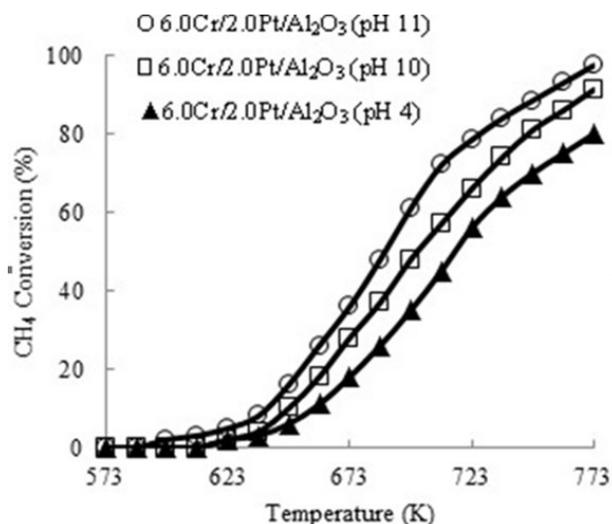
Fig. 4. Methane conversion as a function of temperature for $6.0Cr/2.0Pt/Al_2O_3$ (pH 4), $6.0Cr/2.0Pt/Al_2O_3$ (pH 10), $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalysts.

As shown in figure 4, at 723 K the conversion of methane was 56% on $6.0Cr/2.0Pt/Al_2O_3$ catalyst, meanwhile $6.0Cr/2.0Pt/Al_2O_3$ (pH 10) and $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) gave 66% and 79%, respectively. If no synergistic effect between Cr and Pt, the catalytic of these catalysts should be the same. The catalytic activities decrease as follows: $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) > $6.0Cr/2.0Pt/Al_2O_3$ (pH 10) > $6.0Cr/2.0Pt/Al_2O_3$ (pH 4).

Table 1. CO chemisorptions results.

Catalyst	Pt size (nm)	T 723 K (CH4 conv, %)
$6.0Cr/2.0Pt/Al_2O_3$ (pH 4)	2.5	56
$6.0Cr/2.0Pt/Al_2O_3$ (pH 10)	1.8	66
$6.0Cr/2.0Pt/Al_2O_3$ (pH 11)	1.5	79

The binding energy (eV) was recorded on XPS using Mg Kα (1253.6 eV) radiation at 10 kV and 10 mA. The XPS was measured on calcined catalysts. The binding energies of catalysts were measured with accuracy of ± 0.1 eV and used C 1s at 284.3 eV as standard. It has been known that the interaction of Pt-alumina will results a strong metal surface interaction. Due to this condition, the peak of Pt is difficult to obtain using XPS spectra. The catalysts shown an overlaps between Pt 4f with main peak of Al 2p at 74.6 eV, on the other hand, the peak of oxygen and aluminum oxides is also appeared simultaneously. In order to observe a clear peak for the presence of Cr 2p on catalysts, the XPS was conducted on curve-fitting area of Cr in range of 555-595 eV.

The XPS spectra are showed in figure 5. For $6.0Cr/2.0Pt/Al_2O_3$ (pH 4) catalyst, somewhat a broad peak was obtained on the surface of this catalyst after 500 sweeps. On this broad peak, a low peak is located at binding energies 576.7 eV, this binding energies indicates the presence of Cr 2p3/2. Our results agree well with numbers of researchers who have determined the

position of Cr 2p on supported alumina [18, 19]. The XPS spectra on curve-fitting area of Cr for $6.0Cr/2.0Pt/Al_2O_3$ (pH 10) and $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalyst recorded higher intensities and clear peaks, the catalyst's peaks are shifted to the left compared with $6.0Cr/2.0Pt/Al_2O_3$ (pH 4) catalyst. This indicates that in high pH catalyst, more Cr-Pt metals exist as co-existence than presence separately. The highest peak's binding energy for $6.0Cr/2.0Pt/Al_2O_3$ (pH 10) catalyst is 578.3 eV, this binding energy is higher than the binding energy for Cr 2p3/2 Cr_2O_3 and closer to the binding energy for Cr 2p3/2 CrO_3. The same peak's binding energy is also recorded on $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalyst. The synergistic effect of Cr and Pt could be enhanced by the addition of NH_4OH.
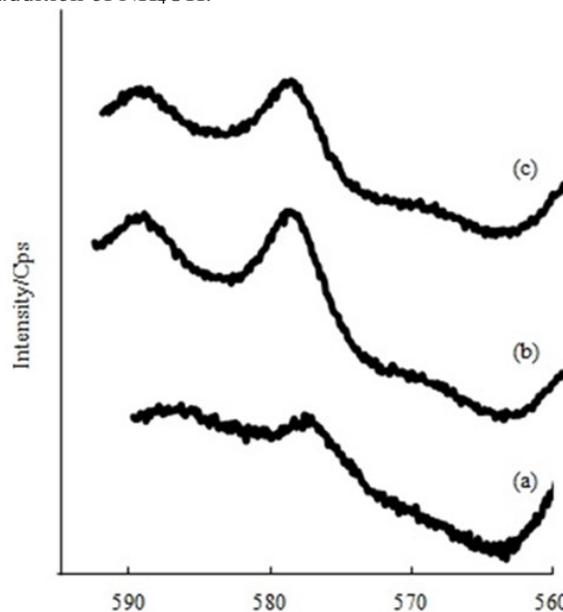

Fig. 5. Xps spectra Cr 2p for (a) $6.0Cr/2.0Pt/Al_2O_3$ (pH 4), (b) $6.0Cr/2.0Pt/Al_2O_3$ (pH 10), (c) $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalysts.

4 Conclusions

We investigated the catalytic activity of binary chromium-platinum catalysts. The oxidation of methane was dependent on chromium loading, Pt particle size, and pH of solution. In this experiment, the pH of solution of binary catalysts was adjusted to ca. 10 and ca. 11by the addition of NH_4OH drop by drop during the catalysts preparation. The catalytic activity results showed that $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalyst has the highest catalytic activity and CO chemisorptions results showed that this catalyst has the smallest Pt particle size compared to other catalysts. The addition of NH_4OH affected the Pt particle size. The XPS spectra showed higher intensities and clear peak of binding energy for $6.0Cr/2.0Pt/Al_2O_3$ (pH 11) catalyst, indicates more aggregation between Cr-Pt-Al_2O_3 occurred. However, the formation of Cr_2O_3 was not observed on the XPS results.

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