Observation of Increased Dispersion of Pt and Mobility of Oxygen in Pt/γ-Al₂O₃ Catalyst with La Modification in CO Oxidation

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Abstract

The study focuses on an improvement of the catalytic activity via CO oxidation for Pt/γ-Al₂O₃ catalyst by addition of La onto the support prior to impregnation with Pt metals. The molar ratios of La/Al were varied from 0.01 to 0.15. Based on temperature-programmed desorption (TPD) of CO₂, La addition apparently resulted in increased basicity of the catalysts, which is related to increasing of oxygen mobility. However, when considered the Pt dispersion measured by CO chemisorption, it was found that Pt dispersion also increased with increasing the amount of La addition up to La/Al = 0.05. It is suggested that too high amount of La addition can inhibit the dispersion Pt due to surface coverage of La. It is worth noting that the catalytic activity toward CO oxidation essentially depends on both Pt dispersion and oxygen mobility and they can be superimposed on each other. Based on this study, the Pt/γ-Al₂O₃ catalyst with La addition of La/Al molar ratio = 0.05 showed the highest activity due to its optimal Pt dispersion and oxygen mobility leading to its highest value of turnover frequency (TOF). Copyright © 2019 BCREC Group. All rights reserved

Keywords: Pt/γ-Al₂O₃; La modification; Pt dispersion; CO oxidation; Oxygen mobility


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1. Introduction

For decades, noble metals such as Pt, Pd, and Au are widely used for CO oxidation catalyst because of their high catalytic activity at low reaction temperature [1-3]. However, a major disadvantage of using noble metals is their high cost. Among noble metals, Pt is mainly used due to its incomparable selectivity to desired products [4,5]. In most case, alumina is used as support for Pt catalyst due to its high thermal stability and high surface area, particularly the γ-Al₂O₃ support [6,7]. However, due to the high cost of Pt, several researches have aimed for the enhancement of Al₂O₃ support properties that can facilitate the Pt dispersion instead of using high loading Pt metal [8]. In fact, the properties of Al₂O₃ support can be improved by using some dopants including La, Ce and Si. Previously, Sun et al. [9] reported that the addition of La or Ce on CuO/γ-Al₂O₃ catalyst can result in a high CO oxidation activity at low
temperatures. However, La doped on CuO/γ-Al₂O₃ catalyst exhibited a higher activity than Ce modified catalyst [9]. Moreover, Chotikrai et al. [10] found that the Si addition on Pt/γ-Al₂O₃ catalyst not only improved the dispersion of Pt sites, but also enhanced the thermal stability of catalyst. Nevertheless, a disadvantage of Si containing catalyst is a decrease in oxygen mobility, which is one of the most important factors for CO oxidation [11,12].

Later, the oxygen mobility of different types of metal oxide was investigated by Martin and Duprez [11]. They found that the oxygen mobility increased with increasing the amounts of surface basicity. As mentioned above, it seems that La is the interesting dopant that can be used to improve the dispersion and the thermal stability for active metal of catalyst, which relate to high activity of catalyst [13]. Furthermore, it is evident that the addition of La can inhibit the sintering of high-surface-area alumina support as well [14]. In addition, La also potentially improves the oxygen mobility because of its high basicity that can overcome the decrease of oxygen mobility as observed in Si addition [10,15]. To the best of our knowledge, no work in the literature has been yet reported on the use of La modified Pt/γ-Al₂O₃ catalysts in catalytic CO oxidation reaction.

Therefore, in this present work, effects of La modification on γ-Al₂O₃ support for Pt/γ-Al₂O₃ catalysts were first used as catalysts for CO oxidation. It is expected that Pt dispersion and oxygen mobility of the catalyst can be improved and subsequently enhanced the catalytic activity of Pt/γ-Al₂O₃ catalysts for CO oxidation. The amounts of La addition are varied and the effects of La addition on Pt dispersion and oxygen mobility of different Pt/γ-Al₂O₃ catalysts are observed.

2. Materials and Methods

2.1 Catalyst Preparation

The γ-Al₂O₃ support was obtained by calcination of the commercial boehmite (Pural SB) in air at 550 °C for 4 h. A series of La doped on γ-Al₂O₃ support were prepared via impregnation method using an aqueous solution of lanthanum nitrate hexahydrate [La(NO₃)₃·6H₂O]. The La-doped γ-Al₂O₃ supports having five different molar ratios of La to Al at 0 (undoped), 0.01, 0.05, 0.10, and 0.15 were obtained. The supports were dried at 110 °C for 24 h and calcined in air at 500 °C for 3 h (heating rate of 10 °C/min). Then, the Pt/γ-Al₂O₃ catalysts with La modification were obtained by the incipient wetness impregnation method using 0.3 wt% of Pt in the aqueous solution of H₂PtCl₆·6H₂O. After that, the ready-to-use samples obtained after dried in an oven at 110 °C overnight and calcined in air at 500 °C for 3 h at the same heating rate. The Pt/γ-Al₂O₃ catalysts were denoted as Pt-XLa; where X is the molar ratio of La to Al in the alumina supports.

2.2 Catalyst Characterization

The crystalline phases were identified by XRD measurement (Bruker D8 Advance). The scanning was carried out by using nickel filtered (Cu-Kα radiation) and a VÂNTEC-1 detector, and scattered radiation was measured with a proportional counter detector at a scan rate of 1 °C/min⁻¹. The scanning angle was from 20° to 80° (degrees 2θ), operating at a voltage of 40 kV applying potential current of 30 mA.

The adsorption-desorption isotherms of nitrogen at -196 °C were obtained from gas sorption techniques (Micromeritics ASAP 2010 Analyser). The specific surface areas were determined by adsorption values for relative pressure (P/P₀) by using the BET method. The total pore volume was estimated from the total amount of adsorbed nitrogen by using the BJH method.

The active sites per gram of catalysts and the relative percentages dispersion of platinum metal are determined by CO-pulse chemisorption technique using Micromeritics ChemiSorb 2750 (pulse chemisorption system). This was performed by first, 0.05 g of catalysts was reduced in H₂ at 500 °C for 1 h. After reduction, H₂ was evacuated by He at 510 °C for 10 min and cooled down with He. After cooling down, the 20 µL of CO gas was fed to the catalyst by syringe injection at He flow rate of 25 mL/min at 30 °C. The CO gas was pulsed on catalyst until it was saturated. Active site of the Pt catalysts was calculated by assuming that ratio of CO_adsorbed/Pt is 1:1 (Pt denotes surface Pt atoms).

The basicity of all catalysts were determined by temperature programmed desorption of carbon dioxide (CO₂-TPD). It was performed by first, 50 mg of catalyst powder was pretreated in He at 500 °C with flowing of helium (30 mL/min⁻¹) for 1 h before cooling down to 30 °C. After, the catalyst was saturated with pure CO₂ (20 mL/min⁻¹) at 40 °C for an hour. Then, the physisorbed CO₂ was desorbed in a He flow until a constant baseline level was attained. The TPD profile of desorbed CO₂ was recorded with TCD (Micromeritics 2750 with a computer) from 30 to 600 °C with a heating rate of 10 °C/min.
2.3 Catalyst Test in CO Oxidation

All catalysts were tested for their catalytic performance in CO oxidation. First, 0.05 g of catalyst was packed into the quartz reactor with 5 mm (ID) that was placed in a furnace. After that, He was purged to remove air inside the reactor. The catalyst was then reduced with H₂ at 500 °C with a heating rate of 10 °C/min for 1 h. The H₂ remained in the quartz reactor was removed by purging with He at 510 °C for 30 min before cooling down to ambient temperature. The reactant gas mixture (1% CO, 2% O₂ and balanced He) was fed through the catalyst bed at a total flow rate of 100 mL/min (GHSV = 30,600 h⁻¹) and maintained at a desired temperature for 20 min. The concentration of CO was carried out by an online using a Shimadzu GC-8ATP gas chromatograph (thermal conductivity detector, TCD) with a Parapak Q column (3 mm i.d. × 7 m) and a molecular sieve 5A column (3 mm i.d. × 3 m). Catalytic activity was evaluated in terms of the light-off temperature, defined as the temperature used to obtain 50% conversion of CO. The calculation of CO conversion was based on CO reacted. The turnover frequency (TOF) of the reaction per active site (at 150 °C) was calculated based on Pt active sites measured by CO chemisorption with CO conversion < 20%. They were calculated following Eqs. (1) and (2):

\[
\% \text{CO conversion} = \frac{n_{\text{CO(in)}} - n_{\text{CO(out)}}}{n_{\text{CO(in)}}} \times 100
\]

\[
\text{TOF} = \frac{\text{Rate of reaction}}{\text{Metal active site}}
\]

Where \(n_{\text{CO(in)}}\) is the number of moles of carbon monoxide in feed, \(n_{\text{CO(out)}}\) is the number of moles of unreacted carbon monoxide, respectively.

3. Results and Discussion

3.1 Catalyst Characterization

The XRD patterns of Pt/γ-Al₂O₃ catalysts with different La modification at θ = 20° to 80° are shown in Figure 1. The XRD patterns of γ-Al₂O₃ support exhibited the expected main peaks of gamma phase at θ = 38°, 46° and 67°, corresponding to the reflections of the (311), (400) and (440) planes, respectively [16]. After Pt metal (0.3 wt%) was loaded to γ-Al₂O₃, the characteristic peaks of Pt were not observed. This may be due to well dispersion of Pt on support or very low amount of Pt loading [17]. In the similar way, the characteristic peaks of La were not seen in the XRD patterns of all Pt/γ-Al₂O₃ catalysts containing La modification probably due to high dispersion of La species. However, the addition of La led to decreased peak intensities of γ-Al₂O₃. This suggests that the crystallinity of γ-Al₂O₃ was decreased by La modification.

Some textural properties of the synthesized catalysts were determined by N₂ physisorption.
methods and the results are shown in Table 1. The results show that the BET surface area of the unmodified Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalyst was 210 m\(^2\)/g. It apparently decreased to 203, 162, 107, and 75 m\(^2\)/g with the increase of La loading to 0.01, 0.05, 0.10, and 0.15 molar ratio, respectively. This was due to the surface coverage of Al\(_2\)O\(_3\) by La content [14,18]. Similarly, the pore volume of the samples also diminished with increasing the La loading. After La addition, the pore size of Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalysts essentially tended to decrease with increasing La contents. The decrease in pore size diameter was related to the accumulation of La\(_2\)O\(_3\) and pore blockages [10]. However, at higher molar ratio of La/Al than 0.10, it led to the increasing of pore size diameter. This can be attributed to the presence of an amorphous structure with higher La contents was used. These results corresponded to the XRD results as previously explained [19,20].

The basicity of catalysts was determined by CO\(_2\)-TPD. The CO\(_2\)-TPD profiles and the amounts of desorbed CO\(_2\) of all Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalysts containing La modification are shown in Figure 2 and Table 1, respectively. As seen from Figure 2, the results show that the CO\(_2\) desorption peaks of Pt-0La and Pt-0.01La were clearly observed only at a low temperature around 100 °C. This peak was attributed to the weak basic sites of Pt-0La and Pt-0.01La catalysts and was related to the desorption of associated CO\(_2\) [21]. For the catalysts with higher loading of La (Pt-0.05La, Pt-0.10La, and Pt-0.15La), another peak was additionally observed at higher temperature around 300 °C. This peak was attributed to the strong basic sites of the catalysts and was related to the strong CO\(_2\) interaction with La\(_2\)O\(_3\) [21]. The amounts of basic sites of catalysts calculated from the peak areas of CO\(_2\) desorption peak were listed in Table 1. It revealed that the basicity of catalysts increased with increased amounts of La loading on alumina support. It should be mentioned that the La-modified supports induced the construction of stronger base centers that could be correlated with free lanthanum highly dispersed on alumina surface [22,23].

The number of active sites of the catalysts from CO-pulse chemisorption were also shown in Table 1. The results show that the number of active sites of Pt/\(\gamma\)-Al\(_2\)O\(_3\) was 7.20×10\(^{-18}\) molecules of CO/g.cat and it was increased to 8.87 and 7.55×10\(^{-18}\) molecules of CO/g.cat after loading of La with molar ratio of 0.01 and 0.05, respectively. When La was added as a dopant to \(\gamma\)-Al\(_2\)O\(_3\), it disperses as a monolayer. This monolayer of La changes the surface properties of the support and thereby effects the dispersion and crystallite size of the supported metal. This in turn enhances the dispersion of active Pt metals on the catalysts surface compare with the unmodified catalyst [13,14]. However, at high La loading in the catalysts, the active Pt sites was found to decrease because of the high coverage of \(\gamma\)-Al\(_2\)O\(_3\) surface by La\(_2\)O\(_3\) resulting in more sintering of Pt metals [10].

### 3.2 Catalytic Performance via CO Oxidation

The CO conversion profile as a function of reaction temperature is shown in Figure 3 and a curve of light off temperature (\(T_{50}\)) as a function of active Pt sites is shown in Figure 4. The Pt-0.01La sample showed superior catalytic ac-

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**Figure 2.** CO\(_2\)-TPD profiles of Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalysts containing La modification.

**Figure 3.** The CO conversion profiles of Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalysts containing La modification.
tivity in CO oxidation with the lowest temperatures at 170 °C for 50 % conversion. With increasing of La molar ratio from 0.05 to 0.1 and 0.15, T_{50} increased from 170 to 173, 180, and 183 °C, respectively. Compared to the unmodified Pt/γ-Al₂O₃ catalyst, the La-modified catalysts showed higher catalytic activity. For the Pt-0.05La and Pt-0La catalysts, T_{50} of the former was much higher than the latter despite similar amount of active sites (ca. 7.20 and 7.55 × 10^{−18} molecules of CO/g.cat). Thus, differences in catalytic activities between these two catalysts suggested that there might be some other effects besides the amount of active Pt sites including in the CO oxidation on Pt/γ-Al₂O₃ catalysts. According to the previous work of Chotikrai et al. [10], one of the most significant factors influencing the CO oxidation activity is the oxygen mobility. Therefore, effect of La addition on the oxygen mobility was also investigated. Based on the research reported by Martin et al. [11], the rate of oxygen surface diffusion was essentially related to the amount of basic sites in which the higher basic sites showed high oxygen mobility. This is corresponding to the CO₂-TPD results as seen in Figure 2. The results showed that the addition of La can increase the amount of basic sites of Pt/γ-Al₂O₃ catalyst and perhaps provided high catalytic activity. This is because the Pt–O bond strength also decreases as optical basicity increases [24], thus, the O₂ movement on the surface is easier. As the result, adsorbed oxygen can easily react with the adsorbed carbon monoxide. Interestingly, it is found that the oxygen mobility on γ-Al₂O₃ supports is similar with that of the catalytic performance of the corresponding Pt/γ-Al₂O₃ catalyst, suggesting that the surface oxygen mobility of γ-Al₂O₃ support is the key factor in causing the difference in catalytic performance as well as the turnover frequency (TOF). The important role of oxygen mobility on a catalyst support has also been observed in other catalytic system [25,26]. In order to highlight the effect of oxygen mobility on CO oxidation besides the major effect of active Pt sites, the TOFs of a reaction can often be related to the function of basicity, for it is typically unresponsive to the Pt particle size [27,28]. Figure 5 shows a relationship between TOFs and basicity. It can be observed that the TOFs increased as the amount of basicity increased (increasing La content). This is highlight the effect of oxygen on support basicity in oxidation reaction. However, higher amounts of La addition with resulting in too strong basicity not only decreased active Pt sites, but also inhibited the activity of oxidation reaction [29,30]. As revealed by second metal dopants such as Si [10], the addition of La can improve oxygen mobility of Pt/γ-Al₂O₃ catalyst, which is opposite to the Si addition. Therefore, La is more suitable to modify the Pt/γ-Al₂O₃ catalyst than Si.

4. Conclusions

The catalytic oxidation of carbon monoxide (CO) over La-modified catalysts proposed that the catalytic performance seemingly depended not only on dispersion of Pt, but also on the oxygen mobility of the supports. The noteworthy relationship between TOF and desorbed CO₂ also reinforced the effect of oxygen mobility relating to basicity of catalysts. The desorbed

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Figure 4. Relationship between light off temperature T_{50} and active sites of Pt/γ-Al₂O₃ catalysts containing La modification.

Figure 5. Relationship between TOF and basicity of Pt/γ-Al₂O₃ catalysts containing La modification.
CO₂ as illustrative of oxygen mobility was tremendously increased with increased amounts of La addition on the γ-Al₂O₃. Moreover, Pt dispersion was highly improved on 0.01 and 0.05 molar ratios of La addition to the support and declined afterward. The suitable amount of La addition needs to be optimized due to trade-off effects between the dispersion of Pt sites and oxygen mobility. These effects are superimposed on each other. Among all La-modified Pt/γ-Al₂O₃ catalysts obtained in this study, the catalyst containing 0.05 molar ratio of La to the support (Pt-0.05La) exhibited the highest catalytic activity because it optimized the Pt dispersion and the oxygen mobility.

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References


