ENHANCEMENT OF OXYGEN MOBILITY ON CO OXIDATION REACTION OVER PT/Γ-AL2O3 BY LA

[1]THANAWAT WANDONDAENG, [2]WIPARK ANUTRASAKDA, [3]PIYASAN PRASERTHDAM

[1,3]Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand,
[2]Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: mcthanawat@gmail.com

Abstract - Effects of La doped Pt/γ-Al_2O_3 catalysts on oxygen mobility of catalyst were investigated by CO oxidation reaction. 0.05 molar ratio of La to Al was doped by impregnation method and compare with Pt/γ-Al_2O_3. The catalytic activities in CO oxidation reaction in terms of light-off temperature (T_{50}) corresponded to Pt active sites, oxygen mobility as characterized by various analytical techniques such as CO-pulse chemisorption and temperature program desorption of CO_2(CO_2-TPD). The results indicated that the addition of La on Pt/γ-Al_2O_3 can increase oxygen mobility of catalyst. As a result, the catalyst activity for CO oxidation was significantly improved.

Index Terms - Pt-La/γ-Al_2O_3, La Modified Catalyst, CO Oxidation, Oxygen Mobility

I. INTRODUCTION

CO oxidation reaction is normally used in order to treat CO gas in catalytic process [1, 2]. Furthermore, CO oxidation reaction is suitable to investigate the performance of catalysts because of its structure insensitivity[3]. Noble metals such as Pt, Pd and Au are widely used for CO oxidation catalyst because they have high catalytic activity at low temperature [4-6]. However, a major disadvantage of using noble metals is the price. Among noble metals, Ptis widely used because it has highly selective desired product [7, 8]. Alumina is mostly used as support in Pt catalyst due to its high thermal stability and high surface area especially the γ-Al_2O_3 phase [9, 10].

One important factor for the CO oxidation is oxygen mobility. According to Chotikrai et al. [11], the addition of Si into Pt/γ-Al_2O_3 catalyst not only improved the dispersion of Pt sites, but also enhanced the thermal stability of catalyst.Nevertheless, a disadvantage of Si containing catalyst was the decreasing of oxygen mobility. According to D.Martin and D.Duprez[12], the oxygen mobility of different types of metal oxide was investigated, the results show that the rate of oxygen diffusion increased with the amount of surface basicity. La is the interesting dopant that may improve the oxygen mobility because of its highly basicity properties [13-15].

In the present work, the effects of La modified γ-Al_2O_3 supported Pt catalysts on oxygen mobility of catalyst were investigated by CO oxidation. 0.05 mole ratio of La to Al was doped into Pt/γ-Al_2O_3 by impregnation method.

II. EXPERIMENTAL

A. Catalyst preparation

The γ-Al_2O_3 support was prepared by calcination of the commercial boehmite (Pural SB) in air at 550 °C for 4 h.

La-modified γ-A_2O_3 support was prepared via impregnation method using the solution of lanthanum nitrate hexahydrate ($La(NO_3)_3.6H_2O$). The molar ratios of La to Al 0.05 were studied. The impregnated solids were dried in an oven at 110 °C overnight and calcined in air at 500 °C for 3 h. The La modified γ-Al_2O_3 supported Pt catalyst was prepared by impregnation method using

0.3 wt.% Pt with aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ that impregnated into La modified γ-Al_2O_3 support. After that, the impregnated sample was dried in an oven at 110 °C overnight and calcined in air at 500 °C for 3 h.

B. Catalyst characterization

The active sites of platinum metal was determined via CO-Pulse chemisorption technique using Micromeritics ChemiSorb 2750 and ASAP 2101C V.3.00 software.

50 mg of catalysts was reduced in H_2 at 500 °C for 1 h. After reduction, H_2 was driven with 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 flow rate of He is 25 ml/min at 30 °C. CO was pulsed until catalysts were saturated. Active site of the Pt catalysts was calculated by assuming that ratio of $CO_{adsorbed}$/Pt atom is unity.

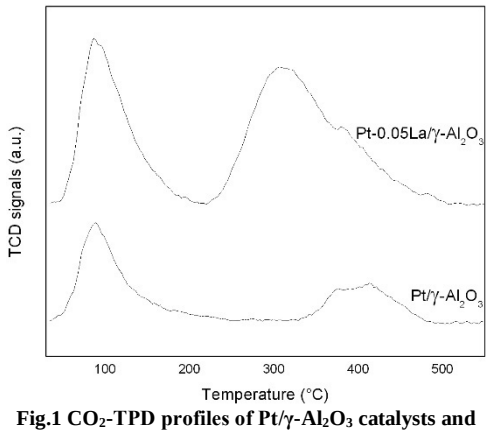


Fig.1 CO_2-TPD profiles of Pt/γ-Al_2O_3 catalysts and Pt-0.05La/γ-Al_2O_3 catalysts.

Table.1 Basicity and active sites of $Pt/\gamma\text{-}Al_2O_3$ catalysts and $Pt\text{-}0.05La/\gamma\text{-}Al_2O_3$ catalysts

Catalysts	Desorbed CO_2[a] (area/g)	Basicity[a] (mmol CO_2/g)	Active sites[b] (molecule$COx10^{-18}$/g.cat)
$Pt/\gamma\text{-}Al_2O_3$	1.6	0.6	7.2
$Pt\text{-}0.05La/\gamma\text{-}Al_2O_3$	4.8	1.7	7.6

a calculated from CO_2 TPD method
b calculated from CO Chemisorption method

The basicity of the supports was evaluated by CO_2-TPD. 50 mg of catalyst powder was treated in He at 510 °C for 1 h before cooling down to 30 °C. After that, 20 ml/min of CO_2 was applied through sample for 20 min. Then, CO_2-saturated sample was purged with He until baseline stable. The TPD profile was recorded with TCD (Micromeritics 2750) with a heating rate of 10 °C/min.

C. Catalyst performance test

The synthesized catalysts were tested for their catalytic performance of CO oxidation. 50 mg of each catalyst was packed into the quartz reactor with 5 mm inside diameter that was placed in the furnace heated by variable voltages. After that, He was purged to remove air inside the reactor. The sample was then reduced with H_2 at 500 °C with a heating rate of 10 °C/min for 1 h. The H_2 remained in the quartz reactor was removed by purging He at 510 °C for 30 min before cooling down at ambient temperature.The reactant gas mixture (1% CO, 2% O_2 and balanced He) was flown through the catalyst bed at a total flow rate of 100 ml/min (GHSV ≈ 30600 h^{-1}) and maintained at a desired temperature for 20 min. The concentration of CO was monitored by an on-line GC-8ATP (Shimadzu) gas chromatograph equipped with a TCD detector and a Molecular Sieve 5A column.Catalytic activity was evaluated in terms of the light-off temperature, defined as the temperature at 50% conversion obtained. The calculation of CO conversion was based on CO consumption. The turnover frequency (TOF) of the catalysts at 150 °C was calculated based on Pt active sites measured by CO chemisorption and at CO conversion < 15%.

III. RESULTS & DISCUSSION

A. Characterization

CO_2-TPD profiles and the amounts of desorbed CO_2 of the catalysts were shown in Fig. 1 and Table 1, respectively. From Fig. 1, the results show that the peak of CO_2desorption of $Pt/\gamma\text{-}Al_2O_3$ and $Pt\text{-}0.05La/\gamma\text{-}Al_2O_3$ wasobserved two main peaks. At a low temperature, this peak could be attributed to the weak basic sites and was related to the desorption of undissociated CO_2[16]. For a high temperature, this peak could be attributed to the strong basic sites and was related to the strong CO_2 interaction with La_2O_3[16]. The amounts of basic sites of catalysts calculated from the peak area ofCO_2 desorption peak (Table 1) show that the amount of basicity of $Pt/\gamma\text{-}Al_2O_3$ was 0.6mmol CO_2/g and was increased to 1.7mmol CO_2/g after add La into $Pt/\gamma\text{-}Al_2O_3$. The results suggest that the basicity of catalysts were increased with the increase of La loading. The La-modified supports induced the construction of stronger base centers that could be correlated with free lanthanum highly dispersed on alumina surface [17, 18].

The amount of active sites of the catalysts from CO-pluse chemisorption were shown in Table 1. The results show that the amount of active sites of $Pt/\gamma\text{-}Al_2O_3$ was 7.2 molecule $COx10^{-18}$/gcat and slightly increased to 7.5 molecule $COx10^{-18}$/gcat after loading La. The results suggest that the addition of La can enhance the dispersion of Pt active metal on the catalysts [19, 20].

B. CO oxidation reaction and effect on oxygen mobility

The light off temperature (T_{50}) of two catalysts was shown in Fig. 2. The $Pt\text{-}0.05La/\gamma\text{-}Al_2O_3$ showed much lower activity temperatures at 170 °C than $Pt/\gamma\text{-}Al_2O_3$ (194 °C) for 50 % conversion despite closing amount of active sites (about 7.2 and 7.6 molecule $COx10^{-18}$/gcat). The differences in catalytic performances between two catalysts suggest that there might be some other effect besides the amount of Pt active sites involve in the CO oxidation on $Pt/\gamma\text{-}Al_2O_3$ catalysts. According to N. Chotikrai et al. [11], the significant factor influencing CO oxidation activity is oxygen mobility. According to D.Martin et al. [12], the rate of oxygen mobility was practically linked to the amount of basic sites in which the higher basic sites exhibited higher oxygen that correlate with CO2-TPD result in Table 1. The result show that the addition of La can increase the amount of basic sites of $Pt/\gamma\text{-}Al_2O_3$ catalyst from 0.6 to 1.7 mmol CO_2/g that could be attributed to increasing of oxygen mobility and resulted to high catalytic activity because the Pt–O bond strength decreases as optical basicity increases, the O_2 movement on the surface is easier [21].

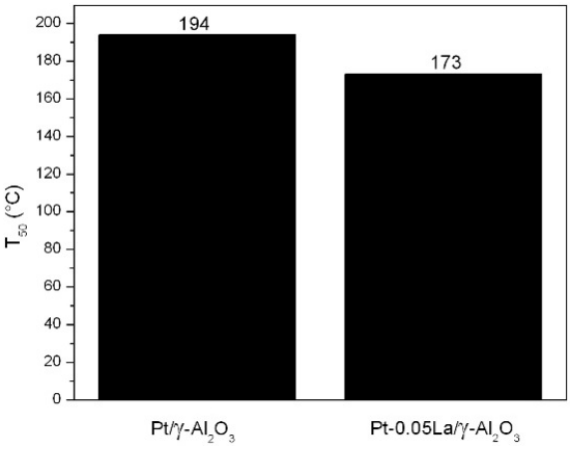


Fig.2The CO oxidation results of catalysts: the light off temperature (T_{50}) of $Pt/\gamma\text{-}Al_2O_3$ catalysts and $Pt\text{-}0.05La/\gamma\text{-}Al_2O_3$ catalysts.

CONCLUSION

The results of CO oxidation over La-modified catalysts suggested that the catalytic activity apparently depended not only on Pt dispersion but also oxygen mobility of the supports. The desorbed CO_2 as representative of oxygen mobility was substantially increased with increasing amount of La loading on the $Pt/\gamma\text{-}Al_2O_3$. The results suggest that the highly oxygen mobility results to a high catalytic performance of CO oxidation.

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