

Effect of water vapor on carbon monoxide oxidation over promoted platinum catalysts

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This study focuses on investigation of the effects of magnesium on catalyst and moisture in reactant on the catalytic activity in CO oxidation using Pt catalysts. The CO conversion rate over Pt–Mg/Al₂O₃ with temperature was higher than that of Pt/Al₂O₃. With the reactants containing moisture, the CO conversion rate over Pt–Mg/Al₂O₃ was significantly improved. It is observed that addition of magnesium to Pt catalysts enriches the hydroxyl group with the increase of basicity and the content of Pt⁰ which is weakly interacted with CO.

KEY WORDS: CO oxidation; Pt/Al₂O₃; magnesium; hydroxyl; basicity.

1. Introduction

The CO oxidation has been applied in the industrial processes such as ammonia synthesis or the emission control of pollutants [1]. Recently an intensive research on the CO oxidation reaction is required because of its importance in the hydrogen purification processes for fuel cell system (preferential CO oxidation) [2]. Many researchers made efforts to enhance the rate of CO oxidation through changing a character of catalyst with promoter. Some showed their outstanding result that alkali metal oxide as promoter was helpful to CO oxidation over Pt catalyst [3,4]. They explained that the enhancement of CO oxidation rate is related to the surface electron density of Pt catalyst [5], and alkali metal promoted a generation of active oxygen on the surface of catalysts.

The oxidation activity on Pt catalysts was increased by the moisture contained in the reactants too [2,6]. Though the role of moisture in CO oxidation reaction has not been clarified yet, it is recently reported the moisture has direct effects on the active sites of catalysts and improves oxidation activity. In the CO oxidation of Au catalysts [7,8], the moisture forms Au⁺-OH⁻ through adsorption on Au clusters with low electron density and then Au-hydroxycarbonyl produced by the reaction of CO with Au⁺-OH⁻ is oxidized by dissociated oxygen which is adsorbed on Au clusters with high electron density. For CO oxidation on Pt catalysts, the moisture makes effects on CO oxidation activity through the mechanism similar to Au catalysts.

This study is to compare the effect of moisture on CO oxidation reaction of both Pt–Mg/Al₂O₃ and Pt/Al₂O₃ catalysts.

2. Experiment

2.1. Preparation and characterization of catalyst

Activated alumina (Aldrich Co.) with specific surface of 150 m²/g was used as support. Pt catalysts were prepared by the incipient wetness impregnation of support with aqueous solutions, as following procedures.

Al₂O₃ power of 5 g was contacted with an aqueous solution of PtCl₄ (Aldrich Co.), followed by drying at 100 °C for 24 h. The dried catalyst powder was calcined at 400 °C for 4 h. A promoted Pt–Mg/Al₂O₃ catalysts were prepared by the incipient wetness impregnation with an aqueous solution of PtCl₄ + Mg(NO₃)₃·6H₂O (Aldrich Co.). Pt–Mg/Al₂O₃ catalysts were dried and calcined by the same method above.

TPR and TPD-CO₂ test were carried out using the Autochem 2910 equipped with a thermal conductivity detector. Before TPR test, the catalyst was reduced at 300 °C for 2 h and oxidized in the atmosphere at 400 °C for 0.5 h. The change of hydrogen concentration in the reactants was measured with the increase of temperature from –50 to 400 °C at a flow rate of 2 °C/min with 5.0 vol% H₂/Ar.

X-ray photoelectron spectroscopy (XPS) analysis was performed using ESCALAB MK-2 (England, VG Scientific Ltd.) spectrometer with an Mg $\kappa\alpha$ anode (1253.6 eV) at an acceleration voltage of 13 kV and current of 20 mA. Collected XPS data of each catalyst

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was adjusted by the C1s peak to a position of 285.0 eV. Only freshly prepared catalysts were analyzed first by a wide-scan of 0–1100 eV region of binding energy and then by single scan analysis of Pt 4d_{5/2} regions.

In order to analyze the type of adsorbed CO on Pt catalysts, we used FT/IR-660 (JASCO Inc.) equipped with MCT narrow band detector. After the reduced powder catalyst of 0.1 g was filled with in the reaction cell, it is pretreated by He at 300 °C for 2 h. The gas mixture was put into the reaction cell at a rate of 30 mL/min. Though this experiment, we investigated the effects of oxygen and moisture on CO adsorption using the following different composition of reactants: (a) 0.4 vol% CO/He, (b) 0.4 vol% CO/He+0.8 vol% H₂O/He, (c) 0.4 vol% CO/He+0.3 vol% O₂/He, (d) 0.4 vol.% CO/He+0.8 vol.% H₂O/He+0.3 vol.% O₂/He.

2.2. Experimental procedure

Catalytic activity was measured in a micro-fixed bed reactor. The micro-reactor was a quartz tube of 6 mm in internal diameter and 50 mm in length. O₂(99.999%), N₂(99.999%) and 20% CO(N₂ balance) were used as received without further purification. Water was introduced from the vaporization chamber. The catalyst loading corresponded to 0.1 g and the flow rate was set at 100 mL (STP)/min. Activity of catalysts was examined at 130–230 °C.

3. Result

3.1. Characterization

3.1.1. CO₂-TPD

Figure 1 shows the change of surface basicity through CO₂-TPD measurements for the addition of Mg to Pt/

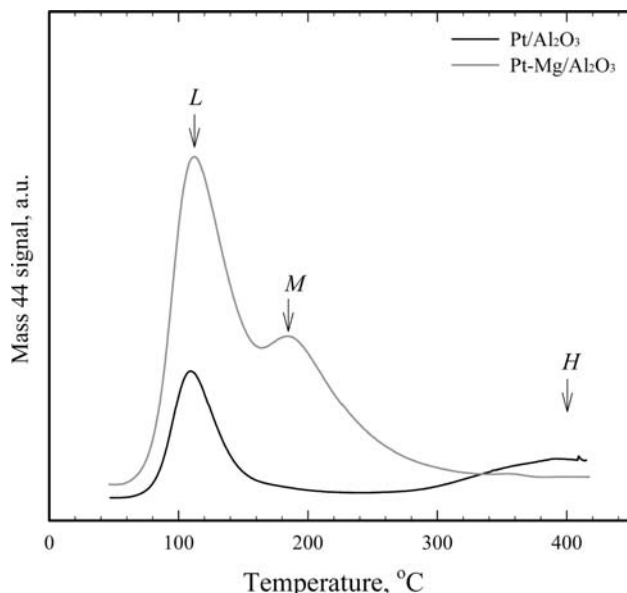


Figure 1. CO₂-TPR pattern of Pt/Al₂O₃ and Pt–Mg/Al₂O₃.

Al₂O₃ catalysts. Desorption temperature of CO₂ can be divided into three ranges according to the basic strength on catalyst surface [8–10]. For prepared catalyst, the ranges were also shown due to basicity as follows: low basicity sites (L) where CO₂ is desorbed within the range of 80–140 °C; medium basicity sites (M) where CO₂ is desorbed within the range of 160–240 °C; and high basicity sites (H) where CO₂ is desorbed at over 300 °C. In figure 1, low basicity sites (L) and high basicity sites (H) were also observed in Pt/Al₂O₃ catalysts, but the concentration of low basicity sites (L) for Pt–Mg/Al₂O₃ catalysts was improved higher than that in Pt/Al₂O₃ and medium basicity sites (M) were detected.

3.1.2. XPS

Figure 2 shows the result of curve fitting of Pt 4d_{5/2} core level spectra for Pt/Al₂O₃ and Pt–Mg/Al₂O₃ which are pre-reduced by hydrogen at 300 °C for 2 h. As shown in XPS analysis of figure 2, Pt existed in metallic state (Pt⁰) and partially oxidized state (PtO) in the reduced Pt/Al₂O₃ and Pt–Mg/Al₂O₃ catalysts, and the ratio of Pt⁰ to PtO in Pt 4d_{5/2} core level spectra in each catalyst was 0.82 for Pt/Al₂O₃ and 0.56 for Pt–Mg/Al₂O₃. This is because interaction between Pt and Al₂O₃ is affected by Mg added.

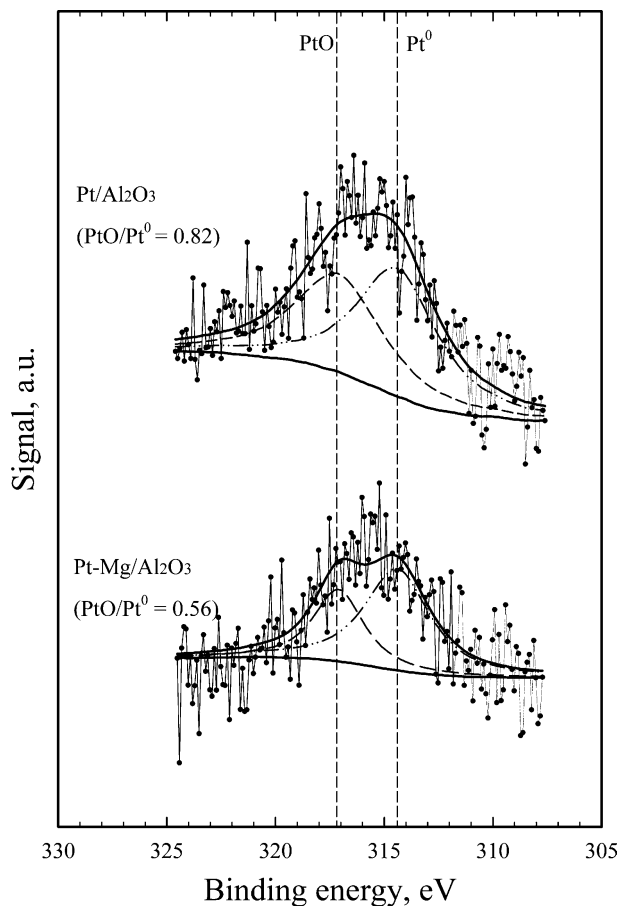


Figure 2. Curve fit of the Pt 4d_{5/2} core level spectra for the Pt/Al₂O₃ and Pt–Mg/Al₂O₃ catalysts reduced by H₂.

3.1.3. TPR

TPR patterns for Pt/Al₂O₃ catalysts are known to be divided into three according to oxidation state of Pt [11]. TPR peak of oxygen adsorbed on Pt⁰ appears at -25 °C, PtO at 50 °C and PtO₂ at 100 °C. These PtOx reduction temperatures are somewhat different with contents of noble metal. Figure 3 shows the TPR patterns of Pt/Al₂O₃ and Pt-Mg/Al₂O₃ reduced under air at 400 °C. Pt of Pt/Al₂O₃ was mainly detected as PtOx (1 < x < 2), while Pt of Pt-Mg/Al₂O₃ existed in the mixed form of Pt⁰ and PtOx (1 < x < 2). The oxidation state of Pt in the two reduced catalysts of figure 3 showed the existence of Pt⁰ and Pt⁺ although there was difference in the contents. According to TPR data obtained after calcination under atmosphere at 400 °C, however, Pt on Pt/Al₂O₃ existed mostly as an oxidized state, but Pt on Pt-Mg/Al₂O₃ existed as a very stable neutral state.

3.1.4. DRIFTS

Figure 4 shows the DRIFTS spectra of CO adsorbed on Pt/Al₂O₃ catalysts at 100 °C. In case of 0.4% CO/He (a), CO adsorption spectrum was composed of three bands at 1826, 2068 and 2124 cm⁻¹. The first two bands are known to be related to CO adsorbed as the bridging form and the linear form into the Pt⁰ of the reduced Pt/Al₂O₃[12,13]. The band of 2124 cm⁻¹ indicates the symmetric stretching of the thermally stable Pt^{δ+}-(CO)₂ [14]. In the condition of (c), the band of the linearly adsorbed CO shifted a little to left. However, when moisture was added to the two reaction conditions (b) and (d), the bands of bridging form and linear form of adsorbed CO moved to lower wave number. In particular, 2124 cm⁻¹ band did not

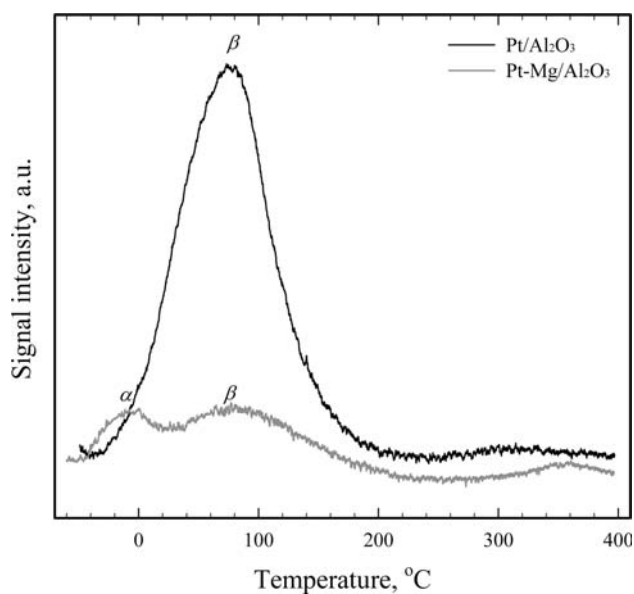


Figure 3. TPR patterns of Pt/Al₂O₃ and Pt-Mg/Al₂O₃.

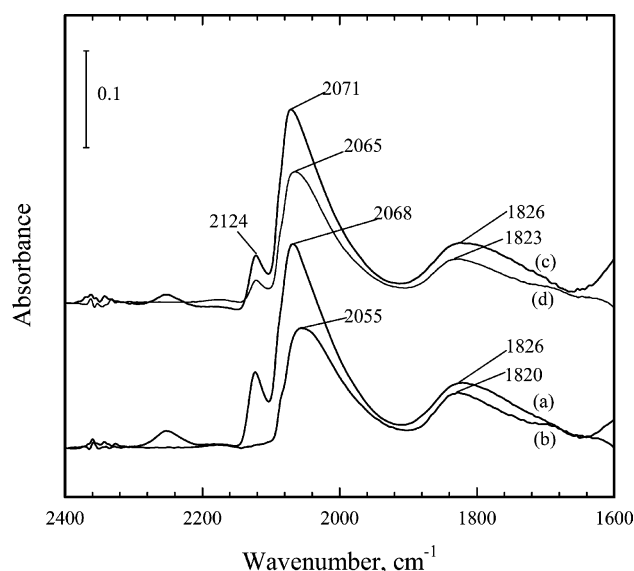


Figure 4. *In situ* IR spectra of adsorbed CO at 100 °C on Pt/Al₂O₃: (a) CO only; (b) CO + H₂O; (c) CO + O₂; (d) CO + O₂ + H₂O.

appear in the condition (b) containing CO and moisture.

Figure 5 shows IR spectra of CO adsorbed under Pt-Mg/Al₂O₃ catalysts of the same condition as that in figure 4. In case of (a), a band (1816 cm⁻¹) of a bridging form and bands (2054 and 2077 cm⁻¹) of two linear forms are appeared, but 2124 cm⁻¹ band did not appear on Pt-Mg/Al₂O₃ in the every condition. The band at 2054 cm⁻¹ is the linear form of CO adsorbed into Pt, being affected by Mg addition. Albertazzi and coworkers showed that a band of linear form in reduced Pt/Al-Mg(O) appeared at 2060 cm⁻¹ [15], because the electron

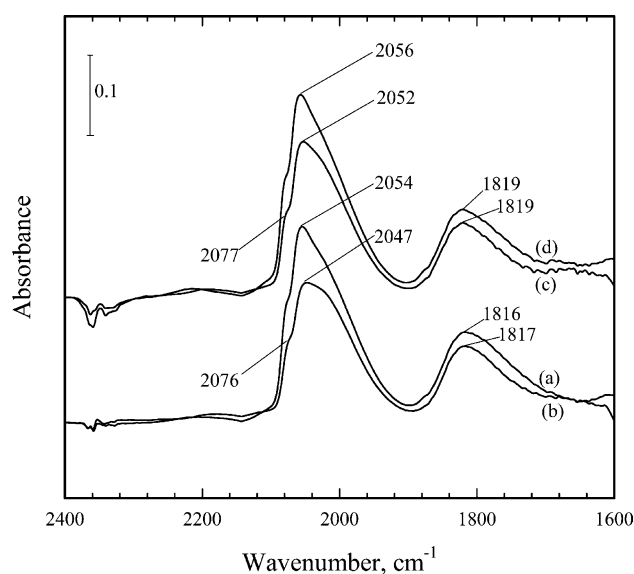


Figure 5. *In situ* IR spectra of adsorbed CO at 100 °C on Pt-Mg/Al₂O₃: (a) CO only; (b) CO + H₂O; (c) CO + O₂; (d) CO + O₂ + H₂O.

density of Pt was increased by Mg [12]. Results of Pt–Mg/Al₂O₃ with variation of reaction condition were similar to those for Pt/Al₂O₃ catalysts.

3.2. The effect of magnesium and water vapor in reactant on CO oxidation over Pt/Al₂O₃

Figure 6 shows the effects of magnesium on catalyst and moisture in reactants on catalytic activity in CO oxidation reaction over Pt/Al₂O₃ and Pt–Mg/Al₂O₃ catalysts. Temperatures with CO conversion of 30% (T_{30}) and 50% (T_{50}) in dry condition were 192 and 199 °C, respectively for Pt/Al₂O₃ catalysts and 186 and 191 °C, respectively for Pt–Mg/Al₂O₃ catalysts. As shown in figure 1, the activity of Pt/Al₂O₃ and Pt–Mg/Al₂O₃ catalysts in the reactants containing moisture was improved. T_{30} of 177 °C and T_{50} of 189 °C for Pt/Al₂O₃ catalyst in the moisture condition were 2–9 °C lower than those in dry condition. CO oxidation activity of Pt–Mg/Al₂O₃ catalysts was improved by moisture much higher than that of Pt/Al₂O₃ catalysts. T_{30} of 158 °C and T_{50} of 169 °C in the moisture condition were about 20 °C lower than those in dry condition.

CO oxidation activity of Pt–Mg/Al₂O₃ in dry condition of figure 6 is a little higher than that of Pt/Al₂O₃. Mg did not extremely affect the activity of Pt catalyst for CO oxidation, but water vapor in reactants did influenced by water vapor.

It is consistent with several reports [6] on CO oxidation activity of noble metal with moisture improvement. Costello and coworkers presented that hydroxyl group (OH⁻) produced by moisture is adsorbed on noble metals with low electron density [8]. These hydroxyl groups react with CO in reactants and produces hydroxycarbonyl. In this reaction, oxygen is easily dissociated and adsorbed into noble metals with high electron density.

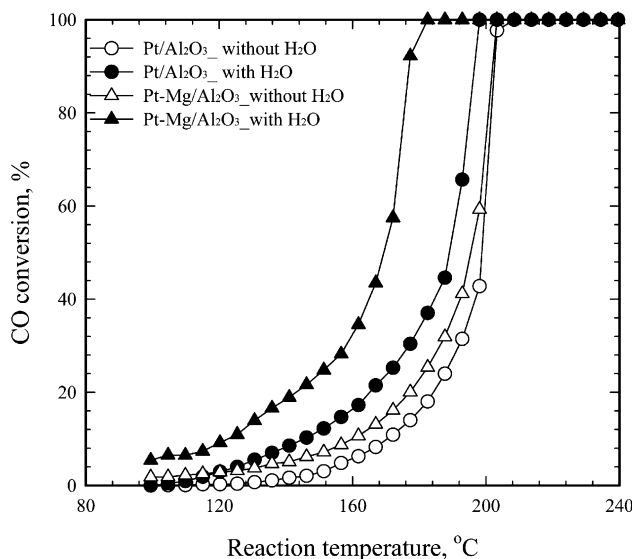


Figure 6. The effect of water vapor on CO oxidation over Pt/Al₂O₃ and Pt–Mg/Al₂O₃.

As shown in figure 4, the thermally stable Pt^{δ+}-(CO)₂ was disappeared by water vapor. In addition, the band of linearly adsorbed CO under condition (a) and (b) or (c) and (d) showed that the wave number shifted toward right by moisture. This was because CO coverage of catalyst surface was lowered by moisture. Muraki and coworkers investigated the effects of moisture on activation energy and the order of reaction of CO in CO oxidation reaction using Pt/Al₂O₃ catalysts [6].

As shown in figure 6, Pt–Mg/Al₂O₃ catalysts are more influenced by moisture than Pt/Al₂O₃ catalysts in CO oxidation reaction. The surface basicity of Pt–Mg/Al₂O₃ catalysts in figure 1 is much higher than that of Pt/Al₂O₃ catalysts. The experimental results of Pt/Mg(Al)O using TPD-CO₂ show that low basicity sites (L) appear in relation to OH⁻ group on the surface and medium basicity sites (M) appear in relation to oxygen in Mg²⁺-O²⁻ pairs [16]. Here, O²⁻ which indicates medium basicity sites (M) reacts with moisture and increases OH⁻ concentration on the surface [17]. Accordingly, Pt–Mg/Al₂O₃ catalysts are more affected by moisture than Pt/Al₂O₃ catalysts because of the increase of OH⁻ concentration on the surface.

Generally CO conversion can be improved by moisture through water-gas shift reaction (WGS) and CO conversion via WGS over Pt–Mg/Al₂O₃ was shown in figure 7. We obtained result that CO conversion via WGS is a negligible quantity under 200 °C.

4. Conclusions

We examined the effects of magnesium on Pt catalyst and moisture in reactant on the CO oxidation. Pt–Mg/Al₂O₃ catalysts are superior to Pt/Al₂O₃ catalysts in CO oxidation due to the following two results. One is that Pt

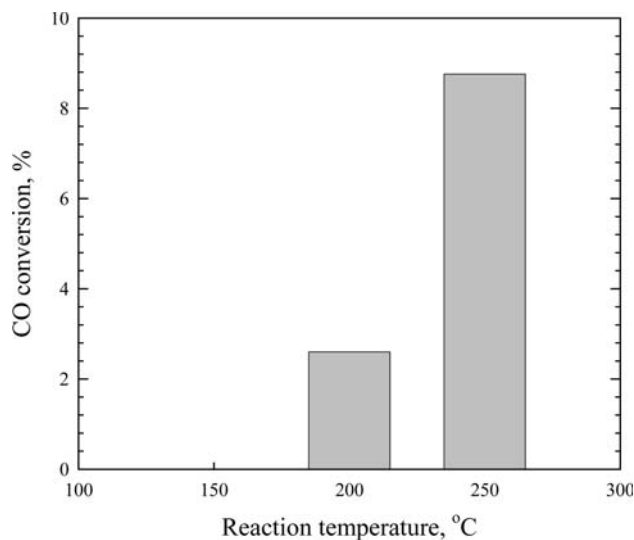


Figure 7. CO conversion on water gas shift reaction over Pt–Mg/Al₂O₃: 1.0 vol% CO, 2.0 vol% H₂O, rest N₂.

in Pt–Mg/Al₂O₃ has weaker interaction with CO than Pt in Pt/Al₂O₃, and the dissociative adsorption of oxygen is easier. As Mg increases the electron density of Pt, it induces the production and stabilization of Pt⁰. The other is that basicity improved by addition of Mg enriches the concentration of hydroxyl group on the surface of Pt catalysts, and then increases reaction activity. Some of moisture in reactant increases the CO oxidation rate by preventing CO from being adsorbed into the surface of Pt metal.

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