

# Study of Ce-Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the selective oxidation of CO in H<sub>2</sub> for application to PEFCs: Effect of gases

In Hyuk Son\*

Fuel Cell Team, Energy Laboratory, Corporate R&D Center in Samsung SDI Co. Ltd. 575, Shin-dong, Yeongtong-gu, Suwon-si, Gyeonggi-Do 443-391, Republic of Korea

Received 30 October 2005; received in revised form 10 December 2005; accepted 12 December 2005  
Available online 19 January 2006

## Abstract

In order to supply pure hydrogen to proton exchange membrane (PEM) fuel cells and avoid CO poisoning, selective CO oxidation in H<sub>2</sub> was studied over Ce-Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Adding the Ce promoted the CO conversion and selectivity of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with changing loading weights of Pt and Ce, oxygen concentration, residence time, and the composition of gases (H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>). At 250 °C, adding H<sub>2</sub>O to the feed gas enhanced the CO conversion due to the water–gas shift reaction. While, adding CO<sub>2</sub> to the feed gas suppressed the CO conversion due to the reversible water–gas shift reaction. In situ BET and XRD tests showed that well-dispersed metallic Pt particles (–2 nm) existed on the Ce oxide over the alumina support, which helps to supply oxygen to the Pt for a high activity of CO oxidation and selectivity.  
© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Pt; Ce; Alumina; PROX; CO oxidation; Fuel cells

## 1. Introduction

Fuel cells for both stationary and mobile applications are being studied as a way to provide clean and economical energy. Due to their durability and high power generation, *phosphoric acid fuel cells* (PAFC), *molten carbonate fuel cells* (MCFC) and *solid oxide fuel cells* (SOFC) are being used for central power plant applications. On the other hand, *polymer electrolyte fuel cells* (PEFC) are being used for propulsive automotive power plants. The low operating temperature (80 °C) solves the problem of fast start up, high power densities and dynamic response characteristics [1].

Ideally, supplying pure hydrogen to the PEFC could provide a simple system integration, maximum efficiency and zero emissions. However, the lack of a hydrogen refueling infrastructure, the difficulty and safety of storage, consumer acceptance, and commercial viability make the supply of pure hydrogen a major difficulty. Thus, three catalytic process steps are used to obtain pure hydrogen from liquid fuels such as methanol and gasoline: (1) *autothermal reforming* (fuel + O<sub>2</sub> + H<sub>2</sub>O ↔ CO<sub>x</sub> + H<sub>2</sub>),

*partial oxidation reforming* (fuel + O<sub>2</sub> ↔ CO<sub>x</sub> + H<sub>2</sub>) or *steam reforming* (fuel + H<sub>2</sub>O ↔ CO<sub>x</sub> + H<sub>2</sub>), (2) *the water–gas shift reaction* (CO + H<sub>2</sub>O ↔ CO<sub>2</sub> + H<sub>2</sub>), and (3) remaining CO is reduced to ppm levels by *preferential oxidation* (PROX) [2].

In the PEFC, the platinum electrocatalyst is easily poisoned by CO, sulfur, and other chemical species produced by the reforming processes. CO is especially serious, poisoning the catalysts at levels higher than 10 ppm. The PROX reactor is used between the water–gas shift reactor and the fuel cell anode in order to decrease the CO concentration: the CO concentration of the water–gas shift at thermodynamic equilibrium reaction is 1 mol%. Higher activity and selectivity of catalytic PROX reactors are required to oxidize the CO without significant hydrogen oxidation, an undesired side reaction. Since the PROX unit is placed between the low-temperature shift reactor (–200 °C) and the PEFC (–80 °C), it should operate between these temperatures.

For the PROX reaction, Pt and Au catalysts have mainly been investigated. Au catalysts show high low temperature activities (–80 °C) for fast start up. Schubert et al. [3] reported that small Au particles produced high activities on inert supports such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO. In addition, enhanced oxygen supply by the supports (Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, NiO<sub>x</sub>, and CoO<sub>x</sub>) to Au produced high activities. However, the activity strongly depended on the

\* Tel.: +82 31 210 7034; fax: +82 31 210 7374.  
E-mail address: [Inhyuk74.son@samsung.com](mailto:Inhyuk74.son@samsung.com).

preparation of the catalysts. The CO conversion and selectivity were lower at higher temperatures (150–200 °C) because of H<sub>2</sub> oxidation and the selectivity decreased at low CO concentrations.

A Pt catalyst on alumina was applied in a multi-stage PROX reactor by the Los Alamos National Laboratory at higher reaction temperatures (150–250 °C). The activities of Pt catalysts could also be improved using small Pt particles on alumina [4] and other oxygen supplying supports [5,6].

Adding a Ce promoter to the Pt supported alumina catalyst improved the activity and selectivity of CO oxidation in H<sub>2</sub> (100–200 °C), which enhances the oxygen supply to Pt along with stability [2]. This study was performed with dry streams with no CO<sub>2</sub> in the feed. A real PROX gas, produced after the water–gas shift reaction, is composed of CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. Thus, the study of selective CO oxidation with a realistic gas mixture is important.

In this study, the activity and selectivity of CO oxidation in H<sub>2</sub> over Pt/γ-Al<sub>2</sub>O<sub>3</sub> and Pt-Ce/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were tested with changing loadings of Pt and Ce, oxygen concentration, residence time, and composition of the gases (H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>) in order to understand the characteristics of the catalysts and apply them to real conditions. In addition, characterizations were performed over the catalysts to find the Ce effects on the reactions related to the Pt dispersions.

## 2. Experimental

Platinum (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Alfa) and Ceria (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Alfa) were co-impregnated with γ-Al<sub>2</sub>O<sub>3</sub> (150 m<sup>2</sup> g<sup>-1</sup>, basic type, >60 mesh, Alfa) using the incipient wetness method. The catalysts were dried in an oven at 120 °C for 24 h and then calcined in air at 400 °C for 2 h. Catalysts were kept in a desiccator to avoid water adsorption. Before testing the catalysts, they were heated in O<sub>2</sub> at 500 °C for 1 h, purged in He for 10 min, and reduced in H<sub>2</sub> at 500 °C for 1 h. The reaction tests started at room temperature after cooling down to the reaction temperature in H<sub>2</sub>. This procedure is based on other researchers' reports [5,7,8]. The following notation identifies the catalysts: *X Pt Y Ce/Al* where *X* and *Y* are wt% and *Al* is γ-Al<sub>2</sub>O<sub>3</sub>.

The pure gas (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, He, and CO (ultra high purity grade, Air Gas Corp.)) and the gas mixture (9.01% CO balanced CO<sub>2</sub>) were used to simulate the reformat or to supply carrier gas to a GC.

Catalysts were tested using a continuous-flow, vertical quartz tube reactor (6 mm i.d.) in a furnace. A temperature controller was used for adjusting reaction temperatures (100–350 °C in 50 °C steps). The loading weight of the catalyst was 0.1–0.3 g, total flow rate was 100 ml min<sup>-1</sup> (STP). Reaction pressure was atmospheric pressure. Four mass flow controllers (Tylan Co., USA) were used for controlling the gas flows rates (1% CO, 0.5–1% O<sub>2</sub>, 10.09% CO<sub>2</sub>, 30% N<sub>2</sub>, and H<sub>2</sub> balance). The water (–2.3%, saturated water percent in air at room temperature) was supplied by a bubbler system. In order to avoid water condensation, the feed gas pipe was heated by heating tapes around 100 °C. The preheated mixing feed gases were passed upwards towards a catalyst bed, which was held in place by glass-wool

plugs. The reaction temperature was measured in the reactor with two thermocouples, which were located on both sides of the catalyst bed. The distance between the two thermocouples was –4.4 cm. The top thermocouple, which was placed directly on top of the catalyst bed, was used with the furnace to control the reaction temperature. The maximum temperature difference was almost 20 °C between the thermocouples because of the highly exothermic reactions [9].

An on-line CO analyzer (Thermo-Environmental Instrument, 48C, USA) was used for analyzing the CO concentration after removal of water in the out let gas with a drierite moisture trap. A gas chromatograph (HP 6890) was used with a TCD detector through a Hayesep DB column to measure the concentrations of O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> using a syringe. The concentrations of H<sub>2</sub>O and H<sub>2</sub> were only measured approximately by a GC. All experimental data were collected for a period of 1–2 h in the steady state. The conversions of CO and O<sub>2</sub> and the selectivity of CO were defined as follows:

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

$$\text{O}_2 \text{ conversion (\%)} = \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \times 100$$

$$\text{CO selectivity (\%)} = \frac{0.5 \times [\text{CO}]_{\text{out}}}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100$$

In situ BET surface areas were measured by N<sub>2</sub> adsorption (30% N<sub>2</sub>/70% He) at liquid nitrogen temperature using a Quantasorb<sup>®</sup> sorption (Quantachrome Corp.) instrument. In order to test in situ BET with changing conditions (after oxidation, after reduction, and after reaction), a BET test cell was used as a reactor and all gases were flowed using mass flow controllers without exposure to air. For the BET test on post-oxidation catalyst, the calcined catalyst was oxidized in O<sub>2</sub> at 500 °C for 1 h. For the test of after-reduction BET test, the oxidized catalyst was reduced in H<sub>2</sub> at 500 °C for 1 h and then the in situ BET test performed after cooling down to room temperature. In addition, for the test of after-reaction BET test, the reduced catalyst was reacted in 1% CO, 1% O<sub>2</sub>, 10.09% CO<sub>2</sub>, 2.03% H<sub>2</sub>O, and H<sub>2</sub> balance at 200 °C for 2 h and then the BET test performed.

X-ray diffraction (XRD) was performed with a Rigaku power diffractometer using nickel-filtered Cu Kα radiation (40 kV tube voltage and 40 mA tube current). For crystal phase identification, typical operating parameters were as follows: 20–75° 2θ scan range, 1° min<sup>-1</sup> scan rate, and 0.02° data interval. The average particle size was calculated from the Pt(1 1 1) peak using Scherrer's formula [10–12].

## 3. Results and discussion

### 3.1. Reaction study

#### 3.1.1. Effect of loading weight of Pt and Ce

Fig. 1 shows the effects of loading weights of Pt and Ce on CO and O<sub>2</sub> conversions as well as selectivity. With decreasing Pt loading weights, the CO conversion decreased over the

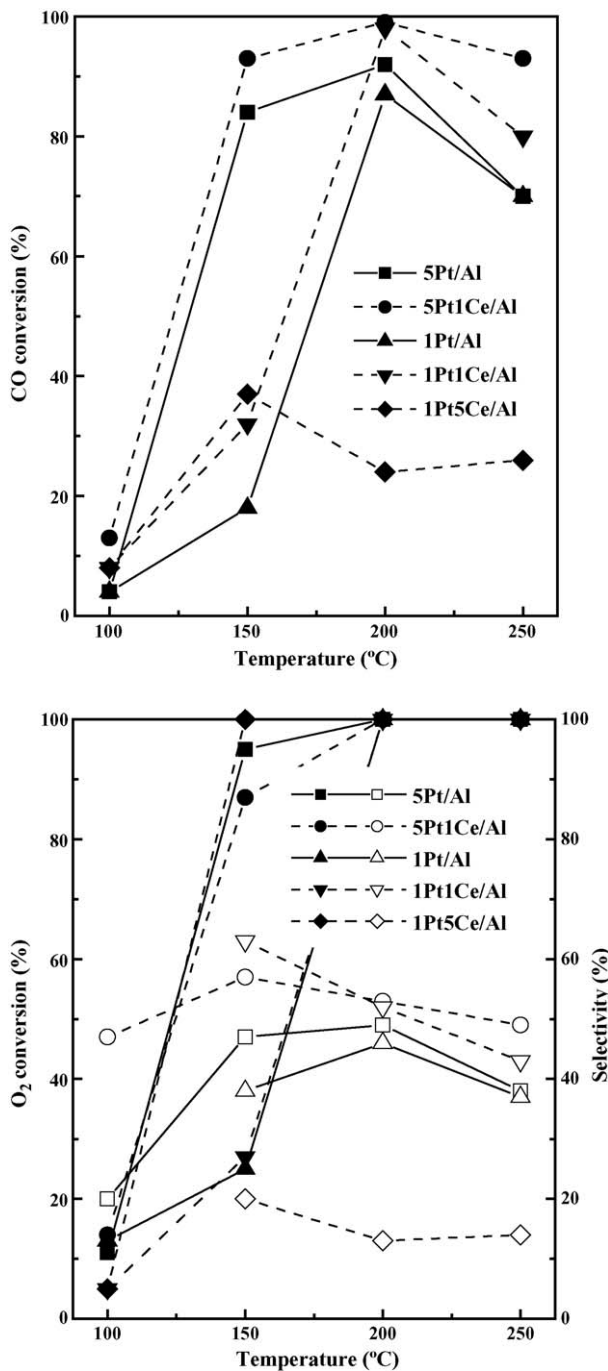


Fig. 1. CO conversion, O<sub>2</sub> conversion (filled symbol), and selectivity (open symbol) over 5Pt/Al, 5Pt1Ce/Al, 1Pt/Al, 1Pt1Ce/Al, and 1Pt5Ce/Al (1% CO, 1% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup>).

entire temperature range and significantly decreased at 150 °C while the selectivity improved below 150 °C, agreeing with others [13]. The selectivity decreased due to higher competing H<sub>2</sub> oxidation at higher temperatures, thus the selectivity could be improved at lower temperatures by suppressing the competing H<sub>2</sub> oxidation [6,13–16]. The 5Pt/Al and 1Pt/Al with 1 wt% Ce showed higher CO conversion and selectivity over the entire temperature range. This is due to the enhancement of the oxygen supply to Pt by Ce [2]. Table 1 shows CO and O<sub>2</sub> conver-

Table 1  
CO conversion, O<sub>2</sub> conversion, and selectivity of 5Pt/Al and 5Pt5Ce/Al

Temperature (°C)	CO conversion		O <sub>2</sub> conversion		CO selectivity	
	5Pt/Al	5Pt5Ce/Al	5Pt/Al	5Pt5Ce/Al	5Pt/Al	5Pt5Ce/Al
100	35	90.2	33.1	90.2	52.9	60.3
150	90.4	95.6	98.6	95.6	45.8	48.4
200	92.3	88.2	100	88.2	46.2	44.4
250	63	56.7	100	56.7	31.5	28.4

1% CO, 1% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 300 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup>.

sion and selectivity of 5Pt/Al and 5Pt5Ce at a higher flow rate (300 ml min<sup>-1</sup> with 0.3 g catalyst) as noted in previous work [2] for comparison. Below 200 °C, the CO conversion and selectivity of 5Pt/Al at 100 ml min<sup>-1</sup> was lower than that of 5Pt/Al at 300 ml min<sup>-1</sup> because of the external mass transfer-limited reaction. In addition, at lower temperatures, the CO conversion of 5Pt1Ce/Al at 100 ml min<sup>-1</sup> was significantly lower than that of 5Pt5Ce/Al at 300 ml min<sup>-1</sup>. Higher total gas flows and loading weights of Ce could produce the differences. The higher loading weight of Ce could supply more oxygen to Pt, which yielded higher CO conversion and higher selectivity. On the other hand, 1Pt5Ce/Al showed the worst CO conversion and selectivity since the too high loading weight ratio of Ce to Pt yielded higher H<sub>2</sub> oxidation: the oxygen conversion was 100% above 150 °C and higher water peaks could be observed by a GC. Therefore, there were optimum loading weights of Ce to Pt for improving the activity.

### 3.1.2. Effect of the mole ratio O<sub>2</sub> to CO

Fig. 2 shows the CO conversion and selectivity of all catalysts were significantly decreased by decreasing the mole ratio O<sub>2</sub> to CO from excess stoichiometric (1% O<sub>2</sub>) to stoichiometric (0.5% O<sub>2</sub>). 5Pt1Ce/Al and 1Pt1Ce/Al also showed higher CO conversion and selectivity than 5Pt/Al and 1Pt/Al over the entire temperature range. The Ce effect is greater at low temperatures. Table 2 shows CO and O<sub>2</sub> conversion and the selectivity of 5Pt/Al and 5Pt5Ce/Al with different mole ratios of O<sub>2</sub> to CO (%) at 150 °C at 300 ml min<sup>-1</sup> as noted in the previous work [2]. The selectivity of 5Pt5Ce/Al is much higher than that of 5Pt/Al. Therefore, the selectivity can be improved by using a higher loading weight ratio of Ce to Pt at low temperatures with a lower ratio of O<sub>2</sub> to CO because a higher Ce loading can improve the oxygen supply to Pt for selective CO oxidation.

Table 2  
CO conversion, O<sub>2</sub> conversion, and selectivity of 5Pt/Al and 5Pt5Ce/Al with changing the ratio O<sub>2</sub> to CO

Ratio of O <sub>2</sub> to CO	CO conversion		O <sub>2</sub> conversion		CO selectivity	
	5Pt/Al	5Pt5Ce/Al	5Pt/Al	5Pt5Ce/Al	5Pt/Al	5Pt5Ce/Al
0.5	52	77.5	100	100	52	77.5
1	90.4	93.2	98.6	98.8	45.8	48.4

1% CO, 0.5–1% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 300 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup> at 150 °C.

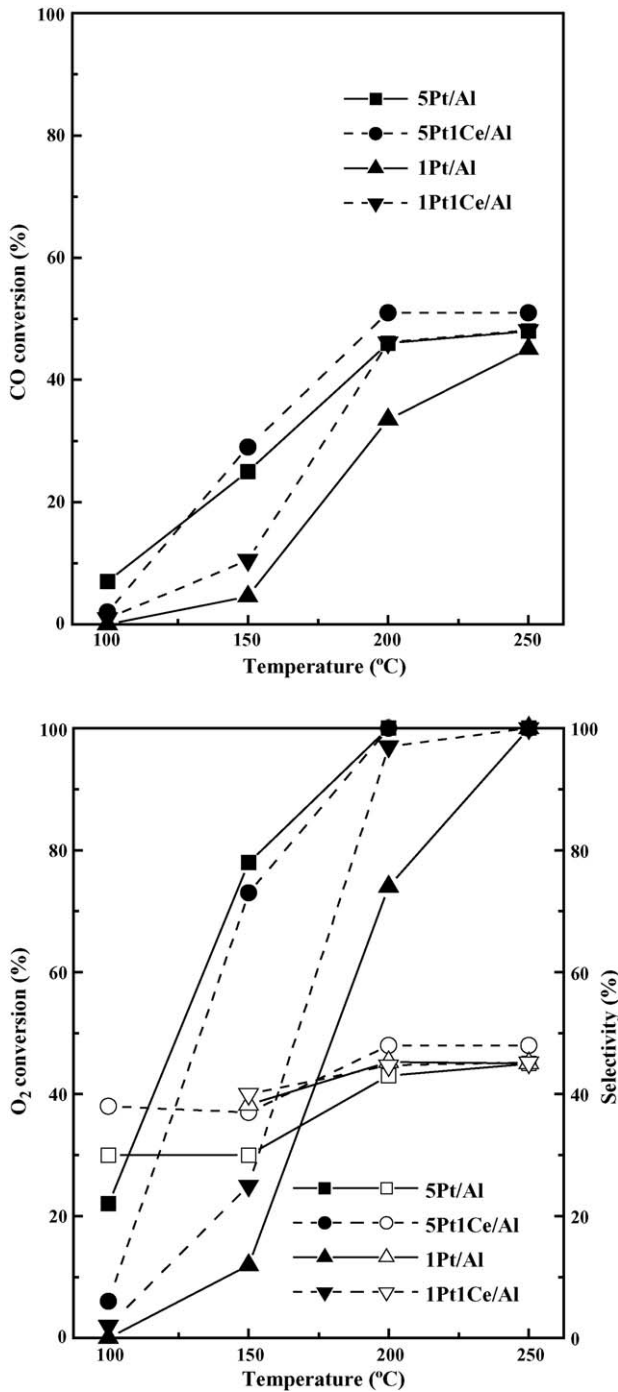


Fig. 2. CO conversion, O<sub>2</sub> conversion (filled symbol), and selectivity (open symbol) with lower ratio of O<sub>2</sub> to CO over 5Pt/Al, 5Pt1Ce/Al, 1Pt/Al, and 1Pt1Ce/Al (1% CO, 0.5% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup>).

### 3.1.3. Effect of the contact time

In Fig. 3, the study of contact time was investigated with changing loading weights of 1Pt1Ce/Al, which has a higher Ce effect as observed in Fig. 1. Table 3 shows the CO conversion, O<sub>2</sub> conversion, and selectivity of 5Pt/Al with increasing contact time at 300 ml min<sup>-1</sup> [2]. The CO conversion of 5Pt/Al improved with increasing contact time over the entire temperature range and its selectivity was constant [7,13,16,17]. On the

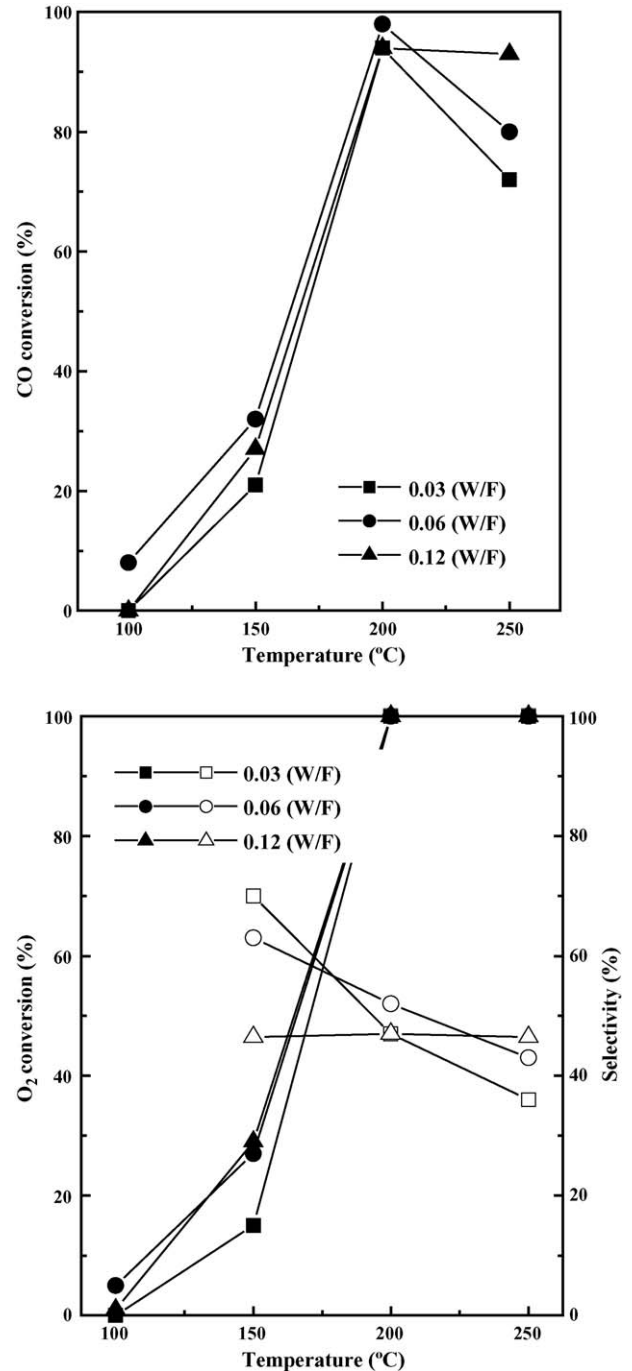


Fig. 3. CO conversion, O<sub>2</sub> conversion (filled symbol), and selectivity (open symbol) with changing ratios of W/F over 1Pt1Ce/Al (1% CO, 1% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, and W/F: 0.03–0.12 g s cm<sup>-3</sup>).

other hand, the CO conversion of 1Pt1Ce/Al slightly decreased. The selectivity of 1Pt1Ce/Al was significantly enhanced with decreasing W/F (ratio of the catalyst weight to the feed rate) at 150 °C. Due to the oxygen supply from Ce to Pt, the selectivity of CO oxidation is higher with a lower contact time and at lower reaction temperatures. At 250 °C, the CO conversion and selectivity was enhanced with increasing contact time. The selectivity of 5Pt/Al and 1Pt1Ce/Al remained constant over the entire temperature range for a high contact time (0.12 W/F).

Table 3  
CO conversion, O<sub>2</sub> conversion, and selectivity of 5Pt/Al with changing W/F

Temperature (°C)	CO conversion		O <sub>2</sub> conversion		CO selectivity	
	0.06	0.12	0.06	0.12	0.06	0.12
100	35	98.22	33.1	100	52.87	49.11
150	90.35	99.44	98.6	100	45.82	49.72
200	92.26	97.65	100	100	46.18	48.83
250	63	93.51	100	100	31.5	46.76

1% CO, 1% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 300 ml min<sup>-1</sup>, and W/F: 0.06–0.12 g s cm<sup>-3</sup>.

### 3.1.4. Effect of H<sub>2</sub>O

With H<sub>2</sub>O in the feed gas, the CO conversion and selectivity of 1Pt1Ce/Al were also higher than that of 1Pt/Al over the entire temperature range (Fig. 4). At 150 °C, the CO conversions of 1Pt/Al and 1Pt1Ce/Al slightly decreased. The selectivity of 1Pt/Al remains constant while that of 1Pt1Ce/Al significantly decreased. Adsorbing H<sub>2</sub>O on the support or Ce, suppressed the oxygen supply to Pt for the selective CO oxidation while it helped the H<sub>2</sub> oxidation, in agreement with other results [12]. On the other hand, at 250 °C, the CO conversions on 1Pt/Al and 1Pt1Ce/Al were much improved due to the water–gas shift reaction [14]. Therefore, adding H<sub>2</sub>O yielded increasing CO conversion at high temperature due to the water–gas shift reaction, while it suppressed CO conversion at low temperature due to enhancing the H<sub>2</sub> oxidation.

### 3.1.5. Effect of CO<sub>2</sub>

The effect of CO<sub>2</sub> in the feed gas on the CO conversion and selectivity of 1Pt/Al and 1Pt1Ce/Al was small in 1% O<sub>2</sub> below 200 °C. However, at 250 °C, the effect became larger due to the reversible WGS reaction (CO<sub>2</sub> + H<sub>2</sub> → CO + H<sub>2</sub>O) (Fig. 5). Thus, CO conversion and selectivity of 1Pt/Al and 1Pt1Ce/Al decreased and 1Pt1Ce/Al was affected by the reversible reaction more. The reversible reaction is more effective than the water–gas shift reaction [12]. However, under 0.5% O<sub>2</sub>, the negative effect of the CO<sub>2</sub> was small over the entire temperature range. The CO conversion and selectivity of 1Pt/Al was slightly enhanced due to the water–gas shift reaction. The reversible reaction was suppressed since the temperature of the catalyst's surface was lowered by decreasing the CO and H<sub>2</sub> oxidation reaction.

### 3.1.6. Effect of N<sub>2</sub>

The activity of 1Pt/Al and 1Pt1Ce/Al was not affected by adding N<sub>2</sub>, decreasing H<sub>2</sub> concentration, over the entire temperature range (no data in this paper). In the catalytic combustion reactions, the activation energy of CO oxidation with hydrogen oxidation was much lower than that of homogeneous CO oxidation owing to the coupling effects [7,8]. This was explained by the interaction between the CO adsorbed on Pt and hydroxylated alumina support, which could help free Pt active sites for oxygen dissociation or adsorption [6]. Changing the hydrogen concentration would affect the reaction due to the changing interaction. However, 30% of hydrogen was decreased by adding N<sub>2</sub> to the feed gas, while the CO conver-

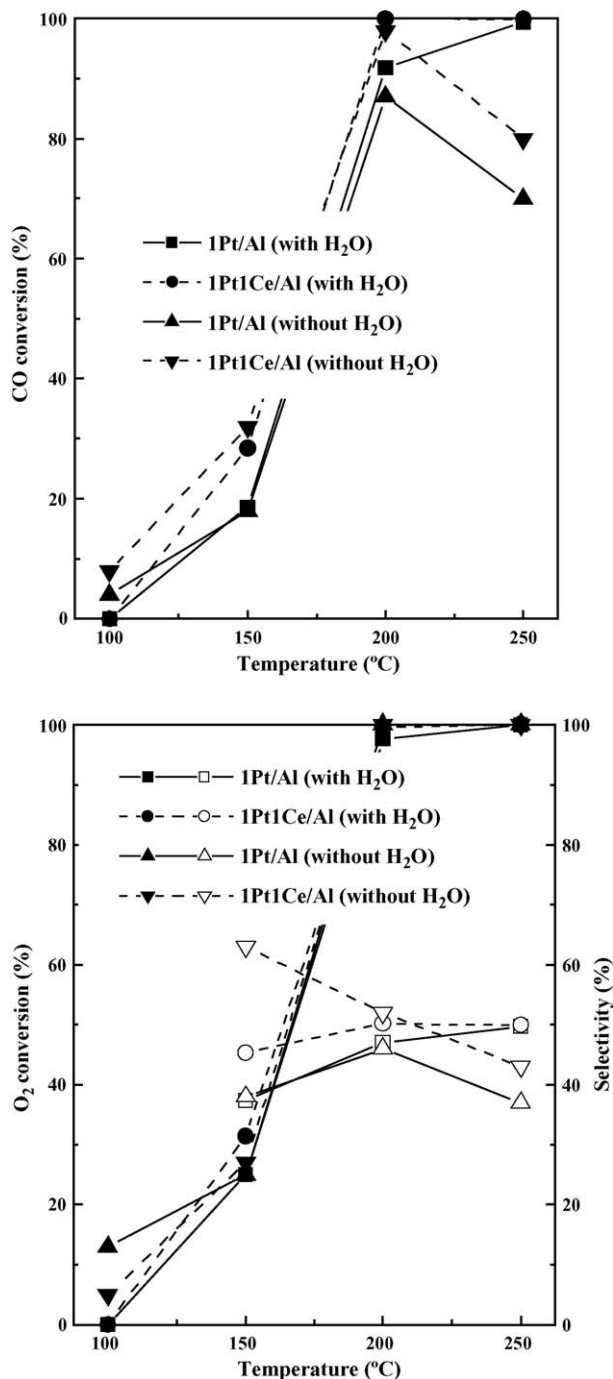


Fig. 4. Effect of adding H<sub>2</sub>O in the feed gas on CO conversion, O<sub>2</sub> conversion (filled symbol), and selectivity (open symbol) over 1Pt/Al and Pt1Ce/Al (1% CO, 1% O<sub>2</sub>, 0–2.3% H<sub>2</sub>O, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup>).

sion and selectivity were unchanged. Thus, the H<sub>2</sub> effects are primary.

### 3.1.7. Methanation

Pt/γ-Al<sub>2</sub>O<sub>3</sub> did not show the methanation side reaction as noted in previous results [5–7]. The methane GC peaks could not be observed over PtCe/Al with changing reaction conditions (changing loading weights of Pt and Ce, oxygen concentration, residence time, and the composition of gases (H<sub>2</sub>O, CO<sub>2</sub> and

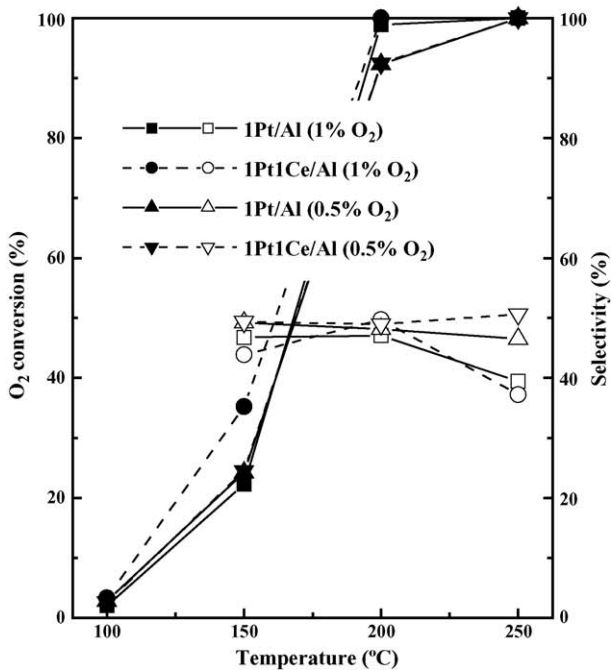
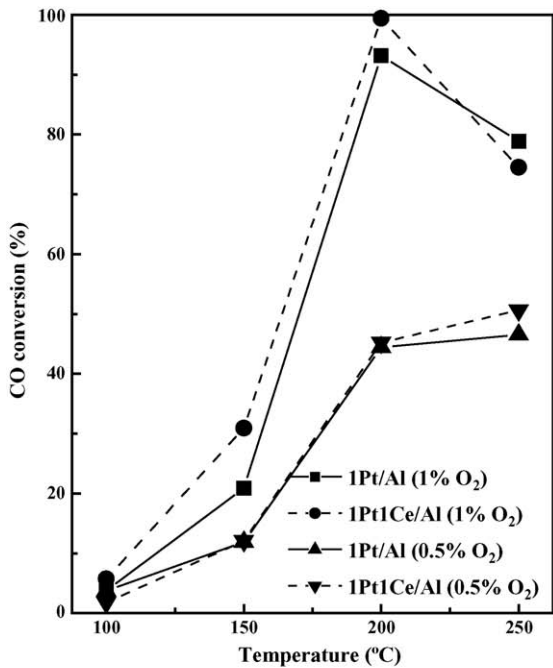


Fig. 5. Effect of adding H<sub>2</sub>O and CO<sub>2</sub> in the feed gas and changing ratios of O<sub>2</sub> to CO on CO conversion, O<sub>2</sub> conversion (filled symbol), and selectivity (open symbol) over 1Pt/A and 1PtCe/Al (1% CO, 0.5–1% O<sub>2</sub>, 2.3% H<sub>2</sub>O, 10.09% CO<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup>).

N<sub>2</sub>) over the entire temperature range. Thus, methane could not be an intermediate in the CO oxidation over Pt/Al and the Pt/Al with Ce, and so it is convenient to apply the catalysts to real PROX reaction for fuel cells.

### 3.2. Characterization

#### 3.2.1. Support and Ce effects on the reaction

In order to understand the role of the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and Ce in the reaction, the reaction tests were performed with-

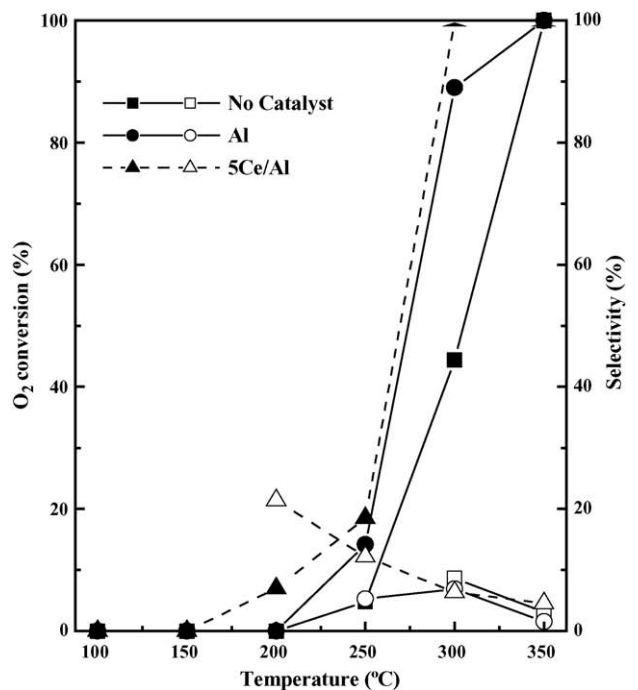
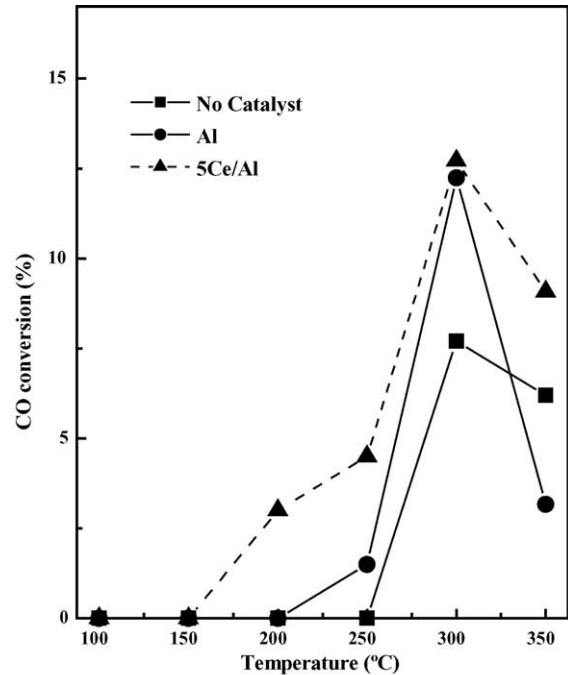


Fig. 6. CO conversion, O<sub>2</sub> conversion (filled symbol), and selectivity (open symbol) over no catalyst, Al and 5Ce/Al (1% CO, 1% O<sub>2</sub>, 2.3% H<sub>2</sub>O, 10.09% CO<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, and W/F: 0.06 g s cm<sup>-3</sup>).

out the catalyst, support (Al), and 5Ce/Al (Fig. 6). The CO conversion and O<sub>2</sub> conversion were significantly suppressed without a Pt loading. Thus, the loaded Pt particles were active sites for the CO oxidation. The order of CO and oxygen conversion rates, even though the CO conversions were low, is 5Ce/Al > Al > no catalyst. The CO could oxidize due to the heat from hydrogen oxidation, which yielded lower selectivity at high temperatures.

Table 4  
In situ BET results

Sample name	After calcination	After reduction	After reaction
5Pt/Al	138.9	146.5	144.9
5Pt1Ce/Al	132	138.3	124.2
1Pt/Al	143.4	168.3	170.2
1Pt1Ce/Al	166.8	166.5	139.3
1Pt5Ce/Al	145.8	145.5	122.6
5Ce/Al	160	142.8	132.3

### 3.2.2. In situ BET test

In situ BET tests were performed to understand the changing of the catalysts' surface areas since the characteristic of Ce can be easily changed by exposure to air (Table 4). The surface areas of 5Pt/Al and 1Pt/Al increased after reduction and remained constant after reaction, due to a higher amount of smaller metallic Pt particles. Thus, the well-dispersed metallic Pt particles existed on the alumina after reduction. While, the surface areas of 5Pt1Ce/Al, 1Pt1Ce/Al, and 1Pt5Ce/Al decreased after reaction. The results were caused by changing morphology of Ce in the reaction since the surface area of 5Ce/Al significantly decreased after reduction and after reaction. The lower surface area can be caused by blocking pores of alumina by Ce oxides [18].

### 3.2.3. XRD test

X-ray diffraction tests were applied to determine the structure of Pt and Ce and sizes of particles after reaction (Fig. 7). The

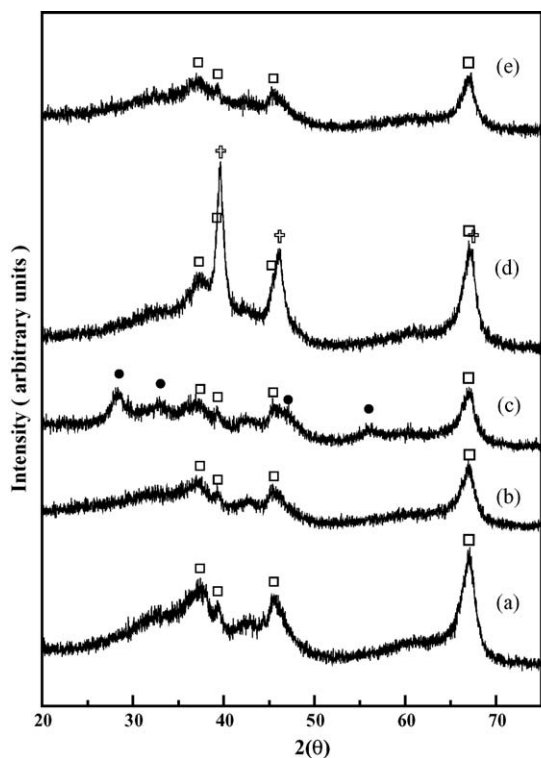


Fig. 7. XRD spectra of: 1Pt/Al (a), 1Pt1Ce/Al (b), 1Pt5Ce/Al (c), 5Pt/Al (d), and 5Pt1Ce/Al (e) after reaction (1% CO, 1% O<sub>2</sub>, H<sub>2</sub> balance, total flow rate: 100 ml min<sup>-1</sup>, W/F: 0.06 g s cm<sup>-3</sup>, (□) γ-Al<sub>2</sub>O<sub>3</sub> peak, (●) cerium oxide (CeO<sub>2</sub>) peak and (⊕) metallic Pt peak).

XRD spectra of 1Pt/Al and 1Pt1Ce/Al only showed broad alumina peaks since the loading weight of Pt and Ce was small or their particles were negligibly small or amorphous to be detected by XRD tests. While, the alumina peaks of 1Pt1Ce/Al were significantly broader than that of 1Pt/Al, which was caused by existence of small metallic Pt particles on alumina [4]. With increasing the loading weight of Ce, 1Pt5Ce/Al showed the CeO<sub>2</sub> peaks. The XRD spectrum of 5Pt/Al showed metallic Pt crystal peaks while that of 5Pt1Ce/Al only showed broad alumina peaks. Since the well-dispersed small metallic Pt particles (less than 2–5 nm) existed on 5Pt1Ce/Al while the big metallic Pt particles (~16 nm) existed on 5Pt/Al, calculated from the Pt(1 1 1) peak using Scherrer's formula [10–12]. Thus, well-dispersed Pt particles existed on the Ce oxide over alumina support, which helps in supplying oxygen to Pt for highly selective CO oxidation [19].

## 4. Conclusions

Adding Ce to Pt/γ-Al<sub>2</sub>O<sub>3</sub> produced higher CO conversion and selectivity at lower temperatures and lower O<sub>2</sub> to CO ratios because of an enhanced oxygen supply to the Pt. The CO conversion and selectivity were enhanced with an optimum loading wt% of Ce and Pt: too high a loading weight ratio of Ce to Pt yielded lower CO conversion and selectivity due to higher H<sub>2</sub> oxidation. With decreasing contact time, the catalyst Pt/γ-Al<sub>2</sub>O<sub>3</sub> with Ce showed a higher CO selectivity at lower temperatures because of the Ce effect of supplying oxygen to Pt, which became larger. At 250 °C adding H<sub>2</sub>O produced a higher CO conversion owing to the water–gas shift reaction, while adding CO<sub>2</sub> yielded a lower CO conversion due to the reversible water–gas shift reaction. Adding N<sub>2</sub>, which decreased the H<sub>2</sub> mole fraction, did not affect the activity. Reaction tests of the support alone or with Ce, using in situ BET and XRD tests, showed well-dispersed metallic Pt particle (~2 nm) active sites, which existed on the Ce oxide over the alumina support, which helped in supplying oxygen to the Pt for higher selectivity in CO oxidation.

## Acknowledgements

The work presented in this paper is supported by the corporate R&D center of Samsung SDI for development of mobile fuel cell system. The authors thank all members involved in the fuel cell in Samsung SDI Co.

## References

- [1] S. Ahmed, M. Krumpelt, Int. J. Hydrogen Energy 26 (2001) 291–301.
- [2] I.H. Son, A.M. Lane, Catal. Lett. 76 (3–4) (2001) 151–154.
- [3] M.M. Schubert, S. Hackenberg, A.C. Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113–122.
- [4] I.H. Son, M. Shamsuzzoha, A.M. Lane, J. Catal. 210 (2) (2002) 460–465.
- [5] A. Wootsch, C. Descorme, D. Duprez, J. Catal. 225 (2) (2004) 259–266.
- [6] O. Korotkikh, R. Farrauto, Catal. Today 62 (2000) 249–254.
- [7] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93–105.
- [8] N.D. Hoyle, P. Kumarasamy, V.A. Self, P.A.M. Sermon, S.W. Vong, Catal. Today 47 (1999) 45–49.

- [9] I.H. Son, A.M. Lane, D.T. Johnson, *J. Power Sources* 124 (2) (2003) 415.
- [10] J.B. Cohen, *Ultramicroscopy* 34 (1990) 41–46.
- [11] J. Pielaszek, J.B. Cohen, R.L. Burell, J.B. Butt, *J. Catal.* 80 (1983) 479–481.
- [12] P. Georgopoulos, J.B. Cohen, *J. Catal.* 92 (1985) 211–215.
- [13] A. Manasilp, E. Gulari, *Appl. Catal. B* 37 (2002) 17–25.
- [14] S.H. Oh, R.M. Sinkevitch, *J. Catal.* 142 (1993) 254–262.
- [15] M. Watanabe, H. Uchida, H. Igarashi, M. Suzuki, *Chem. Lett.* (1995) 21–22.
- [16] G. Avgouropoulos, T. Ioannides, C. Papadopoulou, J. Batista, S. Hocevar, H.K. Matralis, *Catal. Today* 75 (1/4) (2002) 157–167.
- [17] D.H. Kim, M.S. Lim, *Appl. Catal. A* 224 (2002) 27–38.
- [18] M.J. Tiernan, O.E. Finlayson, *Appl. Catal. B* 19 (1998) 23–35.
- [19] S. Bernal, J.J. Calvino, M.A. Cauqui, J.M. Gatica, C. Latase, P. Omil, J.M. Pintado, *Catal. Today* 50 (1999) 175–256.