

## Selective CO oxidation in the presence of hydrogen over supported Pt catalysts promoted with transition metals

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**Abstract**—Selective CO oxidation in the presence of excess hydrogen was studied over supported Pt catalysts promoted with various transition metal compounds such as Cr, Mn, Fe, Co, Ni, Cu, Zn, and Zr. CO chemisorption, XRD, TPR, and TPO were conducted to characterize active catalysts. Among them, Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed high CO conversions over wide reaction temperatures. For supported Pt-Ni catalysts, Alumina was superior to TiO<sub>2</sub> and ZrO<sub>2</sub> as a support. The catalytic activity at low temperatures increased with increasing the molar ratio of Ni/Pt. This accompanied the TPR peak shift to lower temperatures. The optimum molar ratio between Ni and Pt was determined to be 5. This Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed no decrease in CO conversion and CO<sub>2</sub> selectivity for the selective CO oxidation in the presence of 2 vol% H<sub>2</sub>O and 20 vol% CO<sub>2</sub>. The bimetallic phase of Pt-Ni seems to give rise to stable activity with high CO<sub>2</sub> selectivity in selective oxidation of CO in H<sub>2</sub>-rich stream.

Key words: CO Oxidation, PROX, Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Promoter, Fuel Cell

### INTRODUCTION

The polymer electrolyte membrane fuel cell (PEMFC) has been considered to be a promising candidate for utilizing hydrogen gas to produce heat and electricity in the application to electric vehicles or residential power-generation [Son, 2004]. Hydrogen is generally produced from hydrocarbons such as oil, natural gas, and biomass via several catalytic reactions including reforming and water-gas shift reactions. Typically, 0.5-1 vol% of carbon monoxide exists unavoidably after them. Because platinum, an anode of PEMFC, is prone to be poisoned in the presence of small amounts of CO in hydrogen stream, carbon monoxide should be removed to a trace-level. The acceptable CO concentration is <10 ppm at Pt anode and <100 ppm at CO-tolerant alloy anodes [Shore and Farrauto, 2003]. Several different methods for the CO removal have been studied including purification with metal membrane [Wieland and Melin, 2003], selective CO oxidation [Shore and Farrauto, 2003], and CO methanation [Takenaka et al., 2004]. Among them, selective oxidation has been accepted as the most attractive way to achieve this goal [Lee et al., 2002]. In this system, the following two reactions can occur.



A number of catalysts more active for the first reaction than the second reaction have been reported [Shore and Farrauto, 2003]. Among them, supported platinum catalysts have been considered to be promising. However, they usually showed noticeable activities only above 423 K [Oh and Sinkevitch, 1993; Manasilp and Gulari, 2002]. Because PEMFC is operated below 423 K not to degrade polymer

membrane, catalysts operating at low temperatures can be more plausible. To increase catalytic activities at low temperatures, different methods have been tried for supported platinum catalysts. The pretreatment of Pt catalyst with water vapor was reported to enhance low-temperature catalytic activities for selective CO oxidation by increasing Pt dispersion [Son et al., 2002]. Several groups have reported that the selective CO oxidation at low temperatures could be enhanced by the addition of 2<sup>nd</sup> metals such as Fe [Korotkikh and Farrauto, 2000; Liu et al., 2002; Sirijaruphan et al., 2004; Watanabe et al., 2003], Ce [Son and Lane, 2001], Co [Suh et al., 2005; Kwak et al., 2005], Ni [Suh et al., 2005], Mn [Suh et al., 2005], and alkali metals [Pedrero et al., 2005; Kwak et al., 2005; Minemura et al., 2005; Cho et al., 2005]. Even though each catalyst has proven its superiority by comparison with Pt catalyst, it is difficult to assess each catalyst because different reaction conditions have been adopted. Until now, no comparison among promoted platinum catalysts has been conducted at the same reaction condition. Furthermore, most groups have utilized Pt precursors containing chlorine compounds, which can cause different activities depending on the residual chloride. In this work, transition metal-promoted platinum catalysts were prepared by a co-impregnation method using catalyst precursors containing no chloride, and their catalytic performance was compared at the same reaction condition. The promotional effect of alkali and alkali earth metals was not examined in this work because they generally showed much less catalytic activity compared with those containing transition metals at low temperatures in the presence of H<sub>2</sub>O and CO<sub>2</sub>.

### EXPERIMENTAL

All the catalysts were prepared by a wet impregnation method from an aqueous solution of Pt precursor, Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>6</sub>, and transition metal precursors, metal nitrates. Different supports such as  $\gamma$ -

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alumina (Alfa), TiO<sub>2</sub> (P-25, Degussa), and ZrO<sub>2</sub> (TZ-8YS, Tosoh) were utilized. The content of Pt was 1 wt% and the molar ratio between each transition metal and Pt was 10 for all catalysts if not mentioned explicitly. All the catalysts were calcined at 573 K with air and reduced at 573 K with hydrogen stream for 1 h before a reaction.

Bulk crystalline structures of catalysts were determined with an X-ray diffraction (XRD) technique. XRD patterns were obtained by using Cu K $\alpha$  radiation using a Rigaku D/MAC-III instrument at room temperature.

Temperature programmed reduction (TPR) was conducted over 0.2 g sample in a 10 vol% H<sub>2</sub>/Ar stream from 313 K to 573 K at a heating rate of 10 K/min, monitoring TCD signals after samples were pretreated with air at 573 K for 1 h.

Temperature programmed oxidation (TPO) was conducted over 0.2 g sample in a 2 vol% O<sub>2</sub>/He stream from 313 K to 573 K at a heating rate 10 K/min monitoring TCD signals after samples were pretreated with H<sub>2</sub> at 573 K for 1 h.

CO chemisorption was conducted over 0.2 g sample in an He stream at 300 K by a pulsed injection of 50  $\mu$ l of CO after samples were pretreated sequentially with air and H<sub>2</sub> at 573 K for 1 h.

Experiments were carried out in a small fixed bed reactor with catalysts that had been retained between 45 and 80 mesh sieves. A standard gas of 1.0 vol% CO, 1.0 vol% O<sub>2</sub>, 2 vol% H<sub>2</sub>O and 10 (or 80) vol% H<sub>2</sub> balanced with helium was fed to a reactor at atmo-

spheric pressure. The catalytic activity with increasing reaction temperature was measured from 313 K to 473 K at a heating rate 1 K/min. The effect of CO<sub>2</sub> was examined with a gas mixture of 1.0 vol% CO, 1.0 vol% O<sub>2</sub>, 20 vol% CO<sub>2</sub>, and 50 vol% H<sub>2</sub> balanced with helium. For all experiments, 0.10 g of catalyst without diluents was contacted with a reactant gas at a flow rate of 100 ml/min. The conversion of CO and O<sub>2</sub> and the yield of CH<sub>4</sub> were determined through gas chromatographic analysis (HP5890A, molecular sieve 5A column) of the effluent from the reactor. The detection limit of CO was 10 ppm. The CO conversion, O<sub>2</sub> conversion, CO<sub>2</sub> selectivity, and the CH<sub>4</sub> yield were calculated by using the following formulas:

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

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

$$\text{CO}_2 \text{ selectivity (\%)} = \{0.5 \times ([\text{CO}]_{in} - [\text{CO}]_{out} - [\text{CH}_4]_{out}) / ([\text{O}_2]_{in} - [\text{O}_2]_{out})\} \times 100;$$

$$\text{CH}_4 \text{ yield (\%)} = ([\text{CH}_4]_{out}) / [\text{CO}]_{in} \times 100.$$

## RESULTS AND DISCUSSION

The BET surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> was determined to be 170 m<sup>2</sup>/g, 55 m<sup>2</sup>/g, and 9 m<sup>2</sup>/g, respectively. The preferential oxidation of CO in H<sub>2</sub>-rich gas mixture was conducted over transition metal-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as shown in Fig. 1 and Fig. 2. CO conversion of more than 90% was obtained over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> cata-

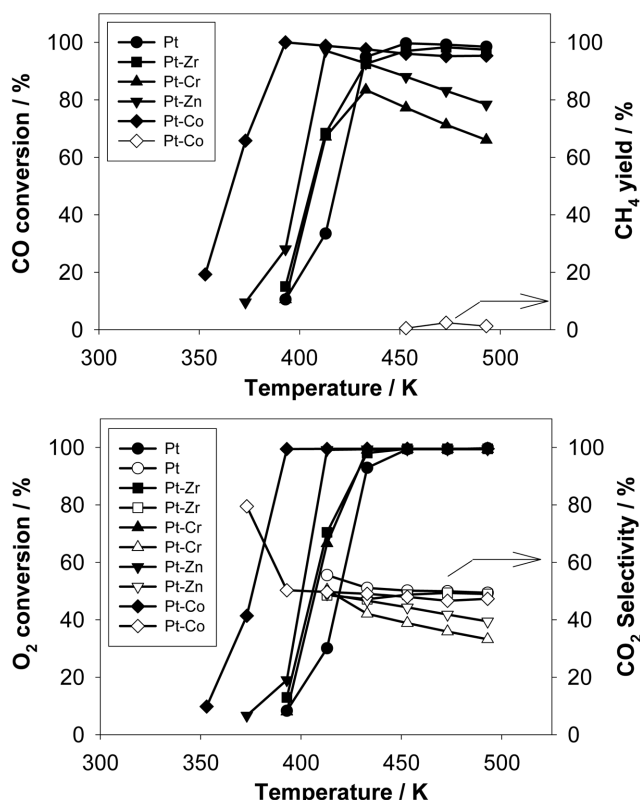


Fig. 1. CO conversion, CH<sub>4</sub> yield, O<sub>2</sub> conversion, and CO<sub>2</sub> selectivity for the selective CO oxidation over transition metal-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with increasing reaction temperatures. Reactants: 1% CO, 1% O<sub>2</sub>, 10% H<sub>2</sub>, and 2% H<sub>2</sub>O in He. F/W=1,000 ml/min/g<sub>cat</sub>.

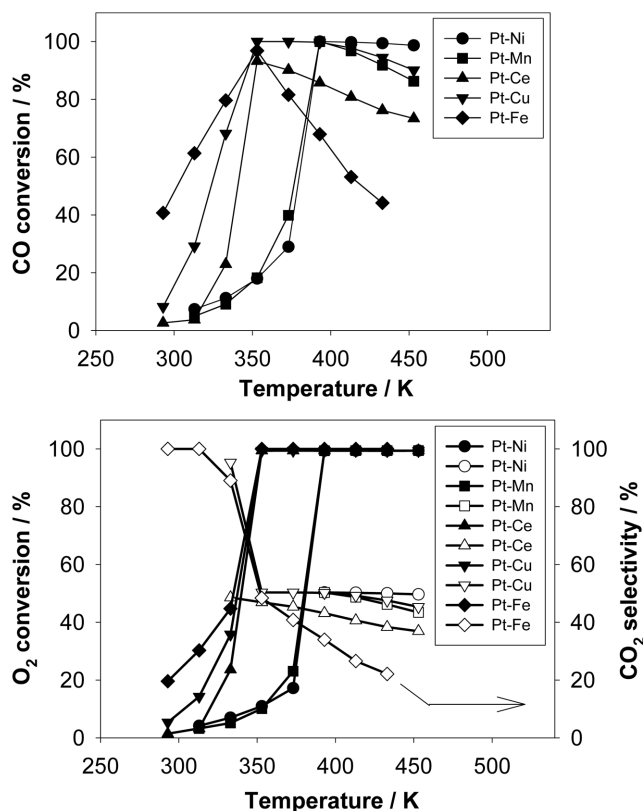


Fig. 2. CO conversion, O<sub>2</sub> conversion, and CO<sub>2</sub> selectivity for the selective CO oxidation over transition metal-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with increasing reaction temperatures. Reactants: 1% CO, 1% O<sub>2</sub>, 10% H<sub>2</sub>, and 2% H<sub>2</sub>O in He. F/W=1,000 ml/min/g<sub>cat</sub>.

lyst when the reaction temperature was higher than 433 K. As the reaction temperature increased further from 453 K to 493 K, the CO conversion decreased gradually from 100% to 98% due to O<sub>2</sub> depletion via the side reaction ( $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ ). Therefore, the CO<sub>2</sub> selectivity decreased from 50% to 49% when the reaction temperature increased from 453 to 493 K. The dispersion of Pt was determined to be 0.68 by CO chemisorption. Compared with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, Pt-ZrOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the higher CO conversion at low temperatures but the lower CO<sub>2</sub> selectivity for all reaction temperatures. This catalyst also showed more than 90% CO conversion over a wide reaction temperature similar to Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. When chromium oxide was added in Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 100% O<sub>2</sub> conversion was achieved at lower temperature compared with that of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. However, the maximum CO conversion was only 83% at 433 K and much less CO conversion was obtained above 433 K. Higher CO conversion was observed over Pt-ZnOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at low temperatures compared with those above catalysts. But, the CO<sub>2</sub> selectivity was lower than that of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst when the CO conversion was more than 50%. When cobalt oxide was added in Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 100% CO and O<sub>2</sub> conversion was achieved at 393 K. The CO conversion decreased from 100% to 95% gradually as the reaction temperature increased from 393 K to 493 K. The methanation reaction proceeded at the same time over this catalyst with consumption of H<sub>2</sub> when the reaction temperature was above 450 K. This could be observed by formed CH<sub>4</sub> species as shown in Fig. 1. In Fig. 2, the catalytic performance for the selective oxidation of CO was compared with other transition metal-promoted Pt catalysts. Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed 100% CO and O<sub>2</sub> conversion at 393 K. The CO conversion decreased from 100% to 99% gradually as the reaction temperature increased from 393 K to 453 K. When manganese oxide was added to Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 100% CO and O<sub>2</sub> conversion was obtained at 393 K. The CO conversion decreased rapidly with increasing reaction temperatures above 393 K. Therefore, the CO<sub>2</sub> selectivity over this catalyst was lower than that of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst when the CO conversion was more than 50%. For Pt-CuOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 100% CO and O<sub>2</sub> conversion was achieved at 353 K. CO<sub>2</sub> selectivity over this catalyst was quite high at low temperatures. As the reaction temperature increased from 353 K to 453 K, CO conversion gradually decreased from 100% to 90%. Therefore, the CO<sub>2</sub> selectivity over this catalyst was slightly lower than that of Pt catalyst at high temperatures. When cerium or iron oxide was added to Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 100% O<sub>2</sub> conversion was achieved at much lower temperature compared with that of Pt catalyst. CO<sub>2</sub> selectivity over Pt-FeOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was quite high at low temperatures. However, maximum CO conversion was only 95% at 353 K and much less CO conversion was obtained above 353 K. The dispersion of Pt in Pt-FeOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was determined to be 0.57. With the results of the above screening test for the selective oxidation of CO over various transition metal-promoted Pt catalysts, we could compare catalytic performance at the same condition. Upon various transition metal-promoted Pt catalysts, each of them seems to have unique characters for the reaction of selective oxidation of CO, especially for CO conversion and CO<sub>2</sub> selectivity, which are most important requirements for excellent catalysts for this specific reaction of selective oxidation of CO. In most cases of selective oxidation of CO, there is another requirement for active and selective catalysts such as se-

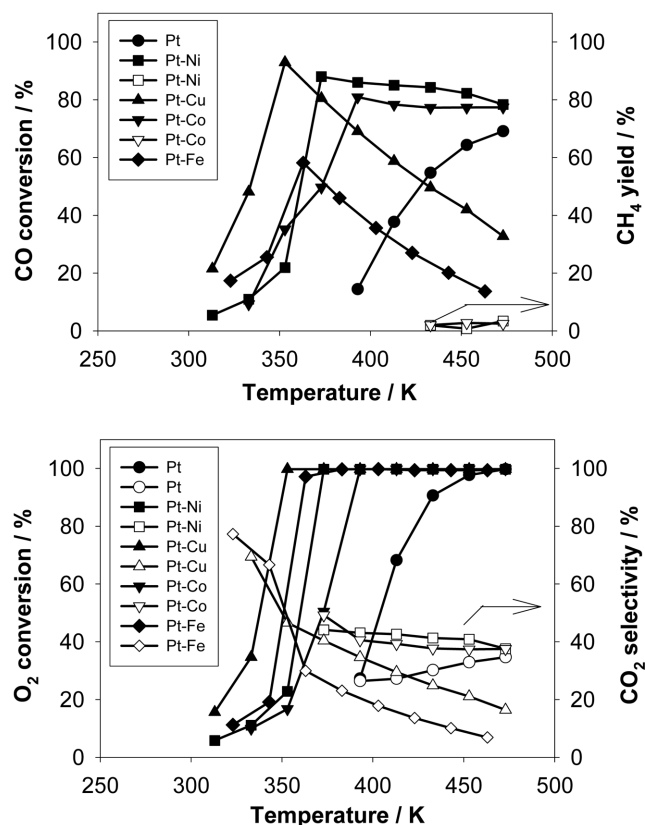


Fig. 3. CO conversion, CH<sub>4</sub> yield, O<sub>2</sub> conversion, and CO<sub>2</sub> selectivity for the selective CO oxidation over transition metal-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with increasing reaction temperature. Reactants: 1% CO, 1% O<sub>2</sub>, 80% H<sub>2</sub>, and 2% H<sub>2</sub>O in He. F/W=1,000 ml/min/g<sub>cat</sub>.

lectivity in extremely high concentration of H<sub>2</sub> in the reactant stream. Under that harsh condition, most catalysts could be easily compared for CO<sub>2</sub> selectivity in the selective oxidation of CO with that of undesired reaction with H<sub>2</sub>. As shown in previous results in Fig. 1 and Fig. 2, much higher conversion of CO and the CO<sub>2</sub> selectivity at lower temperature was achieved over Pt catalysts promoted with transition metals such as Fe, Cu, Co, and Ni compared with those of Pt catalyst. Therefore, FeOx-, CuOx-, CoOx-, and Ni-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst were selected for the selective CO oxidation in the presence of 80% H<sub>2</sub>. As shown in Fig. 3, CuOx-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest CO conversion at low temperatures, but the CO conversion decreased rapidly with increasing reaction temperatures. This was also observed over FeOx-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with much less CO conversion at all reaction temperatures compared with Pt-CuOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Compared with the remarkable decrease in CO conversions and CO<sub>2</sub> selectivity over CuOx- and FeOx-promoted Pt catalysts under the extremely high concentration of H<sub>2</sub> (80 vol%) in the reactant stream, both CoOx- and Ni-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts showed high CO conversion over wide reaction temperatures as revealed in Fig. 3. Furthermore, these catalysts showed the higher CO<sub>2</sub> selectivity for CO oxidation than that in Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst even with higher CO conversions. Thus, these catalysts could be suggested as excellent catalysts for the selective oxidation of CO among various transition metal-promoted Pt catalysts. Especially for the Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, it showed higher

CO conversions from 373 K to 493 K than those in Pt-CoOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Therefore, Ni-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was selected for further study. The methanation reaction proceeded over both catalysts at high temperatures above 433 K as shown in Fig. 3.

TPR was conducted to find the interaction between platinum and transition metal oxides as shown in Fig. 4. Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed

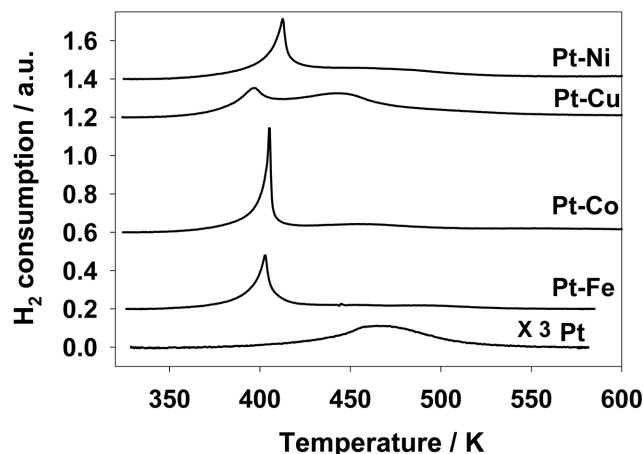


Fig. 4. TPR patterns of transition metal-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

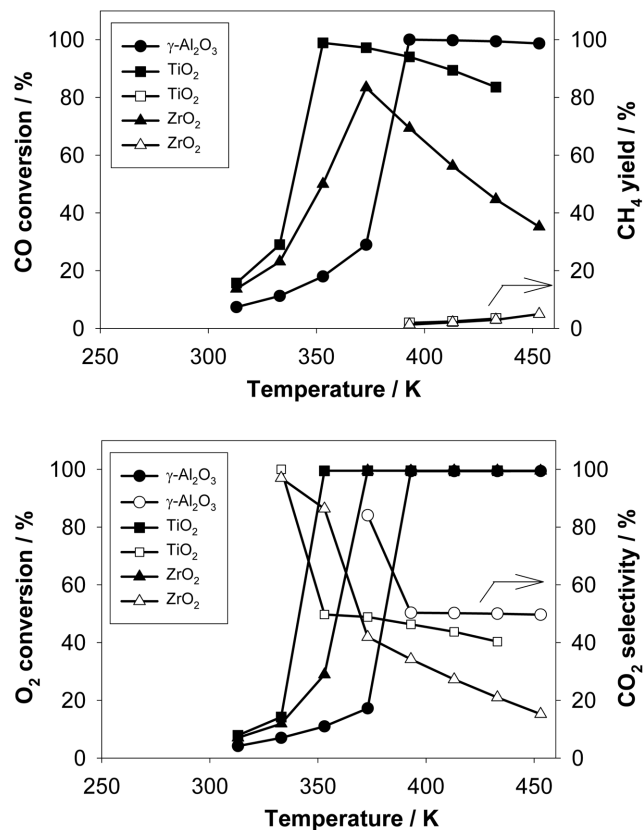


Fig. 5. CO conversion, CH<sub>4</sub> yield, O<sub>2</sub> conversion, and CO<sub>2</sub> selectivity for the selective CO oxidation over supported Pt-Ni catalysts with increasing reaction temperatures. Reactants: 1% CO, 1% O<sub>2</sub>, 10% H<sub>2</sub>, and 2% H<sub>2</sub>O in He. F/W=1,000 ml/min/g<sub>cat</sub>.

one reduction peak at 465 K. For Fe oxide-, Co oxide-, and Ni oxide-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, one strong reduction peak at 405 K with a weak broad shoulder reaching till 540 K was observed. Pt-CuOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed two strong reduction peaks at 395 K and 440 K. Compared with each supported metal oxide, the reduction peak for transition metal oxides shifted to a much lower temperature in the presence of Pt.

The effect of support on catalytic activities was studied over Pt-Ni catalyst as shown in Fig. 5. The low temperature catalytic activity was enhanced when ZrO<sub>2</sub> and TiO<sub>2</sub> were used as a support.

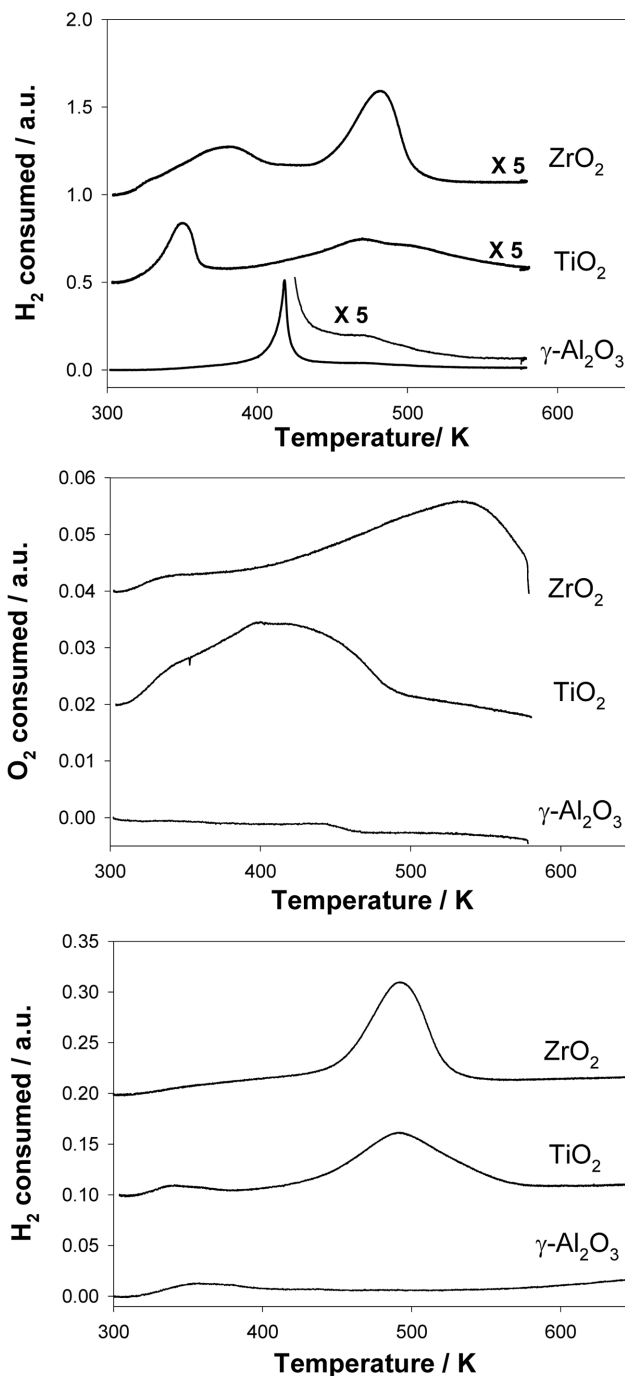


Fig. 6. TPR-TPO-TPR patterns of Pt-Ni catalysts supported on different supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>.

However, catalysts supported on them showed rather narrow operating temperature window showing more than 95% CO conversion. The methanation reaction proceeded at much lower temperatures compared with Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

TPR was also conducted to find the interaction between platinum and nickel oxides for Pt-NiO catalysts supported on different supports as shown in Fig. 6. Pt-NiO/ZrO<sub>2</sub> showed two reduction peaks at 380 K and 480 K. These can originate from reduction of Pt-Ni oxide and NiO, respectively. The reduced Pt-Ni/ZrO<sub>2</sub> catalyst consumed O<sub>2</sub> from room temperature to 573 K, which was determined by TPO experiment. Only one reduction peak at 490 K was observed in TPR after TPO experiment. This can be due to reduction of NiO which was oxidized in TPO experiment. Pt-NiO/TiO<sub>2</sub> showed two reduction peaks at 350 K and 470 K. With similarity to the Pt-NiO/ZrO<sub>2</sub>, these also can originate from reduction of Pt-Ni oxide and NiO, respectively. The reduced Pt-Ni/TiO<sub>2</sub> catalyst consumed O<sub>2</sub> from room temperature to 523 K, which was also determined by TPO experiment. Two reduction peaks at 340 K and 490 K were observed in TPR after TPO experiment as revealed in Fig. 6. These peaks were due to reduction of Pt-Ni oxide and NiO, respectively. However, no noticeable O<sub>2</sub> consumption was observed over Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in TPO and only a very weak reduction peak at 350 K was observed in TPR after TPO experiment in Fig. 6. Therefore, the metallic phase of Pt-Ni should play an important role in the selective CO oxidation over Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The pres-

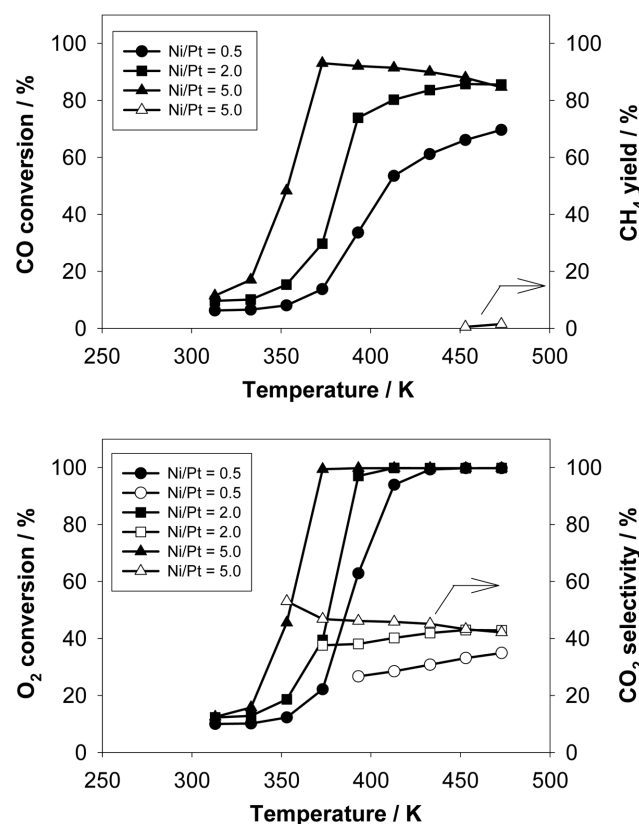


Fig. 7. CO conversion, CH<sub>4</sub> yield, O<sub>2</sub> conversion, and CO<sub>2</sub> selectivity for the selective CO oxidation over Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different molar ratio of Ni/Pt with increasing reaction temperature. Reactants: 1% CO, 1% O<sub>2</sub>, 80% H<sub>2</sub>, and 2% H<sub>2</sub>O in He. F/W=1,000 ml/min/g<sub>cat</sub>.

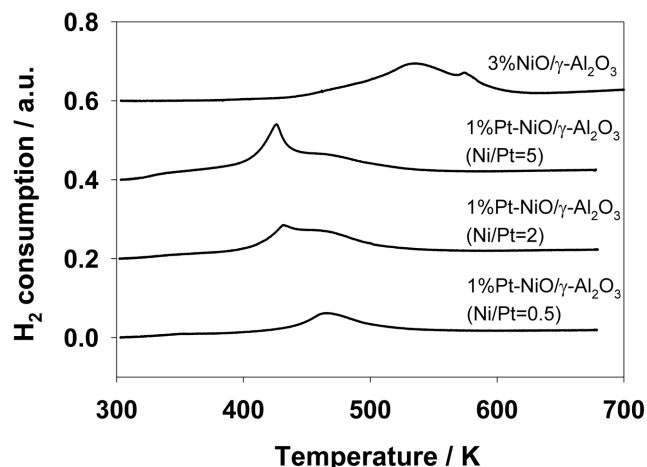


Fig. 8. TPR patterns of Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different molar ratio of Ni/Pt.

ence of NiO, which can be formed over TiO<sub>2</sub> and ZrO<sub>2</sub>, can promote low temperature catalytic activity but cause a decrease in the CO<sub>2</sub> selectivity at high reaction temperatures. For the Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, the metallic phase of Pt-Ni seems to lead to stable activity and selectivity in selective oxidation of CO without sacrificing additional O<sub>2</sub> consumption for oxidation of metallic compounds.

The effect of molar ratio between Ni and Pt was examined as shown in Fig. 7. As the molar ratio of Ni/Pt increased from 0.5 to 5, the catalytic activity at low temperatures increased. The CO<sub>2</sub> selectivity also increased with increasing the molar ratio of Ni/Pt. No noticeable increase in activity could be found when the molar ratio of Ni/Pt increased from 5 to 10.

TPR was also conducted to find the interaction between platinum and nickel oxides with different molar ratio of Ni/Pt as shown in Fig. 8. When the molar ratio of Ni/Pt was 0.5, one reduction peak at 465 K was observed, which was similar to Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Pt-NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed one reduction peak at 430 K with a broad shoulder reaching until 550 K when the molar ratio of Ni/Pt was 2.0. As the molar ratio of Ni/Pt increased further, the reduction occurred at lower temperature and its peak intensity increased, which could be compared in TPR peak in Fig. 6 and Fig. 8 for Pt-NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The strong peak around 450 K and a broad shoulder above 450 K in TPR pattern can be due to the reduction of Pt-Ni oxide and NiO, respectively. The increase of peak intensity around 450 K with a molar ratio of Ni/Pt appeared to be closely related to the increase of the interaction between Pt and Ni. NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed one reduction peak at 540 K with a shoulder at 573 K. The addition of nickel oxide appeared to decrease the reduction temperature of platinum oxide. The presence of Pt also decreased the reduction temperature of NiO.

XRD patterns were obtained to determine bulk crystalline structure of all the above catalysts. However, no peak representing crystalline phase due to platinum and transition metal compounds was found except peaks representing supports. Therefore, it can be assumed that these metals were present in a highly dispersed form, which was also supported by the CO chemisorption for some catalysts.

The effect of presence of H<sub>2</sub>O and CO<sub>2</sub> on the selective CO oxi-

dition was further examined over Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 393 K. 99% CO conversion and 100% O<sub>2</sub> conversion was achieved when 100 ml/min of reactant composed of 1 vol% CO, 1 vol% O<sub>2</sub>, and 50 vol% H<sub>2</sub> in He was contacted with 0.10 g of catalyst. The same CO conversion and CO<sub>2</sub> selectivity was obtained in the presence of 20 vol% CO<sub>2</sub> and 2 vol% H<sub>2</sub>O. Furthermore, deactivation did not occur during 10 h reaction.

Finally, we could compare catalytic performance of various transition metal-promoted Pt catalysts on the selective oxidation of CO under the same reaction condition. Among various Pt catalysts promoted with different transition metal species, Pt-CoOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> could be proposed as effective catalysts for selective oxidation of CO in the presence of H<sub>2</sub> in the reactant stream. Especially for the Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which showed better catalytic performance over wide operating temperature window, the bimetallic phase of Pt-Ni seems to give rise to stable activity and selectivity in selective oxidation of CO in H<sub>2</sub>-rich stream.

## CONCLUSIONS

Pt-CoOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed high CO conversion over wide reaction temperatures in the selective CO oxidation in the presence of excess H<sub>2</sub> among supported Pt catalysts promoted with various transition metals such as Cr, Mn, Fe, Co, Ni, Cu, Zn, and Zr. Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was superior to Pt-CoOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of high concentration of H<sub>2</sub>. The alumina-supported Pt-Ni catalyst showed high CO conversion over a wide range of reaction temperatures compared with TiO<sub>2</sub>- and ZrO<sub>2</sub>-supported ones. The catalytic activity at low temperatures increased with increasing the molar ratio of Ni/Pt. This accompanied the TPR peak shift to lower temperatures. The optimum molar ratio between Ni and Pt was determined to be 5. The bimetallic phase of Pt-Ni can enhance the catalytic activity for the selective CO oxidation. This Pt-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed no decrease in CO conversion and CO<sub>2</sub> selectivity in the presence of 2 vol% H<sub>2</sub>O and 20 vol% CO<sub>2</sub>.

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