ELSEVIER

Chemical Engineering Journal 93 (2003) 61–68

Chemical Engineering Journal

www.elsevier.com/locate/cej

Reaction and surface characterization studies of titania-supported Co, Pt and Co/Pt catalysts for the selective oxidation of CO in H_2-containing streams

William S. Epling[1], Praveen K. Cheekatamarla, Alan M. Lane*

Department of Chemical Engineering, The University of Alabama, Box 870203, Tuscaloosa, AL 35487, USA

Abstract

The selective, catalytic oxidation of CO in H_2-containing streams was investigated over titania-supported Co, Pt and Co/Pt catalysts. The work was motivated by the need to remove CO from the reformate fed to a polymer electrolyte fuel cell (PEFC) before it can poison the Pt anode. Pt/TiO_2 catalysts were active over a broad range of temperatures with a maximum at 120 °C. Co/TiO_2 catalysts were effective for CO oxidation at high temperatures (>100 °C). Mixed metal Co/Pt catalysts were quite effective, even at room temperature. The presence of H_2O and CO_2, major components of actual reformate, reduced the activity of all the catalysts tested, but less so for the Co/Pt catalyst. Activity decreased over long times but an intermittent, high-temperature "purge" regenerated the original activity. X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) were used to understand the synergism between metal components. The Pt either influenced activity by helping reduce the Co, or the Pt and/or Co stabilized a Ti suboxide state that may play a role in the reaction process. The latter is most likely attributable to the strong metal support interaction (SMSI) effect previously noted on Pt/TiO_2 catalysts.

Keywords: Selective oxidation; Polymer electrolyte fuel cell; Suboxide

1. Introduction

Polymer electrolyte fuel cells (PEFCs) show considerable promise for fuel-efficient vehicles and therefore a substantial effort has recently been directed at their production and optimization. The PEFC currently requires hydrogen as its fuel source. In order to avoid storing high-pressure hydrogen, the fuel can be generated in an onboard fuel processor. Although the term "reformer" is often used for the whole system, the production of hydrogen actually occurs in three processes: (1) hydrogen is produced by autothermal reforming of a hydrocarbon ($\text{fuel} + O_2 + H_2O \leftrightarrow CO_x + H_2$) where without water it is partial oxidation and without oxygen it is steam reforming; (2) the water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) eliminates most of the CO, producing more hydrogen; (3) and any remaining CO is reduced to parts per million levels by selective, catalytic oxidation, usually referred to as preferential oxidation (PROX) [1]. Many auxiliary processes such as fuel vaporization, sulfur removal, heat integration, water management and effluent gas combustion can make this a very complicated device.

The CO concentration from the low-temperature water-gas shift reaction is typically about 1 mol%, which is set by thermodynamic equilibrium at about 200 °C. The PEFC anode uses a Pt catalyst, however, that is very sensitive to CO poisoning at its low operating temperature. The Partnership for a New Generation of vehicles (PNGV) has therefore set a CO target concentration for the fuel processor at 10 ppm [2]. In order to achieve this low CO concentration, the PROX reactor is placed between the shift reactor and the fuel cell anode. Los Alamos National Laboratory (DOE's lead laboratory for PROX systems) has developed a PROX catalyst and reaction system. It can achieve low concentrations of CO (10–20 ppm) in a multi-stage reactor over a Pt/Al_2O_3 or Ru/Al_2O_3 catalyst. The reaction chemistry is complicated, involving not only oxidation of both CO and H_2, but also methanation and water-gas shift.

Typical of catalytic reactions, the challenges here are activity, selectivity, stability and cost. The conversion of CO has to be 99.9% in order to achieve a concentration of 10 ppm. 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. At

---

* Corresponding author. Tel.: +1-205-348-1729; fax: +1-205-348-7558. *E-mail address:* alane@coe.eng.ua.edu (A.M. Lane).

[1] Present address: EmeraChem, 2375 Cherahala Boulevard, Knoxville, TN 37932, USA.

1385-8947/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1385-8947(02)00109-2

the same time, the reformate is mostly hydrogen and its coincident oxidation obviously decreases the overall fuel efficiency. The activity should be maintained in the presence of typical reformate gases such as H_2O and CO_2 and over the life of a car. The most common catalyst is supported Pt so the cost could be reduced by using a non-precious metal.

The selectivity is defined as the ratio of CO oxidized (to CO_2) over the total O_2 consumed. Producing water by burning hydrogen wastes fuel and reduces the system efficiency. A selectivity of 50% with a reformate containing 2 mol% CO would reduce the fuel efficiency about 2% [3].

A number of catalysts have been investigated for the PROX reaction. Some of the more effective ones include supported Pt [3,4], Ru, Rh [5], and Au [6–8]. The Pt-based catalysts tested thus far achieve maximum conversions at approximately 200 °C, with selectivities approaching 40–60% in a 1% CO, 1% O_2, and H_2 balance mixture [3]. Introducing the O_2 into the reactor at different stages, enhances this selectivity. Using Au-containing catalysts, it has been reported that the operating temperatures can be lowered to ∼80 °C to achieve similar results [10]. However, preliminary experiments in our laboratory indicate that exposing the Au catalysts to CO_2 and H_2O (typical components of the reformate) results in significant activity loss over time.

Other non-precious metals, such as the first row transition metal oxides, are also active as oxidation catalysts and are substantially cheaper. Cobalt is particularly active and possesses a high activity for CO and hydrocarbon oxidation [9]. Promotion of Pd with Co results in increased CO and propene oxidation activities under stoichiometric conditions [10].

Our objective is to study Co-based catalysts for the selective oxidation of CO in a stream rich in H_2, determine the effects of CO_2 and H_2O on their performance, and study the influence of Pt addition to the Co catalyst. Three model catalysts containing platinum and/or cobalt were selected for this study: Pt/TiO_2, Co/TiO_2, $Pt/Co/TiO_2$. The first two were chosen to study the active components separately and the last to study any synergistic effects. These catalysts were tested for activity and then characterized using X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR).

2. Experimental

The catalysts were prepared from precursor materials obtained from Johnson Mathey and Aldrich Chemical. The TiO_2 support material is anatase and has a purity of 99.9%. The Co precursor is $Co(NO_3)_2 \cdot H_2O$ and the Pt originates from $(NH_3)_2Pt(NO_2)_2$. Each catalyst was prepared by the incipient wetness method using distilled water as the solvent for the precursor materials. Catalyst compositions are given in weight percent. The catalysts were then dried in air at 110 °C overnight. Each was also calcined in air at 500 °C for 2 h. The Pt/Co catalysts were prepared by depositing the Co first, drying, calcining and then depositing the Pt, with subsequent drying and recalcination. Each catalyst was then pretreated in a mixture of 5% H_2 and N_2 for 1 h at 350 °C.

A quartz tube with a diameter of 3/16 in. was used as the reactor. A bypass flow tube was also built in to verify the reactant stream composition intermittently. The tube was placed in a tube furnace with digital control for heating. The catalysts tested were in powder form. A thermocouple was placed inside the reactor tube and the tip was typically located just above the powder during the reaction tests. Mass flow controllers were used to control reactant flowrates. The pressure drop was always less than 3 psig. In each test, 700 mg of non-diluted catalyst and a total flowrate of 550 sccm were used. The exit stream was attached to a Drierite bed to remove water, then a Thermo Environmental CO analyzer, capable of reading CO levels in the ranges of 0–1 to 0–8000 ppm. GC analysis was also performed with an HP 5890 using a Haysep DB column and thermal conductivity detector to monitor CO, O_2, CO_2, and CH_4 levels.

BET surface area and TPR measurements were obtained using a Quantachrome CHEMBET 3000. The BET surface areas of all catalysts used in this study ranged from 10 to 12 m^2/g. For TPR experiments, a temperature ramp rate of 10 °C/min was used and the reductant gas was a 5% H_2/N_2 mixture. XPS data were obtained using a Kratos Axis 165 using an Al anode as the X-ray source.

3. Results and discussion

3.1. Activity and selectivity comparison

CO conversions as a function of reactor temperature are shown in Fig. 1 for three catalysts: 3.32% Co/TiO_2; 1.44% Pt/TiO_2; and 3.32% Co/1.44% Pt/TiO_2. The aerial reaction rates are comparable to others presented in the literature [3,7]. Dispersions (and therefore “true” TOF) could not be accurately attained due to the presence of reduced titanium as will be discussed below. The inlet stream for this test

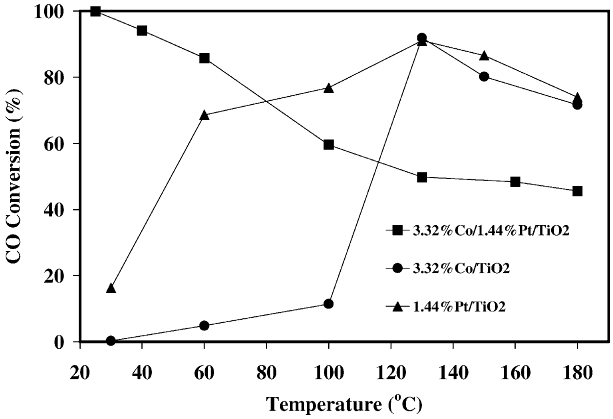

Fig. 1. CO conversion as a function of reactor temperature for the titania-supported Pt, Co and Pt/Co catalysts.

consisted of 1.0% CO, 1.25% O_2 and a balance of H_2. The reactor temperature reported is that of the reactor furnace itself; the temperature at the outlet of the catalyst bed was always higher due to the exothermic reactions. The experiments were performed in short time frames relative to the decay/lifetime study described below. Stable readings were obtained quickly and these are reported. Bare TiO_2 was tested for activity but no CO conversion was observed below 250 °C (data not shown since no activity was observed).

Supported Pt is known as an active CO oxidation catalyst and is considered our “standard” for these experiments. The most active Pt catalyst tested was a 1.44% Pt/TiO_2 and is shown Fig. 1. The CO conversion reached a maximum at about 125 °C. Remarkably, this catalyst oxidized some of the entering CO at room temperature (~17%), probably due to localized heating of the catalyst bed by the H_2 oxidation. Similar results have been reported over Pt/Al_2O_3 catalysts [3,4], but the active temperature range is usually higher. The lower temperature for Pt/TiO_2 may be due to active participation of the reducible TiO_2 support in the reaction.

The supported Co catalyst is as active as the Pt catalyst at high temperatures. However, at low temperatures, it is inactive for CO oxidation. This may be due to its water sensitivity as described later. Based on activity, Co could be a good replacement for Pt at operating temperatures above 120 °C. However, as will be seen, it is inhibited by the other reformate gases, H_2O and CO_2.

The mixed metal $Co/Pt/TiO_2$ catalyst showed remarkable low-temperature activity. The improvement is much more than the additive effect of a higher metal loading. The synergistic mechanism will be explored below.

Oxygen was never observed in the product, indicating that at both low and high temperatures, H_2 was being oxidized to H_2O, and the O_2 was completely consumed. Therefore, the selectivity will be directly proportional to the CO conversion. A maximum selectivity of 40% can be achieved with these flowrates. The Co/TiO_2 catalyst produced some methane at temperatures above 150 °C. Therefore, actual selectivities above 150 °C would be lower than expected. None of the Pt- or Co/Pt-containing catalysts were active for methanation.

Activity data for $Co/Pt/TiO_2$ catalysts with different Co loading are presented in Fig. 2. To illustrate the effect of O_2 concentration on the reaction, the experiment with the 5% Co catalyst was run with 0.85% O_2. At this lower concentration, the selectivity can be much higher, almost 59%. Each catalyst showed high activity beginning at room temperature and the activity decreased as the temperature approached 100 °C. The optimum Co loading would depend on the desired operating conditions. The activity was reversible—it could be regained by lowering the temperature from 100 °C. Conversions greater than 99% were noted with all three catalysts at operating temperatures of 40 °C or below. An obvious drawback to this low operation temperature is the potential accumulation of water in the reactor bed or on the catalyst and this problem will be discussed below.

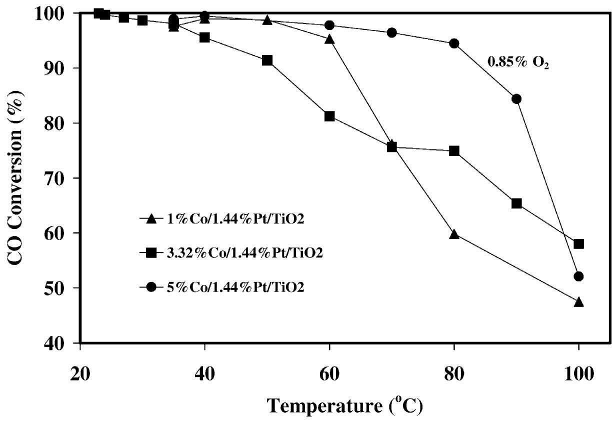

Fig. 2. CO conversion as a function of reactor temperature using $Co/Pt/TiO_2$ catalysts with different Co loadings. Feed concentrations were 1% CO, 0.85% or 1.25% O_2 and a balance of H_2.

The same trend is again noted in the selectivity shown in Fig. 3, illustrating that it is H_2 oxidation that causes the decrease in CO conversion. The selectivity was much improved for the 5% Co catalyst by decreasing the O_2 concentration. The higher Co loading more than compensated for the loss in activity expected with lower O_2 concentrations.

3.2. *Effect of reformate gases—CO_2 and H_2O*

In order to determine the effects of other components that will be present in the reactant stream and their potential influence on the catalytic activity, CO_2 (18%) and H_2O (7%) were introduced separately and then together. Fig. 4 shows the effect for the $Co/Pt/TiO_2$ catalyst at low temperatures. Both CO_2 and H_2O have a small detrimental effect, with water alone being the worst. The effect of combined CO_2 and H_2O in the feed on the three types of catalysts is shown in Fig. 5. Comparing with Fig. 1, the Pt/TiO_2 catalyst looses significant activity but the Co/TiO_2 catalyst is

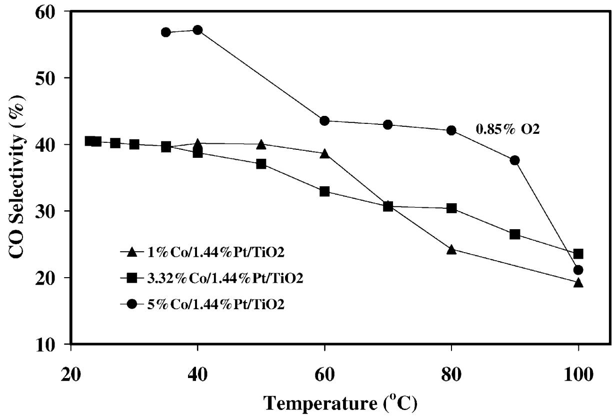

Fig. 3. CO selectivity as a function of reactor temperature using $Co/Pt/TiO_2$ catalysts with different Co loadings. Feed concentrations were 1% CO, 0.85 or 1.25% O_2 and a balance of H_2.

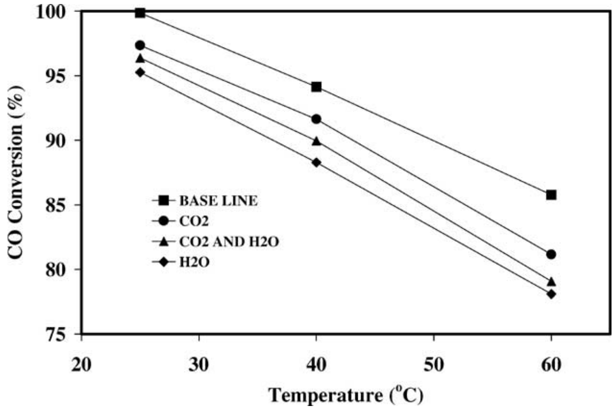

Fig. 4. CO conversion as a function of temperature for the 3.32% Co/1.44% Pt/TiO_2 catalyst with 18% CO_2 and/or 7% H_2O added to the feed.

virtually killed. The low-temperature activity of the Co/Pt/TiO_2 catalyst by comparison was only slightly affected.

Since it is not feasible to remove the H_2O and CO_2 from the reformer outlet and prior to the PROX reactor, the Co/TiO_2 catalysts will not be a good alternative to Pt for a low-temperature PROX catalyst. The only obvious solution would be more catalyst in the reactor, but under the conditions examined in this experiment, a space velocity of only 22,000 h^{-1} was used and would be much further reduced to obtain acceptable conversions. Such a solution would dramatically increase the PROX reactor volume, which must be kept small along with all other components of the H_2 generating system to fit in the small spaces of a car.

3.3. Stability

The mixed metal catalysts performed quite well at low temperatures under the conditions examined. Even in the presence of apparent inhibitors, high conversions could be attained, which led to the next test, whether the conversions could be maintained. The 3.32% Co/1.44% Pt/TiO_2 catalyst was chosen as a test candidate and the reactor was operated at 45 °C, with the data shown in Fig. 6. An initial drop in activity occurred over the first 8 h of operation, but then a slower pace of deactivation was maintained over the next >100 h. After 117 h, the conversion was approximately 79%. At this time, the reactor temperature was raised to 100 °C, held there for 1 h, and then lowered to 45 °C again. This heat treatment restored the catalyst performance. Adsorbed water is the presumed cause of the slow but steady deactivation of the catalyst. The higher temperature resulted in more rapid evaporation of the water from the catalyst surface and re-attainment of the activity. The reason that water does not deactivate the catalyst more rapidly is due to the elevated temperatures along the catalyst bed due to the exothermic reactions occurring during the oxidation process. Although the furnace temperature was set at 45 °C, the temperature just above the catalyst bed was approximately 110 °C. The experiment indicates that if an intermittent high-temperature “purge” can be accomplished, the mixed metal catalyst would be a good candidate as a low-temperature PROX catalyst.

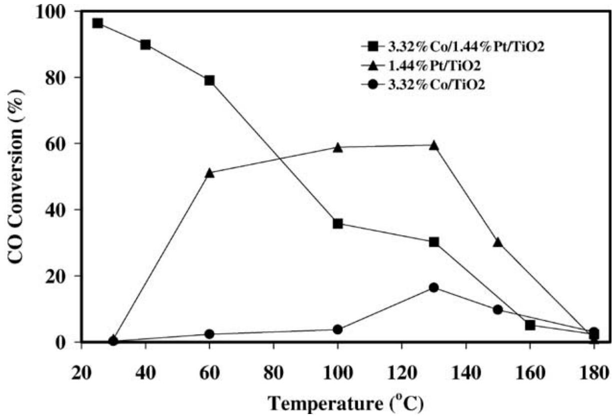

Fig. 5. CO conversion as a function of reactor temperature for the titania-supported Pt, Co and Pt/Co catalysts in the presence of 7% H_2O and 18% CO_2.

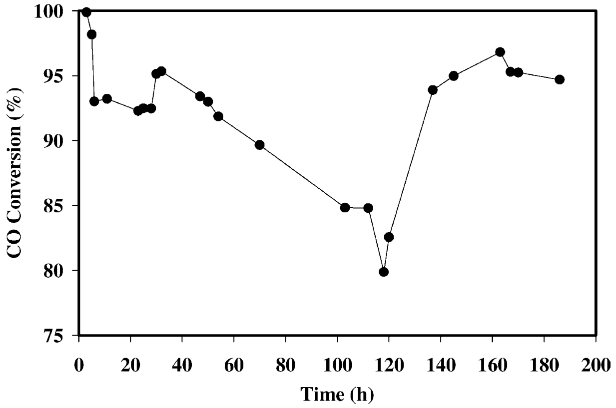

Fig. 6. CO conversion as a function of time on stream for a 3.32% Co/1.44% Pt/TiO_2 catalyst at 45 °C. Temperature increased to 100 °C for 1 h after 117 h of operation.

The activity of the catalyst is a function of time and this would seem to influence the conversion obtained as a function of temperature. However, the short time frames used in the temperature ramp experiments are quite different (∼1.5 versus 117 h). The decrease in activity as a function of reactor temperature was more significant than with time.

3.4. Characterization by X-ray photoelectron spectroscopy and temperature-programmed reduction

The best performance was obtained using the mixed metal catalysts. Simply adding the two activities from the single metal component catalysts does not result in the conversions noted although identical reaction conditions were used in each experiment. Therefore, some synergistic effect must be present. Exploring this possibility was accomplished using XPS and TPR and these results are presented below.

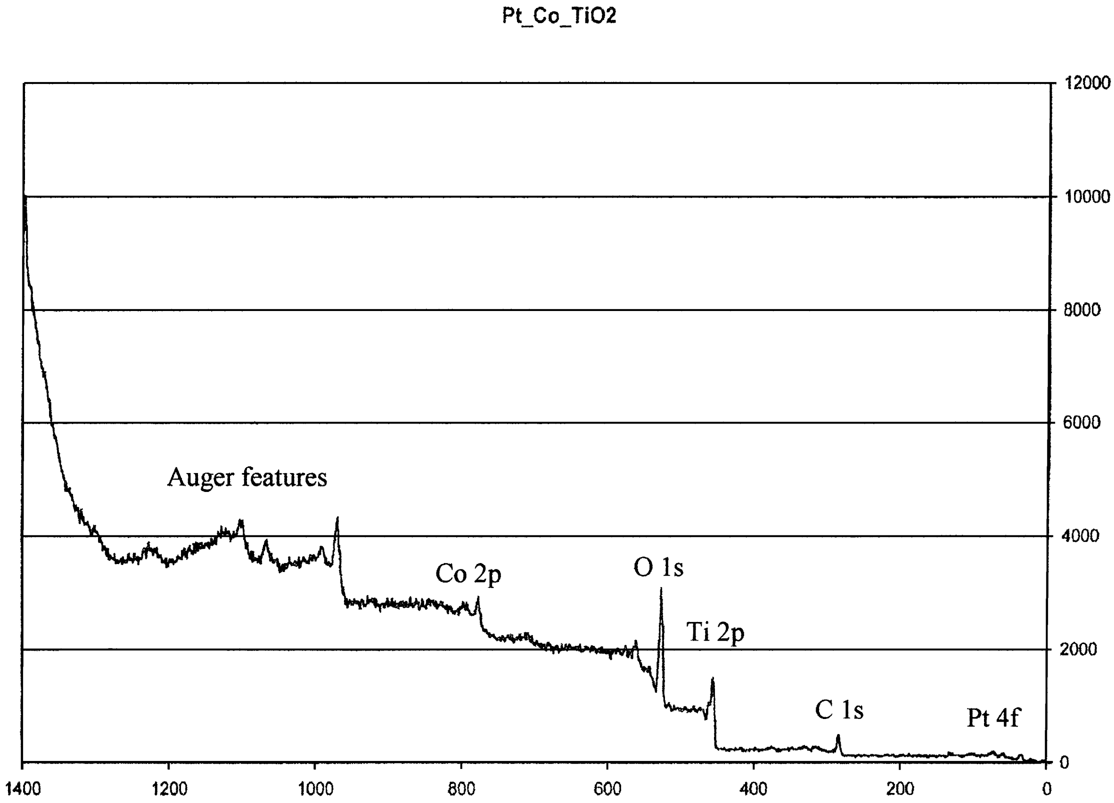

Fig. 7. An XPS survey spectra of the 3.32% Co/1.44% Pt/TiO catalyst after reduction.

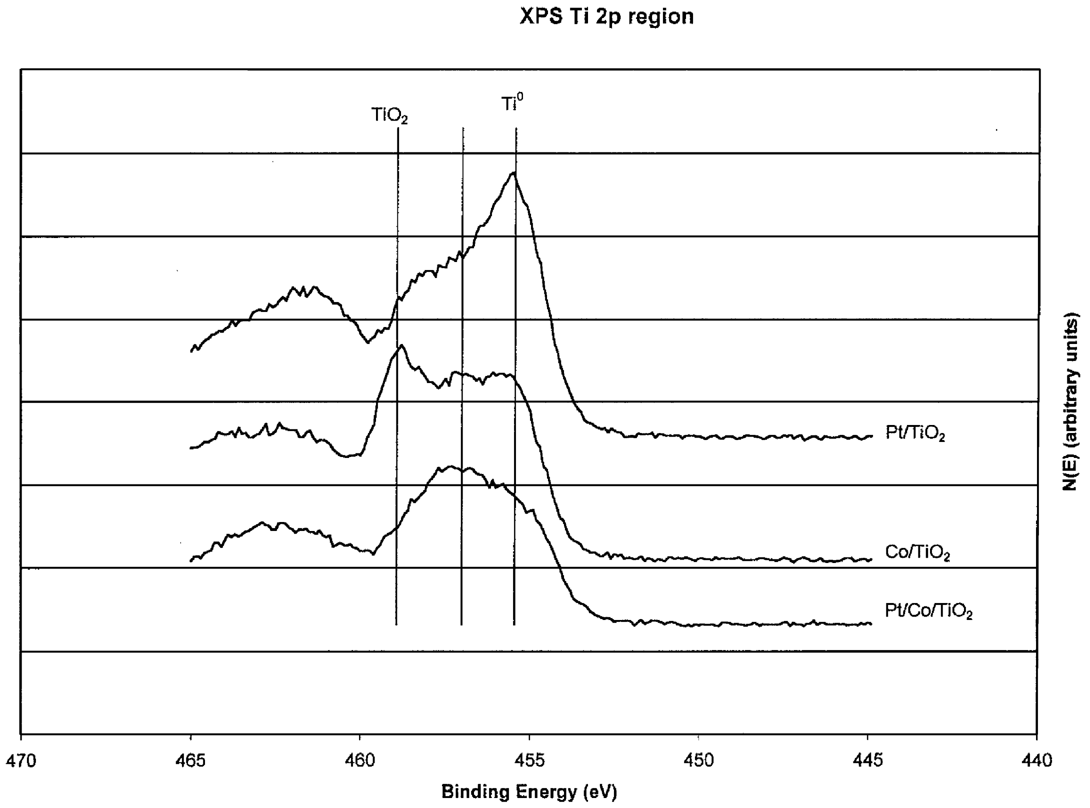

Fig. 8. High-resolution XPS spectra of the Ti 2p binding energy region obtained from the titania-supported Co, Pt and Co/Pt catalysts after reduction.

An XPS survey spectrum obtained from the 3.32% Co/1.44% Pt/TiO_2 catalyst is shown in Fig. 7. This catalyst was calcined at 500 °C and reduced in a 5% H_2/N_2 mixture at 350 °C for 2 h. Features originating from the presence of Co, Pt, Ti, O and C are all evident. The presence of the carbon signal is not surprising because of exposure to air during transfer from the reactor to the XPS. Otherwise, all the other features are expected. The intensity of the O signal may also be larger than expected due to the air exposure. This would be caused by a Co–O presence but most of the signal originates from the support. How much cannot be determined at this stage, but O_2 is present in the reaction feed so this room temperature exposure to air may not influence the interpretation dramatically. The spectra obtained from the single-metal catalysts are identical except that they do not contain the other metal's features and they are therefore not presented.

The high-resolution XPS spectra of the Ti 2p binding energy region obtained from the 3.3% Co/TiO_2, 1.4% Pt/TiO_2 and 3.3% Co/1.4% Pt/TiO_2 catalysts are shown in Fig. 8. A mixture of Ti states exists in the near-surface region of all three catalysts. The chemical state of the Ti in the near-surface region of the Co/TiO_2 catalyst is primarily TiO_2, with both Ti metal and a suboxide present also. The suboxide may correspond to either a cobalt titanate species [11] or to a suboxide such as Ti_2O_3 that has been previously proposed [12]. An XPS spectrum of this same binding energy region obtained from the bare titania (data not shown) indicates that both the metal and TiO_2 species are present, but not the suboxide or titanate states. Therefore, this state must be associated with the Co or is stabilized/formed by the presence of the Co.

The presence of the Pt results in a further degree of Ti reduction. Significantly, more Ti metal is evident in comparison to the amount of TiO_2. Furthermore, the amount of suboxide is also apparently decreased due to the presence of the Pt, possibly due to its effect in further reducing the suboxide species preferentially. Due to the presence of the Ti metal states, calculations of the amounts of Co or Pt and the associated dispersions could not be attained since the methods for these measurements rely on the support remaining as an oxide during the process.

The mixed metal Co/Pt/TiO_2 catalyst contains primarily the suboxide/titanate species in the near-surface region, thus it has become a mixture of the two spectra above. One cannot definitively assign this state to the enhanced low-temperature activity of this catalyst, but this possibility is enhanced by the trend in activity noted. As the suboxide/titanate or metal

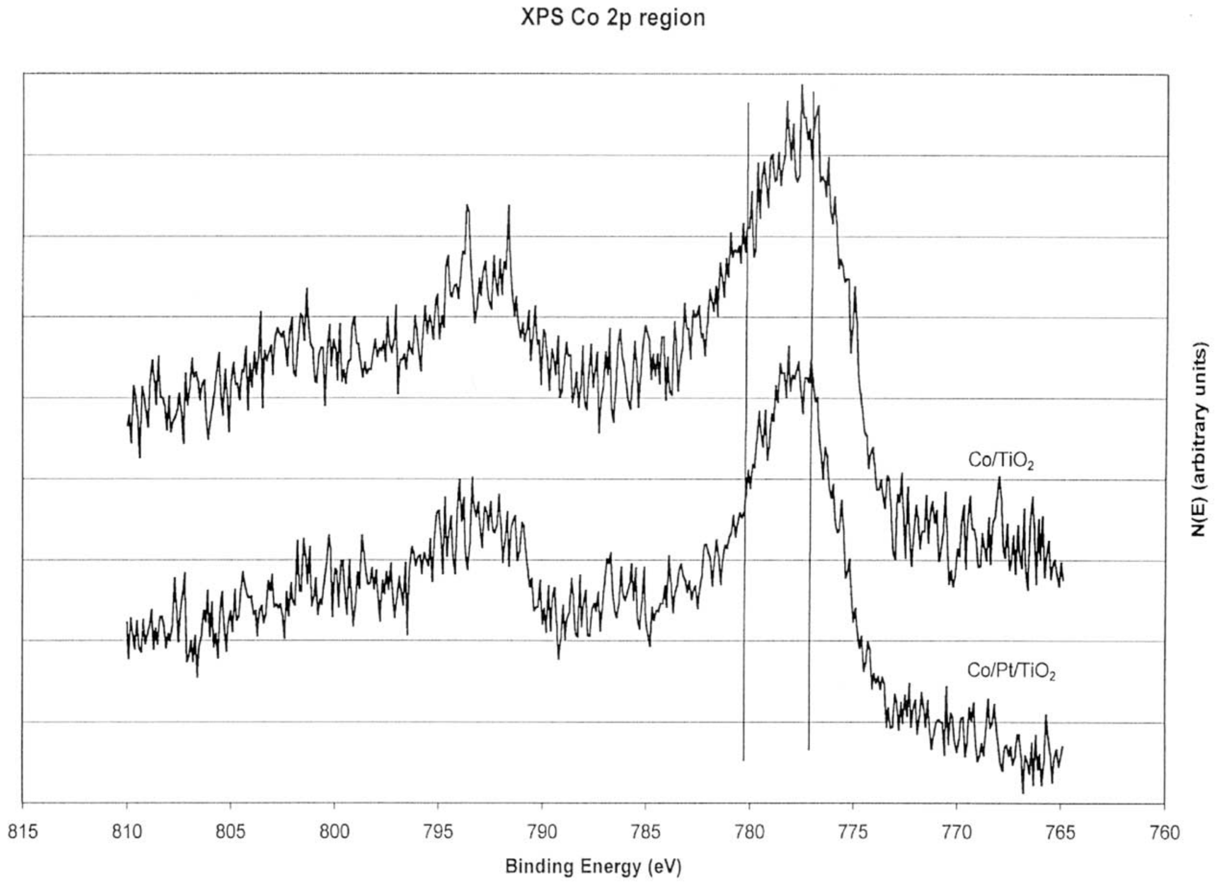

Fig. 9. High-resolution XPS spectra of the Co 2p binding energy region obtained from the titania-supported Co and Co/Pt catalysts after reduction.

presence is increased, lower temperature activities are realized. This growth in suboxide or metal trend occurs as: Co/TiO_2; Pt/TiO_2; $Co/Pt/TiO_2$; with the low temperature activity increasing with each catalyst.

A well-known phenomenon in catalysis is the strong metal support interaction (SMSI) effect. The original work concerning the SMSI effect concerned Pt/TiO_2 [12] catalysts and originally meant the migration of TiO_x particles to and over the Pt during certain high temperature excursions in a reductive environment [13]. The SMSI effect, in many cases, has been expanded to include most effects between a support and metal. It is very probable that in the present study the SMSI effect plays a role. Moderately high-temperature reductions were used and a continuous exposure to H_2 existed in the experiments. The existence of the suboxide, seen in the XPS data, could be attributed to the migrated TiO_x species on the Pt particles. The activity should be affected either through covering the active Pt species with TiO_x or the Ti suboxide may have some activity toward oxidation and assist in the reaction. The latter seems to be true as the activity of the catalyst is quite high even at room temperature.

The XPS spectra of the Co 2p binding energy region obtained from the Co/TiO_2 and $Co/Pt/TiO_2$ catalysts are shown in Fig. 9. The Co species in the near-surface region of the first is composed of metallic and Co_3O_4 states. The presence of the Pt has the same effect on the Co as it did on the titania, as more metal is evident with the addition of the Pt. These results are not surprising since Pt is known to lower the reduction temperature of other oxide species and each of these catalysts was pretreated in a reducing environment. Upon exposure of these catalysts to a reductive pretreatment, more Co oxide is reduced when the Pt is present than not. However, the binding energy values for a Co bound to the titanate should be near that of the metal and may account for the increased signal in this region also.

The TPR experiments shown in Fig. 10 are consistent with the above conclusions. There are two primary features associated with the Co/TiO_2 catalyst. The first corresponds to a temperature of approximately 200 °C and likely originates from reaction with the surface of the support material. This was verified in an experiment using the bare support, which resulted in a peak at the same temperature and exactly the same size on a weight basis. The higher

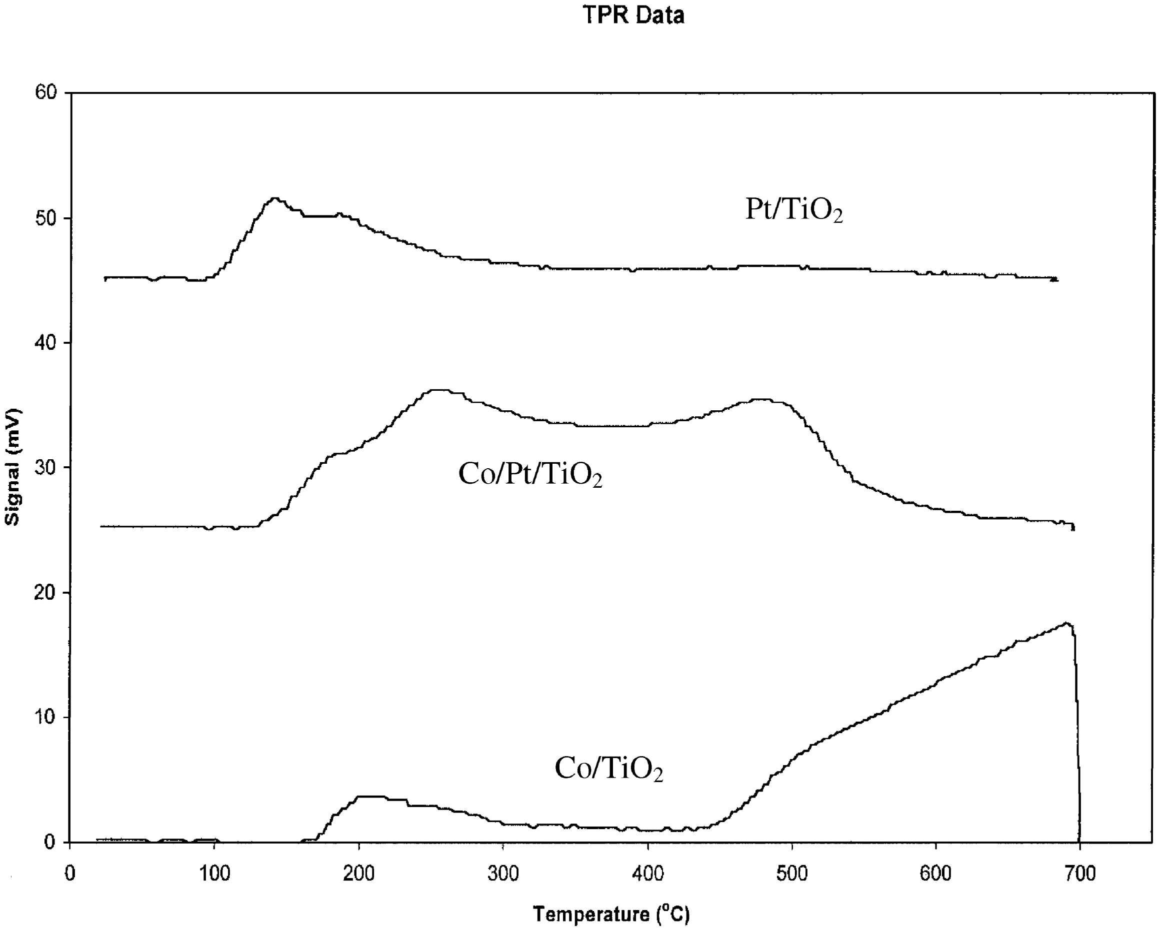

Fig. 10. TPR patterns obtained from the titania-supported Co, Pt and Co/Pt catalysts using a 5% H_2/N_2 mixture with a heating ramp of 10 °C/min.

temperature features are due to the reduction of the Co or bulk TiO_2. The first reduction occurs at about 520 °C and it has been associated with the formation of titanate species [11]. The titanate species is more difficult to reduce and the Co titanate reduces to Co metal at even higher temperatures. Alternatively, this is bulk reduction of TiO_2.

The Pt/TiO_2 catalyst also has several features in its TPR spectrum. The low-temperature peak, residing at approximately 150 °C, is caused by partial reduction of some of the TiO_2, as discussed above. But this peak is larger and at lower temperature than that originating from the bare TiO_2. The Pt may help in the further reduction of some of the near-surface TiO_2. Another possibility is the coincident reduction of any Pt oxide species present at the surface.

The TPR spectrum obtained from the Co/TiO_2 catalyst has three major features at 180, 260 and 470 °C. The latter is associated either with the reduction of the Co species or with bulk TiO_2 reduction but now at a lower temperature with assistance from the Pt. The lower-temperature features are larger than any others and may also be associated with an initial reduction of the Co oxides to the titanate or suboxide species. Also, the peak associated with support reduction is large and occurs at a lower temperature than bare titania.

These data suggest two possible scenarios that may cause low-temperature activity enhancement in the presence of both the Co and Pt. First, the presence of Pt on oxide supports or an interaction with an oxide is known to affect the temperature of reduction of that oxide. If a suboxide species or metal site is needed in this reaction sequence, then the presence of Pt and H_2 in the stream may influence the activity of the catalyst. A possible mechanism is that the Pt causes a further reduction in neighboring Co sites which adsorb more of the O_2 and lend this reactant to the CO adsorption sites, most likely associated with the Pt. Pt readily adsorbs CO but does not readily adsorb O_2 at these low temperatures. Since O_2 is never found in the effluent, it must be chemisorbed on some part of the catalyst. Therefore, this limiting step may be partially overcome by the presence of the more reduced Co species at the surface. The second scenario involves the Ti suboxide presence noted with XPS. Although possibly a Co titanate species, in either case the TiO_x may also act as an O_2 adsorption site, again overcoming the limiting step associated with CO oxidation over Pt-based catalysts.

4. Summary

The selective oxidation or PROX of CO in H_2-rich streams was investigated for potential applications downstream from fuel cell reformers. Co, Pt and Co/Pt supported on TiO_2 catalysts were tested. The Pt/TiO_2 catalyst was active over a broad range of temperature centered at 120 °C. The Co/TiO_2 was just as active at high temperatures but was particularly inhibited by other reformate gases CO_2 and H_2O. The Co/Pt/TiO_2 catalyst was very active at low temperatures and not significantly inhibited by the reformate gases. A lifetime study indicates that the Pt/Co/TiO_2 catalyst decays with time, but that the activity can be reattained with a short, high-temperature "purge". Overall, the Pt/Co catalysts performed much better than the Pt or Co catalysts separately, and simply adding the activities of the two does not result in the activity observed with the mixed metal catalyst. Therefore, some synergistic affect must be present. XPS and TPR experiments were performed to validate this hypothesis and indeed, the presence of both metal components results in different Co and Ti species concentrations at the surface, which may account for the noted activity enhancement.

References

[1] M. Prigent, Revue De L'Institut Francais Du Petrole 52 (1997) 349.

[2] J.A. Milliken, DOE/OATT Perspective, in: Proceedings of the DOE/ONR Fuel Cell Workshop, Baltimore, 6–8 October 1999.

[3] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93.

[4] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, Appl. Catal. A Gen. 159 (1997) 159.

[5] M.L. Brown, A.W. Green, G. Cohn, H.C. Andersen, Ind. Eng. Chem. 52 (1960) 841.

[6] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, K. Catal. 182 (1999) 430.

[7] G.K. Betlike, H.H. Kung, Appl. Catal. A Gen. 194/195 (2000) 43.

[8] R.M. Torres Sanchez, A. Ueda, K. Tanaka, M. Haruta, J. Catal. 168 (1997) 125.

[9] P. Thormahlen, M. Skoglundh, E. Fridell, B. Andersson, J. Catal. 188 (1999) 300.

[10] A. Troncrona, M. Skoglundh, P. Thorrnahlen, E. Fridell, E. Jobson, Appl. Catal. B Environ. 14 (1997) 131.

[11] R. Riva, H. Miessner, R. Vitali, G. Del Piero, Appl. Catal. A Gen. 196 (2000) 111.

[12] S.J. Tauster, S.C. Fung, R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.

[13] G.L. Hailer, D.E. Resasco, Adv. Catal. 36 (1989) 173.