Available online at BCREC Website: http://bcrec.undip.ac.id

Bulletin of Chemical Reaction Engineering & Catalysis, 6 (1), 2011, 1 - 14

Review Article

A Review on Preferential Oxidation of Carbon Monoxide in Hydrogen Rich Gases

A. Mishra, and R. Prasad *

Department of Chemical Engineering & Technology, Banaras Hindu University, Varanasi 221005, India

Received: 22nd October 2010, Revised: 12nd January 2011, Accepted: 19th January 2011

Abstract

In this review, recent works on the preferential oxidation of carbon monoxide in hydrogen rich gases for fuel cell applications are summarized. H_2 is used as a fuel for polymer-electrolyte membrane fuel cell (PEMFC). It is produced by reforming of natural gas or liquid fuels followed by water gas shift reaction. The produced gas consists of H_2, CO, and CO_2. In which CO content is around 1%, which is highly poisonous for the Pt anode of the PEMFC so that further removal of CO is needed. Catalytic preferential oxidation of CO (CO-PROX) is one of the most suitable methods of purification of H_2 because of high CO conversion rate at low temperature range, which is preferable for PEMFC operating conditions. Catalysts used for CO-PROX are mainly noble metal based; gold based and base metal oxide catalysts among them Copper-Ceria based catalysts are the most appropriate due to its low cost, easy availability and result obtained by these catalysts are comparable with the conventional noble metal catalysts. Copyright © 2011 by BCREC UNDIP. All rights reserved.

.

Keywords: Hydrogen purification, CO-PROX, PEMFC, Methods for CO-removal, Catalysts for CO- PROX

1. Introduction

Fuel cells convert chemical energy directly into electrical energy with high efficiency and practically zero emission of pollutants. Fuel cell technology has a number of applications, such as micro/ portable power, stationary power for buildings and distributed generation for remote areas. Prototype vehicles adopting fuel cells in an effort to reduce atmospheric pollution are becoming very popular [1-3]. Fuel cells come in many varieties; however, they all work in the same general manner [4]. A variety of fuel cells for different applications is under development [5-7]: solid polymer fuel cells (SPFC), also known as proton-exchange membrane fuel cells (PEMFC) operating at 80 ^{0}C, alkaline fuel cells (AFC), operating at 100 ^{0}C, phosphoric acid fuel cells (PAFC) for 200 ^{0}C operation, molten carbonate fuel cells (MCFC) at 650 ^{0}C, solid oxide fuel cells (SOFC) for high temperature operation, 800-1100 ^{0}C.

PEMFC have attracted significant interest due to their low temperature of operation (80 ^{0}C), high power density, high efficiency and the environmentally benign nature of their exhaust. PEMFC promises to be clean and efficient alternative to combustion of fuels for power generation in stationary and mobile applications [8]. The PEMFC's ideal fuel is hydrogen; it can be produced through steam reforming, partial oxidation or auto-thermal reforming of liquid fuels or natural gas in combination with the water gas shift reaction. Hydrogen could likely be generated

---

* Corresponding Author, E-mail: rprasad.che@itbhu.ac.in (R. Prasad)
Tel.: +91 542 2367323, fax: +91 542 2368092.

on-board using a reformer, together with significant amounts of CO and CO_2. A subsequent water-gas-shift (WGS) reaction reduces the amount of CO to 1% [9]. The anode catalysts of PEMFC which are operated at relatively low temperatures (80-120 ^0C) have been demonstrated to be easily poisoned by traces of CO (even around 1ppm) in the hydrogen rich feed gas. Therefore it is necessary to eliminate the traces of CO in the hydrogen stream with a minimum hydrogen loss [10].

Several different methods for CO removal from the hydrogen stream have been reported [1]. The main methods are as follows: i) Purification with hydrogen selective membrane, ii) CO methanation, iii) Pressure swing adsorption, and iv) Preferential oxidation (PROX) of CO. For the application of small-scale fuel processor, the selective membrane purification, CO methanation, and the CO-PROX have been considered to be promising. Many research projects sanctioned [8, 87, 92, 94-100], several Ph.D. theses approved [11-14], a number of patents granted [15-21] and numerous studies have been conducted on preferential oxidation of CO in H_2 rich gases. Ghenciu [3] reviewed fuel processing catalysts for hydrogen production in PEM fuel cell systems, emphasising WGS reaction. Park et al. [4] reviewed progress in selective CO removal in a H_2-rich stream. This brief article is an attempt to summarise the recent progress on main methods of CO removal in brief and detailed of preferential oxidation of CO. This review paper will be beneficial to the application of fuel cells as well as chemical, petrochemical industries and refineries utilizing very pure hydrogen.

1.1. Purification with hydrogen selective membrane

One alternative to purify hydrogen is the use of hydrogen selective membranes due to their easy preparation, low energy consumption and cost effectiveness at low gas volumes [22, 23]. There are several kinds of membranes which can be organized into three categories: (i) polymeric, (ii) metallic and (iii) inorganic membranes like zeolite membranes. Polymer membranes have several advantages like having a low cost and not causing significant pressure drops. However, mechanical strength problems and high sensitivity to swelling and compacting reduce their usefulness for this purpose [24, 25]. The second type, metallic membranes, has an excellent hydrogen permeance but suffer from hydrogen embrittlement at low temperatures [26]. This is eliminated by using alloys but the product is more expensive. The latter, zeolite membranes, combine the general advantages of inorganic membranes like temperature stability and solvent resistance with those of polymeric membranes as they are composed of a thin homogeneous layer.

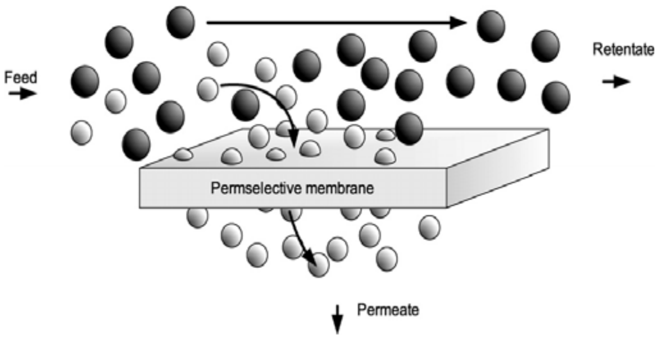

Figure 1. Simplified concept schematic of membrane separation

Fig. 1 shows a schematic of the semi-permeable membrane separation process, in which the driving force is often pressure or concentration gradient across the membrane. Hydrogen separations from highly supercritical gases, such as methane, carbon monoxide, and nitrogen are easy to achieve by polymeric membranes, because of the extremely high diffusion coefficient of hydrogen relative to all other molecules except helium.

To meet the requirements of PEMFC feed such as a high perm-selectivity for H_2 and a high H_2 permeability, the dense phase metal membrane in which the solution diffusion is dominant has been considered to be most plausible [27]. Sotowa et al. [28] compared the Pt-loaded Y-type zeolite membrane (PtY membrane) and a Rh-loaded γ-Al_2O_3 membrane and found that in PtY membrane the H_2 permeance is very high because of the large zeolitic pores. The permeation selectivity for H_2 over other gases is of the order of 10. CO oxidation can be largely attributed to the slow diffusivity of CO in the pores, resulting in a long residence time of CO in the micro-pores. While in $SiO_2/Rh/\gamma\text{-}Al_2O_3$ membrane the H_2 permeance is smaller than that of the PtY membrane, but the separation selectivity of H_2 is very high. Most of the CO molecules are rejected at the feed side surface of the H_2-selective SiO_2 layer. The oxidation rate in the $Rh/\gamma\text{-}Al_2O_3$ layer is greatly increased because the CO concentration is decreased nearly to the threshold value. Bernardo et al. [29] observed that the best CO removal was obtained using a low-permeance zeolite catalytic membrane (Q) at low pressure. This catalytic membrane was found to be very stable with no detectable deactivation over many hours (200 h) of operation. In recent work, Varela-Gandía et al. [30] prepared membranes by ion-exchange of Na-LTA/carbon membranes, they concluded that selectivity for hydrogen purification was very high but further efforts need to be undertaken in order to improve the flux through the composite membrane materials.

1.2. CO Methanation

CO methanation is another method for the purification of hydrogen gas mixture. The following reactions (1-2) can be carried out over the hydrogenation catalyst in the presence of CO, CO_2, and H_2 which are main gaseous components in the exit of water-gas shift reactor.

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \quad \Delta H^0_{298} = -205.813 \text{ kJ/mol} \quad (1)$$

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g) \quad \Delta H^0_{298} = -164.647 \text{ kJ/mol} \quad (2)$$

The selective CO Methanation (Eq. 1) can be promising because this does not require the introduction of any gases such as air in the PROX system [4]. Complete removal of CO by methanation in H_2-rich gas stream is performed over different metal catalysts. Ni/ZrO_2 and Ru/TiO_2 were the most effective catalysts for complete removal of CO through the methanation. These catalysts can decrease a concentration of CO from 0.5% to 20 ppm in the gases formed by the steam reforming of methane with a significantly low conversion of CO_2 into methane [31]. Dagle et al. [32] used Ru-based catalysts and found that it was capable of reducing CO in a reformate to less than 100 ppm over a wide temperature range from 240 to 280 ^{0}C, while keeping hydrogen consumption below 10%. [33-36]. CO methanation experiments showed that it is difficult to reach the goal of deep CO removal depth of below 10 ppm. A two-stage methanation method by applying two kinds of catalysts is proposed by Li et al. [37] that is, one catalyst with relatively low activity and high selectivity for the first stage at higher temperatures, and another one with relatively high activity for the second stage at lower temperatures. CO can be removed from 10000 ppm to below 1000 ppm at the first stage and to below 10 ppm at the second stage. Generally all catalysts used for CO-methanation are noble metal based which are very costly and temperature (300-340 ^{0}C) for the reaction was also very high. Besides that in CO methanation, hydrogenation of CO takes place in which hydrogen is consumed in large amount so popularity of this method is less than preferential oxidation of carbon monoxide [4].

1.3. Pressure swing adsorption

The current technology used to purify hydrogen from synthesis gas is pressure swing adsorption (PSA). It is a technology used to separate some gas species from a mixture of gases under pressure according to the species molecular characteristics and affinity for an adsorbent material (activated

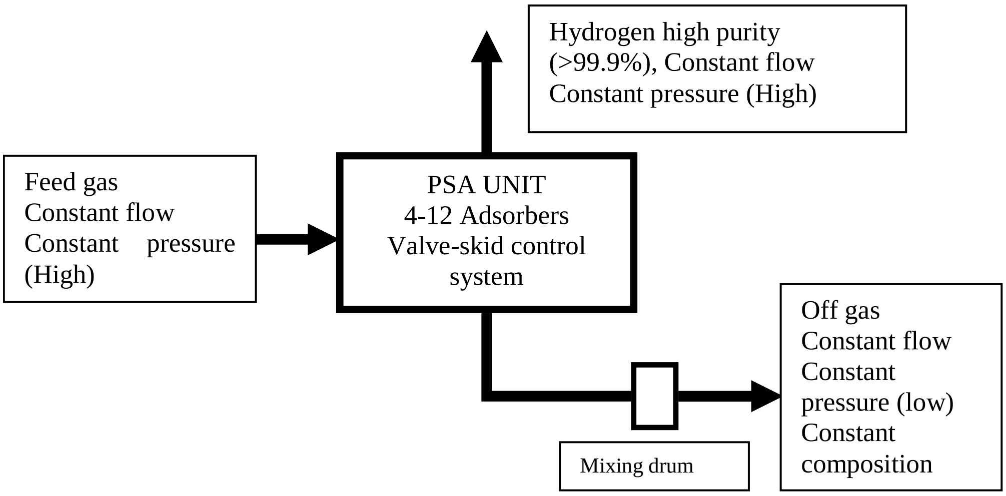

Figure 2. Pressure swing adsorption basic flow scheme

carbon, molecular sieve 5A, silica gel, alumina, and zeolite) [38, 39] that preferentially adsorbs a family of related components from a mixed feed. Pressure swing adsorption processes rely on the fact that under pressure, gases tend to be attracted to solid surfaces, or "adsorbed". The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. PSA processes can be used to separate gases in a mixture because different gases tend to be attracted to different solid surfaces more or less strongly. Although many adsorbents are commercially available, there are still demand for robust (high chemical stability against other contaminants, high mechanical stability against attrition), cheap (low synthesis cost since adsorbent cost represents a significant part of the investment cost) and energy efficient materials [40-41]. The basic schematic flow diagram of PSA technology is shown in fig. 2.

Production of pure hydrogen from a gas mixture containing 60-90 mol% hydrogen by using pressure swing adsorption (PSA) processes has become the state-of-the-art technology in the chemical and petrochemical industries [42]. Several hundred PSA-H_2 process units have been installed around the world (USA, France, Spain, Argentina, Brazil, China, etc). The two most common gas streams used for this application are (a) the steam-methane reformer off-gas after it has been further treated in a water-gas shift reactor and (b) the refinery off-gas from various sources. The typical feed gas compositions to the PSA system for these cases are (a) 70-80% H_2, 15-25% CO_2, 3-6% CH_4, 1-3% CO, and trace N_2; and (b) 65-90% H_2, 3-20% CH_4, 4-8% C_2H_6, 1-3% C_3H_8, and less than 0.5% C_{4+} hydrocarbons. Both feed gases are generally available at a pressure of 8 to 28 atm and at a temperature of 21 to 38 ^{0}C, and they are generally saturated with water. The PSA processes are designed to produce a dry hydrogen-rich product stream at the feed gas pressure containing 98-99.999 mol% H_2 with a H_2 recovery of 70-90%. Yang et al. [44] Used a layered bed of activated carbon and zeolite for PSA process and reported that High purity H_2 product (99.999%) can be produced at feed gas pressure (8 atm) from synthesis gas (H_2: 72.2%, CH_4: 4.17%, CO: 2.03%, CO_2: 21.6%).

The H_2 recovery increased with increasing the linear velocity and adsorption time. Majlan et al. [45] reported that Adsorption of CO and CO_2 in mixtures of H_2/CO/CO_2 was achieved using compact pressure swing adsorption (CPSA) system to produce purified hydrogen for use in fuel cell. A CPSA system was designed by combining four adsorption beds that simultaneously operate at different processes in the pressure swing adsorption (PSA) process cycle. They concluded that Activated carbon has been successfully used to adsorb CO. The adsorption capacity was 0.13 mmol CO/g. CPSA was able to reduce the CO concentration in H_2/CO/CO_2 mixture from 4000 ppm to 1.4 ppm and CO_2 from 5% to 7 ppm. For the continuous adsorption but it is not suitable for non-stationary applications, due to the large dimensions and high costs of the compressor.

1.4. Preferential oxidation of CO

The preferential oxidation (PROX) process is one of the most effective methods for the removal of CO trace from the reformate stream. PROX of CO is a reaction to convert CO in a H_2-rich gas mixture to CO_2 with minimal H_2 consumption. Therefore, preferential oxidation process is an indispensable step to reduce the concentration of CO to 10 ppm level in a H_2 generation process [4]. The flow diagram of hydrogen purification by CO-PROX is shown in fig. 3.

The following reactions (3-4) can occur in the PROX system.

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g) \quad \Delta H^0_{298} = -282.98 \text{ kJ/mol} \tag{3}$$

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(g) \quad \Delta H^0_{298} = -241.82 \text{ kJ/mol} \tag{4}$$

In the first reaction (eq. 3) an excess of oxygen is provided, at around a factor of two, and about 90% of the CO is transformed. In the second step a substantially higher oxygen excess is used, at approximately a factor of 4, which is then processed with the remaining CO, in order to reduce the CO concentration to less than 10 ppm to also avoid excess CO-fraction loading, the

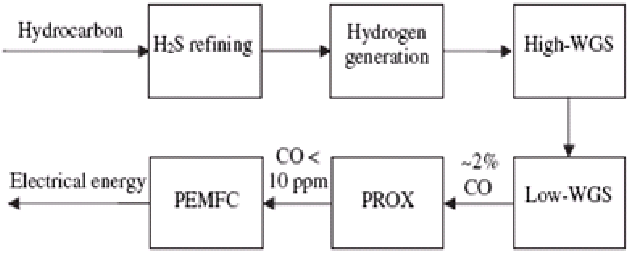

Figure 3. Flow diagram of hydrogen purification by CO-PROX

transient operation of a CO adsorber may be important.

Equation (4) is highly undesirable due to the consumption of hydrogen as 100% selectivity is not possible, oxidation of H_2 takes place and H2O formed, which reduces the activity of prox catalyst. The disadvantage of this technology is its very strong exothermic nature, coupled with a very narrow optimal operation temperature window, and is best operated between 80 ^{0}C and 177 ^{0}C, yielding a steam loss of around one percent [36, 62, 65, 80], Effective cooling is therefore required. In order to minimise steam generation (eqn. 2), excessive dilution with nitrogen is used. Additionally the reaction is interrupted with an intermediary cooler before proceeding to a second stage.

The instrumentation and process control complexity requirements are relatively high. The advantage of this technique over selective methanation is the higher space velocity, which reduces the required reactors size. The PROX of CO is a catalytic reaction where the catalyst plays a significant role in enhancing the CO oxidation and suppressing H_2 oxidation. The key factors to achieve very low CO concentration fuel, is synthesizing a highly active, stable, and selective catalyst for PROX reaction in H_2-rich gas mixture at the lower temperature range [45].

2. Catalysts for CO-PROX

The reported promising catalysts for CO-PROX can be grouped into three classes:

1. Supported noble metal catalysts, such as Pt, Pd, Ir, Ru or Rh [46-74],
2. Nano-gold catalysts [75-94] and
3. Base metal oxides catalysts which mainly concentrate on CuO-CeO_2 [8-10, 45, 95-125].

2.1. Supported noble metal catalysts

Many workers [46-71] studied about preferential oxidation of CO over noble metal based catalysts. Generally, Pt, Rh, Ru and Ir based catalysts fall in this category. The noble metal based catalysts are conventionally used for the CO-PROX. Hulteberg et al. [46] studied different noble metal catalysts for activity in the CO-PROX in hydrogen-rich streams and concluded that Pt on Co-oxide is a highly active catalyst for the reaction. Huang et al. [47, 48] used iridium based catalysts (Ir/CeO_2) which exhibited excellent performance in PROX process. Reductive pre-treatment of Ir/CeO_2 was found to be beneficial to obtain higher CO oxidation activity at low temperatures. The presence of 1.60 wt% of Ir was essential for obtaining high activity in the PROX reaction. Recently, Zhang et al. [49] prepared bi-functional catalyst Ir-$FeOx/SiO_2$, which was very active and selective for preferential oxidation of CO under H_2-rich atmosphere.

Tanaka et al. [50] reported high performance in preferential oxidation of CO in rich hydrogen over K-promoted Rh/USY (K/Rh=3) catalysts. The concentration of CO was below 10 ppm after this process. The addition of potassium to Rh/USY also promoted the activity of CO oxidation without hydrogen. Chin et al. [51] reported over SiO_2- and Al_2O_3-supported Ru Catalysts, and concluded the three major advantages over a conventional Pt catalyst: first lower operating temperatures, second ability to completely eliminate CO in a single step under realistic space velocities (120,000 mL/g h) and O_2 concentrations ($O_2/CO = 1$) without compromising the CO_2 selectivity, and third wide operating temperature windows which yield CO outlet concentration of less than 30 ppm even in the presence of H_2O and CO_2 (120-170 $_0$C for Ru/SiO_2 and 180-200 ^{0}C for Ru/Al_2O_3). Kim et al. [52] prepared various Ru catalysts supported on different supports such as yttria-stabilized zirconia (YSZ), ZrO_2, TiO_2, SiO_2 and γ-Al_2O_3 with a wet impregnation method. Among them, Ru/YSZ showed the highest CO conversion especially at low temperatures and it can reduce the high inlet CO concentration to be less than 10 ppm even in the presence of H_2O and CO_2.

Pt and Pt based catalysts are the most commonly used catalysts of this category and shows better results than other noble metal catalysts. Ayastuy et al. [53] used $MnO_x/Pt/Al_2O_3$ and reported that high CO conversion at high temperature range. Ceria supported Pt with alumina also reported high activity and selectivity for CO-PROX [54-59]. Many works [60-65] have been done over Pt-Fe/mordenite catalysts and concluded that these catalysts gives good result even in presence of H_2O. Alkali metal modified catalyst increases the activity but not effect the selectivity of CO-PROX [66]. Guerrero et al. [67] studied the promotional effect of Nb on Pt supported on alumina or on niobia, for the preferential oxidation of CO (PROX) in hydrogen.The results show a unique effect of Nb as a promoter to Pt. At low Nb loadings on Pt/alumina, the CO oxidation activity and selectivity are significantly increased. The CO selectivity is 100% at conversions up to about 60%. Pt-Co silica or alumina aerogel catalyst exhibited excellent ability for the carbon monoxide removal but at comparatively higher temperature [68, 69].

Sebastian et al. [71] studied Pt supported on different zeolitic materials (MOR, ZSM-5, FAU and ETS-10). The behaviour of the Pt-ETS-10 and Pt-FAU catalysts has been investigated in more depth and the results obtained have been compared and related to the different characteristics of the supports. The best results in the presence of H_2O and CO_2 were obtained with Pt-FAU catalysts, showing stable catalytic activity and complete conversion of CO at 166 ^{0}C.

Luengnaruemitchai et al. [72] reported that complete CO conversion obtained at temperature around 200 ^{0}C over A-type zeolite-supported Pt catalysts; the presence of H_2O depressed the activity. But bimetallic AuPt supported on zeolite catalysts have no effect of H_2O or CO_2 present in the reaction [72]. Pt_3Co and PtCu intermetallic catalyst give high CO conversion at low temperature [73]. Recently, Consuegra et al. [74] reported that the activity and selectivity for the PROX process can be strongly enhanced by the phenomenon of electrochemical promotion. This phenomenon would allow optimizing the amount of promoter under the expected dynamic conditions of a PROX unit which is not possible with a conventional promoted heterogeneous catalyst.

2.2. Gold based catalysts

Gold based catalysts have high activity for the CO-PROX especially at low temperature. Luengnaruemitchai et al. [75] found that the performance of catalyst depends on the preparation method of Au/CeO_2 catalysts. They reported that the Au/CeO_2 catalyst prepared by co-precipitation method exhibited the highest activities but presence of CO_2 in feed stream reduces the CO conversion. Wang et al. [76] used Au/CeO_2-Co_3O_4 catalysts with a Ce/Co atomic ratio from 0.1 to 0.6 which were prepared by deposition-precipitation. CO conversion is 91% while selectivity is around 51 % at temperature 80 ^{0}C. Several workers [77-79] reported good results for CO-PROX on nano gold catalysts. Quinet et al. [80] studied the effect of molecular hydrogen on CO Oxidation over an unsupported silver-free gold powder and concluded that the support-free pathway for the oxidation of CO exists and is enhanced by the presence of hydrogen. However, even with hydrogen, our unsupported particles are found to be less efficient than the oxide-supported ones to activate oxygen, probably because of a low concentration of low-coordination active sites present at the surface of large gold particles. Au/TiO_2 catalyst possesses good catalytic activity for PROX between 25 and 50 ^{0}C and raising the reaction temperature up to 180 ^{0}C has a distinct influence on the reaction and deactivation behaviour of catalysts in the CO oxidation increased [81-84].

Bimetallic Au-Cu catalysts prepared by the deposition-precipitation method for selective CO oxidation reaction showed that Cu addition increased the selectivity for CO oxidation decreasing the H_2 consumption [85]. The interaction between Cu and Au seemed to be able to modify the catalytic properties of Au active sites for CO oxidation. Other than titania, ZrO_2 supported Au catalysts obtained by direct oxidation of bulk alloy shows good results for CO-PROX at high temperature [86]. Ceria supported bimetallic catalyst [87] and rare earths-modified ceria-supported gold catalysts [88] exhibited the highest catalytic activity, selectivity, and high stability.

Manzoli et al. [89] prepared Au/doped ceria catalysts by deposition-precipitation method modified by various cations (Sm^{3+}, La^{3+} and Zn^{2+}). The following activity order was observed: Au/Zn-CeO_2 > Au/Sm-CeO_2 > Au/CeO_2 > Au/La-CeO_2. Catalysts showed improved tolerance towards the presence of CO_2 and H_2O in the PROX feed. Little amount of gold with ceria catalyst showed suppressed activity in presence of CO_2 [90]. Au/iron oxide system reported less selectivity at high temperature range for CO oxidation [91]. Naknam et al. [92] studied over Au/ZnO and Au/ZnO-Fe_2O_3 catalysts prepared by photo-deposition method under UV light, exhibited higher catalytic activity, where it achieves a complete conversion of CO at 30 ^{0}C and 50-73% CO selectivity. The presence of a mixed oxidation state of Au is the active site for the PROX reaction. In recent work Laguna et al. [93] concluded that gold catalyst prepared with the $CeFe_{10}$ as support is a very active for PROX reactions, especially at low temperatures compared with Au/CeO_2. Overall gold based catalysts are suitable only for low temperature range, same as the noble metal based catalysts.

A comparative study was investigated, in which [94] nano-structured gold catalysts supported on CeO_2 and MnO_2 prepared by deposition-precipitation method. The authors concluded that Au/CeO_2 is more active than Au/MnO_2 towards selective CO oxidation.

2.3. Base metal oxide catalysts

The preferential oxidation of carbon monoxide in the presence of large quantities of hydrogen was carried out over different supported base metal catalysts. The catalytic formulations [95] involved several transition metals (Co, Cr, Cu, Ni, Zn) supported on oxides with different acidic, basic and redox properties (MgO, La_2O_3, SiO_2-Al_2O_3, CeO_2, $Ce_{0.63}Zr_{0.37}O_2$). Out of them, the only ceria- and ceria-zirconia-supported copper catalysts appeared to be as active as the costly platinum group catalysts classically used for this reaction. The well-known enhancement of oxidation activity of copper, when supported on reducible oxides like CeO_2, was attributed to a "synergistic" effect [96]. It is proposed that well-dispersed CuO on CeO_2, which is reducible at a lower temperature with respect to bulk CuO, could adsorb CO better. As a result, this catalyst exhibited high activity/ selectivity for low-temperature CO oxidation [97]. Easy availability and low cost make these catalysts able to replace the other noble metal and gold based catalysts [98]. The characteristics of catalysts change according to the preparation method used.

The catalytic properties are strongly affected by the synthesis procedures of the base metal catalysts. Avgouropoulos [99] reported the influence of the preparation method on the physicochemical and catalytic properties of CuO-CeO_2 catalysts for the selective CO oxidation in simulated reformate gas. They reported ranking order of the preparation methods of the CuO-CeO_2 catalyst in CO oxidation activity is as follows: urea-nitrates combustion > citrate-hydrothermal > co-precipitation > impregnation. Liu et al. [100] reported that CuO-CeO_2 catalyst prepared by chelating method has a superior catalytic performance for the preferential oxidation of CO in rich hydrogen, compared with the CuO-CeO_2 catalyst prepared by co-precipitation method. Cu supported ceria catalysts give very good results for CO-PROX even in presence of CO_2 and H_2O in feed stream and at the PEMFC operating condition [100-107].

Different combination with CuO-CeO_2 as α-Fe_2O_3-promoted [108], KOH/K_2CO_3 on CuO-CeO_{2-x} [109], CuO-CeO_2-ZrO_2 system [110,111], CuO-CeO_2/Al_2O_3/FeCrAl mono-lithic catalysts [112], mesomacro-porous monolithic CuO-CeO_2/α-Al_2O_3 catalysts [113], increase the activity and make copper-ceria system stable which is most important characteristic of any catalyst. CuO-ZnO/TiO_2 catalysts were found to have interesting CO conversion values and resulted totally selective toward the CO oxidation in the technologically important 65-120 ^{0}C temperature range [114]. CuO/$Ce_xZr_{1-x}O_2$.Al_2O_3 catalysts exhibited much larger selectivity than, that of the noble catalyst 5%Pt/Al_2O_3 [115]. Hernández et al. [116] synthesized transition metal (Cu, Co, Ni and Zn)-modified cryptomelane-type manganese dioxide nano-materials by the milling method. All the solids were active in the preferential oxidation of CO in the presence of hydrogen, being the modified with copper the most active. $CuMn_2O_4$ nanocatalysts [117] synthesised by silica aquagel confined co-precipitation were analysed for CO-PROX. at moderate temperature, even at high spatial velocities.

Cobalt is another base metal which gives good results for CO-PROX reaction [118-123]. Zhao et al. [118] prepared Cobalt catalysts supported on metal oxides (ZrO_2, CeO_2, SiO_2, Al_2O_3, and TiO_2). It was found that the Co/ZrO_2 catalyst had the highest CO oxidation activity from the series. CoOx/ZrO_2 catalyst was synthesized and studied for the PROX reaction under various reaction conditions and indicated that in the temperature window of interest (80-200^{0}C), this catalyst had potential for obtaining high conversions of CO with high O_2 selectivity to CO_2 [119]. MnOx modified Co_3O_4-CeO_2 catalysts shows almost 100% conversion of CO present in gas mixture as MnO_x into Co_3O_4-CeO_2 led to more uniform mixing of Co_3O_4 and CeO_2 particles and led to finely dispersed and high valence state cobalt oxides species, which contributed to high catalytic activity of Co-Ce-Mn mixed oxides catalysts [120]. Co_3O_4/meso-CeO_2 catalysts with Co_3O_4 content of 10% or higher were very active and selective for preferential oxidation of CO in H_2-rich gases. The catalysts exhibited wide temperature windows for 100% CO conversion and stability is also very high. However, negative effects were observed when CO_2 or H_2O was added to the reaction mixture [121].

The catalytic activity and the selectivity of the CO oxidation of the CuO-CeO_2/γ-Al_2O_3 catalyst in the selective CO oxidation in excess hydrogen were significantly improved by the addition of a small amount of Co. It was found that the temperature window of CO conversion >99.9% within 210-224 ^{0}C [122,123]. In recent work Woods et al. [8] prepared a highly active CoO_x/CeO_2 nano-particle catalyst with high surface area (78 m^2/g). They claimed that the 10% CoO_x/CeO_2 catalyst was able to achieve near 100% CO conversion under a wide range of conditions. This catalyst was stable with time-on-stream at the temperature of highest CO conversion. H_2 concentration seems to have a negative effect on the CO oxidation. They observed three distinct temperatures regions of catalyst activity occur. Below 175 ^{0}C CO oxidation is dominant. Between 175 and 275 ^{0}C, CO oxidation competes with H_2 combustion. Above 275 ^{0}C, methanation dominates.

3. Precious metal vs base metal catalysts

Several authors [95, 124-126] compared the performance of base metal catalysts with precious metal catalysts for the CO-PROX. Marino et al [95] reported that ceria-zirconia-supported copper catalysts appeared to be as active as the costly platinum group catalysts classically used for this reaction. A comparative study between ceria-supported gold and copper oxide catalysts for preferential CO oxidation reaction was carried out by Avgouropoulos et al. [124] both catalysts were prepared by deposition-precipitation method. Au/ceria catalysts showed higher activity than CuO/ceria for the PROX reaction at temperatures lower than 120 ^{0}C, while the CuO/ceria catalysts were able to operate at higher temperatures, with a remarkably better selectivity. The presence of CO_2 and H_2O caused a significant decrease in the catalytic performance of the gold catalyst, while the CuO/ceria catalyst could still achieve complete removal of CO in the presence of CO_2 and H_2O.

Chen et al. [125] worked on $Ce_xSn_{1-x}O_2$-Al_2O_3 mixed oxides catalysts prepared by the suspension/co-precipitation method and found that its activity was comparable with, and its selectivity was much larger than, that of the noble catalyst 5% Pt/Al_2O_3.

Ko et al. [126] concluded that Pt-Ni/γ-Al_2O_3 catalyst showed the highest activity and selectivity among various PROX catalysts such as metal oxides as CoO and CuO-CeO_2, supported gold catalysts as Au/γ-Al_2O_3, Au/CuO, Au/CeO_2/γ-Al_2O_3, Au/CuO-CeO_2 and Au/CeO_2, and supported Pt catalysts such as Pt/γ-Al_2O_3, and Pt-Co/γ-Al_2O_3.

Table 2.1. Recent literature review at a glance on PROX of CO in H_2 rich gases

Catalyst	Preparation method	Operating parameter	Remarks	Reference
Base metal oxide catalysts				
5%CuO-CeO_2	Urea gelation/ Co-precipitation	50%H_2, 20%CO_2, 0.5-1%CO, 10% H_2O-N_2, 150-250^{0}C 79980ml/g h	100% CO conversion, selectivity ≈ 90% in absence of CO_2 &H_2O presence of both it is 99% & 65% at 165^{0}C respectively.	Liu (2004) [97]
7% CuO / $Ce_{0.9}$ $Zr_{0.1}O_2$.Al_2O_3	Suspension/ Co-precipitation	0.3-1%CO,40-75 % $H_2$20-25%CO_2 155^{0}C 10000ml/g h	100% conversion, comparable activity& much larger selectivity than that of the noble catalyst.	Chen (2007) [115]
MnOx modified Co_3O_4-CeO_2,Co: Ce:Mn=8:1:1	Co-precipitation	1% CO, 1% O_2, 50 %H_2-N_2, 80-180^{0}C 40000 ml/g h	100% conversion, MnOx into Co_3O_4-CeO_2 increases the interaction between Co_3O_4/CeO_2, selectivity 98.2%, at 80^{0}C.	Guo(2008) [120]
Meso-porous CeO_2 Supported Co_3O_4,10%	Surfactant-templated	1% CO, 1% O_2, 50% H_2- N_2, 200-300^{0}C, 40000 ml/g h	100% conversion, very active, selective and stable. CO_2 / H_2O effects negatively over activity.	Guo et al. (2007) [121]
CuO-CeO_2	Chelating	1%CO,1 or 1.25%O_2, 50% H_2 H_2O, CO_2, 120^{0}C,120000 ml/g h	99.6% conversion, superior performance to CuO-CeO_2 catalyst prepared by co-precipitation method.	Liu (2007) [100]
α-Fe_2O_3 on CuO-CeO_2	Urea-nitrate combustion	1%CO,1-2%O_2, 40 % H_2, 0-10%H_2O, 0-20% CO_2, 150 ^{0}C	100% conversion, increasing O_2/CO ratio from 1.0 to 1.5, CO conversion increases. 66.5% selectivity at150^{0}C	Sirichai-praert (2008) [108]
KOH/K_2CO_3 on CuO-CeO_{2-x}	Co-precipitation	1%CO,1.25%O_2, 50% H_2, H_2O, CO_2. 90-110 ^{0}C, 30000-120000 ml/ g h	99%conversion, 100 %Selectivity, particle sizes decreases on KOH addition, CuO-CeO_{2-x} catalysts have larger surface areas	Liu (2006) [109]
CuO-CeO_2-ZrO_2	Co-precipitation	74.17% H_2, 0.49% CO, 23.26% CO_2 2.08% CH_4, 177^{0}C	99.5%conversion, stable, activity decreased in the order CuO-CeO_2 > CuO-CeO_2-ZrO_2 > CuO-ZrO_2	Ratnasamy (2004) [110]
Nd- or Zr-modified CuO -CeO_2/ Al_2O_3 /FeCrAl	In situ combustion	0.5% CO, 0.5% O_2, 7.5% CO_2, 10 %H_2O, 50% H_2-N_2, 205 ^{0}C, 7000 h^{-1}	99%conversion, influences the dispersion of CuO & ceria, lowers the activity of H_2 oxidation & wide temp range.	Zeng (2008) [112]
CuO-ZnO/TiO_2	Co-precipitation	1.2%CO, 1.2% O_2 & 50% H_2-He, 65-240^{0}C, 18000 h^{-1}	96%conversion, stable & compa- rable performance with binary systems CuO/ZnO & CuO/ TiO_2.	Moretti (2008) [114]
Co-promoted CuO-CeO_2/γ-Al_2O_3	Impregnation	53%H_2,13%CO_2,1.3% CH_4, 0.5-1% CO, 20-30%H_2O, 205-230^0 C,	>99%conversion, small amount of Co increases the selectivity and activity of the catalyst.	Park (2004) [123]
10%Co/CeO_2 nanoparticles	Incipient wetness, Impregnation	1%CO, 1%O_2, 60% H_2,1%CO_2,175& 275 ^{0}C, 30000 ml/ g h	≈100%conversion,stable, presence of excess H_2 decreases the CO oxidation rate	Woods (2010) [8]

Table 2.1. (continued)

Gold based catalysts				
1%Au/CeO_2	a. Impregnation b.Co-precip. c. Sol-gel	1% CO, 0.5 -2%O_2 2%CO_2, 2-6% H_2O, 40% H_2- He, 110 ^{0}C, 30000 ml /g h	98%conversion, stable, co-precip Au/CeO_2 exhibiting the highest activities. No signifycant effect of H_2O & CO_2 on CO selectivity.	Luengnaru-emitchai (2004) [75]
Pt-Au bimetallic catalyst	a. Impregnation on sol-gel, **b.** Single step sol-gel	0.5-1%CO, 1% O_2, 40% H_2, 0-10% H_2O, and 0-25% CO_2, 50-90 ^{0}C	90%conversion,Catalyst prepared by single step sol- gel method exhibited an excellent catalytic activity for PROX of CO.	Monyanon (2007) [87]
nano-gold catalysts	Photo-deposition (PD)	1.33%CO, 1.33%O_2, 65.33%H_2- He, 50 ^{0}C, 30000 ml/g h	99%conversion, not stable, PD method facilitates to prepare gold particles as small as 1.5 nm. Very active and selective in PROX.	Chang [2008] [77]
Au/CeO_2- Co_3O_4	Deposition-precipitation	1%CO,1% O_2, 50% H_2, 80 ^{0}C, 30000 ml/g h	91%conversion shows higher activity than Au/ Co_3O_4, Au/CeO_2 &CeO_2- Co_3O_4 composite oxide.	Wang (2008) [76]
Au/doped Ceria	Deposition–precipitation	1%CO,1.25%O_2, 50% H_2, 15%CO_2 10% H_2O -He, 50^{0}C	96.6 %conversion, improved tolerance towards the presence of CO_2 and H_2O in the PROX feed.	Manzoli (2008) [89]
Au/ZnO nanocatalysts	Ultrasonication Double impregn. Washing dry.	5% CO, 10% O_2-He, 200^{0}C	100%conversion, best results obtained with ZnO prepared by chemical vapour-deposition with Au loaded by ultrasonication	Carabineiro (2010) [79]
Cu-Au/Al_2O_3 catalysts	Deposition-precipitation	1%CO,0.5-1.5% O_2, 30%H_2,0-30% CO_2, 0-10% H_2O -He, 50 ^{0}C	97%conversion, H_2O positively effects CO conversion & selecti- vity, CO_2 diminishes the same	Mozer (2009)[85]
Au/ZnO Au/ZnO-Fe_2O_3	Photo-deposition under UV-light	1%CO,1%O_2,40%H_2,0-10%CO_2, 10 %H_2O-He,50^{0}C	100%conversion, catalysts exhibited excellent activity, even in presence of CO_2 & H_2O	Naknam (2009) [92]
Supported noble metal catalysts				
Ir/CeO_2	a. Impregnation b. DP c. HDP	2%CO,1%O_2 40% H_2, He,80^{0}c, 40000 ml/g h	70% conversion, stable, negligible influence of H_2O on activity, CO_2 affected negatively.	Huang (2007) [47]
15 wt.% MnO_x Pt/ Al_2O_3	Successive impregnation	1%CO,1%O_2,60% H_2-He 160 ^{0}C, 12000 h^{-1}	100%conversion, stable, CO_2 enhances activity, H_2O inhibits activity with higher MnOx content	Ayastuy (2007) [53]
A-type zeolite-supported Pt	Sol-gel	40% H_2,1% CO, 1% O_2, 0-10 % CO_2, 0-10% H_2O, 100-300 ^{0}C	~95%conversion, Stable, no effect of CO_2on the conversion; H_2O depressed the selectivity and conversion both.	Luengnaru-emitchai (2008) [71]
Electrochemically promoted Pt	Electrochemical	1%CO,1%O_2,40% H_2-He,195^{0}C	83%conversion, activity & selecti- vity strongly enhanced by electro chemical promotion.	Consuegra (2010) [74]
Pt -Fe/ mordenite	Ion-exchange	1%CO,1%O_2, 20% CO_2, 20%H_2O, 68% H_2, 150^{0}C, 50000 h^{-1}	100%conversion,Stable,extremely high reactivity & selectivity	Kotobuki (2005) [63]
Pt-Co-Al_2O_3 aerogel	Sol-gel impregnation	1%H_2, 0.1%CO, 0.1% O_2 -N_2, 75-200 ^{0}C, 23100 h^{-1}.	99% conversion, Co increases activity. Sol-gel > impregnation method.	Kwak (2005) [68]
K-promoted Rh/USY	Impregnation	75% H_2, 0.2%CO 0.2% O_2 , 140^{0}C	>99.5% conversion, potassium increases activity of CO oxidation	Tanaka (2003) [50]

This, Pt-Ni/γ-Al_2O_3 catalyst showed the best performance even in the presence of 2 vol % H_2O and 20 vol% CO_2. The conflicting conclusions regarding performance of precious metal Vs base metal catalysts for CO-PROX by various authors may be due to different experimental conditions followed. Table 2.1 provides a list of representative recent literature survey at a glance on CO-PROX in H_2 rich gases.

3. Conclusions

It can be concluded after thorough scanning of the literature that among all the hydrogen purification methods, preferential oxidation of CO shows the best result for CO removal up to the trace amount. Conventionally noble metal based (Pt, Pd, Rh, Ir, supported) catalysts are used for CO-PROX besides these gold based and base metal oxide (Cu, Ce, Co, Zr, Zn supported etc.) catalysts are also used. The presence of CO_2 and H_2O in feed stream reduces the activity of noble metal and gold catalysts. Au/ceria catalysts are significantly more active, while CuO/ceria ones are remarkably more selective. CuO-CeO_2 modified with Zr and Sn shows better results than Pt supported noble metal catalysts. Thus CuO-CeO_2 based catalysts gives most appropriate result for CO-PROX, these are the cheaper than other classes of the catalysts and easily available hence it also reduces the cost of PEMFC. The catalytic properties are strongly affected by the synthesis procedures of the base metal catalysts. Reported ranking order of the preparation methods of the CuO-CeO_2 catalyst in CO oxidation activity is as follows: urea-nitrates combustion > citrate-hydrothermal > co-precipitation > impregnation method.

References

[1] Gray, P.G.; and Frost, J.C. 1998. Impact on clean energy in road transportation. *Energy Fuels* 12: 1121-1129.

[2] Docter, A.; and Lamm, A. 1999. Gasoline fuel cell systems. *J. Power Sources* 84: 194-200.

[3] Ghenciu, A.F. 2002. Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Curr. Opin. Solid State Mater. Sci.* 6: 389-399.

[4] Park, E. D.; Lee, D.; and Lee, H. C. 2009. Recent progress in selective CO removal in a H_2-rich stream. *Catal. Today* 139: 280-290.

[5] Fuel cells handbook. 2000. EG&G Services, Parson (Ed), Science Applications International Corporation-US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 5th Ed.

[6] Acres, G.J.K.; Frost, J.C.; Hards, G.A.; Potter, R.J.; Ralph, T.R.; and Thompsett, D. 1997. Electrocatalysts for fuel cells. *Catal. Today* 38: 393-400

[7] Ralph, T.R.; and Hards, G. 1998. Fuel cells: clean energy production for the new millennium. *Chem. Eng.* (London) 8: 334-335.

[8] Woods, M. P.; Gawade, P.; Tan, B.; and Ozkan, U.S. 2010. Preferential oxidation of carbon monoxide on Co/CeO_2 nanoparticles. *Appl Catal B: Environ.* 97: 28-35.

[9] Cortes, A. G.; Marquez, Y.; Alatorre, J. A.; and Dıaz, G. 2008. Selective CO oxidation in excess of H_2 over high-surface area CuO/CeO_2 catalysts. *Catal. Today* 133-135: 743-749.

[10] Schonbrod, B.; Marino; Baronetti; F.; and Laborde, M. 2009. Catalytic performance of a copper-promoted CeO_2 catalyst in the CO oxidation: Influence of the operating variables and kinetic study. *Int. J. Hydrogen Energy* 34: 4021-4028.

[11] Al-Ghamdi, M. S. 2006. Studies on Catalysts for Preferential Oxidation of CO in H_2-Rich Gas Mixture. *M.S. Thesis*. The Research Institute King Fahd University of Petroleum & Minerals Dhahran, Saudi Arabia.

[12] Caputo, T. 2005. CuO/CeO_2 catalysts for the preferential oxidation of CO in H_2 rich mixture for fuel cell applications. *Ph.D Thesis*. Department of Chemical and Biological Engineering of the Northwestern University (Evanston, IL, USA).

[13] Chin, P. 2004. Preferential Oxidation of Carbon Monoxide on Structured Supports. *Master's Thesis* North Carolina State University.

[14] Lakshmanan, P. 2006. Design of nanosized ceria-zirconia mixed oxides for catalytic applications, *M.Sc. Thesis*. Indian Institute of Chemical Technology Hyderabad, India.

[15] Zhang, Y.; Ruhl, J.; Brenner, A.M.; and Gittleman, C.S. 2005. Carbon monoxide clean-up in a PEM fuel cell system. *US 2005/0193627 A1.*

[16] Abdo, S.F.; Deboy, C.A.; and Schroeder, G.F. 2003. Preferential oxidation catalyst *US 6573214 B2.*

[17] Shore, L.; and Farrauto, R.J. 2006. Preferential oxidation catalyst containing platinum, copper & iron. *US 2006/0276332 A1.*

[18] Lee, H-C; Kim, S.H.; Lee, D-H; Park, E-D; and Ko, E-Y. 2008. Catalyst for oxidizing monoxide and method of preparing the same *US 2008/0008926 A1.*

[19] We, M-C; and Weissman, J.G. 2006. Selective carbon monoxide oxidation catalyst method of making the same & systems using the same. *US 7147947 B2.*

[20] Vanderspurt, T.H.; Wijzer, F.; Tang, X.; Leffler, M.P.; Willigan, R.R.; Newman, C.A.; Radhakrishnan, R.; Feng, F.; Laube, B. L.; Dardas, Z.; Opalka, S.M.; and She, Y. 2007. Ceria based mixed-metal of structure, including method of making & use. *US 7166263 B2.*

[21] Kim, M.C.; Dong, Y.; Gu, S.; Si, C.; Do, C.; Son, I.H.; Dong, S.; Si, U.; and Do, G. 2007. Preferential oxidation catalyst and process for preparing the same. *US 7247599 B2.*

[22] Freemantle, M. 2005. Membranes for gas separation. *Chem. Eng. News* 83: 49-57.

[23] Adhikari, S.; and Fernando, S. 2006. Hydrogen membrane separation techniques. *Ind. Eng. Chem. Res.* 45: 875-881.

[24] Ockwig, N. W.; and Nenoff, T. M. 2007. Membranes for Hydrogen Separation. *Chem. Rev.* 107: 4078-4110.

[25] Lu, G.Q.; Diniz da Costa, J.C.; Duke, M.; Giessler, S.; Socolowe, R.; Williams, R.H.; and Kreutz, T. 2007. Inorganic membranes for hydrogen production and purification: A critical review and perspective. *J. Colloid Interface Sci.* 314: 589-603

[26] Adams, T. M.; and Mickalonis, J. 2007. Hydrogen permeability of multiphase V-Ti-Ni metallic membranes. *Mater. L*ett. 61: 817-820

[27] Roa, F.; Block, M.J.; and Way, J.D. 2002. The influence of alloy composition on the H_2 flux of composite Pd-Cu membranes. *Desalination* 147: 411-416.

[28] Sotowa, K.I.; Hasegawa, Y.; Kusakabe, K.; and Morooka, S. 2002. Enhancement of CO oxidation by use of H_2-selective membranes impregnated with noble-metal catalysts. *Int. J. Hydrogen En*ergy 27: 339-346.

[29] Bernardo, P.; Algieri, C.; Barbieri, G.; and Drioli, E. 2008. Hydrogen purification from carbon monoxide by

means of selective oxidation using zeolite catalytic membranes. *Sep. Purif. Technol.* 62:629-635.

[30] Varela-Gandía, F.J.; Berenguer-Murcia, A.; Lozano-Castelló, D.; and Cazorla-Amorós, D. 2010. Hydrogen purification for PEM fuel cells using membranes prepared by ion-exchange of Na-LTA/carbon membranes; *J. Membr. Sci.* 351:123-130

[31] Takenaka, S.; Shimizu, T.; and Otsuka, K. 2004. Complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts; *Int. J. Hydrogen Energy* 29:1065-1073.

[32] Dagle, R. A.; Wang, Y.; Xia, G-G; Strohm, J. J.; Holladay, J.; and Palo, D. R. 2007. Selective CO methanation catalysts for fuel processing applications. *Appl. Catal. A: General* 326:213-218.

[33] Chen, S.Q.; and Liu, Y. 2009. $LaFe_yNi_{1-y}O_3$ supported nickel catalysts used for steam; reforming of ethanol. *Int. J. Hydrogen Energy* 34:4735-4746.

[34] Profeti L.P.R; Dias, J.A.C; Assaf, J.M.; and Assaf, E.M. 2009. Hydrogen production by steam reforming of ethanol over Ni-based catalysts promoted with noble metals. *J. of Power Sources* 190: 525-533.

[35] Galletti, C.; Specchia, S.; Saracco, G.; and Specchia, V. 2010. CO-selective methanation over Ru-γAl_2O_3 catalysts in H_2-rich gas for PEMFC applications. *Chem. Eng. Sci.* 65:590-596.

[36] Xua, G.; Chen, X.; and Zhang, Z-G. 2006. Temperature-staged methanation: An alternative method to purify hydrogen-rich fuel gas for PEMFC. *Chem. Eng. J.* 121: 97-107.

[37] Li, Z.; Mi, W.; Liu, S.; and Su, Q.2010. CO deep removal with a method of two-stage methanation; *Int. J. Hydrogen Energy* 35:2820-2823.

[38] Sunny, E. I.; Mohammed, A. B.; Daud, W. R.; Kadhum, A. H.; Fisal, Z.; and Sheriff, A. M. 2000. Removal of CO from process with Sn-activated carbon in pressure swing adsorption; *Journal of chemical technology and biotechnology* 75: 803-811.

[39] Teiseh, E.; and Capareda, S. 2010 Purification of Hydrogen from a Thermo-chemical Process using a Single-Column Pressure Swing Adsorption System with Compound Adsorbent. *An ASABE Meeting Presentation* Paper Number: 1009782.

[40] Barelli, L.; Bidini, G.; Gallorini, F.; and Servili, S. 2008. Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: A review. *Energy* 33: 554-570.

[41] Tagliabue, M.; Farrusseng, D.; Valencia, S.; Aguado, S.; Ravon, U.; Rizzo, C.; Corma, A.; and Mirodatos, C. 2009. Natural gas treating by selective adsorption: Material science and chemical engineering interplay. *Chem. Eng.J.* 155: 553-566.

[42] Sircar, S.; and Golden, T. C. 2000. Purification of Hydrogen by Pressure Swing Adsorption. *Sep. Sci. Technol.* 35: 5, 667-687.

[43] Yang, S-I; Choi, D-Y; Jang, S-C; Kim, S-H; and Choi, D-K 2008. Hydrogen separation by multi-bed pressure swing adsorption of synthesis gas. *Adsorption* 14: 583-590

[44] Majlan, E. H.; Daud, W. R. W.; Iyuke, S. E.; Mohamad, A. B.; Amir, A.; Adhum, H. K.; Mohammad, A.W.; Takriff, M. S.; and Bahaman N. 2009. Hydrogen purification using compact pressure swing adsorption system for fuel cell. *Int. J. Hydrogen Energy* 34: 2771-2777.

[45] López, I.; Valdés-Solís, and T.; Marbán, G. 2008. An attempt to rank copper-based catalysts used in the CO-PROX reaction. *Int. J. Hydrogen Energy* 33: 197-205.

[46] Hulteberg, P.C.; Brandin, J.G.M.; Silversand, F.A.; and Lundberg, M.2005. Preferential oxidation of carbon monoxide on mounted and unmounted noble-metal catalysts in hydrogen-rich streams. *Int. J. Hydrogen Energy* 30:1235-1242.

[47] Huang, Y.; Wang, A.; Wang, X.;and Zhang, T. 2007. Preferential oxidation of CO under excess H_2 conditions over iridium catalysts; *Int. J. Hydrogen Energy* 32: 3880 -3886.

[48] Huang, Y.; Wang, A.; Li, L.; Wang, X.; Su, D.; and Zhang T. 2008. Ir-in-ceria: A highly selective catalyst for preferential CO oxidation. *J. Catal.* 255: 144-152.

[49] Zhang, W.; Huang, Y.; Wang, J.; Liu, K.; Wang, X.; Wang, A.; and Zhang, T. 2010. $IrFeO_x/SiO_2$ A highly active catalyst for preferential CO oxidation in H2. *Int. J. Hydrogen Energy* 35: 3065-3071.

[50] Tanaka, H.; Ito, S.; Kameoka, S.; Tomishige, K.; and Kunimori, K. 2003. Catalytic performance of K-promoted Rh/USY catalysts in preferential oxidation of CO in rich hydrogen. *Appl Catal. A: general* 250: 255-263.

[51] Chin, S.Y.; Alexeev, O.S.; and Amiridis, M.D. 2005. Preferential oxidation of CO under excess H_2 conditions over Ru catalysts. *Appl. Catal. A: general* 286: 157-166.

[52] Kim, Y.H.; Park, E.D.; Lee, H.C.; and Lee, D. 2009. Selective CO removal in a H_2-rich stream over supported Ru catalysts for the polymer electrolyte membrane fuel cell (PEMFC); *Appl. Catal. A: general* 366: 363-369.

[53] Ayastuy, J.L.; Gonzalez-Marcos, M.P.; Gonzalez-Velasco, J.R.; and Gutierrez-Ortiz, M.A. 2007. $MnO_x/Pt/Al_2O_3$ catalysts for CO oxidation in H2-rich streams. *Appl. Catal. B: environ.*70: 532-541.

[54] Jo, M-C; Kwon, G-H; Li, W.; and Lane, A. M. 2009. Preparation and characteristics of pretreated Pt/alumina catalysts for the preferential oxidation of carbon monoxide. *J. Ind. Eng. Chem.*15: 336-341.

[55] Huanling, L.; Lei, M.; Saibing, S.; Zenghe, L.; Aiqin, W.; Yanqiang, H.; and Ta, Z. 2007. Preferential CO Oxidation on Ce-Promoted Pt/γ-Al_2O_3 Catalysts under H2-Rich Atmosphere. *Chin. J. Catal.* 28(12): 1077-1082.

[56] Atalik, B.; and Uner, D. 2006. Structure sensitivity of selective CO oxidation over Pt/γ -Al_2O_3. *J. of Catal.* 241: 268-275.

[57] Wootsch, A.; Descorme, C.; and Duprez, D. 2004. Preferential oxidation of carbon monoxide in the presence of hydrogen (PROX) over ceria-zirconia and alumina-supported Pt catalysts. *J. of Catal.* 225: 259-266.

[58] Kwak, C.; Park, T.J.; and Suh, D.J. 2005. Effects of sodium addition on the performance of $PtCo/Al_2O_3$ catalysts for preferential oxidation of carbon monoxide from hydrogen-rich fuels; *Appl. Catal. A: general* 278: 181-186.

[59] Kuriyama, M.; Tanaka, H.; Ito, S.i; Kubota, T.; Miyao, T.; Naito, S.; Tomishige K.; and Kunimori, K. 2007. Promoting mechanism of potassium in preferential CO oxidation on Pt/Al_2O_3. *J. of Catal.* 252: 39-48.

[60] Kotobuki, M.; Watanabe, A.; Uchida, H.; Yamashita, H.; and Watanabe, M. 2006. High catalytic performance of Pt-Fe alloy nanoparticles supported in mordenite pores for preferential CO oxidation in H2-rich gas. *Appl. Catal. A: general* 307:275-283.

[61] Maeda, N.; Matsushima, T.; Kotobuki, M.; Miyao, T.; Uchida, H.; Yamashita, H.; and Watanabe, M. 2009. H_2O-tolerant monolithic catalysts for preferential oxidation of carbon monoxide in the presence of hydrogen; *Appl. Catal. A: general* 370: 50-53.

[62] Chin, P.; Sun, X.; Roberts, G.W. and Spivey, J.J. 2006. Preferential oxidation of carbon monoxide with iron-promoted platinum catalysts supported on metal foams. *Appl. Catal. A: general* 302: 22-31.

[63] Kotobuki, M.; Watanabe, A.; Uchida, H.; Yamashita, H.; and Watanabe, M. 2005. Pt-Fe/mordenite catalysts reaction mechanism of preferential oxidation of carbon monoxide on Pt, Fe, and Pt-Fe/mordenite catalysts. *J of Catal* 236: 262-269.

[64] Huang, C-Y; Chen, Y-Y; Su, C-C; and Hsu, C-F. 2007. The cleanup of CO in hydrogen for PEMFC applications using Pt, Ru, Co, and Fe in PROX reaction. *J. of Power Sources* 174: 294-301.

[65] Maeda, N.; Matsushima, T.; Uchida, H.; Yamashita, H.; and Watanabe, M. 2008. Performance of Pt-Fe/mordenite monolithic catalysts for preferential oxidation of carbon monoxide in a reformate gas for PEFCs; *Appl. Catal. A: general* 341: 93-97.

[66] Tanaka, H.; Kuriyama, M.; Ishida, Y.; Ito, S.; Tomishige, K. and Kunimori K. 2008. Preferential CO oxidation in hydrogen-rich stream over Pt catalysts modified with alkali metals Part I. Catalytic performance; *Appl. Catal. A: general* 343: 117-124.

[67] S., Guerrero; J.T., Miller; and E.E., Wolf. 2007. Activity and selectivity control by niobium for the preferential oxidation of co on pt supported catalysts; *Appl. Catal. A: general* 328: 27-34.

[68] Kwak, C.; Park, T.J.; and Suh, D.J. 2005. Preferential oxidation of carbon monoxide in hydrogen-rich gas over platinum-cobalt-alumina aerogel catalysts; *Chem. Eng. Sci.* 60: 1211-1217.

[69] Choi, J.; Shin, C. B.; Suh, D.J. 2008. Co-promoted Pt catalysts supported on silica aerogel for preferential oxidation of CO *Catal. Commun.* 9: 880-885.

[70] Sebastian, V.; Irusta, S.; Mallada, R.; and Santamarıa, J. 2009. Selective oxidation of CO in the presence of H_2, CO_2 and H_2O, on different zeolite-supported Pt catalysts. *Appl. Catal. A: general* 366: 242-251.

[71] Luengnaruemitchai, A.; Nimsuk, M.; Naknam, P.; Wongkasemjit, S.; Osuwan, S. 2008. A comparative study of synthesized and commercial A-type zeolite-supported Pt catalysts for selective CO oxidation in H_2-rich stream. *Int. J. Hydrogen Energy* 33: 206-213

[72] Naknam, P.; Luengnaruemitchai, A.; Wongkasemjit, S.; and Osuwan, S. 2007. Preferential catalytic oxidation of carbon monoxide in presence of hydrogen over bimetallic AuPt supported on zeolite catalysts. *J. of Power Sources* 165: 353-358.

[73] Komatsu, T.; and Tamura, A. 2008. Pt_3Co and PtCu intermetallic compounds: Promising catalysts for preferential oxidation of CO in excess hydrogen. *J. of Catal.* 258: 306-314.

[74] de Lucas-Consuegra, A.; Princivalle, A.; Caravaca, A.; Dorado, F.; Guizard, C.; Valverde, J.L.; and Vernoux, P. 2010. Preferential CO oxidation in hydrogen-rich stream over an electrochemically promoted Pt catalyst. *Appl. Catal. B: environ.* 94: 281-287.

[75] Luengnaruemitchai, A.; Osuwan, S.; Gulari E. 2004. Selective catalytic oxidation of CO in the presence of H_2 over gold catalyst. *Int. J. Hydrogen Energy* 29: 429-435.

[76] Wang, H.; Zhu, H.; Qin, Z.; Wang, G.; Liang, F.; Wang, J. 2008. Preferential oxidation of CO in H_2 rich stream over Au/CeO_2-Co_3O_4 catalysts. *Catal. Commun.* 9: 1487-1492.

[77] Chang, L.H.; Yeh, Y.L.; Chen, Y.W. 2008. Preferential oxidation of CO in hydrogen stream over nano-gold catalysts prepared by photodeposition method. *Int. J. Hydrogen Energy* 33: 1965-1974.

[78] Imai, H.; Date, M.; and Tsubota, S. 2008. Preferential Oxidation of CO in H_2-Rich Gas at Low Temperatures over Au Nanoparticles Supported on Metal Oxides. *Catal. Lett.* 124: 68-73.

[79] Carabineiro, S.A.C.; Machado, B.F.; Bacsa, R.R.; Serp, P.; Drazic, G.; Faria, J.L.; Figueiredo, J.L. 2010. Catalytic performance of Au/ZnO nano-catalysts for CO oxidation; *J. of Catal.* Article in press.

[80] Quinet, E.; Piccolo, L.; Daly, H.; Meunier, F. C.; Morfin, F.; Valcarcel, A.; Diehl, F.; Avenier, P.; Caps, V.; and Rousset, J-L. 2008. H_2-induced promotion of CO oxidation over unsupported gold *Catal Today* 138: 43-49.

[81] Liotta, L.F.; Di Carlo, G.; Pantaleo, G.; and Venezia, A.M. 2010. Supported gold catalysts for CO oxidation and preferential oxidation of CO in H_2 stream:Support effect. *Catal. Today*. Article in press.

[82] Yu, W.Y.; Lee, W. S.; Yang, C.P.; and Wan, B.Z. 2007. Low-temperature preferential oxidation of CO in a hydrogen rich stream (PROX) over Au/TiO_2: Thermodynamic study and effect of gold-colloid pH adjustment time on catalytic activity. *J. Chin. Inst. Chem. Eng.* 38: 151-160.

[83] Yang, Y-F; Sangeetha, P.; and Chen Y-W. 2009. Au/TiO_2 catalysts prepared by photo-deposition method for selective CO oxidation in H_2 stream; *Int. J. Hydrogen Energy.* 34: 8912-8920.

[84] Dai, W.; Zheng, X.; Yang, H.; Chen, X.; Wang, X.; Liu, P.; and Fu, X. 2009. The promoted effect of UV irradiation on preferential oxidation of CO in an H_2-rich stream over Au/TiO_2. *J. of Power Sources* 188: 507-514.

[85] Mozer, T. S.; Dziubal, D. A.; Vieira, C.T.P.; and Passos, F. B. 2009. The effect of copper on the selective carbon monoxide oxidation over alumina supported gold catalysts. *J. of Power Sources* 187: 209-215.

[86] Tafin, M.L.; Chaou, A.A.; Morfin, F.; Caps, V.; and Rousset, J.L. 2005. Preferential oxidation of CO in H_2 over highly loaded Au/ZrO_2 catalysts obtained by direct oxidation of bulk alloy. *Chem. Commun.*, 388-390.

[87] Monyanon, S.; Pongstabodee, S.; and Luengnaruemitchai, A. 2007. Preferential oxidation of

carbon monoxide over Pt, Au monometallic catalyst, and Pt-Au bimetallic catalyst supported on ceria in hydrogen-rich reformate. *J. Chin. Inst. Chem. Eng.* 38: 435-441.

[88] Ilieva, L.; Pantaleo, G.; Ivanov, I.; Zanella, R.; Venezia, A.M.; and Andreeva D. 2009. A comparative study of differently prepared rare earths-modified ceria-supported gold catalysts for preferential oxidation of CO. *Int. J. Hydrogen Energy* 34: 6505- 6515

[89] Manzoli, M.; Avgouropoulos, G.; Tabakova, T.; Papavasiliou, J.; Ioannides, T.; and Boccuzzi, F. 2008. Preferential CO oxidation in H2-rich gas mixtures over Au/doped ceria catalysts. *Catal. Today* 138: 239-243.

[90] Deng, W.; Jesus, J. D.; Saltsburg, H.; and Stephanopoulos M. F. 2005. Low-content gold-ceria catalysts for the water-gas shift and preferential CO oxidation reactions. *Appl. Catal. A: genera*l 291: 126-135.

[91] Scire, S.; Crisafulli, C.; Minico, S.; Condorelli, G.G.; and Mauro A. D. 2008. Selective oxidation of CO in H_2-rich stream over gold/iron oxide:An insight on the effect of catalyst pre-treatment. *J. Mol. Catal. A: Chem.* 284: 24-32.

[92] Naknam, P.; Luengnaruemitchai, A.; and Wongkasemjit, S. 2009. Preferential CO oxidation over Au/ZnO and Au/ZnO-Fe_2O_3 catalysts prepared by photodeposition. *Int. J. Hydrogen Energy* 34: 9838-9846.

[93] Laguna, O.H.; Centeno, M.A.; Arzamendi, G.; Gandía, L.M.; Romero-Sarria, F.; Odriozola, J.A. 2010. Iron-modified ceria and Au/ceria catalysts for Total and Preferential Oxidation of CO (TOX and PROX). *Catal. Today* Article in press.

[94] Chang, L-H; Sasirekha, N.; Rajesh, B.; and Chen, Y-W. 2007. CO oxidation on ceria- and manganese oxide-supported gold catalysts. *Sep. Purif. Technol.* 58: 211-218.

[95] Marino, F.; Descorme, C.; and Duprez, D. 2005. Supported base metal catalysts for the preferential oxidation of carbon monoxide in the presence of excess hydrogen (PROX). *Appl Catal. B: environ.*58:75-183.

[96] Ramaswamy, V.; Malwadkar, S.; and Chilukuri, S. 2008. Cu-Ce mixed oxides supported on Al-pillared clay: Effect of method of preparation on catalytic activity in the preferential oxidation of carbon monoxide. *Appl. Catal. B: environ* 84: 21-29.

[97] Liu, Y.; Fu, Q.; and Stephanopoulos, M.F. 2004. Preferential oxidation of CO in H_2 over CuO-CeO_2 catalysts. *Catal. Today* 93-95: 241-246.

[98] Prasad, R.; and Rattan, G. 2010. Preparation Methods and Applications of CuO-CeO_2 Catalysts: A Short Review. *Bull. Chem. React. Eng. Catal.* 5 (1): 7 -30.

[99] Avgouropoulos, G.; Ioannides, T.; Matralis, H. 2005. Influence of the preparation method on the performance of CuO-CeO_2 catalysts for the selective oxidation of CO. *Appl. Catal. B: environ* 56 (2005) 87-93

[100] Liu, Z.; Zhou, and R.; Zheng, X. 2007. Preferential Oxidation of CO in Excess Hydrogen over CuO-CeO_2 Catalyst Prepared by Chelating Method. *J. Nat. Gas Chem.* 16: 167-172.

[101] Marino, F.; Baronetti, G.; Laborde, M.; Bion, N.; Le Valant, A.; Epron, F.,and Duprez, D. 2008. Optimized CuO-CeO_2 catalysts for CO-PROX reaction. *Int. J. Hydrogen Energy* 33:1345-1353.

[102] Derekaya, F. B.; Kutar, C.; and Güldür, C. 2009. Selective CO oxidation over ceria supported CuO catalysts. *Mater. Chem. Phys.* 115: 496-501.

[103] Kim, D.H.; Cha, and J.E. 2003. A CuO-CeO_2 mixed-oxide catalyst for CO clean-up by selective oxidation in hydrogen-rich mixtures. *Catal. Lett.* 86: 1-3.

[104] Moreno, M.; Bergamini, L.; Baronetti, G.T.; Laborde, M.A. and Marino, F.J. 2010. Mechanism of CO oxidation over CuO/CeO_2 catalysts. *Int. J. Hydrogen Energy* 35: 5918-5924

[105] Wu, Z.; Zhu, H.; Qin, Z.; Wang, H.; Ding, J.; Huang, L.; and Wang, J. 2010. CO preferential oxidation in H_2-rich stream over a CuO/CeO_2 catalyst with high H_2O and CO_2 tolerance. *Fuel* Article in press.

[106] Zhang, Y.; Liang, H.; Gao, X.Y.; and Liu, Y. 2009. Three-dimensionally ordered macro-porous CuO-CeO_2 used for preferential oxidation of carbon monoxide in hydrogen-rich gases. *Catal. C*ommun.. 10: 1432-1436.

[107] Marban, G.; Lopez, I.; and Valdes-Solıs, T. 2009. Preferential oxidation of CO by CuO_x/CeO_2 nanocatalysts prepared by SACOP Mechanisms of deactivation under the reactant stream. *Appl. Catal. A: general* 361: 160-169.

[108] Sirichaiprasert, K.; Pongstabodee, S.; and Luengnaruemitchai, A. 2008. Single- and double-stage catalytic preferential CO oxidation in H2-rich stream over an α-Fe_2O_3-promoted CuO-CeO_2 catalyst; *J. Chin. Inst. Chem. Eng* 39: 597-607.

[109] Liu, Z.; Zhou, R.; and Zheng, X. 2006. The preferential oxidation of CO in excess hydrogen: A study of the influence of KOH/K_2CO_3 on CuO-CeO_{2-x} catalysts. *J. Mol. Catal. A: Chem.* 255: 103-108.

[110] Ratnasamy, P.; Srinivas, D.; Satyanarayana, C.V.V.; Manikandan, P.; Senthil Kumaran, R.S.; Sachin, M.; and Shetti, V. N. 2004. Influence of the support on the preferential oxidation of CO in hydrogen-rich steam reformates over the CuO-CeO_2-ZrO_2 system. *J. of Catal.* 221: 455-46.

[111] Pakharukova, V.P.; Moroz, E.M.; Kriventsov, V.V.; Zyuzin, D.A.; Kosmambetova, G.R.; and Strizhak, P.E. 2009. Copper-cerium oxide catalysts supported on monoclinic zirconia: Structural features and catalytic behavior in preferential oxidation of carbon monoxide in hydrogen excess. *Appl. Catal. A: general* 365: 159-164.

[112] Zeng, S.H.; and Liu, Y. 2010. Nd- or Zr-modified CuO-CeO_2/Al_2O_3/FeCrAl monolithic catalysts for preferential oxidation of carbon monoxide in hydrogen-rich gases. *Appl. Surf. Sci.* 254: 4879-4885.

[113] Gu, C.; Lu, S.; Miao, J.; Liu, Y.; and Wang, Y. 2010. Mesoemacroporous monolithic CuO-CeO_2/α-Al_2O_3 catalysts for CO preferential oxidation in hydrogen-rich gas: Effect of loading methods. *Int. J. Hydrogen Energy* 35: 6113 -6122.

[114] Moretti, E.; Storaro, L.; Talon, A.; Patrono, P.; Pinzari, F.; Montanari, T.; Ramis, G.; and Lenarda, M. 2008. Preferential CO oxidation (CO-PROX) over CuO-ZnO/TiO_2 catalysts *Appl. Catal. A: general* 344: 165-174

[115] Chen, Y-Z; Liaw, B-J; Chang, W-C; and Huang, C-T.

2007. Selective Oxidation of CO in Excess Hydrogen over CuO/$Ce_xZr_{1-x}O_2.Al_2O_3$ catalysts. *Int. J. Hydrogen Energy* 32: 4550-4558.

[116] Hernández, W.Y.; Centeno, M.A.; Romero-Sarria, F.; Ivanova, S.; Montes, M.; and Odriozola, J.A. 2010. Modified cryptomelane-type manganese dioxide nanomaterials for preferential oxidation of CO in the presence of hydrogen. *Catal. Today* Article in press.

[117] Valdes-Solıs, T.; Lopez, I.; and Marban, G. 2010. Copper manganite as a catalyst for the PROX reaction.Deactivation studies. *Int. J. Hydrogen Energy* 35: 1879-1887.

[118] Zhao, Z.; Yung, M.M.; and Ozkan, U.S. 2008. Effect of support on the preferential oxidation of CO over cobalt catalysts. *Catal.. Commun.* 9: 1465-1471.

[119] Yung, M.M.; Zhao, Z.;Woods, M.P.; and Ozkan, U.S. 2008. Preferential oxidation of carbon monoxide on CoO_x/ZrO_2. *J. Mol. Catal. A: Chem.* 279: 1-9.

[120] Guo, Q.; and Liu,Y. 2008. MnO_x modified Co_3O_4-CeO_2 catalysts for the preferential oxidation of CO in H2-rich gases. *Appl. Catal. B: Environ* 82: 19-26.

[121] Guo, Q.; Wu, M.; Liu, Y.; and Bai, X. 2007. Mesoporous CeO_2- Supported Co_3O_4 Catalysts for CO Preferential Oxidation in H_2-Rich Gases. *Chin. J. Catal.* 28(11): 953-957.RESEARCH

[122] Park, J.W.; Jeong, J.H.; Yoon, W.L.; Jung, H.; Lee, H.T.; Lee, D.K.; Park, Y.K.; and Rhee, Y.W. 2004. Activity and characterization of the Co-promoted CuO-CeO_2/γ-Al_2O_3 catalyst for the selective oxidation of CO in excess hydrogen. *Appl. Catal. A: general* 274: 25-32.

[123] Park, J.W.; Jeong, J. H.; Yoon, W.L.; and Rhee, Y.W. 2004. Selective oxidation of carbon monoxide in