Catalytic preferential oxidation of carbon monoxide over platinum supported on lanthanum ferrite–ceria catalysts for cleaning of hydrogen
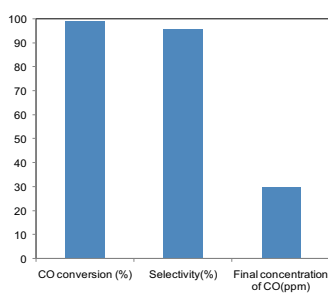
Priti V. Gosavi, Rajesh B. Biniwale*

National Environmental Engineering Research Institute, Council of Scientific and Industrial Research, Nagpur-440020, India

HIGHLIGHTS

► Chitosan complex method resulted in LaFeO$_3$ with pure phase, crystalline, open porous morphology and higher surface area.
► Higher CO conversion in the range of 99% and selectivity for CO conversion in the range of 93–96%.
► Minimization of CO concentration in hydrogen to the extent of 30 ppm by PROX–CO reaction.
► Synergistic effect observed for PROX –CO activity using LaFeO$_3$ and CeO$_2$ as support for Pt catalyst.

GRAPHICAL ABSTRACT

ABSTRACT

Since hydrogen is produced by reforming of hydrocarbon it contains carbon monoxide (CO). In order to make hydrogen suitable for proton exchange membrane fuel cell application there is need to reduce concentration of CO less than 100 ppm. Water–Gas-Shift reactions subsequent to reforming lower CO concentration in H$_2$ to about 1–1.5% by volume. Preferential oxidation of CO (PROX–CO) using a catalyst is therefore important for further cleaning up of CO from H$_2$. The catalyst in this study is platinum supported over lanthanum ferrite–ceria (Pt/LaFeO$_3$–CeO$_2$) exhibits excellent activity of 99.8% and selectivity of 95.7% at a relatively lower temperature of 100 °C with an equivalence ratio of 3 for PROX –CO. The concentration of CO is reduced from 1% v/v in feed to ca. 30 ppm in product gas with relatively lower loss of hydrogen is the most significant achievement in this study. The catalyst is selective towards CO oxidation as the hydrogen loss is relatively low (ca. 3.8%) and there is no methane formation. The improvement in catalytic activity and selectivity is attributed to the strong metal support interaction and open morphology of catalyst. The results obtained in this study reveal the excellent catalytic activity by using LaFeO$_3$–CeO$_2$ as support for Pt catalyst.
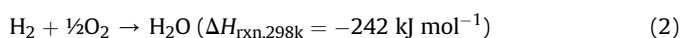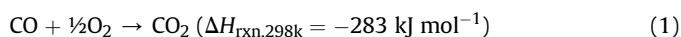
1. Introduction

Availability of hydrogen free from contaminants such as CO and CO$_2$ is a prerequisite for fuel cell, particularly proton exchange membrane fuel cell (PEMFC) application. Hydrogen is produced from liquid hydrocarbons by the process of steam reforming or autothermal reforming. In addition to H$_2$, the product gas of reforming processes includes CO and CO$_2$. Presence of CO in hydrogen fuel above 100 ppm poisons the anode of PEMFC [1–3]. In order to reduce CO in reforming product gas, water–gas-shift (WGS) reactions are used. This reduces CO concentration to the extent of 1% v/v [4]. For further removal of CO from a hydrogen stream, catalytic preferential oxidation of CO (PROX–CO) remains one of the best choice [5]. Low cost, higher CO conversion and

* Corresponding author. Tel.: +91 712 2249885; fax: +91 712 224900.
E-mail addresses: gosavipriti@gmail.com (P.V. Gosavi), rb_biniwale@neeri.res.in (R.B. Biniwale).

achieving desired low concentration of CO without excessive hydrogen consumption are some of the important attributes, which make PROX—CO method highly potential method for removal of CO from H_2 [6]. The PROX—CO catalysts must have higher selectivity towards oxidation of CO as compared to oxidation of H_2. Occurrence of WGS reaction on the catalysts surface at metal support has been reported as mechanism facilitating higher selectivity. The WGS reaction during PROX consumes CO converting H_2O back to H_2. Usually catalysts favour the reverse Water—Gas-Shift (r-WGS) reaction at a high temperature ($\Delta G_{rxn,298k} = +28.6$ kJ mol^{-1}). PROX—CO catalysts must inhibit the reverse water—gas-shift (r-WGS) reaction while should promote WGS reaction. Due to the exothermic nature of oxidation reactions and thermodynamics of WGS reaction, two adiabatic reactors are used in series in many commercial PROX—CO reactors [7—9]. The following reactions are carried out throughout the reaction.

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \; (\Delta H_{rxn,298k} = -283 \text{ kJ mol}^{-1}) \quad (1)$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \; (\Delta H_{rxn,298k} = -242 \text{ kJ mol}^{-1}) \quad (2)$$

$$CO_2 + H_2 \rightleftarrows H_2O + CO \left(\Delta H_{rxn,298k} = +41.2 \text{ kJ mol}^{-1}\right) \quad (3)$$

Several metal catalysts such as Pt, Ru, Au, dispersed on metal oxides are promising catalysts for PROX—CO reaction. Similarly the transition metals such as Cu, CO and Fe are also used as catalysts for PROX—CO reaction [5,10,11]. The catalyst composition designs are targeted for promoting PROX—CO reaction mechanisms. There are several independent mechanisms proposed for PROX—CO namely non-competitive L—H mechanism, reaction of adsorbed CO and O_2 over bimetallic sites in closed vicinity and promotion of water—gas-shift reaction on Pt—CeO_2 interface subsequent to oxidation reaction. The PROX catalysts are reported to follow either of the reaction mechanisms.

Huang et al., reported Pt/Al_2O_3 and Ru/Al_2O_3 as catalysts to clean up CO in hydrogen. The feed composition for PROX reaction was 69% H_2, 28.5% CO_2, 0.5% CO and balance O_2. Increase in Pt and Ru content from 0.5 to 5 wt% in the catalysts reported to lower the temperature for complete CO conversion from 100 to 80 °C. However, methane formation was favoured using 5 wt% noble metal with an increase in temperature [10].

Tabakova et al. reported gold supported on Ce—Fe mixed oxides and compared the activity with Au/CeO_2 and Au/Fe_2O_3 catalysts. The feed used for PROX reaction was 1% CO, 1.25% O_2, 50% H_2 and balance He. Maximum CO conversion of 99.4% was observed for catalyst Au/CeO_2 at 110 °C. According to their report Fe_2O_3 addition to support helps to improve the resistance towards deactivation by CO_2 [11].

Similarly, Huang et al., suggested that addition of Fe to Pt/A_2O_3 and Ru/Al_2O_3 significantly enhanced the CO conversion rate below 160 °C. The CO conversion rate could be enhanced by adding cobalt for reactions carried out at temperatures above 200 °C [10].

According to the above discussions, it is evident that the roles of metal catalyst and support are important in PROX—CO reaction. Out of the various oxides, CeO_2 has been reported as one of the most preferred support for PROX—CO catalysts. CeO_2 fascinated the researchers due to high dispersion of active component over its surface and facilitation of PROX—CO mechanism through change in the oxidation state between 3+ and 4+, depending on redox conditions [12]. Use of mixed oxides is also reported as a potential alternative for PROX—CO reaction. CuO—CeO_2 exhibits higher CO conversion in presence of excess of hydrogen with lower oxygen excess (λ) [5]. Addition of Co_3O_4 in CeO_2 reported to impart stability to the catalyst. In addition to CO oxidation, mixed oxides CeO_2—Fe_2O_3 reported to exhibit catalytic activity for several reactions such as

oxidation of p-cumaric acid, CO oxidation, CH_4 selective oxidation, Fischer—Tropsch synthesis and N_2O decomposition [13—17].

In spite of lower surface area of perovskite, their ability to involve lattice oxygen in reaction makes it as potential catalysts in various oxidation reactions. The studies reported for PROX—CO reaction over perovskite are limited. Some of the perovskite-based catalysts reported for PROX—CO include Pt/$Ce_xZr_{1-x}O_2$ [18] and CuO/$Ce_{1-x}Ti_xO_2$ [19]. $Ce_{0.8}Zr_{0.2}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$ catalysts reported to exhibit CO conversion of 100% with selectivity of 50% at 65 and 91 °C respectively at $\lambda = 2$. For mixed oxides catalyst CuO/$Ce_{0.2}Ti_{0.8}O_2$, CO conversion of ca. 99.5% is reported at the temperature of 110 °C.

Perovskite $LaFeO_3$ is widely reported in the field of environmental catalysis [20]. PROX—CO is not reported over $LaFeO_3$. However the properties of Fe such as improving resistance towards deactivation by CO_2, desorption of oxygen etc. enhances CO oxidation at relatively lower temperatures. This study targets PROX—CO reaction over Pt/$LaFeO_3$ and to evaluate the effect of combination of $LaFeO_3$—CeO_2 as support for the reaction. The aim is to lower the CO concentration below 100 ppm with relatively lower hydrogen loss and without methane formation.

2. Experimental

2.1. Catalyst synthesis

The structure of chitosan—metal hydroxide complex is shown in Fig. 1. As reported for formation of alumina by chitosan complex route, NH_2 group of chitosan binds metal ions from salt solution [21]. During calcination chitosan is combusted and removed along with formation of metal oxides [22]. The removal of chitosan template during calcinations results into voids and help in formation of porous metal oxides. Similar approach could be followed for preparation of other metal oxides or mixed metal oxides. Therefore, we have synthesised perovskite $LaFeO_3$ by chitosan complex method. There may be a possibility of preferential uptake of a cation by chitosan and may result into the different chemical compositions of mixed metal oxide or perovskite. However, this can be controlled by carefully selecting cations and maintaining proper
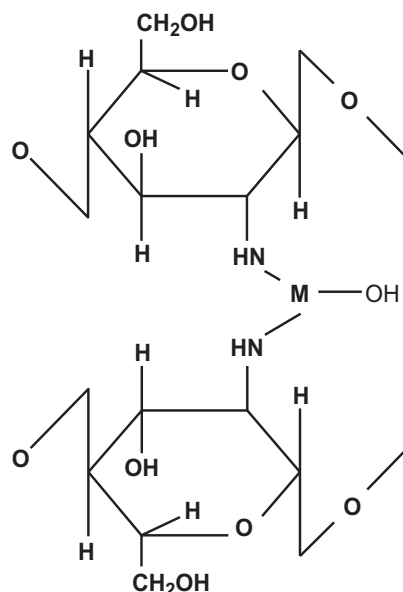

Fig. 1. Chitosan metal complex structure.