Short Communication

High catalytic activity in CO PROX reaction of low cobalt-oxide loading catalysts supported on nano-particulate CeO_2–ZrO_2 oxides

Zhongkui Zhao [a,*], Xiaoli Lin [a], Ronghua Jin [a], Yitao Dai [a], Guiru Wang [b]

[a] State Key Laboratory of Fine Chemicals, Department of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China
[b] Department of Catalytic Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China

ABSTRACT

Co_3O_4/NP-ZrO_2, Co_3O_4/NP-CeO_2 and Co_3O_4/NP-$Ce_{0.8}Zr_{0.2}O_2$ catalysts were prepared via a reverse microemulsion/incipient wetness impregnation (RM–IWI) method. The catalytic properties for CO preferential oxidation (CO PROX) reaction in H_2-rich stream were investigated. The Co_3O_4/NP-$Ce_{0.8}Zr_{0.2}O_2$ catalyst with 1.8 wt.% Co_3O_4 loading has exhibited higher catalytic activity than that of the other two catalysts. The higher catalytic activity might be attributed to the combination effect of the highly dispersed cobalt oxide, the improvement in CeO_2 reducibility due to ZrO_2 incorporation in CeO_2 structures, and the strong cobalt oxide-support interaction.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells are considered as the most attractive method for power generation in the 21st century [1]. Proton exchange membrane fuel cells (PEMFCs) with a number of advantages of high energy density of work, long working life, fast response and low operating temperature have become widely accepted [2]. The fuel of PEMFCs is H_2, whose production is mainly through coal gasification [3], natural gas reforming [4] or partial oxidation [5], etc., followed by a Water–Gas-Shift (WGS) process to obtain pure H_2. Nevertheless, due to thermodynamic and kinetic restrictions of WGS reaction, the H_2 stream contains 40–75% H_2, 15–25% CO_2, 10–20% H_2O, 0–25% N_2 and 0.5–1% CO. The anode of a PEMFC is very sensitive to CO content in the feed due to poisoning. Pt electrodes require the concentration of CO to be less than 10 ppm, and even with the most advanced Pt–Ru alloy electrode, more than 100 ppm is not allowed [6]. Therefore, the elimination of CO from H_2-rich gas has become the key step for the application of H_2-fueled PEMFCs. CO PROX reaction is one of the direct and effective methods to purify H_2, thus having been a hot topic in catalysis [7–9]. CO PROX reaction unit can be attached to Fuel Cell (application temperature 80–120 °C) or to WGS (operation temperature 200–250 °C), and as well as to be a medium unit between Fuel Cell and WGS. A good catalyst for CO PROX reaction basically need have high CO conversion and O_2 selectivity to CO_2 within a wide operation temperature range (100–250 °C) [9–12].

Using Au, Pt, etc. precious metals as catalysts, 100% CO conversion and good selectivity can be achieved at low temperature [13,14]. However, considering their high cost and limited availability, replacing them by non-precious metals is mandatory. The Cu based materials have been widely studied [15,16]. To date, the reports about Cu catalysts used for CO PROX reaction are endless stream, and have achieved fruitful results. But some deficiencies, such as less anti-H_2O, CO_2 capability, not satisfactory CO selectivity (a large number of oxygen and H_2 consumption) and also narrow temperature window, etc. remain to be overcome. Researches on the other non-precious metals are gaining increasing attention. Co_3O_4 as a kind of non-precious metal catalytic material with excellent properties has shown better low-temperature activity, selectivity and the H_2O resistance than CuO_x, which has a good prospect for the CO PROX reaction in excess H_2 [17–19].

The support can affect the catalytic properties by improving the dispersion of active component or interacting with the active sites [11,20]. The support effect for CO PROX reaction has been studied by preparing supported cobalt catalyst on commercially available supports. It shows that support type has significant effects on catalytic activity [11]. The Cerium based composites now were used as supports for the Cu catalysts [15,16], and also for Co catalysts [10,11,21]. As is well known, ceria has a super oxygen storage property, but due to the decrease in surface area with thermal treatment, the oxygen storage is weakened. The addition of zirconium improves its thermal stability, and as well as the structural defects

---

* Corresponding author. Tel./fax: +86 411 84986231.
   E-mail address: zkzhao@dlut.edu.cn (Z. Zhao).

responsible to zirconium boosted the oxygen mobility. All of above benefit the catalytic activity [22]. Nowadays, ceria–zirconia composites were widely used as catalyst or as supports to prepare the supported Cu, Au, Pt catalysts for CO low-temperature oxidation, as well as to support Co for methane combustion, etc., and the good catalytic properties were found [23–25]. However, no report on ceria–zirconia composite supported Co for CO PROX reaction can be found, which initiates us to study $Co_3O_4/Ce_xZr_{1-x}O_2$ catalyst for CO PROX reaction.

In the present paper, we prepared three ceria-zirconia composite nanomaterials by a RM method (see FESEM images in supporting information), and then support cobalt to prepare $Co_3O_4/NP-ZrO_2$, $Co_3O_4/NP-CeO_2$ and $Co_3O_4/NP-Ce_{0.8}Zr_{0.2}O_2$ via IWI method. Firstly, the ceria–zirconia composite oxide supported cobalt catalyst was employed in CO PROX reaction in H_2-rich stream, and the $Co_3O_4/NP-Ce_{0.8}Zr_{0.2}O_2$ catalyst with 1.8 wt.% loading exhibited high catalytic activity for the aimed reaction.

2. Experimental

2.1. Preparation of catalysts

$Ce_xZr_{1-x}O_2(x = 0, 0.8, 1)$ was prepared by reverse microemulsion method with cyclohexane as the organic phase and NP-10 as the surfactant. After drying overnight at 105 °C and calcinating at 400 °C for 5 h in the muffle, they were used as the supports. Through incipient wetness impregnation method, cobalt nitrate as the precursor was loaded on the support. Then, the same drying (105 °C overnight) and calcinating process (400 °C for 5 h) as support preparation were performed to prepare supported cobalt oxide catalysts.

2.2. Characterization of catalysts

The redox behavior and the metal-support interactions on the catalysts were evaluated via TPR using an in-house constructed system equipped with a TCD detector to measure H_2 consumption. A quartz tube was loaded with 100 mg of catalyst which was pretreated by calcination process in 2.5% O_2/Ar at 400 °C for 30 min, and then the sample was cooled to ambient temperature in Ar. The samples were heated in 10% H_2/Ar mixture gas (30 mL/min) from 50 °C to 800 °C at a ramp rate of 10 °C/min. The effluent gas flowed through a tube filled with silica to remove water before reaching TCD detector. The hydrogen consumption was measured by TCD detector. XRD profiles were collected from 5° to 80° at a step width of 0.02° using Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a CuKa source ($\lambda = 1.5406$ Å). The average crystalline particle size estimation was performed according to the Scherrer equation over multiple characteristic diffraction peaks. FESEM photograph was obtained by using HITACHI S4800 Field Emission Scanning Electron.

2.3. Measurement of catalytic performance

Steady-state reaction experiments were performed in a stainless steel, fixed-bed flow reactor (6 mm O.D.) with 200 mg of catalyst with 200–250 mesh particle size held between quartz wool plugs. The feed consisted of 50 cm^3 (STP)/min of 1% CO, 1% O_2 and 50% H_2 in Ar and was controlled with Huibolong mass flow controllers. Samples were pretreated in 2.5% O_2 at 300 °C for 30 min. Temperatures were measured using K-type thermocouples and controlled by a PID controller (Xiamen Yudian). The analysis of the effluent gas was performed using a gas chromatograph (FuLi) on-line with a molecular sieve column and a Porapaq Q column. The CO and CO_2 signals were detected by the high sensitive FID detector after the gas passing through a methanizer. CO

conversion and CO_2 selectivity were calculated on the basis of the equations as follows:

$$CO\ Conversion = 100 \times ([CO]_{in} - [CO]_{out}) / [CO]_{in}$$

$$CO_2\ Selectivity = 100 \times ([CO]_{in} - [CO]_{out}) / 2 \times ([O_2]_{in} - [O_2]_{out})$$

3. Results and discussion

Fig. 1 shows the CO conversion and CO_2 selectivity on the three supported cobalt oxide catalysts. Among the supported Co_3O_4 catalysts, $Co_3O_4/NP-Ce_{0.8}Zr_{0.2}O_2$ had the best catalytic activity, although a little lower selectivity. CO can't be fully converted within the investigated temperature region on $Co_3O_4/NP-CeO_2$. On $Co_3O_4/NP-ZrO_2$ catalyst, only at 225 °C, CO can be completely converted, although best selectivity can be observed. Moreover, due to the competitive oxidation of CO and H_2, the noticeable decrease in CO conversion was detected while the temperature being above 225 °C. For all samples, no methanation reaction took place at our operation temperatures (only happened while the temperature was not less than 300 °C, see the GC for the reaction effluent gas at 250 °C and 300 °C in supporting information). As is well known, the only supported precious metals like Au, Pt, Re, Pd, etc. catalysts with as low as active component loadings can exhibit so high catalytic activity. We were surprised that the ceria–zirconia composite supported cobalt oxide catalyst with 1.8 wt.% loading exhibited high excellent catalytic activity, and CO could be converted completely at lower temperature. Therefore, temperature programmed reduction (TPR) and X-ray diffraction (XRD) experiments were employed to explore the possible reason why it had high catalytic activity although with the low active component loading (no obvious catalytic activity was observed with the $NP-Ce_{0.8}Zr_{0.2}O_2$ as the only catalyst).

The H_2-TPR profiles of the six samples are exhibited in Fig. 2, and the quantitative results are provided in Table 1. The peaks between 200 and 400 °C of catalysts are assigned to the H_2 consumption for the reduction of highly dispersed Co_3O_4 besides some surface reducible CeO_2 [26–28]. Compared with CeO_2, the reduction of ZrO_2 can be negligible (only 8.6% and 2.6% reducible ZrO_2 in support and catalyst, respectively), but the doping of ZrO_2 can improve the reducibility of CeO_2 through the interaction between ZrO_2 and CeO_2. From Table 1, the reducible CeO_2 of $Co_3O_4/NP-Ce_{0.8}Zr_{0.2}O_2$ is much more than that of $Co_3O_4/NP-CeO_2$. Correlated to reaction results, we can see the obvious enhancement of reducible CeO_2. However, the very poor catalytic activity over $NP-Ce_{0.8}Zr_{0.2}O_2$ support (less than 12% for CO

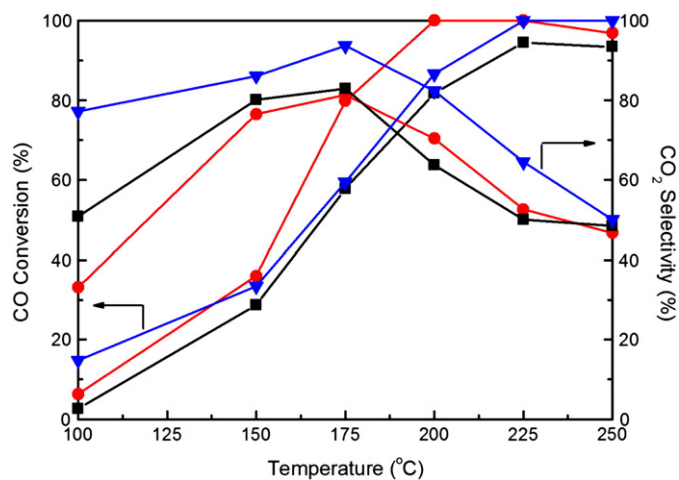**Fig. 1.** CO conversion and CO_2 selectivity on the three samples: (■) $Co_3O_4/NP-CeO_2$, (●) $Co_3O_4/NP-Ce_{0.8}Zr_{0.2}O_2$ and (▼) $Co_3O_4/NP-ZrO_2$ for CO PROX reaction.