Selective oxidation of CO with modified Pd/ZnO catalysts in the presence of H_2: Effects of additives and preparation variables

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Abstract

Supported Pd catalysts on various support materials, ZnO, Ga_2O_3, SiO_2, CeO_2, In_2O_3, and Al_2O_3, exhibit poor activity and selectivity for the selective oxidation of CO in H_2-rich gas with O_2. The most active catalyst is Pd/ZnO among the six samples examined. The Pd species exist in the form of PdZn alloy in this catalyst and the alloy is more effective for the reaction compared with metallic Pd species of the other catalysts. The activity of Pd/ZnO catalyst can be significantly improved by the addition of alkali compounds, in particular Cs and Rb. These additives were shown to enhance the CO oxidation but suppress the undesired H_2 oxidation. With the optimized Cs-modified Pd/ZnO catalyst (Cs/Pd = 3), the CO concentration of a mixture of $CO/O_2/H_2/CO_2$ (0.5/2.0/23/7.0) can be reduced to a 40 ppm level at 433 K, while controlling the H_2 conversion level to <10%. Temperature programmed desorption measurements indicate that the addition of Cs affects the adsorption/desorption behavior of CO and H_2 on PdZn alloy particles in the Pd/ZnO catalyst but not the size of PdZn alloy crystallites. The Cs promoter is effective to weaken the strength of CO adsorption on the catalyst and increase the amount of H_2 weakly interacting with them in the presence of both CO and H_2, resulting in the enhanced selective CO oxidation activity of the Cs-modified Pd/ZnO catalyst.
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1. Introduction

Among various types of fuel cells, proton exchange membrane fuel cell (PEMFC) seems to be the most technically advanced system for transportation and stationary power units because of compact size, low operation temperature, high power density and rapid start up [1,2]. In this system, hydrogen is used as a fuel but it is not suitable for transportation due to its low boiling point. The hydrogen can be produced from natural gas, gasoline or alcohols (methanol and ethanol) by partial oxidation or steam reforming [3]. The reformate gases always contain CO and the Pt electrode of PEMFC is easily deteriorated by the adsorbed CO. Therefore, it is important that CO concentration must be kept at the level to a tolerable range below 50 ppm [4]. CO can be partially converted to CO_2 via the water gas shift reaction (WGSR), but the concentration of CO is thermodynamically limited to levels of about 0.5–1% [5]. Hence, further effective CO removal process is required. The selective oxidation of CO has been regarded to be one of the most promising methods to reduce the CO concentration down to ppm level in the H_2-rich reformate gases [6].

The catalysts that have so far been reported for the selective oxidation of CO are alumina supported platinum-group metals (Pt, Ru and Rh) [2,5,7–10], zeolite supported Pt catalysts [11–13] and gold-based catalysts [14,15]. The gold-based catalysts are more active than platinum-group metal catalysts at lower temperatures below 400 K, but deactivation occurs in the presence of CO_2 in the feed stream [16]. Pd-based catalysts are less active for the selective oxidation of CO in the presence of H_2 [7,13,17]. The performance of supported metal catalysts may be changed by adding some promoter or modifier [2,18–29]. When alkali metals, such as Na or K, are added to Pt or Rh-based catalysts, their catalytic performance is significantly improved [18–22]. Tanaka et al. found a highly active and

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selective new catalyst, which was prepared by loading a large amount of Fe-oxide on 1 wt% Pt supported on TiO_2, Al_2O_3 and CeO_2 [27,28]. More recently, Mirkelamoglu and Karakas [26] have reported that alkali metal enhances CO oxidation activity of PdO/SnO_2 catalysts. In this work, however, experiments were run with only CO and O_2 in the absence of H_2.

Recently, we have communicated that Pd/ZnO catalysts are active for the selective CO oxidation in H_2-rich than several supported Pd catalysts using different supports and, in addition, the activity of Pd/ZnO catalysts can be significantly improved by the addition of such alkali metals as Ca and Rb [30]. The present work has been undertaken to optimize preparation parameters for the design of more active Cs-promoted Pd/ZnO catalysts and examine their activity under different reaction conditions. Further, the adsorption/desorption behavior of CO and H_2 has been investigated using TPD methods to consider reasons for the enhanced CO oxidation activity of those catalysts.

2. Experimental

2.1. Catalyst preparation

Various supported Pd catalysts, such as Pd/Ga_2O_3, Pd/SiO_2, Pd/CeO_2, Pd/In_2O_3, and Pd/Al_2O_3 were prepared by impregnation methods similar to those used previously [31]. CeO_2 was obtained by thermal decomposition of $Ce_2(CO_3)_3 \cdot nH_2O$ at 773 K and the others were purchased and used without further purification, Ga_2O_3 (Kishida Chemical, 99.99%), SiO_2 (GL Sciences, 99.0%), In_2O_3 (Wako Pure Chemical, 99.9%) and Al_2O_3 (Nishio Industry, 99.7%). The support material was impregnated with a solution of palladium nitrate at 353 K. Pd/ZnO catalyst was prepared by a precipitation method [32], in which an aqueous solution of sodium carbonate was added to a mixed solution of palladium and zinc nitrates until pH 8 at 353 K under continuous stirring. The precipitate formed was then filtered out, washed with cold and hot distilled water, and dried in air at 383 K. The residual amount of sodium remaining in the Pd/ZnO samples obtained was examined by X-ray fluorescence and it was found to be below the detectable limit. Alkali metal modified Pd/ZnO catalysts were prepared by impregnation of a Pd/ZnO sample with a solution of alkali metal carbonate, such as Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3 or Cs_2CO_3. For Cs-modified Pd/ZnO catalysts, $CsNO_3$ and CsOH were also used as a source of Cs. The Pd loading was 1 wt% unless otherwise stated. The catalyst samples thus prepared were calcined in air at 773 K for 3 h, followed by reduction before reaction runs, as described below.

2.2. Activity measurement

The preferential oxidation of CO was carried out with a glass fixed bed flow-type reactor in a temperature range of 353–473 K. A weighed sample of catalyst (0.1 g) was pretreated in the reactor under a stream of O_2 (20 vol.% O_2) diluted with N_2 at 773 K for 2 h and then cooled to room temperature. The sample was then reduced in a H_2 stream (4 vol.% in N_2) at room temperature at 1 h and at increasing temperatures at 5 K min^{-1} up to 773 K. After the reduction, pure N_2 stream was introduced and the sample was cooled to reaction temperature. The reaction was started by introducing a mixture of $CO/O_2/H_2/CO_2/N_2$. The composition of inlet gases was 1.6% CO, 1.6% O_2, 7.0% CO_2 and 23.0% H_2 in N_2 as a diluents. In some cases, the concentration of CO and O_2 was changed from 0.3% to 1.6% and from 0.5% to 2.0%, respectively. The effluent gases were analyzed by gas chromatographs equipped with TCD and FID. For quantitative analysis for trace amount of CO, it was converted to methane by a Ni catalyst before supplying to FID.

The CO or H_2 conversion was calculated from the concentration of CO or H_2 at inlet and outlet: Conversion of $X = ([X]_{in} - [X]_{out})/[X]_{in}$ (X = CO, H_2). Under the conditions used, only CO_2 and H_2O were observed to form without any other products. The O_2 conversion was calculated from the concentration of O_2 at inlet and those of CO and H_2: $\{([CO]_{in} - [CO]_{out})/2 + ([H_2]_{in} - [H_2]_{out})/2\}/[O_2]_{in}$. This was because the quantitative analysis of O_2 at outlet was not good in our GC measurements when it was small at large O_2 conversion. Selectivity for the CO oxidation was defined as the ratio of O_2 used for the oxidation of CO to the total amount of O_2 consumed by the oxidation of CO and H_2:

$$\text{Selectivity} = \{([CO]_{in} - [CO]_{out})/2\}/\{([CO]_{in} - [CO]_{out})/2 + ([H_2]_{in} - [H_2]_{out})/2\}.$$

2.3. Catalyst characterization

The catalysts prepared were characterized by X-ray diffraction (JEOL JDX-8020) using Cu Kα radiation ($\lambda = 0.15405$ nm) to examine their structural features. Temperature programmed reduction (TPR) was used to examine the reduction behavior of Pd precursors (mostly in the form of PdO) dispersed on different supports in the above-mentioned manners. A catalyst sample (1.0 g) was calcined in a 20% O_2 (in N_2) stream at 100 cm^3 min^{-1} and at 773 K for 2 h and cooled down to room temperature. Then, the sample was reduced by 4% H_2 (in N_2) stream at room and increasing temperatures at 5 K min^{-1}. The amount of H_2 consumed was measured by TCD. The adsorption and desorption behavior of CO and H_2 over the surface of catalysts was examined with temperature programmed desorption (TPD) using a TPD apparatus (Nippon BEL TPD-A1) equipped with a TCD and a mass spectrometer. A catalyst sample (1.0 g) was calcined and reduced with the same procedures and finally reduced at 773 K for 90 min. Then, CO, H_2, or CO + H_2 was adsorbed on the catalyst sample; for CO, 5% CO (in He) was passed at room temperature for 60 min and, after flushing with pure He, the catalyst sample was heated at 5 K min^{-1} up to 873 K in a He stream at 50 cm^3 min^{-1}. For H_2, a higher temperature of 373 K was used to avoid the formation of metal hydrides. The sample was exposed to a 4% H_2 (in N_2) stream at 100 cm^3 min^{-1} and at 373 K for 60 min and cooled to room temperature in a pure N_2 stream. The catalyst temperature was raised at 5 K min^{-1} up to 1073 K in a N_2 flow at 500 cm^3 min^{-1}. For co-adsorption of CO