Oxidizing-Resistant PdZn Catalyst for Hydrogen Production for Fuel Cell

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ABSTRACT

In the real application of on board hydrogen production for fuel cell powered vehicle, the catalyst concerning steam reforming of methanol (MSR) for hydrogen production suffered frequent oxidation considering the intermittent driving of vehicle. In this study, the environment effect on the PdZn catalyst concerning MSR was investigated and the reason was discussed. It was found that a high molar ratio of Zn to Pd for intermetallic PdZn catalysts is favorable for the formation of PdZn intermetallic compound when the catalyst was oxidized and then reduced. The high molar ratio of Zn to Pd can guarantee the negligible influence of frequent oxidation on the catalytic activity and selectivity.

Keywords: PdZn intermetallic compound; oxidation; hydrogen production; steam reforming of methanol

NONMENCLATURE

Abbreviations	
MSR	steam reforming of methanol
NPs	nanoparticles

1. INTRODUCTION

Hydrogen is being contemplated as the future fuel in view of its high energy content, and its combustion without creating any environmental pollution. It has been rapidly developed and got extensive application. The efficiency of proton exchange membrane fuel cell (PEMFC) vehicle powered by hydrogen is 2-3 times higher than that of diesel locomotive. The research and development of hydrogen production technology for PEMFC has been attracting much attention. Out of various liquid hydrogen sources, methanol is considered as an ideal choice for on-demand production of hydrogen because it is sulfur-free and can be reformed at lower temperatures (200-250ºC) than most other fuels since it contains no carbon-carbon bonds that must be broken [1].

Currently, Cu is known to be highly active and selective towards the MSR, but this catalyst suffers from serious drawbacks, such as low thermal stability, tendency to sintering, and pyrophoric nature [2-3]. Research for alternative MSR catalysts providing higher stability than the Cu based systems led to the investigation of Pd and Pt-based catalysts. In the first publication by Iwasa et al., Pd and Pt on different supports were evaluated [4]. Normally, elemental Pd selectively catalyzes the decomposition of methanol to CO, even in the presence of water, resulting in high CO contents in the product [5]. Surprisingly, Iwasa et al. observed that in the case of Pd/ZnO the CO_2 selectivity improved drastically from 0 to 97% with prior reduction of the catalyst [6]. This was attributed to the bulk PdZn intermetallic compound which was formed by the spill-over of atomic hydrogen from the Pd metal to the ZnO, leading to facile reduction of the ZnO and migration of Zn to the metallic surface [7]. In the real application of on board hydrogen production for fuel cell powered vehicle, the MSR usually stopped in air at a high reaction temperature and then restarted after a given time considering the intermittent driving of vehicle. That is, the catalyst suffered frequent oxidation. The most important issue is to clarify the desirable environment of the PdZn intermetallic compound, which can guarantee the negligible influence of frequent oxidation on the catalytic activity and selectivity. However, no report can be found on this issue.

To this end, in this study, intermetallic PdZn catalysts with different molar ratios were prepared by wet impregnation and modified co-reduction method. Catalytic performance of MSR were tested before and after oxidation. The effect of the environment of the PdZn intermetallic compound was investigated and the

reason was discussed based on the characterization results of the catalyst.

2. EXPERIMENTAL

2.1 Catalyst preparation

We firstly prepared the catalyst of intermetallic PdZn using Al_2O_3 as the support by wet impregnation method. A solution of Pd and Zn nitrates (Pd/Zn molar ratio = 1/22.5) was added drop wise to the Al_2O_3 and the mixture was shaken to ensure even distribution of the nitrate precursor. The resultant mixture was further stirred at room temperature for 3 h. After being dried at $105^{o}C$ for 8 h and subsequently calcined at $400^{o}C$ for 2 h. Then the precursors were reduced in H_2 at $400^{o}C$ with a flow rate of 20 ml*min^{-1} for 3 h. The Pd loadings of PdZn/Al_2O_3 determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) is 2.5% and catalysts were denoted as $Pd_1Zn_{22.5}$. As a comparison, the ordered PdZn intermetallic compound catalyst (Pd/Zn molar ratio = 1/1) was prepared by a modified co-reduction method using butyllithium as reducing agents, then certain amounts of Al_2O_3 powders were added into the above colloid to prepared 2.5wt.% PdZn/Al_2O_3. Hereafter, the catalyst was denoted as Pd_1Zn_1. For the synthesis of 2.5wt. % Pd/Al_2O_3 catalysts, the synthetic procedure was the same as that of $Pd_1Zn_{22.5}$ except that the Zn nitrates was not added. The catalyst was denoted as Pd_1.

2.2 Reactivity measurements

MSR was studied in presence of water using a fixed-bed flow reactor at 350°C under atmospheric pressure with molar ration of H_2O to CH_3OH being 1.5. The MSR tests were performed using 50 mg of catalysts placed in a glass tubular reactor with a coaxially centered thermocouple. The reactants were fed independently into the preheater using liquid pumps and the mixture was led by a flowmeter of N_2 passing through the catalyst bed. The feed and the reactor outflow gases were analyzed on-line by gas chromatograph (GC) with thermal conductivity detector (TCD) equipped with Haysep Q (CO_2, CH_4) and molecular sieve (H_2, CO) using argon as carrier gas.

2.3 Catalyst characterization

High-resolution transmission electron microscope (HR-TEM) images with selected-area electron diffraction (SAED) patterns corresponding to the reflections of (111) and (200) of the PdZn intermetallic phase were obtained on a JOEL JEM 2100F transmission electron microscope operated at 200 kV [8]. X-ray diffraction (XRD) patterns of samples were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation in the 2θ range from 20° to 80°. The spectra of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) were achieved on a Nicolet-6700 Fourier transform infrared spectrometer. Prior to test, the samples were purged with He at room temperature for 30 min. Before the DRIFT spectra were recorded, the catalysts were treated with pure CO at a gas flow rate of 20 mL min^{-1} at room temperatures for 30 min and then purged with He to remove the free CO.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

The HR-TEM images with SAED patterns of the $Pd_1Zn_{22.5}$ and Pd_1Zn_1 samples are shown in Fig. 1. For fresh $Pd_1Zn_{22.5}$, the size of particles ranged in 5-15 nm and the interplanar spacing (d) was observed to be 2.2 Å (Fig. 1A) which is in good agreement with the PdZn intermetallic compound plane of (111) [9], demonstrating the formation of PdZn intermetallic compound nanostructure. After the $Pd_1Zn_{22.5}$ was oxidized, the structure of PdZn intermetallic compound disappeared and a large number of PdO appeared which was evidenced by the d value of 2.7 Å corresponding to that of (101) planes of PdO compounds (see Fig. 1B). Subsequently, when the $Pd_1Zn_{22.5}$ was reduced using hydrogen, the formation of PdZn intermetallic compound structure can be confirmed by the the d value of 2.2 Å corresponding to the (111) refection of PdZn (see Fig. 1C). In contrast, for fresh Pd_1Zn_1, the structure of PdZn intermetallic compound structure (Fig.1D) changed to PdO and ZnO (Fig. 1E) when the catalyst was oxidized in air at $400^{o}C$ using air. But after the following reduction by hydrogen, the nanoparticles of Pd not PdZn intermetallic compound formed. Therefore, a high molar ratio of Zn to Pd for intermetallic PdZn catalysts is favorable for the formation of PdZn intermetallic compound when the catalyst was oxidized and then reduced.

The XRD patterns of the $Pd_1Zn_{22.5}$ and Pd_1Zn_1 are shown in Fig. 2. For the fresh $Pd_1Zn_{22.5}$, no reflection of Pd metallic phase was observed. Two small reflection peaks at 2θ of 41.2° and 44.1° were detected. After the $Pd_1Zn_{22.5}$ catalysts were oxidized, formation of PdO phase can be confirmed. When the $Pd_1Zn_{22.5}$ catalysts were subsequently reduced, the PdZn interme-

tallic compound appeared. For fresh Pd_1Zn_1, the ordered PdZn intermetallic compound was observed with the absence of ZnO, indicating the perfect formation of intermetallic compound nanostructure. The species of PdO and ZnO appeared when Pd_1Zn_1 was oxidized. Different from $Pd_1Zn_{22.5}$, only Pd and ZnO were observed for Pd_1Zn_1. The PdZn phase can be retrieved by reduction for $Pd_1Zn_{22.5}$. The XRD patterns agree well with the results of TEM as shown in Fig. 1, indicating the important role of molar ratio of Pd to Zn in the reappearance of PdZn intermetallic compound after the oxidation of catalyst.
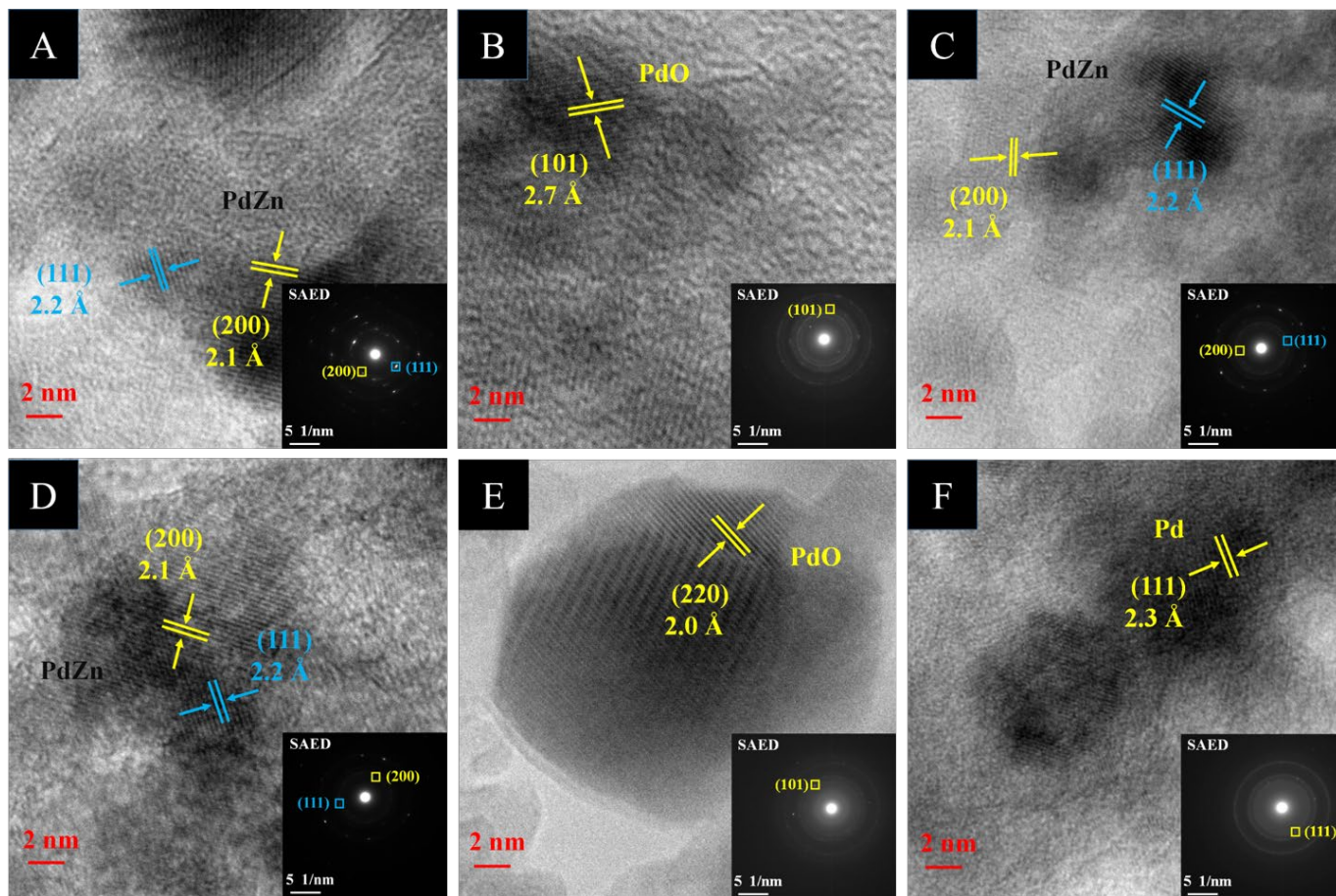

Fig. 1. HR-TEM images and SAED patterns of fresh $Pd_1Zn_{22.5}$ (A), after oxidization at 400 °C (B), and after reduction at 400 °C using hydrogen. HR-TEM images and SAED patterns of fresh Pd_1Zn_1 (D), after oxidization at 400 °C (E), and after reduction at 400 °C using hydrogen (F).
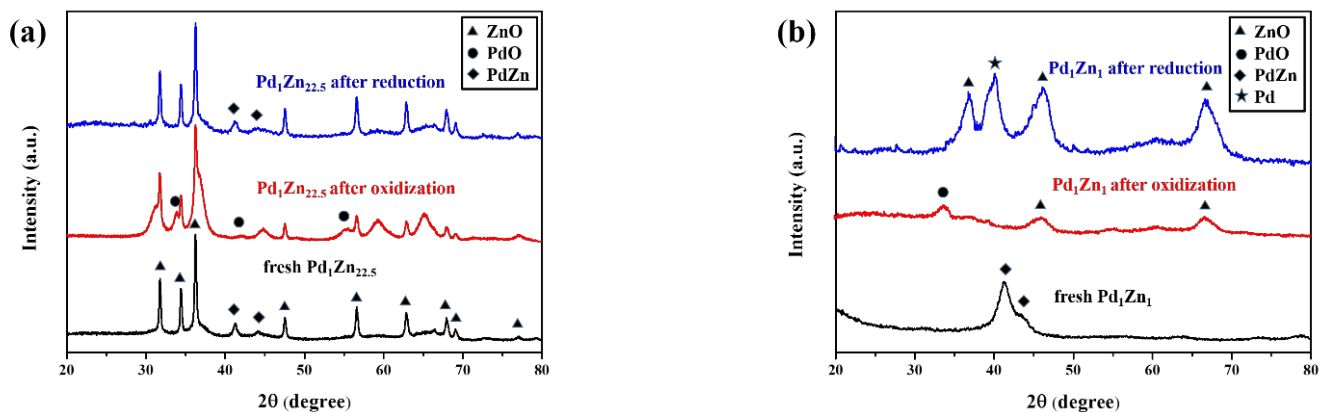

Fig. 2. XRD patterns of $Pd_1ZnO_{22.5}$ (a) and Pd_1ZnO_1 (b) (under three conditions: fresh, after oxidization and after reduction).

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To further confirm the formation of PdZn intermetallic compound, in situ DRIFT measurements with the CO adsorption to characterize the surface of the catalysts. As shown Fig. 3(a), for Pd_1, two peaks of 2076 cm^{-1} and 1941 cm^{-1} were observed, which are assigned to the CO adsorption in linear and bridge manners on Pd particles, respectively [10]. For fresh $Pd_1Zn_{22.5}$, no bands at around 1941 cm^{-1} could be observed, indicating that the CO molecules were only absorbed in a linear manner. The absence of bridged CO can be explained by the proposal that the distance between adjacent Pd atoms on the surface of the PdZn intermetallic compound is greater than that on the surface of pure Pd [11]. Interestingly, a shift was detected from 2076 cm^{-1} for Pd_1 to 2090 cm^{-1} for Pd_1Zn_1. Compared with Pd_1, no shift of linear CO linear adsorption peak was observed for $Pd_1Zn_{22.5}$. This tendency is different from those reported by Shinya et al.[12] that the linear CO linear adsorption peak on Pd red-shifted when intermetallic compound PdZn formed. The red shift can be understood by the transfer of 0.4 electrons from zinc to palladium upon ZnPd formation. This increases the back donation of electrons from palladium to the antibonding $\pi*$-state of the C-O bond, thus weakening the bond. It is well known that the CO adsorbed infrared spectroscopy probes the vibrational mode of CO that is sensitive to the electronic and geometric structure of the adsorption site on a metal surface. The shift of the adsorbed CO peak was also influenced by the particle size [13] and/or to the support effects [14]. It was reported that a blue shift of CO adsorption occurred when the particle size increased. The average size of $Pd_1Zn_{22.5}$ and Pd_1Zn_1 were 13.2 nm and 5.0 nm, exceeding that of 4.7 nm of Pd_1. Theoretically, blue shift existed. In addition, for $Pd_1Zn_{22.5}$, the PdZn was supported on ZnO not on Al_2O_3 considering a very high molar ratio of Zn to Pd. Therefore, the complicated electron donation, size and support effect worked together, resulting in the DRFIT spectra as shown in Fig. 3. When Pd_1Zn_1 and $Pd_1Zn_{22.5}$ were oxidized, the CO linear and bridge manners on PdO were observed. Subsequently, as the catalyst were reduced by hydrogen, the CO linear adsorption peak at 2075 cm^{-1} appeared for $Pd_1Zn_{22.5}$, corresponding to PdZn intermetallic compound. Whereas, for Pd_1Zn_1, the presence of Pd not PdZn was detected given the existence of the CO linear and bridge adsorption manners at 2070 and 1963 cm^{-1}, respectively. Therefore, from the combination of HR-TEM, XRD and DRIFT studies, it is concluded that the for $Pd_1Zn_{22.5}$, PdZn intermetallic compound could be regenerated after oxidation and the following reduction.

But for Pd_1Zn_1, the PdZn intermetallic compound was completely lost and transferred to pure Pd and ZnO. For MSR catalytic applications, PdZn intermetallic compound NPs are desired, which produce highly active sites for catalysis as well as stability.
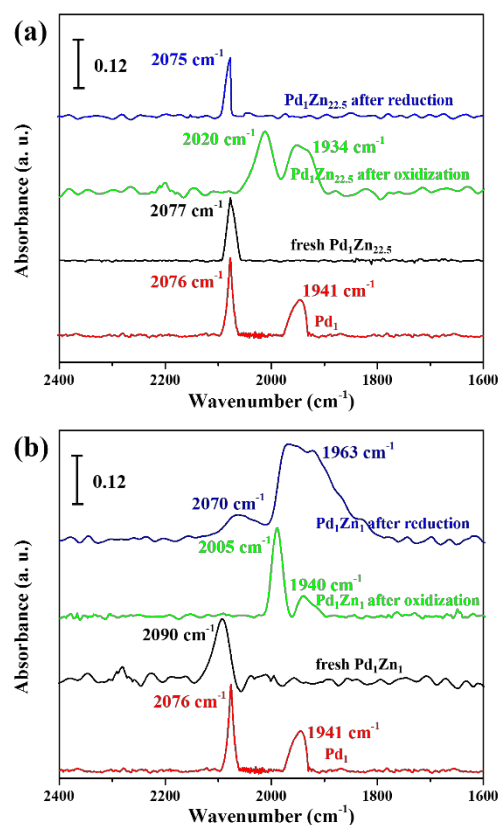

Fig. 3. DRIFT spectra with CO probes of $Pd_1ZnO_{22.5}$ (a) and Pd_1ZnO_1 (b) (under three conditions: fresh, after oxidization and after reduction).

3.2 Catalytic performance

The catalytic activities of $Pd_1Zn_{22.5}$ and Pd_1Zn_1 concerning MSR were investigated. As shown in Fig. 4(a) and 4(b), the CH_3OH conversions of fresh $Pd_1Zn_{22.5}$ and after reduction maintained around 99% throughout 180 min, coupling with the CO concentration being below 2%. After oxidation, the CH_3OH conversion decreased to around 72% and the CO concentration rose to around 20%, which is similar to the catalytic behavior of Pd metal. This tendency indicates the intermetallic compound transferred to Pd and ZnO, which agrees well with the characterization results as shown in Figs. 1-3. For Pd_1Zn_1, as shown in Fig. 4(c) and 4(d), the relatively low CH_3OH conversions of fresh prepared Pd_1Zn_1 and it is impossible to analyze the composition of the gas due to the slow gas flow at the outlet of the pipeline. The low

activity is attributed to organic compounds covering the active sites without calcination. After oxidation, the CH_3OH conversion remained at ca. 75% with the CO concentration of Ca. 22.5%. After the following reduction, the CH_3OH conversion slightly increased to ca. 80% with the same CO concentration of Ca. 22.5%. The high CO concentration indicates that the Pd-ZnO not the intermetallic PdZn compound existed for the reduced Pd_1Zn_1. Therefore, for the Al_2O_3 supported PdZn catalyst, a high molar ratio of Zn to Pd is an essential prerequisite for guaranteeing the negligible influence of frequent oxidation on the catalytic activity and selectivity.
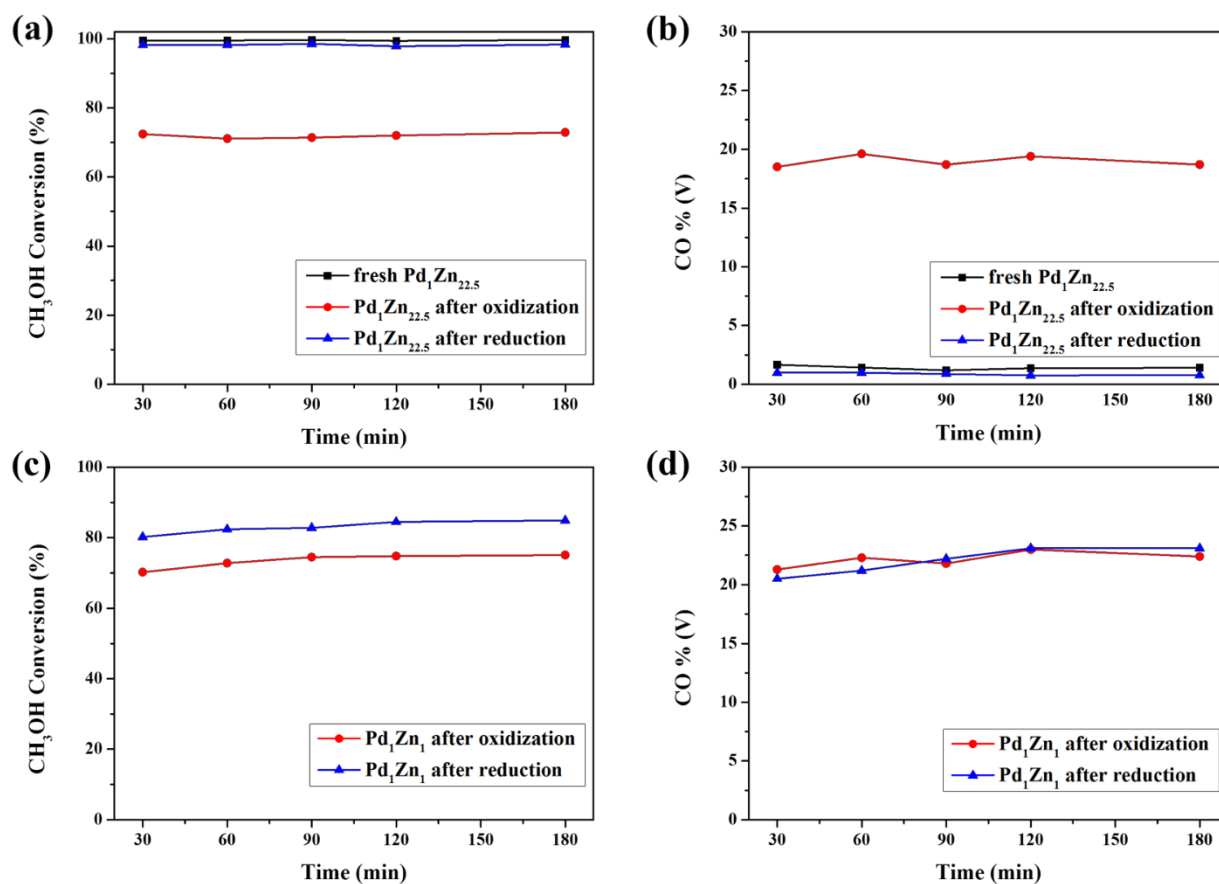

Fig. 4 Catalytic activities of of $Pd_1ZnO_{22.5}$ (a) and Pd_1ZnO_1 (b) (under three conditions: fresh, after oxidization and after reduction).

4. CONCLUSION

Intermetallic PdZn catalysts with different molar ratios were prepared by wet impregnation and modified co-reduction method. From the combination of HR-TEM, XRD and DRIFT studies, it is concluded that for $Pd_1Zn_{22.5}$, PdZn intermetallic compound could be regenerated after oxidation and the following reduction. Meanwhile, activity and seletivity of $Pd_1Zn_{22.5}$ for steam reforming of methanol are excellent. Therefore, for the Al_2O_3 supported PdZn catalyst, a high molar ratio of Zn to Pd is an essential prerequisite for guaranteeing the negligible influence of frequent oxidation on the catalytic activity and selectivity.

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