Catalysis Today 175 (2011) 430–434

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic decomposition of methanol to carbon monoxide and hydrogen over palladium supported on $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ and La–Al_2O_3

Ming Zhao, Xue Li, Lihua Zhang, Chao Zhang, Maochu Gong, Yaoqiang Chen*

Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, Number 29, Wangjiang Road, Chengdu 610064, PR China

ARTICLE INFO

Article history:
Received 14 October 2010
Received in revised form 10 May 2011
Accepted 16 May 2011
Available online 22 June 2011

Keywords:
$Ce_{0.65}Zr_{0.30}La_{0.05}O_2$
Palladium based catalysis
XPS
Methanol decomposition

ABSTRACT

In this article, La–Al_2O_3 and $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ were used as support to prepare palladium catalyst for methanol decomposition to synthesis gas at low temperature. The catalysts were characterized by nitrogen adsorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and NH_3-temperature-programmed desorption (TPD). XPS results confirm that palladium exists as oxidation state in the two catalysts and has strong interaction with ceria–zirconia solid solution. The result of H_2-TPR reveals that the reduction temperature of PdO slightly shifts to high temperature due to the strong interaction between palladium and $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$. For Pd/$Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ catalyst, the higher oxygen storage capacity is beneficial to the Pd species in a more active $Pd^{\delta+}$ state. Furthermore, the results of the methanol decomposition reaction show that the Pd/$Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ catalyst has high catalytic activity. The conversion of methanol achieves 100% at 220 °C over Pd/$Ce_{0.65}Zr_{0.30}La_{0.05}O_2$.

1. Introduction

Methanol is regarded as an alternative fuel for automobiles in the future. Recently the decomposition of methanol to H_2 and CO has attracted much attention as a method of increasing fuel efficiency for methanol powered vehicles. The decomposition of methanol is endothermic reaction and can recover the waste heat from methanol-fuelled vehicles in which the decomposition gas is fed to the engine [1]. In past years, Cu, Ni, and Mn containing catalysts have been extensively investigated. But these catalysts still suffer a slow deactivation and a by-product is usually observed [2,3]. Noble metal-containing catalysts, especially the Pd-containing catalysts, exhibit high activity and selectivity for methanol decomposition at low temperature (200–250 °C) and the activity is greatly affected by the supports. Recently, Usami et al. [4] tested a number of metal oxides as support for Pd and found that Pd/ZrO_2, Pd/Pr_2O_3 and Pd/CeO_2 catalysts prepared by a deposition–precipitation method were active for the selective decomposition of methanol to H_2 and CO at low temperature. The authors clarified that the interaction between Pd and metal oxides affected the catalytic activity. Lanthanum-modified Pd has been reported to be very active in the synthesis of methanol from CO and H_2 [5–7]. Lanthana is a particularly attractive support because it permits the combined achievement of high selectivity and specific activity for methanol synthesis. CeO_2-based catalysts have been investigated intensely in the last years [8]. Yang reported that Pd supported on CeO_2/γ-Al_2O_3 has excellent catalytic performance towards the decomposition of methanol [9]. The $Ce_xZr_{1-x}O_2$ solid solution has been reported to be a good support of noble metals for decomposition of methanol [10].

The objective of this work is to investigate the effect of palladium supported on $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ and La–Al_2O_3 on catalytic activity of monolithic catalysts towards the decomposition of methanol. In this paper, fabrication and the activity of the Pd-supported on La–Al_2O_3 and $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ catalysts towards methanol decomposition were studied and the state of Pd was characterized by XRD, TPR and XPS techniques.

2. Experimental

2.1. Catalyst preparation

$Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ solid solution was prepared by co-precipitation method from the corresponding raw materials: $Ce(NO_3)_3{\cdot}6H_2O$, $ZrO(NO_3)_2$ and $La(NO_3)_3$ in stoichiometric ratio. The precursors were mixed in an aqueous solution, then the mixed solution was added dropwise to ammonia and pH of the solution was adjusted to ca. 10. The precipitates were filtered, washed, dried at 105 °C overnight, then calcined at 600 °C for 5 h. Finally, $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ was obtained. La_2O_3–Al_2O_3 was pre-

---

* Corresponding author. Tel.: +86 28 85418451; fax: +86 28 85418451.
E-mail address: nic7501@scu.edu.Cn (Y. Chen).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.05.014

pared by co-precipitation method. $Al(NO_3)_3{\cdot}9H_2O$ was dissolved in distilled water, then mixed with solution of $La(NO_3)_3$. The mixed solutions were precipitated by adding excessive ammonia. During the precipitation reaction, pH was kept at 9.5. The precipitates obtained were boiled, filtered, washed, dried and then calcined at 900 °C for 4 h. The nominal content of La_2O_3 was about 4.6 wt%.

The Pd catalysts were prepared by impregnating the supports using $PdCl_2$ solutions. The loading amount of Pd was 1.4 wt%. Then the catalysts were dried at 120 °C overnight, calcined at 550 °C for 2 h. Monolithic catalysts were prepared according to the following procedure: the prepared powder catalysts were ball-milled with desired deionized water to obtain slurry, then the resulting slurry was washcoated onto a honeycomb cordierite (2.5 cm^3, the weight is 1.1 g, Corning, China); The excess slurry was blown off using compressed air. The obtained Pd loading was about 2.0 g L^{-1} and the washcoat loading was 140 g L^{-1} (about 24 wt%). The coated catalysts were dried at 120 °C for 2 h, calcined at 550 °C for 3 h. They were labeled as PCZ and PA, respectively.

2.2. Characterization of catalysts

The catalytic activity towards decomposition of methanol was evaluated in a multiple fixed bed continuum flow micro-reactor. Firstly, the catalysts were reduced in a steam of 5% hydrogen diluted with nitrogen at 400 °C for 1 h, methanol diluted with argon (MeOH, 15%; The gas space velocity was 4000 h^{-1}) was fed at 160–360 °C. The outlet reaction gas was analyzed by on-line gas chromatography equipped with TCD and FID. A TDX-01 column (2 m) was used for the analysis of H_2, CO, CH_4, CO_2, and Porapak-Q column (2 m) was used for CH_3OH, CH_3OCH_3 and $HCOOCH_3$.

X-ray diffraction (XRD) data were recorded on a DX-1000 X-ray diffractometer (China Fangyuan) using Cu Kα radiation (λ = 0.15406 nm). The X-ray tube was operated at 40 kV and 25 mA. Samples were scanned in 2θ range of 10–90° with a step size of 0.02°. The crystalline phases were compared with the reference data from the International Center for Diffraction Data (1999-JCPDS).

X-ray photoelectron spectroscopy experiments were carried out on a spectrometer (XSAM-800, KRATOS Co.) with Mg K radiation under UHV, the X-ray photoelectron spectra were referenced to the C 1s peak (E_b = 284.80 eV) resulting from adventitious hydrocarbon (i.e., from the XPS instrument itself) present on the sample surface.

The BET specific surface area and pore size measurement were performed on a ZXF-4500 automatic surface analyzer. The samples were evacuated at 350 °C for 1 h, and then cooled to −196 °C using liquid N_2 at which point N_2 adsorption was measured. Total oxygen storage capacity (OSC) was measured after reducing the catalyst (200 mg) at the appropriate temperature (550 °C) under H_2 flow (40 min). Before measuring O_2 uptake, the catalyst after reduction was cooled to 200 °C under N_2 flow, then pulses of oxygen were injected up to the breakthrough point. OSC was evaluated from oxygen consumed. Carbon monoxide chemisorptions were used to determine the dispersion of Pd catalysts. Before analyses, all the samples (500 mg) were reduced in a quartz U-tube in H_2 stream at 300 °C for 30 min, then cooled down to 25 °C under pure N_2 stream. Then pulse of carbon monoxide was injected up to the breakthrough point. Dispersion of Pd was evaluated from the consumption of carbon monoxide. Temperature-programmed reduction (H_2-TPR) experiments were carried out in a conventional system equipped with a thermal conductivity detector. All samples (80 mg) were pretreated in a quartz U-tube in a flow of pure N_2 at 400 °C for 1 h, then cooled down to room temperature. The reduction was carried out in a flow of H_2 (5%) in N_2 (20 ml min^{-1}) from 25 °C to 800 °C with a linear heating rate of 10 °C min^{-1}.

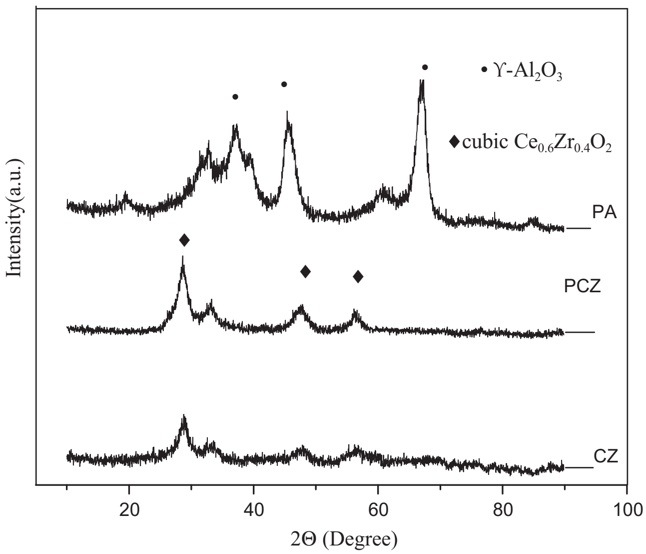

Fig. 1. XRD patterns of two catalyst samples and $Ce_{0.65}Zr_{0.35}La_{0.05}O_2$. PA: Pd/La–$Al_2O_3$ and PCZ: Pd/$Ce_{0.65}Zr_{0.30}La_{0.05}O$.

3. Results and discussion

3.1. XRD characterization

XRD patterns of the samples are shown in Fig. 1. No diffraction peaks of palladium (2θ = 40.0°) and PdO (2θ = 34.0°) or PdO_2 (2θ = 54.6°) were observed in the patterns of PCZ and PA catalysts. This result indicates that Pd species are highly dispersed on the surface of the carrier. The XRD patterns of PCZ are consistent well with the characteristic peaks of cubic CeO_2, which indicates the formation of CeO_2–ZrO_2 solid solutions. There are no separated ZrO_2 or La_2O_3 peaks, which imply the Zr^{4+} or La^{3+} enters into the CeO_2 lattice formation of $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ solid solution. PA catalyst shows only γ-Al_2O_3 phase. No separated peaks of PdO and La_2O_3 were detected. Similar results have been reported by some researchers [11,12]. The high degree of dispersion of Pd species will promote the catalytic activity. This result is in good harmony with the catalytic activity.

3.2. NH_3-TPD

NH_3-TPD profiles of the catalyst samples are presented in Fig. 2. The PCZ and PA have different NH_3 desorption peaks. As shown in Fig. 2, NH_3 desorption peaks of the two catalysts are at 50–400 °C, the peaks are attributed to $Pd^{\delta+}$ species on the surface of the two carriers. PCZ catalyst shows only one type of adsorption sites for NH_3, the area of the peak is small, indicating that the relatively small adsorption amount; As for PA catalyst, the desorption diagram shows two well resolved peaks at 50–400 °C and 450–650 °C, respectively, this result indicates that two types of adsorption sites present on the PA catalyst. The PA catalyst has stronger surface acidity than that of PCZ catalyst, the stronger surface acidity is, the worse selectivity is. The peak at 50–400 °C can be assigned to desorption from $Pd^{\delta+}$ species, while the small peak at higher temperature is assigned to desorption from alumina [13]. In addition, the acromion appeared at 300 °C indicates that Pd dispersed on La–Al_2O_3 can affect the oxygen coordination center of acid Al^{3+}. PCZ catalyst favors the decomposition of methanol to generate CO and H_2; these results are consistent with the results of activity.

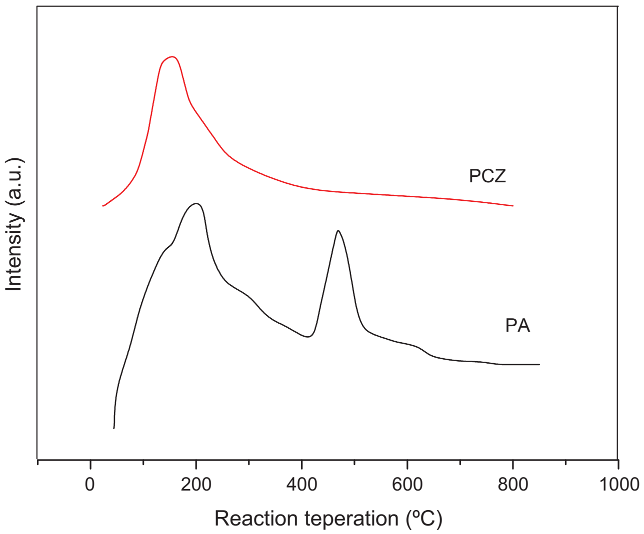

Fig. 2. NH_3-TPD profiles of the catalyst samples.

3.3. H_2-TPR

H_2-TPR experiments were carried out to evaluate the relationship between the catalytic activity and the reducibility of supported catalysts. The redox ability of catalysts is closely related to the catalytic activity. It has been generally agreed that the mainly active phase for methanol decomposition is PdO_x $(0 < x < 2)$. The transformation between PdO and Pd, the rate of PdO_x species reduction and Pd reoxidation are critical to catalytic activity. The H_2-TPR profiles of two catalysts are displayed in Fig. 3. The sharp peak below 100 °C is attributed to the reduction of small PdO species. The reduction temperature at 60 °C and 80 °C are attributed to PA catalyst, PCZ catalyst, respectively. In the PCZ catalyst, the strong metal-support interaction may promote the oxygen transfer, which can help maintain PdO in a more cationic state, hindering the reduction of PdO. This result is in good agreement with reference [14]. The other peak located at 460 °C is attributed to the reduction of surface CeO_2 interacted with Pd. The results suggest that the strong Pd–Ce interaction improves the reduction of surface CeO_2. According to Ref. [15], the reducibility of the surface oxygen species in the ceria–zirconia support may be altered after loading palladium metals and the peak of high temperature shifts to lower temperature. The strong interaction between CeO_2 and Pd has a great impact on the reduction behavior, which causes the reduction temperature of PdO slightly shifts to higher temperature. The results are in good consistent with that of catalytic activity for methanol decomposition.

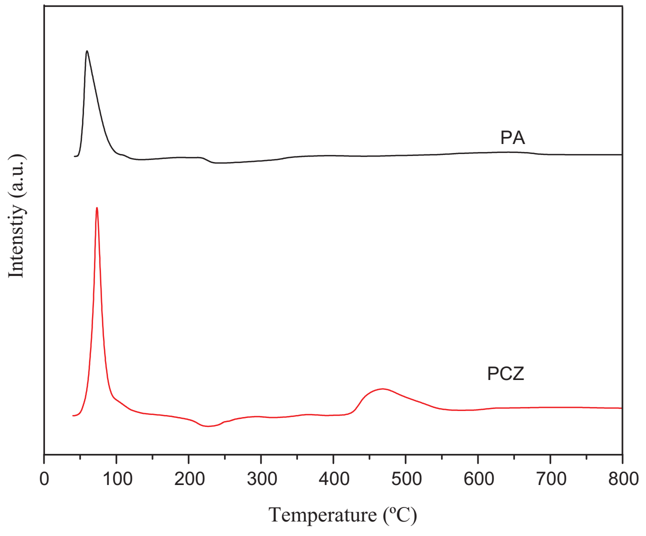

Fig. 3. H_2-TPR profiles of the catalyst samples.

3.4. OSC and XPS

The textural properties such as surface area and the oxygen storage capacity play an important role in the performance of catalytic. Table 1 shows the textural properties and the oxygen storage capacity of the two catalysts. It is clear that the specific surface areas of the two catalysts are similar; the surface areas are up to 130 $m^2\,g^{-1}$. As shown in Table 1, the OSC of PCZ catalyst is higher than that of the PA catalyst. The OSC of the PCZ catalyst is 361 $\mu mol\,g^{-1}$, while the OSC of the PA catalyst is 17 $\mu mol\,g^{-1}$. The higher OSC exhibits that the catalyst has stronger ability of storage and release oxygen, which greatly promotes the oxygen transfer from the bulk to the support surface and from the support surface to the Pd particles [16]. For PCZ catalyst, the distinct chemical defect of ceria can provide lattice oxygen and transfer oxygen from the support to the metal, which can help the Pd in a more active $Pd^{\delta+}$ state. In $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ solid solution mobile of oxygen has been enhanced, indicating that bulk oxygen from the body can easily spread to the catalyst surface, and there has been $Ce^{4+} \rightarrow Ce^{3+}$ response, the release of atomic oxygen will cause part of the Pd^0 (zero price of palladium) into PdO_x and maintains the higher activity of palladium $Pd^{\delta+}$ state [5]. It is also proposed that some of the Ce^{3+} ions are possibly formed through direct reduction by Pd^0 particles, which could form $Pd^{\delta+}$ species, according the following scheme [17], $Ce^{4+} + Pd^0 \rightarrow Ce^{3+} + Pd^+$. Simultaneously, the electron transfers from methoxy to the $Pd^{\delta+}$, which would weaken the CH bond of methoxy. In the PCZ catalyst, there exists more oxygen vacancy on the PdO_x surface, which can accelerate to weaken the C–H bond. The $Pd^{\delta+}$ is considered to be highly active in the methanol decomposition, which agrees well with the result of catalytic activity.

The metal dispersion and particle size are estimated from CO chemisorption and the results are shown in Table 1. Compared to the PA catalyst (18%), the PCZ catalyst possesses higher dispersion (26%). It is clear that the PCZ catalyst forms smaller Pd particles due to high dispersion than the PA catalyst. The absence of metallic Pd or PdO_x phase in XRD suggests the presence of well-dispersed nano-size Pd particles.

The XPS results are shown in Fig. 4. In the PA catalyst, the peaks of the Pd $3d_{5/2}$ appear at 335.2 eV with shoulder at 336.5 eV. It suggests that the most of the palladium on the surface is reduced to metallic palladium, whereas the rest are still in the form of Pd^{2+}, while the Pd $3d_{5/2}$ binding energy of PCZ catalyst is 335.9 eV. According to the standard manual [18], the binding energy of Pd $3d_{5/2}$ in Pd^0 and PdO are 335 eV and 336.8 eV, respectively, which may be inferred that the palladium of PCZ catalyst is cationic state. The Pd $3^d{}_{5/2}$ binding energy of PCZ catalyst is 0.7 eV higher than that of PA. The valence of Pd may be between 0 and +2 in PCZ catalyst, the cationic species is considered to be highly active in the methanol decomposition [19,20].

This species can be produced by electron transfer from palladium to ceria, indicating the strong interaction between palladium

Table 1
BET, OSC, XPS results of two catalysts samples.

Sample	BET surface area ($m^2\,g^{-1}$)	OSC ($\mu mol\,g^{-1}$)	Dispersion of Pd (%)	Pd (XPS)%	O (XPS)%
PA	134	23	18	1.31	48.60
PCZ	131	361	26	3.41	58.63

Table 2
The decomposition gas under different working conditions of $Pd/Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ at 300 °C.

Rotate speed (r/min)	Torsion (N m)	H_2 (%)	CO (%)	CH_3OH (%)	DME (%)	CO_2 (%)	CH_4 (%)
2400	20	50.4	22.2	4.9	17.7	4.0	0.7
2400	50	54.9	24.2	0.7	16.0	3.6	0.7
2270	60	56.9	25.6	0.5	13.1	3.4	0.5

particles and the support as mentioned above. According to the catalyst activity, the lower the Pd combination value is, the higher catalytic activity is. Since XPS reflects the condition of few surface atomic layers, the dispersion of palladium on the surface of PCZ (3.14%) is higher than that of PA (1.31%). No such peak was detected in the XRD patterns for either of the samples after reaction, indicating palladium particles are highly dispersed. It is supposed that chemical bonding such as Pd–O–Ce can be formed in the interface of palladium particles and the support. We may infer that the high activity of the PCZ catalyst is caused by the strong interaction between palladium particles and the support.

3.5. Catalytic activities

As seen from Fig. 5, the catalytic activity of PCZ towards the methanol decomposition is significantly higher than that of PA. PCZ has high activity, the methanol conversion is up to 100% at 220 °C; PA catalyst has relatively poor activity, the conversion is 80% at 300 °C. According to the results of dispersion, Pd is in highly decentralized state on $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ solid solution. In short, the conversion of methanol is different due to different carrier, the interaction between the Pd and carrier is different which affects the active sites of the Pd [21]. Since Pd and CZ oxygen storage materials have strong interaction which reduces the activation energy for methoxy into CO and H_2, PCZ catalyst has higher activity. So single Pd supports on different carriers will produce different effects.As can be seen from Table 2, the main components of methanol decomposition contain H_2, CO, DME, CO_2 and a small amount of CH_4 at different rotate speed and torsion, these five components accounted for 95% in the decomposition gas, the total content of H_2 and CO is about 80%, caloric value increases by 18–20% compared to liquid methanol. In addition, the catalyst also maintains high activity after it has been use for 100 h, the conversion of methanol still remains 90%.

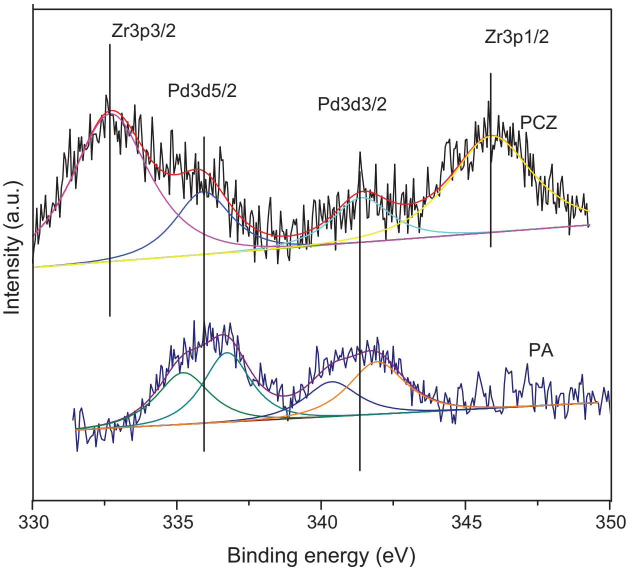

Fig. 4. XPS spectra of the catalyst samples after reduced at 400 °C.

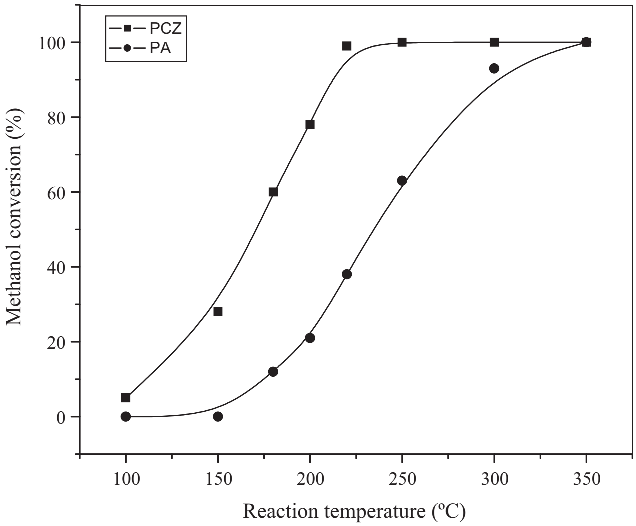

Fig. 5. The conversion of methanol at different temperature.

4. Conclusion

PA and PCA catalysts were prepared by impregnating the $La–Al_2O_3$ and $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$ using $PdCl_2$ solutions. Result of XRD indicates that Pd species is highly dispersed on the surface of the support; at the same time, the PCZ catalyst possesses higher dispersion (26%) compared to the PA catalyst (18%). XPS results show that the Pd $3d_{5/2}$ binding energy of PCZ catalyst is 0.7 eV higher than that of PA. The valence of Pd is between 0 and +2 in PCZ, the $Pd^{\delta+}$ is considered to be highly active in the methanol decomposition. H_2-TPR reveals that the reduction temperature of PdO slightly shifts to high temperature because of the strong interaction between palladium and the $Ce_{0.65}Zr_{0.30}La_{0.05}O_2$. NH_3-TPD confirms that the PA catalyst has stronger surface acidity than that of PCZ catalyst. Surface acidity and the chemical state of palladium affect the catalytic behavior of the methanol decomposition. The PCZ catalyst has higher catalytic activity than that of PA catalyst.

Acknowledgments

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant 20773090, 20803049).Young Teachers Foundation of Sichuan University (20091007) and Laboratory and Equipment Management of Sichuan University.

References

[1] O.A. Kutlar, A.T. Çalik, H. Arslan, T. Özaktaş, F. Karaosmanoğlu, [M] World Renewable Energy Congress VI, 2000, p. 2508.
[2] W.H. Cheng, C.Y. Shiau, T.H. Liu, H.L. Tung, J.F. Lu, C.C. Hsu, Appl. Catal. A: Gen. 170 (1998) 215.
[3] Y. Matsumura, K. Kagawa, Y. Usami, M. Kawazoe, H. Sakurai, M. Haruta, J. Chem. Soc.: Chem. Commun. (1997) 657.
[4] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai, M. Haruta, Appl. Catal. A: Gen. 171 (1998) 123.
[5] M.P. Koppor, A. Raj, Y. Matsumura, Micropor. Mesopor. Mater. (44–45) (2001) 565.

[6] G. Mul, A.S. Hirschon, Catal. Today 65 (2001) 69.
[7] A. Gotti, R. Prins, J. Catal. 125 (1998) 302.
[8] S. Imamuraa, T. Higashiharaa, Y. Saitoa, H. Aritania, H. Kanaib, Y. Matsumurac, N. Tsuda, Catal. Today 50 (1999) 369.
[9] C. Yang, J. Ren, Y.H. Sun, Catal. Commun. 2 (2001) 353.
[10] Y.Y. Liu, T. Hayakawa, T. Ishii, M. Kumagai, H. Yasuda, K.S.S. Hamakawa, K. Murata, Appl. Catal. A: Gen. 210 (2001) 301.
[11] H.R. Wang, Y.Q. Chen, Q.L. Zhang, Q.C. Zhu, M.C. Gong, M. Zhao, J. Nat. Gas. Chem 18 (2009) 211.
[12] D.T. Wickham, B.W. Logsdon, S.W. Cowley, C.D. Butler, J. Catal. 128 (1991) 198.
[13] C. Yang, J. Ren, Y.H. Sun, Chin. J. Catal. 22 (2001) 283.
[14] K.P. Sun, W.W. Lu, M. Wang, X.L. Xu, Appl. Catal. A: Gen. 268 (2004) 107.
[15] E. Bekyarova1, P. Fornasiero, J. KasÏpar, M. Graziani, Catal. Today 45 (1998) 179.
[16] P. Fornasiero, J. Kaspar, V. Sergo, M. Graziani, J. Catal. 182 (1999) 56.
[17] A. Bensalem, F. Bozon-Verduraz, V. Perrichon, J. Chem. Soc.: Faraday Trans. 91 (1995) 2185.
[18] C.B. Vincent, Handbook of Monochromatic XPS Spectra [M], XPS International Inc., CA, 1999.
[19] L. Fan, K. Fujimoto, J. Catal. 172 (1997) 238.
[20] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai, M. Haruta, Stud. Surf. Sci. Catal 118 (1998) 83.
[21] W.J. Shen, Y. Matsumura, Phys. Chem. Chem. Phys. 2 (2000) 1519.