

负载型 Pd 三效催化剂:载体 $\text{CeO}_2\text{-ZrO}_2\text{-BaO}$ 的制备及催化性能

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摘要: 制备了不同 BaO 含量的 $\text{CeO}_2\text{-ZrO}_2$ 储氧材料,并以此材料为载体浸渍 H_2PdCl_6 制得三效催化剂。结果表明,不论新鲜还是 1000 °C 老化状态下,以 10% BaO 添加 $\text{CeO}_2\text{-ZrO}_2$ 储氧材料制备的 Pd 三效催化剂活性最佳,起燃和完全转化温度最低。XPS 结果证实,10% BaO 添加,通过稳定 PdO 活性组分并改变其电子环境使得催化剂有最佳活性。而随着 BaO 含量持续增加,Pd 活性组分相对处于较氧化状态。储氧量、低温 N_2 吸附-脱附测试以及 XRD 测试结果均表明 10% BaO 添加的材料储氧量,比表面积以及孔容均最大,而且有适应三效催化的孔径。这些结果均有助于以其制备的 Pd 三效催化剂获得更好的活性以及热稳定性。

关键词: 储氧材料(OSM); 氧化钡; 催化剂; 晶体结构

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Pd Supported Three-Way Catalyst: Preparation of $\text{CeO}_2\text{-ZrO}_2\text{-BaO}$ Support and Catalytic Performance

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Abstract: The three-way catalysts were prepared by impregnating BaO doped $\text{CeO}_2\text{-ZrO}_2$ solid solutions with H_2PdCl_6 . The results show that Pd catalyst prepared by the support with 10wt% BaO has the best activity and the lowest light-off temperature both before and after aging at 1 000 °C for 5 h. The XPS results confirm that a doping of 10% BaO can improve the catalytic activity by stabilizing the active phase of PdO and changing the electronic environment of the active phase of Pd. With more doped BaO, Pd will be at lower oxidation state. The oxygen storage capacity(OSC), low temperature nitrogen adsorption-desorption and XRD tests of the supports show that the support material containing 10% BaO has the largest specific area and pore volume, proper pore diameter and the highest OSC, which can improve the catalytic performance and the thermal stability of Pd three-way catalysts.

Key words: oxygen storage material(OSM); BaO; catalyst; crystal structure

Three-Way-Catalysts(TWCs) have been widely used to control pollutant emissions from gasoline engine-powered vehicles, CeO_2 used to be the key to TWCs because of its oxygen storage-release capacity^[1,2]. But easy sintering of CeO_2 after high temperature aging would

result in catalyst deactivation. This problem has been obviously prevented by doping ZrO_2 into CeO_2 . The doping of ZrO_2 into CeO_2 also helps the oxygen storage material get better oxygen storage capacity and faster oxygen storage/release speed. TWCs with $\text{CeO}_2\text{-ZrO}_2$

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(CZ) solid solution gain better low-temperature catalytic activity^[3-6] due to the higher thermal stability of CZ. As a matter of fact, CZ solid solution becomes the key material to TWCs. Erik Fridell and coworkers^[7] have concluded that catalysts containing BaO have the capacity to store NO_x after studying the NO_x storage capacity over the models of Pt/BaO/Al₂O₃, BaO/Al₂O₃, Pt-Rh/Al₂O₃, and Pt-Rh/BaO/Al₂O₃. The results of Min C N and coworkers^[8] demonstrate that Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1} with thermal stability, high specific surface area and good CO oxidation activity is a better catalyst support. According to the report of Masakazu Iwamoto et al^[9], catalysts containing Mg, Ba and Ca can obviously improve the reduction conversion of NO to N₂. Also, as reported by Annika Amberntsson et al^[10], NO_x can be stored and released by the formation and decomposition of Ba(NO₃)₂. In addition, Pt, Pd and Rh are widely used as the active component of TWCs. Pd is considered to be the most useful one because of its lower price. By doping appropriate amount of BaO into CZ support, Pd can be well dispersed and have excellent catalytic performance.

Here we report the preparation of Pd TWCs catalyst by impregnating BaO doped CZ with H₂PdCl₆, and the corresponding characterization by XRD and XPS. The three-way catalytic activities of Pd TWCs are also studied.

1 Experimental

1.1 Ceria-based compound preparation

The sample of CeO₂-ZrO₂-BaO(the mass fraction of BaO is 0, 0.05, 0.1, 0.15, 0.2 and 0.25 respectively, and CeO₂ shared the same mass fraction with ZrO₂) samples (CZB0, CZB1, CZB2, CZB3, CZB4, CZB5) were prepared by the co-precipitation method from the corresponding chemicals: Ce(NO₃)₃·6H₂O, ZrO(NO₃)₂ and Ba(NO₃)₂ in stoichiometric ratios. The precursors were mixed in an aqueous solution, and then the mixed metal salt solution was added dropwise to a container containing a mixed aqueous solution of ammonia and ammonium carbonate to reach a pH value of 10. The precipitates were filtered, washed, and dried at 105 °C overnight, then were calcined at 600 °C for 5 h. Finally, CeO₂-ZrO₂-BaO powders were obtained.

1.2 Preparation of catalysts

All the catalysts were prepared by impregnation method. The catalysts powders were prepared by impregnating the CeO₂-ZrO₂-BaO powders with H₂PdCl₆ aqueous solutions then dried at 105 °C overnight and calcined at 500 °C for 3 h in air. 3% La(NO₃)₃ and 3% ZrO(Ac)₂ were added as the promoter, also 45wt% water was added, then the mixture was ballmilled to form a slurry. The resulting slurry was coated on a honeycomb cordierite(2.5 cm³, Corning, Shanghai), and the excessive slurry was blown away by compressed air, then the washcoat was dried and calcined at 500 °C for 3 h in air. Finally, a monolithic catalyst was obtained. The catalysts prepared by CZB0, CZB1, CZB2, CZB3, CZB4, CZB5 were labeled as Ca0, Ca1, Ca2, Ca3, Ca4, Ca5, respectively. In all samples, the noble metal loadings were 2 g·L⁻¹.

1.3 Catalytic activity measurements

The three-way catalytic activity was evaluated in a multiple fixed bed continuum flow micro reactor by passing a gas mixture that was similar to that of an exhaust from a gasoline engine. Before entering a blender, the gases were regulated using mass-flow controllers. The simulated exhaust was a mixture with O₂, CO (0.86%), C₃H₈(600×10⁻⁶), NO(1 200×10⁻⁶), CO₂(12%), H₂O(10%) balanced by N₂. The gas space velocity was 30 000 h⁻¹. The concentrations of CO, C₃H₈ and NO were analyzed on-line by a five-component analyzer FGA24100 before and after the stimulated gas passed the micro-reactor. The activity of the fresh catalysts was taken from 200 to 360 °C while that of the aged catalysts were taken from 280 to 440 °C.

1.4 Characterization

Low temperature nitrogen adsorption-desorption of the catalysts was carried out using Autosorb-ZXF-05 (Xibei Chemical Engineering Institute, China). The samples were evacuated 3 h at 623 K, and then cooled to 77 K using liquid N₂ while N₂ adsorption was measured.

Oxygen storage capacity(OSC) is measured by oxygen pulse. 200 mg sample was first reduced in H₂ at 400 °C for 40 min, and then the sample was cooled down to 200 °C. With oxygen pulse of 16.4 μmol O₂ im-

pulses, the excessive oxygen which cannot be stored was measured by TCD. When oxygen was no longer stored, the amount of all the stored oxygen was calculated.

Powder X-ray diffraction (XRD) was performed with a D/Max-rA Rotating Anode Diffractometer(Rigaku International Corp. Japan), using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) using graphite curved-crystal monochromator, operated at 40 kV and 100 mA with proportional counter detection for 2θ from 10° to 90° . The crystalline phases were identified by comparison with the reference data(PDF) from the International Center for Diffraction Data (ICDD)

XPS were recorded with a Karatos XSAM 800 Spectrometer(United Kingdom), using Mg $K\alpha$ -radiation, operated at 13 kV and 20 mA. The binding energy of electrons was corrected by C1s(284.8 eV).

2 Results and discussion

2.1 XRD studies

Fig.1 shows the XRD patterns of the fresh and aged supports. Bae Jong Sung and coworkers^[11] have reported that when ZrO_2 and BaO are simultaneously introduced into CeO_2 , a stable solid solution is obtained after calcination at 1000°C . In that way, CZ solid solution is stabilized. Therefore, when BaO is added to the material by co-precipitation, BaO and CZ can form CeO_2 - ZrO_2 -BaO (CZB) solid solution. In our study, the XRD peaks of all CZB containing BaO are with a slight shift from that of CZB0. The shift indicates the unit cell parameter changes because BaO comes into the lattice of CZ. The stability of CZB at high temperature is better than that of CZ solid solution^[12]. The XRD patterns of fresh CZB1 and CZB2 show a stable phase of CZB and all BaO in this system is in the cell of CZ. The absence of free BaO phase in CZB1 and CZB2 also implies the formation of CZB solid solution^[13]. The XRD patterns of the fresh CZB3, CZB4 and CZB5 with more than 15% BaO show the presence of $BaCO_3$, indicating the sepa-

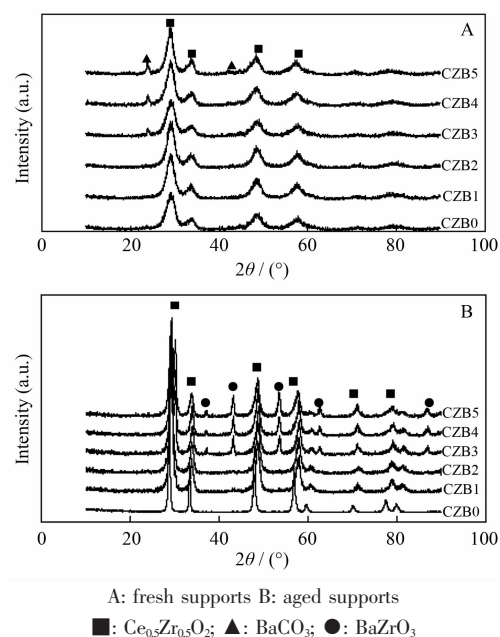


Fig.1 XRD patterns of supports

ration of the single phase. According to this result, the $BaZrO_3$ is visualized in aged CZB3, CZB4 and CZB5. The $BaCO_3$ phase transforms to $BaZrO_3$ by reaction with ZrO_2 after calcination at 1000°C for 5 h. In addition to the phase separation, phase transformation from $BaCO_3$ to $BaZrO_3$ is another cause for the instability of the system.

The grain size was calculated using the Scherrer equation with corrections for instrumental line broadening and the half width of the diffraction peak of the $Ce_{0.5}Zr_{0.5}O_2$ (111) plane. As shown in Tab.1, crystallite size of CZ in CZB0 is 3.9 nm, and it is 3.8 nm, 4.4 nm, 3.4 nm, 3.9 nm and 4.5 nm in CZB1, CZB2, CZB3, CZB4 and CZB5, respectively. No significant difference is observed among the crystallite size of all the fresh samples. As phase separations occur in CZB3 CZB4 and CZB5, these samples could not be the most stable one. And we can see that CZB0 without BaO sees the greatest change in crystallite size after aging. Thus, better stability from BaO doping can be confirmed. At the same time, among the left two, CZB2 exposed less change on its crystallite size. As the structure of CZB2

Table 1 Crystallite size of CeO_2 - ZrO_2 -BaO in all the supports

Sample	CZB0	CZB1	CZB2	CZB3	CZB4	CZB5
Fresh / nm	3.9	3.8	4.0	3.4	3.9	4.5
Aged / nm	13.1	10.1	9.6	10.1	9.9	8.7

shows the least change, surely, the catalyst prepared by CZB2(Ca2) will show the best tolerance to high temperature aging. With the results of activity test, we can say the better thermal stability of Ca2 due to the stability of CZB2.

2.2 BET surface area, pore volume, pore size and OSC test

The results of low temperature nitrogen adsorption-desorption are listed in Table 2. As can be seen, the specific area continually decreases with the BaO content in the system. The specific area of CZB0 is 90 m²·g⁻¹, and it is 96, 82, 80, 73 and 64 m²·g⁻¹ for CZB1, CZB2, CZB3, CZB4 and CZB5, respectively. After aging, the specific surface area of CZB2 changes least among the three CZBs with one single phase. The other two, CZB0 and CZB1 have the largest specific surface area for the fresh sample but the smallest one after aging. This means the two will easily sinter after aging, and are instable. It is clear that the presence of 10% BaO significantly improves the thermal stability of the CeO₂-ZrO₂-BaO system. The other three, CZB3, CZB4 and CZB5 show a similar stability on specific surface area after aging. In the other hand, doping of BaO also affects the pore volume of the samples. Fresh CZB2 also has the highest pore of 0.22 mL·g⁻¹, with more BaO doped in the materials, the pore volume decreases from 0.22 mL·g⁻¹ of CZB with lower content of BaO to 0.16 mL·g⁻¹ of CZB with higher content of BaO. The largest pore volume of CZB2 after aging shows its excellent

thermal stability. The average pore sizes of the fresh and aged samples are shown in Table 2 too. CZB0, CZB1 and CZB2 with one single phase have smaller change on average pore size than that of CZB3 CZB4 and CZB5 with two different phases in them. The greater change of mesopore will surely result in the encapsulating of the active compounds Pd in the supported catalyst system, which is the main reason to the deactivation of the catalysts. According to this, the smaller change of the mesopore is one of the keys to the stability of the catalysts. According to the pore diameter of the fresh and aged samples, CZB1 and CZB2 are suitable to be used as support of TWC. But only 10 m²·g⁻¹ specific area of CZB1 after aging takes a great disadvantage. Rossignol et al.^[12] reported that the textural properties of CZ mixed oxides prepared by co-precipitation were the best. Furthermore, in our study, it is found that the textual property is affected evidently by the content of BaO. Olivier Demoulin^[14] et al. reported that the loading of low content of noble metal on supports slightly changed the textural property of the supports. Thus, the result in Table 2 also shows the textural property of this Pd/CeO₂-ZrO₂-BaO catalytic system. The target of our research is to prepare a better nano-material with good thermal stability and to make the material ready to be used in TWC as support. Considering both the structure and textural parameters, CZB2 may be the most stable one related to the most stable catalyst of Ca2.

Table 2 Textural and OSC results for the supports

	CZB0		CZB1		CZB2		CZB3		CZB4		CZB5	
	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged
BET _s /(m ² ·g ⁻¹)	90	11	96	10	82	18	80	17	73	22	64	16
V _s /(mL·g ⁻¹)	0.21	0.07	0.2	0.07	0.22	0.08	0.17	0.06	0.18	0.07	0.16	0.07
R _m /nm	8.8	5.9	7.7	6.2	8.9	6.2	7.4	4.4	7.7	4.7	8.5	5.1
OSC/(μmol·g ⁻¹)	420	270	460	334	430	277	360	264	283	215	278	176

Note: BET_s=BET specific surface area; V_s=Pore volume; R_m=average pore diameter; OSC=Oxygen storage capacity

According to Table 2, CZB0 exhibits nearly the same OSC as that of CZB2 before and after aging, but fresh CZB1 shows the largest OSC of 460 μmol·g⁻¹. The effect of small amount of doped BaO is found to improve the OSC of CZ system. With the increasing of BaO content, the OSCs of all the supports show continuously

decreasing from 360 μmol·g⁻¹ of CZB3 to 278 μmol·g⁻¹ of CZB5. Among the five supports containing BaO, the redox couple of Ce(III)~Ce(IV) is of greater quantity on oxygen storage due to the higher content of CeO₂. CZB2 has the OSC of 430 μmol·g⁻¹, which is slightly decreased in comparison to CZB1 but still much higher

than the other three CZBs with BaO. The second phase in this $\text{CeO}_2\text{-ZrO}_2\text{-BaO}$ system will affect the migration of the oxygen anions and the formation of oxygen vacancy, which makes the $\text{Ce(III)}\sim\text{Ce(IV)}$ redox couple less efficient. The $\text{Ce(III)}\sim\text{Ce(IV)}$ redox couple became less efficient after aging, the amount of oxygen vacancy decreases and becomes less movable, and all OSCs of these samples decrease. They also follow the rule that the increase in BaO will result in the decrease of OSC.

2.3 XPS characterization

XPS characterization results are shown in Table 3.

Table 3 Binding energy of $\text{Pd}3d_{5/2}$ in fresh Ca2 and Ca4

Sample	Ca2	Ca4
Binding energy/eV	336.44	336.31

The binding energy (BE) of pure $\text{Pd}3d_{5/2}$ for metal Pd is 335.8 eV, while that in pure PdO is 336.3 eV. In Ca2, the BE of $\text{Pd}3d_{5/2}$ electron is 336.44 eV and shifts to 336.31 eV for Ca4. This shift implies a significant electron environment change of palladium when BaO content in support is increased, resulting in the formation of lower palladium oxidation state with the survival of a few metallic palladium species. According to the work of Kobayashi and coworkers^[15], the electron environment of Pd on CZ changes due to the electron transfer from Pd to the support CZ. Here, alkaline-earth metals have stronger ability pushing electron towards Pd. Therefore, Pd in fresh Ca4 with 20% BaO has lower oxidation state than that of Ca2 with 10% BaO. According to the report^[16,17], PdO is the active site of TWC. For this reason, the more PdO is stabilized in the TWC system, the better is the TWC activity. This means that higher Pd oxidation state leads to higher catalytic per-

formance. In this study, Ca2 is chosen due to its higher Pd oxidative state and better catalytic activity.

2.4 Catalytic performance

Table 4 shows the three-way catalytic performance for the CO and C_3H_8 oxidation and NO reduction conversion under a stoichiometric simulated exhaust-mixed gas over the fresh and aged catalysts. $T_{50\%}$ value ($T_{50\%}$ corresponding to the temperature at which 50% conversion of a given compound is achieved) and $T_{90\%}$ value ($T_{90\%}$ corresponding to the temperature at which 90% conversion of a given compound is achieved) are listed. In Table 4, one can see that both the $T_{50\%}$ and $T_{90\%}$ of C_3H_8 over the fresh catalyst prepared by BaO containing support first decrease then increase with the increase in BaO content. And that over fresh Ca2 are 265 °C and 300 °C respectively, which are the lowest among the five catalysts. In Table 4, catalyst without BaO shows a slight worse activity than Ca1, which shows that the BaO doping is beneficial for the conversion of C_3H_8 . In this $\text{Pd/CeO}_2\text{-ZrO}_2\text{-BaO}$ catalytic system, $\Delta T(T_{90\%}-T_{50\%})$ of C_3H_8 is the highest of the three pollutants, but those over the five catalysts are less than 40 °C. The small differences between $T_{50\%}$ and $T_{90\%}$ of C_3H_8 over the five catalysts imply a fact that soon after light-off, the complete conversion of the pollutant is reached. After aging, Ca2 still has the lowest $T_{50\%}$ and $T_{90\%}$ for C_3H_8 . And the difference of $T_{50\%}$ and $T_{90\%}$ between the five catalysts is much larger than that under the fresh condition. Actually, the $T_{50\%}$ and $T_{90\%}$ of C_3H_8 over aged Ca2 are 368 °C and 416 °C, respectively. ΔT over aged Ca2 is larger than that over fresh catalyst, due to the damage of high temperature aging. But, the ΔT rises to 48 °C which is less than 50 °C.

Table 4 Light-off temperature of catalysts

Sample	$T_{50\%}$ for catalyst / °C				$T_{90\%}$ for catalyst / °C			
	C_3H_8		NO	CO	C_3H_8		NO	CO
	Fresh	Aged	Fresh	Fresh	Fresh	Aged	Fresh	Fresh
Ca0	288	396	260	230	320	437	300	269
Ca1	286	407	230	210	315	433	247	236
Ca2	265	368	218	200	300	416	236	225
Ca3	275	390	221	221	303	440	237	242
Ca4	280	416	228	220	309	440	243	237
Ca5	285	425	233	228	319	—	246	256

This means that the temperature property of this catalyst is not bad after aging.

NM(noble metal)/CZ always plays the role to remove NO and CO in the three-way catalytic system^[2]. In Table 4, the $T_{50\%}$ and $T_{90\%}$ of NO and CO over the fresh catalyst is also shown. The nearly 40 °C higher $T_{50\%}$ and $T_{90\%}$ of NO over CaO with no BaO doping shows us the effect of BaO doping on NO conversion. According to the report^[7], BaO doping makes the catalytic system able to store NO and activate NO in order to remove it. This effect is proved in this study. The changing rule of $T_{50\%}$ and $T_{90\%}$ of NO and CO over the fresh catalyst is the same as that of C₃H₈, first decrease then increase as the BaO content increases, and that over CaO is the lowest, 218 °C and 236 °C for NO and 200 and 225 °C for CO, respectively, which are lower than the regular three-way catalytic system^[18]. And the ΔT of these two reactants is even less than that of C₃H₈. All these show good temperature properties of this catalytic system. After aging, all CO and NO are completely converted on aged catalysts during the test temperature range. That means $T_{90\%}$ for NO and CO are less than 300 °C. The aged catalysts with a specific surface area less than 20 m² · g⁻¹ also have good conversion on NO and CO. This means that OSC of the catalysts and the chemical environment of the active compounds are the key to remove NO and CO.

3 Conclusions

The doping of less than 10% BaO in the Ce-Zr system will form the CZB solid solution, more BaO doping will cause the formation of a new phase. The material is most stabilized by 10% BaO doping owing to a stable texture. The stable texture helps the Pd catalyst hold its active components dispersion and maximize its high temperature tolerance. BaO changes the electron environment of Pd. With more BaO doping, activitive PdO gets into lower oxidation state. And that makes the catalyst less efficient. Most importantly, the doping of BaO into Ce-Zr system has great influence on the catalytic activity, especially NO conversion. TWC prepared by 10% BaO doping CZ has the best catalytic

activity on the conversion of C₃H₈ and thermal stability. But with BaO doping, NO can be stored over the catalyst and well converted on all the fresh and aged catalysts. According to the high OSC, CO is also well converted.

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