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Article

Effects of ZnO content on the performance of Pd/Zr_{0.5}Al_{0.5}O_{1.75} catalysts used in lean-burn natural gas vehicles

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ABSTRACT

Mixed oxides obtained by adding varying amounts of ZnO into Zr_{0.5}Al_{0.5}O_{1.75} were used as supports to prepare 1.5% Pd catalysts. The catalyst activity and H₂O tolerances of the catalysts were evaluated in a gas mixture simulating the exhaust of lean-burn natural gas-fueled vehicles. The catalysts were further characterized by N₂ adsorption-desorption, X-ray diffraction, H₂ temperature programmed reduction and X-ray photoelectron spectroscopy. The catalytic activity was greatly influenced by ZnO contents in Zr_{0.5}Al_{0.5}O_{1.75} support. The catalyst containing 15% ZnO exhibited a light-off temperature and complete conversion temperature for CH₄ in the absence of H₂O of 278 and 314 °C, respectively; while these same values in the presence of H₂O were 342 and 371 °C, respectively. These results indicate that this combination of materials offers excellent catalytic activity at low temperature and also exhibits significant H₂O tolerance.

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1. Introduction

The complete catalytic oxidation of CH₄ under lean-burn conditions (in which the amount of oxygen exceeds the stoichiometric ratio) has received gradually increasing attention in recent years and one of the most likely applications of this technology is in lean-burn natural gas vehicles (NGVs) [1,2]. Because of the rapid development of China's economy and the associated increasing demand for energy, there is a need to find new energy sources to partially replace oil. For the purposes of powering automobiles, natural gas is the most mature alternative fuel since sizeable reserves and the appropriate technology exist. Compressed natural gas (CNG) vehicles are currently very popular in Europe and are also growing rapidly in China, espe-

cially buses and taxis [3]. With regard to exhaust emissions, natural gas vehicles (NGVs) have many advantages, including low emissions of CO, NO_x, hydrocarbons (HC) and particulate matter, which has practical significance in terms of reducing fog and haze and addressing air pollution in large cities [4]. However, the primary pollutant emissions of NGVs still exceed current emission regulations and so the exhaust requires treatment to meet these standards.

Under lean-burning conditions, CO can be readily converted to CO₂ and the NO_x emissions of NGVs fall below China's Standard V limit because of the low engine temperatures. In general, the main difficulty is the incomplete combustion of CH₄ in the exhaust gas, since this compound has a pronounced greenhouse effect (35 times greater than that of CO₂ over 20 years)

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[5]. CH₄ is the most stable HC and is very difficult to oxidize catalytically to CO₂ and H₂O under the specific conditions found in automobile exhaust. Compared with HC from gasoline, the oxidation of CH₄ requires higher temperatures and a better catalyst. Unfortunately, the temperature of lean-burning exhaust gas is relatively low (300–550 °C) [5], and therefore one of the most significant challenges is the oxidation of CH₄ at low temperatures (300 °C).

Due to the high activity and stability, Pd and Pt are widely used as the active components of exhaust purification catalysts [6–8], however, under lean-burn conditions, Pd shows higher activity than Pt [7,8]. To improve the utilization of these precious metals, they are usually dispersed as microcrystalline or polycrystalline form within the nano-pores of support materials, Al₂O₃ and ZrO₂ are two of the most widely used support materials [9–13]. The initial activity of Pd/Al₂O₃ catalyst is very high, but the conversion rate gradually declines over time. In contrast, Pd/ZrO₂ catalysts are not as active but do not exhibit the same level of reduced performance during using [14].

The activity of these catalysts is greatly inhibited by the presence of H₂O, which is primarily due to the adsorption of H₂O and various reactants species on active sites and to the slow generation of Pd(OH)₂ via the reaction of PdO and H₂O under certain conditions [15]. Thus another difficulty associated with these catalysts is increasing their H₂O tolerance [2,5], and it has been widely reported that modification of the supports and the active components can assist in this regard. In a previous study, Pd/Zr_{0.5}Al_{0.5}O_{1.75} catalyst was prepared that exhibited excellent low-temperature activity and outstanding H₂O resistance [16]. When such catalysts are intended to meet improved emission regulations, they must also work with higher space velocities, higher concentrations of H₂O and lower concentrations of CO. Thus, to further improve the catalyst activity and the H₂O tolerance, ZnO is added to the Zr_{0.5}Al_{0.5}O_{1.75} to prepare a Pd/ZnO-Zr_{0.5}Al_{0.5}O_{1.75} catalyst that has improved activity compared with the original Pd/Zr_{0.5}Al_{0.5}O_{1.75}.

In this work, Pd/ZnO-Zr_{0.5}Al_{0.5}O_{1.75} catalysts with differing ZnO contents were prepared to examine the effects on the catalytic activity and H₂O tolerance. Various techniques, including N₂ adsorption-desorption, X-ray diffraction (XRD), H₂ temperature programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS), were employed to characterize the results of varying the ZnO content on the physicochemical properties of the prepared catalysts.

2. Experimental

2.1. Catalyst preparation

ZnO-Zr_{0.5}Al_{0.5}O_{1.75} catalysts with different ZnO contents were prepared by a co-precipitation method. Following the co-precipitation process, the precipitates were boiled, filtered, dried and then calcined at 950 °C for 3 h. The nominal ZnO contents (mass fraction) were 0, 5%, 10%, 15%, 20% and 30% in the Zr_{0.5}Al_{0.5}O_{1.75} supports, and these materials were termed Mat-1, Mat-2, Mat-3, Mat-4, Mat-5, and Mat-6, respectively.

1.5% Pd catalysts were prepared by impregnation of sup-

ports with Pd(NO₃)₂ solutions. The catalysts thus obtained were dried at 120 °C overnight and then calcined at 550 °C for 3 h. The prepared catalysts were ball-milled with water to a homogeneous slurry and then spread on a honeycomb cordierite (2.5 cm³, Corning) to obtain monolithic catalysts. The coated catalysts were dried overnight at 120 °C and calcined at 550 °C for 3 h. These were termed Cat-1, Cat-2, Cat-3, Cat-4, Cat-5 and Cat-6 according to their support material had been applied.

2.2. Catalytic activity measurements

Catalytic activities were assessed using a multiple fixed-bed continuous flow micro-reactor, by passing a gas mixture simulating the exhaust emissions from a lean-burning NGV through the reactor. The simulated exhaust without H₂O consisted of 0.075% CH₄, 0.10% CO, 5.0% O₂, 12.0% CO₂ and/or 12.0% H₂O, with N₂ as the balance. The gas space velocity in the reactor was 50000 h⁻¹. The CH₄ concentration was determined using an on-line gas chromatograph equipped with an FID detector both before and after the simulated gases passed through the reactor.

2.3. Sample characterization

The BET specific surface areas and pore-size distribution curves (generated using BJH theory) of supports were obtained by N₂ adsorption-desorption at -196 °C on a Quantachrome automated surface area and pore-size analytical apparatus (Autosorb SI, Quantachrome, Boynton Beach, FL, USA). Prior to measurements, samples were degassed under vacuum for at 300 °C for 3 h.

H₂-TPR was carried out using a quartz tubular micro-reactor, in which 100 mg samples (20–40 mesh) were pretreated in a flow of 10% O₂ in N₂ (30 ml/min) at 450 °C for 45 min, then cooled to room temperature in N₂. Reduction was subsequently performed under a flow of 5%H₂/N₂ (20 ml/min) between room temperature and 200 °C at a heating rate of 10 °C/min. The consumption of H₂ was monitored by TCD.

The crystal structures of the samples were determined by power XRD on D/Max-rA using Cu K_α radiation (λ = 0.15406 nm) and operating at 40 kV and 25 mA. The XRD data were recorded for 2θ values between 10° and 70° with an interval of 0.06°.

XPS data were acquired with a spectrometer (XSAM-800, KRATOS Co.) with Al K_α radiation and UHV, calibrated internally using carbon deposit C 1s binding energy at 284.8 eV.

3. Results and discussion

3.1. Catalyst activity

The activity for the complete oxidation of CH₄ over the series of Pd catalysts are shown in Fig. 1 (for gas compositions without H₂O). The values of *T*₅₀ (the light-off temperature at which CH₄ conversion reaches 50%), *T*₉₀ (the complete conversion temperature at which CH₄ reaches 90%) and Δ*T* (the temperature range from *T*₅₀ and *T*₉₀) are obtained from Figs. 1 and

Fig. 1. CH₄ conversion versus temperature over the series of catalysts. Reaction conditions: 0.075% CH₄, 0.10% CO, 5.0% O₂, 12.0% CO₂, and N₂ as the balance at GHSV = 50000 h⁻¹.

2 and are summarized in Table 1. As can be seen from Table 1, the T_{90} values increase in the following order: Cat-1 < Cat-4 < Cat-3 < Cat-2 < Cat-5 < Cat-6. Within these six temperature values, the highest value is 165 °C higher than the lowest, indicating that the addition of ZnO has a significant effect on the activity of the catalysts. At ZnO levels below 15%, the differences in catalytic activity are very small and the value of T_{90} varies by about 10 °C, while adding ZnO at above 15% sharply decreases the catalytic activity. The T_{50} values of the Cat-1, Cat-2 and Cat-4 samples are all 278 °C, showing excellent low-temperature activity higher than the previously reported results [17,18]. We have previously systematically researched Pd catalysts supported on both pure and modified Al₂O₃ and ZrO₂ [19,20]. Using the same simulated exhaust and a space velocity of 30000 h⁻¹, T_{50} and T_{90} values of Pd/Al₂O₃ are 309 and 347 °C, respectively; while these for Pd/ZrO₂ are 353 and 437 °C, respectively. In this study, however, T_{90} is less than 320 °C and T_{50} is below 285 °C when ZnO is less than 15%, meaning that the present results are superior to our previous findings. The ΔT values for Cat-1 and Cat-3 are 32 and 33 °C, respectively, which suggest that CH₄ reaches complete conversion immediately at light-off and thus these catalysts exhibit remarkably good temperature properties [21]. The ΔT values achieved here are significantly smaller even than that of the HC obtained from gasoline vehicles.

The catalyst activity results obtained with simulated exhaust containing 12% H₂O for CH₄ complete oxidation over the series of catalysts are presented in Fig. 2. As seen in Table 1, the T_{90} values increase in the following order: Cat-4 < Cat-3 < Cat-2 < Cat-5 < Cat-1 < Cat-6, indicating that the catalytic activity and H₂O tolerance are both improved at ZnO levels below 20%. Within these catalysts, Cat-4 exhibits the highest T_{90} value, with 42 °C less than Cat-1. In our previous study [16], Pd/Zr_{0.5}Al_{0.5}O_{1.75} shows excellent resistance to H₂O in terms of its catalyst activity and has T_{90} and T_{50} values of 356 and 325 °C at GHSV = 30000 h⁻¹ and with 10% H₂O. The activity undergoes an obvious decline and its T_{90} and T_{50} values are increased to 413 and 383 °C when the GHSV was raised to 50000 h⁻¹, the H₂O content is increased to 12.0% and the proportion of CO is

Fig. 2. CH₄ conversion versus temperature over the series of catalysts in a simulated exhaust gas: 0.075% CH₄, 0.10% CO, 5.0% O₂, 12.0% CO₂, 12.0% H₂O and N₂ as the balance at GHSV = 50000 h⁻¹.

Table 1

Light-off temperatures (T_{50}), complete conversion temperatures (T_{90}) and ΔT for methane oxidation over the catalysts.

Catalyst	ZnO content* (%)	T_{50} (°C)		T_{90} (°C)		ΔT^{**} (°C)	
		Without H ₂ O	With H ₂ O	Without H ₂ O	With H ₂ O	Without H ₂ O	With H ₂ O
Cat-1	0	278	383	310	413	32	30
Cat-2	5	278	365	320	397	42	32
Cat-3	10	285	350	318	388	33	38
Cat-4	15	278	342	314	371	36	29
Cat-5	20	312	365	360	400	48	35
Cat-6	30	396	468	475	505	79	37

* Mass fraction of ZnO in the catalyst support (Zr_{0.5}Al_{0.5}O_{1.75}).

** $\Delta T = T_{90} - T_{50}$.

decreased from 0.40% to 0.10%. Compared with these prior results, further improvements in the catalytic activity under higher GHSV and H₂O content have been realized with Pd/ZnO-Zr_{0.5}Al_{0.5}O_{1.75}, which shows T_{90} and T_{50} values of 371 and 342 °C following the addition of 15% ZnO with H₂O content from 10% to 15% and GHSV from 30000 to 100000 h⁻¹, simulating lean-burning NGVs exhaust. Therefore this material shows significant promise in terms of practical applications since its catalytic activity has been demonstrated under conditions close to actual exhaust environments.

3.2. Textural properties

Because of the high GHSV values (30000–100000 h⁻¹) associated with the exhaust purification catalytic reaction, the textural properties of supports are one of their most important aspects. The textural properties greatly affect not only mass transfer but also the dispersion of the noble materials. BJH pore-size distribution curves of supports are shown in Fig. 3, compared with Mat-1, the pore-size distributions of Mat-2 and Mat-3 are obviously increased to between 10 and 20 nm, meaning that the textural properties of the supports are enhanced by the addition of ZnO. As the amount of ZnO is increased, the peak area continually decreases, demonstrating that the pores volumes are reduced along with the high-temperature resistance of the material. The textural property data

Fig. 3. Pore distributions of the supports.

for the supports are summarized in Table 2. The specific surface area and average pore diameter are obviously enhanced at ZnO levels below 10%, and are optimized at 10% ZnO, increasing from 66 m²/g and 0.26 ml/g to 92 m²/g and 0.32 ml/g, respectively. Both the specific surface area and the average pore diameter gradually decrease above 15% ZnO and reach minimums of 20 m²/g and 0.11 ml/g for Mat-6 (30% ZnO). This occurs because pores about 10 nm in size tend to rapidly sinter, leaving only a few pores about 20 nm in size.

3.3. XRD results

Figure 4 presents the XRD patterns of the various Pd catalysts. No Pd or PdO peak is seen, which is primarily attributed to the low loading of Pd (1.5%), the small size of the Pd particles (below the detection limit) and the presence of PdO in a highly dispersed microcrystalline form on the surface of support pores. Three peaks at $2\theta = 30.5^\circ$, 50.5° and 60.2° are all attributed to $\text{Zr}_{0.48}\text{Al}_{0.52}\text{O}_{1.74}$ mixed oxides, which is consistent with the theoretical composition of $\text{Zr}_{0.5}\text{Al}_{0.5}\text{O}_{1.75}$. The $\text{Zr}_{0.48}\text{Al}_{0.52}\text{O}_{1.74}$ peak intensity is not obviously changed and there is no ZnO peak when ZnO content is less than 10%, indicating that ZnO enters into the lattice of $\text{Zr}_{0.48}\text{Al}_{0.52}\text{O}_{1.74}$ or that the microcrystalline state is below the XRD detected limit. When the ZnO content is more than 15%, the intensities of diffraction peaks gradually strengthen and the peaks sharpen, hence the crystal state in the material increases in size and becomes more perfect. In addition, obvious peaks attributed to monolithic ZrO_2 (at $2\theta = 28.3^\circ$ and 31.4°) and ZnO ($2\theta = 36.8^\circ$ and 55.6°) become evident. These changes indicate that the high-temperature (950 °C) resistance of the materials is re-

Fig. 4. XRD patterns of the Pd catalysts.

duced with increasing in the ZnO content above a certain amount as a new crystalline phase appears.

3.4. H₂-TPR results

Pd-catalyzed oxidation of CH₄ occurs through a redox mechanism [22] and it is widely accepted that the main active phase during the CH₄ oxidation is either PdO or PdO_x ($0 < x < 2$). The catalysts will therefore demonstrate excellent activity during the complete oxidation of CH₄ when Pd is present as PdO and PdO_x. The redox of supported PdO, which is greatly influenced by its interactions with supports, is therefore closely related to the catalytic activity.

H₂-TPR experiments are carried out to evaluate the relationship between the catalytic activity and the reducibility of the supported catalysts. Figure 5 shows the H₂-TPR profiles of the series of catalysts. The reduction peaks are obtained only below 200 °C attributed to the reduction of PdO. The negative peaks at 50–80 °C can be attributed to H₂ from the decomposition β -phase Pd hydride [23,24]. It is well known that H₂ can be adsorbed in Pd at room temperature to form Pd hydride under partial pressures of H₂ greater than 1.32 kPa [25]. Dispersed Pd catalysts (as opposed to bulk Pd) can adsorb less H₂ and the ratio of H₂ to Pd is thus a linear function of Pd dispersion, such

Fig. 5. H₂-TPR profiles of the Pd catalysts.

Table 2

Textural properties of the supports.

Sample	ZnO content (%)	S_{BET} (m ² /g)	Pore volume (ml/g)	Pore diameter (nm)
Mat-1	0	66	0.26	16.0
Mat-2	5	82	0.31	15.0
Mat-3	10	92	0.32	14.2
Mat-4	15	54	0.22	16.2
Mat-5	20	41	0.24	23.6
Mat-6	30	20	0.11	21.8

that the amount of adsorption approaches zero as dispersion reaches 100% and increases with increasing Pd particle size [26,27]. As shown in Fig. 5, the negative peaks initially decrease and then increase as the ZnO content is elevated. In the case of Cat-4, the negative peak is the smallest, which indicates that this material had the highest metal dispersion. The addition of ZnO thus produces obvious changes in the Pd dispersion. The improved dispersion associated with a certain ZnO range should improve the activity of the catalyst. Generally speaking, the reduction of pure PdO occurs at about 55 °C and the reduction of supported PdO appears at about 100 °C [23]. With the exception of Cat-5 and Cat-6, the reduction temperatures of the catalysts are all between 80 and 100 °C. Higher reduction temperatures are associated with stronger interactions between PdO and the support, which can facilitate the transfer of oxygen, resulting in a greater proportion of cationic PdO. Compared with Cat-4, the other catalysts exhibit lower active component dispersions and larger particle sizes, which lead to higher reduction temperatures.

3.5. XPS results

Catalysts with differing ZnO contents were characterized by XPS to investigate the effects of ZnO contents on surface properties. As shown in Fig. 6, two peaks are evident, attributed to Pd 3d, Pd 3d_{5/2} and Pd 3d_{3/2}. The Pd 3d_{5/2} binding energy is about 336.5 eV, suggesting that the Pd exists primarily as Pd²⁺ [28]. The Pd 3d binding energy may be slightly shifted because of the strong interaction between the supports and PdO. The binding energy of Pd 3d_{5/2} in Cat-6 (336.6 eV) is the highest among the six catalysts, while Pd 3d_{5/2} of Cat-4 (335.9 eV) is the lowest. There are three effects that may lead to low binding energy: PdO may be completely reduced to metal Pd, the PdO surface may be covered with a layer of Pd or the PdO may have a metallic Pd core [3]. In the case of Cat-4, a portion of the PdO has been oxidized to PdO_x (1 < x < 2) with oxygen defects around the PdO. The activity for the complete oxidation of CH₄ is related to oxygen defects on the PdO_x surface because PdO_x with strong Pd-O bonds can enhance the amount of oxygen available for the reaction [11,29]. In this study, PdO is the main active component during the complete oxidation of CH₄, while a

Fig. 6. Pd 3d XPS spectra of the catalysts.

Table 3

Surface atomic concentrations in the catalysts.

Catalyst	ZnO content (%)	Surface atomic concentration (%)				
		Pd	Zn	Zr	Al	O
Cat-1	0	0.60	—	13.20	20.40	65.80
Cat-2	5	0.65	0.76	12.35	19.94	66.30
Cat-3	10	0.54	0.64	11.03	20.35	67.44
Cat-4	15	0.53	0.54	12.85	18.90	67.18
Cat-5	20	0.50	3.75	11.30	18.82	65.63
Cat-6	30	0.66	12.28	4.44	16.25	62.37

lesser quantity of reduced PdO is also available to increase the catalytic activity. Epling et al. [14] find that metal Pd could facilitate the dissociative adsorption of CH₄, which is the rate-determining step in the complete oxidation; this is the primary reason for the high catalyst activity of the Cat-4. The surface contents of all atoms are listed in Table 3. It is evident that the surface ZnO levels increase in concert with the theoretical amounts, although all the actual values are lower than the theoretical ones. The surface ZnO content is only about 1% compared with a theoretical value of 15%, which indicates that Zn(NO₃)₂ is not transformed to Zn(OH)₂ by the co-precipitation method.

4. Conclusions

The supported Pd catalysts exhibit the highest catalytic activity when 15% ZnO is added to the Zr_{0.5}Al_{0.5}O_{1.75} support. The Mat-4 supported Pd catalyst can suitably purify lean-burning NGVs exhaust. The activity of the catalysts is greatly influenced by the contents of ZnO, and the catalyst containing 15% ZnO shows a light-off temperature (*T*₅₀) and complete conversion temperature (*T*₉₀) for CH₄ of 278 and 314 °C in the absence of H₂O, respectively; and *T*₅₀ and *T*₉₀ values of 342 and 371 °C in the presence of H₂O, respectively. These results indicate that this catalyst provides excellent catalytic activity at low temperatures and also possesses significant H₂O tolerance.

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Graphical Abstract

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Pd/15% ZnO/Zr_{0.5}Al_{0.5}O_{1.75} exhibited $T_{50} = 278\text{ }^{\circ}\text{C}$ and $T_{90} = 314\text{ }^{\circ}\text{C}$ in the absence of H₂O and $T_{50} = 342\text{ }^{\circ}\text{C}$ and $T_{90} = 371\text{ }^{\circ}\text{C}$ in the presence of H₂O. This material thus shows excellent catalytic activity at low temperature and exhibits significant H₂O tolerance.

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ZnO添加量对Pd/Zr_{0.5}Al_{0.5}O_{1.75}催化剂净化稀燃天然气汽车尾气性能的影响

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摘要: 以掺杂不同含量ZnO的Zr_{0.5}Al_{0.5}O_{1.75}为载体, 制备了系列1.5% Pd催化剂. 在模拟稀燃天然气汽车尾气条件下, 测试了催化剂的活性和抗水性, 并用N₂吸附-脱附、X射线衍射、H₂程序升温还原和X射线光电子能谱等手段对催化剂进行了系统表征. 研究表明, ZnO的添加及添加量对催化剂的活性和抗H₂O性有明显影响, 其中以ZnO添加量为15%时制备的复合氧化物为载体的催化剂活性最佳. 当模拟尾气中不含H₂O时, 该催化剂对甲烷的起燃温度(T_{50})和完全转化温度(T_{90})分别为278和314 $^{\circ}\text{C}$; 在含H₂O时, 该催化剂的 T_{50} 和 T_{90} 分别为342和371 $^{\circ}\text{C}$.

关键词: 钯; 铝; 锌; 钼; 复合氧化物; 稀燃; 天然气汽车; 水抑制

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1. 前言

近年来, CH₄在稀燃(燃料在氧气量超过化学计量比的燃烧方式)条件下的完全氧化逐渐受到人们的重视^[1], 而其中最主要的一个应用是稀燃天然气汽车尾气的净化^[2]. 中国正处于高速发展阶段, 对石油的需求量逐年增加, 但石油资源的储量是有限的, 因此需要寻找新能源来部分替代石油, 以减少石油的用量. 就汽车燃料来说, 天然气是目前储量最多且技术最为成熟的替代燃料. 压缩天然气(CNG)汽车, 目前在欧洲很受欢迎^[3]. 中国天然气汽车的数量也正在快速增长, 尤其像城市的公交车和出租车. 从尾气排放的角度考虑, 天然气汽车有很多优势, 如CO, NO_x和HC的排放量大大降低, 且几乎没有颗粒物^[4], 这对降低空气中PM_{2.5}, 减少大城市的雾霾天气, 解决城市空气污染, 具有实际意义. 但是, 即使清洁能源的天然气汽车, 其主要污染物的排放量仍然超过目前的排放法规, 也必须经过尾气后处理才能达到排放要求.

在稀燃条件下, CO容易转化, 且排气温度较低, NO_x排放量在国V排放限以下, 因此, 主要难点是尾气中未完全燃烧, 具有强温室效应的CH₄ (20年期的温室效应是CO₂的35倍^[5])的净化. CH₄是最稳定的HC化合物, 通过催化的手段在汽车尾气特定的条件下, 与O₂发生完全氧化反应生成CO₂和H₂O的难度很大. 相对于汽油车尾气中HC化合物的净化, CH₄的氧化需要更高的温度和性能更优异的催化剂, 然而, 稀燃CNG汽车的尾气温度仅有300–550 °C^[5]. 因此, CH₄在低温(300 °C)条件下的完全氧化是研究的难点之一.

Pd和Pt具有较高的活性和稳定性, 被广泛用于汽车尾气净化催化剂的活性组分^[6–8]. 在稀燃条件下, Pd比Pt具有更高的活性^[7,8]. 为提高贵金属的利用率, 通常将活性组分以微晶或多晶的形式高度分散在载体的孔道体系中. Al₂O₃和ZrO₂是目前报道最多的两类载体材料^[9–13]. 反应初期Pd/Al₂O₃对CH₄氧化具有很高的活性, 但随着时间的延长, 会逐渐下降; 虽然Pd/ZrO₂活性不如Pd/Al₂O₃, 但稳定性更高^[14].

H₂O对催化剂的活性有很强的抑制作用, 它与反应物竞争吸附催化剂的活性位, 还会与活性组分在一定条件下反应, 缓慢生成活性很低或几乎没有活性的Pd(OH)₂^[15]. 因此, 人们通过调变载体与活性组分来研究水蒸气对催化剂的抑制作用^[2,5]. 本课题组曾制备了对CH₄低温活性和抗H₂O性能优异的

Pd/Zr_{0.5}Al_{0.5}O_{1.75}催化剂^[16], 但为研究能满足更高排放法规的催化剂时, 将其在更高空速, 更高浓度H₂O, 更低浓度CO的条件下测试时发现, 催化剂活性下降较为明显. 为了进一步提高催化剂的活性和抗H₂O性, 我们通过多种方法调变载体和活性组分的物化性能, 均未取得明显效果. 近期研究发现, 将ZnO添加到Zr_{0.5}Al_{0.5}O_{1.75}中, 制备的Pd-ZnO/Zr_{0.5}Al_{0.5}O_{1.75}催化剂, 抗H₂O性较Pd/Zr_{0.5}Al_{0.5}O_{1.75}催化剂明显提高.

本文详细考察了ZnO的添加量对Pd/Zr_{0.5}Al_{0.5}O_{1.75}催化剂低温活性及抗H₂O性的影响, 并采用N₂吸附-脱附、X射线衍射(XRD)、H₂程序升温还原(H₂-TPR)和X射线光电子能谱(XPS)对催化剂进行了表征, 系统研究了ZnO含量的变化对催化剂物化性能的影响.

2. 实验部分

2.1. 催化剂的制备

采用共沉淀法制备不同ZnO添加量的Zr_{0.5}Al_{0.5}O_{1.75}复合氧化物. 将ZrOCO₃用HNO₃溶解后与Al(NO₃)₃和Zn(NO₃)₂按一定比例配成混合盐溶液, 以氨水为沉淀剂进行并流滴定沉淀. 滴完后经洗涤, 干燥, 焙烧后即得所需载体材料. 材料1为Zr_{0.5}Al_{0.5}O_{1.75}, 记为Mat-1, 在Mat-1中分别加入5%, 10%, 15%, 20%和30%的ZnO, 所得材料依次记为Mat-2, Mat-3, Mat-4, Mat-5, Mat-6.

以Mat-1–Mat-6为载体, 采用等体积浸渍法将Pd(NO₃)₂溶液浸渍于其上, 经120 °C干燥一晚后, 550 °C焙烧3 h, 可得负载型Pd催化剂粉末. 之后, 将催化剂粉末调成浆料, 涂覆于体积约2.5 cm³圆柱体的堇青石(Corning)基体小样上, 后经120 °C干燥一夜, 550 °C焙烧3 h, 得到整体式催化剂. 对应的催化剂依次记为: Cat-1, Cat-2, Cat-3, Cat-4, Cat-5和Cat-6.

2.2. 催化剂活性评价

催化剂活性测试在自组装的专用多路固定床连续流动微型反应器中进行, 各路气体流量分别用质量流量计控制, 并在进入反应器之前混合均匀. 模拟气组成为: 0.075% CH₄, 0.10% CO, 5.0% O₂, 12.0% CO₂, 或含12% H₂O, N₂为平衡气体, 空速(GHSV)为50000 h⁻¹. 反应前后的CH₄含量用配有氢火焰离子检测器(FID)的气相色谱检测.

2.3. 催化剂及材料的表征

采用美国康塔公司的全自动比表面及孔径测试仪(Autosorb SI)在–196 °C进行N₂吸附-脱附测试载体材料的结构性能. 测试前样品在300 °C下抽真空预处理3 h.

H₂-TPR实验在自组装微型反应装置上进行. 称取20–40目样品100 mg置于U型石英管中, 在N₂(30 ml/min)中加热至450 °C, 保持45 min后降至室温, 再通入5%H₂–95%N₂ (20 ml/min)混合气, 并以10 °C/min的速率升温至200 °C, TCD检测.

XRD实验在日本理学D/Max-rA型旋转阳极X射线衍射仪上进行, 激发光源为Cu K α ($\lambda = 0.15406$ nm), 扫描范围: $2\theta = 10^\circ$ – 70° .

XPS: 在英国Kratos公司XSAM-800型电子能谱仪上进行, 采用Al K α 激发源, 13 kV的高压和20 mA的电流. 以C 1s (284.8 eV)来标定各元素的电子结合能数值.

3. 结果与讨论

3.1. 催化剂活性测试结果

图1为模拟尾气中不含H₂O时各催化剂上CH₄转化率随温度变化曲线. 由此得到各催化剂上CH₄转化的起燃温度(T_{50} , 即CH₄转化率达到50%时的温度), 完全转化温度(T_{90} , 即对CH₄转化率达到90%时的温度)和从起燃到完全转化的温度区间 ΔT ($\Delta T = T_{90} - T_{50}$)的数值. 表中数据显示, T_{90} 的高低顺序为: Cat-1 < Cat-4 < Cat-3 < Cat-2 < Cat-5 < Cat-6, 这6个温度最高温与最低温差为165 °C, 可见ZnO的添加及添加量对催化剂的活性影响非常明显. ZnO的添加量小于15%时, 各催化剂的活性差异较小, T_{90} 的变化值在10 °C内; 但当ZnO的添加量大于15%时, 各催化剂的活性急剧下降. 系列催化剂中, Cat-1, Cat-2和Cat-4的 T_{50} 值均等于278 °C, 表现出优异的低温活性, 优于文献[17,18]报道结果. 我们曾对纯Al₂O₃、纯ZrO₂及其改性材料为载体的单Pd催化剂做过系统的研究^[19,20], 在模拟尾气组成相同, 测试空速为30000 h⁻¹时, Pd/Al₂O₃的 T_{50} 和 T_{90} 分别为309和347 °C; Pd/ZrO₂的分别为353和437 °C; 而本文制备的ZnO改性的Zr_{0.5}Al_{0.5}O_{1.75}, 当ZnO的添加量小于15%时, 制备的Pd催化剂在50000 h⁻¹条件下, T_{90} 低于320 °C, T_{50} 低于285 °C, 优于上述结果^[19,20]. 除Cat-5和Cat-6外, 其它催化剂上 ΔT 均小于50 °C, 其中Cat-1和Cat-3的 ΔT 甚至分别仅为32和33 °C小于大多文献数据, 甚至比容易转化的汽油车尾气中HC化合物的温度区间还要小^[21].

图2为模拟尾气中加入12%H₂O后, 各催化剂上CH₄转化率随温度的变化曲线. 表1列出了各催化剂 T_{50} , T_{90} 和 ΔT 三个特征温度值. 可以看出, 各催化剂的 T_{90} 大小顺序为: Cat-4 < Cat-3 < Cat-2 < Cat-5 < Cat-1 < Cat-6, 即当ZnO的添加量不超过20%时, 各催化剂抗H₂O性能明显

提高, 其中Cat-4的抗H₂O性最好, T_{90} 较Cat-1的 T_{90} 降低42 °C. 本实验室制备的Pd/Zr_{0.5}Al_{0.5}O_{1.75}催化剂^[16], 在空速为30000 h⁻¹和10.0%H₂O存在下, 具有优异的抗H₂O性, T_{90} 和 T_{50} 分别为356和325 °C. 当模拟尾气的空速从30000升至50000 h⁻¹, H₂O含量从10%升至12.0%, CO浓度从0.40%降到0.10%时, 催化剂活性明显下降, T_{90} 和 T_{50} 分别升至413和383 °C, 均升高55 °C以上. 在此基础上, 本文为进一步提高催化剂在更高空速, 更高水蒸气含量下的抗H₂O性, 成功制备了ZnO改性的Zr_{0.5}Al_{0.5}O_{1.75}负载的单Pd催化剂, 当ZnO添加量为15%时, 活性最好, T_{90} 和 T_{50} 分别为371和342 °C. 稀燃CNG汽车尾气中H₂O含量为10%–15%, 空速在30000–100000 h⁻¹, 因此, 研究高水蒸气含量和高空速条件具有高活性的催化剂, 更具实际意义.

3.2. 材料的织构性能

汽车尾气净化的催化反应是在高空速(30000–100000 h⁻¹)下进行的, 而高空速对载体材料的织构性能有着较高的要求. 载体材料的织构性能不仅对传质, 并且对贵金属的分散也有很大影响. 图3是载体材料的BJH孔径分布曲线. 由图可见, 对于Mat-1, Mat-2和Mat-3孔径小于10 nm的小孔数量几乎没有变化, 但10–20 nm间的孔数量明显增加, 可见, 一定量ZnO的加入, 是有利于载体材料织构性能提高的, 但随着ZnO的继续添加, 孔径分布图中的峰面积逐渐减小, 孔体积变小, 孔烧塌严重, 载体的抗高温老化性能下降. 表2列出了各载体材料的织构性质. 可以看出, 当ZnO添加量小于10%时, 样品比表面积和孔体积随着ZnO含量的增加而明显提高; ZnO添加量为10%时, 样品的织构性能最好, 其比表面和孔容分别从66 m²/g和0.26 ml/g提高到92 m²/g和0.32 ml/g. 当ZnO添加量超过15%后, 比表面和孔体积均开始下降; 至30%时, 其比表面和孔体积分别仅为20 m²/g和0.11 ml/g, 这主要是由于10 nm左右的孔急剧烧塌减少, 变成少量的大孔所致.

3.3. XRD结果

图4是系列催化剂的XRD谱. 由图可见, 未在图谱中出现Pd或PdO的衍射峰, 这主要是由于Pd的负载量较低, 颗粒尺寸小于XRD的检测限, Pd以微晶的形式高度分散于载体孔道表面. 各样品在 $2\theta = 30.5^\circ$, 50.5° 和 60.2° 出现的衍射峰属于Zr_{0.48}Al_{0.52}O_{1.74}, 与理论上制备的Zr_{0.5}Al_{0.5}O_{1.75}复合材料成分一致. 当ZnO含量小于10%时, Zr_{0.48}Al_{0.52}O_{1.74}衍射峰的强度变化不大, 也未观察到ZnO衍射峰, 说明ZnO进入了Zr_{0.48}Al_{0.52}O_{1.74}晶格内或者

形成的微晶小于XRD检测限;但当ZnO的添加量大于15%后,衍射峰逐渐增强且峰形变得尖锐,晶粒逐渐长大且晶形更加完善,并且开始逐渐出现明显单斜相的 ZrO_2 ($2\theta = 28.3^\circ, 31.4^\circ$)和 ZnO ($2\theta = 36.8^\circ, 55.6^\circ$)衍射峰,这说明当ZnO含量增加到一定量后,材料的抗高温(950 °C焙烧)老化能力降低,开始出现分相。

3.4. H_2 -TPR结果

Pd催化剂对 CH_4 的完全氧化是通过氧化-还原机理进行的^[22],研究表明, Pd对 CH_4 的完全氧化活性相是PdO,且当Pd以PdO和 PdO_x ($1 < x < 2$)存在时,具有最好的活性^[5];此外,活性组分的氧化-还原性对催化剂的活性起至关重要的作用,而载体与活性组分间相互作用是影响催化剂氧化-还原性的主要因素。 H_2 -TPR可以表征催化剂的还原性能,探究催化剂活性与活性组分还原性能间的关系。图5是各Pd催化剂的 H_2 -TPR谱。在室温–200 °C区间内的还原峰均归属为PdO的还原。在50–80 °C,各催化剂均有一个明显的倒峰,这是在常温下饱和吸附的 H_2 随温度升高而脱附所致^[23,24]。室温下,当 H_2 的分压超过1.32 kPa, H_2 会吸附到Pd的表面,形成Pd- H_2 ^[25]。Pd催化剂对 H_2 的吸附量与其分散度有关: Pd总量相同时,分散度越高,饱和吸附的 H_2 量越少,当Pd分散度达100%时, H_2 吸附量为0^[26,27]。如图5所示,随着载体中ZnO添加量的增加, Pd与 H_2 形成脱附峰面积先减小后增大,其中以Cat-4的最小,说明其吸附的 H_2 量最少,分散度最高。还可以看出, ZnO的添加能明显调变活性组分在载体表面的分散性,而一定范围内活性组分分散度的增加可以提高催化活性,与本文结果是一致的。研究表明,在PdO粒径相当条件下,纯PdO的还原温度仅为55 °C,而负载型的则在100 °C左右,可见, Pd与载体间的相互作用越强,还原温度越高^[23]。此外,催化剂的分散度越低, Pd的颗粒就越大,还原温度也会升高。除Cat-5和Cat-6外,其余4个催化剂的还原峰温均在80–100 °C,从Cat-1到Cat-4, Pd的分散度依次减小,可见,载体与活性组分间相互作用则是依次增强。载体与活性组分间的强相互作用可以促进氧的移动,有利于PdO以阳离子形态存在。相对于Cat-4, Cat-5和Cat-6上Pd分散度明显降低,其颗粒度增

大,还原温度升高。

3.5. XPS结果

为了考察ZnO对催化剂表面性质的影响,图6给出了不同ZnO含量的催化剂XPS谱。对于负载型Pd催化剂, Pd 3d轨道结合能对应有两个峰,分别是Pd 3d_{5/2}和Pd 3d_{3/2}。前者的电子结合能在336.5 eV附近,属于典型的Pd²⁺^[28]。由于负载型Pd催化剂载体与PdO间存在强相互作用,结合能会略有偏移。对于这6个催化剂, Cat-6的Pd 3d_{5/2}的电子结合能最大,为336.6 eV;而Cat-4的最小,是335.9 eV。结合能变小的原因有: (1) PdO完全被还原成金属态的Pd; (2) PdO上覆盖了一层Pd; (3) PdO的内部有金属Pd核^[3]。在这6个催化剂中,即使是Pd 3d_{5/2}偏移最大的Cat-4,也仅仅只降低了0.6 eV,这很可能是由于有部分氧缺陷的 PdO_x ($1 < x < 2$)在PdO的表面或周围形成。 CH_4 的完全氧化活性与 PdO_x 表面的氧缺陷有关, PdO_x 含有强的Pd-O键,并在反应过程中可提高氧浓度^[11,29]。PdO是 CH_4 完全氧化的活性组分,但部分还原的PdO可以促进催化剂的活性。Epling等^[14]研究发现,金属态Pd的存在可以促进 CH_4 的解离吸附,而该步被认为是 CH_4 完全氧化的速率控制步骤,这也是Cat-4具有高活性的一个主要原因。表3列出了各催化剂表面原子含量。由表可见,表面ZnO含量随着添加量的增加逐渐增加,但均小于理论值。当ZnO含量低于15%时,其表面Zn原子含量均小于1%,这很可能是由于在共沉淀法制备的过程中, $\text{Zn}(\text{NO}_3)_2$ 并未以 $\text{Zn}(\text{OH})_2$ 形式完全沉淀下来。

4. 结论

制备了不同ZnO添加量的 $\text{Zr}_{0.5}\text{Al}_{0.5}\text{O}_{1.75}$ 复合氧化物载体,当ZnO含量达到15%时,其负载的Pd催化剂活性最高,该载体材料的织构性能也可以很好地满足稀燃CNG汽车尾气净化催化剂的要求。ZnO含量对 CH_4 低温活性和抗 H_2O 性影响很大,当ZnO添加量15%时,催化剂表现出较好的低温活性和优异的抗 H_2O 性,在GHSV = 50000 h⁻¹条件下,无 H_2O 时, CH_4 的 T_{50} 和 T_{90} 分别为274和315 °C,表现出优异的低温活性;含 H_2O 时,该催化剂对 CH_4 的 T_{50} 和 T_{90} 仅提高到342和371 °C,具有很好的抗 H_2O 性。