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Article

Ultrasonic-assisted fabrication and catalytic activity of CeZrAl oxide-supported Pd for the purification of gasohol exhaust

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ABSTRACT

CeZrAl oxides (CZA) using as the support of Pd catalyst for purification of gasohol exhausts are synthesized by co-precipitation assisted by ultrasonic vibration. CZA are characterized by surface analysis, X-ray diffraction, temperature-programmed reduction by hydrogen, oxygen storage capacity (OSC), and X-ray photoelectron spectroscopy. The results show that ultrasonic vibration promotes the formation of smaller, more uniform pores in CZA, which is beneficial to the dispersion of Pd species. Ultrasonic vibration can also improve the OSC and uniformity of the composition of CZA on its surface and in bulk. Catalytic tests demonstrate that ultrasonic treatment of CZA widens the window of the full use of oxygen from 0–0.64% to 0–1.16% of Pd-CZA catalysts in the purification of gasohol exhaust, and decreases the light-off temperature of ethanol, propane, and carbon monoxide by 30, 28, and 24 °C, respectively. Moreover, the interaction between Pd species and CZA can enhance the reaction of NO with propane and ethanol.

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1. Introduction

Using environmentally friendly alternative fuels is one of the ways to solve the problem of increasing air pollution from automobile exhaust. Ethanol is the most widely used alternative fuel because it contains oxygen, is reproducible, shows good anti-knock characteristics, and can reduce the emission of CO and hydrocarbons (HCs) [1–3]. However, the use of alcohol-based fuels for automobiles will lead to new organic pollutants such as unburned ethanol, acetaldehyde, acetone, acetic acid, and ethers [4–7], which can be involved in photochemical air pollution. In addition, acetaldehyde is also a toxic compound [8,9]. The purification of organic contaminants produced by alcohol-based fuels has not yet been paid sufficient attention in

many countries. It is well known that three-way catalysts (TWCs) are the most effective way to treat the exhaust from gasoline vehicles. However, existing TWCs have not yet been used to purify gasohol exhaust.

According to reports, the support of TWCs determines the catalyst performance and life [10]. At present, CeZrAl oxides (CZA) are the most studied support for exhaust catalysts because of their excellent textural properties, thermal stability, and oxygen storage capacity (OSC) [11–15]. The performance of CZA is closely related to its method of preparation [10,16,17]. Currently, CZA is typically prepared by co-precipitation [18–22] or sol-gel [17,23] methods. Meanwhile, ultrasonic treatment has been successfully used in nanomaterial synthesis to make particles more uniform, increase

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specific surface area, shorten reaction time, and purify phases [24–26]. However, ultrasonic treatment has not yet been used in the synthesis of CZA. As far as the active component of automobile exhaust catalysts is concerned, palladium (Pd) exhibits excellent catalytic activity for the combustion of HCs, CO, and ethanol [27–31], so it was used here as the active species to purify gasohol exhaust.

The present work uses ultrasonic treatment to synthesize CZA. The textural, structural, and redox properties, Pd dispersion, and OSC of CZA samples prepared with and without ultrasonic treatment are investigated by surface analysis, X-ray diffraction (XRD), temperature-programmed reduction by hydrogen (H_2 -TPR), oxygen pulse adsorption, and X-ray photoelectron spectroscopy (XPS). The obtained CZA oxides are also used as supports for Pd catalysts in the purification of gasohol exhausts. The catalytic activities of Pd catalysts supported on different CZA samples are investigated in detail.

2. Experimental

2.1. Preparation of CZA

All chemicals (analytical grade) were supplied by Chengdu Ke Long Chemical Reagent Factory and used as received. $ZrOCO_3$ was first dissolved in concentrated nitric acid, and then mixed with an aqueous solution of $Ce(NO_3)_3$ and $Al(NO_3)_3$. The molar ratio of Ce:Zr:Al in the resulting solution was 2:3:5. Ammonia was slowly titrated into the above solution until pH = 10 under the vigorous agitation. The suspension was stirred at 70 °C for 1 h, and then filtered, washed with distilled water, and dried at 120 °C overnight. For comparison, the same suspension was treated under ultrasonic vibration for 1 h, and then filtered, washed with distilled water, and dried at 120 °C overnight. CZA samples were obtained after calcination in air at 600 °C for 3 h. Samples prepared without and with ultrasonic treatment are denoted as CZA-S and CZA-U, respectively.

2.2. Preparation of Pd catalysts

CZA-S or CZA-U was added to aqueous solutions of $Pd(NO_3)_2$ to obtain catalysts designated Pd-CZA-S and Pd-CZA-U, respectively. The nominal Pd loading was 2.0 wt%. The resulting powder was dried at 120 °C for 24 h, and then added to desired water and ground to form a slurry. The slurry was coated on honeycomb cordierite (2.5 cm³, Corning Ltd., New York, USA), and the precious metal content was 0.70 g/L. The sample was dried and calcined at 550 °C for 3 h in air to obtain the monolithic Pd-CZA-S or Pd-CZA-U catalyst.

2.3. Characterization

The texture of CZA was characterized by the Brunauer-Emmett-Teller (BET) method using an SSA-4200 analyzer (Builder Co., Beijing, China) at –196 °C following degassing at room temperature for 2 h. The structure of CZA was determined by powder XRD on an X-ray diffractometer (DX-1000, Dandong, China) in the range of $2\theta = 10^\circ$ – 80° using $Cu K\alpha$ radi-

ation ($\lambda = 0.154$ nm), and operating at 40 kV and 25 mA. H_2 -TPR experiments were performed in a quartz apparatus equipped with a thermal conductivity detector (TCD) to monitor the consumption of H_2 . Each sample (100 mg) was first pre-treated at 500 °C for 1 h under a flow of N_2 (30 cm³/min). After cooling, the samples were heated from room temperature to 800 °C with a 5% H_2 -95% N_2 mixed gas (flow rate of 30 cm³/min, temperature ramp 10 °C/min), and the consumption of H_2 was detected by a TCD. The total OSC was measured by oxygen pulse adsorption. Each sample (200 mg) was reduced at 550 °C for 60 min under a flow of H_2 of 30 cm³/min and then cooled to 200 °C under a flow of N_2 (20 cm³/min). Then, a pulse of oxygen (27.0 μ mol) was injected into the sample until no consumption of O_2 was detected by the TCD. The dispersion of Pd was evaluated by CO pulse chemisorption at room temperature assuming a chemisorption stoichiometry of 1:1 between CO and Pd. Before chemisorption, Pd catalyst (300 mg) in a U-type quartz tube was first activated at 500 °C in a flow of 5% H_2 -95% N_2 for 1 h. The remnant H_2 was removed under a flow of Ar at 550 °C for 30 min, and then the sample was cooled to room temperature. XPS measurements were carried out on a spectrometer (Kratos XSAM 800, Manchester, UK) equipped with a Mg $K\alpha$ source. The binding energy (BE) correction was performed using the C 1s peak of adventitious carbon at 284.8 eV as a reference.

2.4. Catalytic tests

The catalytic activity of Pd-CZA-S or Pd-CZA-U was evaluated by the purification of simulated gasohol exhaust in a fixed-bed continuous flow microreactor. The simulated exhaust contained an adjustable mixture of CO (1.1%–1.2%), propane (C_3H_8 ; 0.06–0.07%), nitric oxide (NO; 0.07%–0.08%), O_2 (0–15%), ethanol (0.03%–0.04%), and N_2 (balance) using mass-flow controllers. Typically, the monolithic catalyst was placed in a quartz tube reactor and activated in air at 350 °C for 1 h. After the temperature was adjusted to the desired value, the simulated exhaust gas with a gas hourly space velocity (GHSV) of 30000 h^{–1} was passed through the catalyst bed. The tested reaction temperature range was 100–400 °C. The organic products were analyzed by gas chromatography (GC-2000, Shanghai, China) equipped with a flame ionization detector (FID) and Porapak Q column. The amounts of CO, HCs, NO, O_2 , and CO_2 were analyzed online using a five-component vehicle exhaust gas analyzer (FGA-4001, Foshan, Guangdong, China).

3. Results and discussion

3.1. Texture of CZA samples

The textural properties of the supports are presented in Table 1. CZA-U possesses smaller pore volume and pore size (0.27 cm³/g and 6.14 nm, respectively) than CZA-S (0.39 cm³/g and 9.08 nm, respectively). This shows that ultrasonic treatment promotes the formation of small pores, resulting in reduced pore volume, and increased surface area.

Table 1

Textural properties and OSC of supports and Pd dispersion of catalysts.

Sample	A_{BET} (m^2/g)	V_{p} (cm^3/g)	D_{mean} (nm)	OSC ($\mu\text{mol}/\text{g}$)	Pd dispersion (%)	Pd particle size (nm)
CZA-S	169.9	0.39	9.08	263	39.0	1.99
CZA-U	174.6	0.27	6.14	291	52.2	1.48

A_{BET} : specific surface area; V_{p} : pore volume; D_{mean} : average pore diameter.

Fig. 1. Pore distribution curves of the supports. (1) CZA-S; (2) CZA-U.

Figure 1 shows the pore-size distribution curves of the supports. The pore distribution is very narrow and homogeneous for CZA-U, probably because of the cavitation-induced effect of ultrasonic treatment [32,33]. Propagation of acoustic vibrations through the liquid CZA hydroxide precursor can cause cavitation bubbles to form. These bubbles can concentrate the acoustic energy within very small spatial domains in a medium [32], which makes pores smaller and uniform.

3.2. Pd dispersion in the catalysts

The dispersion of Pd in the Pd-CZA catalysts is also listed in Table 1. Pd-CZA-U possesses a higher Pd dispersion (52.2%) with a smaller Pd particle size (1.48 nm) than Pd-CZA-S, probably because of the higher surface area of CZA-U and the smaller Pd particles interacting strongly with the support [34]. A good correlation is observed between Pd dispersion and catalytic activity, and the better dispersion of Pd should be one of the reasons for the excellent activity of Pd-CZA-U [35].

3.3. XRD

XRD patterns of the supports (Fig. 2) revealed that both samples exhibit the characteristic peaks of a cubic ceria-zirconia (CZ) solid solution. No obvious characteristic diffraction peaks for aluminum species are observed, which is attributed to the incorporation of Al^{3+} into the CZ lattice [36,37]. CZA-U shows broader diffraction peaks than CZA-S, indicating a decrease of crystallite size [38] resulting from the effect of ultrasonic vibration during its preparation. Using the half-band width of the reflection peak at $2\theta = 29^\circ$ characteristic of the (111) crystal plane for a CZ solid solution, the crystal size of CZA-U can be calculated with the Scherrer formula as 3.5 nm,

Fig. 2. XRD patterns of the supports. (1) CZA-S; (2) CZA-U.

which is smaller than that of CZA-S (4.1 nm). This result further confirms that ultrasonic treatment induces the formation of smaller CZA particles, which is consistent with the results of BET analysis.

3.4. H_2 -TPR

The H_2 -TPR profiles of the supports (Fig. 3(a)) show that both CZA-S and CZA-U have two main H_2 consumption peaks at about 450 and 550 $^\circ\text{C}$ (denoted as α and β) that are attributed to the reduction of surface and subsurface Ce^{4+} , respectively [39]. CZA-U has a larger total peak area than CZA-S and especially a more intense α peak, indicating that more Ce species are present on the surface of CZA-U. As the surface Ce increases, the OSC of CZA improves, which is in accordance with the OSC results in Table 1. Meanwhile, an increase of the reduction temperature of Ce species in CZA-U is related to strengthening

Fig. 3. H_2 -TPR profiles of the supports (a) and catalysts (b). (1) CZA-S; (2) CZA-U; (3) Pd-CZA-S; (4) Pd-CZA-U.

Table 2

Binding energy (eV) of core electrons of elements in the supports and catalysts.

Sample	Ce 3d _{5/2}		Zr 3d _{5/2}	Al 2p	Pd 3d _{5/2}	O 1s		
	Ce ⁴⁺	Ce ⁿ⁺				Π ₁	Π ₂	Π ₃
CZA-S	882.7	—	181.4	74.0	—	529.1	530.4	531.7
CZA-U	882.9	—	181.8	73.8	—	529.4	530.7	532.0
Pd-CZA-S	882.7	886.1	181.8	74.1	336.7	530.0	531.2	532.3
Pd-CZA-U	882.3	884.4	181.8	74.1	336.4	529.9	531.3	532.6

of Ce-O formed under ultrasonic treatment.

Obviously, the presence of Pd lowers the reduction temperature significantly, indicating that metal-support interactions occur between Pd and CZA (Fig. 3(b)). This phenomenon is often interpreted in terms of the well-known spillover of hydrogen from Pd to Ce [40]. The H₂-TPR profiles of the catalysts (Fig. 3(b)) show a large H₂ consumption peak below 100 °C, which is ascribed to the reduction of PdO and species related to PdO-CeO₂ interactions [41]. Moreover, the reduction temperature of PdO on CZA-U is about 27 °C lower than that of Pd-CZA-S, indicating that Pd supported on CZA-U is reduced more easily because of the smaller particles of CZA [42]. The Pd-CZA-U catalyst exhibits a higher H₂ consumption peak related to Pd species, indicating there is more PdO on this support because ultrasonic-assisted synthesis improves the dispersion of CZA [43] and increases the concentration of Ce species, as mentioned above. Apparently, ultrasonic vibration treatment during the preparation of the CZA support can significantly affect the redox properties of the Pd catalyst.

3.5. XPS

XPS measurements were obtained to further investigate the properties of the supports and catalysts. The BE data for Pd, Ce, and O is listed in Table 2. The BE of Ce 3d_{5/2} for both supports was about 882.7 eV, indicating Ce species are mainly in the form of Ce⁴⁺ [44]. However, the presence of Pd in the catalysts can lead to the presence of Ce species at 886.1 and 884.4 eV. The former is assigned to Ce³⁺ [45], and the latter corresponds to Ce in CePd₃ [46] caused by the strong interaction between small PdO particles with Ce in CZA-U. It has been reported that the BE of PdO and metallic Pd⁰ are 336.8 and 335.1–335.3 eV, respectively [47,48]. In this work, the BE of Pd 3d_{5/2} for Pd-CZA-S and Pd-CZA-U are 336.7 and 336.4 eV, respectively. These values indicate that Pd is partially oxidized, which probably corresponds to a dispersed state [49]. Meanwhile, three different oxygen bands can be discerned at 529.1–530.0, 530.4–531.2, and 531.7–532.5 eV. The band at 529.1–530.0 eV can be assigned to oxygen species bonded to Ce (denoted as Π₁)

[35,50]. The other two peaks at 530.4–531.2 and 531.7–532.5 eV are assigned to lattice oxygen (denoted as Π₂) and surface hydroxyl groups (denoted as Π₃) [35], respectively. From Table 2, the presence of Pd increases the BE of oxygen species at Π₁, Π₂, and Π₃, which is a result of the interaction between Pd and the supports.

The surface atomic ratios are shown in Table 3. The oxygen species in CZA-U can transfer from Π₁ and Π₃ to Π₂ during ultrasonic treatment, resulting in a higher OSC for CZA-U as mentioned above. Another noticeable point is that the measured ratio of Ce/Zr for CZA-U is equal to the theoretical one, indicating that ultrasonic vibration is beneficial to forming a uniform surface and bulk composition of CZA. Meanwhile, the ratios of Pd/Ce, Pd/(Ce+Zr+Al), and Pd/O in Pd-CZA-U are all greater than those in Pd-CZA-S, indicating that more Pd species are exposed on the surface of Pd-CZA-U than in Pd-CZA-S. This result is consistent with the results of Pd dispersion and H₂-TPR discussed above.

3.6. Purification of gasohol exhaust

3.6.1. Effect of O₂ concentration

The effects of the O₂ concentration in gasohol exhaust on the conversion of CO, C₃H₈, NO, and ethanol at 350 °C over Pd-CZA-S and Pd-CZA-U and O₂ use were investigated. As shown in Fig. 4, NO is completely transformed when the gasohol exhaust lacks O₂, indicating that NO mainly acts as the oxidant for the oxidation of CO, C₃H₈, and ethanol over both catalysts in fuel-rich conditions. However, NO conversion decreased rapidly when the O₂ concentration was above a certain value, showing that O₂ exhibits a stronger oxidation capacity than NO. Therefore, the presence of O₂ in high concentration hinders the removal of NO. At the same time, the O₂ concentration window for the full use of O₂ over Pd-CZA-U (0–1.16%) is broader than that over Pd-CZA-S (0–0.64%). This result is assigned to the higher OSC of Pd-CZA-U. Moreover, the conversions of CO, C₃H₈, NO, and ethanol over Pd-CZA-U are also higher than those over Pd-CZA-S in the presence of O₂. Overall, the Pd catalyst supported on CZA synthesized by ultrasonic

Table 3

Surface atomic ratios of supports and catalysts obtained from XPS.

Sample	Π ₁ :Π ₂ :Π ₃	Pd/Ce	Pd/(Ce+Zr+Al)	Pd/O	Ce ⁿ⁺ /Ce ⁴⁺	Ce/Zr	
						XPS	Calculated
CZA-S	25.2:42.5:32.3	—	—	—	—	0.43	0.67
CZA-U	22.1:46.2:31.7	—	—	—	—	0.67	0.67
Pd-CZA-S	30.8:46.6:22.6	0.29	0.014	0.007	0.511	—	—
Pd-CZA-U	29.4:47.5:23.1	0.59	0.022	0.012	0.365	—	—

Fig. 4. Conversion of ethanol, C_3H_8 , CO, and NO at different O_2 concentrations. (a) Pd-CZA-S; (b) Pd-CZA-U.

treatment exhibits excellent catalytic performance for the purification of gasohol exhaust.

3.6.2. Effect of reaction temperature

Figure 5 presents the effect of reaction temperature on the conversion of C_3H_8 , CO, NO, and ethanol over Pd-CZA-S and Pd-CZA-U. The temperature at which a conversion reaches 50% (T_{50}) is used as an index of catalytic activity. Pd-CZA-U exhibits lower T_{50} towards ethanol, C_3H_8 , and CO than Pd-CZA-S by 30, 28, and 24 °C, respectively. This shows that Pd-CZA-U exhibits higher catalytic activity than Pd-CZA-S, probably because Pd is better dispersed and more Pd species are exposed on the sur-

face of CZA-U. Moreover, a rapid increase of NO conversion can be observed in the temperature range of 150–240 °C, in which the CO conversion increases remarkably. This result indicates that the reaction $CO + 2NO \rightarrow N_2 + CO_2$ can take place over Pd-CZA-S promoted by the Ce^{3+} species detected by XPS, which is consistent with previously reported results [51]. However, NO conversion begins to decrease over 240 °C because CO can react completely with O_2 . Therefore, Pd-CZA-S shows better catalytic activity for NO at low temperature. The reduction of NO over Pd-CZA-U mainly occurs in the temperature range of 250–350 °C, along with increasing conversion of ethanol and C_3H_8 , so NO conversion may be caused by the two reactions $C_3H_8 + 2NO + 4O_2 \rightarrow N_2 + 3CO_2 + 4H_2O$ and $C_2H_5OH + 2NO + 2O_2 \rightarrow N_2 + 2CO_2 + 3H_2O$.

4. Conclusions

CZA synthesized by co-precipitation assisted by ultrasonic treatment exhibits better textural, OSC, and redox properties than that prepared without exposure to ultrasound. Ultrasonic treatment improves the uniformity of the surface and bulk composition of CZA, increasing the bonding between Ce, Zr, and O. A Pd catalyst supported by a CZA sample prepared by ultrasonic treatment exhibited higher catalytic activity towards the conversion of ethanol, C_3H_8 , CO with T_{50} decreased by 30, 28, and 24 °C, respectively, compared with those of a catalyst on a support prepared without ultrasonic treatment. The reactions $C_3H_8 + 2NO + 4O_2 \rightarrow N_2 + 3CO_2 + 4H_2O$ and $C_2H_5OH + 2NO + 2O_2 \rightarrow N_2 + 2CO_2 + 3H_2O$ are promoted by the improved interactions between Pd species and CZA prepared with ultrasonic treatment.

References

- [1] Demirbas A. *Energy Policy*, 2007, 35: 4661
- [2] Hsieh W D, Chen R H, Wu T L, Lin T H. *Atmos Environ*, 2002, 36: 403
- [3] Cooney C P, Worm J J, Naber J D. *Energy Fuels*, 2009, 23: 2319
- [4] Corrêa S M, Martins E M, Arbilla G. *Atmos Environ*, 2003, 37: 23
- [5] Graham L A, Belisle S L, Baas C L. *Atmos Environ*, 2008, 42: 4498
- [6] Di Y, Cheung C S, Huang Z H. *Sci Total Environ*, 2009, 407: 835
- [7] Corrêa S M, Arbilla G, Martins E M, Quitério S L, de Souza Guimarães C, Gatti L V. *Atmos Environ*, 2010, 44: 2302

Fig. 5. Conversion of ethanol (a), C_3H_8 (b), CO (c), and NO (d) at different temperatures over Pd-CZA-S (1) and Pd-CZA-U (2).

Graphical Abstract

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Ultrasonic vibration leads to more Ce on the surface of a CeZrO_x solid solution, and therefore more Pd species that interact with Ce.

- [8] Baez A P, Belmont R, Padilla H. *Enviro Pollut*, 1995, 89: 163
- [9] Pouloupoulos S G, Samaras D P, Philippopoulos C J. *Atmos Environ*, 2001, 35: 4399
- [10] Wu X D, Fan J, Ran R, Yang J, Weng D. *J Alloys Compd*, 2005, 395: 135
- [11] Zhao M, Chen Sh H, Zhang X Y, Gong M Ch, Chen Y Q. *J Rare Earths*, 2009, 27: 728
- [12] Wei Z L, Li H M, Zhang X Y, Yan Sh H, Lü Zh, Chen Y Q, Gong M Ch. *J Alloys Compd*, 2008, 455: 322
- [13] Morikawa A, Suzuki T, Kanazawa T, Kikuta K, Suda A, Shinjo H. *Appl Catal B*, 2008, 78: 210
- [14] Kaspar J, Fornasiero P, Hickey N. *Catal Today*, 2003, 77: 419
- [15] Kaspar J, Fornasiero P, Graziani M. *Catal Today*, 1999, 50: 285
- [16] Zhao B, Li G F, Ge Ch H, Wang Q Y, Zhou R X. *Appl Catal B*, 2010, 96: 338
- [17] Frolova E V, Ivanovskaya M I, Kosareva Y A. *Thin Solid Films*, 2006, 495: 139
- [18] Li H M, Zhu Q C, Li Y L, Gong M Ch, Chen Y D, Wang J L, Chen Y Q. *J Rare Earths*, 2010, 28: 79
- [19] Pan Y L, Wen Y Y, Chen Y Q, Gong M Ch. *Chem J Chin Univ* (潘依浪, 温怡芸, 陈耀强, 龚茂初. 高等学校化学学报), 2009, 30: 337
- [20] Li H M, Zhou J F, Zhu Q C, Zeng S H, Wei Z L, Chen Y Q, Gong M Ch. *Chem J Chin Univ* (李红梅, 周菊发, 祝清超, 曾少华, 魏振玲, 陈耀强, 龚茂初. 高等学校化学学报), 2009, 30: 2484
- [21] Shen M Q, Yang M, Wang J, Wen J, Zhao M W, Wang W L. *J Phys Chem C*, 2009, 113: 3212
- [22] Mei D J, Chen Y Q, Zhong J B, Wei Z L, Ma D, Gong M Ch. *J Rare Earths*, 2007, 25: 311
- [23] Frolova E V, Ivanovskaya M I, Hlushonak H K. *Opt Mater*, 2006, 28: 660
- [24] Yao S Y, Xie Z H. *J Mater Process Technol*, 2007, 186: 54
- [25] Pinjari D V, Pandit A B. *Ultrason Sonochem*, 2011, 18: 1118
- [26] Tu Y B, Luo J Y, Meng M, Wang G, He J J. *Int J Hydrogen Energy*, 2009, 34: 3743
- [27] Zheng H T, Li Y L, Chen S X, Shen P K. *J Power Sources*, 2006, 163: 371
- [28] Dimos M M, Blanchard G J. *J Phys Chem C*, 2010, 114: 6019
- [29] Greca M C, Moraes C, Morelli M R, Segadaes A M. *Appl Catal A*, 1999, 179: 87
- [30] Galvita V V, Belyaev V D, Semikolenov V A, Tsiakaras P, Frumin A, Sobyannin V A. *React Kinet Catal Lett*, 2002, 76: 343
- [31] Davidson J M, McGregor C M, Doraiswamy L K. *Ind Eng Chem Res*, 2001, 40: 108
- [32] Baranchikov A Y, Ivanov V K, Tretyakov Y D. *Uspekhi Khimii*, 2007, 76: 147
- [33] Bang J H, Suslick K S. *Adv Mater*, 2010, 22: 1039
- [34] Wang H R, Chen Y Q, Zhang Q L, Zhu Q Ch, Gong M Ch, Zhao M. *J Nat Gas Chem*, 2009, 18: 211
- [35] Zhang X Y, Long E Y, Li Y L, Zhang L J, Guo J X, Gong M Ch, Chen Y Q. *J Mol Catal A*, 2009, 308: 73
- [36] Zhao B, Yang C Q, Wang Q Y, Li G F, Zhou R X. *J Alloys Compd*, 2010, 494: 340
- [37] Cai L, Zhao M, Pi Zh, Gong M Ch, Chen Y Q. *Chin J Catal* (蔡黎, 赵明, 皮展, 龚茂初, 陈耀强. 催化学报), 2008, 29: 108
- [38] Wang J Q, Shen M Q, An Y, Wang J. *Catal Commun*, 2008, 10: 103
- [39] He H, Dai H X, Au C T. *Catal Today*, 2004, 90: 245
- [40] Hamoudi S, Sayari A, Belkacemi K, Bonneviot L, Larachi F. *Catal Today*, 2000, 62: 379
- [41] Zhu H Q, Qin Z F, Shan W J, Shen W J, Wang J G. *J Catal*, 2004, 225: 267
- [42] Wang N, Chu W, Huang L Q, Zhang T. *J Nat Gas Chem*, 2010, 19: 117
- [43] Wahlberg A, Pettersson L J, Bruce K, Andersson M, Jansson K. *Appl Catal B*, 1999, 23: 271
- [44] Bera S, Mittal V K, Krishnan R V, Saravanan T, Velmurugan S, Nagarajan K, Narasimhan S V. *J Nucl Mater*, 2009, 393: 120
- [45] Long Q, Cai M, Rogers J D, Rong H L, Li J R, Jiang L. *Nanotech*, 2007, 18: 1
- [46] Padilla J M, Del Angel G, Navarrete J. *Catal Today*, 2008, 133-135: 541
- [47] de la Peña O'Shea V A, Alvarez-Galvan M C, Requies J, Barrio V L, Arias P L, Cambra J F, Güemez M B, Fierro J L G. *Catal Commun*, 2007, 8: 1287
- [48] Otto K, Haack L P, deVries J E. *Appl Catal B*, 1992, 1: 1
- [49] Thevenin P O, Alcalde A, Pettersson L J, Järås S G, Fierro J L G. *J Catal*, 2003, 215: 78
- [50] Ma Y Ch, Ge Q J, Li W Zh, Xu H Y. *Appl Catal B*, 2009, 90: 99
- [51] Fornasiero P, Balducci G, Kaspar J, Meriani S, di Monte R, Graziani M. *Catal Today*, 1996, 29: 47

超声辅助合成铈锆铝氧化物及其负载 Pd 催化剂对乙醇汽油车尾气的净化性能

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摘要: 在共沉淀法的基础上辅助以超声制备了铈锆铝复合氧化物 (CZA), 采用比表面分析仪、X 射线衍射、程序升温还原、储氧量和 X 射线光电子能谱对材料进行了表征. 结果表明, 超声振荡有助于小而均匀的孔生成, 有利于 Pd 物种的分散; 超声振荡还能提高 CZA 的储氧量, 使材料的表面组成与体相组成趋于一致. 催化活性测试表明, 材料经过超声处理的 Pd-CZA 净化乙醇汽油车尾气时, 可以将氧气的完全利用窗口从 0~0.64% 拓宽至 0~1.16%; 并且使乙醇、C₃H₈ 和 CO 起燃温度分别下降了 30, 28 和 24 °C. 此外, Pd 物种与 CZA-U 的相互作用有利于 NO 与 C₃H₈ 和 C₂H₅OH 的反应.

关键词: 铈锆铝; 超声; 钯; 乙醇汽油; 尾气; 净化

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