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Preparation of binary washcoat deposited on cordierite substrate for catalytic applications

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Abstract

The deposition of binary M–ZrO_2 (M = Al_2O_3, SiO_2 or TiO_2) as secondary support on cordierite substrate by dip-coating was investigated and the as-prepared M–ZrO_2/cordierite was characterized by means of XRD and SEM techniques. After two successive dip-coating processes, the highest washcoat loading of 25.1% was achieved in Al_2O_3–ZrO_2/cordierite, followed by 18.7% in TiO_2–ZrO_2/cordierite and then 17.4% in SiO_2–ZrO_2/cordierite. The optimal parameters to prepare Al_2O_3–ZrO_2 washcoat on cordierite were investigated in detail. After introduction of noble metal active components (Rh and Pd) to the secondary support, the obtained Rh/M–ZrO_2/cordierite and Pd/M–ZrO_2/cordierite were further tested as monolithic catalysts for the decomposition of nitrous oxide and the deep oxidation of benzene, respectively.

Keywords: D. Al_2O_3; D. ZrO_2; D. Cordierite; Dip-coating; Monolith

1. Introduction

Structured monoliths and reactors have been widely used in heterogeneous catalysis, especially in gas-phase catalytic reactions [1]. In a typical structured monolith, there are many channels and large open frontal area for reactants and products to traverse through. As a consequence, lower resistance to gas flow and corresponding lower pressure drop are achieved in structured monoliths than those in packed-beds. A simple way to obtain catalyst monolith is to deposit a catalytic layer on the non-catalytic structured substrate [2,3]. Honeycomb cordierite (2MgO–$2Al_2O_3$–$5SiO_2$), is the substrate in common use because of its superior mechanical stability and hydrothermal stability as well as its plasticity. Various methods, *e.g.* dip-coating [4–6], direct synthesis [7,8], chemical vapor deposition [9], have been applied to deposit catalytic coatings on cordierite substrate. For the preparation of monolithic catalyst by dip-coating, the ready-made catalysts with or without binders can be directly deposited from the slurry. In an alternative way, a high-surface area secondary support is first deposited on cordierite substrate and then active component is introduced to the secondary support. As for monolithic catalyst with noble metals as main active component, the latter is preferred to realize the maximal utilization of noble metals. Then, the choice of secondary support is very important for the dip-coating process. γ-Al_2O_3 is the most prevalent secondary support materials, due to its advantages in porosity and large specific surface area (150–300 m^2/g). Besides, thanks to its outstanding adhesiveness, no extra binders are needed in the dip-coating process. Up to now, much attention has been focused on the details of washcoat of γ-Al_2O_3 on cordierite substrate. The catalyst monoliths with γ-Al_2O_3 as secondary support also exhibit quite good performance and make great successes in catalytic application [10]. ZrO_2 is known as very important additive in dip-coating process to enhance the thermal stability of washcoat or to prevent the washcoat against agglomeration. However to our knowledge, much less attention is given on the preparation of ZrO_2-containing binary washcoat on cordierite.

In this study, the deposition of M–ZrO_2 (M = Al_2O_3, SiO_2 or TiO_2) on cordierite substrate by dip-coating is studied. The main goal of this study is to present an optimal route to

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prepare ZrO_2-containing binary secondary support on cordierite. Finally, after introduction of noble metal as active component, the obtained monoliths are tested as promising catalysts for two typical environmental catalysis reactions, *e.g.* the deep oxidation of VOCs and the decomposition of nitrous oxide.

2. Experimental

2.1. Preparation of washcoat on cordierite by dip-coating

Cordierite honeycomb monoliths (Corning Incorporated, 60 cells/cm^2, 0.2 mm average wall thickness) were used as substrates. The commercial cordierites were cleaned in HCl (0.1 M) by ultrasonic for 20 min and washed by deionized water before used.

In a typical preparation, γ-alumina (Sinopec, BET surface area 125 m^2/g), $Zr(CH_3COO)_2$ (22%) and H_2O were mixed based on the mass composition of $1\gamma\text{-}Al_2O_3:2H_2O:0.2Zr(CH_3COO)_2$ and vigorously stirred for 4 h to form slurry. The pH value of the slurry was adjusted to the desired value by the addition of CH_3COOH or NH_3–H_2O. Then, two successive dip-coating processes were performed by immersing the pretreated cordierite into the slurry. After each immersion the obtained monolith was blown by hot air to remove the excess slurry, dried at 150 °C for 12 h and calcined at 450 °C in flowing air for 4 h. The as-prepared monolith was defined as Al_2O_3–ZrO_2/cordierite. In a similar preparation process, TiO_2–ZrO_2/cordierite and SiO_2–ZrO_2/cordierite were obtained by using TiO_2 (anatase, BET surface area 57 m^2/g) and SiO_2 (amorphous, BET surface area 147 m^2/g) instead of Al_2O_3.

2.2. Preparation of monolithic catalyst

The monolithic catalysts were prepared by impregnating the as-prepared monolith with aqueous solution of metal salt ($RhCl_3$ or $PdCl_2$) in an evaporator at the constant temperature. In a typical preparation process of Rh/Al_2O_3–ZrO_2/cordierite, 10 mL $RhCl_3$ aqueous solution (Rh concentration: 1.0 mg/mL) was added to 5 g Al_2O_3–ZrO_2/cordierite to achieve Rh loading of ca. 0.2%. The impregnated sample was mixed well and then evaporated in a rotary evaporator at constant temperature of 80 °C. The as-prepared samples were carefully washed by distilled water and then dried at 100 °C overnight.

2.3. Characterization techniques

The X-ray diffraction (XRD) patterns of all samples were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu-Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4°/min in $2\theta = 5$–$80°$.

The scanning electron microscopy (SEM) images were acquired on a HITACHI S-3500N scanning electron microscope to observe the surface morphology of samples. The samples were covered with a thin layer of gold film by sputtering before observation. The washcoat loadings on as-prepared monolith were calculated based on the following formulation:

$$W = \frac{m - m_0}{m_0} \times 100\%$$

In this formulation, W is the washcoat loading, m is the weight of as-prepared monolith and m_0 is the weight of blank cordierite before dip-coating.

2.4. Catalytic test

N_2O decomposition experiments were performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 0.5 g monolith sample was placed in a quartz reactor and pretreated in He at 600 °C for 1 h. After cooling to 300 °C, the reactant gas (1% N_2O, He balance) was fed to the reactor. The total flow rate of gas mixture was 60 mL/min corresponding to a gas-hourly space velocity of 9000 h^{-1}. The steady-state tests were conducted isothermally every 25 °C from 300 °C to 600 °C. The gas products (after 1 h steady-state reaction) were analyzed on-line using a gas chromatograph (Agilent 6820 series) equipped with a TCD detector and two serial columns (a Porapak Q column served for the separation of N_2O and a molecular sieve 5A column for the separation of N_2 and O_2).

The catalytic combustion of volatile organic compound benzene was also performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 0.5 g monolith sample was placed in a quartz reactor and pretreated in O_2 at 350 °C for 1 h. After cooling to 150 °C, the reactant gas (1000 ppm benzene, air balance) was fed to the reactor. The total flow rate of gas mixture was 100 mL/min corresponding to a gas-hourly space velocity of 15,000 h^{-1}. The steady-state tests were conducted isothermally every 25 °C from 150 °C to 350 °C. The gas products (after 1 h steady-state reaction) were analyzed on-line using a gas chromatograph (Agilent 6890 series) equipped with a FID detector and a GasPro capillary column.

3. Results and discussion

3.1. Characterization of as-prepared washcoat on cordierite

Fig. 1 shows the XRD patterns of blank cordierite and as-prepared M–ZrO_2/cordierite (M = Al_2O_3, SiO_2 or TiO_2). Typical diffraction peaks at 10.4°, 18.03°, 19.0°, 21.6°, 26.4°, 28.4°, 29.4° and 33.9° are observed in the XRD pattern of blank cordierite, corresponding to the structure of cordierite ($2MgO$–$2Al_2O_3$–$5SiO_2$). These diffraction peaks are also clearly observed in the XRD patterns of as-prepared M–ZrO_2/cordierite. For Al_2O_3–ZrO_2/cordierite, diffraction peaks corresponding to tetragonal ZrO_2 are observed besides the typical diffraction peaks corresponding to cordierite while the diffraction peaks corresponding to γ-Al_2O_3 are not observed. For SiO_2–ZrO_2/cordierite, diffraction peaks corresponding to cordierite substrate and tetragonal ZrO_2 are observed while no diffraction peaks corresponding to SiO_2 can be found. For TiO_2–ZrO_2/cordierite, diffraction peaks corresponding to cordierite and anatase TiO_2 are observed and the diffraction

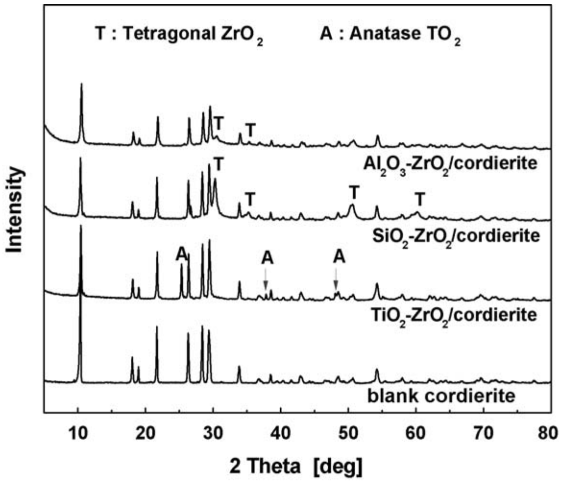

Fig. 1. XRD patterns of blank cordierite and as-prepared Al_2O_3–ZrO_2/cordierite, SiO_2–ZrO_2/cordierite and TiO_2–ZrO_2/cordierite.

peaks corresponding to ZrO_2 are missing. On the whole, binary M–ZrO_2 secondary supports are expected to be coated on cordierite substrate by dip-coating, however, due to the interaction between each component and the great difference in the intensities of typical X-ray diffraction peaks, some diffraction peaks corresponding to certain component disappear. The coating results are further examined by SEM and weight increase in the following sections.

Fig. 2 shows the SEM photographs of blank cordierite and as-prepared M–ZrO_2/cordierite from top-view. The cordierite substrate has irregular flat surface, as seen in the figure, and such structure is good for dip-coating. After dip-coating, the crystal grains with different regular shapes completely and compactly cover the irregular surface of cordierites so that the irregular surface of cordierite substrate could not be observed any more. The Al_2O_3 (or SiO_2, TiO_2) and ZrO_2 form the homogeneous mixture and cannot be easily distinguished. The EDAX analysis results confirm the existence of Zr species in obtained M–ZrO_2/cordierite with weight loadings of 5–15%. Besides, Al_2O_3 with weight loading of above 20% is determined by EDAX analysis. The obvious enrichment of surface Al in Al_2O_3–ZrO_2/cordierite compared to cordierite substrate (ca. 16%) indicating the introduction of Al_2O_3 by dip-coating.

Based on the results from XRD and SEM, we conclude that M–ZrO_2 (M = Al_2O_3, SiO_2 or TiO_2) have been successfully coated on cordierite substrate. The highest washcoat loading of 25.1% is achieved in as-prepared Al_2O_3–ZrO_2/cordierite, followed by 18.7% in TiO_2–ZrO_2/cordierite and then 17.4% in SiO_2–ZrO_2/cordierite. For Al_2O_3–ZrO_2/cordierite, homogeneous Al_2O_3–ZrO_2 coating of ca. 200 μm is observed to coat tightly on cordierite substrate, as shown in Fig. 3. Al_2O_3–ZrO_2 appears to be a good secondary support on cordierite substrate and the optimal conditions to prepare Al_2O_3–ZrO_2 coating are investigated in detail in the following section.

3.2. Study on the optimal conditions to prepare Al_2O_3–ZrO_2 coating

First, the optimal pH value to prepare Al_2O_3–ZrO_2 coating is studied. At pH >5, bulk zirconium oxides will precipitate from the slurry and the cordierite substrate will dissolve under strong acidic conditions at pH <3. So, the range of pH values for

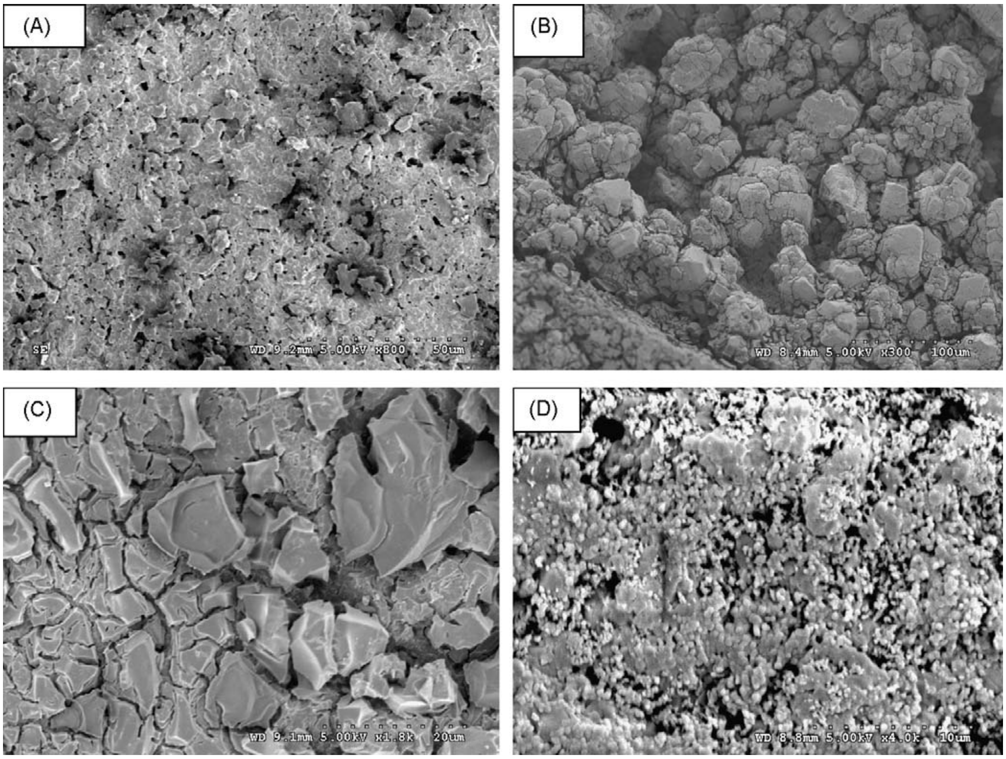

Fig. 2. Top-view SEM photographs of blank cordierite (A), Al_2O_3–ZrO_2/cordierite (B), SiO_2–ZrO_2/cordierite (C) and TiO_2–ZrO_2/cordierite (D).

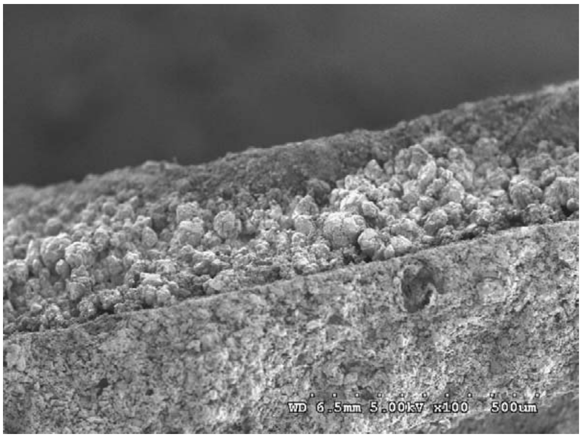

Fig. 3. Side-view SEM photograph of as-prepared Al_2O_3–ZrO_2/cordierite.

investigation is from 3 to 5. As shown in Fig. 4, the weight loading of Al_2O_3–ZrO_2 coating after first dip-coating process (m_{10}) decreases with increasing pH value from 3 to 5 while the weight loading of Al_2O_3–ZrO_2 coating after second dip-coating process (m_{21}) nearly keeps unchanged in this range. On the whole, the highest Al_2O_3–ZrO_2 loading of ca. 25% (m_{20}) is achieved after two successive dip-coating process at pH 3. It is also found that the pH values mainly affect the first dip-coating process. In our opinion, adjusting the pH value of slurry changes the adsorption ability of particles in the slurry onto the surface of cordierite substrate and then changes the initial loading of Al_2O_3–ZrO_2 coating. In the experiments hereafter, the optimal pH of ca. 3 is employed to prepare Al_2O_3–ZrO_2 coatings on cordierite by dip-coating.

Thermal treatment at certain temperature is absolutely necessary in the preparation of washcoat [11]. During the thermal treatment, the decomposition of $Zr(CH_3COO)_2$ takes place and volatile compounds, *e.g.* H_2O, CO_2, are removed from the coatings. It is shown in Fig. 5 that the weight loading of Al_2O_3–ZrO_2 through calcination at different temperatures (350–950 °C) are quite similar (ca. 25%). It is obvious that the calcination temperatures do not have direct influence on the dip-coating results. We further test the thermal stability of Al_2O_3–ZrO_2 coatings. As shown in Table 1, an average weight loss of as low as ca. 0.5% (three groups of parallel experiments) is observed after thermal treatment at 600 °C or 800 °C for 24 h, indicating the good thermal stability and the Al_2O_3–ZrO_2 coating on cordierite.

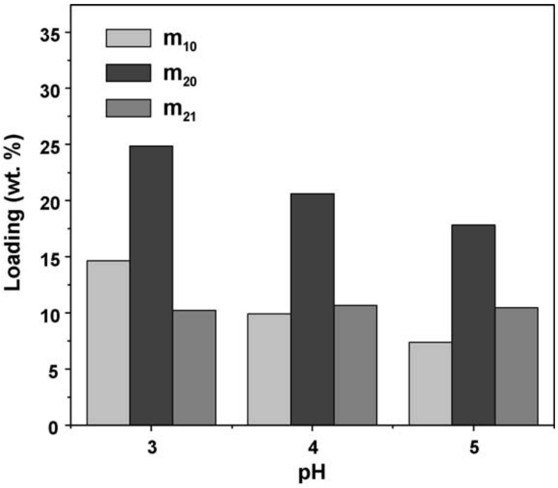

Fig. 4. Effect of pH values on Al_2O_3–ZrO_2 loading on cordierite substrate.

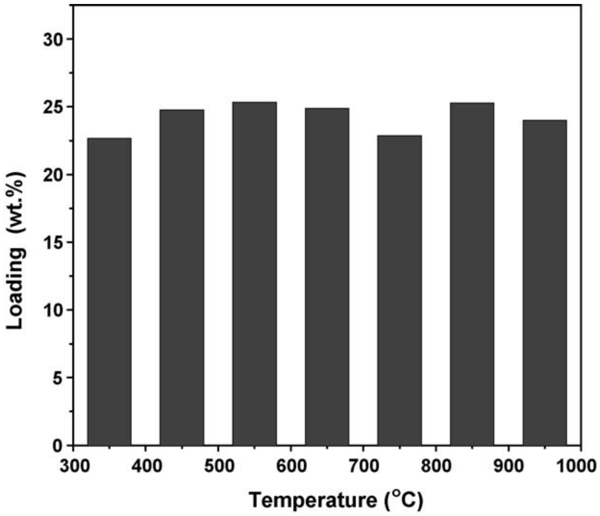

Fig. 5. Effect of calcination temperatures on Al_2O_3–ZrO_2 loading on cordierite substrate.

The water plays an important role in dip-coating process. In the presence of water, Al_2O_3 and $Zr(CH_3COO)_2$ mix well and transform into homogeneous suspension, with the viscosity and solid content adjustable by controlling the content of water added. The effect of H_2O/Al_2O_3 ratios on the weight loading of obtained Al_2O_3–ZrO_2 coatings is presented in Fig. 6. It is seen that with increasing H_2O/Al_2O_3 ratios from 1.59 to 2.53, the weight loading of Al_2O_3–ZrO_2 on cordierite after first dip-coating process (m_{10}) first increase to a maximum (H_2O/Al_2O_3 ≈ 2) and then begins to drop gradually. While for the second dip-coating process, the H_2O/Al_2O_3 ratios do not show obvious effect on the weight increase (m_{21}). On the whole, the highest Al_2O_3–ZrO_2 weight loading (m_{20}) of ca. 25% can be achieved at the H_2O/Al_2O_3 of 2 after two successive dip-coating processes.

The effect of H_2O/Al_2O_3 ratios on dip-coating results can be essentially ascribed to the adjusting of apparent viscosity. Increasing the H_2O/Al_2O_3 ratios means decreasing solid content and thus decreasing apparent viscosity. At high H_2O/Al_2O_3 ratios, the interaction between cordierite and slurry is not enough to support high Al_2O_3–ZrO_2 loadings on cordierite due to the low apparent viscosity while at low H_2O/Al_2O_3 ratios, the diffusion of slurry with high viscosity inside cordierite channels

Table 1
Thermal stability of Al_2O_3–ZrO_2 on cordierite.

Sample	Weight loss (%)	
	600 °C	800 °C
Al_2O_3–ZrO_2/cordierite-1	0.34	0.49
Al_2O_3–ZrO_2/cordierite-2	0.52	0.58
Al_2O_3–ZrO_2/cordierite-3	0.41	0.45

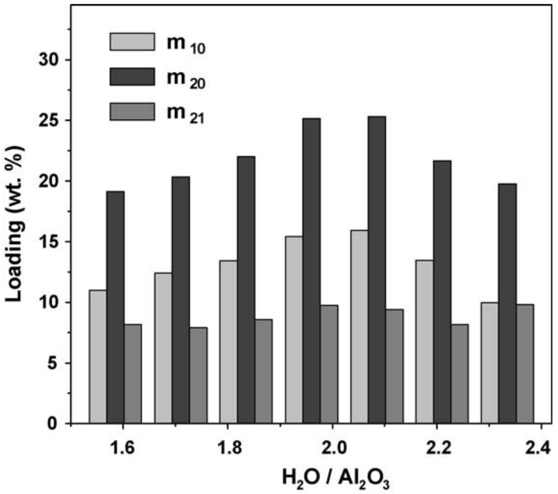

Fig. 6. Effect of H_2O/Al_2O_3 ratios on Al_2O_3–ZrO_2 loading on cordierite substrate.

is limited and the capillary action of cordierite to slurry is reduced. As discussed, an optimal H_2O/Al_2O_3 ratio of ca. 2 is determined to achieve high weight loading of Al_2O_3–ZrO_2 coatings on cordierite by dip-coating.

Zirconium acetate can be used as thermal stabilizer in the preparation of Al_2O_3 coatings and the decomposition product ZrO_2 can greatly reinforce Al_2O_3 coatings on cordierite surface [12]. In this study, Al_2O_3–ZrO_2 composite is employed as secondary support on cordierite and the effect of $Zr(CH_3COO)_2/Al_2O_3$ ratios on the dip-coating results is shown in Fig. 7. It is seen that the weight loading of Al_2O_3–ZrO_2 coatings increases obviously with increasing $Zr(CH_3COO)_2/Al_2O_3$ ratios from 0 to 0.32 after first dip-coating. In this process, ZrO_2 from the decomposition of zirconium acetate can go into the crystal defects of Al_2O_3 particles and Al_2O_3 in cordierite during calcination step. In such a way, strong combination between Al_2O_3–ZrO_2 coating and cordierite substrate is obtained. From Fig. 7, it is seen that high total weight loadings of Al_2O_3–ZrO_2 (m_{20}) can be achieved at high $Zr(CH_3COO)_2/Al_2O_3$ ratios. It should be mentioned that the ZrO_2/Al_2O_3 ratios in obtained coatings also increase with increasing batch $Zr(CH_3COO)_2/Al_2O_3$ ratios. As a consequence, we can adjust the $Zr(CH_3COO)_2/Al_2O_3$ ratio by turning batch $Zr(CH_3COO)_2/Al_2O_3$ ratios. In this work, a medium $Zr(CH_3COO)_2/Al_2O_3$ ratio of ca. 0.2 is employed and a maximal BET surface area of ca. 17.3 is obtained on Al_2O_3–ZrO_2/cordierite.

3.3. Catalytic test of monolithic catalysts

After introduction of active component into the as-prepared M–ZrO_2/cordierite, the monolithic sample can be used as structured catalysts for various heterogeneous catalytic reactions. In this work, Rh/M–ZrO_2/cordierite and Pd/M–ZrO_2/cordierite are tested as catalysts for N_2O decomposition and benzene deep oxidation, respectively. As shown in Fig. 8, Rh/Al_2O_3–ZrO_2/cordierite exhibits the best N_2O decomposition activity, followed by Rh/TiO_2–ZrO_2/cordierite and then Rh/SiO_2–ZrO_2/cordierite. For the best catalyst Rh/Al_2O_3–ZrO_2/cordierite, 100% N_2O conversion can be achieved at 500 °C. While for benzene deep oxidation, Pd/SiO_2–ZrO_2/cordierite exhibits the best activity, followed by Pd/TiO_2–ZrO_2/cordierite and then Pd/Al_2O_3–ZrO_2/cordierite, as shown in Fig. 9. A 100% benzene conversion can be obtained at 325 °C over Pd/SiO_2–ZrO_2/cordierite. From the catalytic results we can see that catalytic activity of monolithic catalyst in different reactions is very related to the choice second support. Though Al_2O_3–ZrO_2 is the most easily obtained second support on cordierite with highest weight loading, we should select suitable second support based on the different catalytic reactions.

The effects of calcination temperatures during dip-coating process on N_2O decomposition activity over Rh/Al_2O_3–ZrO_2/cordierite are investigated, as displayed in Fig. 10. Calcination

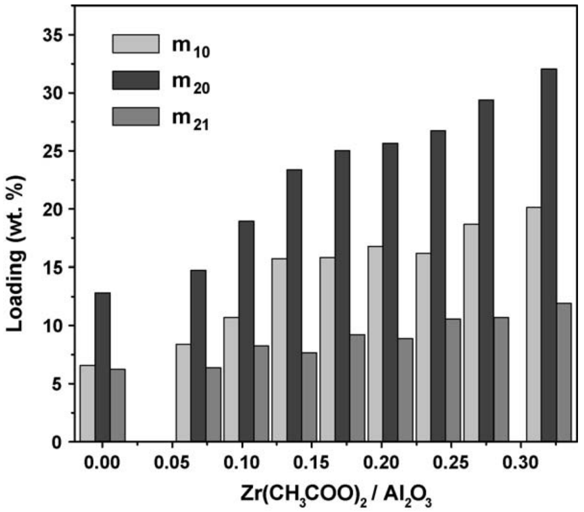

Fig. 7. Effect of $Zr(CH_3COO)_2/Al_2O_3$ ratios on Al_2O_3–ZrO_2 loading on cordierite substrate.

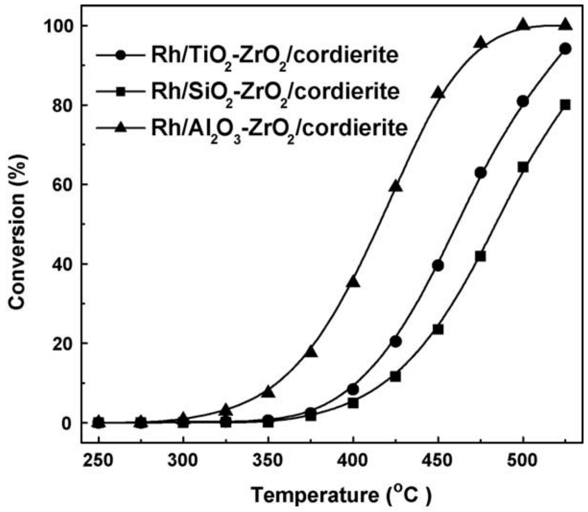

Fig. 8. Decomposition of nitrous oxide over Rh-based monolithic catalyst. Reaction conditions: 0.5 g monolithic catalyst, 1% N_2O, and the balance He, GHSV = 9000 h^{-1}.

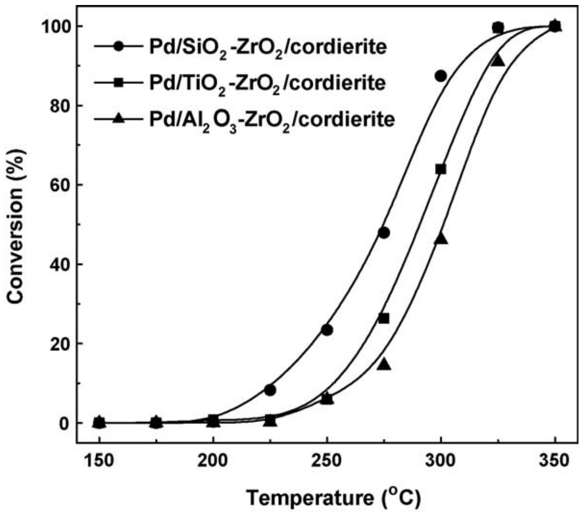

Fig. 9. Deep oxidation of benzene over Pd-based monolithic catalyst. Reaction conditions: 0.5 g monolithic catalyst, 1000 ppm C_6H_6, and the balance air, GHSV = 15,000 h^{-1}.

at 650 °C results in a slight decrease in N_2O decomposition activity compared to that calcined at 550 °C while further increase in calcination temperature to 950 °C results in more serious decrease in catalytic activity of $Rh/Al_2O_3–ZrO_2$/cordierite. Nevertheless, a 100% N_2O conversion can still be obtained at 600 °C on $Rh/Al_2O_3–ZrO_2$/cordierite pre-calcined at 950 °C. The loss of activity may be attributed to the sintering of Rh species during calcination. In this study, ZrO_2 acts as anti-sintering component in $Rh/Al_2O_3–ZrO_2$/cordierite and the sintering of Rh species can be prevented to a great extent. In the absence of ZrO_2, Rh/Al_2O_3/cordierite shows a little high activity for N_2O decomposition than $Rh/Al_2O_3–ZrO_2$/cordierite. However disappointedly, the activity of Rh/Al_2O_3/cordierite at below 500 °C is completely lost after calcined at 950 °C. It is thus established that ZrO_2 in the coatings plays an important role on the stabilization of active component.

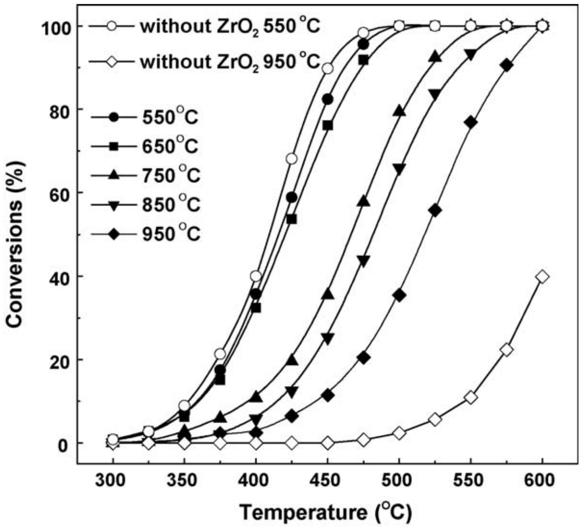

Fig. 10. Decomposition of nitrous oxide over $Rh/Al_2O_3–ZrO_2$/cordierite and Rh/Al_2O_3/cordierite calcined at different temperatures. Reaction conditions: 0.5 g monolithic catalyst, 1% N_2O, and the balance He, GHSV = 9000 h^{-1}.

4. Conclusion

Binary secondary supports $M–ZrO_2$ ($M = Al_2O_3$, SiO_2 or TiO_2) have been successfully coated on cordierite substrate by dip-coating method. $Al_2O_3–ZrO_2$ is the most easily obtained binary second support on cordierite and a weight loading of ca. 25% can be obtained after two successive dip-coating processes. The optimal slurry composition for $Al_2O–ZrO_2$ wash coating is determined to be $1\gamma\text{-}Al_2O_3:2H_2O:0.2Zr(CH_3COO)_2$ and the pH value is ca. 3. After introduction of noble metal as active component, the obtained $Rh/M–ZrO_2$/cordierite and $Pd/M–ZrO_2$/cordierite exhibit considerable activity for the decomposition of nitrous oxide and the deep oxidation of benzene, respectively. It is clearly observed that catalytic activity of monolithic catalyst in different reactions is very much related to the choice of second support. From the catalytic results, it is also proved that ZrO_2 in secondary support coatings plays an important role on the stabilization of active component against sintering.

Acknowledgements

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