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doi: 10.3866/PKU.WHXB201403101

www.whxb.pku.edu.cn

浸渍法制备的Pd-MnO_x/γ-Al₂O₃催化剂及不同载体对地表O₃降解的影响

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摘要: 在γ-Al₂O₃载体上用等体积浸渍法浸渍Pd、MnO_x活性组分, 然后涂覆于堇青石基体上制备Pd-MnO_x/γ-Al₂O₃整体式催化剂. 分别用X射线衍射(XRD)、H₂-程序升温还原(H₂-TPR)、低温N₂吸附-脱附及X射线光电子能谱(XPS)对制备的催化剂进行表征. 研究了Pd、MnO_x浸渍顺序对催化剂活性、氧化还原性能及结构性质的影响. 实验结果表明, Pd、MnO_x共浸渍较分别浸渍制备的催化剂活性好, Pd和MnO_x之间存在一定的协同作用. 考察了不同载体如La-Al₂O₃、SiO₂、γ-Al₂O₃和Zr-Al₂O₃对催化剂活性、氧化还原性能、结构性质及表面电子性能的影响. 研究表明, 以La-Al₂O₃或SiO₂为载体的催化剂活性最好, 即, 14 °C时O₃转化率为82%, 完全转化温度为36 °C. γ-Al₂O₃载体次之, Zr-Al₂O₃载体较差. 不同载体制备的催化剂中MnO_x的氧化还原性能顺序为: Pd-MnO_x/SiO₂>Pd-MnO_x/La-Al₂O₃>Pd-MnO_x/γ-Al₂O₃>Pd-MnO_x/Zr-Al₂O₃.

关键词: 锰氧化物; 钯; 臭氧; 催化分解; 浸渍法; 载体

中图分类号: O643

Pd-MnO_x/γ-Al₂O₃ Monolithic Catalysts Prepared by Impregnation Method and Effect of Different Supports on Ground-Level Ozone Decomposition

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Abstract: Pd-MnO_x/γ-Al₂O₃ catalysts were prepared by impregnating Pd and MnO_x on γ-Al₂O₃ supports, using an incipient wetness impregnation method, and then coating on a cordierite substrate to obtain monolithic catalysts. The catalysts were characterized using X-ray diffraction (XRD), temperature-programmed reduction of H₂ (H₂-TPR), low-temperature N₂ adsorption-desorption measurements, and X-ray photoelectron spectroscopy (XPS). The effects of the Pd and MnO_x impregnation order on the catalytic activity, redox performance, textural properties, and surface electronic characteristics of the catalysts were studied. The experimental results showed that the activity of the catalyst co-impregnated with Pd and MnO_x on γ-Al₂O₃ was better than that of the catalyst impregnated sequentially with Pd and MnO_x. A synergetic effect was observed between Pd and MnO_x on the Pd-MnO_x/γ-Al₂O₃ catalysts for ozone decomposition. The effects of various supports on catalytic activity, redox performance, textural properties, and surface electron characteristics of the catalysts were also investigated. The results indicated that the catalytic activities of Pd-MnO_x/La-Al₂O₃ and Pd-MnO_x/SiO₂ catalysts were the best; ozone conversion reached 82% at 14 °C and ozone was completely decomposed at 36 °C. The activity of the Pd-MnO_x/γ-Al₂O₃ catalyst was second better, but the activity of the Pd-MnO_x/Zr-Al₂O₃ catalyst was poor. The support clearly affects the reducibility of PdO and MnO_x. The redox performances of MnO_x impregnated on different supports followed the order:

Received: December 25, 2013; Revised: March 10, 2014; Published on Web: March 10, 2014.

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The project was supported by the National Natural Science Foundation of China (J1103315, J1310008).

国家自然科学基金(J1103315, J1310008)资助项目

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$\text{Pd-MnO}_x/\text{SiO}_2 > \text{Pd-MnO}_x/\text{La-Al}_2\text{O}_3 > \text{Pd-MnO}_x/\gamma\text{-Al}_2\text{O}_3 > \text{Pd-MnO}_x/\text{Zr-Al}_2\text{O}_3$.

Key Words: Manganese oxide; Palladium; Ozone; Catalytic decomposition; Impregnation method; Support

1 Introduction

The researchers have found that ground-level ozone would increase cardiovascular mortality and respiratory disease, decrease lung function.¹ Ozone is a powerful oxidant. The woody plants including arbor and shrubs had already suffered the harm of ambient ozone.² Karlsson *et al.*³ investigated the negative impacts of ozone on crop yields and forest production. Moreover, ozone can deteriorate valuable materials.⁴ According to OSHA (Occupational Safety and Health Administration) regulations, the threshold level for allowable exposure during an 8 h time period is 1.0×10^{-7} (volume fraction, the same below).⁵ The allowable concentration in the working environment is also 1.0×10^{-7} in Japan.⁶ In March 2012, State Environmental Protection Administration of China promulgated “ambient air quality standard” regulation (GB3095-2012) that ozone average concentration must be lower than $100\text{--}160 \mu\text{g} \cdot \text{m}^{-3}$ ($4.6 \times 10^{-8}\text{--}7.5 \times 10^{-8}$) in 8 h and it will be carried out in January 2016. Therefore, the catalytic decomposition of ozone is an important area of research from the point of view of environmental protection and health.^{7–11}

Ground-level ozone was formed from nonlinear reactions between volatile organic compounds (VOCs) and nitrogen oxides (NO_x) under ultraviolet light,^{12–14} which are released from power plants and automobile exhaust gases. The numbers of vehicle are dramatically increased with rapid development of economy in recent years. Ozone gradually becomes one of the major air pollutions. Our group^{8–11} focused on improving the activity of catalysts in early work. If the as-prepared catalysts were coated on vehicle radiators, where temperature ranged from 20 to 90 °C, ozone would be completely decomposed. However, automobiles often run at high speed, and may jolt and rattle on the rough ground. The washcoat of catalysts could be fallen away. Therefore, it is necessary that the catalysts have not only excellent activity but also better viscosity.

The Al_2O_3 is used as both support and binder due to its large surface area and better viscosity in this paper. MnO_x is acted as active species owing to its highly activity.^{5,11,15,16} Moreover, there is high relative humidity on the surface of water tank in automobiles. H_2O molecules would compete with ozone for adsorption leading to decrease of MnO_x activity. Therefore, Pd is employed both as a resistant to water vapor and active species.^{11,16,17} The $\gamma\text{-Al}_2\text{O}_3$ support was prepared by peptizing method, and $\text{Mn}(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$ were impregnated on the $\gamma\text{-Al}_2\text{O}_3$ support, and then, the $\text{Pd-MnO}_x/\gamma\text{-Al}_2\text{O}_3$ was coated on the cordierite substrate to obtain $\text{Pd-MnO}_x/\gamma\text{-Al}_2\text{O}_3$ monolith catalysts. In addition, $\text{Mn}(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$ were impregnated on SiO_2 , $\text{La-Al}_2\text{O}_3$, and $\text{Zr-Al}_2\text{O}_3$ supports, respectively. The per-

formance of catalysts for O_3 decomposition was investigated under high space velocities (380000, 450000, 510000, and 580000 h^{-1}) and high relative humidity ($\text{RH}=85\%\text{--}90\%$). The prepared catalysts were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction (TPR) technologies. And the significant results were obtained.

2 Experimental

2.1 Preparation of catalysts

2.1.1 Supports

A support of $\gamma\text{-Al}_2\text{O}_3$ was prepared by peptizing method. Firstly, concentrated nitric acid (A.R.) and water were added into an appropriate amount of boehmite (A.R.). Subsequently, a clear sol was formed after high-energy ball milling, and aged at 90 °C for 6 h in water bath. Then, the precipitates were filtered *via* vacuum filtration, washed with distilled water, and dried at 110 °C overnight. The dried precipitates were calcined at 600 °C for 3 h.

$\text{La-Al}_2\text{O}_3$ support calcined at 900 °C was purchased from Rhodia Corporation.

SiO_2 support was prepared, for which the SiO_2 aqueous sol (A.R.) was heated in water bath until vapor was removed, and then, dried at 110 °C overnight. The dried powders were calcined at 600 °C for 3 h.

$\text{Zr-Al}_2\text{O}_3$ support was prepared by co-precipitation method. $\text{ZrOCO}_3 \cdot 6\text{H}_2\text{O}$ (A.R.) was dissolved into concentrated nitric acid. Then, the aqueous solutions of ZrOCO_3 and $\text{Al}(\text{NO}_3)_3$ (A.R.) were mixed in a mass ratio of 1:9 (ZrO_2 to Al_2O_3), and adjusted to pH 8.8 by $\text{NH}_3 \cdot \text{H}_2\text{O}$ (A.R.). The precipitates were filtered off, washed with distilled water, and dried at 110 °C overnight. The dried precipitates were calcined at 600 °C for 3 h.

2.1.2 $\text{Pd-MnO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst powders

$\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst powders were prepared, for which $\text{Mn}(\text{NO}_3)_2$ (A.R.) was impregnated on the $\gamma\text{-Al}_2\text{O}_3$ support, and then, was heated in water bath until vapor was removed, and then dried at 110 °C overnight. The dried powders were calcined at 400 °C for 6 h. The amount of MnO_x was 8% (mass fraction).

$\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst powders were prepared, for which $\text{Pd}(\text{NO}_3)_2$ (ChengDu Guangming Equipment Company, A.R.) was impregnated on the $\gamma\text{-Al}_2\text{O}_3$ support, then was heated in water bath until vapor was removed, and then dried at 110 °C overnight. The dried powders were calcined at 400 °C for 3 h. The amount of Pd was 2% (mass fraction).

Catalyst (MP) was prepared. Firstly, $\text{Mn}(\text{NO}_3)_2$ was impregnated on the $\gamma\text{-Al}_2\text{O}_3$ support, then was heated in water bath until vapor was removed, and then dried at 110 °C overnight. The

dried powders were calcined at 400 °C for 6 h. Subsequently, Pd(NO₃)₂ was impregnated on the MnO_x/γ-Al₂O₃ support, then was heated in water bath until vapor was removed, and then dried at 110 °C overnight. The dried powders were calcined at 400 °C for 3 h. The amount of Pd was 2% (mass fraction), and the amount of MnO_x was 8% (mass fraction).

Catalyst (PM) was prepared. At first, Pd(NO₃)₂ was impregnated on the γ-Al₂O₃ support, then was heated in water bath until vapor was removed, and dried at 110 °C overnight. The dried powders were calcined at 400 °C for 3 h. Subsequently, Mn(NO₃)₂ was impregnated on the Pd/γ-Al₂O₃ support, then was heated in water bath until vapor was removed, and then dried at 110 °C overnight. The dried powders were calcined at 400 °C for 6 h. The amount of Pd was 2% (mass fraction), and the amount of MnO_x was 8% (mass fraction).

Catalyst (CPM) was prepared, which Mn(NO₃)₂ and Pd(NO₃)₂ were co-impregnated on the γ-Al₂O₃ support, then was heated in water bath until vapor was removed, and then dried at 110 °C overnight. The dried powders were calcined at 400 °C for 6 h. The amount of Pd was 2% (mass fraction), and the amount of MnO_x was 8% (mass fraction).

2.1.3 Pd-MnO_x/γ-Al₂O₃ monolith catalyst

The above mentioned powders were ball-milled with distilled water to form slurry. The slurry was coated on cordierite substrate of 0.28 cm³ (Coring Corporation in American, 400 pore · inch⁻², diameter (Φ)=5 mm, length (L)=14 mm) and the excess slurry was blown off. The catalyst was dried at 110 °C overnight and calcined in air at 200 °C for 3 h to prepare the Pd-MnO_x/γ-Al₂O₃ monolith catalyst. The loading of catalyst washcoat was 350 mg · mL⁻¹.

When the support was SiO₂, La-Al₂O₃, or Zr-Al₂O₃, the monolith catalysts were prepared by the above-mentioned methods, respectively.

2.2 Catalyst characterization

The XRD analysis was conducted on DX-1000 X-ray diffractometer, using Cu K_α radiation (λ=0.15406 nm) at 40 kV and 25 mA. The XRD data were recorded for 2θ values from 10° to 80° at an interval of 0.05 (°) · s⁻¹. The specific surface area and pore size of the catalysts were determined by N₂ adsorption-desorption at -196 °C on a QUADRASORB SI, an automated surface area and pore size analyzer (Uuantachrome Instruments). Before the measurements, the samples were degassed in vacuum at 350 °C for 1 h. X-ray photoelectron spectra of samples were acquired at room temperature using a Vacuum Generator Scientific XSAM800 system from Kratos Co. in U.K. The spectra were recorded with the Mg K_α (hν=1253.6 eV). X-ray radiation by setting the electron energy analyzer was operated at 180 W (12 kV, 15 mA). Temperature programmed reduction of H₂ was carried out using an automated instrument. In a typical experiment, 100 mg of sample was loaded in a U-shaped quartz micro-reactor. The sample was heated from room temperature to 550 °C at a heating rate of 10 °C · min⁻¹ in a flowing hydrogen mixed gas of 5% (volume

fraction) H₂ and 95% (volume fraction) N₂ at 30 cm³ · min⁻¹. Hydrogen consumption was monitored using a thermal conductivity detector.

2.3 Catalytic tests

The catalyst tests were carried out in a continuous flow tubular quartz reactor (inner diameter: 10 mm) placed in a temperature-programmed furnace. The catalyst temperature was controlled by a thermocouple mounted internally. Ozone gases were generated from ozone generator (JY-3 type, Chengdu Qianguai Purification Equipment Company) and were fed from independent mass-flow controller. Air was come into being from air compressor, and then was separated by an oil-water separator and dried by a silica gel, its flow rate was controlled by a rotameter. Measurements over the samples were performed at a RH of 85%–90% using a gas hourly space velocity (GHSV) of 380000, 450000, 510000, and 580000 h⁻¹, respectively. The feed consists of 6.0 × 10⁻⁷ O₃, and balance air. The outlet flow of the reactor was analyzed using an ozone analyzer (Nanjing 8Shang Technology Co., Ltd.). The activity of the catalyst was calculated on the basis of the following equation:

$$\text{O}_3 \text{ conversion} = (C_{\text{inlet}} - C_{\text{outlet}}) / C_{\text{inlet}}$$

where C_{inlet} and C_{outlet} are inlet concentration of O₃ and outlet concentration of O₃, respectively.

3 Results and discussion

3.1 Activity of catalysts and synergetic effect between Pd and MnO_x

As shown in Fig.1, initial O₃ conversions at 12 °C are 53.3%, 73.3%, and 30.0%, O₃ complete conversion temperatures are 56, 38, and 70 °C, corresponding to MnO_x/γ-Al₂O₃, Pd-MnO_x/γ-Al₂O₃, and Pd/γ-Al₂O₃ catalysts, respectively. The activity of the Pd/γ-Al₂O₃ catalyst for decomposition of O₃ is poor, and the activity of MnO_x/γ-Al₂O₃ catalyst is better than Pd based catalyst. The performance of the Pd-MnO_x/γ-Al₂O₃ catalyst is the best, where both Pd and MnO_x species are involved. Namely, there was some synergetic effect between Pd and MnO_x. For the Pd-MnO_x/γ-Al₂O₃ catalyst, Pd is functionalized both as active spe-

Fig.1 O₃ conversion as a function of reaction temperature on Pd/γ-Al₂O₃, MnO_x/γ-Al₂O₃, and Pd-MnO_x/γ-Al₂O₃ catalysts

reaction conditions: O₃ inlet concentration=(6.0±0.2)×10⁻⁷, GHSV=380000 h⁻¹, RH=85%–90%

Fig.2 H₂-TPR profiles of Pd/γ-Al₂O₃, MnO_x/γ-Al₂O₃, and Pd-MnO_x/γ-Al₂O₃ catalysts

cies and resistant to humidity, which would suppress deactivation aroused by the adsorption of H₂O molecules.^{16,17} It benefits to O₃ molecules interacting with more MnO_x active species. Therefore, the Pd-MnO_x/γ-Al₂O₃ catalyst has an excellent activity under high relative humidity.

Fig.2 shows H₂-TPR profiles of Pd/γ-Al₂O₃, MnO_x/γ-Al₂O₃, and Pd-MnO_x/γ-Al₂O₃ catalysts. It is seen that a weak peak at 121 °C was present in the Pd/γ-Al₂O₃ catalyst, it is attributed to the reduction of PdO species.^{18,19} For the MnO_x/γ-Al₂O₃ catalyst, the broad peaks around 150–370 °C and 420–610 °C are observed. The broad peak around 150–370 °C can be divided into two peaks at 181 and 258 °C, which are ascribed as MnO₂ and Mn₂O₃ reduction to Mn₃O₄.¹⁹ The broad peak around 420–610 °C can be divided into two peaks at 475 and 538 °C, which represent Mn₃O₄ reducing to MnO.¹⁹ For the Pd-MnO_x/γ-Al₂O₃ catalyst, a peak at 155 °C is attributed to the reduction of PdO species,¹⁸ and a peak around 210 °C is due to MnO₂ and Mn₂O₃ reduction to Mn₃O₄,¹⁹ and a peak at 430 °C is ascribed to Mn₃O₄ reduction to MnO.¹⁹ The reduction temperature of MnO_x is lowered in the presence of Pd, implying that there is an obvious interaction between Pd and MnO_x. Xu *et al.*²⁰ reported that the presence of Pd lowered the reduction temperature of MnO₂ due to hydrogen spillover from Pd to the oxides. This phenomenon can be explained as follows: PdO is easily reduced to Pd by H₂. Namely, PdO has changed to Pd before MnO₂ reduction. The Pd adsorbs H₂ and dissociates it into H, and then, H spills over onto MnO₂ to promote its reduction. The interaction of Pd and MnO_x improves the reducibility of MnO_x. Dhandapani and Oyama⁵ thought that the activity of MnO_x is relevant to its reducibility. Therefore, the activity of the Pd-MnO_x/γ-Al₂O₃ catalyst is enhanced for decomposition of O₃.

3.2 Effect of impregnation orders of Pd and MnO_x on performance of catalysts

3.2.1 TPR results of catalysts

Fig.3 displays the TPR profiles of the catalysts prepared by different impregnation orders of Pd and MnO_x. For the catalyst co-impregnated Pd and MnO_x, as mentioned in Fig.2, there are three reduction peaks around 155, 210, and 430 °C. A broad peak around 60–330 °C and a peak at 426 °C were observed

Fig.3 H₂-TPR profiles of the samples prepared by different impregnation orders of Pd and MnO_x

MP: MnO_x was first impregnated on γ-Al₂O₃ and then PdO was impregnated on MnO_x/γ-Al₂O₃; PM: PdO was first impregnated on γ-Al₂O₃ and then MnO_x was impregnated on Pd/γ-Al₂O₃; CMP: MnO_x and PdO were co-impregnated on γ-Al₂O₃.

in the catalyst impregnated MnO_x and then impregnated Pd. The broad peak can be divided into two peaks at 153 and 218 °C. For the catalyst impregnated Pd and then MnO_x, three peaks at about 151, 260, and 437 °C were present, the peak at 260 °C shifted towards high temperature. Although there are slight difference of the reduction temperatures of Pd and MnO_x, the reduction peak areas of Pd and MnO_x are obviously different from the other two samples. The reduction peak area is the largest in the catalyst co-impregnated Pd and MnO_x, indicating that the catalyst has the best reducibility.

3.2.2 Textural property of catalysts

As shown in Table 1, the surface areas are similar in three samples. However, the pore volume and average pore diameter of the catalyst co-impregnated Pd and MnO_x are slightly larger than those of the catalysts impregnated Pd and MnO_x sequentially. Large pore volume is favorable of more O₃ molecules activated by the active species on the surface of catalyst. Large pore diameter is in favor of O₃ coming into pores rapidly under high space velocity. Therefore, better textural property of the co-impregnated catalyst is beneficial to decomposition of O₃.

3.2.3 Activity of catalysts

Fig.4 indicates the activity of catalysts impregnated Pd and MnO_x by different impregnation orders. It is seen that initial O₃ conversions at 12 °C are 73.3%, 69.7%, and 66.7%, complete conversion temperatures of O₃ are 38, 46, and 48 °C, corresponding to the catalyst co-impregnated Pd and MnO_x, the catalyst impregnated MnO_x and then Pd, and the catalyst impregnated Pd and then MnO_x, respectively. The impregnation order has some impacts on the activity of catalysts, the activity of the co-

Table 1 Textural property of the samples prepared by different impregnation orders of Pd and MnO_x

Sample	Surface area	Pore volume	Average pore diameter
	(m ² ·g ⁻¹)	(cm ³ ·g ⁻¹)	nm
MP	221	0.33	6.0
PM	210	0.32	6.0
CMP	216	0.36	6.7

Fig.4 O₃ catalytic performance of samples prepared by different impregnation orders of Pd and MnO_x

reaction conditions: O₃ inlet concentration=(6.0±0.2)×10⁻⁷,
GHSV=380000 h⁻¹, RH=85%–90%

impregnated catalyst is the highest in the three samples. For the co-impregnated catalyst, Mn⁴⁺ and Pd²⁺ were uniformly mixed in ionic form before impregnation, in favor of MnO_x and Pd dispersion evenly onto the surface of γ-Al₂O₃ support. It is possible that more active species were exposed on the surface of the co-impregnated catalyst. In general, the more the active species exposed (such as Pd or MnO_x), the better the activity of the catalyst. Moreover, when Pd or MnO_x was loaded on the surface of γ-Al₂O₃ support, the negative charges of Al₂O₃ would be transferred into PdO or MnO_x due to strong interaction of metal and support. For the co-impregnated catalyst, the interaction could be more obvious, resulting in better reducibility of PdO and MnO_x, which is helpful to O₃ decomposition. In addition, the activity of the catalyst impregnated MnO_x and then Pd is slightly better than that of the catalyst impregnated Pd and then MnO_x. It can be ascribed to good reducibility of MnO_x in the catalyst (see Fig.3, H₂-TPR). Furthermore, a little Pd was possibly covered by MnO_x on the surface of the catalyst impregnated Pd and then MnO_x, the amount of Pd exposed decreased more or less.

3.3 Effect of supports on the performance of the catalyst co-impregnated Pd and MnO_x

3.3.1 Activity of catalysts

Fig.5 reveals the activity of the catalyst co-impregnated Pd and MnO_x on various supports under different space velocities, respectively. For space velocity of 380000 h⁻¹, O₃ conversions, at 14 °C are 82%, 82%, 77%, and 68%, O₃ complete conversion temperatures are 36, 36, 38, and 48 °C corresponding to La-Al₂O₃, SiO₂, γ-Al₂O₃, and Zr-Al₂O₃ supports, respectively. For space velocity of 450000 h⁻¹, O₃ conversions at 14 °C are 72%, 68%, 64%, and 58%, O₃ complete conversion temperatures are 50, 56, 59 and 65 °C corresponding to La-Al₂O₃, SiO₂, γ-Al₂O₃, and Zr-Al₂O₃ supports, respectively. For space velocity of 510000 h⁻¹, O₃ conversions at 14 °C are 60%, 52%, 50%, and 40%, O₃ complete conversion temperatures are 66, 78, 80, and 88 °C corresponding to La-Al₂O₃, SiO₂, γ-Al₂O₃, and Zr-Al₂O₃ supports, respectively. For space velocity of 580000 h⁻¹,

Fig.5 Effect of supports on the catalytic performance of samples co-impregnated Pd and MnO_x under different space velocities

reaction conditions: O₃ inlet concentration=(6.0±0.2)×10⁻⁷, RH=85%–90%

O₃ conversions at 14 °C are 43%, 34%, 36%, and 28%, O₃ complete conversion temperatures are 86, 100, 94, and 112 °C corresponding to La-Al₂O₃, SiO₂, γ-Al₂O₃, and Zr-Al₂O₃ supports, respectively. It can be seen that the Pd-MnO_x/La-Al₂O₃ catalyst has the best activity; the Pd-MnO_x/SiO₂ catalyst has better activity when the space velocity varied from 380000 to 510000 h⁻¹, however, its activity is slightly weaker than that of the Pd-MnO_x/γ-Al₂O₃ catalyst at the space velocity of 580000 h⁻¹; the activity of the Pd-MnO_x/Zr-Al₂O₃ catalyst is the worst in all the catalysts.

3.3.2 XRD characterization of catalysts

Fig.6 shows XRD patterns of samples co-impregnated Pd and MnO_x on different supports. The diffraction peaks of supports were observed in XRD patterns for all of the samples. For example, SiO₂ was observed in the Pd-MnO_x/SiO₂ catalyst. The γ-Al₂O₃ was present in the Al₂O₃-based catalysts. The weak diffraction peaks of MnO₂ were appeared, indicating that MnO₂ was in the presence of microcrystalline due to low MnO₂ content and high dispersion on the surface of supports. In addition, a weak diffraction peak of PdO was also emerged, implying that PdO was evenly dispersed on the surface of supports, and was a microcrystalline.

3.3.3 Textural property of catalysts

As shown in Table 2, the surface areas of the Pd-MnO₂/SiO₂,

Fig.6 XRD patterns of samples co-impregnated Pd and MnO_x on different supports

Table 2 Textural properties of the samples co-impregnated Pd and MnO_x on different supports

Sample	Surface area	Pore volume	Average pore diameter
	(m ² ·g ⁻¹)	(cm ³ ·g ⁻¹)	nm
La-Al ₂ O ₃	156	0.37	9.4
SiO ₂	232	0.27	4.6
γ-Al ₂ O ₃	216	0.36	6.7
Zr-Al ₂ O ₃	244	0.36	6.0

Pd-MnO₂/γ-Al₂O₃ and Pd-MnO₂/Zr-Al₂O₃ are large, whereas the surface area of the Pd-MnO₂/La-Al₂O₃ is the least. Total pore volume is almost the same for the Pd-MnO₂/γ-Al₂O₃, Pd-MnO₂/La-Al₂O₃, and Pd-MnO₂/Zr-Al₂O₃, while pore volume of the Pd-MnO₂/SiO₂ is the least. The average pore diameter of the Pd-MnO₂/La-Al₂O₃ is the largest, in favor of O₃ mass transfer under high space velocity. The average pore diameter of the Pd-MnO₂/SiO₂ catalyst is the least. The textural property of the Pd-MnO₂/SiO₂ catalyst is related to its support, which has large surface area and small average pore diameter.^{21,22} Large surface area is in favor of O₃ adsorption on the SiO₂ support. However, its small pore volume and small average pore diameter make against the mass transfer of O₃ molecules, especially, under high space velocity. Therefore, the activity of the Pd-MnO₂/SiO₂ catalyst sharply declined with the increase of space velocity.

3.3.4 XPS of catalysts

Fig. 7 shows Mn 2p_{3/2} XPS spectra for the samples co-impregnated Pd and MnO_x on different supports. According to literature,^{23,24} the binding energies of Mn 2p_{3/2} were 640.8, 641.8, and 642.6 eV for Mn(II), Mn(III), and Mn(IV), respectively.^{24,25} As shown in Fig. 7, valence state of Mn is +3 on the surface of the Pd-MnO_x/SiO₂ catalyst. Although XRD pattern (Fig. 6) shows MnO₂ microcrystalline, it is possible that negative charge in SiO₂ support was transferred into Mn⁴⁺ due to strong interaction between MnO_x and SiO₂ support, resulting in the forma-

Fig. 7 Mn 2p_{3/2} XPS spectra for the samples co-impregnated Pd and MnO_x on different supports**Table 3** XPS results of Mn 2p_{3/2} for the samples co-impregnated Pd and MnO_x on different supports

Sample	Mn ²⁺		Mn ³⁺		Mn ⁴⁺	
	Peak position/eV	A/%	Peak position/eV	A/%	Peak position/eV	A/%
La-Al ₂ O ₃	640.6	39.6	641.9	60.4	—	—
SiO ₂	—	—	641.8	100	—	—
γ-Al ₂ O ₃	640.7	32.5	—	—	642.3	67.5
Zr-Al ₂ O ₃	640.6	39.9	—	—	642.6	60.1

A: atomic percent of Mn²⁺, Mn³⁺, and Mn⁴⁺

tion of Mn₂O₃ on the surface of the catalyst. Valence states of Mn are +2 and +3 on the surface of the Pd-MnO_x/La-Al₂O₃ catalyst. It indicates that MnO_x is in the presence of MnO and Mn₂O₃ on the surface of the catalyst, and there is a strong interaction between MnO_x and La-Al₂O₃ support. Valence states of Mn are +2 and +4 on the surfaces of the Pd-MnO_x/γ-Al₂O₃ catalyst and the Pd-MnO_x/Zr-Al₂O₃ catalyst. Namely, MnO, Mn₃O₄, or Mn₂O₈ formed by Mn⁴⁺ got electrons from the support (γ-Al₂O₃ or Zr-Al₂O₃) on the surface of the catalysts. The relative amount of Mn²⁺, Mn³⁺, and Mn⁴⁺ species on the surface of samples is listed in Table 3.

3.3.5 TPR of catalysts

Fig. 8 exhibits H₂-TPR profiles of samples co-impregnated Pd and MnO_x on different supports. It can be seen that support obviously affects the reducibility of PdO and MnO_x. For the Pd-MnO_x/SiO₂ catalyst, a large reduction peak around 66–160 °C can be divided into two peaks at 102 and 132 °C, which represent the reduction of PdO and MnO_x, respectively. The reduction peak of MnO_x obviously shifted towards low temperature due to strong interaction between MnO_x and SiO₂ support, in agreement with the result of XPS analysis. Namely, MnO_x species is highly active and is easily reduced for the Pd-MnO_x/SiO₂ catalyst. For the Pd-MnO_x/La-Al₂O₃ catalyst, a large reduction peak around 58–200 °C can be divided into two peaks at 116 and 145 °C, which are ascribed to the reduction of PdO and MnO_x, respectively.¹⁸ The reduction temperatures of PdO and MnO_x are low for Pd-MnO_x/SiO₂ and Pd-MnO_x/La-Al₂O₃, implying high reducibility and better activity of PdO and MnO_x. The peak at 155 °C is due to the reduction of PdO,¹⁸ the peak at

Fig. 8 H₂-TPR profiles of samples co-impregnated Pd and MnO_x on different supports

210 °C is ascribed as MnO₂ reduction to Mn₃O₄, the peak at 430 °C belongs to Mn₃O₄ reducing to MnO.¹⁹ The reduction peak areas of PdO and MnO_x are large for the Pd-MnO_x/γ-Al₂O₃ catalyst, leading to better catalytic performance for O₃ decomposition. A peak at 120 °C is attributed to the reduction of PdO, small peaks around 180 and 260 °C are ascribed to the reduction of MnO_x for the Pd-MnO_x/Zr-Al₂O₃ catalyst. The catalyst has less activity, which is related to poor reducibility of MnO_x.

Lin *et al.*²⁶ supposed an interaction of metal with catalyst support, and adsorption ability of support affected the activity of catalyst. According to the result of H₂-TPR, MnO_x has high reducibility due to strong interaction between MnO_x and SiO₂ support, in favor of Mn²⁺ participating in O₃ decomposition.²⁷ SiO₂ is a good adsorbent for O₃, and H₂O molecules were weakly adsorbed on the surface of SiO₂, hardly compete with O₃ for adsorption under high humidity.²⁶ Moreover, mild acidic SiO₂ support promotes the formation of oxygen species intermediates (e.g., O₃⁻ and O⁻), which would enhance the adsorption and decomposition of O₃.²⁸ These factors are in favor of O₃ decomposition. Therefore, the Pd-MnO_x/SiO₂ catalyst has excellent catalytic activity. However, when the space velocity increased a lot, the activity of the Pd-MnO_x/SiO₂ catalyst was drastically declined due to small pore diameter going against mass transfer of O₃ molecules and its products. For the Pd-MnO_x/La-Al₂O₃ catalyst, both high reducibility of PdO and MnO_x and large average pore diameter are in favor of O₃ decomposition under high space velocity. Therefore, the catalyst shows the best catalytic performance.

3.4 Durability of catalyst

O₃ (6.0 × 10⁻⁷) was continuously decomposed at 90 °C for 10 days on the Pd-MnO_x/γ-Al₂O₃ catalyst under space velocity of 580000 h⁻¹ and RH of 85%–90%. The activity of the catalyst hold steady, and the washcoat of catalyst did not desquamate, which are related to stable physicochemical properties of the γ-Al₂O₃ support, active species of Pd and MnO_x, and better viscosity of the support.

4 Conclusions

When active Pd and MnO_x coexist in the Pd-MnO_x/γ-Al₂O₃ catalyst, its activity is higher than that of the Pd or MnO_x catalyst (e.g., Pd/γ-Al₂O₃ or MnO_x/γ-Al₂O₃). The catalyst co-impregnated Pd and MnO_x has better activity than the catalyst impregnated Pd or MnO_x sequentially. The supports have significant impacts on catalytic activity for O₃ decomposition. The Pd-MnO_x/La-Al₂O₃ catalyst has the best activity. Next is the catalyst using SiO₂ as a support. Again is the catalyst using γ-Al₂O₃ as a support. Finally, the Pd-MnO_x/Zr-Al₂O₃ sample has the worst catalytic performance in all of the catalysts. The activity of catalysts prepared on different supports is nearly in agreement with the reducibility of Pd and MnO_x. Ground-level ozone would be completely decomposed if the Pd-MnO_x/La-Al₂O₃ catalyst was coated on vehicle radiators, in which their tempera-

ture ranged from 20 to 90 °C. Therefore, the as-prepared catalyst has a potential applicable value.

References

- (1) Gryparis, A.; Forsberg, B.; Katsouyanni, K.; Analitis, A.; Touloumi, G.; Schwartz, J.; Samoli, E.; Medina, S.; Anderson, H. R.; Niciu, E. M. *American Journal of Respiratory and Critical Care Medicine* **2004**, *170*, 1080. doi: 10.1164/rccm.200403-333OC
- (2) Wan, W. X.; Xia, Y. J.; Zhang, H. X.; Wang, J.; Wang, X. K. *Acta Ecologica Sinica* **2013**, *33* (4), 1098. [万五星, 夏亚军, 张红星, 王 娇, 王效科. 生态学报, **2013**, *33* (4), 1098.] doi: 10.5846/stxb
- (3) Karlsson, P. E.; Pleijel, H.; Belhaj, M.; Danielsson, H.; Dahlin, B.; Andersson, M.; Haneon, M.; Munthe, J.; Grennfelt, P. *AMBIO* **2005**, *34*, 32.
- (4) Weschler, C. J. *Indoor Air* **2000**, *10*, 269. doi: 10.1034/j.1600-0668.2000.010004269.x
- (5) Dhandapani, B.; Oyama, S. T. *Appl. Catal. B* **1997**, *11*, 129. doi: 10.1016/S0926-3373(96)00044-6
- (6) Japan Air Cleaning Association. *Air Cleaning Handbook*; Ohm Press: Tokyo, 1981; p178
- (7) Zhang, B.; Shi, R.; Zhang, P. Y.; Xu, J. H. *Rare Metal Mat. Eng.* **2010**, *39* (4), 692. [张 博, 史 蕊, 张彭义, 徐九华. 稀有金属材料与工程, **2010**, *39* (4), 692.]
- (8) Zhang, B.; Zhang, P. Y.; Shi, R.; Wang, H. J. *Chin. J. Catal.* **2009**, *30* (3), 235. [张 博, 张彭义, 史 蕊, 王化军. 催化学报, **2009**, *30* (3), 235.]
- (9) Yu, Q. W.; Zhao, M.; Liu, Z. M.; Zhang, X. Y.; Zheng, L. M.; Chen, Y. Q.; Gong, M. C. *Chin. J. Catal.* **2009**, *30* (1), 1. [余全伟, 赵 明, 刘志敏, 张晓玉, 郑灵敏, 陈耀强, 龚茂初. 催化学报, **2009**, *30* (1), 1.] doi: 10.1016/S1872-2067(08)60082-0
- (10) Pan, H.; Zhou, L. N.; Zhu, Y.; Peng, N.; Gong, M. C.; Chen, Y. Q. *Chin. J. Catal.* **2011**, *32* (6), 1040. [潘 浩, 周丽娜, 朱 艺, 彭 娜, 龚茂初, 陈耀强. 催化学报, **2011**, *32* (6), 1040.]
- (11) Zhou, L. N.; Chen, Y. Q.; Ren, C. J.; Gong, M. C. *Chin. J. Inorg. Chem.* **2013**, *29* (11), 2363. [周丽娜, 陈耀强, 任成军, 龚茂初. 无机化学学报, **2013**, *29* (11), 2363.]
- (12) Thompson, A. M. *Science* **1992**, *256*, 1157. doi: 10.1126/science.256.5060.1157
- (13) Russell, A.; Milford, J.; Bergin, M. S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W. R.; Croes, B. *Science* **1995**, *269*, 491. doi: 10.1126/science.269.5223.491
- (14) Yu, L. P.; Jia, J. J. *J. Shandong Univ. Sci. Technol. Nat. Sci.* **2001**, *20* (4), 111. [于林平, 贾建军. 山东科技大学学报(自然科学版), **2001**, *20* (4), 111.]
- (15) Sadao Terui, H.; Yoshiyuki Yokota, S. Catalyst and Method of Preparing the Catalyst. US Patent, 5187137, 1993-02-16.
- (16) Kameya, T.; Urano, K. *J. Environ. Eng.* **2002**, *128*, 286. doi: 10.1061/(ASCE)0733-9372(2002)128:3(286)
- (17) Wu, M. C.; Kelly, N. A. *Appl. Catal. B* **1998**, *18*, 93.

- doi: 10.1016/S0926-3373(98)00028-9
- (18) Yao, Y. L.; Fang, R. M.; Shi, Z. H.; Gong, M. C.; Chen, Y. Q. *Chin. J. Catal.* **2011**, *32* (4), 589. [姚艳玲, 方瑞梅, 史忠华, 龚茂初, 陈耀强. 催化学报, **2011**, *32* (4), 589.]
- (19) Rezaei, E.; Soltan, J.; Chen, N.; Lin, J. R. *Chem. Eng. J.* **2013**, *214*, 219. doi: 10.1016/j.cej.2012.10.044
- (20) Xu, G. P.; Zhu, Y. X.; Ma, J.; Yan, H. J.; Xie, Y. C. *Stud. Surf. Sci. Catal.* **1997**, *11*, 333.
- (21) Ren, C. J.; Qiu, W.; Chen, Y. Q. *Sep. Purif. Technol.* **2013**, *107*, 264. doi: 10.1016/j.seppur.2013.01.037
- (22) Qiu, W.; Ren, C. J.; Gong, M. C.; Hou, Y. Z.; Chen, Y. Q. *Acta Phys. -Chim. Sin.* **2011**, *27*, 1487. [仇 伟, 任成军, 龚茂初, 侯云泽, 陈耀强. 物理化学学报, **2011**, *27*, 1487.] doi: 10.3866/PKU.WHXB20110621
- (23) Santos, V. P.; Pereira, M. F. R.; Órfão, J. J. M.; Figueiredo, J. L. *Appl. Catal. B* **2010**, *99*, 353. doi: 10.1016/j.apcatb.2010.07.007
- (24) Wei, Y. J.; Yan, L. Y.; Wang, C. Z.; Xu, X. G.; Wu, F.; Chen, G. *J. Phys. Chem. B* **2004**, *108*, 18547. doi: 10.1021/jp0479522
- (25) O'Shea, V. A. D. P.; Álvarez-Galván, M. C.; Fierro, J. L. G.; Arias, P. L. *Appl. Catal. B* **2005**, *57*, 191. doi: 10.1016/j.apcatb.2004.11.001
- (26) Lin, J. J.; Kawai, A.; Nakajima, T. *Appl. Catal. B* **2002**, *39*, 157. doi: 10.1016/S0926-3373(02)00081-4
- (27) Einaga, H.; Harada, M.; Futamura, S. *Chem. Phys. Lett.* **2005**, *408*, 377. doi: 10.1016/j.cplett.2005.04.061
- (28) Kumar, N.; Konova, P.; Naydenov, A.; Salmi, T.; Murzin, D. Y.; Heikillä, T.; Lehto, V. P. *Catal. Today* **2007**, *119*, 342. doi: 10.1016/j.cattod.2006.08.048