



# Influence of calcination temperature on the performance of Pd–Mn/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts for ozone decomposition

Quanwei Yu, Hao Pan, Ming Zhao, Zhimin Liu, Jianli Wang, Yaoqiang Chen, Maochu Gong\*

Key Laboratory of Green Chemistry & Technology of the Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, PR China

## ARTICLE INFO

### Article history:

Received 15 April 2009

Received in revised form 13 July 2009

Accepted 13 July 2009

Available online 18 July 2009

### Keywords:

Ozone

Calcination temperature

Manganese dioxide with deficient oxygen atom

Catalytic decomposition

Monolithic catalyst

## ABSTRACT

The catalytic decomposition of ozone was investigated over Pd–Mn/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts in the ground air. The catalysts were prepared by incipient wetness impregnation method and characterized by powder X-ray diffraction (XRD), thermo gravimetric (TG) analysis, and N<sub>2</sub> adsorption/desorption measurements (Brunauer–Emmett–Teller method). The influence of calcination temperature on the catalytic activities, and the lifetime test of the catalyst pretreated at 350 °C had been studied. XRD and TG results show that when calcined in the temperature range of 300–450 °C, manganese carbonate (MnCO<sub>3</sub>) is partly decomposed to MnO<sub>x</sub> ( $x = 1.6\text{--}2.0$ ) species in the catalysts. However, when calcined at 500 °C, MnO<sub>x</sub> partly turns into Mn<sub>2</sub>O<sub>3</sub> in the catalyst. The catalytic activity test indicates that the catalysts calcined at 300–400 °C exhibit the best performance for O<sub>3</sub> decomposition, and the completely conversion temperature of ozone ( $T_{100}$ ) is in the region of 30–35 °C, which is lower than surface temperature of water tanks of running automobile. Under gas hour space velocity (GHSV) of 635,000 h<sup>-1</sup> and reaction temperature of 40 °C, after lifetime test for 80 h, the catalyst calcined at 350 °C keeps 90% conversion, which indicates that they have excellent ability to resist deactivation. The catalysts calcined at 300–400 °C show great potential to be applied at lower temperature, especially in winter and at the stage of automobile engine cold start.

Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.

## 1. Introduction

It is well known that the ozone layer in the Earth's stratosphere can resist ultraviolet light to protect life on the Earth. However when it resides in the ground atmosphere, ozone is a harmful pollutant that causes health problems to human beings. When the ozone concentration in the air is beyond  $1 \times 10^{-7}$  (volume ratio), people will feel uncomfortable. Increasing of the ozone concentration further will cause cancer even death [1,2]. Hydrocarbons and nitrogen oxides in automobile exhaust emissions will generate a certain concentration of ozone on the surface of the Earth with the effect of sunlight [3]. Another major source of high concentration of ground ozone comes from high-temperature, high-discharge mechanical work, such as air-condition, photocopiers, aircraft cabin, and so on [1]. To reduce the ground ozone and protect human lives, the United States and the World Health Organization constituted the laws to limit the ozone concentration in the air which should be lower than  $1 \times 10^{-7}$  [4,5]. Chinese "indoor air quality standards" (GB/T 18883-2002) required that indoor ozone concentration should not exceed 0.16 mg/m<sup>3</sup> [6].

Ozone is relative unstable and can easily decompose to O<sub>2</sub> molecule. The decomposition increases with the increasing of temperature. Two approaches for ozone decomposition have been established, namely catalytic decomposition and photocatalytic decomposition. Currently, the former has been extensively studied in the world. For example, Terui et al. [7,8] calcined MnCO<sub>3</sub> solid at different temperature to produce MnO<sub>x</sub> ( $x = 1.6\text{--}2.0$ ) which was used as the active component. Hoke et al. [9,10] used Pd, Pt and MnO<sub>x</sub> ( $x = 1.6\text{--}2.0$ ) as the active component, respectively, and the prepared catalysts coated on wave-shaped heat patches of the automobile water tanks. When cars run at high speed, the water tanks use the waste heat of their surface (surface temperature was 45–105 °C) to treat ground O<sub>3</sub>. The PremAir catalyst from Engelhard Corporation was used on the automobile water tanks, and the O<sub>3</sub> conversion was about 80% [11]. In China, Au/Fe<sub>2</sub>O<sub>3</sub> and manganese catalysts were prepared to decompose high concentration O<sub>3</sub> by Hao et al. [12] and Liu et al. [13–15], respectively. He et al. [16] used Au/TiO<sub>2</sub> catalysts for the photocatalytic decomposition of O<sub>3</sub> in air. The experimental results show that at low relative humidity (RH), MnO<sub>2</sub> has the best capacity to treat O<sub>3</sub> [17], but at high RH, H<sub>2</sub>O and O<sub>3</sub> molecules adsorb competitively on the surface of catalysts; the pores are blocked, and the activity of MnO<sub>2</sub> becomes poor. The addition of Pd can resist water and slow down the activity reduction of the catalysts [18–20]. It is expected that the combination of Pd with

\* Corresponding author. Tel.: +86 28 85418451; fax: +86 28 85418451.  
E-mail address: [nic7501@email.scu.edu.cn](mailto:nic7501@email.scu.edu.cn) (M. Gong).

MnO<sub>2</sub> in the same catalysts will contribute to O<sub>3</sub> decomposition, and MnO<sub>2</sub> in two active components Pd and MnO<sub>2</sub> is main below 70% RH at room temperature [20]. It was reported that catalysts containing MnCO<sub>3</sub> but without Pd calcined at different temperature would exhibit different catalytic performance [8].

In the paper, the preparation and characterization of Pd–Mn/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts was reported. The influence of different calcination temperature on the catalytic performance to decompose ozone at low temperature was investigated.

## 2. Experimental

### 2.1. The preparation of support and catalyst

SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support was prepared by peptizing method [21]. First, sodium silicate (AR grade, Chengdu Kelong Chemical Reagents Factory, China) solution and HNO<sub>3</sub> solution were mixed and stirred to form SiO<sub>2</sub> sol. Meanwhile, water and HNO<sub>3</sub> were mixed with pseudo-boehmite and then milled to form Al<sub>2</sub>O<sub>3</sub> sol. Then, the prepared SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> sol were mixed, milled and deposited. After washed, sprayed, dried and calcined at 600 °C for 4 h. SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support was obtained (specific surface area: 199 m<sup>2</sup>/g).

Activated MnCO<sub>3</sub> (CR grade, Chengdu Kelong Chemical Reagents Factory, China) was prepared by heating MnCO<sub>3</sub> solid at 300 °C for 2 h in air [8].

Pd–Mn catalysts were prepared by incipient wetness impregnation method [22]. Palladium nitrate solution was divided into two parts with the volume ratio of 2:1, and impregnated on active MnCO<sub>3</sub> and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support, respectively. After calcined at 300 °C for 2 h, the catalyst powder were mixed and milled to form slurry. Then the resulting slurry was coated onto ceramic honeycomb substrate (400 cell/in.<sup>2</sup>, Corning, America) with the volume of 0.30 cm<sup>3</sup>. After dried at 120 °C for 2 h, the catalysts were calcined for 2 h at 300, 350, 400, 450, and 500 °C, respectively. The obtained catalyst was denoted as PM300, PM350, PM400, PM450, and PM500, respectively. All catalysts had the same Mn content, with Pd:Mn = 1:100 (molar ratio), and the loading of washcoat is 250–265 g/L.

### 2.2. Characterization of catalysts and MnCO<sub>3</sub>

Powder XRD data of catalysts were obtained by D/max-rA X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) operating at 50 kV and 180 mA. Samples were scanned in the  $2\theta$  range from 10° to 90°.

TG analysis data of MnCO<sub>3</sub> solid were obtained by NETZSCH TG209F1 instrument under N<sub>2</sub> atmosphere with a heating rate of 10 °C/min from 30 to 700 °C.

The BET specific surface areas of all catalysts were determined by N<sub>2</sub> adsorption/desorption method on a ZXF-6 automatic surface analyzer (Xibei Chemical Institute, China).

### 2.3. Catalytic activity measurement

The test apparatus consists of the air compressor, O<sub>3</sub> generator (JY-3 model, Qianguai purification equipment plant, China), the catalytic reactor, and O<sub>3</sub> analyzer (M4+ model, Bashang Technology Co. Ltd., China). The gas flow passing the reactor is 3.15 L/min.

The temperature of the 100% O<sub>3</sub> conversion is defined as the completely conversion temperature ( $T_{100}$ ). When the O<sub>3</sub> concentration passing into the reactor with  $(6.0 \pm 0.2) \times 10^{-7}$  (volume ratio, 27 °C testing), GHSV = 635,000 h<sup>-1</sup>, RH = 55–65% (at 23–27 °C), activity test was performed with the heating rate of 1–1.5 °C/min.

## 3. Results and discussion

### 3.1. XRD and TG analyses

The catalysts PM300, PM400, PM450 and PM500 were characterized by XRD, as shown in Fig. 1. The XRD patterns show that MnCO<sub>3</sub> solid did not decompose completely in all the catalysts except PM500. The diffraction peaks should be ascribed to MnCO<sub>3</sub> and MnO<sub>x</sub> for PM300, PM400, while be ascribed to MnCO<sub>3</sub>, MnO<sub>x</sub> and Mn<sub>2</sub>O<sub>3</sub> for PM450, while be ascribed to MnO<sub>x</sub>, Mn<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for PM500. MnCO<sub>3</sub> solid decomposed to MnO<sub>x</sub> for PM300, PM400 and PM450, and MnO<sub>x</sub> partly transforms to Mn<sub>2</sub>O<sub>3</sub> for PM500. In other word, MnCO<sub>3</sub> firstly decomposes to MnO<sub>x</sub> with the increasing of temperature; then, MnO<sub>x</sub> gradually turns into Mn<sub>2</sub>O<sub>3</sub> after MnCO<sub>3</sub> has been decomposed greatly at 450 °C. The results of XRD are in good agreement with that reported by Kitaguchi et al. [8].

The decomposition behavior of MnCO<sub>3</sub> solid was characterized by TG measurement with a heating rate of 10 °C/min in N<sub>2</sub> atmosphere. As shown in Fig. 2, three approximate platforms exist in the temperature range of 200–400, 460–500 and 550–700 °C, respectively, so the mass of calcination solid becomes unchanged nearly in the three temperature range. It indicates that the phases of calcination solid become unchanged nearly in the three temperature range

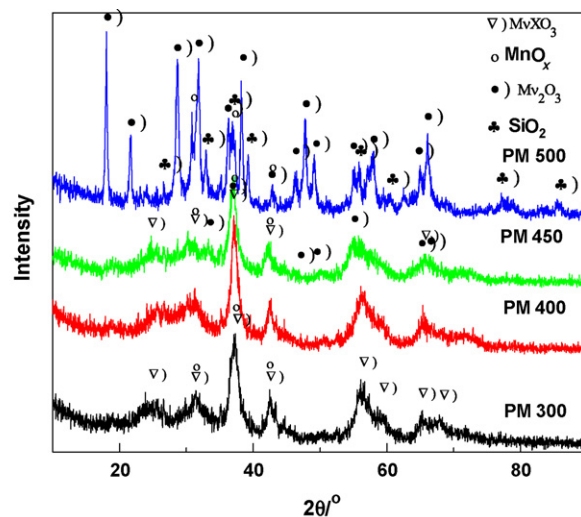


Fig. 1. XRD patterns of the catalysts calcined at different temperature. PM300: 300 °C; PM400: 400 °C; PM450: 450 °C; PM500: 500 °C.

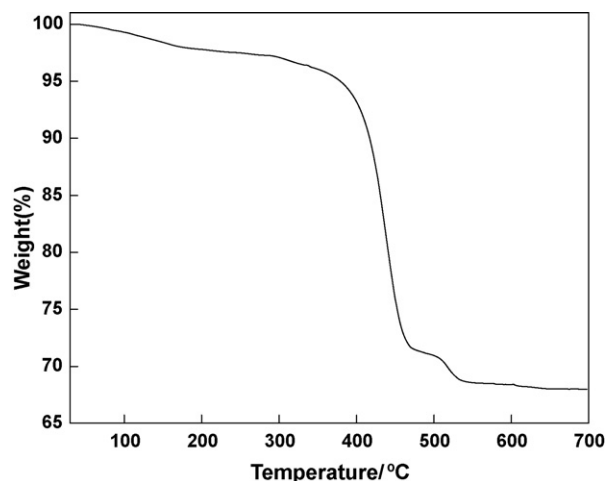


Fig. 2. TG curve of MnCO<sub>3</sub> solid under a flow of N<sub>2</sub> with a heating rate of 10 °C/min.

**Table 1**

The textural performance of Pd-Mn/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts calcined at different temperature.

	PM300	PM350	PM400	PM450	PM500
Surface area (m <sup>2</sup> /g)	96.60	97.70	88.13	86.54	87.85
Pore volume (cm <sup>3</sup> /g)	0.18	0.18	0.16	0.22	0.20
Average pore diameter (nm)	5.98	6.20	5.88	5.84	6.75

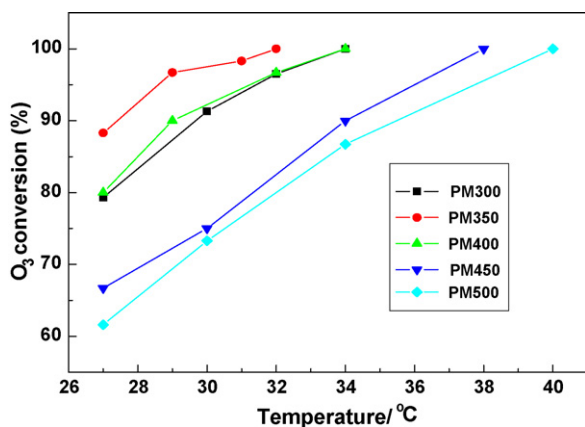
too. The slight mass loss below 150 °C is likely due to the removal of water molecules adsorbed on the surface of MnCO<sub>3</sub> solid. At the temperature of 300, 350, 400 and 450 °C, it is 5.4%, 9.8%, 21.7% and 93.9% of MnCO<sub>3</sub> decomposition, respectively (the result is obtained according to mass reduction of the solid by TG). And a drastic weight loss in the range of 400–460 °C is found which should be the great decomposition of MnCO<sub>3</sub> solid with the increasing of temperature. The results of TG and XRD analyses reveal: (1) MnCO<sub>3</sub> solid turn into MnOx and form the mixture of MnCO<sub>3</sub> and MnOx in the temperature range of 200–460 °C; (2) as soon as MnCO<sub>3</sub> solid completely decompose, a small amount of MnOx turns into Mn<sub>2</sub>O<sub>3</sub>; (3) MnOx phase is mainly present at about 460–500 °C; (4) most MnOx turns into Mn<sub>2</sub>O<sub>3</sub> at the temperature range of 500–550 °C; (5) only Mn<sub>2</sub>O<sub>3</sub> phase is presented at 550–700 °C.

### 3.2. Texture of catalysts

The textural performances of the five catalysts at different calcination temperature were characterized by N<sub>2</sub> adsorption/desorption measurements and the results are listed in Table 1. It is obvious that all of the catalysts exhibit similar specific surface area and the pore volume. However, with the increasing of calcination temperature, the pore diameter first decreases then increases. The texture of these catalysts had little influence on their catalytic activity. The reason is that, at the condition of high GHSV, O<sub>3</sub> molecules are only adsorbed on the surface of the catalysts for a very short time and cannot diffuse into the inner pores of the catalysts to reach the reaction sites.

### 3.3. Catalytic activity

The catalytic performances of the five catalysts were measured. As shown in Fig. 3, the activity of the catalysts increases with the increasing of reaction temperature. The T<sub>100</sub> of PM300, PM350, PM400, PM450, and PM500 is 34, 32, 34, 38 and 40 °C, respectively. The conversion at 27 °C is 79.3%, 88.3%, 80.0%, 66.7% and 61.6%, respectively. These results show that the catalysts calcined at



**Fig. 3.** The curve of O<sub>3</sub> conversion of the catalysts calcined at different temperatures. PM300: 300 °C; PM350: 350 °C; PM400: 400 °C; PM450: 450 °C; PM500: 500 °C. Reaction condition: O<sub>3</sub> concentration of entrance = (6.0 ± 0.2) × 10<sup>-7</sup> (volume ratio), GHSV = 635,000 h<sup>-1</sup>, RH = 55–65%.

300–400 °C have the best activity for ozone decomposition. Especially at room temperature (i.e. 27 °C), the conversion over PM300, PM350 and PM400 is about 80%, and the T<sub>100</sub> of the catalysts is relative low (at 30–35 °C); and the catalysts can treat ground O<sub>3</sub> completely by the waste heat on the surface of water tanks. These results indicate that these catalysts can be applied in ozone decomposition at lower temperature, especially in winter and at the stage of automobile engine cold start. And the catalysts are also used on the heat patches of the air-conditioner to decompose O<sub>3</sub>, which the air-conditioner produces in work. So, the catalysts calcined at 300–400 °C make the contribution to environment-protection and saving energy sources.

From characterization and catalytic activity measurements above-mentioned, we can see that the Mn species in the calcination solid, instead of texture, plays an important role for O<sub>3</sub> decomposition. The reason is that MnCO<sub>3</sub>, MnOx and Mn<sub>2</sub>O<sub>3</sub> have different catalytic activity for O<sub>3</sub> decomposition [8]. Especially when a small amount of MnCO<sub>3</sub> solid in the catalysts decomposes to MnOx at calcination temperature of 300–400 °C, the mutual effect between MnCO<sub>3</sub> and MnOx is likely to exist in the catalysts and results in the best activity. Therefore, the mutual effect can contribute to O<sub>3</sub> decomposition and be responsible for the activity of the catalysts.

### 3.4. Lifetime test of PM350

At 40 °C (test conditions as above), PM350 catalyst still keeps excellent performance of O<sub>3</sub> conversion by 90%. So, it has excellent ability to resist deactivation after the lifetime test of 80 h. The higher the test temperature is, the longer the lifetime of the catalyst become. When the automobile run at normal conditions, the surface temperature of water tank is about 90 °C, under which the lifetime of the catalyst will lengthen greatly. So, the catalysts calcined at 300–400 °C exhibit great potential to be applied in water tank of automobile in future.

## 4. Conclusion

A series of catalysts can effectively decompose O<sub>3</sub> in ground air. Four conclusions can be made in this work. (1) The compositions of the calcination solid play a crucial role in the catalytic activity. (2) The catalysts calcined at 300–400 °C have the best performance. T<sub>100</sub> of them is relative low (at 30–35 °C). (3) They can be applied to decompose O<sub>3</sub> when the automobile are running, especially in winter and at the stage of engine cold start. (4) The catalysts have excellent ability to resist deactivation. Therefore, the catalysts have wide application in the reduction of ground O<sub>3</sub> at lower temperature.

## Acknowledgements

We gratefully acknowledge the financial support from the National High Technology Research and Development Program of China (863 Program, No. 2006AA06Z347) and the National Natural Science Foundation of China (No. 20773090). We also thank Prof. Qian Zhou for TG, Prof. Jumu Zhu for XRD, Prof. Zhien Lin and Dr. Xiaoyu Zhang for revision.

## References

- [1] C. Subrahmanyam, D.A. Bulushev, L. Kiwi-Minsker, Dynamic behaviour of activated carbon catalysts during ozone decomposition at room temperature. Dynamic behaviour of activated carbon catalysts during ozone decomposition at room temperature, *Appl. Catal. B: Environ.* 61 (2005) 98–106.
- [2] Y.L. Gu, S.W. Liu, X.L. Xu, Preparation and properties of binary metal oxide ozone decomposition catalyst, *Ind. Catal.* 10 (2002) 39–42.
- [3] J.B. Hoke, R.M. Heck, T.C. Poles, PremAir® Catalyst System—A New Approach to Cleaning the Air, SAE, 1999-01-3677.

- [4] J. Lin, A. Kawai, T. Nakajima, Effective catalysts for decomposition of aqueous ozone, *Appl. Catal. B: Environ.* 39 (2002) 157–165.
- [5] T.L. Rakitskaya, A.A. Ennan, I.V. Granatyuk, A.Y. Bandurko, G.G.A. Balavoine, Y.V. Geletii, V.Y. Paina, Kinetics and mechanism of low-temperature ozone decomposition by Co-ions adsorbed on silica, *Catal. Today* 53 (1999) 715–723.
- [6] D.M. Yang, P.K. He, F. Dong, M. Zhang, J.J. Yang, Effect of water vapor at room temperature on photocatalytic decomposition of gaseous ozone over Au/TiO<sub>2</sub>, *Chin. J. Catal.* 27 (2006) 1122–1126.
- [7] S. Terui, Y. Yokota, Catalyst and method of preparing the catalyst, US Patent 5,187,137 (1993).
- [8] S. Kitaguchi, S. Terui, A. Nose, Catalyst and a method of preparing the catalyst, US Patent 5,296,435 (1994).
- [9] J.B. Hoke, F.M. Allen, P.W. Blosser, Z. Hu, R.M. Heck, Stable slurries of catalytically active materials, US Patent 6,818,254 (2004).
- [10] J.B. Hoke, R.M. Heck, Catalyst and adsorption compositions having improved adhesion characteristics, US Patent 6,863,984 (2005).
- [11] R.J. Farrauto, R.M. Heck, Environmental catalysis into the 21st century, *Catal. Today* 55 (2000) 179–187.
- [12] Z.P. Hao, D.Y. Cheng, Y. Guo, Y.H. Liang, Supported gold catalysts used for ozone decomposition and simultaneous elimination of ozone and carbon monoxide at ambient temperature, *Appl. Catal. B: Environ.* 33 (2001) 217–222.
- [13] J. Liu, M.L. Luo, Z. Xu, J.L. Xie, H.L. Yin, Y.J. Feng, Decomposition of high concentrated ozone under high humidity condition, *Chem. Res. Appl.* 14 (2002) 191–193.
- [14] Q.L. Yang, J.L. Xie, Z. Xu, S.Y. Tan, Y.J. Feng, Manganese oxide catalysts for decomposition of ozone under high humidity condition, *Environ. Eng.* 20 (2002) 65–67.
- [15] H.L. Yin, D.P. Zhou, Q.L. Yang, Y.J. Feng, Decomposition of ozone on MnOx–AgOx/cordierite catalysts, *J. Func. Mater.* 36 (2005) 307–310.
- [16] P.K. He, J.J. Yang, D.M. Yang, X.H. Wang, M. Zhang, Photocatalytic decomposition of gaseous ozone on Au/TiO<sub>2</sub>, *Chin. J. Catal.* 27 (2006) 71–74.
- [17] B. Dhandapani, S.T. Oyama, Gas phase ozone decomposition catalysts, *Appl. Catal. B: Environ.* 11 (1997) 129–166.
- [18] M.C. Wu, N.A. Kelly, Clean-air catalyst system for on-road applications. I. Evaluation of potential catalysts, *Appl. Catal. B: Environ.* 18 (1998) 79–91.
- [19] M.C. Wu, N.A. Kelly, Clean-air catalyst system for on-road applications. II. Mechanistic studies of pollutant removal, *Appl. Catal. B: Environ.* 18 (1998) 93–104.
- [20] T. Kameya, K. Urano, Catalytic decomposition of ozone gas by a Pd impregnated MnO<sub>2</sub> catalyst, *J. Environ. Eng.* 128 (2002) 286–292.
- [21] L.J. Zhang, W.P. Dong, J.X. Guo, S.H. Yuan, L. Zhang, M.C. Gong, Y.Q. Chen, Performance of La–Ba Co-modified alumina prepared by peptizing method, *Acta Phys.-Chim. Sin.* 23 (2007) 1738–1742.
- [22] J.X. Guo, M.C. Gong, S.H. Yuan, Y.Q. Chen, Effect of BaO on catalytic activity of Pt–Rh TWC, *J. Rare Earth* 24 (2006) 27–31.