

Catalytic decomposition of ozone: from laboratory fixed bed reactor to design of adiabatic monolithic reactor

A. I. Naydenov

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev St., Block 11, 1113 Sofia, Bulgaria*

Received September 29, 2015; Revised October 28, 2015

The purpose of the present paper is to demonstrate an approach to establish kinetics parameters of ozone decomposition aimed at being suitable for further application to design monolithic reactors for neutralization of waste gases. A catalytic system of Ag/anodized alumina/aluminium foil was selected for this purpose. To obtain kinetic data close to plug-flow reactor conditions, the catalyst was tested in the form of 2×5 mm sheets loaded randomly in the reactor. The same amount of catalyst has been rolled to create tubes of circular cross-section (diameter of 2.5 mm) to resemble a geometrical configuration of a single monolithic channel. Two kinetic equations of first order and partial order reaction were selected to fit experimental data. Purification of waste gases containing ozone in a monolithic reactor was simulated by a two-dimensional heterogeneous model accounting for concentration and temperature profiles inside both the gas phase in the channel and the catalytic active phase.

Keywords: ozone, catalytic decomposition, reaction kinetics, two-dimensional model, monolithic channel.

INTRODUCTION

The reaction of catalytic decomposition of ozone is of practical interest for several reasons. Exit gases from ozonation of wastewater and drinking water, sterilization, and deodorization contain residual ozone and because ozone itself is very toxic, these gases must be neutralized [1]. The catalytic decomposition of ozone is required for purification of indoor ventilation air including aircrafts, where ozone peak levels without catalytic converters exceeds 100 ppb, with some flights having long periods when these levels are above 75 ppb [2]. The role of aerosol particles in depleting the stratospheric ozone layer is a problem of major importance. There has been long evidence for a negative correlation between ozone and aerosols during desert dust outbreaks [3]. *In situ* measurements show a significant reduction in ozone layer under high dust concentrations [4, 5].

Ag-containing catalysts exhibit highest activity when compared with oxides of Co, Ni, Fe, Mn, Ce, Cu, Pb, Bi, Sn, Mo, V, and Si [6]. It has been reported that a silver-based catalyst demonstrate a remarkable activity and stability even at low temperatures [7–12]. During the catalytic decomposition of ozone, a highly reactive oxygen species is produced that is able to oxidize completely toxic compounds at room temperature [13]. There is an increased interest in the complete oxidation of VOCs (volatile organic compounds) [13–20] and

CO [21, 22] in waste gases by catalytic ozonation. Most of the available data in the literature related to the catalytic decomposition of ozone are based on testing the catalysts in the form of small particles (sizes below 1 mm) of irregular shape and, at the same time, significant results on monolithic (structured) catalysts are missing.

The aim of the present paper was to demonstrate an alternative approach to establish kinetic parameters of ozone decomposition that are suitable for further application to design monolithic reactors. The active phase of the catalyst (Ag) was supported on a thin layer of γ -alumina obtained by anodizing an aluminium foil. The catalyst had well defined geometrical characteristics, which were proper for operation under plug-flow conditions by testing catalytic samples in the form of rectangular-shaped sheets thus ensuring almost perfect mixing around each catalytic element. For tests in a laminar gas flow inside a monolithic element, the same catalyst was examined in the form of a channel of circular cross-section. A possibility to apply the results of fixed bed reactor experiments by simulating the behaviour of a monolithic reactor for ozone-containing waste gas abatement by a two-dimensional heterogeneous model of monolithic channel is also considered.

EXPERIMENTAL

The catalytic support was prepared by anodizing an aluminium foil (thickness of 0.30 mm, 99%

* To whom all correspondence should be sent
E-mail: naydenov@svr.igic.bas.bg

purity) and rolled to create tubes of circular cross-section of a 153-mm length and diameter of 2.5 mm to achieve a geometrical configuration of a single monolithic channel. Anodizing was applied to obtain a thin film layer of γ - Al_2O_3 , which is suitable for a catalyst supports for Ag. A scanning electron micrograph (SEM) of the catalyst revealed an average thickness of the alumina layer of 15 μm , while a BET surface area of 14 $\text{m}^2\cdot\text{g}^{-1}$ was measured on a Quantachrome Nova 1200 instrument.

A catalytically active phase of 2 wt.% silver, measured by a Perkin-Elmer atomic absorption analyser, was deposited on the support by direct impregnation with an aqueous solution of AgNO_3 , then dried, and calcined at 400°C for 2 h.

The following experimental conditions were applied to obtain kinetic data. A catalyst sample (12 cm^2) was tested in the form of 2×5 mm sheets, then loaded randomly in the reactor (quartz glass tube, i.d. 5.5 mm), and mixed with α -alumina spherical particles of 0.6–0.7-mm size. The pressure drop was measured to be below 1 kPa and it was disregarded. Radial concentration profiles and axial dispersion effects were also neglected.

Ozone was synthesized in a flow of oxygen (99.7%) using an ozone generator with silent discharge and coaxial electrodes. The inlet concentration of ozone was varied from 0.04 to 0.17 $\text{mol}\cdot\text{m}^{-3}$. Ozone concentration was measured by an Ozomat GM ozone analyser (Anseros, Germany). The reaction temperature was varied from –40 to +40°C and was kept with an accuracy of $\pm 0.5^\circ\text{C}$ by

means of a thermostat with a mixture of acetone and dry ice (carbon dioxide, $T = -78^\circ\text{C}$).

RESULTS

The decomposition of ozone on an Ag/anodized alumina catalyst loaded in the reactor in the form of 2×5 mm sheets proceeds at a measurable rate at a temperature below -40°C (Fig. 1). Further, analysis of catalyst behaviour was extended by investigation of reaction kinetics. To calculate kinetic parameters both inlet concentration of the ozone and gas hourly space velocity (GHSV) were varied.

Data on conversion-temperature dependencies were used to fit kinetic parameters by applying the method described by Duprat [23] and Harriot [24]. The results are presented in Table 1. Details on the calculation procedure were published elsewhere [25]. In brief, it consists of a direct integration of the reaction rate based on data on temperature-conversion curves by using a one-dimensional pseudo-homogeneous model of plug-flow isothermal reactor. The residual squared sum (RSS) between experimental data and model predictions was minimized (an optimization criterion) and the square of correlation coefficient (R^2) was calculated and used as a measure of model applicability. Values for the effectiveness factor of first-order kinetics and slab geometry were calculated by Thiele modulus [26, 27]. Calculations showed that at temperatures above -10°C , where resistance due to internal diffusion plays a significant role, the decrease of the effectiveness factor could not be neglected.

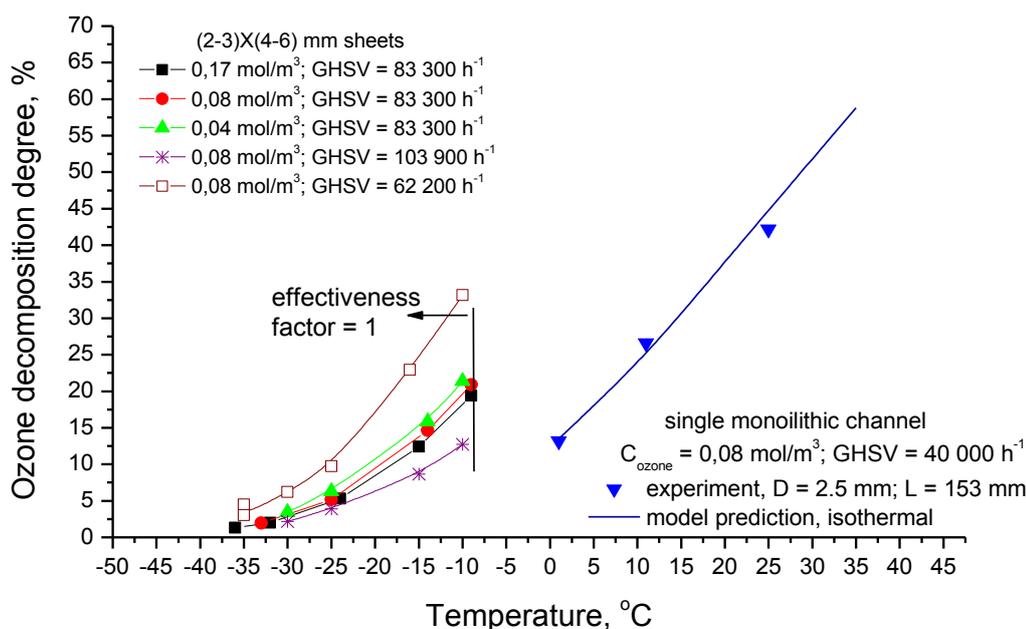
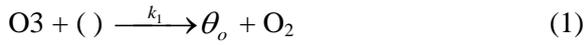


Fig. 1. Measured conversions of ozone decomposition over Ag/anodized Al-catalyst tested under conditions of plug-flow reactor and single monolithic channel with circular cross-section: comparison with model prediction.

Table 1.

Model	k_o	E_a	m	RSS	R^2
First order kinetics:					
$r_a = kP_{O_3}$	2.25E+12	52.0		1,7	0.988
Power-law kinetics:					
$r_a = kP_{O_3}^m$	2.25E+12	52.7	0.95	1.6	0.989
$k = k_o \cdot \exp(-E_a/RT)$; E_a , kJ.mol ⁻¹ ; k_o , mol.s ⁻¹ .m ⁻³ .atm ^{-(1-m)} .					

In general the heterogeneous catalytic decomposition of ozone can be presented by the following scheme [28]:



$$r = 2 \frac{k_1 \cdot k_2}{k_1 + k_2} \cdot P_{o_3} \quad (3)$$

Obviously, equation (3) applies for a first-order reaction (stoichiometric equation is $2O_3 \rightarrow 3O_2$). However, the present experimental results show an increased conversion value at a lower inlet concentration of ozone, i.e. the observed reaction order is somewhat lower than unity. A similar observation has been reported by Oyama and Li [29]. These authors proposed a simple rate expression of global kinetics: a power rate law dependence on ozone partial pressure that was linear over several orders of magnitude of ozone partial pressure change, $r = kP^{0.94}$.

Results of fixed bed reactor tests were applied to simulate the behaviour of a monolithic reactor for

abatement of waste gases containing ozone. A two-dimensional heterogeneous model of monolithic channel was used to simulate ozone decomposition in a monolithic reactor. The basic principles of the model have been described in detail by Belfiore [28] and Nauman [29]. A single channel model was the subject of mathematical description. A finite difference method was applied and the corresponding computational code was written by using a standard Excel® (Microsoft) program. Verification of the model was performed by a comparative calculation with the corresponding analytical solutions for certain boundary cases.

Figure 2 shows results of experiments with the monolithic element and calculations using the kinetics parameters as given in Table 1. Channel dimensions were selected in a way that channel area be the same as for a tested sample in a fixed bed reactor in the form of rectangular shaped sheets. The results are related to calculated conversion and temperature profiles inside the monolithic channel using data on first-order reactions at different channel dimensions (diameter and channel length), gas-hourly space velocities, inlet ozone concentrations, and data on an isothermal or adiabatic reactor operation. Furthermore, it was of practical interest to calculate the necessary amount of catalyst to achieve a specified degree of waste gas purification (e.g., if 98% of containing ozone is to be decomposed or to simulate the process in monoliths at a different channel/aspect ratio). For the purpose, experimental results acquired by means of an isothermal laboratory reactor (Fig. 2a) were used to simulate the abatement of methane containing gases under adiabatic conditions (Fig. 2b).

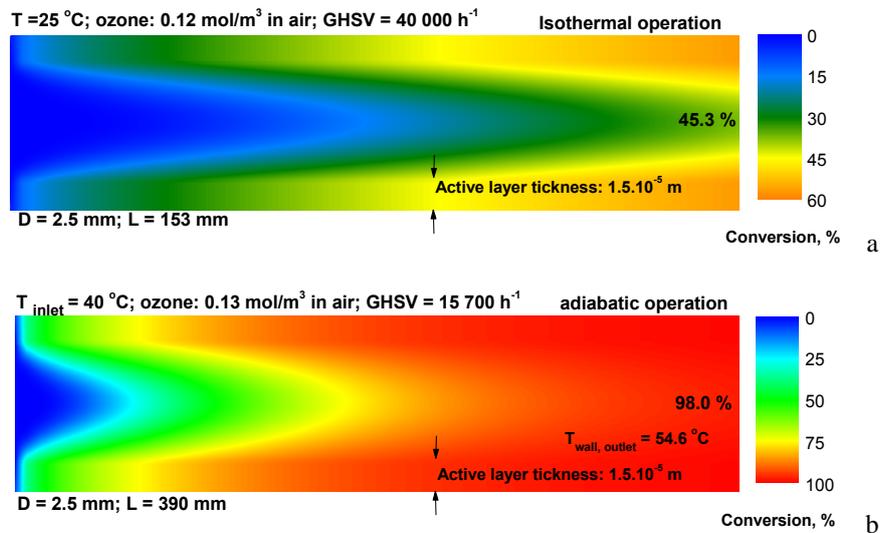


Fig. 2. Experimental (a) and calculated (b) conversion profiles inside the monolithic channel at a different channel length using the obtained data on first-order kinetics.

The proposed experimental approach can also be used to collect data on a detailed reaction mechanism by applying the co-called transient response method, first developed by Kobayashi [30]. It is based on analysis of the response of the catalytic system when a fast step-wise change of reaction parameters is applied.

CONCLUSION

Based on experimental results and performed calculations one may conclude that the reaction of catalytic decomposition of ozone was investigated under proper experimental conditions and data on further application to design structured (monolithic) reactors for abatement of ozone in waste gases could be provided.

Acknowledgements: Financial support by the European Social Fund through Contract BG051PO001-3.3.06-0050 and by a Collaborative project between the Bulgarian Academy of Sciences and the Macedonian Academy of Sciences and Arts is gratefully acknowledged. The author also thanks the Bulgarian Science Fund for Grant No TO1/6.

REFERENCES

1. S. Rakovsky, G. Zaikov, Kinetics and Mechanism of Ozone Reactions with Organic and Polymeric Compounds in Liquid Phase, Nova Science Publishers, Inc., Commack, New York, 1999.
2. C. Weisel, C. J. Weschler, K. Mohan, J. Vallarino, J. D. Spengler, *Environ. Sci. Technol.*, **47**, 4711 (2013).
3. J. Andrey, E. Cuevas, M. C. Parrondo, S. Alonso-Pérez, A. Redondas, M. Gil-Ojeda, *Atmos. Environ.*, **84**, 28 (2014).
4. M. de Reus, F. Dentener, A. Thomas, S. Borrmann, J. Ström, J. Lelieveld, *J. Geophys. Res.*, **105**, 15263 (2000).
5. E. Cuevas, Y. González, S. Rodríguez, J. C. Guerra, A. J. Gómez-Peláez S. Alonso-Pérez, J. Bustos, C. Milford, *Atmos. Chem. Phys.* **13**, 1973 (2013).
6. S. Imamura, M. Ikebata, T. Ito, T. Ogita, *Ind. Eng. Chem. Res.*, **30**, 217 (1991).
7. A. Naydenov, P. Konova, P. Nikolov, F. Klingstedt, N. Kumar, D. Kovacheva, P. Stefanov, R. Stoyanova, D. Mehandjiev, *Catal. Today.*, **137**, 471 (2008).
8. N. Kumar, P. Konova, A. Naydenov, T. Heikillä, T. Salmi, D. Yu. Murzin, *Catal. Lett.*, **98**, 57 (2004).
9. N. Kumar, P. Konova, A. Naydenov, T. Salmi, D. Yu. Murzin, T. Heikillä, V.-P. Lehto, *Catal. Today*, **119**, 342 (2007).
10. P. Nikolov, K. Genov, P. Konova, K. Milenova, T. Batakliiev, V. Georgiev, N. Kumar, D. K. Sarker, D. Pishev, S. Rakovsky, *J. Hazard. Mater.*, **184**, 16 (2010).
11. K. Genov, V. Georgiev, T. Batakliiev, D. K. Sarker, *Int. J. Civ. Environ. Eng.*, **33**, 205 (2011).
12. T. Batakliiev, G. Tyuliev, V. Georgiev, M. Anachkov, A. Eliyas, S. Rakovsky, *Ozone: Sci. Eng.*, **37**, 3, 216 (2015).
13. A. Naydenov, D. Mehandjiev, *Appl. Catal. A: General*, **97**, 17 (1993).
14. H. Einaga, S. Futamura, *J. Catal.*, **227**, 304 (2004).
15. H. Einaga, S. Futamura, *Appl. Catal. B: Environ.*, **60**, 49 (2005).
16. H. Einaga, S. Futamura, *J. Catal.*, **243**, 446 (2006).
17. H. Einaga, M. Harada, A. Ogata, *Catal. Lett.*, **129**, 422 (2009).
18. H. Einaga, A. Ogata, *J. Hazard. Mater.*, **164**, 1236 (2009).
19. H. Einaga, N. Maeda, S. Yamamoto, Y. Teraoka, *Catal. Today*, **245**, 22 (2015).
20. Y. Liu, X. Li, J. Liu, C. Shi, A. Zhu, *Chin. J. Catal.*, **35**, 1465 (2014)
21. A. Naydenov, R. Stoyanova, D. Mehandjiev, *J. Mol. Catal.*, **98**, 9 (1995).
22. K. Soni, S. C. Shekar, B. Singh, A. Agrawal, *Ind. J. Chem.*, **53A**, 484 (2014).
23. F. Duprat, *Chem. Eng. Sci.*, **57**, 901 (2002).
24. P. Harriot, Chemical Reactor Design, Marcel Dekker Inc., 2003.
25. S. Todorova, A. Naydenov, H. Kolev, J. P. Holgado, G. Ivanov, G. Kadinov, A. Caballero, *Appl. Catal. A:General*, **43**, 413 (2012).
26. C. N. Satterfield, Mass Transfer in Heterogeneous Catalysis, MIT Press, Cambridge, Mass., 1970.
27. O. Levenspiel, Chemical Reactor Engineering, 3rd edn., John Wiley & Sons Inc., 1999.
28. G. I. Golodetz, Heterogeneous catalytic reactions involving molecular oxygen, Elsevier, 1983, ISBN: 978-0-444-42204-0.
29. S. T. Oyama, W. Li, *Topics in Catalysis.*, **8**, 75 (1999).
30. L. A. Belfiore, Transport Phenomena for Chemical Reactor Design, John Wiley & Sons Inc., 2003.
31. E. B. Nauman, Chemical Reactor Design, Optimization, and Scaleup, McGraw-Hill, 2002.
- H. Kobayashi, M. Kobayashi, *Catal. Rev. Sci. Eng.*, **10**, 1 (1974).

КАТАЛИТИЧНО РАЗЛАГАНЕ НА ОЗОН – ОТ ЛАБОРАТОРЕН РЕАКТОР С НЕПОДВИЖЕН СЛОЙ КЪМ ОРАЗМЕРЯВАНЕ НА МОНОЛИТЕН АДИАБАТЕН РЕАКТОР

Ант. Ил. Найденов

*Институт по обща и неорганична химия, Българска академия на науките,
ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

Постъпила на 29 септември 2015 г.; Преработена на 28 октомври 2015 г.

(Резюме)

Целта на настоящата работа е да се покаже възможността за определяне на кинетичните параметри на реакцията на каталитично разлагане на озон с оглед последващо им приложение при оразмеряването на монолитни реактори за обезвреждане на отпадъчни газове. Каталитичната система Ag/анодиран алуминий/алуминиево фолио бе избрана за настоящото изследване. За получаване на данни за кинетиката при условия в реактора, близки до режим на идеално изместване, катализаторът бе тестван под формата на ленти с размери 2×5 mm, заредени в неподреден вид в каталитичния реактор. От същото количество катализатор бяха изработени и тръбни елементи с кръгло сечение с диаметър 2.5 mm с цел доближаване до геометричните характеристики на единичен канал от монолитен каталитичен елемент. За изчисляване на кинетичните параметри бяха подбрани две уравнения: от първи и от дробен порядък спрямо озона. Очистването на отпадъчни газове, съдържащи озон, бе симулирано чрез двумерен хетерогенен модел на реактор, предвиждащ концентрационния и температурния профил както в газова фаза, така също и в активната фаза на катализатора.