

# Volatile Organic Compounds Destruction by Catalytic Oxidation for Environmental Applications

Mohammed Nasir Kajama, Ngozi Claribelle Nwogu, Edward Gobina

**Abstract**—Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane catalysts were prepared via an evaporative-crystallization deposition method. The obtained Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst activity was tested after characterization (SEM-EDAX observation, BET measurement, permeability assessment) in the catalytic oxidation of selected volatile organic compound (VOC) i.e. propane, fed in mixture of oxygen. The VOC conversion (nearly 90%) obtained by varying the operating temperature showed that flow-through membrane reactor might do better in the abatement of VOCs.

**Keywords**—VOC combustion, flow-through membrane reactor, platinum supported alumina catalysts.

## I. INTRODUCTION

VOLATILE organic compounds (VOCs) encompass all organic compounds that boil at 50-260°C excluding pesticides but including dichloromethane (which boils at 41°C) [1]. VOCs are grouped as aliphatic hydrocarbons (compounds containing carbon and hydrogen joined together in straight chains, such as propene and ethane) and aromatic hydrocarbons, aldehydes, ketones, halogenated hydrocarbons, alcohols, ethers among others [2]. VOCs are extremely harmful compounds when emitted to the environment due to their elevated photochemical ozone [3]. VOCs are mostly emitted from the industrial processes such as petroleum refineries, chemical and pharmaceutical plants, automobile manufacturer, food processors and transport at variable degrees and also from household products. Some common VOCs are ethane, propane, n-butane, acetaldehyde, benzene, carbon tetrachloride, toluene, and naphthalene among others [4]-[6]. VOCs have many health and adverse impact on humans and plants which are associated with the pollution they produce. Some symptoms associated to short term exposure of VOCs include; allergic skin reaction, headaches, dizziness, coughing, visual disorders, eye and respiratory tract irritation and fatigue. Similarly, kidney, brain damage, liver, damage to the nervous, reproductive and immune systems are caused by long term exposure [7].

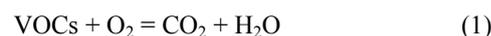
The release of VOCs into the environment will be harnessed by imposing strict regulations [3]. In recent years, VOCs emissions are strictly regulated in different countries

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around the globe. For example, in the air quality standards developed by the United States Environmental Protection Agency states that the maximum 3-hour concentration of hydrocarbon content is  $1.6 \times 10^{-4}$  kg/m<sup>3</sup> (0.24 ppm), not to be exceeded for a period of more than a year [4], [8]. The Gothenburg protocol states that by 2020 the European Union (EU) was adopted to reduce VOCs emission levels by 50% compared to the year 2000 [3].

The most widely implemented VOCs destruction methods are thermal and catalytic oxidation in which VOCs are combined with oxygen at specific temperatures and yield carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). In general, the reaction takes the form:



### A. Thermal Oxidation

The temperature range used to achieve VOCs combustion for thermal oxidation systems is typically between 704°C to 982°C (1,300°F to 1,800°F). The actual operating temperature is a function of the type and concentration of the material within the exhaust stream and the desired destruction and removal efficiency (DRE). Some compounds that are difficult to combust or are present at low inlet concentrations will need greater heat input and retention time in the combustion zone. Inlet concentrations above 25% of the lower explosive limits (LEL) are avoided due to explosion hazards [4], [6], [9].

### B. Catalytic Oxidation

Catalytic oxidation or catalytic incineration systems also combust VOCs in a similar way as thermal oxidation does. As its name proposes, catalytic oxidation uses a catalyst in order to facilitate the rate of a chemical reaction without itself being consumed. The main difference between thermal and catalytic oxidation is that, catalytic oxidation operates at a lower temperature typically between 371°C to 482°C (700°F to 900°F) [4], [6]; 260°C to 482°C (500°F to 900°F) [7], [10]. They offer many advantages for the appropriate application. The required energy for catalytic oxidation is lower than that for thermal oxidation due to the presence of catalyst resulting in lower operating and/or capital cost [4], [6], [7], [10].

Catalytic systems design in controlling VOC emissions is regarded as one of the most significant instruments for environmental protection [11]-[13]. However, catalytic combustion is applied for the removal of VOC at low concentrations at a higher range of total gas flow rate [11], [13]. The well recognized catalysts for these activities are the supported noble metal catalysts which are famous in oxidation reactions because of their high activity [12]. The most

efficient catalytic system for VOC destruction is the platinum supported on gamma-alumina ( $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ ) which can operate at a lower temperature and achieve total VOC conversion [11], [13]-[16]. For example, in the case of the flow-through contactor configuration, the reactants gas mixtures are forced to go through the catalytic pores from the reactor entrance after been heated to the desired temperature. The catalyst (Pt) lower the reaction's activation energy to produce a wide dispersion of the catalytically active metal and create a large surface area, oxidation of the reactants will occur on the catalyst surface whereby heat will be released as the VOCs are converted and yield the product from the exit side of the reactor as shown in Fig. 1.

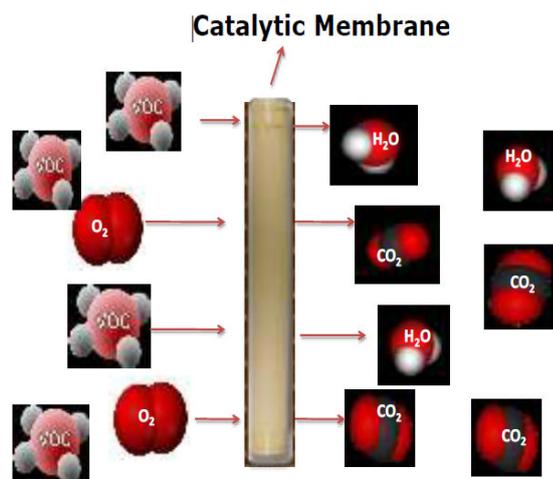


Fig. 1 Typical VOC catalytic membrane reactor conversion

Generally, VOC conversion can be achieved on the following categories of catalyst: (a) noble metals (platinum (Pt), titanium (Ti), palladium (Pd), copper (Cu), among others) which can be supported on (e.g. aluminum oxide ( $\text{Al}_2\text{O}_3$ ), silicon dioxide ( $\text{SiO}_2$ ), among others) or may not be supported, and (b) transition metal oxides (e.g. iron-III oxides ( $\text{Fe}_2\text{O}_3$ ), chromium-III oxides ( $\text{Cr}_2\text{O}_3$ ), vanadium-V oxides ( $\text{V}_2\text{O}_5$ ), among others). The most commonly applied catalysts include noble metals (e.g. Pt, Rh, Pd) supported on oxide supports (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ) due to their high intrinsic action for VOC destruction [11], [16]-[18]. It is indeed for this reason that to achieve total combustion for toluene and propene supported noble metals on alumina are more frequently used than transition metal catalysts [11], [19]. Nonetheless, some literatures disclosed that platinum supported on alumina are more superior for the catalytic combustion of toluene and propene [11], [16], [17], [20]-[24]. Noble-metal based catalysts are mostly obtained with  $\gamma\text{-Al}_2\text{O}_3$  as a support with over 65% dispersion [11]. Performance of catalysts robustly relies on the method of preparation. This will dictate the degree of metal dispersion on the surface of the support and the metallic nano-particles size. The content of the noble metal should be low due to its high cost. Consequently, particle size and dispersion are among the key parameters ensuing in preparing such catalysts [11].

The present work was conducted by depositing of a low Pt loading on  $\text{Al}_2\text{O}_3$  support using tubular alumina membrane reactor for the destruction of VOCs in the presence of oxygen and yield carbon dioxide and water.

## II. EXPERIMENTAL

### A. Materials

Commercial supports of tubular configuration supplied by Ceramiques Techniques et Industrielles (CTI SA) France, consisted of 77% alumina + 23%  $\text{TiO}_2$  have been used in this study. The support consisted of 7 and 10 mm internal and outer diameter respectively. The support possesses a permeable length of 348 mm and 45% porosity. In most cases, a solution of hexachloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , has been used as platinum precursor. Some experiments have also been made using Pt-free support and the Pt-impregnated support.

In all cases the tubular support is first dried at 65 °C. After weighing, it is dipped during 2 hours in pure water before Pt introduction. The deposition method used was based on evaporation-crystallization steps.

### B. Evaporation-Crystallization Deposition Method

This method was based on the so-called "reservoir" method proposed by [25] and [26]. The tube was first dipped for 2 hours in pure water (in our case we used deionised water) afterwards the tube was dipped for 10 hours in a 10g/l of  $\text{H}_2\text{PtCl}_6$  precursor solution. The sample was then dried at room temperature to favour evaporation from the inner side and deposition in the top layer.

### C. Platinum Activation

Metallic platinum is obtained after thermal treatment of the sample under flowing hydrogen at 400 °C for at least 10 min followed by nitrogen flow the same way.

### D. Characterization Methods

Scanning electron microscopy (Zeiss EVO LS10) has been used to determine the position of platinum particles inside the porous structure of the multi-layered ceramic material. Samples for crosswise Pt EDX analyses were prepared by breaking the tube after depositing a film on the section. SEM and EDXA results indicated the presence of Pt. The surface area of the support and ( $\text{Pt}/\text{Al}_2\text{O}_3$ ) was measured using Brunauer-Emmett-Teller (BET) method from nitrogen adsorption-desorption at 77 K, using automated gas sorption analyzer (Quantachrome instrument 2013). All samples were first degassed at 400°C for 2 hours prior to the nitrogen adsorption analysis. Gas permeation measurements of nitrogen were performed before and after Pt deposition using a conventional setup [25], [26]. The gas was introduced inside the tube and the flow permeating outside the tube was measured [15], [25] by a digital flow meter (Cole-Parmer).

The catalytic tests were carried out on a stainless steel shell housing the ceramic membrane by means flow-through contactor configuration. The VOC reactants mixture was composed of propane and oxygen. The products were analysed by  $\text{CO}_2$  analyser (CT2100-Emissions Sensor).

### III. RESULTS AND DISCUSSION

Fig. 2 depicts a typical SEM micrograph of the outside surface of the membrane after impregnation. Pt particles are clearly visible. Fig. 3 depicts the EDXA of the Pt membrane used in carrying out the experiment. Data generated by EDXA were the true composition of the elements within the sample. As observed, Pt element is also present with some other metals.

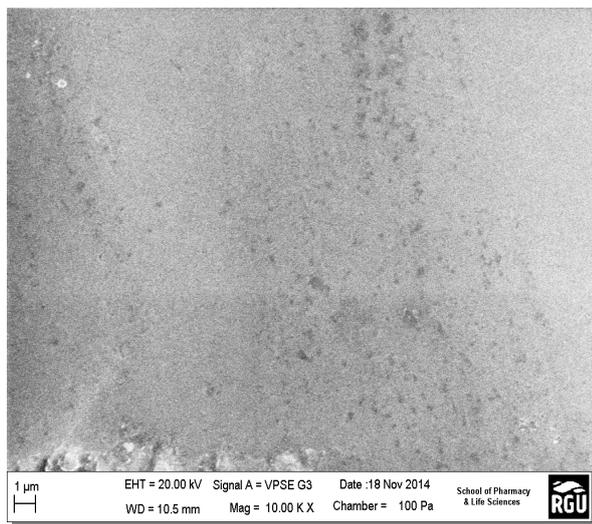


Fig. 2 SEM image of the Pt particles outside diameter

Fig. 4 depicts the relationship between propane conversion and the inlet temperature. Almost 86% VOC conversion has been achieved at a temperature of 333°C. Saracco and Specchia [27] obtained complete oxidation of propane at almost 450 °C on a Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst with 5-wt% Pt content. In their work, they have achieved 86% propane conversion at a temperature of over 350 °C. Therefore, the temperature at which the catalytic combustion takes place for the VOC corroborate, if not even lower, to the one obtained from the literature [27] for the same VOC on Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts.

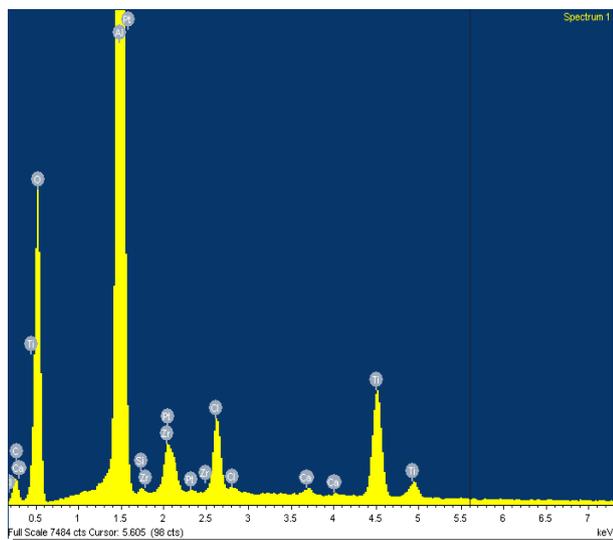


Fig. 3 EDX analysis of Pt/Al<sub>2</sub>O<sub>3</sub> outside diameter

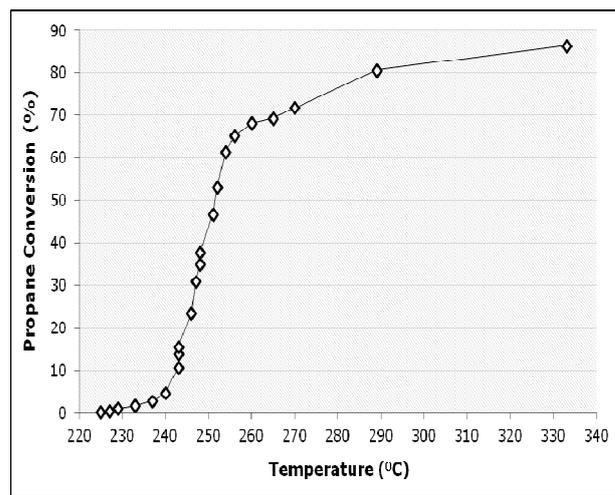


Fig. 4 VOC (propane) conversion against temperature

### IV. CONCLUSION

Platinum membrane was prepared by dipping a γ-Al<sub>2</sub>O<sub>3</sub> support via evaporation-crystallization deposition method. The Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was tested in order to know its performance towards catalytic oxidation of propane as a representative of VOC compound. Nearly 90% of VOC destruction was demonstrated. This confirms that the flow-through membrane reactor operation is a promising alternative for the combustion of VOCs. In addition, the result indicates that it is possible to achieve complete VOC destruction using this simple but effective “reservoir technique” at lower temperature.

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### REFERENCES

- [1] S. Aguado, J. Coronas, and J. Santamaria, “Use of zeolite membrane reactors for the combustion of VOCs present in air at low concentrations,” *Chemical Engineering Research & Design*, vol. 83(A3), 2005, pp. 295-301.
- [2] M. P. Pina, S. Irusta, M. Menendez, and J. Santamaria, “Combustion of volatile organic compounds over platinum-based catalytic membranes,” *Industrial Engineering Chemistry Resources*, vol. 36, 1997, pp. 4557-4566.
- [3] L. F. Liotta, “Catalytic oxidation of volatile organic compounds on supported noble metals,” *Applied Catalysis B: Environmental*, vol. 100(3-4), 2010, pp. 403-412.
- [4] F. I. Khan, and A. Kr. Ghoshal, “Removal of volatile organic compounds from polluted air,” *Journal of Loss Prevention in the Process Industries*, vol. 13(6), 2000, pp. 527-545.
- [5] B. Buzcu-Guven, and R. Harriss, “Extent, impacts & remedies of global gas flaring and venting,” *Carbon Management*, Vol. 3(1), 2012, pp. 95-108.
- [6] E. N. Ruddy, and L. A. Carroll, “Select the best VOC control strategy,” *Chemical Engineering Progress*, Vol. 89(7), 1993, pp. 28-35.
- [7] A. O. Rusu, and E. Dumitriu, “Destruction of volatile organic compounds by catalytic oxidation,” *Environmental Engineering and Management Journal*, vol. 2(4), 2003, pp. 273-302.
- [8] M. Tamaddoni, R. Sotudeh-Gharebagh, S. Nario, M. Hajhosseinzadeh, and N. Mostoufi, “Experimental study of the VOC emitted from crude

- oil tankers,” *Process Safety and Environmental Protection*, vol. 92, 2014, pp. 929-937.
- [9] AIChE, “Current and potential future industrial practices for reducing and controlling volatile organic compounds,” New York, NY: *Centre for Waste Reduction Technologies, AIChE*, 1992.
- [10] <http://www.meca.org/galleries/files/hapwp.pdf> “Catalytic oxidation for the control of hazardous organic air pollutants,” 1995, (Accessed on 29<sup>th</sup> October 2014).
- [11] S. Benard, M. Ousmane, L. Retailleau, A. Boreave, P. Vernoux, and A. Giroir-Fendler, “Catalytic removal of propene and toluene in air over noble metal catalyst<sup>1</sup>,” *Can. J. Civ. Eng.*, vol. 36, 2009, pp. 1935-1945.
- [12] V. P. Santos, S. A. C. Carabineiro, P. B. Tavares, M. F.R. Pereira, J. J. M. Órfão, and J. L. Figueiredo, “Oxidation of CO, ethanol and toluene over TiO<sub>2</sub> supported noble metal catalysts,” *Applied Catalysis B: Environmental*, vol. 99, 2010, pp. 198-205.
- [13] L. F. Liotta, M. Ousmane, G. Di. Carlo, G. Pantaleo, G. Deganello, A. Boreave, and A. Giroir-Fendler, “Catalytic removal of toluene over CO<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> mixed oxide catalysts: comparison with Pt/Al<sub>2</sub>O<sub>3</sub>,” *Catal Lett.*, vol. 127, 2009, pp. 270-276.
- [14] P. Marécot, A. Fakche, B. Kellali, G. Mabilon, M. Prigent, and J. Barbier, “Propane and propene oxidation over platinum and palladium on alumina: Effects of chloride and water,” *Applied Catalysis B: Environmental*, vol. 3, 1994, pp. 283-294.
- [15] S. Benard, A. Giroir-Fendler, P. Vernoux, N. Guilhaume, and K. Fiaty, “Comparing monolithic and membrane reactors in catalytic oxidation of propene and toluene in excess of oxygen,” *Catalysis today*, vol. 156, 2010, pp. 301-305.
- [16] M. Paulis, L. M. Gandia, A. Gil, J. Sambeth, J. A. Odriozola, and M. Montes, “Influence of the surface adsorption-desorption processes on the ignition curves of volatile organic compounds (VOCs) complete oxidation over supported catalysts,” *Applied Catalysis B: Environmental*, vol. 26, 2000, pp. 37-46.
- [17] M. Paulis, H. Peyrard, and M. Montes, “Influence of chlorine on the activity and stability of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in the complete oxidation of toluene,” *Journal of Catalysis*, vol. 199, 2001, pp. 30-40.
- [18] P. Papaefthimiou, T. Ioannides, and X. E. Verykios, “Combustion of non-halogenated volatile organic compounds over group VIII metal catalysts,” *Applied Catalysis B: Environmental*, vol. 13, 1997, pp. 175-184.
- [19] K. Everaert, and J. Baeyens, “Catalytic combustion of volatile organic compounds,” *Journal of Hazardous Materials: B*, vol. 109, 2004, pp. 113-139.
- [20] N. Radic, B. Grbic, and A. Terlecki-Baricevic, “Kinetics of deep oxidation of *n*-hexane and toluene over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts platinum crystallite size effect,” *Applied Catalysis B: Environmental*, vol. 50, 2004, pp. 153-159.
- [21] D. H. Kim, M. C. Kung, A. Kozlova, S. D. Yuan, and H. H. Kung, “Synergism between Pt/Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> in the low temperature oxidation of propene,” *Catalysis Letters*, vol. 98(1), 2004, pp. 11-15.
- [22] S. F. Tahir, and C. A. Koh, “Catalytic destruction of volatile organic compound emissions by platinum based catalyst,” *Chemosphere*, vol. 38(9), 1999, pp. 2109-2116.
- [23] A. C. Gluhoi, N. Bogdanchikova, and B. E. Nieuwenhuys, “Total oxidation of propene and propane over gold-copper oxide on alumina catalysts: Comparison with Pt/Al<sub>2</sub>O<sub>3</sub>,” *Catalysis Today*, vol. 113, 2006, pp. 178-181.
- [24] M. P. Pina, M. Menendez, and J. Santamaria, “The Knudsen-diffusion catalytic membrane reactor: An efficient contactor for the combustion of volatile organic compounds,” *Applied Catalysis B: Environmental*, vol. 11, 1996, pp. L19-L27.
- [25] D. Uzio, S. Miachon, and J.-A. Dalmon, “Controlled Pt deposition in membrane mesoporous top layers,” *Catalysis Today*, vol. 82, 2003, pp. 67-74.
- [26] E. E. Iojoiu, J. Walmsley, H. Raeder, R. Bredesen, S. Miachon, and J.-A. Dalmon, “Comparison of different support types for the preparation of nanostructured catalytic membranes,” *Rev. Adv. Mater. Sci.*, vol. 5, 2003, pp. 160-165.
- [27] G. Saracco, and V. Specchia, “Catalytic filters for the abatement of volatile organic compounds,” *Chemical Engineering Science*, vol. 55, 2000, pp. 897-908.