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VOC oxidation in excess of oxygen using flow-through catalytic membrane reactor

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Abstract

Platinum gamma-alumina (Pt/ γ -Al₂O₃) impregnated membrane was prepared through the evaporative-crystallization deposition method for volatile organic compounds (VOCs) conversion to carbon dioxide (CO₂) and water (H₂O). The catalytic oxidation of VOCs (propane, n-butane and propylene), fed alone with oxygen were obtained after characterization (SEM-EDXA observation, BET measurement, permeability assessment). VOC conversion of 95%, 52% and 82% for propane, n-butane and propylene was achieved at 378⁰C, 245⁰C and 420⁰C respectively, by varying the reaction temperature using the contactor flow-through catalytic membrane reactor operating in the Knudsen flow regime. The BET surface area and the pore diameter of the 3.52 wt% Pt membrane are 0.426m²/g and 3.70nm respectively. The results are comparable with the literature.

Keywords— platinum catalysts; flow-through membrane reactor; VOC oxidation; tubular mesoporous membrane.

1. Introduction

VOC abatement is a great challenge and of paramount importance to the process industry [1]. Some common VOCs are listed in Table 1 [2-4]. Besides the more established VOC abatement processes, destruction of VOC to form CO₂ and H₂O (Fig. 1) has been widely studied using membrane reactors (MRs) [5-12].

A membrane reactor is a process which combines reaction and separation in a single unit [13]. They can be made from different materials such as metals, ceramics and polymers. Different definitions exist for MRs [14]. The International Union of Pure and Applied Chemistry (IUPAC) define a membrane reactor as a device for simultaneously carrying out a reaction and membrane-based separation in the same physical enclosure [15]. According to a wider definition any reactor in which a chemical reaction is performed in presence of a membrane is called membrane reactor [16]. The application of membrane

reactors have received a lot of attention over the past five decades and quite a large number of papers have been published on the subject [17-21]. The membrane can also be used as an active candidate in a chemical conversion for increasing the reaction rate, selectivity and yield [17]. The interest of membrane reactors has been demonstrated at the laboratory scale for dehydrogenation, hydrogenation, decomposition and oxidation reactions among others [17]. The concept has yet to be used widely for industrial applications although some small industrial installations already exist. The drawback for commercial development of membrane reactors are the membrane themselves, their support and issues such as performance, cost and stability among others which still need to be optimized [17].

TABLE 1: Some common VOCs [2-4]

Number	VOCs
1	Acetaldehyde
2	Acetamide
3	Acetone
4	Acetonitrile
5	Benzene
6	Benzyl chloride
7	Carbon tetrachloride
8	Cyclohexane
9	Ethyl acetate
10	Ethylene glycol
11	Formaldehyde
12	Heptane
13	Hexane
14	Isopropyl alcohol
15	Methyl ethyl ketone
16	Methylene chloride
17	Naphthalene
18	Propylene
19	Styrene
20	Toluene

In recent years, the concept applied in the combination of membranes and reactors is being proposed. The concept is classified into three groups namely; extractor, distributor and contactor which are related to the role of the membrane in the process [17]. Extractor mode is used to selectively remove the product(s) from the reaction mixture. Distributor mode is used to control the addition of reactants to the reaction mixture. And lastly, the contactor mode used to intensify the contact between reactants and the catalyst.

The active contactor mode membrane reactor involves a forced flow-through membrane reactor, where the membrane acts as a diffusion barrier and is catalytically active [17, 18]. This type of membrane is used to provide a reaction space where the catalyst is deposited inside the membrane pores. The catalyst-membrane arrangement leads to high catalytic activity [1, 18].

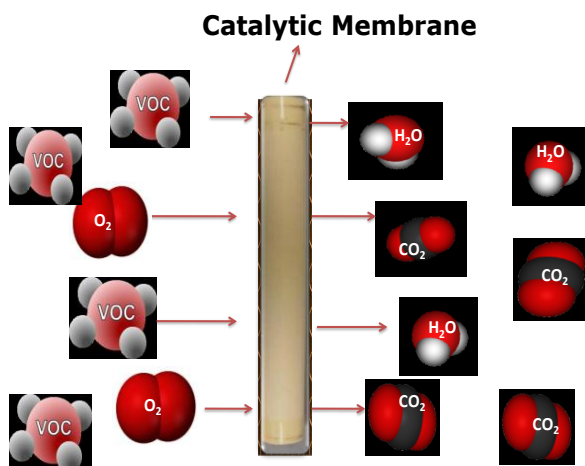


Figure 1: Flow-through catalytic membrane reactor.

The forced flow-through contactor mode has been widely employed by many researchers in the total oxidation of VOCs [5, 22-32]. Our aim is to investigate the catalytic oxidation of propane, n-butane and propylene as a chemical reaction using membrane catalysts prepared via an evaporative-crystallization deposition method. The influence parameters such as platinum (Pt) loading, total gas flow rate, VOC concentration, oxygen content and conversion reaction temperature were examined.

2. Experimental procedure

2.1 Materials

Commercially available tubular porous alumina supplied by Ceramiques Techniques et Industrielles (CTI SA) France was used in this study. The tubular alumina possesses an internal and outer diameter of 7 and 10 mm respectively, with a permeable length of 348 mm and a porosity of 0.45. The support was found to be defect free after characterization.

2.2 Membrane preparation

Hexachloroplatinic acid solution (H_2PtCl_6) was impregnated into the tubular alumina using dip-coating method. The tubular support was first dried at $65\text{ }^\circ\text{C}$. The support was dipped for 2 hours in deionised

water before Pt introduction. The deposition procedure used was based on evaporation-crystallisation. This method was based on the so-called “reservoir” method proposed by Uzio et al. [33]; Iojoiu et al. [34] and Kajama et al. [35]. The tube was dipped for 10 hours in a 10g/l Pt/H₂PtCl₆ precursor solution. The sample was then dried at room temperature overnight to favour evaporation from the inner side and deposition in the top layer. Platinum membrane was obtained after thermal treatment of the sample under flowing hydrogen at 400 °C for at least 10 min followed by nitrogen flow for 10 min at 400 °C.

2.3 Characterization of catalytic systems

Scanning electron microscopy (SEM) (Zeiss EVO LS10) image was obtained in order to determine the position of platinum particles on the porous structure of the ceramic material. Samples for crosswise Pt-impregnated membrane energy diffraction X-ray analysis (EDXA) were also obtained. SEM and EDXA results indicated the presence of Pt. The surface area of the bare support and Pt/Al₂O₃-impregnated membrane were measured using Brunauer-Emmett-Teller (BET) method from nitrogen adsorption-desorption at -196.15 °C using automated gas sorption analyzer (Quantachrome instrument version 3.0) [35]. All samples were first degassed at 400 °C for 2 hours prior to the nitrogen adsorption analysis. Gas permeation measurements of hydrogen [35] were performed before and after Pt deposition using a conventional setup [35]. The gas was introduced inside the tube and the flow permeating outside the tube was measured by a digital flowmeter (Cole-Parmer 32908-71).

2.4 Catalytic activity measurements

Oxidation of the VOCs was carried out in a lab-scale tubular reactor in which 3.52 wt% of catalyst was loaded and a total flow rate ranging from 166 to 270, 310 to 445 and 187 to 297 (ml/min) for propane, n-butane and propylene respectively, passed through the catalytic membrane. The catalytic tests were carried out using a stainless steel shell housing the membrane tube by means flow-through contactor configuration. Leak test was carried out by flowing N₂ through the system prior to the experiment. Permeate was measured to ensure the system was leak-free. The reactor was then heated up to experimental temperature. The temperature in the reactor was regulated by an electro thermal power regulator. Temperatures in the tube side were measured using a k-type thermocouples. Pressures were also measured by pressure gauges along the reactor. The reactants (VOCs and oxygen) were fed using mass flow controllers to the feed side of the membrane reactor. Products (CO₂ and H₂O) flows from the permeate stream through a moisture trap where the moisture trap absorbs the H₂O, and the CO₂ flows through the digital flowmeter to the CO₂ analyzer (CT2100-Emissions Laser Sensor). After each experiment, the reactor was cooled down to room temperature. Before starting each experiment, N₂ gas

was purged through the system and hoses to remove residual reaction gases from the system. This was used in order to minimize error that any residual gases may cause.

3. Results and discussion

3.1 Pt membrane characterization

SEM micrograph and EDXA of the outer side surface of the membrane after Pt impregnation is depicted in Figs. 2 and 3. Pt metallic particles are clearly visible (Fig. 2). From Fig. 3, the Pt wt% is 3.52 wt%.

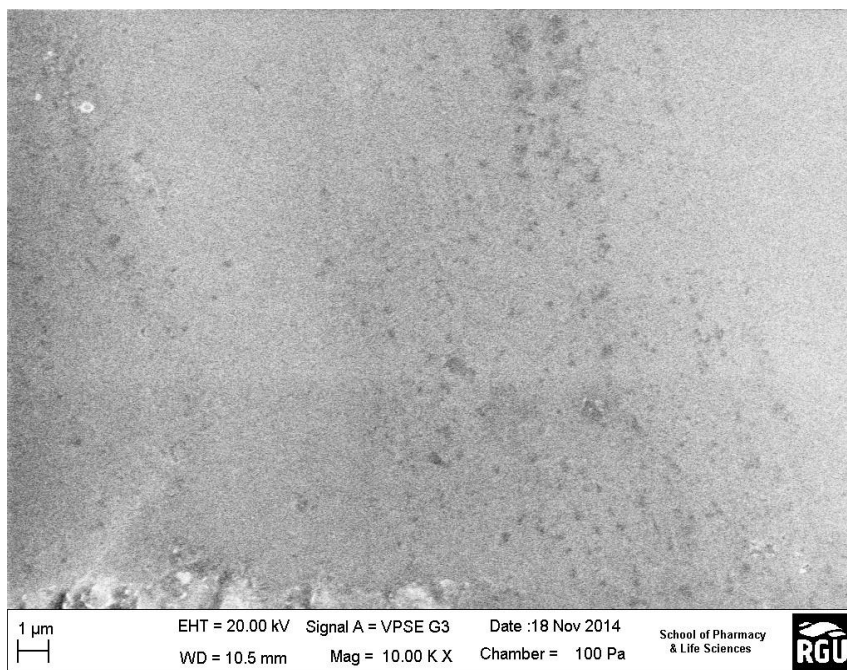


Figure 2: SEM image of the Pt particles outside diameter.

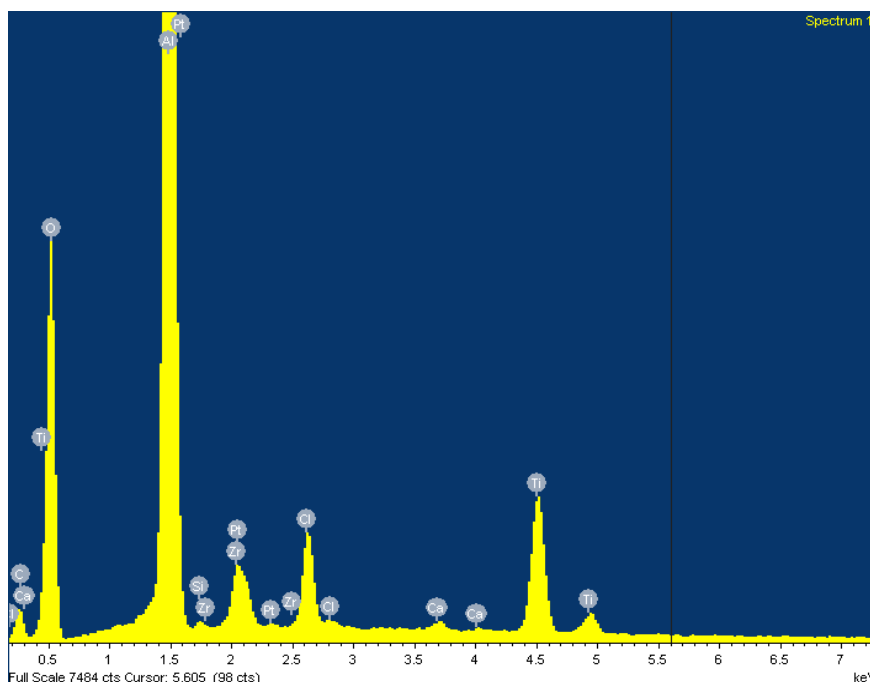


Figure 3: EDXA image of the Pt membrane outer surface.

The Pt/Al₂O₃ membrane sample was subjected to BET surface area and pore size measurement. The data of specific surface area, average pore diameter and pore volume for the samples are presented in Table 2. The effect of the Pt weight gain using the reservoir method was studied by measuring the BET surface area. The results clearly showed an increase in BET surface area between the support and the Pt-alumina membrane, which may be attributed to the formation of nano-dispersed platinum particles. As may be expected, there was also a reduction in pore diameter which is possibly due to pore blockage caused by the metal platinum particles. Although, no changes in the pore volume were observed.

TABLE 2: BET surface area, average pore diameter and pore volume measurements

Catalyst	BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
Support	0.364	4.171	0.005
Pt-alumina	0.426	3.70	0.005

3.2 Catalytic results

The influence of reaction temperature on the conversion efficiency of the concentration of VOCs in air over the catalyst was tested on a tubular reactor and some data was obtained on the activity. This influence is illustrated by the rise in conversion efficiency for the VOCs which occurred with increasing reaction temperature (Figs. 4-6). The alumina support provides the surface for the metallic phase dispersion which has a great influence on VOC oxidation. The conversion efficiencies as a function of

reaction temperature was evaluated when converting the VOCs in air at a flow rate ranging from 166 up to 445 ml/min.

Various VOCs such as propane, n-butane and propylene typically found in industrial gaseous emissions were selected to examine their activity on 3.52 wt% Pt/Al₂O₃ catalyst. Fig. 4 depicts the propane conversion versus reaction temperature on the Pt membrane. It can be seen that 95.47% propane conversion is achieved at a reaction temperature of 378 °C. Saracco and Specchia, (2000); Gluhoi, Bogdanchikova and Nieuwenhuys, (2006) obtained complete oxidation of propane at almost 450 °C with 5-wt% Pt content. Saracco and Specchia, (2000) in their work, have achieved 95% propane conversion at a temperature of nearly 430 °C. Therefore, in this study, the temperature at which the catalytic combustion takes place for propane is lower to the one obtained from the literature [32] for the same VOC on Pt/γ-Al₂O₃ catalysts.

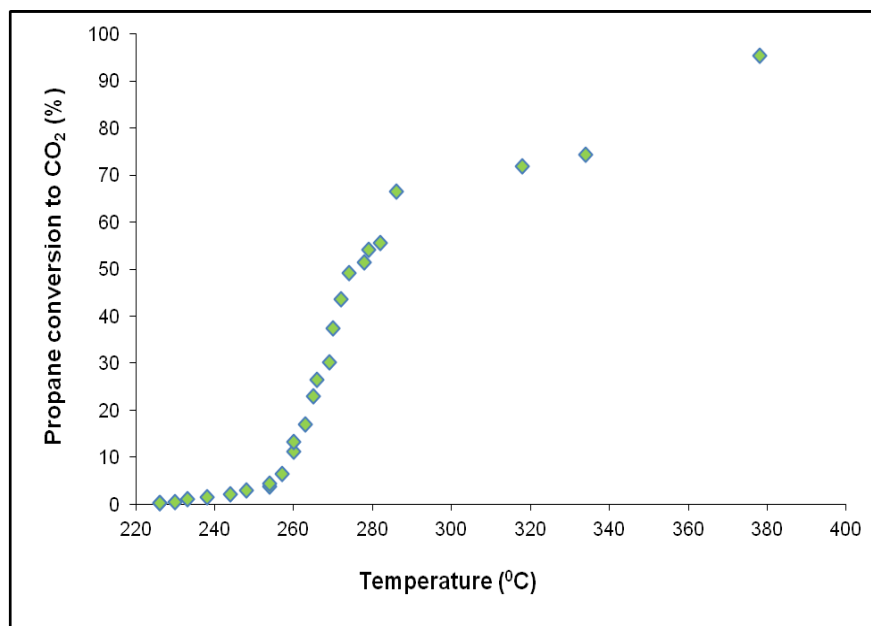


Figure 4: Propane conversion against reaction temperature.

Fig. 5 depicts the relationship between n-butane conversion versus reaction temperature on the Pt catalyst. As can be seen from Fig. 5, 52% n-butane conversion is achieved at a temperature of 245 °C on Pt/γ-Al₂O₃ catalyst. This result corroborates with the literature [36] using 4.6% Ru/γ-Al₂O₃ catalyst where they achieved 52% n-butane conversion at almost 320 °C, were 75 °C temperature difference is observed between Pt and Ru catalysts. This is an indication that Pt/Al₂O₃ is the best catalyst for oxidation reactions if a similar noble metal loading is used [11].

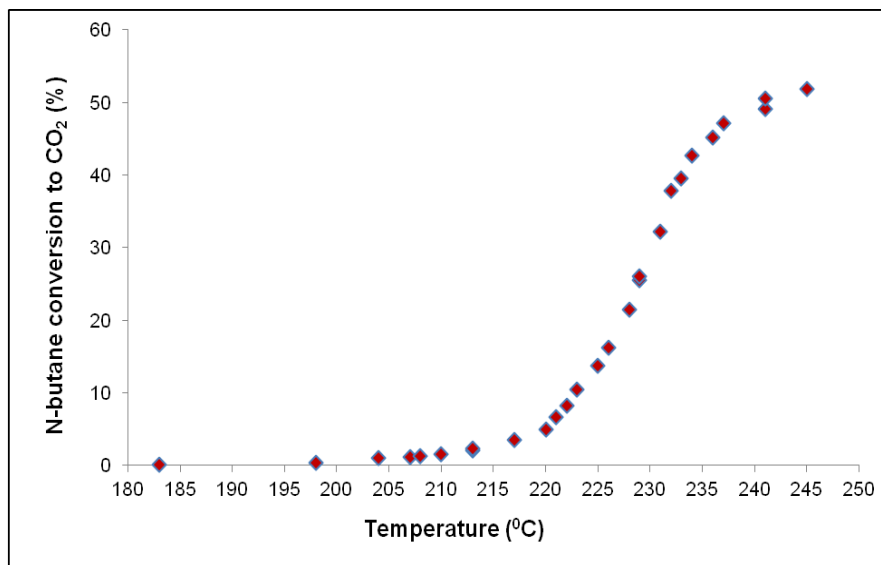


Figure 5: N-butane conversion against reaction temperature.

Fig. 6 depicts the relationship between propylene conversion versus reaction temperature on the Pt catalyst. From Fig. 6, 82% propylene conversion is achieved at a temperature of 420 °C on Pt/Al₂O₃ catalyst. Saracco and Specchia, (2000) obtained similar conversion at nearly 300 °C with 5-wt% Pt content. From Fig. 6, it can be seen that 75% conversion is obtained at 262 °C were it takes up to 372 °C before the next conversion occurred. Therefore, the residence time before the next conversion occurred was longer. This could be as a result of exothermic reaction which takes longer to release energy for the next conversion to occur.

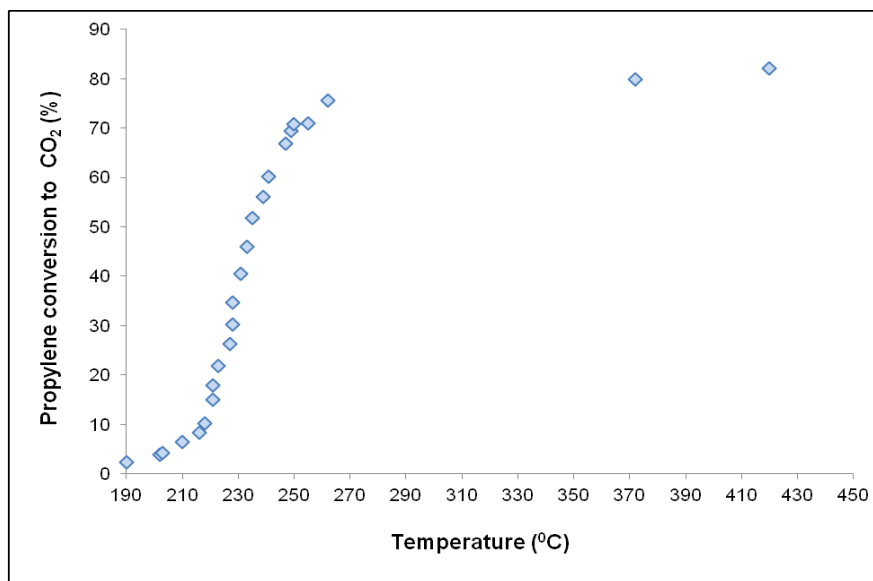


Figure 6: Propylene conversion against reaction temperature.

The above results indicates that the temperature at which the oxidation was performed depend on the nature of the organic compounds present in the waste gas stream. The catalyst was exposed to several activity runs. The same catalyst was then cooled down and the temperature was lowered to ambient temperature before starting each experiment. The activity procedure was repeated for up to three to four runs for each organic compound and no deactivation of the catalyst occurred for over 100 h of operation.

Conclusion

The study of catalytic oxidation of VOCs (propane, n-butane and propylene) as a chemical reaction using platinum catalysts was presented. The catalyst was effective to destruct various aliphatic hydrocarbons and no effect showed on the activity at high temperature (420 °C). These results on VOC combustion also showed that the catalytic membrane reactor performed better in the flow-through membrane reactor using the simple but effective “reservoir technique”. Finally, this confirms that the Pt membrane reactor is a promising alternative for the combustion of VOCs.

Acknowledgement

The authors gratefully acknowledge Petroleum Technology Development Fund (PTDF) Nigeria for funding this research, and School of Pharmacy & Life Sciences RGU Aberdeen for the SEM and EDXA results.

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