

Propylene Oxidation Using Pt-alumina Impregnated Catalytic Membrane Reactor

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Abstract— Pt/ γ -Al₂O₃ membrane was prepared through the evaporative-crystallization deposition method for volatile organic compounds (VOCs) destruction. SEM-EDXA observation, BET measurement, permeability assessment and the catalytic oxidation of propylene was obtained. Nearly 80% propylene conversion was achieved by varying the reaction temperature using flow-through catalytic membrane reactor operating in the Knudsen flow regime.

Key words: Volatile organic compounds (VOCs), Propylene oxidation, Flow-through membrane reactor, Platinum supported alumina catalysts.

I. INTRODUCTION

PROPYLENE and toluene are recognised as among the most harmful volatile organic compounds (VOCs) when emitted to the environment due to their high photochemical ozone generation potential [1]. VOC comprises a large variety of compounds such as aliphatic hydrocarbons (propane, propene and methane), aromatic hydrocarbons (toluene and benzene), aldehydes (formaldehyde), ketones (acetone), halogenated hydrocarbons, alcohols (ethanol, methanol and n-propanol), and esters (ethylacetate) among others [2, 3].

VOCs are mostly generated from the industrial processes (petroleum refineries, chemical and pharmaceutical plants, automobile manufacturers, food processors), transport (at variable degrees) and also from household products. VOCs have many health and adverse impact on animals and plants which are associated with the pollution they produced. About 235 million tonnes of VOCs are released annually into the atmosphere from man-made sources [4]. This has made it imperative to curtail these vapours emissions which may lead to a significant milestone to the process industries. The release of these vapours into the environment can be harnessed by imposing strict regulations [3]. In the last four decades, VOCs emissions have been strictly regulated in different countries around the globe. For example, the air quality standards developed by the United States Environmental Protection Agency (USEPA) stipulates that a maximum 3-hour concentration of hydrocarbon content to be below of 0.24 parts per million (ppm) for a period of more than a year [5, 6].

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Also, the reduction of VOCs emissions that exceeds the current national air quality standard for ozone of 0.12 ppm is mandated under Title I of the US Clean Air Act Amendment (USCAAA) of 1990. Title III of the amendments requires 90% reduction in emissions of 189 toxic pollutants, out of which 70% are VOCs [4, 5]. The Gothenburg protocol states that, by 2020 the European Union (EU) adopt to reduce VOCs emission levels by 50% compared to the year 2000.

A number of technologies have been developed for the destruction of these toxic compounds at low concentration [2]. Thermal and catalytic oxidation are the most widely implemented VOC destruction methods in which VOCs are combined with oxygen at specific temperatures and yield carbon dioxide (CO₂) and water (H₂O).

Thermal oxidation was one of the first techniques to be implemented for VOCs destruction, and can operate at high temperature resulting in the production of even more toxic or rather dangerous compounds such as carbon monoxide and nitrogen oxides than the actual VOC itself [2]. Thermal oxidation is the process of oxidizing combustible materials by increasing their temperature above auto-ignition point and combined with oxygen at a high temperature to yield carbon dioxide and water. The temperature range used to achieve this combustion is typically between 704 °C to 982 °C. 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 [5, 7, 8].

Catalytic oxidation systems also combust VOCs in a similar way as thermal oxidation does. However, unlike thermal oxidation, catalytic oxidation uses a catalyst in order to facilitate the rate of the chemical reaction. The main difference between thermal and catalytic oxidation is that, catalytic oxidation operates at a lower temperature typically between 260 °C to 482 °C [9]. 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, 5, 7, 9].

Catalytic systems design in controlling VOC emissions is regarded as one of the most significant instruments for environmental protection [10-12]. Catalytic combustion is applied for the removal of VOC at low concentrations at a higher range of total gas flow rate [10, 12] and currently, noble and transition metals are famous in the oxidation reaction of VOCs because of their high activity [11]. The most efficient metal for VOC combustion is the platinum supported on gamma-alumina (Pt/ γ -Al₂O₃) which can

operate at a lower temperature and achieve total VOC conversion [10, 12-15]. For example, in the case of the flow-through contactor configuration, the reactant 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 activation energy and the porous support creates, produce a wide dispersion of the catalytically active metal and 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 on the exit side of the reactor as shown in Fig. 1.

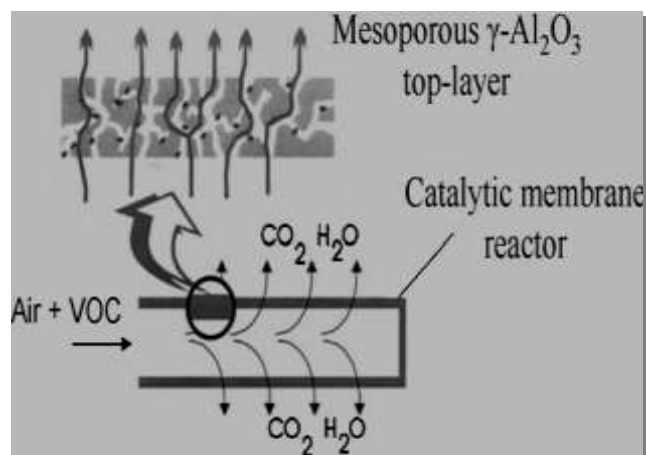


Figure 1: Flow-through catalytic membrane reactor [14].

Nevertheless, literature disclosed that platinum supported on alumina are more superior for the catalytic combustion of toluene and propene [10, 15-20]. Noble-metal based catalysts are mostly obtained on γ - Al_2O_3 as a support with high surface area [10]. 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 [10].

This present study was conducted by depositing a Pt on Al_2O_3 support and applying these in a membrane reactor for the oxidation of propylene in the presence of oxygen to yield carbon dioxide and water.

II. EXPERIMENTAL

A. Materials and Membrane Preparation

Commercially available porous supports of tubular configuration supplied by Ceramiques Techniques et Industrielles (CTI SA) France, consisting of 77% alumina + 23% TiO_2 have been used in this study. The support has an internal and outer diameter of 7 and 10 mm respectively with a permeable length of 348 mm and a porosity of 45%. A solution of hexachloroplatinic acid (H_2PtCl_6) has been used as platinum precursor. The tubular support is first dried at 65°C and after weighing, it is dipped for 2 hours in deionised water before Pt introduction. The deposition method used was based on evaporation-crystallization steps.

This method was based on the so-called “reservoir” method proposed by Uzio et al. [21] and Iojoiu et al. [22]. 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 $\text{Pt}/\text{H}_2\text{PtCl}_6$ precursor solution. The sample was then dried at room temperature to favour evaporation from the inner side and deposition in the top layer.

B. 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 for 10 min at 400°C .

C. Membrane Characterization

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 (not shown) results indicate 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 version 3.0) (not shown). All samples were first degassed at 400°C for 2 hours prior to the nitrogen adsorption analysis. Gas permeation measurements of helium were performed before and after Pt deposition using a conventional setup [21, 22]. The gas permeate flow was measured [14, 21] by a digital flowmeter (Cole-Parmer).

The catalytic tests were carried out on a membrane reactor consisting of a stainless steel shell housing the ceramic membrane and operated by means flow-through contactor configuration. The VOC reactants mixture was composed of propylene and oxygen. The products were analysed by CO_2 analyser (CT2100-Emissions Sensor).

III. RESULT AND DISCUSSION

A. Pt Membrane Characterization

SEM micrograph of the outside surface of the membrane after Pt impregnation is shown in Fig. 2. Pt particles are clearly visible.

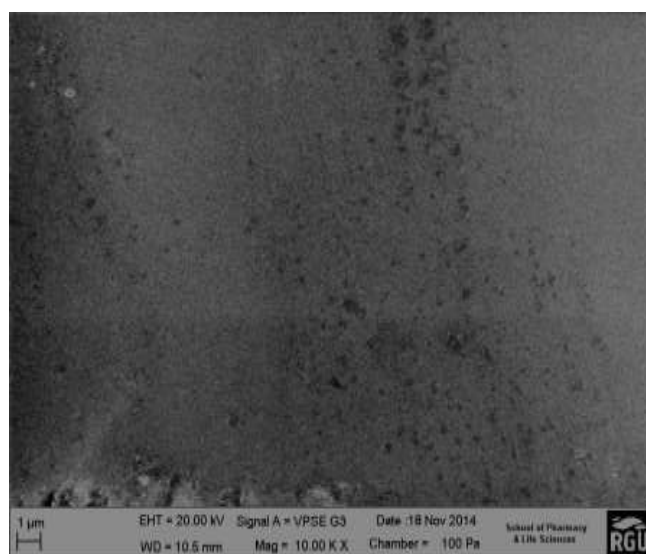


Figure 2: SEM image of the Pt particles outside diameter.

A. Gas Permeation

Permeation experiments were carried out at 100 °C using helium as the permeating gas in order to quantify the viscous and Knudsen flow contributions. Fig. 3 depicts the permeate flux of the Pt/Al₂O₃ membrane. Eqn. (1) was used to relate the permeation flux and mean pressure [23].

$$F = \beta P_{av} + K \quad (1)$$

where β and k equals;

$$\beta = 0.125 \frac{\varepsilon r^2}{L\tau\mu RT}, \text{ and } K = 1.06 \frac{\varepsilon r}{L\tau\sqrt{MRT}} \quad (2)$$

Where, F is the permeation flux per unit of time and area, ε is the porosity of the membrane, r is the mean pore radius (m), $P_{av} = (p_1+p_2)/2$ is the average pressure (Pa), μ is the viscosity (Pa-s) and L is the thickness of the membrane (m), τ is the tortuosity, M is the molecular weight of the diffusing gas (g/mol), R gas constant (8.314 J.K⁻¹.mol⁻¹) and T is the permeation temperature (K). β and K can be regarded as viscous and Knudsen contributions to the permeation flux.

From Fig. 3, it can be seen that almost a horizontal line is obtained on the 3.2 wt% Pt membrane indicating a predominantly Knudsen flow contribution. The obtained results corroborates with the literature [23].

B. Reaction Results

Fig. 4 depicts the relationship between propylene conversion and the reaction temperature. Almost 80% of propylene conversion has been achieved at a temperature of 331 °C on 3.2 wt% Pt/ γ -Al₂O₃ catalysts. This result is comparable with the values obtained by Saracco and Specchia [24] who used 5 wt% Pt/ γ -Al₂O₃ catalysts and achieved 80% propylene conversion at nearly 290 °C.

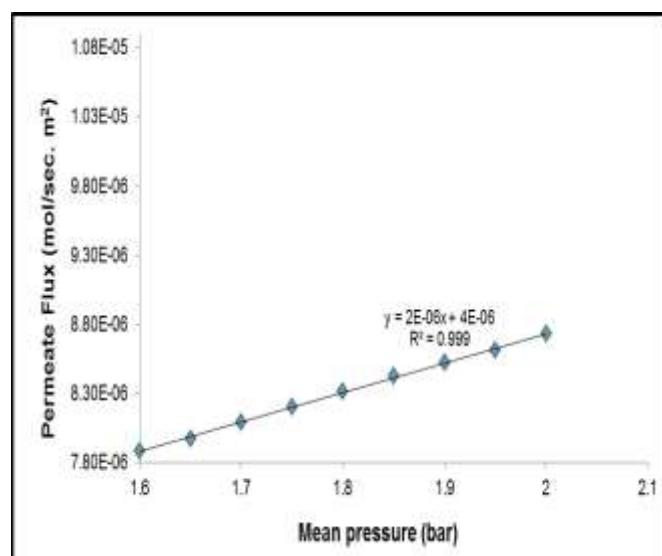


Figure 3: Helium Permeate flux against mean pressure on Pt/Al₂O₃ membrane at 100 °C.

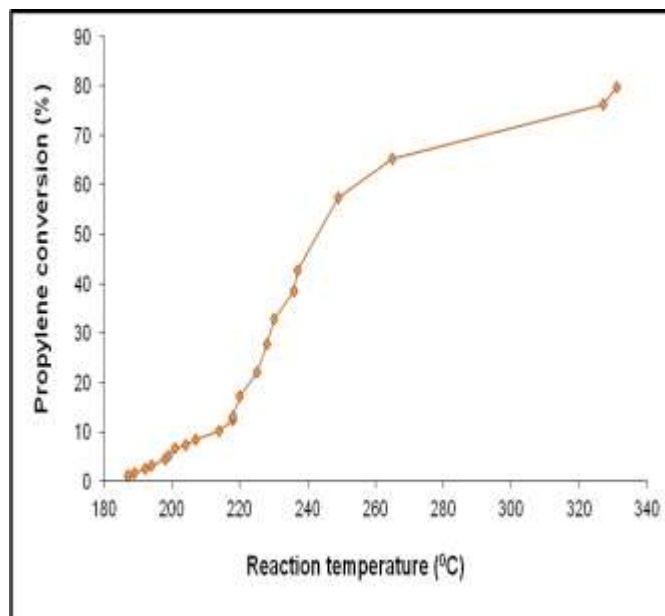


Figure 4: Propylene conversion against reaction temperature.

IV. CONCLUSION

The performance of Pt/ γ -Al₂O₃ catalysts on propylene oxidation was investigated in the flow-through catalytic membrane reactor. The result of propylene oxidation confirms that the flow-through membrane reactor operation is a promising alternative for the oxidation of VOCs. In addition, it is possible to achieve complete VOC destruction using this simple but effective “reservoir technique” for catalyst impregnation. This results in a higher dispersion of the catalyst material and results in a lower operating temperature.

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