

Oxidation of PCE and DCM over Pt, Pd, Rh, and V_2O_5 catalysts supported on Al_2O_3 , $Al_2O_3-TiO_2$ and $Al_2O_3-CeO_2$

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1 Introduction

Chlorinated volatile organic compounds (CVOCs) are widely used in industry e.g. as solvents, dry-cleaning agents, degreasing agents, and intermediates in the production of plastics, synthetic resins or pharmaceuticals [1]. The global warming potential (GWP) of 100 years for CVOCs ranges from 10 to 1800, which is much higher than that of CO_2 (the GWP of CO_2 is 1) [2]. Due to their harmful properties both to the environment and health, the release of CVOCs is controlled by increasingly stringent regulations [3].

Reductions in VOCs, including CVOC emissions, achieved by modifying the process equipment, raw material, and/or by changing the process are the most effective and preferable methods as being primary emission control methods. If primary methods are not feasible, secondary abatement methods for CVOCs can be used. Secondary methods can also be called add-on-control or end-of-pipe techniques and are further classified into two sub groups, recovery and destruction. [4,5] High-value VOCs favour recovery methods whereas mixtures of VOCs or low-value solvents favour methods of destruction. A major advantage in the destruction-based abatement is that there is no requirement for the subsequent disposal of recovered VOC mixture when it does not have commercial value. It is also possible to use hybrid systems, where different techniques are combined for enhanced abatement of VOCs. [6,7]

The main selection criteria for VOC abatement technologies are costs, VOC concentration, vent-gas flow rate, and the required control level i.e. regulatory factors. The cost to treat streams containing halogenated volatile organics is estimated to be at least double the cost of non-halogenated streams. [6,8] The most efficient and most widely used method for the destruction of VOCs in gas effluent streams is oxidation, also called incineration or combustion [5]. Oxidation methods can be divided into thermal and catalytic methods. Low temperature catalytic oxidation of chlorinated volatile organic compounds (CVOCs) appears to be a viable and effective technology for CVOC emission abatement. [7] This technology is especially preferable when emissions contain mixtures of several compounds and low concentrations of halogenated VOCs [8,9].

Through optimization of catalytic materials and the oxidation process itself via intensive research, the reaction products can be directed towards HCl while formation of Cl_2 and other harmful by-products are minimized. Based on a literary review [10-13] and on our earlier studies [14], it can be concluded that there are noble metal catalysts available that can fully oxidize CVOCs to the desired products.

In this study, the complete catalytic oxidation of 500 ppm of dichloromethane (DCM, CH_2Cl_2) and 500 ppm of perchloroethylene (PCE, C_2Cl_4) over Pt, Pd, Rh and V_2O_5 catalysts supported on Al_2O_3 , $Al_2O_3-TiO_2$ and $Al_2O_3-CeO_2$ was evaluated at laboratory scale with the aid of light-off tests. The catalysts used

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were metallic monoliths with cell density of 500 cpsi. The gas phase analysis was carried out with Gasmet DX-4000N FTIR gas analyzer. Experimental conditions were 1.5 vol-% H₂O, GHSV 32 000 h⁻¹, and heating from 100 to 700°C (10°C min⁻¹). The BET surface areas (m²g⁻¹) of the catalysts were determined with N₂ physisorption using Micrometrics ASAP 2020.

2 Objectives of the research

The aim of this study was to find the most active and selective catalyst for CVOCs abatement among the tested catalysts. The formation of harmful by-products such as methyl chloride, carbon tetrachloride, trichloroethylene and perchloroethylene, detected in previous studies [10, 15, 16], was especially taken into consideration.

3 Results

BET surface areas of the tested catalysts varied from 127 to 170 m²g⁻¹ (Table 1).

Table 1 BET surface areas [m²g⁻¹] of the catalysts used in the experiments.

Support/loading	1% Pt	0.5% Pd	0.5% Rh	1% V ₂ O ₅
Al ₂ O ₃	140	152	163	170
Al ₂ O ₃ -TiO ₂	127	140	163	144
Al ₂ O ₃ -CeO ₂	160	151	170	148

3.1 DCM oxidation

The Rh/Al₂O₃-CeO₂ (T₅₀ = 274°C) was the most active of the tested catalysts followed by Rh/Al₂O₃ (T₅₀ = 300°C) and Pt/Al₂O₃-CeO₂ (T₅₀ = 305°C). Light-off curves of DCM oxidation over Pt, Pd, Rh and V₂O₅ supported on Al₂O₃-CeO₂ are shown in Figure 1a. The activity of catalysts decreases in the order Rh > Pt > V₂O₅ > Pd. Conversion of 90% was reached in the order Rh/Al₂O₃-CeO₂ and Rh/Al₂O₃ (T₉₀ = 360°C) > Pt/Al₂O₃-CeO₂ (T₉₀ = 365 °C) > Rh/Al₂O₃-TiO₂ (T₉₀ = 380°C). Total oxidation (T100) was reached at 450°C over Rh/Al₂O₃-TiO₂ followed by V₂O₅/Al₂O₃-TiO₂ (T₁₀₀ = 465°C). Chlorinated by-products were not detected in DCM oxidation. With Pt, Pd and Rh, small amounts (< 6 ppm) of CO were detected but, with V₂O₅, CO was the main by-product reaching the amount of 450 ppm at 400°C. The selectivity towards HCl is shown in Figure 1b.

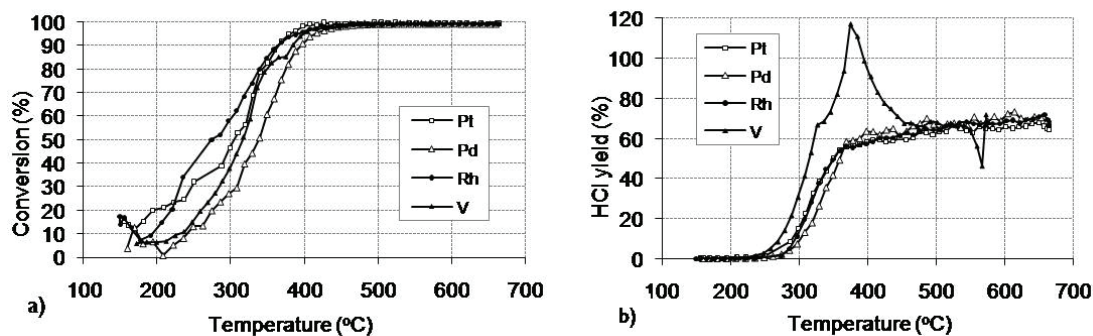


Figure 1 a) DCM conversion and b) HCl yield over Pt, Pd, Rh and V₂O₅ supported on Al₂O₃-CeO₂ (DCM 500 ppm, water 1.5 vol-%, GHSV 32 000 h⁻¹).

3.2 PCE oxidation

The Pt/Al₂O₃-CeO₂ catalyst (T₅₀ = 491 °C) showed the best performance followed by Pd/Al₂O₃-TiO₂ (T₅₀ = 508 °C). Light-off curves of PCE oxidation over Pt, Pd, Rh and V₂O₅ supported on Al₂O₃-CeO₂ are shown in Figure 2a. The activity of catalysts decreases in the order Pt > V₂O₅ > Rh > Pd. The conversion of 90% was exceeded over all the catalysts, and in the following order Pt > V₂O₅ > Pd > Rh. The highest conversions 98.8% and 99.3 % were reached over Pt and Pd, respectively. The maximum conversion was 97 % over Rh. In catalytic tests, small amount (< 10 ppm) of CH₂Cl₂ was detected as a by-product. Other chlorinated by-products were not detected. With Pt, Pd and Rh small amounts (~10 ppm) of CO were detected but, with V₂O₅, CO was the main by-product reaching the amount of 220 ppm at 600 °C. Data on the HCl selectivity is shown in Figure 2b.

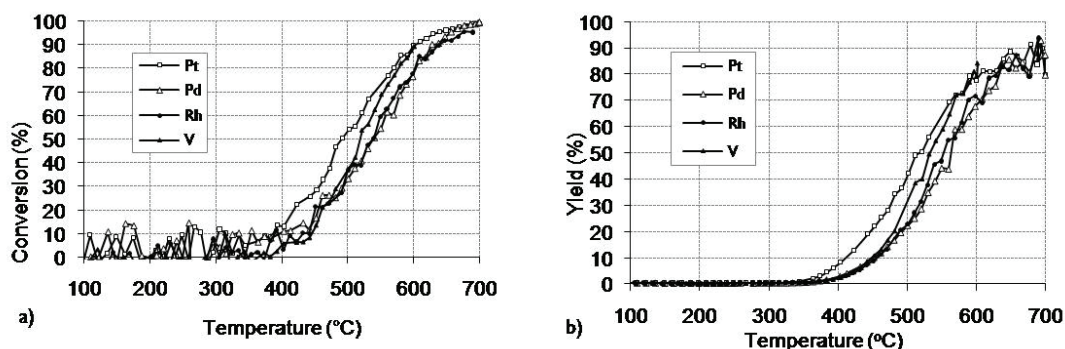


Figure 2 a) PCE conversion and b) HCl yield over Pt, Pd, Rh and V₂O₅ supported on Al₂O₃-CeO₂ (PCE 500 ppm, water 1.5 vol-%, GHSV 32 000 h⁻¹).

4 Relevance of the research

This research subject is extremely essential due to CVOC's strong greenhouse gas effect. Catalytic oxidation is an economic abatement system for industrial VOC emissions and it would be even more favourable should more active and selective, durable and inexpensive catalysts be found.

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