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CATALYTIC OXIDATION OF DICHLORETHANE AND TETRACHLORETHYLENE OVER NOBLE METAL CATALYSTS

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Annotation

Among the chemicals emitted to the atmosphere, volatile organic compounds (VOCs) are classified worldwide as hazardous air pollutants. Most of the VOCs are organochlorine compounds, widely used in industryas the components of detergents and degreasers, chemical extractants, additives for paints, inks and adhesives, raw materials for drug synthesis, pesticides and polymers, solvents for chemicalsand paint strippers. These compounds are released into the atmosphere and pose a significant health hazard due to their pronounced toxicity, high stability and persistence in the environment. In this study, a total of 6 different metal monoliths containing γ-Al$_2$O$_3$ were studied in the oxidation of dichloromethane (DCM) and tetrachlorethylene (perchlorethylene-PCE). Pt, Pd, separately, were used as the active substances. Before the research experiments of the catalysts have been started, the water supply was optimized. Among the studied catalysts, Pt/Al$_2$O$_3$ was the most active in the oxidation of DCM.

Keywords: catalytic oxidation; chlorinated volatile organic compound; dichloromethane; tetrachloroethylene.

КАТАЛІТИЧНЕ ОКИСНЕННЯ ДИХЛОРОМЕТАНА ТА ТЕТРАХЛОРОЕТИЛЕНА НА КАТАЛІЗАТОРАХ ІЗ БЛАГОРОДНИХ МЕТАЛІВ

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Анотація

Серед хімічних речовин, які потрапляють до атмосфери, леткі органічні сполуки (ЛОС) у всьому світі класифікуються як небезпечні забруднювачі повітря. Важливою групою ЛОС є хлороорганічні сполуки, що широко використовуються у промисловості, у таких галузях, як виробництво миючих та знежирюючих засобів; у якості екстрагентів, добавок до барвників, чорнил та клеїв; як сировина для синтеза лікарських засобів, пестицидів та полімерів; як розчинники. Наявність цих сполук у повітрі являє значну небезпеку для здоров'я людини з-за вираженої токсичності, високої стабільності та стійкості у навколишньому середовищі. У даній роботі досліджена каталітична активність щодо реакцій окиснення дихлорометана (DCM) та перхлороетилена (PCE) загалом шести металів зі вмістом γ-Al$_2$O$_3$. У якості активних речовин використовували Pt і Pd окремо. До початку експериментів із каталізаторами оптимізували подачу води. Найбільш активним щодо окиснення DCM серед досліджених виявив себе каталізатор Pt/ Al$_2$O$_3$.

Ключові слова: каталітичне окиснення; хлоровані леткі органічні сполуки; дихлорометан; тетрахлороетилен.

КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ ДИХЛОРМЕТАНА И ТЕТРАХЛОРЭТИЛЕНА НА КАТАЛИЗАТОРАХ ИЗ БЛАГОРОДНЫХ МЕТАЛЛОВ

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Аннотация

Среди химических веществ, выбрасываемых в атмосферу, летучие органические соединения (ЛОС) во всем мире классифицируются как опасные загрязнители воздуха. Важной группой ЛОС являются хлорорганические соединения, которые широко используются в промышленности в таких областях, как производство моющих и обезжиривающих средств; в качестве экстрагентов; добавок для красок, чернил и клеев, как сырье для синтеза лекарств, пестицидов и полимеров; в качестве растворителей. Наличие этих соединений в атмосфере представляют значительную опасность для здоровья человека из-за их выраженной токсичности, высокой стабильности и стойкости в окружающей среде. В данной работе в качестве катализаторов окисления дихлорметана (DCM) и перхлорэтилена (PCE) исследовано в общей сложности шесть различных металлов, содержащих γ-Al_2O_3. В качестве активных веществ использовали Pt и Pd по отдельности. Перед началом экспериментов с исследуемыми катализаторами была оптимизирована подача воды. Среди исследованных наиболее активен в окислении DCM был катализатор Pt/ Al_2O_3.

Ключевые слова: каталитическое окисление; хлорированные летучие органические соединения; дихлорметан; тетрахлорэтилен.

Introduction

For many years, thermal incineration has been considered one of the most efficient decontamination processes. The effluent is burned with air in a furnace or burner using fuel gas as an energy source, as the low VOC concentration (1000 ppm) prevents spontaneous combustion. In addition, due to their chemical stability, these compounds require high temperatures (800–1000 °C) for complete destruction, and the presence of chlorine leads to the formation of a large volume of highly toxic products of incomplete combustion, such as phosgene, dibenzofuran, etc.

In recent decades, the catalytic oxidation of Cl–VOCs has received increased attention for its energy and efficiency benefits in a wide range of operating conditions. Catalytic oxidation opens up a different reaction path with the lower activation energy than gas-phase combustion and allows the oxidation to proceed at lower temperatures. This results in lower energy consumption and lower NOx production. The approximate operating variable ranges are low to moderate temperatures (100–500°C), atmospheric pressure, high space velocity (10^3–10^5 h^{-1}), and low organic contamination. Reagent concentration is 10^2–10^3 ppm in air.

The removal of Cl-VOC by catalytic oxidation over various catalysts has been presented in many scientific papers. One of the main goals in catalyst design is to find a composition that lowers the temperature required to convert contaminants. Also, the reaction path over the catalyst should lead to complete oxidation of the products, i.e., CO_2, H_2O and HCl. The presence of HCl is preferred over Cl_2 as it can be easily purified after the catalytic oxidizer. The stability and durability of the catalyst are just as important as their activity and selectivity. These properties must remain constant during the reaction to comply with international environmental regulations and to be more economically attractive [1; 2].

The primary sources of chlorinated VOC emissions into the atmosphere can be divided into three groups: 1) chemical plants producing halogenated hydrocarbons for the synthesis of plastics, insecticides, anesthetics, etc.; 2) finishing processes based on the use of volatile solvents; 3) cleaning processes [3; 4]. Among the wide range of Cl-VOCs, the compound group has been used for catalytic oxidation studies: trichloroethylene (TCE) and dichloromethane (DCM), common cleaning solvents for dry cleaning, metal degreasing and semiconductor manufacturing, found in groundwater waste gases and soil remediation processes. This work aims to investigate the process of heterogeneous catalytic oxidation of tetrachloroethylene (PCE) and dichloromethane (DCM) on catalysts based on noble metals. The catalyst must bring to the oxidation products that is, CO_2, H_2O and HCl.

Catalysts for the neutralization of chlorinated VOCs. Historically, oxidation reactions have always been carried out over noble metals or transition metal oxides [5]. Noble metals are commonly used for full oxidation, while transition

metal oxides are used for selective and fulloxidation. The cost of treating streams containing halogenated organics is estimated to be double that of simple non-halogenated organics. Catalytic emission reduction is a particularly preferred approach when mixtures of several compounds and low concentrations of halogenated VOCs are present in the emissions [6–9].

For a long time, catalysts based on noble metals and mixed oxides have been intensively studied. In recent years, efforts have been focused on formulating catalysts with enhanced redox properties.

Noble metals are the metals that are not subject to corrosion and oxidation and do not react with hydrochloric acid. The primary noble metals are gold, silver, as well as platinum and the other five platinum-group metals - ruthenium, rhodium, palladium, osmium and iridium.

Platinum-group metals (PGMs) are highly active catalysts. Small amounts (0.1–0.5 %) platinum and palladium dispersed on substrates with a high specific surface area (γ-Al_2O_3, TiO_2, SiO_2, etc.) are widely used for the oxidation of these chlorinated hydrocarbons. Pt promotes the full oxidation of chlorohydrocarbons to CO2, whereas Pd yields CO to a greaterextentof hydrogen chlorides [5]. Due to the excess of oxygen in the reaction medium, noble metals are gradually oxidized, and chlorinated oxides and chloride metals are converted [10; 11].

The use of Pt and Pd is limited by the cost and sensitivity of the catalysts. Noble metals, especially platinum and palladium, show high catalytic activity in many chemical reactions. Platinum catalysts are widely used in oil refining processes; palladium catalysts have found application in the hydrogenation of unsaturated organic compounds. Along with this, the metals of the platinum group exhibit high catalytic activity in the reactions of deep oxidation of organic substances and carbon monoxide, and in their activity (per atom of the active substance), they are significantly superior to other catalysts. Their high cost hinders the widespread use of noble metals as catalysts for deep oxidation; therefore, supporting systems are often used. Most often the oxides of aluminum, silicon and aluminosilicates areused as carriers. However, such catalysts often lose their activity in highly exothermic reactions carried out at high temperatures. The probable reasons for the deactivation of the deposited systems at high temperatures are low thermal stability of the samples, sintering, and agglomeration of the metal particles on the base surface [12; 13].

The catalysts used for CVOC oxidation must be highly active at relatively low temperatures, maintain high resistance to deactivation with chlorine and its compounds, and have high selectivity towards CO_2 and HCl. The reactivity of CVOCs in catalytic oxidation, as well as the distribution of of the products of reaction is highly dependent on the catalyst used and the chemical structure of the oxidized compounds.

Experience shows that noble metal catalysts are often more selective than the catalysts based on metal oxides or perovskites [12; 13].

The total chlorine content of CVOC plays an important role as chlorinated C_1 hydrocarbons are catalytically more active than chlorinated C_2 hydrocarbons and chlorobenzenes. Among chlorinated hydrocarbons C_1, the reactivity increases with an increase in the number of chlorine atoms and a decrease in the number of C-H bonds in the molecule - that is, the catalytic reactivity of chlorinated hydrocarbons C_1 increases with the reduction in the C-Cl bond energy. In addition, the double bond affects the reactivity, but, unlike VOCs, unsaturated CVOS are more stable than saturated ones.

When mixtures of CVOC and VOC are oxidized, each compounds breakdown efficiency can increase or decrease. Generally, compared to noble metal catalysts, the presence of hydrogen-rich compounds (e. g. water or VOCs) positivelyaffectsthe selectivity to HCl, but the CVOC conversion can also be increased. On the other hand, CVDs usually inhibit the oxidation of added non-chlorinated VOCs [14]. The enhanced degradation of CVOC depends on the VOCs used. For example unsaturated VOCs can significantly increase the oxidation of unsaturated chlorinated VOCs, while with the use of saturated VOCs the effect is less.

Materials and methods

The characteristics of the compounds used in the experiments are given in table 1.

Dichloromethane. Exposure to dichloromethane (DCM) is irritating to the skin and eyes and can affect the central nervous system, blood, liver, heart, and lungs. Exposure to high concentrations can cause confusion and even death [15–17].

Table 1

Characteristics of the compounds used in the experiment

Compound formula	Cas №	CHS Classification	Density (g/mL) (typical)	Boiling Point (typical)	Emission limit value	Provider-Purity
Dichlormethane DCM, CH_2Cl_2	75–09-2	H351	1.318 (25 °C)	39.5 °C.	20 mg Nm^{-3} 5.27 ppm	Avantor-99,5%
Terachloroethylene PCE, C_2Cl_4	127–18-4	H411,H351	1.63 g/cm^3 (20 °C)	121.1°C (1013 hPa)	20mg Nm^{-3} 2.70 ppm	Avantor-99%

Tetrachlorethylene. Short-term exposure to tetrachlorethylene (PCE) irritates the eyes, skin, and respiratory tract and can affect the central nervous system. Exposure to high concentrations can cause unconsciousness. Long-term or repeated exposure can cause dermatitis and damage to the liver and kidney [18–20].

Catalysts used in the experiments. Two different catalyst support (Al_2O_3, Al_2O_3–TiO_2) and two other active substances (Pt, Pd) were chosen (Table 2). When preparing the Al_2O_3-TiO_2 catalyst support a mass ratio of 3:1 was used. The amount of support on the metal foil was set constant and amounted to 25 % of the catalysts' total mass. The noble metal loads were fixed the same with moles (n), and therefore the target loads were 1 wt% for Pt and 0.5 wt% for Pd. Used precursor salts: $Pd(NH_3)_4(NO_3)$, $Pt(NH_3)_4(HCO_3)_2$. After the subsequent impregnation of the active material, the catalysts were calcined at 550 °C for 5 hours. The catalysts withtheir actual metal content are presented in Table 2.

Table 2

Catalysts used in the experiments

Usedcatalysts	ActualLoad
Pt/ Al_2O_3	0.98
Pd/ Al_2O_3	0.75
Pt/ Al_2O_3- TiO_2	1,4
Pd/ Al_2O_3- TiO_2	0.66
Al_2O_3	–
Al_2O_3- TiO_2	–

The following methods determined characteristics of the catalyst

Physical adsorption. Specific surface area (SBET), specific pore volume (Vp), and pore size distribution (PSD) wasdetermined by physical nitrogen sorption at –196 °C on a Thermo Scientific Surfer gas adsorption porosimeter. Samples were degassed before analysis for 2 hours at 350 °C in a vacuum (2 Pa).

Chemisorption. The degree of dispersion and the surface area of the CO active sites of Pt, Pd, determined by the iteration of active-site chemisorption method at 35 °C using the Thermo Scientific Surfer chemisorption module.

The formula for calculating the conversion. The formula for calculating the conversion [%] is presented as follows (1):

$$X_{CVOC} = 100 \times \left(1 - \frac{c_{CVOC}^{out}}{c_{CVOC}^{in}} \right) \qquad (1)$$

Gas analysis was carried out using an Agilent 7820A a gas chromatography (Gas Chromatograph) calibrated for the detection of the following chlorinated hydrocarbons: C_2Cl_4, C_2HCl_3, CH_3Cl, CH_2Cl_2, $CHCl_3$, $COCl_2$, HCl as well. H_2O, CO_2, CO, NO, NO_2, N_2O, CH_4, CH_2O, CH_4O, C_2H_6, C_2H_4O, C_2H_6O, C_3H_8, C_7H_8.

The chromatograph was equipped with a high-temperature sample cell and a flame ionization detector (FID) as well as a mass spectrometric (MSD) detector. To analyze the indicators, the OpenLAB CDS EZChrom Compact software was used.

Vertically oriented reactor. In the laboratory, activity experiments were carried out with a vertically aligned tubular quartz reactor operating at atmospheric pressure. The scheme of the experiment is shown in Fig. 1.
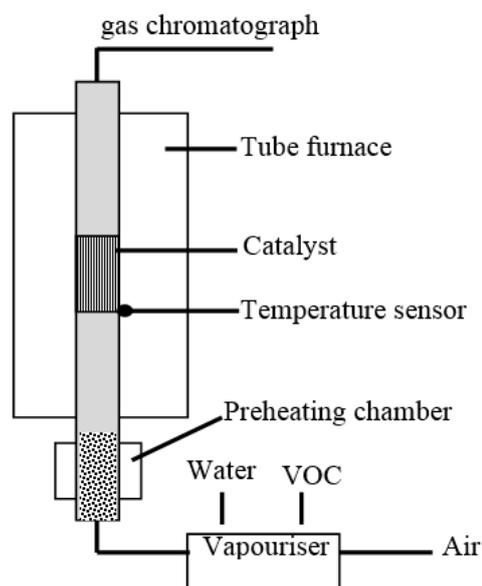
Fig. 1. The experimental Vertically-aligned reactor

Due to the corrosion products, all materials used in the experimental setup were corrosion-resistant: quartz glass, heated Teflon pipes (T = 180 °C) and Teflon connectors. In an evaporation

unit, liquid VOCs and water were supplied by syringe pumps equipped with gastight syringes to an evaporation heater and mixed with air from the mass flow controller. A preheating oven filled with glass spheres for mixing gases was set to 150 °C. The temperature was measured outside the reactor just in front of the monolith and then adjusted to the value inside the reactor. The correction was made based on a calibration performed earlier by measuring the

temperatures inside and outside the reactor at the same time as the furnace temperature was increasing in the same way as during the ignition tests. A monolith 0.8 cm in diameter and 4.0 cm in length was used in all experiments. The CVOC catalysts were packaged in a quartz glass tube.

Results and discussions

Properties of the tested catalysts are given in table 3.

Table 3

Properties of the tested catalysts

Catalyst	Metal dispersion (%)	Metal loading (wt.%)	SBET (m^2g^{-1})
Pt/ Al_2O_3	50	0.98	142
Pd/ Al_2O_3	17	0.74	150
Pt/ Al_2O_3 -TiO_2	50	1.2	131
Pd/ Al_2O_3 - TiO_2	20	0.66	139
Al_2O_3	174	–	–
Al_2O_3 - TiO_2	137	–	–

Dichloromethane oxidation. Ignition tests with catalysts showed that the carriers themselves (Al_2O_3, Al_2O_3–TiO_2) were very active in DCM oxidation, and up to 100 % DCM conversion was achieved (Fig. 2). The substrates also showed high selectivity towards HCl (Fig. 3) and CO_2 formation. HCl yields were up to 99 %, and CO_2 yields up to 100 %. The high activity of the tested carriers, especially γ-Al_2O_3, corresponds to the results of other researchers, was expected since several authors previously reported it [5; 21–25]. The addition of Pt, Pd as the active compound had

a different effect on the activity depending on the carrier (Fig. 2, a–b). In general, the result was small, anyway. On the catalysts supported on Al_2O_3, the impact was positive for all of them except for the Pd catalyst. The temperatures required to achieve 100% DCM conversion were 420 °C for Pt/Al_2O_3. When 26 wt% titanium dioxide was present in the support, the addition of active metal increased the catalysts' activity. For the Pt catalysts, temperatures of 420 °C and 450 °C were required to achieve 100 % DCM conversion, respectively.
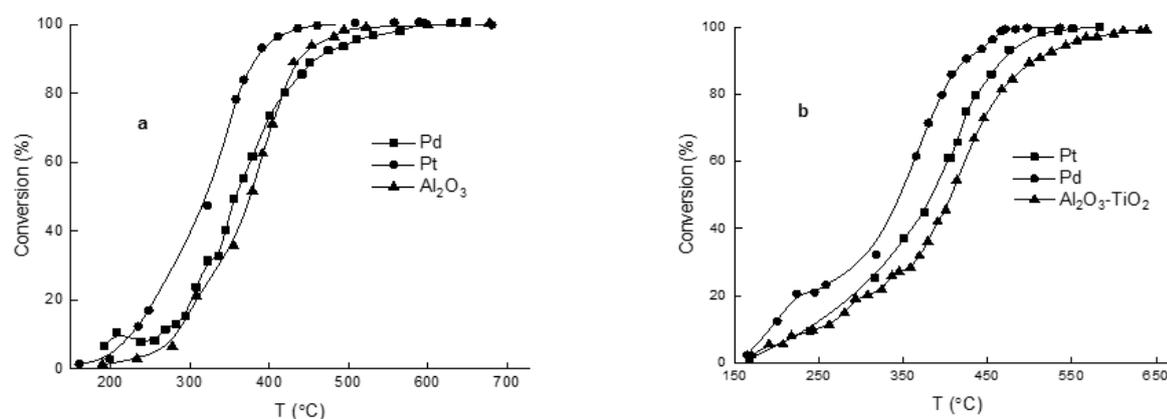
Fig. 2. The DCM conversions over the Al_2O_3 (a), Al_2O_3-TiO_2 (b) (DCM 500 ppm, H_2O 1.5 wt%, GHSV [Gas hourly space velocity] 32000 h^{-1}) supported researched catalysts.
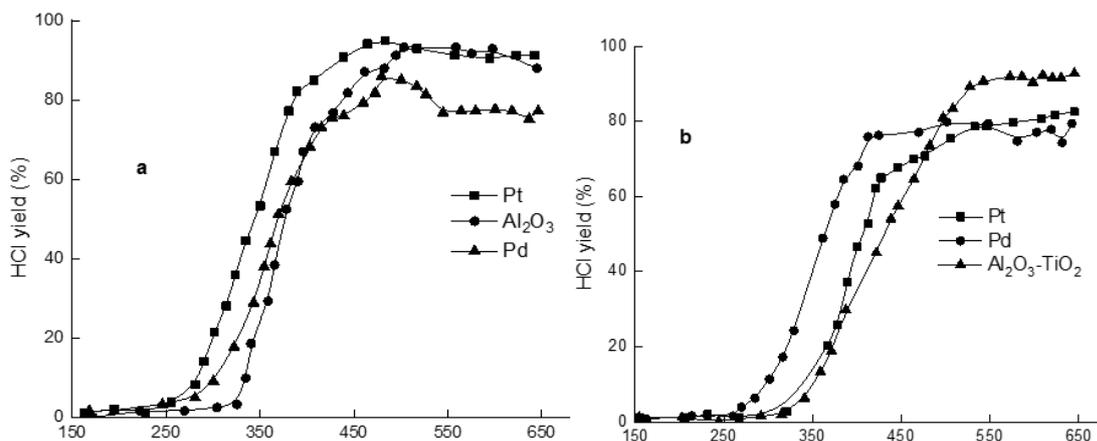
Fig. 3. HCl yields over the Al₂O₃ (a), Al₂O₃- TiO₂ (b) (DCM 500 ppm, H₂O 1.5 wt%, GHSV 32000 h⁻¹) supported researched catalysts in the dichloromethane oxidation.

Perchlorethylene oxidation. Before starting the activity experiments, various concentrations of water were tested (0.2 wt%, 0.6 wt%, 1 wt%, 1.5 wt%, 2 wt%) to determine the appropriate amount of water to be added to the emission stream during testing to act as a hydrogen source to ensure the highest possible HCl yield. In addition to increasing the HCl selectivity from 57 % to 79 %, water also increased the PCE conversion to some extent, that is, from 77 % to 84 %, as the amount of water increased from 0.3 to 3 wt%. Of the various water concentrations tested, 1.5 wt% was chosen for the activity experiments, since the higher PCE conversion and HCl yield increased only slightly, and the same disadvantages as previously for DCM manifested, i.e., unstable water evaporation and interference
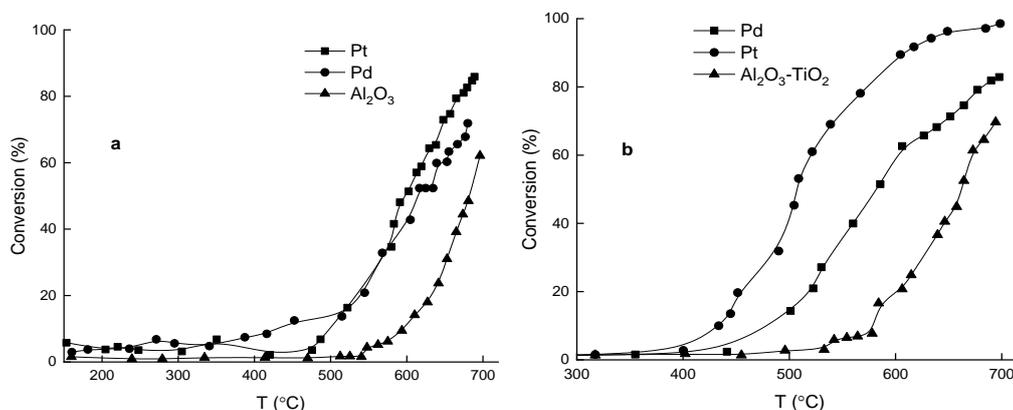
Fig. 4. The PCE conversions over the Al₂O₃ (a), Al₂O₃-TiO₂ (b) (DCM 500 ppm, H₂O 1.5 wt%, HSV 32000 h⁻¹) supported researched catalysts.
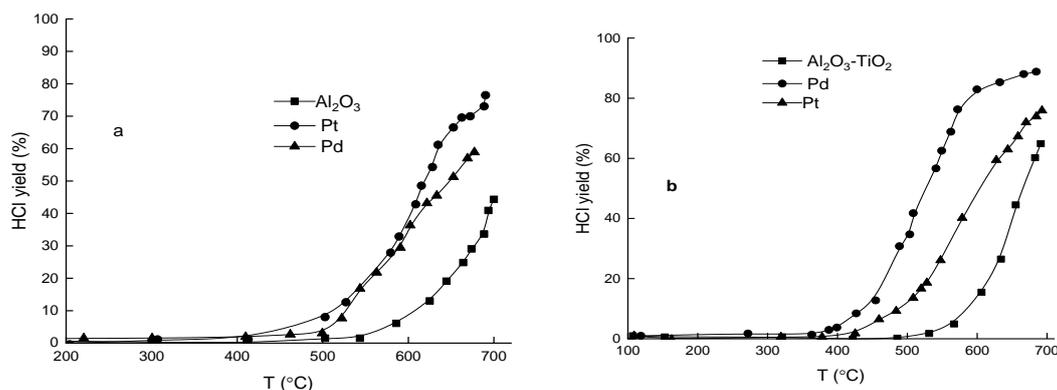
Fig. 5. HCl yields over theAl₂O₃ (a), Al₂O₃- TiO₂ (b) (DCM 500 ppm, H₂O 1.5 wt%, GHSV 32000 h⁻¹) supported researched catalysts in the perchlorethylene oxidation.

The tested carriers, Al_2O_3, Al_2O_3–TiO_2, showed a rather high activity in PCE oxidation (Fig. 4). The supports also showed high selectivity for HCl (Fig. 5), CO_2, and CO- the only end products found during ignition tests. In contrast to the oxidation of DCM Pt, Pd significantly increased the activity and selectivity of the PCE oxidation. In addition, almost all Al_2O_3-TiO_2 supported catalysts showed higher activity, and better HCl selectivity than their corresponding Al_2O_3 supported catalysts. The only exception to this rule was Pt/Al_2O_3–TiO_2 because the activity and selectivity remained the same as compared to the Pt / Al_2O_3 catalyst.

Conclusions

In this study, six different CVOC metal monolithic oxidation catalysts were studied in vitro.

The catalysts used to destroy CVOC must be highly active at relatively low temperatures, have high selectivity towards CO_2 and HCl, and retain high resistance to deactivation by chlorine and its compounds. Pt-Pd catalysts have been proven to be highly active for CVOC oxidation. Pt catalysts were more involved in DCM oxidation than Pd catalysts. Pd catalysts were active in the oxidation of PCE.

GHSV had a marked effect on DCM conversion and HCl yield, followed by DCM concentration and then the amount of water in the feed stream. The optimum water feed was set to 1.35 wt% for both CVOCs. During testing, it was observed that the addition of an active metal to the catalyst significantly increases the selectivity towards CO_2 and reduces the formation of detected by-products. (CH_3Cl, CH_2O, and CO). In DCM oxidation, Pt/Al_2O_3 is the most active and selective for HCl. The data presented in the article have scientific novelty and practical significance.

Bibliography

[1] Vapor phase hydrogenation of aqueous levulinic acid over hydroxyapatite supported metal (M = Pd, Pt, Ru, Cu, Ni) catalysts / M. Sudhakara, V. Vijay Kumara, G.Naresha [et al.] //Applied Catalysis B: Environmental.– 2016. –Vol. 180. – P.113–120

[2] Thermally Induced Strains on the Catalytic Activity and Stability of Pt-M2O3 /C (M=Y or Gd) Catalysts towards Oxygen Reduction Reaction / Luo Yun, Habrioux Aurelien, Calvillo Laura [et al.] // Chem. Cat. Chem. – 2015. –Vol. 7. P. 1573–1582.

[3] Yasuhara A. Formation of Chlorinated Compounds in Pyrolysis of Trichloroethylene / A. Yasuhara, M. Morita //Chemosphere. – 1990. –Vol. 21. – P. 479–486.

[4] Roberto Fiorenza. Bimetallic Catalysts for Volatile Organic Compound Oxidation / Fiorenza Roberto // Catalysts. – 2020. – Vol.10. – P. 661.

[5] Activity and Product Distribution of Alumina Supported Platinum and Palladium Catalysts in the Gas-phase Oxidative Decomposition of Chlorinated Hydrocarbons / J.R. González-Velasco, A. Aranzabal, J.I. Gutiérrez Ortiz [et al.] //Appl. Catal., B: Environ. – 1998. – Vol. 19. – P. 189–197.

[6] Oxidation of dichloromethane and perchloroethylene as single compounds and inmixtures / S. Pitkäaho, S. Ojala, T. Maunula [et al.] // Applied Catalysis B: Environmental. – 2011. – Vol. 102. – P. 395–403.

[7] He C. Recent advances in the catalytic oxidation of volatile organic compounds: A review based on pollutant sorts and sources / C. He, J. Cheng, X. Zhang [et al.] //Chem. Rev. – 2019. – Vol. 119, N7. – P.4471–4568.

[8] Aqueous-phase catalytic hydrodechlorination of 1,2-dichloroethane over palladium nanoparticles (nPd) with residual borohydride from nPd synthesis / El-Sharnouby Omneya, K. Hardiljeet Boparai, Herrera Jose [et al.] //Chemical Engineering Journal. – 2018. – Vol. 342. – P. 281–292.

[9] Spatiotemporal changes of CVOC concentrations in karst aquifers: Analysis of three decades of data from Puerto Rico / X. Yu. R. Ghasemizadeh, I. Padilla [et al.] // Science of the Total Environment. – 2015. – Vol. 511. –P. 1–10.

[10] Giraudon J. Catalytic Oxidation of Chlorobenzene over Pd/Perovskites / J. Giraudon, A. Elhachimi, G. Leclercq // Appl. Catal. B: Environ. –2008. –Vol. 84(1). –P. 251–261.

[11] Oxidation ofdichloromethane over Pt, Pd, Rh, and V2O5 catalysts supported on Al2O3, Al2O3–TiO2 and Al2O3–CeO2 / S. Pitkäaho, T. Nevanperä, L. Matejova [et al.] //Applied Catalysis B: Environmental. – 2013. – Vol. 138–139. – P.33–42.

[12] Oxidative destruction of dichloromethane over protonic zeolites / R. López-Fonseca, S. Gibrián, J.I. Gutiérrez-Ortiz [et al.] //AI. Ch. E. J. – 2004. – Vol. 49. –P. 496–504.

[13] Wang L. Catalytic oxidation of dichloromethane andtoluene over platinum alumite catalyst / Wang, M. Sakurai & H. Kameyama // J. Hazard. Mater. – 2008. – Vol. 154. – P. 390–395.

[14] Physical, chemical, and biological treatment of chemical waste from teaching laboratories at Universidad Nacional, Costa Rica / Rodríguez-Rodríguez Jorengeth Abad, Vargas-Villalobos Seiling, Aparicio-Mora Carmen [et al.] // UNICIENCIA. –2020. – Vol. 34, N 2. – P. 82–94.

[15] Cytotoxic activities of the dichloromethane extracts from *Andrographis paniculata* (Burm. f.) nees / S. Maria Carmen, Glenn G. Oyong, Chien-Chang Shen, Consolacion Y. Ragasa // Journal of Natural Science, Biology and Medicine. – 2018. – Vol. 9. Issue 2. – P. 201–206.

[16] Occupational exposure to solvents and risk of head and neck cancer in women: a population-based case–control study in France / Carton Matthieu, Barul Christine, Menvielle Gwenn, Cyr Diane [et al.] // BMJ Open. – 2017. – Vol.7: e012833.

[17] Reductive/oxidative sequential bioelectrochemical process for /Marco Zeppillia, Bruna Matturrob, Edoardo Dell', Armia Lorenzo [et al.] //Journal of Environmental Chemical Engineering. – 2021. – Vol. 9. Issue 1. – P.104657

[18] Relations Between Residential Proximity to EPA-Designated Toxic Release Sites and Diffuse Large B-Cell Lymphoma Incidence / C. Bulka, L.J. Nastoupil, J.L. Koff [et al.] //Southern Medical Journal. – 2016. – Vol. 109, Iss. 10. – P. 606–614.

[19] Occupational exposure to solvents and bladder cancer: A population-based case control study in Nordic countries / Hadkhale Kishor, Martinsen Jan Ivar, Weiderpass Elisabete, Kjaerheim Kristina [et al.] // International Journal of Cancer. – 2017. – Vol. 140., Iss. 8. – P. 1736–1746.

[20] Catalytic oxidation of dichloromethane on γ-Al₂O₃: A combined flow and infraredspectroscopy study / R. W. van den Brink, P. Mulder, R. Louw [et al.] // J. Catal. – 1998. – Vol. 180. – P. 153–160.

[21] Novel One-Pot Synthesis of Pyrazolopyrano-pyrimidinones Using Newly Produced γ-Alumina Nanoparticles as Powerful Catalyst / S. Kiani, S. Hodabakhshi, A.Rashidi, S. Dasthoon // Iran. J. Chem. Chem. Eng. – 2018. – Vol. 37, N. 3. – P.63–71.

[22] Newly Prepared Nano Gamma Alumina and Its Application in Enhanced oil Recovery: an Approach to Low-Salinity Water flooding / S. Kiani, M. Mansouri Zadeh, S. Khodabakhshi [et al.] //Energy & Fuels. – 2016. – 30(5). – P. 3791–3797.

[23] Correlations between the basicity and the fractal dimension of Rh-nanoparticles supported on Al₂O₃, TiO₂ and WO₃ / Dobrescu Gianina, Papa Florica, Irina Atkinson [et al.] //IOSR Journal of Applied Chemistry (IOSR-JAC). – 2021. – Vol.14. Iss. 1. –P.11–25.

[24] Interface excess on Li₂O-doped γ-Al₂O₃ nanoparticles / Raphael A.M.P. de Oliveira, Andre L. da Silva, Lorena B. Caliman, Douglas Gouvêa. // Ceramics International. – 2020. – Vol.46. – P. 10555–1056.

[25] Oxidation of Dichloromethane over Au, Pt, and Pt-Au Containing Catalysts Supported on γ-Al₂O₃ and CeO₂-Al₂O₃ / Tuomas K. Nevanperä, Satu Pitkäaho, Satu Ojala [et al.] // Molecules. – 2020. – Vol. 25. – P. 4644.

References

[1] Sudhakara, M., Vijay Kumara, V., Naresha, G., Lakshmi Kantama, M., Bhargavab, S.K., Venugopala, A. (2016). Vapor phase hydrogenation of aqueous levulinic acid over hydroxyapatite supported metal (M = Pd, Pt, Ru, Cu, Ni) catalysts. *Applied Catalysis B: Environmental.* 180, 113–120.

[2] Yun, Luo, Aurelien, Habrioux, Laura, Calvillo, Gaetano, Granozzi, and Nicolas, Alonso-Vante. (2015). Thermally Induced Strains on the Catalytic Activity and Stability of Pt-M₂O₃/C (M=Y or Gd) Catalysts towards Oxygen Reduction Reaction. *Chem. Cat. Chem*, 7, 1573–1582, https://doi.org/ 10.1002/cctc.201500130

[3] Yasuhara, A., Morita, M. (1990). Formation of Chlorinated Compounds in Pyrolysis of Trichloroethylene. *Chemosphere.* 21, 479–486.

[4] Roberto, Fiorenza. (2020). Bimetallic Catalysts for Volatile Organic Compound Oxidation. *Catalysts.* 10, 661. https://doi.org/10.3390/catal10060661

[5] González-Velasco, J.R, Aranzabal, A., Gutiérrez Ortiz, J.I., López-Fonseca, R., Gutiérrez-Ortiz, M.A. (1998). Activity and Product Distribution of Alumina Supported Platinum and Palladium Catalysts in the Gas-phase Oxidative Decomposition of Chlorinated Hydrocarbons. *Appl Catal, B: Environ.* 19, 189–197.

[6] Pitkäaho, S., Ojala, S., Maunula, T., Savimäki, A., Kinnunen, T.&Keiski, R.L. (2011). Oxidation of dichloromethane and perchloroethylene as single compounds and inmixtures. *Applied Catalysis B: Environmental*, 102, 395–403. https://doi.org/10.1016/j.apcatb.2010.12.011

[7] He, C., Cheng, J., Zhang, X., Douthwaite, M., Pattisson, S., Hao, Z. (2019). Recent advances in the catalytic oxidation of volatile organic compounds: A review based on pollutant sorts and sources. *Chem. Rev. 119*(7), 4471–4568. https://doi.org/10.1021/acs.chemrev.8b00408

[8] Omneya El-Sharnouby, Hardiljeet K. Boparai, Jose Herrera, Denis M. O'Carroll. (2018). Aqueous-phase catalytic hydrodechlorination of 1,2-dichloroethane over palladium nanoparticles (nPd) with residual borohydride from nPd synthesis. *Chemical Engineering Journal.* 342, 281–292. https://doi.org/ 10.1016/j.cej.2018.02.006

[9] Yu, X.Ghasemizadeh, R. Padilla, I. Irizarry, C. Kaeli, D. Alshawabkeh, A. (2015). Spatiotemporal changes of CVOC concentrations in karst aquifers: Analysis of three decades of data from Puerto Rico. *Science of the Total Environment.* 511, 1–10.

[10] Giraudon, J., Elhachimi, A., Leclercq, G. (2008). Catalytic Oxidation of Chlorobenzene over Pd/Perovskites. *Appl. Catal B: Environ. 84*(1), 251–261. https://doi.org/10.1016/j.apcatb.2008.04.023

[11] Pitkäaho, S., Nevanperä, T., Matejova, L., Ojala, S. & Keiski, R.L. (2013). Oxidation ofdichloromethane over Pt, Pd, Rh, and V₂O₅ catalysts supported on Al₂O₃, Al₂O₃–TiO₂ and Al₂O₃–CeO₂. *Applied Catalysis B: Environmental.* 138–139, 33–42. https://doi.org/10.1016/j.apcatb.2013.01.058

[12] López-Fonseca, R., Gibrián, S., Gutiérrez-Ortiz, J.I., Gutiérrez-Ortiz, M.A. & Gonzáles-Velasco, J.R. (2004). Oxidative destruction of dichloromethane over protonic zeolites. *A. I. Ch. E. J.,* 49, 496–504. https://doi.org/10.1002/aic.690490219

[13] Wang, L., Sakurai, M. & Kameyama, H. (2008). Catalytic oxidation of dichloromethane andtoluene over platinum alumite catalyst. *J. Hazard. Mater.* 154, 390–395. https://doi.org/10.1016/j.jhazmat.2007.10.036

[14] Jorengeth Abad, Rodríguez-Rodríguez, Seiling, Vargas-Villalobos, Carmen, Aparicio-Mora, Nidya, Nova-Bustos. (2020). Physical, chemical, and biological treatment of chemical waste from teaching laboratories at Universidad Nacional, Costa Rica. *UNICIENCIA. 34*(2), 82–94. http://dx.doi.org/10.15359/ru.34-2.5

[15] Maria, Carmen S. Tan, Glenn G. Oyong, Chien-Chang Shen, Consolacion, Y. Ragasa. (2018). Cytotoxic activities of the dichloromethane extracts from *Andrographis paniculata* (Burm. f.) nees. *Journal of Natural Science, Biology and Medicine, 9*(2), 201–206. https://doi.org/10.4103/jnsbm.JNSBM_91_17

[16] Matthieu, Carton, Christine, Barul, Gwenn, Menvielle, Diane, Cyr et al. (2017). Occupational exposure to solvents and risk of head and neck cancer in women: a population-based case–control study in France. *BMJ Open.* 7, e012833. https://doi.org/10.1136/bmjopen-2016-012833

[17] Marco, Zeppillia, Bruna, Matturrob, Edoardo, Dell', Armia, Lorenzo et al. (2021). Cristiania. Reductive/oxidative sequential bioelectrochemical process for. *Journal of Environmental Chemical Engineering. 9*(1), 104657.

[18] Bulka, C., Nastoupil, L.J., Koff, J.L. et al. (2016). Relations Between Residential Proximity to EPA-

Designated Toxic Release Sites and Diffuse Large B-Cell Lymphoma Incidence. *Southern Medical Journal, 109*(10), 606–614. https://doi.org/10.14423/SMJ.0000000000000545

[19] Kishor, Hadkhale, Jan, Ivar Martinsen, Elisabete, Weiderpass, Kristina, Kjaerheim. (2017). Occupational exposure to solvents and bladder cancer: A population-based case control study in Nordic countries. *International Journal of Cancer, 140*(8), 1736–1746. https://doi.org/10.1002/ijc.30593

[20] Brink, R.W. van den, Mulder, P., Louw, R., Sinquin, G., Petit, & C. Hindermann J.-P. (1998). Catalytic oxidation of dichloromethane on γ-Al$_2$O$_3$: A combined flow and infraredspectroscopy study. *J. Catal.*180, 153–160.

[21] Kiani, S., Hodabakhshi, S., Rashidi, A., Dasthoon, S. (2018). Novel One-Pot Synthesis of Pyrazolopyranopyrimidinones Using Newly Produced γ-Alumina Nanoparticles as Powerful Catalyst. *Iran. J. Chem. Chem. Eng., 37*(3), 63–71.

[22] Kiani, S., Mansouri, Zadeh M., Khodabakhshi, S., Rashidi, A., Moghadasi, J. (2016). Newly Prepared Nano Gamma Alumina and Its Application in Enhanced oil Recovery: an Approach to Low-Salinity Waterflooding. *Energy & Fuels*, *30*(5), 3791–3797.

[23] Gianina, Dobrescu, Florica, Papa, Irina, Atkinson, Daniela, Culita, Ioan, Balint. (2021). Correlations between the basicity and the fractal dimension of Rh-nanoparticles supported on Al$_2$O$_3$, TiO$_2$ and WO$_3$. *IOSR Journal of Applied Chemistry (IOSR-JAC).*, *14*(1), 11–25. https://doi.org/10.9790/5736-1401011125

[24] Raphael, A.M.P. de Oliveira, Andre, L. da Silva, Lorena B. Caliman, Douglas Gouvêa. (2020). Interface excess on Li$_2$O-doped γ-Al$_2$O$_3$ nanoparticles. *Ceramics International*, 46, 10555–1056. https://doi.org/10.1016/j.ceramint.2020.01.057

[25] Tuomas, K. Nevanperä, Satu, Pitkäaho, Satu, Ojala and Riitta, L. Keiski. (2020). Oxidation of Dichloromethane over Au, Pt, and Pt-Au Containing Catalysts Supported on γ-Al$_2$O$_3$ and CeO$_2$-Al$_2$O$_3$. *Molecules*. 25, 4644. https://doi.org/10.3390/molecules25204644.