Revista de Chimie
https://revistadechimie.ro
https://doi.org/10.37358/Rev. Chim.1949

Chemical Vapour Deposition (CVD) Technique for Abatement of Volatile Organic Compounds (VOCs)

MARIUS STOIAN[1], LILIANA LAZAR[2], FLORENT UNY[3,4], FREDERIC SANCHETTE[3,4], IOANA FECHETE[3,4]*

[1]Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blvd, 030018, Bucharest, Romania
[2]Gheorghe Asachi Technical University of Iasi-Romania, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, 73 Prof. Dimitrie Mangeron Blvd., 700050, Iasi, Romania
[3]ICD-LASMIS, Université de Technologie de Troyes, Antenne de Nogent, Pôle Technologique de Sud Champagne, Nogent, 52800, France
[4]Nogent International Center for CVD Innovation-NICCI, LRC-CEA-ICD-LASMIS, Université de Troyes-Antenne de Nogent, Pôle Technologique Sud Champagne, 26, rue Lavoisier, 52800 Nogent, France

Abstract: *Chemical vapour deposition (CVD) is an important technique that uses volatile precursors to produce thin film deposits on an exposed substrate, having the capability to generate different types of nanostructures (e.g. nanoparticles, nanotubes, nanofibers or nanocomposites) as catalytic materials. The environmental hazard of volatile organic compounds (VOCs) requires efficient methods to reduce their emission into the atmosphere, due to their high potential to cause severe health issues, along with their extended spread in the environment. Catalytic combustion proves to be one of the most effective means for the abatement of VOCs, employing different catalysts, such as noble metals or non-noble metal oxides, to facilitate the oxidation process of the pollutants. These catalysts can be prepared through various methods as multiple steps wet processes or CVD techniques, indicating the superiority of the CVD-prepared catalysts compared to those prepared using the former type of process, due to the ability to achieve high dispersion of the active material, together with enhanced textural and morphological properties. This paper aims to present the various CVD techniques employed in the fabrication of different catalysts with the possibility of generating materials at nano-scale for use in numerous reactions, mostly in combustion process for VOCs decomposition.*

Keywords*: CVD, VOCs, thin film, total oxidation,* CH_4

1. Introduction

The development of technological processes with high atom economies represent a challenge in all industries and academic research [1-7]. A challenge for the 21st century is the control of technological processes in all industries to develop atom-economical and environmental friendly processes without by-products [8-13]. In this context, excellent comparative studies for several catalysts have been performed to improve catalytic performance in catalytic removal of CH4, NOx, COx, VOCs from flue gases [14-22]. VOCs are known as organic compounds with a low boiling point (≤ 250°C) at atmospheric pressure, according to the European Union (EU) [23]. Such compounds (e.g. toluene, benzene, xylene) are widely used in various industries such as in the fabrication of semiconductors, automobiles, and even as domestic cleaning agents, being so present in the environment [24]. They contribute as the main components of indoor air pollution, are responsible for inducing carcinogenic, mutagenic, and teratogenic effects, also increasing the risk for health issues such as skin allergies, dizziness, vomiting, damage to the liver, kidney, and central nervous system [25,26], thus considered to be the main reason for sick building syndrome [27].

**email: ioana.fechete@utt.fr*

Due to the concerning effects of the volatile organic compounds, the catalytic combustion has attracted a lot of interest in the recent years as one of the most efficient means to reduce VOCs emission in order to control the atmospheric pollution. Compared to the flame combustion, the catalytic process runs at lower temperatures wherein such conditions limit the nitrogen oxide (NO_x) emissions and can enhance the selectivity to CO_2 [28,29]. Most of the investigations on the catalytic combustion process were realized using methane as molecule test, which is the most challenging hydrocarbon to decompose because of its stability due to the high strength of C-H bonds [30]. Considering that methane represents the main constituent of natural gas, its continuous use of energy source rises concerns due to the significant environmental impact of its combustion with regard to the contribution to the global warming, thus the employed catalysts required high activity for its effective combustion [31]. Methane is the most difficult hydrocarbon to oxidize and the 20 times larger global warming potential than carbon dioxide [32-34].

Supported noble metals (e.g. Pd, Pt, Rh, Au) are the most used and efficient known oxidation catalysts in virtue of their high specific activity [35]. However, besides their high activity, these noble metals have some disadvantages: limited availability with low abundance, consequently being expensive, and on the other hand, these metals are susceptible to sintering and to the formation of volatile metal oxide at high temperatures. As the list of drawbacks for the noble metals extends, the transition-metal oxides may represent a valid option in the development of combustion catalysts, providing a range of technical and commercial advantages that make them an attractive alternative as non-noble metal oxide catalysts.

The combustion over metal oxides occurs after an activation of the oxygen molecules through an interaction with the surface of the catalyst in two steps: dissociative adsorption, which includes coordination, electron transfer and dissociation, followed by the incorporation into the lattice [36]. There are available two states of oxygen on the catalyst surface: highly active adsorbed oxygen species for complete oxidation and lattice oxygen, which takes part in selective oxidations.

Among the studied non-noble-metal oxides (3d elements), cobalt oxide (Co_3O_4) exhibits the lowest oxygen bond strength [37] and the highest rate of oxygen binding, showing a promising catalytic efficiency for the total oxidation of hydrocarbons [38,39]. Co_3O_4 is one of the spinel oxides. It has almost the weakest M–O bonds among all transition metal oxides [40,41]. The metal-oxygen bond dissociation energy for Co-O at 773 K is 400 kJ/mol [42] and for other oxides as Al-O, Ce-O, Zr-O, Si-O, Pd-O and Ni-O are 505, 793, 769, 803, 241 and 370 kJ/mol, respectively [42]. It is known, the lower the metal–oxygen bond strength, the higher the oxygen mobility [43]. Moreover, the oxygen mobility also increases with oxide basicity [43], which contributes to the positive expectations from basic Co_3O_4. Oxygen vacancies can be readily generated even at a temperature below 25°C [44,45]. In addition, the barrier for hopping oxygen vacancies on the surface of Co_3O_4 is only 0.23 eV [44]. Furthermore, besides its activity as a main catalyst, cobalt oxide was also used as support catalyst for Au-Pt (or Au-Pd) which resulted in performances exceeding those of Pd/Al_2O_3 for methane combustion [46,47].

Many attempts have been made to develop new preparation methods to improve the physico-chemical properties of catalysts for total oxidation of methane. The noble metals, as well as those non-noble metal oxides catalysts, can be prepared through various methods as multiple steps wet processes or single-step gas-phase preparation technique, e.g. Chemical Vapour Deposition – CVD.

2. Chemical Vapour Deposition (CVD) methods

Chemical vapour deposition (CVD) technique has been developed as a novel manufacturing process in several industrial sectors [52]. Several studies have stressed the superiority of prepared catalyst through CVD technique compared to those prepared using wet processes for both combustion [48] and selective reactions [49,50], due to the ability of the process to achieve high dispersion of the active material with stronger interaction with the support material.

A scientific definition for CVD is a process whereby a thin solid film is deposited onto a substrate through chemical reactions of the gaseous species. CVD it is a reactive process, involving chemical reactions which generates the material for film deposition, that distinguish CVD process from physical vapour deposition (PVD) processes, such as physical evaporation process, sputtering and sublimation processes [51, 52].

A classical definition of CVD is that it is a complex process of depositing solid materials at a high temperature as a result of a chemical reaction. This deposition forms a special type of material commonly known as ordered crystal grown from vapour [52].

CVD methods are classified into seven main types of fabrication (Figure 1) [52]. The parameters used to characterise a CVD process include wall/substrate temperature, depositing time, temperature, pressure, precursor nature, gas flow state and activation manner [53-55].

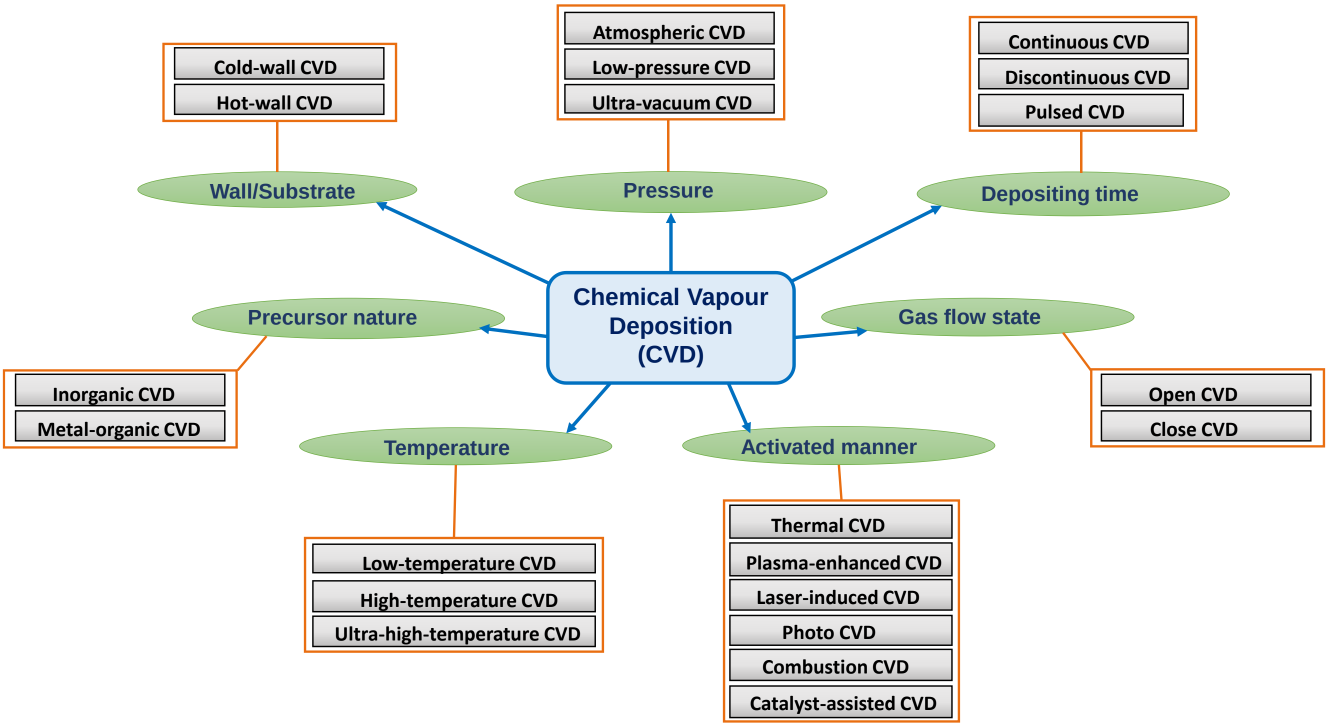

Figure 1. Classification for CVD methods [52]

In chemical vapour deposition, growth of the material takes place through the reaction or decomposition of gaseous species, forming a solid film on a heated surface as one of the reaction by-products. There are also a large number of CVD processes, depending on the operating conditions.

Depending on the operating pressure, there are encountered atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD) and ultra-high vacuum CVD (UHPCVD). There are no differences in equipment upon difference in pressure, but as the pressure goes down, it affects the mass transport inside the reactor, affecting the deposition process [52,56].

Thermodynamics studies of a CVD process are undertaken to provide a basic understanding of chemical reactions under equilibrium conditions. CVD phase diagrams are derived based on the minimisation of Gibbs free energy and are useful in predicting the equilibrium phases present in the chemical reaction system under given processing conditions determined by the deposition temperature, pressure and reactant concentration.

A CVD process is also a non-equilibrium process and typically consists of complex chemical reactions. The kinetics of a CVD system involves many steps which determine the rate of the deposition process. Among them, three important steps are:

- Homogeneous reactions taking place among the gases in a reaction chamber;
- Heterogeneous reactions occurring on the surface of a substrate;
- Mass transportation of the gaseous precursors.

The overall deposition rate of the CVD process is limited by the slowest step in the three aforementioned steps.

The feasibility of the chemical reaction can be determined by calculating the Gibbs free energy of the reaction under given conditions. A negative Gibbs free energy implies that the reaction may occur, whereas a positive Gibbs free energy indicates that the reaction would not take place. If several possible reactions are proposed and all are thermodynamically feasible, the reaction with the most negative Gibbs free energy should be ideally selected since it leads to the most stable products. The next selection is to determine the other processing parameters, such as depositing temperature, pressure, concentration and so forth.

3. CVD technique for the preparation of catalytic materials

Aforementioned before, in general, CVD is a process in which a substrate is exposed to one or more volatile precursors, which reacts and/or decompose on the substrate surface to produce the desired thin film deposit [57]. Also, CVD is an established technique for the production of catalytic materials, being able to generate diverse types of nanostructures by modifying the surface properties of massive or even nano-divided substrates. A need for improving the performance and cost-benefit of catalytic materials has motivated the search of alternatives of synthesis to enhance their textural and morphological properties with consequences on the catalytic activity [57]. Although CVD has been used for the synthesis of dense and continuous films in materials technology, also it has been successfully used in producing catalytically important structures and morphologies such as nanoparticles, nanotubes, nanofibers, nanocomposites and porous or highly orientated films of valuable support, promoter or active materials [59,60]. In the last three decades, new CVD processes were developed to allow the formation of nano-scale structures: catalytic CVD, fluidized-bed CVD, rotary CVD, two-step (precursor vapour adsorption-decomposition) CVD and large spot laser CVD [61,62].

In order to fabricate supported catalysts, the incorporation of active nanoparticles on high surface area porous supports is usually realized at industrial scale by more classic methods like wet chemical methods including ion-exchange, co-precipitation, sol-gel and wet impregnation. However, CVD has represented an attractive alternative for the preparation of supported catalysts because of its significant advantages over the traditional methods. CVD processes have an advantage over the previously employed methods, allowing the incorporation of active nanoparticles in a gaseous phase on porous supports, i.e. without the need of liquid solvents to disperse the active material and the substrate. Moreover, the drying and reduction steps are no longer required, which may induce undesirable changes in the active particles. In addition, higher dispersions and more uniform size distributions of the active phase in catalysts prepared by CVD have been reported to increase the catalytic activity of the materials. CVD has also been used to produce catalytically active films, composites, carbon nanotubes (CNTs) and particles at the micro- or nano-scale size with careful control of the deposition conditions. Furthermore, enhanced CVD techniques such as plasma or laser CVD can be used to prepare porous and favourable oriented catalytic films.

Considered an efficient method, extensively applied in catalytic material preparation, CVD has distinguished itself with the following advantages [55]:

a) CVD can be operated at high deposition rates to produce uniform films with effective reproducibility.

b) Depending on the intended application, the careful control of the deposition rate allows distinctive distribution of the grown material: low deposition rate favours the growth of epitaxial thin films for microelectronic applications, whereas, a high deposition rate is directed for the deposition of thick protective coatings with rates exceeding tens of mm per hour.

c) The deposed materials by CVD processes are highly pure and dense.

d) CVD is capable to reach good coverage, being applied successfully to uniformly coat intricate substrate components, and also in diverse film depositions with greater performance that outweighs the Physical Vapour Deposition (PVD) process.

e) The fine tuning of CVD process parameters is associated with the control of crystal structure, surface morphology and orientation in the deposed materials.

f) In CVD processes, a wide range of volatile chemical reagents such as halides, hydrides, organometallics are employed to afford the deposition of various materials that include metals, carbides, nitrides, oxides, sulphides etc.

g) The reasonable costs of the processing involved in CVD techniques is another reason for their attractive uses.

h) The use of low energies at low deposition temperatures in vapour phase reactions permits the in-situ formation of desired phases and control over the nucleation and growth on the substrate, also allows refractory materials to be deposited at lower temperatures than their melting temperatures, e.g. SiC with melting points of 2700 ^oC is deposited at 1000 ^oC, according to the below chemical reaction.

$$CH_3SiCl_3 \xrightarrow{H_2} SiC + 3\ HCl$$

However, besides the above mentioned advantages, CVD presents some drawbacks, most notably including [55]:

a). CVD processes use a lot of toxic or flammable precursor gases that can raise considerable risks regarding safety and health issues. Nevertheless, recent CVD techniques such as Electrostatic Spray Assisted Vapour Deposition (ESAVD) and Combustion Chemical Vapour Deposition (CCVD) methods have mitigated those risks by using more friendly environmental reagents.

b) Multicomponent materials with well-established stoichiometry are difficult to obtain from multi-source precursors as they present different vaporization rates, so using single source precursors increase the control over the stoichiometry.

c) Multiple CVD variants such as low pressure or ultrahigh vacuum CVD, plasma assisted CVD and photo-assisted CVD tend to increase the cost of fabrication by the usage of more sophisticated reactors and/or vacuum system, but there are also other variants of CVD such as Aerosol Assisted Chemical Vapour Deposition (AACVD) and Flame Assisted Chemical Vapour Deposition (FACVD) that do not require more complicated setup to ensure the adequate conditions. Thus, such variants may provide alternatives for applications where production cost is an issue.

Consequently, the advantages of CVD technique outweigh its limitations, rendering in general, CVD as a versatile technique for the deposition of coating, single-crystalline, amorphous, or polycrystalline thin films for a wide range of applications, comprising of:

a) microelectronics, optoelectronics, energy conversion devices - semiconductors (e.g. Si, Ge, III–V, II–VI group elements)

b) microelectronics - dielectrics (e.g. SiO_2, AlN, Si_3N_4, etc.);

c) electronics - metallic films (W, Pt, Mo, Al, Cu, etc.);

d) hard coatings, protection against wear, corrosion, oxidation, chemical reaction, thermal shock, neutron adsorption or as diffusion barriers - refractory ceramic materials (e.g. TiB_2, SiC, B_4C, BN, TiN, Al_2O_3, ZrO_2, $MoSi_2$, diamond, etc.)

e) mechanic resistant materials - ceramic fibres (e.g. SiC and C) and ceramic matrix composites (e.g. SiC/SiC, SiC/C).

Furthermore, newly developed CVD techniques such as pulsed injection CVD, ESAVD, CCVD have enabled effective control in the deposition of multicomponent films with well-established stoichiometry and controlled microstructure, extending in consequence the CVD applications for the deposition of ferroelectrics (e.g. $PbTiO_3$, $PbZrTiO_3$), superconductors (e.g. $YaBa_2Cu_3O_7$) and perovskite materials (e.g. $La(Sr)MnO_3$ for solid oxide fuel cell applications) [55].

Moreover, the conventional CVD is also perfectly adequate for catalytic materials preparation. Such a technique was able to produce quasi-spherical Ni powder (600 nm mean particle size) by thermal decomposition of nickel carbonyl gas as precursor (Figure 2) [59]. Metal organic precursor employed in CVD process represents a valid alternative to prepare nano-scale noble metal particles. However, the impurity carbon arising from the thermal decomposition of the carbonyl precursors could hinder the growth of continuous films on the substrate, thus resulting porous films that consists of nano-scale metal particles surrounded by carbon (Pt-C, Ir-C, Ru-C, Pt-YSZ and IrO_2-YSZ) [63, 64].

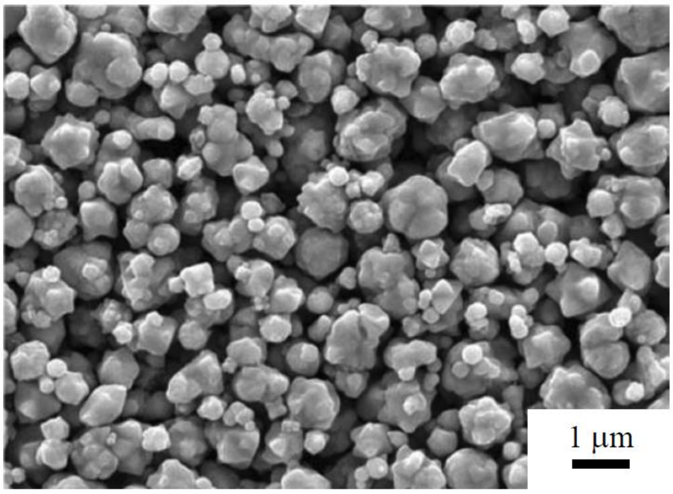

Figure 2. SEM image of quasi-spherical Ni powder prepared by thermal decomposition of nickel carbonyl gas using conventional CVD [59]

Supported catalysts can be obtained through a CVD technique called fluidized bed CVD (FBCVD) wherein an upward flow of precursor and carrier gas mixture fluidizes the solid support particles in a vertical reactor. Compared with conventional methods (wet impregnation, ion exchange and co-precipitation), the production of supported catalysts by FBCVD is more advantageous as liquid solvents are no longer used, consequently drying, calcination and reduction steps are not required. Eliminating these additional steps, otherwise necessary when the conventional methods are applied, prevents the aggregation of active particles during such processing which would lead to a decrease in catalytic activity [65]. For supported catalysts, the dispersion of the catalytic particles is crucial, thus in FBCVD, the surface area available for the deposition becomes extremely high by using porous powders as supports with high specific surface area.

The fluidization of the support particles depends mostly on their properties, such as size, distribution and density as choosing the adequate supports requires proper consideration. However, the most used oxide particles (Al_2O_3, MgO, SiO_2, TiO_2, and aluminosilicates) employed in the preparation of supported catalysts are easy to fluidize, according to their small mean size (20-150 μm) of the powder and their low density [66]. Supported catalysts were obtained by FBCVD where noble metal particles (Rh, Pd and Pt) were deposited on SiO_2, Al_2O_3 and activated carbon (AC) [67,68]. Studies have shown the superiority of CVD techniques as the activity of 1% wt.% Rh/SiO_2 catalyst prepared by FBCVD (Figure 3)was higher in the hydrogenation reaction of 1-octane than that of 1 wt.% Rh/SiO_2 catalyst prepared by impregnation [69]. Besides noble metal catalyst, FBCVD has also been used in the preparation of supported transition metal catalysts (Cu/Al_2O_3, Fe/Al_2O_3, Mo/Al_2O_3 and $Fe\text{-}Mo/Al_2O_3$) by [70,71].

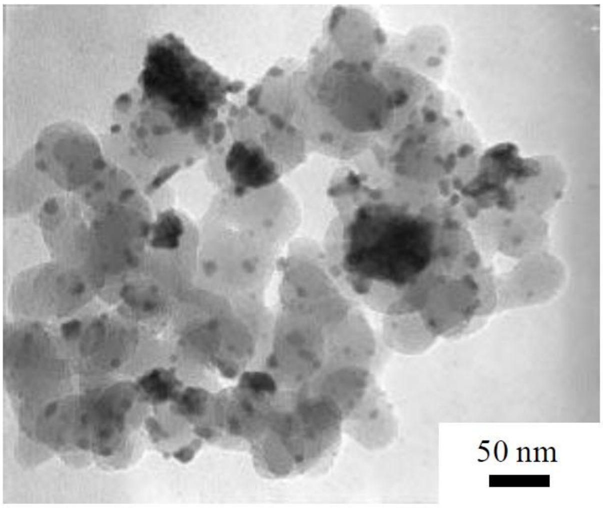

Figure 3. TEM image of 1 wt.% Rh/SiO_2
catalyst prepared by FBCVD [69]

Another CVD variation of for the preparation of supported catalysts is represented by the two-step CVD which consists in a first step of precursor vapour absorption on the support particles, followed by a thermal treatment to obtain the active particles. It is also called vapour-phase impregnation-decomposition method, which has been widely used to obtain catalysts supported on oxide particles in a micro-scale size (20-150 μm). The two-step CVD overcomes the difficulty of the FBCVD to prepare catalysts with particle size less than 20 μm, being applied successfully to prepare catalysts based on nano-scale size supports such as Al_2O_3 nanoparticles, CNTs or titania nanotubes (TNTs) [72]. Pt nanoparticles (2.1 nm mean size) were deposited on TNTs (7-10 nm diameter and several hundred nm in length) in a two-step CVD, wherein the oxide and precursor powders were mechanically mixed and heated at 180°C for vapour impregnation, followed by calcination (400°C). The Pt particles were uniformly distributed on TNTs (even at a high Pt load of 14 wt.%) and had 10 times more activity in naphthalene hydrogenation than a conventionally wet impregnated Pt/TNTs catalyst with the same metallic load (Figure 4) [72].

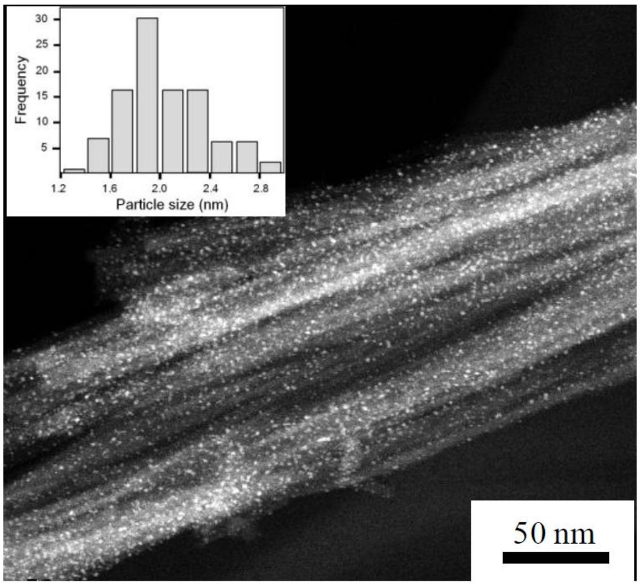

Figure 4. TEM image of the Pt/TNTs
prepared by two-step CVD [72]

More advanced CVD techniques, such as plasma-enhanced CVD and laser CVD, allow catalytic films deposition. For example, films containing Co_3O_4 nanoclusters (4-6 nm) prepared by plasma-enhanced CVD have proved to be promising in the n-hexane oxidation [73]. Laser CVD allowed the growth of CeO_2 films which presented catalytically desirable features such as a highly orientation and a columnar structure with considerable amount of nano-scale voids [74]. The more unstable (100) plane of the fluorite structure of CeO_2 is potentially more reactive than the (110) and (111) planes. The cross-sectional TEM images at the top of the columnar grains of the highly oriented ceria films represented in Figure 5 indicate the alignment of the column in the <100> and <111> directions of the cubic CeO_2 structure, as well as the nano-scale void structure which enables a favourable high surface area, also highly dispersed and accessible catalytic sites.

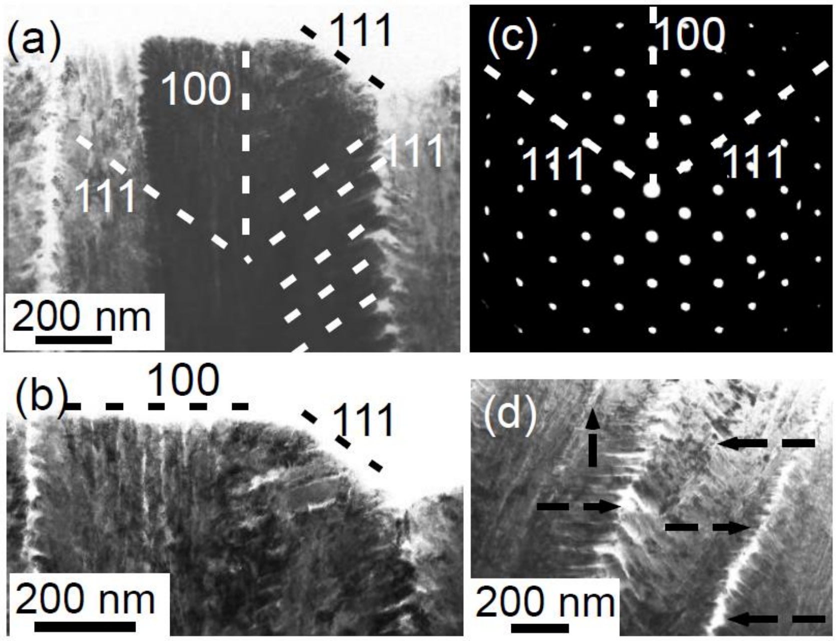

Figure 5. Cross-sectional TEM images at the top-ending f the columnar grains of the highly (100)-oriented CeO_2 films prepared by laser CVD [74]

Performing CVD technique at low pressure (20 mbar) and in the kinetically controlled regime (T = 230 ^oC), cobalt oxide as active phase was deposited on monolithic cordierite supports using cobalt (II) acetylacetonate as the precursor. Its slow decomposition on the support surface allowed the generation of a highly homogeneous layer on the complex surface geometry of the support with an excellent reproducibility [75].

The grown cobalt oxide was identified as cubic spinel Co_3O_4 using X-ray diffraction, and the surface studies revealed a high content of oxygen using Auger electron spectroscopy (AES). In addition, the morphology and the composition of the films were investigated by atomic force microscopy (AFM) and energy dispersive X-ray analysis (EDX), whereas the reducibility of the grown film which was evaluated by H_2-TPR (temperature-programmed reduction) to show the oxidizing character of the oxide [75].

Adjusting the deposition time allowed the preparation of a series consisting of catalysts with different loading of cobalt oxide to investigate the effect upon the methane lightoff [76]. Catalyst loadings above 0.46 wt.% reached complete combustion of methane at ~550 ^oC, also with high reaction rates, having superior performance than that of the other studied perovskites [28,77]. Moreover, further studies involving the partial pressure of oxygen and methane respectively, showed that the activity of cobalt oxide is dependent on the reactant gas partial pressure with increased performance at higher partial pressure of the reactants, confirming that the requirements for high catalyst efficiency are stricter when lean mixtures have to be combusted as intended in pollutant abatement.

These studies have also confirmed the participation of the bulk cobalt oxide in the catalytic reaction, described by the Mars-Van Krevelen mechanism. Such activity is attributed to the concept of oxygen bank function [78], which includes a rapid migration of oxide ions through the bulk diffusion. Furthermore, the catalytic reaction over cobalt oxide is likely to occur similarly to that of Pd, which is the most efficient catalyst for methane combustion, being also described by the Mars-Van Krevelen redox model involving PdO formed at the surface and at the interface with the support [79]. Although having its thermal stability as the major limiting factor, nevertheless, the cobalt oxide represents an attractive choice as combustion catalyst in further investigation of replacing the currently used noble-metal catalysts.

3.1. Non-thermal plasma (NTP) as alternative to catalyst activation in VOCs abatement

Besides the various technologies employed in the decomposition of VOCs including the catalytic combustion, plasma catalysis (PC) has gathered considerable attention, particularly for the removal of low concentration of VOCs (<1000 ppm), as the combination of non-thermal plasma (NTP) and catalysis[80]. Non-thermal plasma is obtained when a sufficiently high electric field is applied between two electrodes in order to produce electrons, excited gas molecules and free radicals which are suitable to transform pollutant molecules in friendlier environmental products [81]. However, plasma applied alone has the following disadvantages such as: formation of unwanted toxic by-products, low energy efficiency and incomplete oxidation of VOCs, whereas the combination of NTP and catalysts could brings together the ability of plasma to activate catalysts at lower temperature and the high selectivity of the catalysts to increase the VOCs abatement potential [82].

The abatement of very low concentrations of VOCs (<100 ppm) in flue gas proves to be challenging for plasma catalysis as most of the discharge energy will be utilized for the excitement of oxygen and nitrogen, which are in higher amounts exceeding the pollutants [83], stressing out the necessity to explore different techniques which are more suitable for the removal of very low concentration of VOCs from a large volume of flue gas. To improve the energy efficiency and to treat larger volumes of gas with low VOC concentration, a concept which combines adsorption and plasma catalysis (APC) has been investigated wherein the NTP discharge is either continuous [84] or cyclic [85,86].

Between these two variations, the continuous treatment presents the main disadvantage as uninterrupted use of the plasma discharge, without regard to the high fluctuations in VOC concentration, results in higher energy consumption for decomposition per VOC molecule. On the other hand, the working principle of the cyclic APC process for VOC removal (Figure 6) allows first a storage stage (plasma off) to store low-concentration VOCs in flue gas on catalysts/ adsorbents and then the oxidation of the stored VOCs to CO_2 by plasma at a discharge stage (plasma on), with enhanced energy eficiency [87,88].

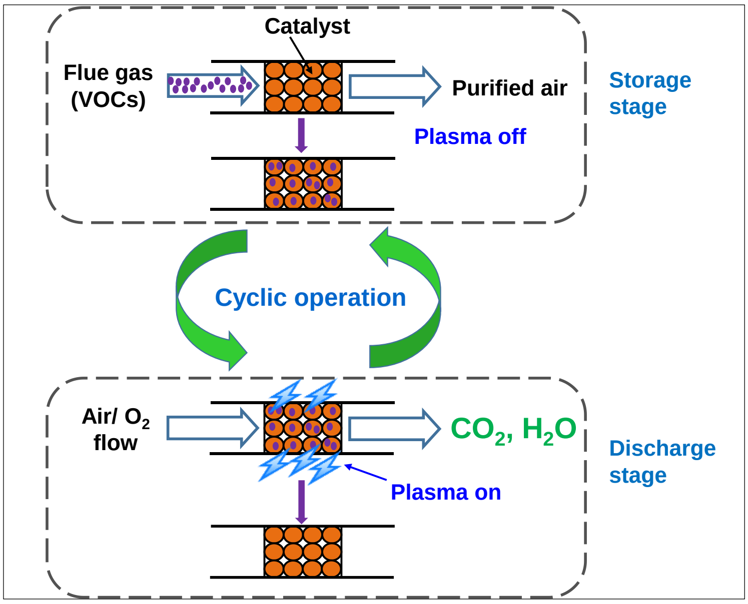

Figure 6. The working principle of the cyclic adsorption-plasma catalytic process for VOC removal [81]

The main advantages of the cyclic APC over continuous APC include:

a) usage of oxygen plasma instead of air avoids the formation of unwanted by-products (e.g. NO_x, N_2O, etc.) and also allows a more efficient regeneration of the catalyst;

b) enhanced selectivity towards CO_2;

c) improved carbon balance;

d) increased energy efficiency with higher power output;

e) accumulation of VOCs in the adsorbents from dilute flue gas through storage stage (compact system);

f) easy adjusting of the system, depending on the change in flow rate and VOC concentration;

g) fast operation

The properties of the adsorbents, namely the adsorbing and catalytic function, can be present in separated form or combined in a dual-functional material. The most used materials with such properties vary from physical adsorbents (e.g. alumina, zeolite and activated carbon), to either chemical adsorbents (e.g. alkaline earth metals and transition metal loaded physical adsorbents). In the case of physisorption, the adsorbed molecules are attached on the surfaces by the Van Der Waals force of attraction and can be desorbed by applying heat; whereas the chemisorption involves chemical reactions that facilitate the fixation of molecules on the adsorbent surface through transfer of electrons or ions. Hence, as the molecules can interact at the surface level, the adsorbents in the plasma discharge region prolong the residence time of VOCs, active species and intermediate by-products, resulting in increased collisional probabilities between them and thus in enhanced CO_2 selectivity [89].

Another noteworthy advantage of combining adsorption and NTP is the increased lifetime of the used adsorbents. The VOCs from diluted flue gas can be accumulated on adsorbing materials and then desorbed and decomposed with the help of plasma to less toxic or more useful products. In many instances, the used adsorbents are to be discarded or incinerated, so from a more economic and practical point of view, it is recommended to decompose the adsorbed VOCs and regenerate the adsorbent [90]. There have been reported in the literature multiple methods that can be used in the regeneration of the adsorbents such as heating [91], microwave heating [92], pressure and temperature swing adsorption [93] and non-thermal plasma [94]. A major advantage for the use of NTP discharge in the desorption and decomposition of VOCs accumulated in the adsorbents, instead of a conventional thermal process, consists of can be used significant reduction in both the size of the treatment equipment and the energy consumption [95]. At the same time, the highly oxidizing environment of plasma promotes the degradation of the adsorbed VOCs with simultaneous regeneration of the adsorbent.

The APC requires an adsorbing/catalytic system which effectively adsorb VOCs and efficiently oxidize the adsorbed VOCs. The selection of adsorbents takes into consideration various material properties that lead to high energy efficiency to decompose diluted VOCs from air, such as pore size, specific surface area, dielectric constant, hydrophobicity etc. As they include many of the desired features, the zeolites represent one of the best adsorbents and catalysts for VOC degradation, being already known as traditional adsorbents due to their unique channel system containing multiple micropores and cavities. The pore diameter of zeolites in the range of 5-20 Å is quite suitable for the adsorption of various VOC molecules [96]. In addition, zeolites can interact with plasma, having a semiconductor character and electrical conductivity [97].

Zeolites are a class of aluminosilicate minerals that are well-known as solid acids used widely in many applications due to their high surface area, ordered pore size and structure, thermal stability, shape selectivity. Other special features of the zeolites include hydrothermal stability, catalytic activity due to their cations, along with the ability to tailor their properties such as wettability and auxiliary mesopore generation in the crystals.

Due to their surface area and pore channels, zeolites are able to increase the residence time of VOCs in the plasma discharge *via* adsorption. They allow higher conversion towards gaseous products CO_x (CO, CO_2) in a setup of cyclic APC which is more suitable for air pollution treatment [98]. More studies on different metal loaded (Cu, Mg, Ce, Co) zeolites for the decomposition of toluene revealed that the metal loading on zeolite enhances the CO and CO_2 yield [99]. This is due to the dissociation of O_3 produced by the NTP discharge on the metal active sites (*) which play a significant role on the complete oxidation of toluene following the equations [100]:

$$O_3 + * \rightarrow O_2 + *O$$

$$O_3 + *O \rightarrow O_2 + *O_2$$

$$*O_2 \rightarrow O_2 + *$$

Among the different metal loaded zeolites studied, the zeolites with Cu and Co showed enhanced CO_2 selectivity, because the active sites of Co and Cu catalysts are represented by Co_3O_4 and CuO_2, respectively, which have large oxygen adsorption capacity and easily convert oxygen to O^- and O^{2-} ions. Another study using zeolites such as Na-ZSM-5 and Cu-ZSM-5 for trichloroethylene (TCE) removal have reported a removal efficiency of 80% without plasma, thanks to the adsorption capacity provided by their large specific surface area[101]. With a good adsorption of TCE at room temperature and plasma discharge usage, Cu-ZSM-5 reached a removal efficiency higher than 95%.

The use of non-thermal plasma brings an innovative method for VOC removal. In combination with zeolites as adsorbent materials and supports for metal loading, the cyclic-adsorption plasma catalysis for VOC abatement represents a suitable option for removal of low concentration of VOCs from large volume of gas. The nature and the amount of metal ions used for loading on zeolites has many implications as it can influence the adsorption of VOCs, the characteristics of the plasma discharge, the oxidation of adsorbed VOCs and the regeneration of adsorbent materials., Therefore, CVD methods could provide new ways to develop different morphologies regarding the metal ion loaded layer. The use of novel emerging approaches in catalyst preparations, combined with more efficient activation systems as NTP for the catalytic process of VOCs conversion, is of great interest to extend their applications to the real world.

4. Conclusions

Chemical vapour deposition has distinguished itself as a superior technique to produce thin films on different substrates with the possibility of generating numerous types of nanostructures, such as nanoparticles, nanotubes, nanofibers or nanocomposites, for the development of active catalyst materials in various reactions, mostly VOCs combustion processes. Depending on the operating conditions, CVD techniques are divided in multiple categories, wherein the most used are the conventional CVD, fluidized bed CVD, two-step CVD, plasma-enhanced CVD and laser CVD. Taking into consideration the advantages and the drawbacks of CVD techniques, the catalysts prepared through these techniques can achieve improved textural and morphological properties with great effects on the performance in catalytic activity, showing superiority over the conventional multiple steps wet processes, often employed in catalyst preparation. CVD processes have evolved during the last years in matter of deposition control, being able to produce particles at the micro- or nano-scale levels, also porous and favourable oriented catalytic films, proving to be quite attractive methods for extensive material development.

References

1. SHELDON, R.A., Atom utilisation, *E* factors and the catalytic solution, *C. R. Acad. Sci. Paris - Séries IIc: Chemistry*, **3**, 2000, 541–551. https://doi.org/10.1016/S1387-1609(00)01174-9.
2. SINGH, U.K., VANNICE, M.A., Kinetics of liquid-phase hydrogenation reactions over supported metal catalysts - a review, *Appl. Catal. A: Gen.*, **213**, 2001, 1–24. https://doi.org/10.1016/S0926-860X(00)00885-1.
3. FECHETE, I., JOUIKOV, V., Double decarbonylation of phthalimide revisited: A facile cathodic synthesis of isoindoline, *Electrochim. Acta*, **53**, 2008, 7107-7110. https://doi.org/10.1016/j.electacta.2008.05.010.
4. DUMITRIU, E., FECHETE, I., CAULLET, P., KESSLER, H., HULEA, V., CHELARU, C., HULEA, T., BOURDON, X., Conversion of aromatic hydrocarbons over MCM-22 and MCM-36 catalysts, *2nd FEZA Studies in Surface Science and Catalysis*, 142, *Conference « Impact of Zeolites and Porous Materials on the New Technologies at the Beginning of the New Millenium »* 2002, 951-958.
5. LIU, H., HADJLTAIEF, H.B., BENZINA, M., GÁLVEZ, M.E., Da COSTA, P., Natural clay based nickel catalysts for dry reforming of methane: On the effect of support promotion (La, Al, Mn), *Int. J. Hydrogen Energy*, **44** (1), 2019, 246-255. https://doi.org/10.1016/j.ijhydene.2018.03.004.
6. DJEDDI, A., FECHETE, I., GARIN, F., Conversion of methylcyclopentane (MCP) on Pt/MoO_2, Ir/MoO_2 and Pt-Ir/MoO_2 catalysts, *Catal. Commun.*, **17**, 2012, 173-178.
7. (a)ROGÉ, V., BAHLAWANE, N., LAMBLIN, G., FECHETE, I., GARIN, F., DINIA, A., LENOBLE, D., Improvement of the photocatalytic degradation property of ZnO ALD thin films: Impact of the film composition and structure, *J. Mater. Chem. A*, **3**, 2015, 11453-11461.(b)IVAN, Ş.-B., POPESCU, I., FECHETE, I., GARIN, F., PÂRVULESCU, V.I., MARCU, I.-C., The effect of phosphorus on the catalytic performance of nickel oxide in ethane oxidative dehydrogenation, *Catal. Sci. Technol.*, **6**, 2016, 6953–6964.
8. MELONI, D., MONACI, R., ROMBI, E., GUIMON, C., MARTINEZ, H., FECHETE, I., DUMITRIU, E., Synthesis and characterization of MCM-22 zeolite for the N_2O oxidation of benzene to phenol, 2nd *FEZA, Studies in Surface Science and Catalysis*, 142, *Conference « Impact of Zeolites and Porous Materials on the New Technologies at the Beginning of the New Millenium»* 2002, 167-174.
9. KLEIN, J., WU, D., TSCHAMBER, V., FECHETE, I., GARIN, F., Carbon - NSR catalyst interaction: impact on catalyst structure and NO_x storage efficiency, *Appl. Catal. B: Environ.*, **132-133**, 2013, 527-534.
10. ISCHENKO, O., KRISHNAMOORTHYA, S., VALLE, N., GUILLOT, J., TUREK, P., FECHETE, I., LENOBLE, D., Investigating vapor phase growth of block copolymer templated titania nanoarrays, *J. Phys. Chem. C*, **120**, 2016, 7067-7076.

11. BENSACIA, N., MOULAY, S., GARIN, F., FECHETE, I., BOOS, A., Effect of grafted hydroquinone on the acid-base properties of poly(acrylic acid) in the presence of copper (II), *J. Chem.*, 2015, 913987, https://doi.org/10.1155/2015/913987.

12. WU, D., TSCHAMBER, V., LIMOUSY, L., WESTERMANN, A., AZAMBRE, B., FECHETE, I**.**, GARIN, F., Simultaneous effect of carbon and water on NO_x adsorption on a stabilized Pt-Ba/Al_2O_3, *C. R. Chim.*, **17**, 2014, 687-700.

13. FECHETE, I., GAUTRON, E., DUMITRIU, E., LUTIC, D., CAULLET, P., KESSLER, H., Studies on the acidity and the stability of Fe^{3+} ions in the framework (Si,Fe)-MCM-22 zeolite. Selective *para*-xylene production by toluene disproportionation, *Rev. Roum. Chim.,* **53**, 2008, 49-54.

14. OKAL, J., ZAWADZKI, M., BARANOWSKA, K., Methane combustion over bimetallic Ru-Re/-Al2O3 catalysts: Effect of Re and pretreatments, *Appl. Catal. B: Environ.*, **194**, 2016, 22–31.

15. WU, D., TSCHAMBER, V., LIMOUSY, L., MICHELIN, L., WESTERMANN, A., AZAMBRE, B., FECHETE, I., GARIN, F., Combined fixed-bed reactor and in situ DRIFTS tests of NO adsorption on a NOx storage-reduction system catalyst, *Chem. Eng. Technol.*, **37**, 2014, 204-212.

16. ERCOLINO, G., GRZYBEK, G., STELMACHOWSKI, P., SPECCHIA, S., KOTARBA, A., SPECCHIA, V., Pd/Co3O4-based catalysts prepared by solution combustion synthesis for residual methane oxidation in lean conditions. *Catal. Today*, **257**, 2015, 66–71.

17. KLEIN, J., FECHETE, I., TSCHAMBER, V., GARIN, F., Effect of carbon black combustion on NO_x trap catalyst performances, *Catal. Today,* **189**, 2012, 60-64.

18. PAREDES, J.R., DÍAZ, E., DÍEZ, F.V., ORDÓÑE, S., Combustion of Methane in Lean Mixtures over Bulk Transition-Metal Oxides: Evaluation of the Activity and Self-Deactivation, *Energy Fuels*, **23**, 2009, 86–93.

19. MENDES, A.N., LAUGA, V., CAPELA, S., RIBEIRO, M.F., DaCOSTA, P., HENRIQUES, C., Application of PdCe-HMOR Catalyst as NO_x CH_4-SCR System for Heavy-Duty Vehicles Moved by Natural Gas, *Top. Catal.*, **59(**10-12), 2016, 982-986. https://doi.org/10.1007/s11244-016-0578-y.

20. COHL, M., LAZAR, L., CRETESCU, I., BALASANIAN,I., Trihalomethanes Issues Drinking Water After Chlorination Treatment, *Rev.Chim,* **66** (9), 2015, 1282-1287.

21. COZMA, D.G., COSTULEANU, C.L., SANDU, I., LUTIC, D., Statistical Analysis of Raw and Potable Water Quality from a Preparation Plant, as a Basis to Purpose the Re-schedule of the Physico-Chemical Current Routine Analysis Periodicit, *Rev.Chim.,* **69**(1), 2018, 2014-221.

22. STOICA,C., DINU, L., LUCACIU, I., NITA-LAZAR, M., ONCU, V., The Toxic Effect of Conventional Treated Mine Water on Aquatic Organism, Rev.Chim., 71(1), 2020, 67-72.

23.EUR-Lex—31999L0013—EN—EUR-Lex. Available online: https://eur-lex.europa.eu/legal-content/EN/ TXT/?uri=celex%3A31999L0013 (accessed on 3 September 2018).

24. FECHETE, I., CAULLET, P., DUMITRIU, E., HULEA, V., KESSLER, H., Study of the conversion of aromatic hydrocarbons on EMT-type zeolite. Influence of the partial substitution of Al by Ga, *Appl. Catal. A: Gen.,* **280**, 2005, 245-254.

25. GUO, H., LEE, S.C., CHAN, L.Y., LI, W.M., Risk assessment of exposure to volatile organic compounds in different indoor environments, *Environ. Res.,* **94**, 2004, 57–66. https://doi.org/10.1016/S0013-9351(03)00035-5.

26. PITTEN, F.A., BREMER, J., KRAMER, A., Air pollution by volatile organic compounds (VOC) and health complaints, *Dtsch. Med. Wochenschr.*, **125**, 2000, 545–550. DOI: 10.1055/s-2007-1024338.

27. WOLKOFF, P., NIELSEN, G.D., Organic compounds in indoor air-their relevance for perceived indoor air quality?, *Atmos. Environ.*, **35**, 2001, 4407–4417. https://doi.org/10.1016/S1352-2310(01)00244-8.

28. CHOUDHARY, T.V., BANERJEE, S., CHOUDHARY, V.R., Catalysts for combustion of methane and lower alkanes, *Appl. Catal. A: Gen.*, **234**, 2002, 1–23. https://doi.org/10.1016/S0926-860X(02)00231-4.

29. NDIFOR, E.N., GARCIA, T., SOLSONA, B., TAYLOR, S.H., Influence of preparation conditions of nano-crystalline ceria catalysts on the total oxidation of naphthalene, a model polycyclic aromatic hydrocarbon, *Appl. Catal. B: Environ.*, **76,** 2007, 248–256.
30. ARYAFAR, M., ZAERA, F., Kinetic study of the catalytic oxidation of alkanes over nickel, palladium, and platinum foils, *Catal. Lett.*, **48**, 1997, 173–183.
31. KEPPLER, F., HAMILTON, J.T.G., BRAß, M., RÖCKMANN, T., Methane emissions from terrestrial plants under aerobic conditions, *Nature,* **439**, 2006, 149–187.
32. ALLEN, G., Biogeochemistry: rebalancing the global methane budget, *Nature*, **538**, 2016, 46–48.
33. LELIEVELD, J., Climate change: a nasty surprise in the greenhouse, *Nature*, **443**, 2006, 405–406.
34. MONTZKA, S.A., DLUGOKENCKY, E.J., BUTLER, J.H., Non-CO_2 greenhouse gases and climate change, *Nature*, **476**, 2011, 43–50.
35. YAO, Y.-F.Y., Oxidation of Alkanes over Noble Metal Catalysts, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 1980, 293–298. https://doi.org/10.1021/i360075a003.
36. SOKOLOVSKII, V.D., Principles of Oxidative Catalysis on Solid Oxides, *Catal. Rev.*, 32, 1990, 1–49.
37. MORO-OKA, Y., MORIKAWA, Y., OZAKI, A., Regularity in the catalytic properties of metal oxides in hydrocarbon oxidation, *J. Catal.*, **7**, 1967, 23–32.
38. LIOTTA, L.F., OUSMANE, M., CARLO, G.D., PANTALEO, G., DEGANELLO, G., MARCÌ, G., RETAILLEAU, L., GIROIR-FENDLER, A., Total oxidation of propene at low temperature over Co_3O_4–CeO_2 mixed oxides: Role of surface oxygen vacancies and bulk oxygen mobility in the catalytic activity**,** *Appl. Catal. A: Gen.*, **347**, 2008, 81–88.
39. SOLSONA, B., VÁZQUEZ, I., GARCIA, T., DAVIES, T.E., TAYLOR, S.H., Complete oxidation of short chain alkanes using a nanocrystalline cobalt oxide catalyst, *Catal. Lett.*, **116**, 2007, 116–121.
40. ZHANG, S.R. et al., WGS Catalysis and In Situ Studies of CoO_{1-x}, $PtCo_n/Co_3O_4$, and $Pt_mCo_{m'}/CoO_{1-x}$ Nanorod Catalysts, *J. Am. Chem. Soc.* **135**, 2013, 8283–8293. https://doi.org/10.1021/ja401967y.
41. HENRICH, V.E., COX, P.A., *The Surface Science of Metal Oxides*, Cambridge Univ. Press, Cambridge, 1994.
42. LUO, Y.-R., *Bond dissociation energies*, in: W.M. Haynes (Ed.), CRC Handb. Chem. Phys. 93rd ed., CRC Press Taylor & Francis Group, Boca Raton, London, New York, 2012, 9–65.
43. MARTIN, D., DUPREZ, D., Mobility of surface species on oxides. 1. Isotopic exchange of 18O2 with 16O of SiO2, Al2O3, ZrO2, MgO, CeO2, and CeO2-Al2O3. Activation by noble metals. Correlation with oxide basicity, *J. Phys. Chem.* **100**, 2002, 9429–9438. https://doi.org/10.1021/jp9531568.
44. JIANG, D.E., DAI, S., The role of low-coordinate oxygen on Co3O4(110) in catalytic CO oxidation, *Phys. Chem. Chem. Phys.* **13**, 2011, 978–984.
45. XIE, X.W., LI, Y., LIU, Z.Q., HARUTA, M., SHEN, W.J., Low-temperature oxidation of CO catalysed by Co3O4 nanorods, *Nature*, **458**, 2009, 746–749.
46. MIAO, S.J., DENG, Y.Q., Au–Pt/Co_3O_4 catalyst for methane combustion, *Appl. Catal. B: Environ.,* **31**, 2001, L1–L4.
47. WU, Z. et al., Three-dimensionally ordered mesoporous Co_3O_4-supported Au–Pd alloy nanoparticles: High-performance catalysts for methane combustion**,** *J. Catal.* **332**, 2015, 13–24.
48. COMINOS, V., GAVRIILIDIS, A., An Experimental Study of Non-Uniform Pd Catalytic Monoliths, *Chem. Eng. Res. Des.*, **79**, 2001, 795–798.
49. KERÄNEN, J., CARNITI, P., GERVASINI, A., LISKOLA, E.I., AUROUX, A., NIINISTÖ, L., Preparation by atomic layer deposition and characterization of active sites in nanodispersed vanadia/titania/silica catalysts, *Catal. Today*, **91–92**, 2004, 67–71.
50. GERVASINI, A., CARNITI, P., KERÄNEN, J., NIINISTÖ, L., AUROUX, A., Surface characteristics and activity in selective oxidation of o-xylene of supported V_2O_5 catalysts prepared by standard impregnation and atomic layer deposition, *Catal. Today*, **96**(4), 2004, 187-194.

51. HITCHMAN, M.L., JENSEN, K.F., *Chemical vapour deposition: principles and applications*, Academic Press, 1993.
52. XU, Y., YAN, X.-T., *Chemical Vapour Deposition-An integrated Engineering Design for Advanced Materials*, Springer-Verlag London, 2010.
53. GLOCKER, D.A., SHAH, S.I., *Handbook of thin process technology*, Inst. of Physics Pub. Inc., 1995.
54. PIERSON, H.O., *Handbook of chemical vapour deposition* (CVD), 2nd ed., William Andrew Inc., 1999.
55. CHOY, K.L., Chemical vapour deposition of coatings, *Prog. Mater. Sci.*, **48**, 2003, 57–170. https://doi.org/10.1016/S0079-6425(01)00009-3
56. YANGUAS-GIL, A., *Growth and Transport in Nanostructured Materials*, Springer International Publishing, 2017, Chapter 2. Physical and Chemical Vapor Deposition Techniques.
57. ROGÉ, V., GUIGNARD, C., LAMBLIN, G., LAPORTE, F., FECHETE, I., GARIN, F., DINIA, A., LENOBLE, D., Photocatalytic degradation behavior of multiple xenobiotics using MOCVD synthesized ZnO nanowires, *Catal. Today*, **306**, 2018, 215-222. https://doi.org/10.1016/j.cattod.2017.05.088.
58. VARGAS-GARCIA, J.R., GOTO, T., Catalytic materials prepared by chemical vapor deposition, *IOP Conf. Ser.: Mater. Sci. Eng.* **20**, 2011, 012001. doi:10.1088/1757-899X/20/1/012001.
59. PASERIN, V., BAKSA, S., ZAITSEV, A., SHU, J., SHOJAI, F., NOWOSIADLY, W., Potential for Mass Production of Nickel-Based Nanomaterials by Carbonyl Process, *J. Nanosci. Nanotechnol.*, **8**, 2008, 4049-4055.
60. TABOADA, C.D., BATISTA, J., PINTAR, A., LEVEC, J., Preparation, characterization and catalytic properties of carbon nanofiber-supported Pt, Pd, Ru monometallic particles in aqueous-phase reactions, *Appl. Catal. B: Environ.*, **89**, 2009, 375-382.
61. DOSSI, C., PSARO, R., UGO, R., ZHANG, C.Z., SACHTLER, W.M.H., Non-acidic Pd/Y Zeolite Catalysts from Organopalladium Precursors: Preparation and Catalytic Activity in MCP Reforming, *J. Catal.*, **149**, 1994, 92-99.
62. GOTO, T., Thermal barrier coatings deposited by laser CVD, *Surf. Coat. Technol.*, **198**, 2005, 367-371.
63. GOTO, T., VARGAS-GARCIA, J.R., HIRAI, T., Preparation of iridium clusters by MOCVD and their electrochemical properties, *Mater. Sci. Eng. A*, **217-218**, 1996, 223-226.
64. TORRES-HUERTA, A.M., VARGAS-GARCIA, J.R., Preparation and characterization of IrO_2–YSZ nanocomposite electrodes by MOCVD, *Solid State Ionics*, **178**, 2007, 1608.
65. VAHLAS, C., CAUSSAT, B., SERP, P., ANGELOPOULOS, G.N., Principles and applications of CVD powder technology, *Mater. Sci. Eng. R*, **53**, 2006, 1-72.
66. GELDART, D., Types of gas fluidization, *Powder Technol.*, **7**(5), 1973, 285-292.
67. VAHLAS, C., JUAREZ, F., FEURER, R., SERP, P., CAUSSAT, B., Fluidization, Spouting, and Metal–Organic CVD of Platinum Group Metals on Powders, *Chem. Vap. Depos.*, **8**(4), 2002, 127-144.
68. MU, X., BARTMANN, U., GURAYA, M., BUSSER, G.W., WECKENMANN, U., FISCHER, R., MUHLER, M., The preparation of Pd/SiO_2 catalysts by chemical vapor deposition in a fluidized-bed reactor, *Appl. Catal. A: Gen.*, **248**, 2003, 85-95.
69. HIERSO, J-C., SERP, P., FEURER, R., KALCK, P., MOCVD of rhodium, palladium and platinum complexes on fluidized divided substrates: Novel process for one-step preparation of noble-metal catalysts, *Appl. Organometal. Chem.*, **12**, 1998, 161-172.
70. XU, C., ZHU, J., One-step preparation of highly dispersed metal-supported catalysts by fluidized-bed MOCVD for carbon nanotube synthesis, *Nanotechnology*, **15**, 2004, 1671-1681.
71. D`Alnoncourt, R.N., Becker, M., Sekulic, J., Fischer, R.A., Muhler, M., The preparation of Cu/Al_2O_3 catalysts via CVD in a fluidized-bed reactor, *Surf. Coat. Technol.*, **201**, 2007, 9035-9040.

72. ENCARNACION-GOMEZ, C., VARGAS-GARCIA, J.R., TOLEDO-ANTONIO, J.A., CORTES-JACOME, M.A., ANGELES-CHAVEZ, C., Pt nanoparticles on titania nanotubes prepared by vapor-phase impregnation–decomposition method, *J. Alloys Compd.*, **495**, 2009, 458-461.
73. TYCZKOWSKI, J., KAPICA, R., LOJEWSKA, J., Thin cobalt oxide films for catalysis deposited by plasma-enhanced metal–organic chemical vapor deposition, *Thin Solid Films*, **515**(16), 2007, 6590-6595.
74. VARGAS-GARCIA, J.R., BELTRAN-ROMERO, L., TU, R., GOTO, T., Highly (100)-oriented CeO_2 films prepared on amorphous substrates by laser chemical vapor deposition, *Thin Solid Films*, **519**, 2010, 1-4.
75. TIAN, Z. et al., Catalytic oxidation of hydrocarbons over Co_3O_4 catalyst prepared by CVD, *Catal. Commun.*, **11**, 2009, 118–122.
76. BAHLAWANE, N., Kinetics of methane combustion over CVD-made cobalt oxide catalysts, *Appl. Catal. B: Environ.*, **67**, 2006, 168–176.
77. KIRCHNEROVA, J., ALIFANTI, M., DELMON, B., Evidence of phase cooperation in the $LaCoO_3$–CeO_2–Co_3O_4 catalytic system in relation to activity in methane combustion, *Appl. Catal. A: Gen.*, **231**, 2002, 65–80. https://doi.org/10.1016/S0926-860X(01)00903-6.
78. MORO-OKA, Y., UEDA, W., LEE, K.H., The role of bulk oxide ion in the catalytic oxidation reaction over metal oxide catalyst, *J. Mol. Catal. A: Chem.*, **199**, 2003, 139–148.
79. HUBER, B., KOSKINEN, P., HÄKKINEN, H., MOSELER, M., Oxidation of magnesia-supported Pd-clusters leads to the ultimate limit of epitaxy with a catalytic function, *Nat. Mater.*, **5**, 2006, 44–47.
80. TANG, X., FENG, F., YE, L., ZHANG, X., HUANG, Y., LIU, Z., YAN, K., Removal of dilute VOCs in air by post-plasma catalysis over Ag-based composite oxide catalysts, *Catal. Today*, **211**, 2013, 39–43.
81. K. P. VEERAPANDIAN, S., DE GEYTER, N., GIRAUDON, J.-M., LAMONIER, J.-F., MORENT, R., The Use of Zeolites for VOCs Abatement by Combining Non-Thermal Plasma, Adsorption, and/or Catalysis: A Review, *Catalysts*, **9**, 2019, 98. https://doi.org/10.3390/catal9010098.
82. KIM, H.-H., OGATA, A., Nonthermal plasma activates catalyst: From current understanding and future prospects, *Eur. Phys. J. Appl. Phys.*, **55**, 2011, 13806.
DOI: https://doi.org/10.1051/epjap/2011100444.
83. YAMAGATA, Y., NIHO, K., INOUE, K., OKANO, H., MURAOKA, K., Decomposition of Volatile Organic Compounds at Low Concentrations Using Combination of Densification by Zeolite Adsorption and Dielectric Barrier Discharge, *Jpn. J. Appl. Phys.*, **45**, 2006, 8251–8254.
84. INOUE, K., OKANO, H., YAMAGATA, Y., MURAOKA, K., TERAOKA, Y., Performance tests of newly developed adsorption/plasma combined system for decomposition of volatile organic compounds under continuous flow condition, *J. Environ. Sci.*, **23**, 2011, 139–144.
85. WANG, W., WANG, H., ZHU, T., FAN, X., Removal of gas phase low-concentration toluene over Mn, Ag and Ce modified HZSM-5 catalysts by periodical operation of adsorption and non-thermal plasma regeneration, *J. Hazard. Mater.*, **292**, 2015, 70–78.
86. LIU, Y., LI, X., LIU, J., WU, J., ZHU, A., Cycled storage-discharge (CSD) plasma catalytic removal of benzene over AgMn/HZSM-5 using air as discharge gas, *Catal. Sci. Technol.*, **6**, 2016, 3788–3796.
87. KIM, H.H., KIM, J.H., OGATA, A., Adsorption and oxygen plasma-driven catalysis for total oxidation of VOCs, *Int. J. Plasma Environ. Sci. Technol.*, **2**, 2008, 106–112.
88. OHSHIMA, T., KONDO, T., KITAJIMA, N., SATO, M., Adsorption and plasma decomposition of gaseous acetaldehyde on fibrous activated carbon, *IEEE Trans. Ind. Appl.*, **46**, 2010, 23–28.
89. NISHIMURA, J., KAWAMURA, T., TAKAHASHI, K., TERAMOTO, Y., TAKAKI, K., KOIDE, S., SUGA, M., ORIKASA, T., UCHINO, T., Removal of ethylene and by-products using packed bed dielectric barrier discharge with Ag nanoparticle-loaded zeolite, *Electron. Commun. Jpn.*, **100**, 2017, 320–327. https://doi.org/10.1002/ecj.11925.

90. KUROKI, T., HIRAI, K., KAWABATA, R., OKUBO, M., YAMAMOTO, T., Decomposition of adsorbed xylene on adsorbents using nonthermal plasma with gas circulation, *IEEE Trans. Ind. Appl.*, **46**, 2010, 672–679. DOI: 10.1109/TIA.2010.2040051.
91. LEE, D.-G., KIM, J.-H., LEE, C.-H., Adsorption and thermal regeneration of acetone and toluene vapors in dealuminated Y-zeolite bed, *Sep. Purif. Technol.*, **77**, 2011, 312–324. https://doi.org/10.1016/j.seppur.2010.12.022.
92. KIM, K.-J., AHN, H.-G., The effect of pore structure of zeolite on the adsorption of VOCs and their desorption properties by microwave heating, *Micropor. Mesopor. Mater.*, **152**, 2012, 78–83. https://doi.org/10.1016/j.micromeso.2011.11.051.
93. GHOSHAL, A.K., MANJARE, S.D., Selection of appropriate adsorption technique for recovery of VOCs: An analysis, *J. Loss Prev. Process Ind.*, **15**, 2002, 413–421. https://doi.org/10.1016/S0950-4230(02)00042-6.
94. FAN, Y., CAI, Y., LI, X., YIN, H., CHEN, L., LIU, S., Regeneration of the HZSM-5 zeolite deactivated in the upgrading of bio-oil via non-thermal plasma injection (NTPI) technology, *J. Anal. Appl. Pyrolysis*, **111**, 2015, 209–215. https://doi.org/10.1016/j.jaap.2014.11.008
95. SHIAU, C.H., PAN, K.L., YU, S.J., YAN, S.Y., CHANG, M.B., Desorption of isopropyl alcohol from adsorbent with non-thermal plasma, *Environ. Technol.*, **38**, 2017, 2314–2323. https://doi.org/10.1080/09593330.2016.1259354.
96. LIU, C., ZOU, J., YU, K., CHENG, D., HAN, Y., ZHAN, J., RATANATAWANATE, C., JANG, B.W.-L., Plasma application for more environmentally friendly catalyst preparation, *Pure Appl. Chem.*, **78**, 2006, 1227–1238. https://doi.org/10.1351/pac200678061227.
97. RHODES, C.J., Electric fields in zeolites: Fundamental features and environmental implications, *Chem. Pap.*, **70**, 2016, 4–21. https://doi.org/10.1515/chempap-2015-0160.
98. XU, X., WANG, P., XU, W., WU, J., CHEN, L., FU, M., YE, D., Plasma-catalysis of metal loaded SBA-15 for toluene removal: Comparison of continuously introduced and adsorption-discharge plasma system, *Chem. Eng. J.*, **283**, 2016, 276–284. https://doi.org/10.1016/j.cej.2015.07.050.
99. YI, H., YANG, X., TANG, X., ZHAO, S., WANG, J., CUI, X., FENG, T., MA, Y., Removal of toluene from industrial gas over 13X zeolite supported catalysts by adsorption-plasma catalytic process, *J. Chem. Technol. Biotechnol.*, **92**, 2017, 2276–2286. https://doi.org/10.1002/jctb.5314.
100. BAHRI, M., HAGHIGHAT, F., Plasma-Based Indoor Air Cleaning Technologies: The State of the Art-Review, *Clean-Soil Air Water*, **42**, 2014, 1667–1680. https://doi.org/10.1002/clen.201300296.
101. ODA, T., Non-thermal plasma processing for environmental protection: Decomposition of dilute VOCs in air, *J. Electrostat.*, **57**, 2003, 293–311. https://doi.org/10.1016/S0304-3886(02)00179-1.

Manuscript received: 21.06.2020