

Review

Utilization of Volatile Organic Compounds as an Alternative for Destructive Abatement

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Abstract: The treatment of volatile organic compounds (VOC) emissions is a necessity of today. The catalytic treatment has already proven to be environmentally and economically sound technology for the total oxidation of the VOCs. However, in certain cases, it may also become economical to utilize these emissions in some profitable way. Currently, the most common way to utilize the VOC emissions is their use in energy production. However, interesting possibilities are arising from the usage of VOCs in hydrogen and syngas production. Production of chemicals from VOC emissions is still mainly at the research stage. However, few commercial examples exist. This review will summarize the commercially existing VOC utilization possibilities, present the utilization applications that are in the research stage and introduce some novel ideas related to the catalytic utilization possibilities of the VOC emissions. In general, there exist a vast number of possibilities for VOC

utilization via different catalytic processes, which creates also a good research potential for the future.

Keywords: catalysis; synthesis gas; methane; chemicals production; circular economy; sustainability; fuels; oxidation; reforming

1. Introduction

Volatile organic compounds (VOCs) are emitted to our environment from various industrial and natural sources. Since one can count several hundreds of compounds that belong in the VOCs category, one can also easily imagine that the environmental and health effects caused by these compounds are diverse. They range from local annoying odor emissions to global effects such as greenhouse phenomena. Furthermore, certain VOCs are even more dangerous as carcinogens and their utilization is limited, for example carbon tetrachlorine and benzene. Due to these harmful effects, different countries have set growingly stringent emission levels for the industrial activities [1]. One example of the legislation is the Industrial Emissions Directive set by the European Commission [2] that replaced the old VOC-directive from 1999 [3].

The VOC emissions can be reduced in several different ways. The primary way should be avoiding the formation of the emissions by process changes and replacing the organic raw materials used. However, this is not always possible or practical. In those cases, the VOCs treatment can be done either by destruction or by recovery-based technologies [4]. In both categories, catalysis has taken its role. Instead of only treatment, this review will concentrate on the recovery of the VOC emissions and further valorization of them. Utilization of gaseous emissions is a rather recent idea, since typically the circular economy principle is connected to solid or liquid waste. There exists research related to the utilization of CO₂, but the utilization of organic gaseous emissions is a somewhat less studied area. In this review, we will take into account also methane, while it is not strictly speaking a VOC compound, but it offers a good potential for utilization. Based on our surveys it seems that the utilization of VOCs as an energy source, either additional or in co-firing purposes [5–10] is the most currently used solution. However, we exclude this alternative from this review and we concentrate on either the direct use, synthesis gas production or hydrogen production from VOC emissions. In this review, different types of utilization of organic compounds in the production of chemicals are presented including existing solutions and those under research. Most of the processes presented here are catalytic, apart from the actual recovery and purification technologies presented here as well. When considering the total concept of the VOC emission utilization, an important part related to the recovery, purification of emission gas to be utilized and the purification of the final product. Since the catalytic processes are considered, the presence of catalyst poisons and the deactivating nature of the VOC compound itself need to be considered. At the end of the review, certain economic issues and the sustainability of the VOC utilization are discussed.

2. Pre- and Post-Processing of the Emissions to Be Utilized

2.1. Recovery of the Raw Emissions

Even in certain rare cases where the direct utilization of VOCs would be possible, typically the concentrations of VOC emissions are so low that one or two pre-treatment methods are needed to recover the compounds from the waste gas stream in order to valorize them. The recovery method therefore needs to be efficient and economically feasible. The technical feasibility can be evaluated by the efficiency of the recovery, the quality of the product, the physical and chemical characterization of the product and the characteristics of the emission stream [11]. In general, the recovery of VOCs is economically feasible from the solvents vapors of low-boiling products and when VOCs are used as energy carriers in incinerators or oxidizers or boilers. The techniques that can be used for the recovery of VOCs are adsorption, membrane separation, wet scrubbing, and condensation and cryogenic condensation [12]. Table 1 presents these most common techniques for the recovery of VOC emissions and they are discussed in more detail in this chapter.

Table 1. Characteristics of the volatile organic compounds (VOC) recovery techniques [13].

Recovery technique	Efficiency (%)	Indication of applied flow (m ³ h ⁻¹)	Critical parameters
Adsorption:			
Activated carbon	80–98	100–100,000	Fluid percentage, VOC concentration
Zeolite	80–99	<100,000	Fluid percentage, dust in inlet gas
Polymeric	95–98	-	Dust in inlet gas
Membrane separation	99.9	<3000	-
Wet scrubbing	30–99	50–500,000	Temperature
Condensation	60–90	100–100,000	Saturation of inlet gas
Cryocondensation	>99	<5000	Fluid percentage in inlet gas

2.1.1. Adsorption

In VOC adsorption the gaseous compounds (adsorbate) are adhered to the surface of the solid sorbent (adsorbent). The interaction between adsorbent and adsorbate may be physical or chemical in nature. In the physical adsorption the gaseous compounds adhere to the adsorbent by van der Waal forces and are therefore more easily desorbed from the sorbent. Desorption of the adsorbed molecule can be carried out either by lowering the pressure or rising the temperature or by a combination of these two [13]. After desorption the concentrations of the molecules are higher than in the original emission gas, and the molecules are therefore more easily used as raw material for new products [12].

Adsorption by activated carbon is the most commonly used method for recovering VOC emissions since it is the most economic process for different kind of gas streams [7]. Activated carbons can be prepared from basically any carbon source, such as coconut, wood, peat, coal, tar, sawdust and cellulose residues [14]. Recent research has been conducted on preparation of activated carbons from many agricultural waste materials [15–18]. Also activated carbon fiber cloth with regeneration by electrothermal desorption has been applied for the recovery of methylene chloride in an industrial scale [19]. The main reason for the activated carbons' very good ability to adsorb molecules is the high surface area and vast structure of pores and micropores they have [20].

Zeolites are an alternative for activated carbons when thermal stability and hydrophobicity are needed. They are inorganic materials, made of Si and Al, and have a crystalline structure and fixed pore sizes. The precise pore size allows the selective adsorption of certain compounds [20]. Zeolites appear naturally, but they can also be produced synthetically. The main applications of zeolite adsorption in VOC recovery are, e.g., in spraying cabins and varnish production. Since zeolites are more expensive than activated carbons, it is rational to combine them together, using zeolites in the final recovery phase [13].

In the polymer adsorption process small porous plastic balls are used as adsorbents. However, the small size of micropores in activated carbon cannot be achieved in polymers even if polymers have rather high adsorption capacity. Polymers have low selectivity in VOC adsorption, but different types of polymers adsorb different types of VOCs. Polymers can also be combined with other adsorbents, activated carbon or zeolites, zeolites being typically the last purification phase [13].

2.1.2. Membrane Separation

Membrane separation of VOCs is based on selective permeability of the membrane for different species. Several organic compounds can be recovered, including alkenes, olefins, chlorinated hydrocarbons, aromatics, ketones, ethers, alcohols and monomers, like vinyl chloride, ethylene or propylene, from gas streams containing nitrogen, oxygen, hydrogen or carbon dioxide. Membrane recovery is applied in the chemical industry, petrochemical industry and pharmaceutical industry [21]. The membrane technologies used in the VOC gas recovery are mainly gas permeation and reverse osmosis [21]. The concentration of VOC gases is rising in the membrane unit as the separation proceeds, and the limits from the lower to the upper explosive limit have to be taken into consideration to prevent the formation of an explosive mixture [12]. However, membrane separation is only a concentration technique and if complete purification of the emission stream is wanted, membrane technology needs to be combined with another technique, e.g., adsorption [13]. If we consider membranes to recover selected VOC compounds, it seems to be a rather feasible method.

2.1.3. Wet Gas Scrubbing

In wet gas scrubbing a gaseous compound is absorbed from a gas phase to a liquid phase. For the recovery of chemical compounds physical absorption is the only possibility since after that process the compounds can be desorbed. Chemical scrubbing is used only for the abatement of compounds from gaseous emissions. The suitable chemicals that can be scrubbed with water are those that are soluble in water, such as alcohols, acetone and formaldehyde. However, absorption is mainly used for the recovery of inorganic compounds rather than VOCs [12].

2.1.4. Condensation and Cryocondensation

In condensation the temperature of the gas is decreased or the pressure is increased to reach its dew point. The use of condensers is favorable when the concentration of VOCs is high in the gas stream. Low-volatility VOCs are easier to condense, since their condensing temperatures are higher. Therefore, volatility is a crucial property of the compound when considering condensation as a recovery method. Condensers can be used as a primary recovery method or together with another recovery technique [22].

Cryocondensation uses very low temperature refrigerants, e.g., liquid nitrogen, as coolants to reduce the temperature for condensation. Cryocondensation is very effective with all VOCs and can be used as the final method for the VOC emission control. The method is very flexible for the changes in the VOC flow rate and solvent loading [12].

2.2. Purification of the Raw Emissions and the Products

In some cases, the raw emission needs to be pretreated for the removal of particulates or water before the recovery of valuable VOC compounds [23]. Often, these compounds are separated from VOCs in the recovery phase and no separate pretreatment is needed. The recovered emission is typically a mixture of several organic compounds and for the chemical utilization it is usually necessary to purify the desired compound from other organic compounds. In this case, a selective technique is needed and also the sequence of the separation of compounds has to be considered carefully.

The recovered gas may contain several impurities, such as catalyst poisons, that are harmful in the utilization of the compounds. The source of the emission gas and the application of the recovered gas determine the need for purifying the recovered gas. Particulates and non-organic gases are typical impurities found in VOC gases. In catalytic utilization of the recovered gas, it is vital that the gas does not affect the activity of the catalyst nor contain catalyst poisons, such as siloxanes and compounds of sulphur, phosphorus and halogens at intolerable amounts. It may also be necessary to concentrate the gas with one organic compound and remove other VOCs that complicate the utilization of the major compounds [24].

Particulates present in the gas mixture to be utilized may cause erosion, compression damages and explosion risks [7]. Methods that remove particles, but not VOCs are gravitational separations and several filtration techniques, namely dry and wet electrostatic precipitator, fabric filter, ceramic and metal filter, two-stage dust filter, absolute filter (HEPA) and high-efficiency air filter (HEAF) [12]. Nitrogen removal is the most critical and expensive process. However, it is possible to remove nitrogen and also CO₂ by pressure swing adsorption with certain carbon molecular sieves. Water can be removed, e.g., by adsorbing it to a zeolite. Oxygen removal is also essential, since it may cause combustion or explosion of VOCs. Oxygen removal can be carried out by catalytic process where some of the organic compounds are oxidized to CO₂. However, this reduces the amount of valuable VOCs to be recovered [7].

One special case of impurities in VOCs is the presence of siloxanes in landfill gases. Siloxanes are added to many domestic products, which is the reason that their concentrations are increasing in landfill gases. Siloxanes are non-toxic silicon containing organic molecules. They are volatile and thus evaporate to the recovered landfill gas. The problem of siloxanes is, that they for example burn together with the other organic gases, but instead of gaseous products they form crystalline solid silica. This product is then fouling the equipment surfaces, deactivating the catalysts, *etc.* Siloxanes can be removed from the gas by condensation (refrigeration) and adsorption (such as carbon adsorption) [25].

To summarize, several mature techniques are available for the recovery of VOCs. Some techniques include the regeneration phase, which increase the costs compared to the abatement of VOCs from emission gases. Membrane techniques, condensation and cryocondensation have the benefit that no regeneration is needed. Selectivity of the recovery technique plays also an important role when the recovered compound will be utilized as raw material to form new products. A thorough planning needs

to be made when the suitable recovery and purification technology is considered. The selection is very case-dependent and not only dependent on the recovered VOC, but also on the potential products concerned.

3. Catalytic Utilization of Methane Emissions

3.1. From Methane to Syngas and Hydrogen

Methane is the simplest form of hydrocarbon and organic gas. Methane is also the major compound in natural gas (NG) and it is the second largest energy source after crude oil. Around the world, abundant NG reserves exist and it is ubiquitous material distributed more evenly than oil and coal [26]. Methane is mainly utilized as a fuel and energy source for many decades, for example in electricity production and as a transportation fuel in the form of liquefied natural gas (LNG) or compressed natural gas (CNG). In this present section, the main focus is on the utilization of methane gas (or NG) emissions from different possible sources. Globally, enormous amounts of NG is extracted, produced, and transported. Methane is one of the major greenhouse gases (GHGs), even though it is present in the atmosphere in low concentrations. It is noteworthy that methane has ~20–23 times higher global warming potential (GWP) than CO₂ [27,28]. Methane emissions originate from a wide variety of natural (such as oceans and wetlands) and anthropogenic sources, typically from oil drilling (NG is vented and flared), shale gas, automobiles' exhaust gas, landfill gas (LFG), coal bed methane (CBM), hydrocarbon processes, agro-farming, mining and metal industries [29,30]. In many places, methane is a waste hydrocarbon source from different process industries and exploration sites, which is not utilized efficiently. There are many ambitious projects around the world on reduction of NG flaring and utilization [31,32]. Moreover, in many geological deposits, in coal mining and process industries, methane exists with CO₂. Henceforth, both, *i.e.*, CH₄ and CO₂ GHGs can be utilized in synthesis gas (*syngas* as short form) production via the dry reforming process. Further, syngas can be converted to valuable fuels, intermediates, and chemicals via Fischer-Tropsch synthesis [26].

Utilization of methane emissions depends on many factors, for example, the amount and concentration or purity levels of CH₄. Further, gas stream originated from different sources contain different concentration levels of methane (e.g., ~50% by volume exist in LFG) [29]. Even the low-concentrations of methane from CBM can be utilized to produce useful energy, for example, by catalytic combustion over a heterogeneous catalyst CuO/ γ -Al₂O₃ [33]. The economic viability and thermal efficiency are the topics that need to be considered in the case of methane emission utilization.

Methane is a symmetrical molecule, with no dipole moment and has strong C–H bond energy (493 kJ mol⁻¹). In order to convert CH₄, a lot of energy is required to activate the C–H bond. This activation is one of the biggest challenges in the catalysis field and has been an important topic of research for academic and industrial communities [34–37]. The kinetic and thermodynamic constraints are critical for developing energy efficient processes in methane conversion technologies [34,37]. As mentioned in Tang *et al.* [38], the C–H bond activation can be done by mainly four ways by reducing the oxidation state of carbon atom, such as (i) complete C–H bond removal by partial oxidation, for example to syngas (CO + H₂), oxygenates (CH₃OH) and hydrocarbons compounds (olefins and aromatics) production; (ii) complete C–H bond removal by decomposition to carbon and H₂; (iii) complete combustion in mobile and stationary applications (such as fuel and energy) and finally; (iv) partial C–H

bond removal by substituting heteroatoms (e.g., CH₃Cl). In the following sections, catalysts development in these four strategies of methane C-H bond activation will be discussed.

3.1.1. Methane Dry Reforming and Partial Oxidation to Syngas

The first and foremost route was the direct methane conversion to syngas production. Currently, there are three main routes to convert CH₄ to syngas, *i.e.*, partial oxidation, and dry and steam reforming (Figure 1). Methane dry reforming (MDR) is a promising route for syngas production, and moreover, it is beneficial in utilizing CO₂ emissions [39]. In the MDR process, the CO/H₂ ratio of one can be achieved, which is ideal for the F-T synthesis. Whereas, methane steam reforming (MSR) is more appropriate for H₂ production than syngas, due to a higher H₂/CO ratio that can be achieved. This topic is discussed more in the next section. Few processes are successful, but still to reach the industrial scale, many challenges exist in catalysis and reactor design. In this perspective, the biggest challenge occurs in developing catalytic materials for the methane conversion routes (Figure 1).

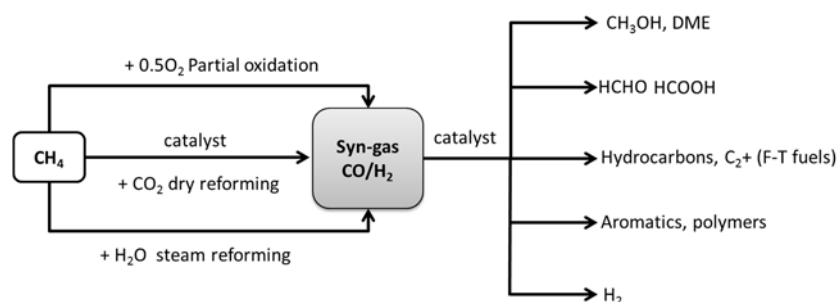
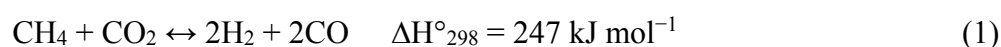


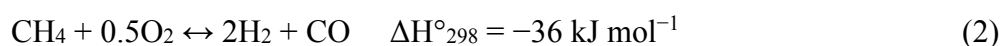
Figure 1. Indirect methane conversion to produce fuels and value-added chemicals via intermediate syngas production.

A list of chemical reactions involved in methane conversion to syngas, hydrogen and direct decomposition is as follows [35].

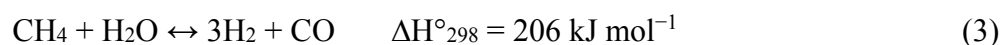
(E1) *Methane dry reforming (MDR)*



(E2) *Methane partial oxidation (POM)*

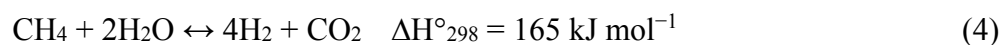


(E3) *Methane steam reforming (MSR)*



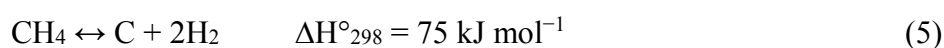
(Insufficient steam)

(E4) *Methane steam reforming*



(Sufficient steam)

(E5) *Methane decomposition*



Several catalysts are developed and tested in syngas production via the MDR and POM process. In the literature, one can find quite a good number of studies and excellent reviews on thermodynamics and heterogeneous catalysts for methane dry reforming reaction (e.g., [40–45]) and also for the methane partial oxidation [46–48]. The recently studied most active catalysts published on MDR and POM process are summarized in Tables 2 and 3. Most of the studies in MDR are related to high-temperature catalysis operated at above 600 °C [41].

Recently, micro-plasma technology coupled with catalysis has gained interest in research communities and promising results at room temperature reaction have been obtained, e.g., using dielectric barrier discharge (DBD) plasma assisted reactor with a packed bed catalyst [49]. This technology is also very promising for the preparation of catalytic materials since it produces a uniform heat distribution [50].

In general, platinum group metals (noble) [41] and non-noble [42–51] metal catalysts were studied in MDR, but non-noble metal catalysts are the preferred ones due to the cost and availability. The noble metal based catalysts have also shown comparable activities and higher durability than non-noble metal catalysts. As presented in Table 2, Ni based catalysts were found to be most popular and widely studied in MDR due to their superior activity and low cost. Most of the studies employed stoichiometric molar ratio $\text{CH}_4/\text{CO}_2 = 1$ and the syngas production was close to the ideal, *i.e.*, $\text{H}_2/\text{CO} = 1$. The influence of the preparation method on the catalytic properties was a crucial parameter. Moreover, the operating conditions had a greater influence on catalytic activity in MDR and POM, such as reaction temperature, which had a significant effect on the products formation at ambient pressure. The catalyst development for MDR was mostly investigated on Ni based catalysts on different carrier materials such as oxides (CeO_2 , MnO_2 , SiO_2 , Al_2O_3 , MgO_2 , ZrO_2 , *etc.*), mixed oxides ($\text{CeO}_2\text{-Al}_2\text{O}_3$, $\text{CeO}_2\text{-ZrO}_2$), tri and ternary oxides, and moreover bimetallic materials such as NiPt, NiCo, NiFe based catalysts [40,41]. Preparation methods for the carrier and active metal catalysts were found to be the most important parameter in preparing active and selective catalysts. In this perspective, calcination temperature had greater influence on the active particle size. As reported by Gould *et al.* [52], an atomic layer deposition method is effective in preparing very small active Ni particles with controlled growth and distribution compared to impregnation. In methane activation, the metal-support interactions are important and they affect strongly the overall catalytic activity [53,54]. In MDR, carbon formation is a serious problem and this results in catalyst deactivation. There are different strategies to reduce and avoid carbon formation [55]. For example, addition of small amounts of noble metals such as Pt, Rh can improve the catalyst performance and coking resistance [56]. Another effective way is to prepare a catalyst with high oxygen storage capacity (OSC) materials such as CeO_2 , for effective carbon removal via gasification by lattice oxygen [57]. In many catalytic applications, OSC materials renders the surface by oxidizing the carbon species. Novel methods were developed by modifying the conventional methods to prepare catalyst with desired physicochemical properties for example refluxed co-precipitation and sequential impregnation [51,58]. The effect of calcination method had a pronounced effect on the activity and selectivity of MDR, for example, freeze drying and NO calcination of Ni based catalysts were superior compared to conventional and air drying and calcination [53]. Nevertheless, the nature of the support material also plays vital role in catalytic activity and deactivation [59,60]. Nano based catalytic materials are most active and robust with optimal size, shape and uniform particle distribution [52,61]. New class of materials are needed and

also modification of conventional mixed metal oxides with lower amount of active metal can lead to reduction of the overall costs.

Table 2. Most recently studied Ni based catalysts in methane dry reforming (MDR) to syngas production.

Catalyst	Prepa-ration method	Reaction conditions	Conversion (%)	H ₂ /CO	Comments	Ref.
LaNiO ₃ @SiO ₂	Stöber	RT Q _{tot} = 50 mL min ⁻¹ CH ₄ /CO ₂ = 1	X _{CH₄} = 67 X _{CO₂} = 57	0.9	NT-plasma, DBD reactor, core shell	[49]
Ni _{4.7} Pt ₁	ALD	T = 600 °C Q _{tot} = 40 mL min ⁻¹ CH ₄ /CO ₂ = 1	X _{CH₄} = 30	na	small Ni particles □8 nm with ALD	[52]
Ni ₁₀ Pt _{0.5} /Al ₂ O ₃	WI	T = 750 °C, Q _{tot} = 20 mL min ⁻¹ CH ₄ /CO ₂ = 1	X _{CH₄} = 78 X _{CO₂} = 95	0.63	Pt addition reduce the carbon deposition and improve the geometric effects	[56]
Ni ₅ Mn ₉₅ O	CP	T = 750 °C, Q _{tot} = 30 mL min ⁻¹ CH ₄ /CO ₂ = 1	X _{CH₄} = 75, X _{CO₂} = 75	na	rapid deactivation due to Mn phase change leads to metal sintering	[59]
Ni ₅ /diatomites	two solvents and DI	T = 650 °C, GHSV = 21,120 mL g ⁻¹ h ⁻¹ CH ₄ /CO ₂ = 1	X _{CH₄} = 39 X _{CO₂} = 49	0.88	deactivation of Ni ⁰ by re-oxidation, only C-β (reactive C-nanotubes)	[62]
Ni ₅ /SiO ₂	two solvents and DI	T = 650 °C, GHSV = 21,120 mL.g ⁻¹ h ⁻¹ CH ₄ /CO ₂ = 1	X _{CH₄} = 61, X _{CO₂} = 70	0.9	deactivation of Ni ⁰ by re-oxidation, two types of carbon forms: C-β and C-γ (less reactive sp ³ C-graphite)	[62]
(NiCo) _{2.5} /Ce ₇₇ Zr ₂₀	Glycothermal synthesis + DP + FD calcination	T = 750 °C p = 1.2 bar	X _{CH₄} = 90 X _{CO₂} = 90	0.85	TOS 20 h, calcination effect	[53]
Ni ₅ -Ce ₆ /SBA-15	two solvents and IWI	T = 600 °C, GHSV = 264 L.g ⁻¹ h ⁻¹	X _{CH₄} = 95, X _{CO₂} = 90	0.96	high dispersion inside pores, smaller NiO particles, mode of NiO addition after Ce	[51]
Ce _{2.5} -Co ₅ -Ni ₁₀ /Al ₂ O ₃	IWI	T = 750 °C CH ₄ :CO ₂ = 1	X _{CH₄} = 60		TOS 5 h, effect of forced periodic cycling	[63]
Ni ₁₅ CeMgAl	refluxed co-precipitation	T = 750 °C GHSV = 48,000 h ⁻¹ CO ₂ /CH ₄ = 1.04	X _{CH₄} = 96.5 X _{CO₂} = 92	0.8	bimodal pore, Ni sites in NiAl ₂ O ₄ spinel structure had longer stability	[58]
Ni ₅ /La ₂ O ₃ -ZrO ₂	IWI	T = 400 °C, 12 mL min ⁻¹	X _{CH₄} = 7.5 X _{CO₂} = 12	na	effect of calcination temperature relation with Ni particle size	[64]
NiFe ₂ O ₄ /SiO ₂	sol-gel	T = 800 °C Q _{tot} = 30 mL min ⁻¹ CH ₄ /CO ₂ = 2	X _{CH₄} = 66 X _{CO₂} = 93	1.1	surface acidity is crucial in limiting RWGSR	[65]
Rh _{0.2} -Ni/SBA-15	DI	T = 650 °C GHSV = 48,000 mL h ⁻¹ g ⁻¹	-	0.82	Rh promoted the Ni reducibility and decrease the Ni particle size and enhances the stability	[54]

Table 2. Cont.

Catalyst	Prepa-Ration Method	Reaction conditions	Conversion (%)	H ₂ /CO	Comments	Ref.
Ni/CNT	IWI	$T = 750\text{ }^{\circ}\text{C}$ $W/F = 1\text{ g}\cdot\text{h}\cdot\text{mol}^{-1}$	$X_{\text{CH}_4} = 66$ $X_{\text{CO}_2} = 79$	0.9	TOS 8 h, Ni particles inside the CNTs are more active than outside, tube confinement effect	[66]
Ni/Al ₂ O ₃	IWI	$T = 850\text{ }^{\circ}\text{C}$ $\text{GHSV} = 24\text{ L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	$X_{\text{CH}_4} = 90$ $X_{\text{CO}_2} = 94$	1	preparation of nano catalyst with high SA, good dispersion,	[61]
Ni ₁₅ /TiO ₂	sonication	$T = 700\text{ }^{\circ}\text{C}$, $\text{GHSV} = 95,500\text{ h}^{-1}$ $\text{H}_2\text{O}/\text{CH}_4 = 1.2$	$X_{\text{CH}_4} = 86$ $X_{\text{CO}_2} = 84$	0.9	sonication is more efficient than impregnation, fine dispersion of Ni NPs,	[67]
Rh ₁ /NiO ₂₀ -Al ₂ O ₃	sol-gel/IWI	$T = 700\text{ }^{\circ}\text{C}$ $Q_{\text{tot}} = 37\text{ L}\cdot\text{min}^{-1}$ $\text{CH}_4:\text{CO}_2 = 1:1$	$X_{\text{CH}_4} = 89$ $X_{\text{CO}_2} = 91$	1.22	210 min TOS, deactivation of Rh avoided by NiAl ₂ O ₄ spinel phase, Ni enhance the Rh dispersion on the surface	[68]

T = reaction temperature ($^{\circ}\text{C}$); p = reaction pressure; RT = room temperature; Q_{tot} = CO₂ + CH₄ volumetric feed gas flow rate; GHSV = gas-hourly-space-velocity; TOS = time-on-stream; X_{CH_4} = methane conversion (%); X_{CO_2} = carbon dioxide conversion (%); IWI = Incipient wetness impregnation; NT = non-thermal; DBD = dielectric barrier discharge; CP = co-precipitation; ALD = atomic layered deposition; DI = dry impregnation; FD = freeze drying.

In POM, stoichiometric CH₄:CO₂ ratio is critical in determining the syngas composition (E2). Most widely studied catalytic materials in POM are the transition metal catalysts (*i.e.*, PGM) due to their high activity in oxidation [47]. Among them, Rh based catalysts were found to be most active and stable and widely reported in scientific literature (Table 3). As reported earlier, noble metals are highly selective for oxidation reactions due to high O₂ adsorption and resistance against carbon formation [69]. POM is thermodynamically an exothermic reaction, but most of the catalysts are active and selective at higher temperatures 700–1000 $^{\circ}\text{C}$ (shown in Table 3). At higher temperatures, deactivation of the catalysts takes place due to active metal sintering or agglomeration [55,70]. Developing new catalytic materials, which are active at low temperatures can be a possible solution to avoid metal sintering and also make the process less energy intensive. Most of the catalysts used in the literature achieved the conversion and selectivity close to equilibrium values (Table 3). Durability of the catalyst is still a challenge, since to the best of our knowledge, only a few catalysts performed excellently when the time-on-stream was longer than 150 h [70].

Table 3. Recently studied catalysts in partial oxidation of methane to syngas.

Catalyst	Prepa-ration Method	Reaction conditions	Conversion and selectivity (%)	H ₂ /CO	comments	ref.
Rh _{0.005} /γ-Al ₂ O ₃	IWI	$T = 900\text{ }^{\circ}\text{C}$ $\text{GHSV} = 24,640\text{ h}^{-1}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = \sim 88$ $S_{\text{CO}} = 90$ $S_{\text{H}_2} = 90$	2	TOS 160 h, CH ₄ conversion and CO selectivity decrease with Rh NP size	[70]
Rh ₅ -doped CeO ₂	solution-based hydrothermal	$T = 700\text{ }^{\circ}\text{C}$ $Q_{\text{tot}} = 100\text{ mL}\cdot\text{min}^{-1}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = 95$ $S_{\text{H}_2} = 93$ $S_{\text{CO}} = 86$	2.2	surface chemistries with <i>in situ</i> studies are important to correlate the catalysts performance	[69]

Table 3. Cont.

Catalyst	Preparation method	Reaction conditions	Conversion and selectivity (%)	H ₂ /CO	Comments	Ref.
Rh-honeycombs in microreactor	micro-structuring Rh foils	$T = 1100\text{ }^{\circ}\text{C}$, $p = 0.15\text{ Mpa}$, $\text{GHSV} = 195 \cdot 10^3\text{ h}^{-1}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = 90$ $S_{\text{H}_2} = 88$ $S_{\text{CO}} = 87$	2	$t > 10\text{ ms}$; high pressure used in Rh honeycomb catalyst; minimizing pressure drop	[71]
Ni-Th-O	controlled oxidation	$T = 750\text{ }^{\circ}\text{C}$ $\text{CH}_4/\text{N}_2\text{O} = 1$ $\text{GHSV} = 8500\text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$	$X_{\text{CH}_4} = 50$ $S_{\text{CO}} = 90$ $S_{\text{H}_2} = 90$	2	using N ₂ O as oxidant, bimetallic Ni thorium used, accessibility and acidity	[72]
Ni-Pt/ La _{0.2} Zr _{0.4} Ce _{0.4} O _x	wash coating and IWI	$T = 800\text{ }^{\circ}\text{C}$ $\text{GHSV} = 820,000\text{ h}^{-1}$ $Q_{\text{tot}} = 4.0\text{ mL} \cdot \text{s}^{-1}$ $\tau = 4.4\text{ ms}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = 82$ $S_{\text{CO}} = 60$	1.5	microchannel reactor, very short residence time, high flow rates	[73]
Ce ₇ -Fe ₃ -O mixed oxide	CP	$T = 900\text{ }^{\circ}\text{C}$	$X_{\text{CH}_4} = 95$ $S_{\text{H}_2} = 99$ $S_{\text{CO}} = 98.8$	2	oxygen carrier showed good, lattice oxygen is crucial and high O mobility	[62]
Ni ₃₀ /MgO	IWI	$T = 800\text{ }^{\circ}\text{C}$ $P = 0.1\text{ MPa}$ $\text{GHSV} = 1200\text{ h}^{-1}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = 94$ $S_{\text{CO}} = 94$ $S_{\text{H}_2} = 94$	2	higher conversion with increasing calcination temperature, highly Ni dispersed	[74]
Rh _{1.5} /CeO ₂ / monolith cordierite	solution combustion synthesis	$T = 800\text{ }^{\circ}\text{C}$ $\text{GHSV} = 400,000\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$ $\text{S/C} = 1.2$ $\text{O/C} = 0.55$	$X_{\text{CH}_4} = 100$	3	Structured catalysts cordierite honeycombs, high performance at high WSV, process intensification	[75]
(CeO ₂) ₅ /Pt ₂ -SiC	micro-emulsion	$T = 805\text{ }^{\circ}\text{C}$ $\text{CH}_4/\text{O}_2 = 2$ $\text{GHSV} = 1500\text{ h}^{-1}$	$X_{\text{CH}_4} = 93$	1	composites with optimal Ce and Pt content to achieve high activity,	[76]
(NiO) ₄₈ /CeO ₂	one-step template	$T = 850\text{ }^{\circ}\text{C}$ $\text{GHSV} = 9.5 \times 10^6\text{ h}^{-1}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = 90$ $S_{\text{CO}} = 84$ $S_{\text{H}_2} = 90$	2	Fibrous nanocatalyst, highly active at very short contact time of 98 μs,	[77]
Ni ₁₀ /CeO ₂ -SiO ₂	sol-gel/DI	$T = 750\text{ }^{\circ}\text{C}$ $\text{CH}_4/\text{O}_2 = 2$ $Q_{\text{tot}} = 30\text{ mL} \cdot \text{min}^{-1}$	$X_{\text{CH}_4} = \sim 84\%$	2	calcined at 700 °C had a weak surface acidity with high surface area and low carbon formation, atomic Ce/Si = 1, 15 h TOS	[78]
Pt ₁₀ Ce _{0.5} Zr _{0.5} O ₂ / Al ₂ O ₃	IWI	$T = 900\text{ }^{\circ}\text{C}$ $Q_{\text{tot}} = 100\text{ mL} \cdot \text{min}^{-1}$ $\text{CH}_4/\text{O}_2 = 2$	$X_{\text{CH}_4} = 70$ $X_{\text{CO}} = 80$ $S_{\text{H}_2} = 96$		high reducibility and O ₂ mobility reduce the carbon formation	[79]

T = reaction temperature (°C); p = reaction pressure; τ = residence time; Q_{tot} = volumetric feed gas flow rate; IWI = Incipient wetness impregnation; CP = co-precipitation; ALD = atomic layered deposition; GHSV = gas-hourly-space-velocity; TOS = time-on-stream; DI = dry impregnation; X_{CH_4} = methane conversion (%); X_{CO_2} = carbondioxide conversion (%); S_{CO} = CO selectivity (%); S_{H_2} = CO selectivity (%).

3.1.2. Methane Steam Reforming and Decomposition to H₂

As reported by many scientists, environmental panelists and governmental organizations, possible solution for the current environmental problems and clean energy security can be the H₂ economy. Hydrogen is known as a clean energy carrier and it is used as a fuel in fuel cell systems. Today, ~50% of H₂ is produced by natural gas steam reforming over industrially applied Ni-based catalyst [80]. Still challenges exist in catalysts development for MSR. MSR is widely studied over several catalytic systems with different configurations, intensified reactors, and process conditions [42,81]. There is a need to improve the efficiency of the existing MSR process using new robust catalytic materials (Table 4) and also by intensifying reformer system (such as membrane assisted reactors (MRs)). Steam reforming of hydrocarbons is studied extensively in MR related to CO_x-free H₂ production [82,83]. MSR at low temperature operation will be one of the main research objectives, but thermodynamically temperatures less than 600 °C are challenging for the reforming reaction [42]. There is a need for active and selective catalysts which can activate the C–H bond and the water molecule at moderate temperatures. Another route in methane to H₂ is the catalytic decomposition. For low temperature fuel cell applications, catalytic decomposition of methane (CDM) is more suitable than MSR since then CO_x free H₂ can be produced [84]. In MSR, carbon formation is relatively lower than in CDM due to steam environment. The challenge in CDM is to avoid deactivation of catalyst due to carbon formation during the H₂ production. The type of carbon formed is very much dependent on the type of the feed and operating conditions. Interestingly, carbon nanotubes can be grown along with H₂, which does not have any influence on catalyst deactivation [84]. Still, MSR is highly matured technology and cost-effective in H₂ production, but process modifications and new catalysts are needed to improve the existing efficiency and to reduce the emissions.

Table 4. Recently studied catalysts in methane steam reforming to hydrogen.

Catalyst	Preparation method	Reaction conditions #	Conversion and H ₂ selectivity (%), yield (% or mole)	Comments	Ref.
Ni ₁₀ /ZrO ₂ -CeO ₂ -La ₂ O ₃	WI	T = 500 °C GHSV = 70,000 h ⁻¹ S/C = 3	X _{CH₄} = 25 Y _{H₂} = 30	Low temperature steam reforming	[85]
Ni/K ₂ Ti _x O _y -Al ₂ O ₃	WI	T = 750 °C GHSV = 15,000 h ⁻¹ S/C = 2.5 TOS = 10 h	X _{CH₄} = 97 Y _{H₂} = 3 mol	high activity due to weak interactions between Ni and support, addition of secondary support K ₂ TiO ₂ improved the resistance to deactivation	[86]
NiO/SiO ₂	sol-gel	T = 700 °C ST = 11.31 kg _{cat} h.kmol ⁻¹ S/C = 3.5	X _{CH₄} = 96 Y _{H₂} = 3.8 mol	crystallite size of NiO catalysts can be controlled by calcination	[81]
Ni/Ce _{0.65} Hf _{0.25} Pr _{0.1} O ₂	EDTA-citrate	T = 700 °C S/C = 2	X _{CH₄} = 85	Dopants redox property crucial in enhancing the OSC in rare earth metals-doped	[87]

Table 4. Cont.

Catalyst	Preparation method	Reaction conditions #	Conversion and H ₂ selectivity (%), yield (% or mole)	Comments	Ref.
Cu ₅ /Co ₆ Al ₂	precipitation and IWI	$T = 650\text{ }^{\circ}\text{C}$ $S/C = 3$ $Q_{\text{tot}} = 50\text{ mL}\cdot\text{min}^{-1}$	$X_{\text{CH}_4} = 96$ $Y_{\text{H}_2} = 2.60\text{ mol}$	Cu favors the WGS reaction	[88]
Ni _{0.5} Mg _{2.5} AlO ₉	co-precipitation	$T = 900\text{ }^{\circ}\text{C}$ $S/C = 3.1$ $Q_{\text{tot}} = 50\text{ mL}\cdot\text{min}^{-1}$	$X_{\text{CH}_4} = 100$	150 h, 20 ms, high WHSV, higher dispersion of Ni particles, small particles	[89]
Ru/Co ₆ Al ₂	IWI	$T = 600\text{ }^{\circ}\text{C}$, $S/C = 3$, $Q_{\text{tot}} = 20\text{ mL}\cdot\text{min}^{-1}$,	$X_{\text{CH}_4} = 95$ $Y_{\text{H}_2} = 24$	100 h, well dispersed at the surface and higher Co loading	[90]
Ni _{0.15} Al _{0.85}	Solution-combustion/ IWI	$T = 850\text{ }^{\circ}\text{C}$ $Q_{\text{tot}} = 100\text{ mL}\cdot\text{min}^{-1}$ $S/C = 4$	$X_{\text{CH}_4} = 97.8$ $Y_{\text{H}_2} = 2.9\text{ mol}$	high surface area and strong interaction between Ni and Al	[91]
Ir ₅ /MgAl ₂ O ₄	IWI	$T = 850\text{ }^{\circ}\text{C}$ GHSV = 284,000 h ⁻¹ $S/C = 3$	$X_{\text{CH}_4} = 55$	Ir particles bind strongly MgAl ₂ O ₄ surface via redox process leading to a strong metal–support interaction and activate facile water dissociation	[92]
Au/Ni ₅ -LaAl	anionic exchange /IWI	$T = 700\text{ }^{\circ}\text{C}$ $S/C = 1.24$ GHSV = 135,000 mL·g ⁻¹ ·h ⁻¹	$X_{\text{CH}_4} = 34$	Au addition enhance the stability and decreases the carbon growth rate	[93]

atmospheric pressure; T = reaction temperature ($^{\circ}\text{C}$); p = reaction pressure; Q_{tot} = volumetric feed gas flow rate; S/C = steam-to carbon ratio; ST = space time; IWI = Incipient wetness impregnation; CP = co-precipitation; ALD = atomic layered deposition; DI = dry impregnation; GHSV = gas-hourly-space-velocity; TOS = time-on-stream; OSC = oxygen storage capacity; X_{CH_4} = methane conversion (%); Y_{H_2} = hydrogen yield (%).

3.2. From Methane to Chemicals

Transportable liquids are more cost-effective than NG due to its low volumetric density. Gas-to-liquid (GTL) technology is a dominant approach to convert gases to liquid fuels and chemicals. Direct methane conversion in a single-step can reduce operating costs, energy consumption, and it is more efficient than producing first syngas and then the chemicals. Transformation of methane to value added intermediates and chemicals is still at the research stage compared to methane to syngas production (Figure 2). Hydrogen cyanide production from methane in the presence of oxygen was the only industrially established process for many decades [94]. One of the strategies in the C–H bond activation is the catalytic oxidation process. Oxidation process is one of the most viable, easy and efficient methods in VOC abatement and utilization technologies [95].

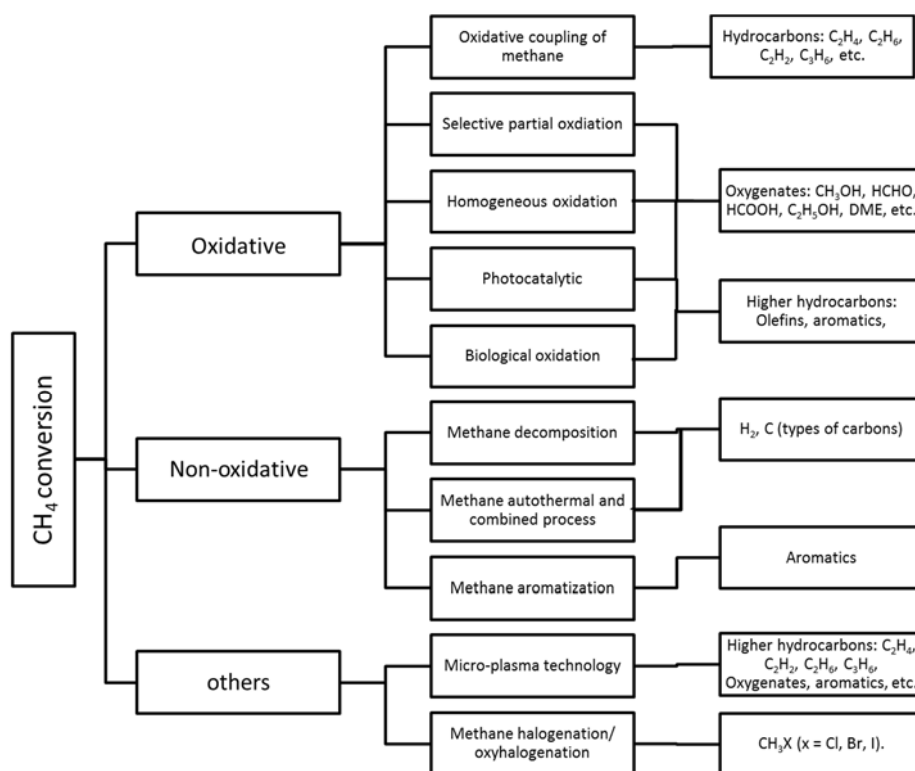
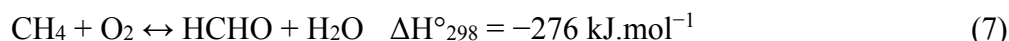
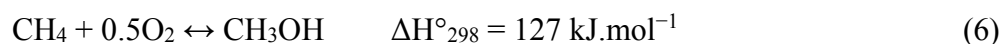


Figure 2. Direct methane conversion technologies to various valuable chemicals, intermediates and fuel compounds.

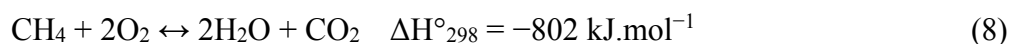
One of the commercially applied conversion technology is the catalytic methane combustion (CMC) (in the form of LNG and/or CNG) in automotive applications. A significant amount of research has been done on catalyst materials for methane combustion in internal combustion engine (ICE) applications. Uncombusted methane is lost through exhaust pipe to the environment. Huge amount of research is devoted to develop an efficient catalytic converter to improve the CH₄ fuel economy [96]. In CMC, PGM metals are good candidates for complete combustion and Pd is more selective in oxidizing the methane. In catalytic combustion of methane, Pd was found to be most active and reported in several studies [96,97].

List of reactions involved in methane to chemical synthesis [35]:

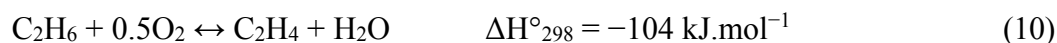
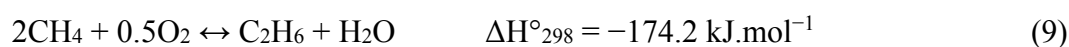
(E6) *Methane partial oxidation*



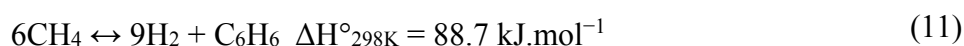
(E7) *Methane combustion or total oxidation*



(E8) *Oxidative coupling of Methane (OCM)*



(E9) *Methane dehydroaromatization (MDA)*



(E10) Methane halogenation and oxyhalogenation



Methane can be selectively converted to a wide variety of products such as oxygenates, olefins, aromatics and methyl halides by oxidation and non-oxidation processes (Figure 2).

3.2.1. Catalysts for Selective Partial Oxidation of Methane to Oxygenates

Thermodynamically the direct conversion of methane to C₁ oxygenates via partial oxidation takes place at temperatures above 300 °C and the process is restricted by the products stability [98,99]. Large amounts of O₂ are needed for methane to chemical synthesis. Instead of using expensive pure O₂, several authors have also utilized oxidants such as GHGs (N₂O, CO₂, CO), H₂O₂ and air [72,100]. Thus, the methane oxidation in the N₂O stream makes the process more efficient and greener. In Table 5, results obtained over few studied catalysts with different operating conditions are summarized (thermal and non-thermal catalysis). Methane to methanol (MTM) synthesis over a Cu₄/MOR catalyst was studied at low temperatures by Alayon in 2012 [101], and he reported that the reaction conditions affect the Cu structure. During the reaction, O₂ is activating the Cu²⁺ active sites; thereafter react with CH₄ to form Cu⁺. The nature of active sites plays an important role in the product selectivity [102]. Wei *et al.* investigated low temperature (at 60 °C) conversion of CH₄ to HCOOH over a VOSO₄ catalyst and they were able to achieve 7% conversion with 70% HCOOH selectivity due to the formation of V⁺⁵ species, which activate methane in the H₂O₂ media. In CH₄ to C₁ oxygenates synthesis, photo-, bio-, plasma, and homogeneous liquid phase oxidation (in H₂SO₄) are widely studied at relatively low temperatures to improve the overall yield and selectivity especially for CH₃OH and HCHO [103–107]. Recently, much attention has been paid to CH₄ photocatalytic conversion and some promising results are shown at relatively low temperatures (below 60 °C) operating in a simplified reactor apparatus [103,108]. Another interesting route is the selective oxidation of methane in homogeneous liquid phase (HLP). HLP carried out over an OsCl₃ catalyst produced highest turnover frequency for the formation of oxygenates compared to other transition metal chlorides reported in Ref. [109].

Table 5. A few selected catalysts studied in methane to C₁ oxygenates (mostly CH₃OH and HCHO) under different reaction conditions.

Catalyst	Preparation method	Reaction conditions	Conversion, selectivity and yield (%)	Comments	Ref.
nano-Au/SiO ₂	HAuCl ₄ + IL in SiO ₂ sol	T = 90 °C p = 20 atm	X _{CH₄} = 25 S _{CH₃OH} = 72 Y _{CH₃OH} = 18	[Bmim]Cl ionic liquid as dissolution solvent, Liquid phase oxidation, 97% Au is recovered	[104]
CuFe ₂ (P ₂ O ₇) ₂	IWI	T = 630 °C p _{CH₄} = 65 kPa p _{N₂O} = 26 kPa Q _{tot} = 3.6 L/h, CH ₄ /N ₂ O = 1.2	X _{CH₄} = 6.4 S _{HCHO} = 26.6 S _{CH₃OH} = 1.8 Y* _{CH₃OH+HCHO} = 1.8	interactions and synergistic effects of Fe and Cu leads to enhanced activity, crystalline phase	[110]

Table 5. Cont.

Catalyst	Preparation method	Reaction conditions	Conversion, selectivity and yield (%)	Comments	Ref.
Fe ₂ O ₃ -CuO/ γ-Al ₂ O ₃	IWI	T = 300 °C	X _{CH₄} = 43 Y _{CH₃OH} = 1.5	Plasma-catalysis, inside packed catalyst configuration is more effective than post catalysis	[105]
Y ₃ /Cu ₆ -Zn _{2.5} -Al _{1.5}	co-precipitation	CH ₄ /O ₂ = 4	X _{CH₄} = 25 S _{CH₃OH} = 27	Plasma-Catalysis, dielectric barrier discharge addition of Yttrium, also Pt and Fe, found to enhance performance	[106]
(V ₂ O ₅) _{0.03} /SiO ₂	IWI	T = 650 °C GHSV = 6.6 × 10 ⁴ h ⁻¹ Q _{tot} = 71 mL·min ⁻¹ CH ₄ /O ₂ = 2	X _{CH₄} = 34 Y _{CH₃OH+HCHO} = 16	1% NO in feed enhanced the conversion and selectivity	[111]
PPFe ⁺³ OH/ AlSiMg Fe/ protoporphyrin	Activation	T = 180 °C H ₂ O ₂ /CH ₄ = 1.4	X _{CH₄} = 50 Y _{CH₃OH} = 60 S _{CH₃OH} = 97	Biomimetic enzyme catalysis, using H ₂ O ₂ oxidant, highest hydroxylating activity due to active O ₂ carriers, deactivates in 5 h	[112]
MoO ₃ /SiO ₂	sol-gel	T = 500	X _{CH₄} = 2.9 S _{HCHO} = 52 S _{CH₃OH} = 8 Y _{CH₃OH+HCHO} = 0.86	catalyst preparation method influences the products selectivity, formation of silicomolybdc acid on the surface reduce the successive oxidation	[113]

T = reaction temperature (°C); p = reaction pressure; Q_{tot} = volumetric feed gas flow rate; S/C = steam-to-carbon ratio; ST = space time; IWI = incipient wetness impregnation; CP = co-precipitation; ALD = atomic layered deposition; DI = dry impregnation; GHSV = gas-hourly-space-velocity; TOS = time-on-stream; OSC = oxygen storage capacity; X_{CH₄} = methane conversion (%); S_{CH₃OH} = CH₃OH selectivity (%); S_{HCHO} = HCHO selectivity (%); Y* = yield of CH₃OH and HCHO (%).

3.2.2. Oxidative Coupling of Methane (OCM) to Ethylene

OCM is extensively studied for C₂ olefin/alkane synthesis over heterogeneous catalysts at higher temperatures (above 700 °C) and recently reported catalysts are Mn-Na₂WO₄/SiO₂ based catalysts [114], Li/MgO [115], Mg- and Al-doped SrTiO₃ and Sr₂TiO₄ [116], Ce-doped La₂O₃ [117], BaCl₂-TiO₂-SnO₂ [118] and La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} [119]. The most commonly studied OCM catalysts are Mn-Na₂WO₄/SiO₂ based catalysts, which are found to be very active and selective when prepared by a sol-gel method. Recently, Godini *et al.* reported promising results on OCM with 78% C₂-selectivity, 64% C₂H₄-selectivity and 24.2% C₂-yield at a low CH₄/O₂ ratio and N₂ dilution. A comparative analysis on the performance was made between different Mn-Na₂WO₄/SiO₂ based catalysts, *i.e.*, taking into account catalyst composition (different Mn (1.9%–2%) and Na₂WO₄ (4.5%–5%)), reaction conditions, reactor type, catalyst preparation methods, and the following results are summarized: methane conversion 7%–40%, C₂-selectivity 58%–80%, yield 5%–27% and the C₂H₄/C₂H₆ ratio of 0.45–2.1 [120]. The synergistic effect of Mn₂O₃ and Na₂WO₄ phases are very important in the OCM activity [114]. Wang *et al.* reported

that the optimal conditions for OCM are 800 °C, flow rate of CH₄/O₂ of 2, and a space velocity (SV) 5000 mL.h⁻¹g⁻¹. In these conditions, 44% conversion with 20% C₂H₄ yield, and C₂ selectivity of 53.3% were achieved over the BaCl₂-TiO₂-SnO₂ catalyst [118]. Still many challenges are involved in improving the conversion and yield of ethylene in OCM. Developing Mn-Na₂WO₄/SiO₂ based catalysts can be one approach. However, there is a need for alternative catalysts for OCM to improve the conversion and yield such as binary, ternary and quaternary mixed oxides (e.g., alkali modified MCl-Mn-Na₂WO₄/SiO₂ (M = Na, Li, K, etc.) [114]. One approach to enhance the performance was to intensifying the OCM reaction by using novel reactors such as membrane assisted reactors (MR) and/or microreactor technology. OCM is performed in oxygen permeable MRs to shift the equilibrium towards the forward direction to improve the overall selectivity and yield. In Oshima *et al.* [100], plasma catalysis in OCM showed good results using a La₅-ZrO₂ catalyst and CO₂ as an oxidant. The electric field and synergistic phase of the La-cation and stabilized tetragonal ZrO₂ were the three main reasons for high activity at 200 °C [100].

3.2.3. Non-oxidative or Pyrolysis of Methane to Aromatics

Methane aromatization process to produce value added H₂ and aromatic compounds such as benzene offers many potential benefits. Non-oxidative conversion of methane (NOM) is a highly endothermic reaction that takes place at higher temperatures (E9). An excellent review on the studied catalysts on methane dehydroaromatization (MDA) or NOM was reported by Spivey and Hutchings [41] and Ma *et al.* [66]. Thermodynamically MDA is an extremely difficult reaction to proceed and involves a highly complex reaction mechanism over the studied catalysts [41]. In MDH, most of the studies dealt with zeolite based catalysts such as Mo/ZSM-5 and Mo/MCM-22 (Ma *et al.* 2013). Zeolite based catalysts exhibit a bifunctional mechanism in the MDA reaction. The additives in the methane feed such as olefins, alkanes and oxygenates had a significant effect on the methane conversion and benzene selectivity. A higher co-conversion of methane/methanol was achieved with high hydrocarbon selectivity (mainly aromatics) over a Zn₂-Mo₅/HZSM-5 catalyst prepared by co-impregnation [121]. Recently, the effect of Fe and Zn promoters on Mo/ZSM-5 were studied in MDA [122] and promoters were observed to change the surface acidity of the ZSM-5. The Fe promoted catalyst had created a higher number of Brønsted acid sites and Fe was bound more strongly to the zeolite structure than Zn, thus, Fe enhances the benzene selectivity [122]. Still more research needs to be done to improve the net aromatic yield, conversion and selectivity before making this process commercially viable.

Membrane assisted reactor (MR) technology is widely studied in gas separation and purification processes [123]. In MR, *in situ* reaction and selective separation takes place simultaneously, thus shifting the equilibrium towards the forward direction. In methane conversion technologies (MCT), oxidant O₂ is a reagent in processing CH₄, and H₂ is one of the products from non-oxidative methane processing, e.g., from OCM, MDH, and steam reforming. Most of the MCT processes are equilibrium limited and kinetically controlled reactions. One approach to enhance the MCT performance is by applying membrane-assisted reactors for example in MDH, wherein H₂ is selectively removed through the membrane and reaction proceeds more towards the forward direction. According to Cao *et al.* [124], MDH in an O₂ permeable MR resulted in a selective removal of product H₂ that leads in superior activity in methane conversions and also avoids the catalyst deactivation.

In methane conversion, predominantly the products are more reactive than methane itself. There is a need for effective product separation and kinetic control over the process. The most favorable option to utilize methane emissions will be syngas and/or H₂ production than chemicals synthesis due to the maturity of the technology and significant research and development that has already been done. Methane to chemicals holds a promising route, but many challenges exist in converting methane efficiently to chemicals with high yield and conversion. In the long run, methane transformation to fuels and chemicals via bio- or photochemical conversion will be potential technologies. Furthermore, biological and photochemical renewable processes are very promising due to enormous amounts of living biological sources and surplus amount of solar energy. Nevertheless, thermal catalytic conversion holds potential route for the short term implementation to convert methane to chemicals due to the existing industrial expertise and infrastructure. The future work will be more focused on developing new catalytic materials (e.g., for low temperature methane activation), process intensification and reactor design (e.g., microstructured reactors), integration of two or more processes such as tri-reforming (MDR+POM+MSR), O₂ and H₂ permeable membrane reactors for yield, conversion and selectivity enhancement.

4. Catalytic Utilization of Volatile Organic Compounds

As an alternative for VOC abatement, VOCs can be used as important sources of energy if collected and valorized effectively. Methanol and ethanol are interesting examples of the use of VOCs in energy conversion systems. However, scientific data are scarcer in the case of other molecules especially those encountered from industrial emanations. The previous chapter of the review was concentrating on the utilization of methane. Now we will proceed further to the other organic emissions.

4.1. From Volatile Organic Compounds to Syngas and Hydrogen

Reforming reaction of alkanes is an important energy conversion process for synthesis gas (mainly H₂ and CO) generation. Methane, as the main component of natural gas, is one of the most studied molecules for reforming reactions. However, several studies have been centered on processing and valorizing a number of higher alkanes such as ethane [125,126], propane [127–130], *n*-butane [131–133] which are present in natural gas, but also generated in engine burners. Among reforming reaction, the steam reforming (SR) of higher alkanes is probably the most common and cost-effective industrial process for H₂ generation. Rhodium based materials have been reported as highly active catalysts for steam reforming of alkane molecules at low temperatures [131]. Schädel *et al.* [125] studied the steam reforming of methane, ethane, propane, butane, separately, over rhodium-based monolithic honeycomb catalyst, and found that ethane, propane, and butane are converted at much lower temperatures than methane. For industrial application, Ni based materials are more studied due to their reasonable activity and significantly lower costs [133–135]. As in the case of methane discussed before, the coke deposition and high temperature of reforming when conventional Ni/ γ -Al₂O₄ is used, lead to rapid catalytic deactivation and reduced H₂ yield. Support modification by catalytic promoters and/or atomic dispersion of Ni in mixed oxide structure has been reported to stabilize the catalytic activity of Ni [133,135]. For instance, CeO₂-doped Ni/Al₂O₃ displayed enhanced resistance toward carbon formation [135].

The generation of aromatic hydrocarbons as by-products of biomass [136] and plastic gasification to synthesis gas [137,138] have driven more interest into investigating in details their catalytic conversion

to hydrogen-rich gas streams. To assess the efficiency of a classical reforming process, model molecules such as benzene [139–141], toluene [142,143] are usually studied and can provide insight for the VOCs utilization and processing. The existing studies are more oriented on steam reforming reaction using conventional catalysts such as Rh based catalyst [144–147], supported Ni catalyst [148–154], Ni-mixed oxide: perovskite [155–159] and hexaaluminate [148]. Rh based catalyst are reported to be highly active for toluene and benzene reforming within the temperature range of 700–850 °C [147,156]. The catalytic activity of Rh is reported to be dependent on the nature of the support used, where benzene/toluene is activated on Rh particles and water activated on the site associated with the support [144]. In concordance with a bifunctional mechanism, Colby *et al.* [146] have reported an enhanced catalytic activity of Rh/Al₂O₃ in the presence of CeO₂ in benzene steam reforming due to probable activation of H₂O on the surface of reduced ceria and by consequence increasing the rate of hydroxyl transfer between the oxide support and metal [146]. Nickel based catalysts were also investigated as a viable alternative to Rh based materials. Yoon *et al.* have evaluated the efficiency of two commercial nickel catalyst, *i.e.*, Katalco 46-3Q and Katalco 46-6Q (from Jonson Matthey) for toluene steam reforming and found that Katalco 46-6Q (zirconia-promoted nickel-based catalyst) displays high efficiency for toluene reforming reaching 100% conversion at relatively low temperature of 600 °C. Although, nickel supported catalysts have been widely proposed as potential substitutes for Rh based catalysts in steam reforming reaction, nickel is more vulnerable to coking leading to severe deactivation [157]. The general scheme adopted to enhance Ni stability towards coking is based on the modification of Ni active site by support modification. The addition of alkali, alkali earth oxides and rare earth metal oxides to the Al₂O₃ support or the use of basic metal oxides as the support improves Ni resistance to coking [152]. In fact, the presence of alkaline additives on the catalyst surface is believed to accelerate the reaction of steam with adsorbed species decreasing the accumulation of carbon deposits on the catalysts. Nevertheless, due to the high temperature of the catalytic process, Ni oxides interacting weakly with the support tend to aggregate and sinter. The presence of large ensemble of Ni atoms stimulates coke formation leading to strong deactivation of the catalyst [158]. In this perspective perovskite materials with the general formula ABO₃, where A is an alkali, an alkali earth oxides or a rare earth metal oxide presenting a basic character, and B is a transition metal principally Ni, Fe and Co, inserted into defined structures, are interesting materials [150,155]. The role of the cation A in the catalytic activity of Ni based perovskite was reported in several studies. For instance, the catalytic activity of La_{1-x}A_xNi_{0.8}Fe_{0.2}O₃ (A = Sr, Ca and Mg) perovskite in toluene steam reforming was found to vary with the nature of the cation A. The catalytic activity was found to vary following the order La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O₃ > La_{0.8}Ca_{0.2}Ni_{0.8}Fe_{0.2}O₃ > La_{0.8}Mg_{0.2}Ni_{0.8}Fe_{0.2}O₃. Oemar *et al.* [156] reported also a lower carbon formation on La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O₃ which was correlating according to the authors to the highest amount of lattice oxygen in this latter.

In the literature, only very few studies are available on the reforming of carbonyl-containing compounds and most of these studies have been conducted with acetone. Thermodynamic prediction for hydrogen production via steam reforming of acetone investigated in a broad range of conditions can be found in the work of Vagia *et al.* [159] and that maximum hydrogen content is obtained at the temperature of 627 °C. At low temperatures, *i.e.*, ≤500 °C, CO₂ and CH₄ are the main products expected. However, as the temperature increases H₂ and CO fractions are expected to be the main products. Steam reforming of acetone is often conducted on classical active reforming catalysts such as Ni/γ-Al₂O₄ [160,161], modified Ni-catalyst [162,163], PtNi alloys [164], Pt/ZrO₂ and Pt/CeO₂ [164].

However, acetone is known to be a coke precursor causing rapid deactivation of the supported Ni catalyst as observed in many reforming materials. PtNi alloys supported on modified alumina by La, Ce and Mg have been reported to display improved catalytic activity as well as enhanced water adsorption and OH-surface mobility of the Al₂O₃ support. Moreover, PtNi catalysts presented a lower carbon deposition and a higher thermal stability with respect to the monometallic Ni reference catalyst [163].

Generation of H₂ from an alcohol substrate, such as methanol and ethanol, is a well-documented subject and several reviews are available in the literature. Special interest is accorded to the 1st generation bioethanol and the 2nd generation bioethanol produced in a fermentation process [165]. Even if generation of H₂ from bioethanol is behind the scope of this review, some investigation related to the impact of by-products of fermentation on the H₂ generation can provide useful information. Devianto *et al.* [166] investigated the effect of higher alcohols as impurities on the direct bioethanol internal reforming for molten carbonate fuel cells (MCFC) [166]. The activity test revealed that the presence of 1-propanol affected negatively the catalytic activity of Ni/MgO catalysts. 1-propanol was found to be partially reformed and negatively influenced the selectivity. In the contrary, methanol is reported to enhance the yield of H₂. The poisoning effect of higher alcohols (1-propanol, 2-propanol) in the H₂ generation process was also reported by Rass-Hansen *et al.* [167] on the 10 wt % Ni/MgAl₂O₄ catalyst [167]. The presence of higher alcohols was found to favor carbon deposition on the Ni based catalyst. In the same manner steam reforming of butanol was found to show a much greater tendency towards coke deposition than ethanol [168]. However, using Gibbs free-energy-minimisation method Nahar *et al.* [169] predicted that carbon formation can be inhibited when steam reforming of butanol is operated between 600 and 800 °C at 1 bar and at water-to-butanol molar feed ratios of 9–12 [169].

From the existing literature, the current technologies for hydrogen production are absolutely transposable to VOCs valorization into syngas and hydrogen. Steam reforming reaction is the most common and cost-effective industrial process to be envisaged for the H₂ generation from VOCs. The actual challenges facing VOC reforming reaction for H₂ production are in fact common to all reforming processes, which are mainly related to the high operating temperature and catalyst deactivation due to carbon deposition. The nature and origin of VOCs for reforming may arise additional difficulties. The low concentration of VOCs in industrial discharge may require an additional step to enhance the concentration of VOCs before the reforming reaction. Furthermore, the heterogeneous composition of VOCs encountered in an industrial site will complicate the optimization process of operating conditions.

4.2. From Volatile Organic Compounds to Chemicals

An interesting approach and not so intensively studied one, is the utilization of VOCs as reactants in the production of valuable chemicals. There exist actually only a few examples of VOC emission utilization, of which one is related to the utilization of contaminated methanol from pulp manufacturing industry. This section of the review concentrates on these few examples, but also presents some of the current technologies and production processes where the organic compounds are used as raw materials. In certain cases, especially in the production of high-value products, there could be room for the VOC utilization.

Organic reactions in general can be categorized based on the type of functional groups involved in the reaction as a reactant and the functional group that is formed as a result of this reaction. The basic

organic chemistry reaction types are addition, elimination, substitution, pericyclic, rearrangement, photochemical and redox reactions. These may all have a potential role in the VOC utilization applications. To simplify the approach, we have grouped here the VOC compounds based on their functional groups, which classification can be found very often also in emission inventories. For example Piccot *et al.* [170] have made a Global inventory of VOC compounds in 1992 where they classified VOCs into paraffins, olefins, aromatic compounds, BTX compounds, formaldehyde, other aldehyde, other aromatics and marginally reactive organic compounds. Later, Wei *et al.* [171] have classified the VOC emissions in China as alkanes, aromatics, alkenes, alkynes and carbonyls. We have decided to group the different types of VOC in this case as *alkanes*, *alkenes*, *alkynes*, *aromatics*, *oxygenated* and *substituted* compounds meaning the compounds having any other atom than oxygen to replace one or more hydrogen atoms in the organic structure. Table 6 summarizes the typical sources of different types of VOCs.

Alkanes are introduced into the environment due to their extensive use as fuels and chemicals. The production, storage and transportation of oil and natural gas are one of the major global sources of hydrocarbons [172]. Due to the presence of single covalent C–C bonds, alkanes are less reactive compared to the other volatile organic compounds. However, several alkanes are natural metabolites and part of the lipophilic fraction in microorganisms, plants and animals [173,174].

Alkenes are hydrocarbons having one double bond between at least one of the carbon atoms. They belong to the group of unsaturated hydrocarbons and they are also called as olefins since they form oil-type liquids when reacting with gaseous chlorine. Alkenes are the raw materials for several different types of plastics, such as polyethylene, polypropylene and PVC. Alkenes are more reactive than alkanes and they are very often used in addition reactions. Alkene compounds exist also in the nature and they are responsible for the characteristic odors of trees and plants (limonene, myrcene) [175,176]. Some of the alkenes (ethene and propene) are efficient atmospheric precursors for the formation of formaldehyde that is typically the compound found at the highest concentrations in the boundary layer atmosphere. Interestingly, the direct emissions of formaldehyde to the atmosphere are small, and therefore formaldehyde can be used as a good indicator for atmospheric VOC oxidation. Alkene emissions followed by formaldehyde formation are typically emitted from oil refining industries [177,178].

An *alkyne* is a hydrocarbon that contains a carbon-carbon triple bond. Alkynes are less reactive and also less stable than alkenes. Acetylene (ethyne), C_2H_2 , is the simplest alkyne. Combustion of acetylene produces a high-temperature flame, because of its triple bond and high enthalpy of formation [179–181]. Acetylene is one of the main alkyne emission compounds. Typically, acetylene emissions are formed from motor vehicle exhaust (mainly gasoline), industrial processes, as well as wood, biofuel and coal combustion [182,183]. Acetylene is an important source material for the production of several chemicals and carbon materials [184].

The simplest and most industrially important *aromatic compound* is benzene (C_6H_6). Benzene is the precursor for many chemicals, which could further be used as end products or intermediates. Benzene is used to produce for example styrene, phenol, cyclohexane, and maleic anhydride. Toluene (C_7H_8) and xylene (C_8H_{10}) are substituted benzenes. Most of the toluene extracted for the chemical use is actually converted to benzene. Toluene is also used to produce important synthetic intermediates such as nitrotoluene and dinitrotoluenes. Xylenes are an aromatic mixture composed of three isomers, *o*-, *m*-, and *p*-xylene. Xylenes are an important chemical raw material and for example *p*-xylene is an important isomer for producing terephthalic acid to manufacture polyesters [185,186].

Aromatic organic emissions can also be classified as the BTEX (Benzene, toluene, ethyl benzene, *p*-xylene, *m*-xylene, *o*-xylene) and BTX (Benzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene) compounds [185,187]. Furthermore, another significant aromatic emission compound not mentioned before is styrene. Some of the aromatic organic compounds such as the Polycyclic Aromatic Hydrocarbon (PAH) compounds (e.g., Naphthalene, anthracene, phenanthrene) and phenols are classified as the semivolatile organic compounds [188]. BTEX compound emissions cause many environmental problems for groundwater, soil and air [187]. BTEX compounds take part in reactions promoting photochemical smog [189], and they have also high reactivity and ozone production potential [186]. BTEX compounds can cause variety of health problems such as respiratory irritation, and central nervous system damage. Benzene is also a carcinogenic compound [190].

Aromatic VOCs are formed in many industrial processes and are also present in vehicle exhausts. In some industrial processes a significant amount of aromatic compounds emissions are formed. For example in iron and steel industry (included coke making, sintering, hot forming, and cold forming) major emissions are aromatic compounds with 46%–64% of total emissions [191]. Aromatic VOCs are also an origin for the problems caused by urban city air. In Shanghai, the share of aromatic compounds from total VOC concentration is 30% [192] and in Los Angeles 20%–25% [193].

Traditionally aromatic VOCs are treated by different methods, such as catalytic oxidation, ozone-catalytic oxidation, and thermo-photocatalytic degradation. However, the reaction products of these treatment technologies are also an environmental concern (CO, CO₂) [187,194–199].

Oxygenated hydrocarbons are the compounds of hydrogen and carbon having at least one oxygen in the structure including alcohols (–OH), ethers (–O–), ketones (–CO–), aldehydes (–CO–H), carboxylic acids (–COOH), esters (–COO–), acid anhydrides (–CO–O–CO–) and amides (–C(O)–NR₂). The most commonly used oxygenates are alcohols and ethers, since they are used as fuel additives. Acetone and phenol are raw materials for many different products. Oxygenated VOCs in general are emitted from the traffic, solvent usage, industry and some natural sources [200–202]. It can be forecasted that the concentrations of oxygenated VOCs in urban atmosphere will increase due to the use of oxygenates to replace the gasoline.

In this paper, when the *substituted compounds* are discussed, we mean the compounds, where one or several hydrogens of an organic compound have been replaced by another element. For example, total reduced sulphur (TRS) compounds is a group of compounds that typically includes hydrogen sulphide, mercaptans, dimethyl sulphide, dimethyl disulphide and other sulphur compounds that are released to the environment by the steel industry, pulp and paper mills, refineries and sewage treatment facilities [203]. Alkyl halides are a class of compounds where a halogen atom or atoms are bound to an sp³ orbital of an alkyl group with a general formula of RX where R is an alkyl or substituted alkyl group and X is a halogen (F, Cl, Br, I) [204]. Alkyl halides are used as flame retardants, fire extinguishers, refrigerants, propellants, solvents, and pharmaceuticals [205]. Dichloromethane (DCM, or methylene chloride) is an organic compound with the formula CH₂Cl₂. This colorless, volatile liquid with a moderately sweet aroma is widely used as a solvent. Alkyl halides are emissions sources are different industrial processes, e.g., paint removals, plastic industries, and the pharmaceutical sector [206]. The correct catalyst selection for utilization of substituted compounds is especially important, since the compounds themselves are potential deactivating agents for certain catalytic materials.

Table 6. Sources of the VOC emissions.

Sources of the Emission	Major Aromatic Compounds Emissions	Ref.
Vehicles exhaust (gasoline, diesel)	BTEX, trimethylbenzenes, ethylene, propene, 1-butene, ethane, acetylene, oxygenates	[182,183,200–202]
Transportation	1,3-butadiene, benzene, toluene, xylene, formaldehyde, acraldehyde	[207]
Fuel evaporation (gasoline, diesel)	Benzene, toluene, iso-pentane, pentenes, n-heptane	[182]
Biomass burning	BTEX, Benzene (major aromatic emission), acetylene, ethylene, propene, ethane, methylchloride, methanol, formaldehyde	[182,183,207]
Coal burning	BTEX, naphthalene, acetylene, ethylene, propylene, propane, ethane	[182,183]
Petrochemical industry	Styrene, benzene, hexane, methylcyclohexane, trichloroethylene, TRS compounds	[172,182,203,206]
Oil-refinery	Benzene, ethylene, hexane, cyclopentane, cyclohexane, methylcyclohexane, TRS compounds	[172,177,178,182,203]
Painting (Coating for building)	BTEX, styrene, n-butane	[182]
Electronics manufacturing (printed circuite board)	Toluene, 2-ethyl-1,3-dimethylbenzene, 1,2,4,5-tetramethylbenzene, ethanol, acetic acid, iso-propyl alcohol	[186]
Vehicle manufacturing	Toluene, ethylbenzene, <i>p</i> , <i>o</i> -xylene, trimethylbenzenes, ethyl acetate, 2-butanone, acetic acid	[186]
Flexographic Printing	<i>o</i> -xylene, acetic acid, ethyl acetate	[186]
Metal and plastic surface spraying	Ethylbenzene, <i>p</i> , <i>o</i> -xylene, ethyl acetate, 2-butanone, butyl acetate, ethanol	[186]
Furniture manufacturing	Toluene, ethylbenzene, <i>p</i> , <i>o</i> -xylene, trimethylbenzenes, trimethylbenzenes, acetic acid	[186]
Plastic waste recycling plants	BTEX, styrene, 1-butene, 2-hexene, pinenes, hexane, octane, 3-methylnonane	[194]
Iron and steel industry (cokemaking, sintering, hot forming, cold forming)	BTEX, trimethylbenzenes, isopentane, n-pentane, n-butane, methylhexanes, n-heptane, butenes, trichloroethylene, TRS compounds	[191,203]
Industrial solvent use (e.g., solvent production, paint and adhesive use)	Toluene, xylenes, n-hexane, oxygenates, substituted compounds	[200–202,205,207]
Pulp and paper production	oxygenates (mainly methanol), TRS compounds	204
Pharmaceutical industry	substituted compounds (alkyl halides)	207

TRS is Total reduced Sulfur, mixture of organic (e.g., methyl mercaptan, dimethyl sulphide, dimethyl disulphide) and inorganic (e.g., hydrogen sulphide) sulphur compounds.

4.2.1. Potential Existing Technologies and New Considerations for VOC utilization in Chemicals' Production

Burning the alkanes or using them as fuels stays the most common methods of valorization [6,208] due to their higher flammability. Another possibility for the utilization of the hydrocarbons that is under development is the metabolization of them following the aerobic or the anaerobic conversion to valuable chemicals [209–212]. Microorganisms have established effective strategies involving specialized enzyme systems and metabolic pathways to access n-alkanes as a carbon and energy source. The reactivity of the n-alkanes depends on the chain length and some of the short chain alkanes (<C9) may be toxic to micro-organisms. The aerobic alkane degraders use O₂ as a reactant for the activation of the alkane molecule. Oxidation of methane renders methanol that is subsequently transformed to formaldehyde and then to formic acid. In the case of longer chain alkanes, the oxidation starts usually in the terminal methyl group to give the primary alcohol, which is further oxidized to the corresponding aldehyde, and finally converted into fatty acid [210,213]. The alkane-activating enzymes are the mono-oxygenases, which are widely used as biocatalysts in several processes [214–216]. Temperature is an important factor in these processes, since it affects the solubility of the alkanes and the stability of the enzymes. For example stability of mono-oxygenase enzyme CYP P450 in *Aspergillus terreus* MTCC6324 ranges between 25 and 40 °C. The presence of molecular oxygen is affecting the activity of the enzymes as well as pH that needs to be between 7 and 8 to support the required reaction [210].

If the conversion of alkanes into more useful and reactive products, such as alkenes, alcohols, aldehydes, and carboxylic acids can occur under milder and better controlled catalytic conditions, then this can offer large economic benefits [217]. The oxidative functionalization following the catalytic route by functionalizing the C–H bond had been studied widely by many researchers [218–220]. Sivaramakrishna *et al.* [217] have reviewed the progress in the oxidation of *n*-alkanes by heterogeneous catalysis, from the partial oxidation to the oxidation, ammoxidation and the oxidative dehydrogenation, that are the three main processes in the heterogeneous catalysis to functionalize hydrocarbons. A mixed metal oxide catalyst containing Mo, V, and Nb was used in the oxidative dehydrogenation of ethane to ethylene. Supported iron (III) and manganese (III) catalysts in the presence of an oxidant were tested in the hydroxylation of alkanes to alcohols. Vanadium oxide supported metal oxides (e.g., MgO, TiO₂, Al₂O₃, ZrO₂, SiO₂) are an important group of catalysts for a variety of reactions, including selective oxidation of hydrocarbons [217].

Maybe the most important reactions of the alkenes are the addition reactions, especially electrophilic addition. For example ethene can be hydrated to ethanol with using phosphoric acid as a catalyst. However, more interesting direction in practice is the producing ethene from ethanol over Fe-ZSM-5 or carbon-based catalyst, since ethene is considered as more valuable than ethanol [221,222]. Ethene can be converted also to methyl propanoate via methoxycarbonylation over a palladium catalyst [223]. Methyl propionate is used as a solvent for cellulose nitrate and as a raw material in the production of paints and varnishes [224]. Other applications for ethene can be found in large amounts, since it is widely used in polymerization, oxidation, halogenation, alkylation, *etc.* About 90% of ethene is used for production of ethylene oxide, ethylene dichloride, ethylbenzene and polyethylene in Europe and US [225]. Since the production of ethene is growingly increasing and it is produced in several countries, it is unlikely that the ethene from the waste gas would be economically interesting to collect and to be used

in the near future. We have used ethene here as an example of alkene reactions due to its wide applications, even if the first alkenes that can be considered as VOCs are the pentenes, which have a rather low boiling point of 30 °C [226]. Pentene itself is not a very interesting chemical, since it does not have very many utilization areas. 1-hexene is used in polymer production as a co-monomer. Heptane, in turn, is used as an additive in lubricants, but also as a catalyst [227]. Alkenes, in general, are mostly emitted from oil refining, where the organic emissions in general are high, and being the potential industrial sector for the VOC utilization applications.

One possibly interesting reaction of the alkenes is the epoxidation. The epoxides are the main raw materials in the production of several chemicals, and therefore significant amount of research have been published related to the development of catalytic systems for alkene epoxidation. For example, Davarpanah and Kiasat [228] have proposed a novel solid polyperoxoacid catalyst for alkene epoxidation. The polyperoxoacid, that showed good activity, was produced by anchoring and oxidation of polyacrylic acid onto the surface of SBA-Im-Allyl and it showed to be stable and recyclable with the help of H₂O₂ solution. The yields of the epoxides were varying from 52% to 98% depending on the alkene used as a raw material [228]. Ionic liquids have also been used as co-solvents in epoxidation of alkenes. The aim of using aqueous/ionic liquid systems is in enhancing the recyclability of the catalysts.

Crosthwaite *et al.* [229] studied alkene epoxidation by using 2-alkyl-3,4-dihydroisoquinolinium salts as catalysts and Oxone™ as an ionic oxidant. Good results of epoxidation were found with the system they used, however, using the bi-phasic system to recycle the catalyst failed [229]. Pescarmona and Jacobs [230] applied high-throughput experimentation to develop transition metal free catalysts for epoxidation of alkenes. They tested epoxidation of 1-hexene, 1-octene, 1-decene, *R*-(+)-limonene, cyclohexene and cis-cyclooctene over gallium oxide, alumino- and gallosilicates (Al-MCM-41, Ga-MCM-41) and USY zeolites. Gallium catalysts showed high activities and the epoxide yields were improved when selecting the correct solvent for the system [230]. An interesting possibility for epoxide production is coming from the possibility to use microreactors in the production. Salmi *et al.* [231] have studied microreactors in the production of ethylene oxide over silver catalysts. They found out that ethylene oxide can be produced with high selectivity in microreactors [231,232]. The advantage of using microreactors in ethylene oxide production is the safety of the small-scale process that is easier to control and the reaction could be potentially run within the explosive regime and conditions where surplus oxygen is present. The usage of microreactors could be considered also in the case of VOC utilization. They allow flexible production from small to larger scale by adding several microreactors together. In addition, multiple products could be produced from the VOCs parallel and simultaneously. Another important industrial application is the production of aldehydes from alkenes. For example the Wacker-type of reaction is important in synthetic chemistry and pharmaceutical industry [233,234]. More recently, several researchers have reported the development of new types of catalysts for aldehyde production with better selectivities and without the C=C bond cleavage. These materials include palladium, copper, ruthenium, ruthenium(IV)-porphyrin catalysts. With these catalysts the aldehyde yields range between 60%–99%, and especially ruthenium(IV)-porphyrin seems to be very potential homogeneous catalyst for the aldehyde production reaction [235,236]. To conclude the findings related to the alkenes, it seems, that one potential route for VOC utilization could be via transforming the VOCs to different types of alkenes that could be further used in the production of variety of chemicals needed in chemical and pharmaceutical industry.

In the 1950s, acetylene was the one of the most important raw material for the production of the synthetic organic chemicals. Thermodynamically unstable acetylene can be used in many different kind of reaction such as carbonylation, dimerization, vinylation, polymerization, ethynylation, and oligomerization. Today, in many cases ethylene and propylene have replaced acetylene as a raw material, because price of the acetylene is high. Still, acetylene-based routes to produce chemicals have been operated on an industrial scale during the past century. For that reason there exists a lot of knowhow related to acetylene-based processes and therefore utilization of acetylene emissions for chemical production is possible. Typically, acetylene is manufactured from coal. Crude acetylene includes small quantities of impurities, such as phosphine, arsine, ammonia, and hydrogen sulfide. For chemicals manufacturing, the purity of acetylene have to be 99 vol % because impurities may poison the catalysts [180,184]. The demand for the high purity creates challenges for the utilization of acetylene emissions in manufacturing of chemicals. However, development of the new selective catalytic materials can be give opportunities for utilization of acetylene containing emissions also in this case.

In the commercial scale acetylene is used in the chemical industry to produce, e.g., acrylic acid, vinyl chloride, ethylene, acetaldehyde, acetic acid, and 1,4-butanediol [180,184,236,237]. Here we have reviewing shortly some chemical production possibilities starting from acetylene that could be interesting in the future. Worldwide annual production of acrylic acid that was traditionally produced from acetylene, is over 1 million metric tons. Acrylic acid has widely used in the manufacturing of acrylate, monomers for polymer synthesis, and plastics. Today, almost all acrylic acid is produced from propylene, because it is more economical. However, the raw material to produce acrylic acid is dependent on the country. Carbonylation of acetylene with a $\text{Ni}(\text{CO})_4$ catalyst was firstly found by Reppe in 1939. Acrylic acid can be produced by hydrocarboxylation of acetylene with carbon monoxide and water over a catalyst [180,184,238,239]. Recently, many researchers have suggested new catalytic material to hydrocarbonylation of acetylene [238]. Ni_2O_3 and cupric bromide are effectively catalysing hydrocarboxylation of acetylene to acrylic acid. Yield of acrylic acid was found to be 72.1% and selectivity 85.2% with a Ni_2O_3 catalyst at 235 °C [180]. Good catalytic conversion of acetylene (85%) and selectivity of acrylic acid (99%) under mild conditions ($T = 40\text{--}50$ °C) is achieved with a catalyst system consisting of a homogeneous catalyst $\text{Pd}(\text{OAc})_2$, with diphenyl-2-pyridylphospine as the phosphine ligands and trifluoromethane sulfonic acid as the acidic promoter [239]. Hydrocarboxylation of other alkynes is an important reaction for production of α,β -unsaturated carboxylic acids [240,241]. The most widely used catalyst in hydrocarboxylation of alkynes are based on Ni, Co, and Pd [242]. New interesting research area is the use of CO_2 as a renewable and environmentally friendly source material of carbon in the hydrocarboxylation process. The promising results for CO_2 process have been obtained with nickel and copper catalysts [241,243,244].

Worldwide annual production of vinyl chloride is over 30 million metric tons. Most of the vinyl chloride is produced from ethylene although the conversion of acetylene to vinyl chloride is inexpensive process when considering the capital and operating costs [180]. For that reason the utilization of acetylene emissions to produce vinyl chloride could be economically feasible. Vinyl chloride can be manufactured by hydrochlorination of acetylene on commercial scale. Vinyl chloride monomer (VCM) is the main raw material to produce polyvinylchloride (PVC). The traditional processes use mercuric chloride supported on activated carbon, which causes lot of environmental pollution problems. For this reason, new catalysts are developed [237,238,245]. N-doped carbon is used as a catalyst in converting acetylene to vinyl

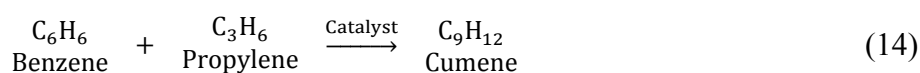
chloride with acetylene conversion 77% and vinyl chloride selectivity >98% [246]. With Au-La/SAC (SAC, spherical activated carbon) catalysts, the conversion of acetylene 98% and selectivity to VCM 99.8% can be obtained [245].

Hydrogenation of acetylene is often used to remove small amount of acetylene in the ethylene feedstock for polyethylene production. Hydrogenation can be used in connection with low concentrations (0.1–1 vol %) of acetylene to ethylene [247,248]. Several types of catalysts are suitable for the hydrogenation of acetylene [249], but the most widely studied hydrogenation catalyst is based on palladium and gold [248–250].

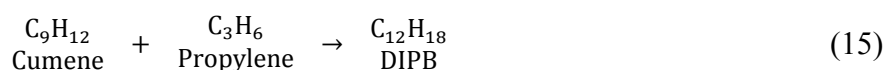
High conversion of acetylene (>99%) and selectivity to ethylene (>70%–80%) are achieved over Cu/Al₂O₃ catalysts modified with different Cu:Pd ratios at the temperature range of 90–100 °C [251]. With gold-based catalyst close to 100% selectivity for hydrogenation of acetylene to ethylene at temperature up to 300 °C is achievable [248]. Good results are obtained for example with a Au/CeO₂ catalyst [249] and a Au/C-TiO₂ catalyst with different Au loadings [248]. BTEX compounds are very important petrochemical intermediates and solvents for the synthesis of organic compounds [185]. A mixture of BTEX emissions compounds or individual compound could be utilized to produce many important intermediates and products. One of the most important processes is the production of phenol from benzene. Phenol is a very important intermediate for synthesis of petrochemicals, plastics, agrochemicals, and pharmaceuticals. Phenols are used in the production of bisphenol A, thermosetting phenolic resins, alkyl phenols, aniline, acetophenone, caprolactam, and other useful chemicals [252,253]. Currently, phenol is produced nearly 8 million tons/year worldwide. More than 90% of the world's phenol production technology is based on the three-step Hock process, which is also called the cumene process. Alternative new methods to the production of phenol are the toluene oxidation and direct hydroxylation of benzene [252–255].

The industrial Hock process is based on a three-step cumene synthesis and oxidation processes. First step of the Hock process is alkylation of benzene with propylene over an acid catalyst to form cumene. Alkylation reaction is catalyzed by, e.g., phosphoric acid, aluminium chloride, boron trifluoride, hydrogen fluoride or MCM22 zeolite. Today, almost all cumene is produced by using zeolite-based processes. The cumene can alkylate with propylene to form diisopropyl benzene (DIPB) by side reaction. The reactions of alkylation are highly exothermic [254–256]:

Main reaction:



Side reaction:



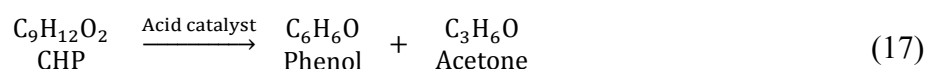
The second step of the Hock process is oxidation of cumene to cumenehydroperoxide (CHP) with air proceeding via a free-radical mechanism that is essentially auto-catalyzed by CHP. (Busca 2008, Schmidt 2005)

Reaction:



Last step of the phenol production is the decomposition of CHP to phenol and acetone. Decomposition reaction is catalyzed by strong mineral acid such as sulphuric acid at 60–100 °C [254,255,257].

Decomposition:



The advantages of the Hock process is the inexpensive raw material (benzene and propylene), and high value useful products (phenol and acetone) [257]. Typical phenol production plant is producing phenol over 500,000 t/year. For example INEOS Phenol is producing almost 2 million tons phenol per year and 1.2 million tons acetone per year [258]. Utilization of the benzene emissions in economic way to produce phenol or other valuable products depends, e.g., price of the products and capital and operating cost of the small-scale plant.

Hydroxylation of benzene is an alternative method for producing phenol (Joseph 2009). The direct hydroxylation of benzene to phenol has potential advantages compared to the cumene process. Hydroxylation process is economic one-step method and no explosive intermediate (cumene hydroperoxide) is formed in the process. Challenge of the process is the thermodynamic limitation, because phenol is oxidized easier than benzene [253,259–261]. Commercially available AlphOx™ process by Solutia Inc. uses oxidation of benzene to phenol with N₂O oxidant. Selectivity to phenol is high 95%–100%, but it is dependent on the used catalyst [255,261]. Benzene's hydroxylation to phenol could be achieved using, e.g., zeolite catalysts containing rhodium, palladium, platinum, or iridium [185], as well as by using Cu-Ca-phosphate catalyst [262]. Multi-step Hock process could be lead to higher capital investment cost than direct benzene's hydroxylation. The simpler hydroxylation process could be more useful for the utilization method. Also, the efficiency of the Hock process strongly depends on price of the acetone. In additional, industrially valuable products can be produced by direct hydroxylation of other aromatic compounds in the same conditions. Therefore different kinds of aromatic emissions mixture could be utilized with direct hydroxylation [257,263].

In addition to N₂O, in hydroxylation of benzene to phenol, also three other oxidants can be used: O₂, H₂O₂, and mixture of H₂ and O₂ [253,259–261,264]. The same oxidants could be used also in hydroxylation of other aromatic compounds. Direct hydroxylation of toluene, ethylbenzene, xylenes and anisole to produce hydroxyaromatic compounds are a significantly less studied topic than benzene hydroxylation. Hydroxylation of toluene is producing *o*, *m*, and *p*-cresol that are valuable compounds to produce for example antioxidants, wood preservers, disinfectants in soap, ore flotation, fiber treatment, and precursors to synthetic tanning agents [264,265]. Hydroxylation of anisole is used to produce methoxy phenols such as *p*-hydroxyanisole [264]. Hydroxylation of toluene and anisole could be carried out over zeolite-based catalyst [266,267], vanadium [264], and iron [268–270]. Hydroxylation of ethylbenzene and xylenes has received limited attention in literature. Generally, ethylbenzene hydroxylation activity is low and often higher temperature and H₂O₂ concentration is needed to increase the reaction rate. Reaction mechanism is also significantly different for ethylbenzene hydroxylation than, e.g., toluene. Major products from ethylbenzene are acetophenone, benzaldehyde and 1-phenylethanol. Also small amounts of the styrene, cumene and phenol are formed [265]. Hydroxylation of *m*-xylene over zeolites produces 2,4- and 2,6-xylenols [271]. Development of new catalyst for hydroxylation of ethylbenzene and xylenes could be achieved higher selectivity and conversion. For example multi-walled carbon nanotube catalysts have been developed for hydroxylation [272]. Studies on the hydroxylation of a mixture of aromatic

compounds could give new knowledge for utilization of aromatic emission compounds as well. At present, aromatic compounds' hydroxylation research is focused on the studies with separate compounds. Table 7 shows hydroxylation process catalysts and operation conditions for selected aromatic compounds.

The bromination and chlorination of BTEX compounds requires a Lewis acid catalyst such as ferric bromide (FeBr₃), ferric chloride (FeCl₃) or chlorides of aluminum or zinc [179,273]. The major disadvantages of the toxic and harmful Lewis acid catalysts are the catalyst disposal difficulties and corrosion problems. Also Lewis catalyst needs to be neutralized after the reaction. Bromination and chlorination of various aromatic compounds over zeolite catalysts are used in many studies [273–278]. Use of the zeolites in the processes will help in avoiding corrosion and disposal problems [273]. Bromination is catalyzed also with chlorides of aluminum and zinc [274]. Nitration of aromatic compounds could be used to produce organic intermediates. Nitration with nitric acid (HNO₃) requires sulphuric acid as a catalyst [179,279–281]. The Figure 3 summarizes possible intermediates and products that are achievable by bromination, chlorination, nitration and hydroxylation of BTEX compounds.

Table 7. Used catalyst and operation conditions hydroxylation of aromatic compounds.

Catalyst	Source compound	Oxidant	Conditions (°C)	Conversion	Product selectivity	Ref.
Zeolites	Benzene	N ₂ O	400–450	N ₂ O: 100%	Phenol: 80%–100%	[255,259]
Palladium membrane	Benzene	O ₂	<250	Benzene: 2%–16%	Phenol: 80%–97%	[259]
VO(acac) ₂	Benzene	H ₂ O ₂	65	Benzene: 11%	Phenol: 100%	[264]
VO(acac) ₂	Toluene	H ₂ O ₂	65	Toluene: 5%	<i>o</i> -cresol 37% <i>m,p</i> -cresol: 56%	[264]
VO(acac) ₂	Anisole	H ₂ O ₂	65	Anisole: 2%	<i>p</i> -hydroxyanisole: 26%	[264]
VOPc ^a	Benzene	H ₂ O ₂	65	Benzene: 22.4%	Phenol: 100%	[264]
VOPc ^a	Toluene	H ₂ O ₂	65	Toluene: 18.74%	<i>o</i> -cresol: 38% <i>m,p</i> -cresol: 57%	[264]
VOPc ^a	Anisole	H ₂ O ₂	65	Anisole: 6%	<i>p</i> -hydroxyanisole: 47%	[264]
Multi-walled carbon nanotubes	Benzene	-	50–70	Benzene: 2%–6%	Phenol: ~98%	[273]
Multi-walled carbon nanotubes	Toluene	-	50–70	-	<i>o,m,p</i> -cresol: <80%	[274]
H-[Al]ZSM-5 zeolites ^b	Benzene	N ₂ O	350	Benzene: 22%	Phenol: ~98%	[267]
H-[Al]ZSM-5 zeolites ^b	Toluene	N ₂ O	350	Toluene: 24%	-	[267]
H-[Al]ZSM-5 zeolites ^b	Anisole	N ₂ O	350	Anisole: 53%	-	[267]

^a Vanadyl tetraphenoxypthalocyanine (VOPc); ^b Zeocat PZ-2/54 Uetikon.

Oxygenated VOCs form a great potential for chemicals production. For example methanol is very important raw material for variety of production. It is commercially used in the production of formaldehyde, esters of different acids that are further processed to the final products. Approximately 30% of methanol is used in formaldehyde production [282,283]. Ethanol, methanol and butanol can also be used as fuels to replace the fossil fuels currently in use [283–287]. There exist also so-called direct-methanol fuel cells that have the potential to be miniaturized and applied in consumer electronics [288–290]. Alcohols are directly used as solvents in production of medicines, perfumes and essential oils [282,285]. Methanol is emitted from pulping industry in rather large amounts [290], and therefore it is a suitable compound for VOC utilization purposes. There exist studies where methanol is used in production of formaldehyde over vanadium-based catalysts [291], but other potential products could be considered as well. An interesting approach to use alcohol is its possible usage in waste water treatment plants as a carbon source for denitrifying bacteria. [292] This could be potential and rather direct VOC emission utilization possibility.

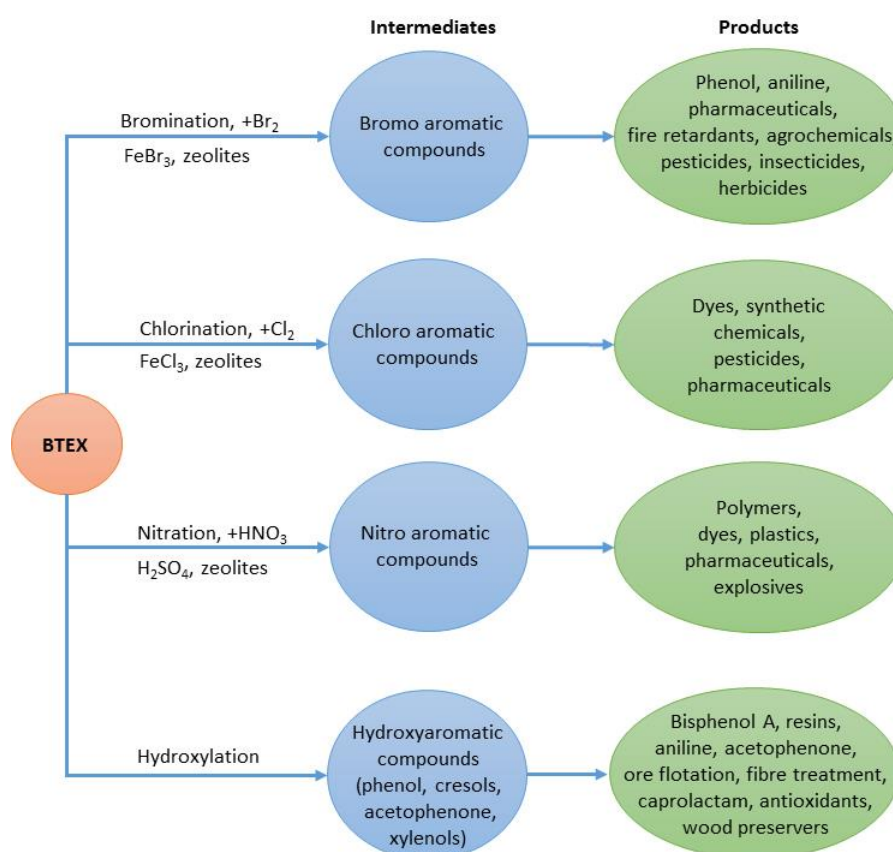


Figure 3. Products and intermediates from BTEX (benzene, toluene, ethylbenzene and xylenes) compounds [179,185,252,253,264,265,274–281].

Ethers are relatively unreactive. They have the uses as solvents for fats, waxes, resins and dyes, for example [293]. Certain ethers find applications as insecticides and they find also important applications in pharmacology. Ethyl ether is used as anesthetic, and codeine is the methyl ether of morphine [293,294]. Codeine can be produced also from diols via chemoenzymatic synthesis [295]. Dimethyl ether is used as a propellant and methyl t-butyl ether (MTBE) is used as octane number increasing additive in gasoline [296]. Dimethyl ether (DME) is considered as a potential alternative fuel for diesel engines,

but it can also be used as a source for other hydrocarbons [297–299]. Yu *et al.* have studied SnO₂/MgO and SnO₂/CaO catalysts in the production of methyl formate, dimethoxyethane and ethanol from DME through catalytic oxidation. The DME conversion of 21.8% was obtained over SnO₂/CaO at 300 °C with the selectivity of 19.1% to methyl formate and 59% to dimethoxyethane [298]. DME can be also converted to propylene over MCM-68 zeolite [300].

Also ketones find applications in pharmacology, since they have important physiological properties. They are present in sugars and different medicines, including steroid hormones and cortisone [301]. Furthermore, they are important chemical intermediates. The most important ketone is acetone, and it is used as a solvent in several applications. Only few ketones are manufactured in a large scale. The synthesis of them can be done via several different ways [301,302]. Ketones are used in for example asymmetric aldol reactions in production of chiral organic structures. Suzuki *et al.* have developed Ca complex structures that can be used as a catalyst in direct asymmetric aldol reaction of acetophenone and aliphatic aldehydes. These catalysts can be used to produce aldol products even with higher than 70% of yield and ee almost 90% [303]. Vetere *et al.* [304] studied hydrogenation of ketones over Pt-based heterogeneous catalysts. The aim was to obtain industrially interesting alcohols that could be used as chemical intermediates of fine chemicals, such as pharmaceuticals and flavors. The main challenge in this reaction is in the optimizing the selectivity of the reaction due to possibility to form several different products [304]. In this purpose, also Ni, Rh, Pd, Ag, Ru-based monometallic catalysts have been studied [305–308]. Unsaturated ketones can be hydrogenated in aqueous medium over anchored Ru(II)-phenanthroline complexes. Desmukh *et al.* [309] applied amino functionalized MCM-41 materials to immobilize the Ru-complexes and tested their activities in 3-methylpent-3-en-2-one hydrogenation to corresponding alcohol. They achieved complete conversion and up to 99% chemoselectivity for the reaction [309]. Chiral tertiary alcohols are produced via alkylation of ketones. They are very important in organic chemistry due to their wide use in pharmaceuticals and appearance in natural products. The main way to produce them is the asymmetric synthesis from ketones by the addition of organometallic complexes derived from Zn, Al, Mg and Li [310].

Maybe the most common use of carboxylic acids is their use in fatty acids in making different types of soaps and detergents [311,312]. They are also used, e.g., in polymer production (maleic acid, terephthalic acid, adipic acid), food preservatives (propionic acid) and beverages (citric acid). Carboxylic acids can be produced for example from aldehydes using Co and Mn catalysts or from alcohols via hydrogenation and using base-catalysts [312]. Carboxylic acid reacts with alcohols to produce esters of which the most important is the polyester [312]. The reduction of carboxylic acids leads to either alcohols or aldehydes, to do this selectively, remains still a challenge. Hydrosilylation of carboxylic acids can be made selectively with using iron-catalyst [313,314]. Recently, it was found that amide bond formation from formamides and carboxylic acids can be achieved over copper catalysts without producing considerable amounts of hazardous waste due to coupling reagents. Amide bonds are present for example in several drug molecules and agrochemicals. Liu *et al.* tested both aromatic and aliphatic carboxylic acids successfully with high yields with Cu-catalysts [315].

Esters are used as artificial flavors and aroma. They can be used in different consumer products and food production and especially they are extensively used in fragrance and flavor industry. They are also used as solvents in paints, for example, and as plasticizers. Nitroglycerin and polyester are well-known examples of esters [316]. Esterification reaction is reversible, and they can undergo hydrolysis under

basic or acidic conditions. Hydrolysis under basic conditions leads to soap formation via saponification [316]. Esters can be also hydrogenated to fatty alcohols over copper chromite catalyst [317] or by iron complexes [313]. Direct reduction of esters to ethers is difficult, but it is possible to carry it out over triethylsilane or variety of Lewis acids [317]. The direct conversion of esters to nitriles is also possible [318]. There exist one interesting potential use for the esters, if we consider utilization of VOC emissions. The methyl esters of fatty acids can be used as bitumen fluxes and therefore in reducing the emissions of VOCs during the road construction [319]. Methyl acetate has also been used as a model for hydrogen production from biodiesel. For example, Rh and Rh/CeO₂-catalysts have been used in this purpose [320].

Converting methyl mercaptan in a gaseous feed to formaldehyde and sulfur dioxide is one rather recent example of the valorization of the TRS [291,320,321]. The process consists of contacting the gaseous stream containing methyl mercaptan with a catalysts under oxidizing conditions for sufficient time. The catalytic materials used during this process can be supported metal oxides or certain bulk metal oxides. Isreal E Wachs studied the activity of different catalysts with different compositions. Supported metal oxides catalysts 1% MO₃/TiO₂, 1% CrO₃/TiO₂ and 1% Re₂O₇/TiO₂ show good activity (around 80% of methyl mercaptan conversion) and important selectivity (around 80%) [320]. The production of formaldehyde from methyl mercaptan is also possible in presence of other compounds (*i.e.*, methanol). Titania-silica-supported vanadium catalysts have been studied in this case [291]. Later, cerium-titanium mixed oxide catalysts where studied in the partial oxidation of the methanol and methyl mercaptan to produce formaldehyde, interesting results were obtained in terms of activity and selectivity [321].

In the beginning of the last century, Krause and Rroka studied production of formaldehyde from methylene chloride. The process consisted of mixing DCM with water in a closed vessel, providing a heating from 140 °C to 170 °C. They found that the production of formaldehyde from DCM is possible [322,323]. From the same family, methyl chloride can be oxidized with air over a catalyst to give formaldehyde and hydrogen chloride. After separating the hydrogen chloride from the reaction products, formaldehyde is obtained. This reaction occur following a catalytic route, where the catalyst consists of particles or pellets of uniform compositions, or it can be an intimate mixture of particles or pellets of two distinct compositions. The first reaction step in which methyl chloride is hydrolyzed to methyl alcohol may be catalyzed by copper chloride, zinc chloride, bismuth chloride or by alumina gel, at a temperature in the range of 280 °C to 350 °C. The second reaction step whereby methyl alcohol is oxidized to formaldehyde is catalyzed by an iron-molybdenum oxide catalyst, which may be enhanced with chromium oxide. Other catalysts that have been reported to oxidize methyl alcohol include vanadium pentoxide and copper. The oxidation reaction is carried out at a temperature in the range of 250 °C to 400 °C [323].

These examples show that there exist indeed several possibilities for the utilization of VOC. It is more likely that economically feasible utilization will be based on the needs of the chemicals in the proximity of where the utilized VOC is produced. This calls for improvements in industrial ecology, Furthermore, the composition of emission mixture is important: Does the mixture contain catalyst poisons? Does it include enough the major compound to make the recovery and separation easier? Will the legislation set requirements for the utilization of gases in the future? What are the most potential industrial sectors for the utilization of VOCs? These questions are still open.

5. Considerations on Catalyst Durability in Utilization of Organic Emissions

As already highlighted before, the catalyst stability is one important issue related to the utilization of the VOC, since VOC emissions are mixtures containing several gaseous compounds and in some cases also solids. The recovery, concentration and purification possibilities are already discussed in detail in Chapter 2 and thus we will not consider the catalyst stability directly related to those aspects here. In general, the selection of the correct catalytic materials is central in VOC utilization. In any case, detailed measurements of the exact composition of the emission would be important to facilitate the selection. It is not very common that the industry knows the exact composition of their emissions, since the emission follow-up programs are related to those compounds that are limited or measurements are required by authorities. Also, one industrial site contains typically several different sources of emissions that compositions are different, which complicates making the general guidelines on the catalyst selection for example. This is why we approach here the catalyst durability through few case examples and by this way aim to demonstrate the importance of the issue.

In methane conversion, catalyst deactivation is a serious problem, which can occur due to various factors such as gas impurities and process conditions [324]. Firstly, the natural gas (NG) or landfill gas (LFG) quality is critical in processing methane further to syngas and hydrogen. Methane from LFG (40%–49% CH₄, 50% CO₂, traces of sulfides, chlorinated compounds, heavy metals, siloxanes, *etc.*) and coal bed methane (CBM, typically 30%–98% CH₄, other hydrocarbons, CO₂, H₂O) are the industrially relevant feedstocks for utilization [325–327]. Fossil based NG consists of many trace impurities as well, such as heavier hydrocarbons, sulfides and nitrous oxides besides CO₂. The contaminants such as H₂O, CO₂ and H₂S exist also in the extracted coal bed methane (CBM) [325]. The main causes for the catalyst deactivation in processing CBM are mainly fouling of the surfaces by ash (Na, K, Ca, and sulphates), chemical poisoning by sulfur and As compounds, hydrothermal sintering and fly ash erosion and abrasion [55]. Developing a catalyst which is sulfur resistant can be achieved by using high oxygen storage materials (such as CeO₂, ZrO₂), which reduce also the coke formation [57,328].

Large amounts of water is released during CBM production, thus there exist a big challenge in water management in a cost-effective and environmentally acceptable way [325,329]. One option in utilizing the methane and CO₂ along with huge quantity of water can be the combination of steam and dry reforming of methane to syngas. The addition of water has both positive effect, *i.e.*, by reducing coke formation and negative effect by energy consumption and re-oxidation of Ni particles to NiO. Nickel supported on alumina based catalysts is widely used industrially for steam reforming of methane and also studied extensively in methane dry reforming. Most common poisons, which are found in NG or coal mine streams are H₂S and As, which deactivate Ni catalysts. The traces of impurities and contaminants can poison the Ni particles and also enhance the coking during the reaction [55,56]. In syngas production via methane dry reforming, the carbon formation is inevitable during the reaction. Carbon diffuses to material and forms filamentous carbon around Ni particles at high temperatures. In order to avoid carbon formation during methane reforming, high steam to carbon ratio is used. Another common deactivation phenomena is Ni sintering at high temperatures, which can be solved by adding promoters (e.g., K, Ca, Mg), stabilizers (e.g., La and Al), and co-catalysts (e.g., noble metals Pt, Pd, metal oxides) and thus, enhance the catalyst durability [55].

The pulp mill chip bin emissions contain in addition to methanol and sulfur-containing volatile organic compounds also hydrogen sulfide, terpenic compounds, amines, higher alcohols, amines, water vapor and solid particulates [290,291,330,331]. Sulfur is a well-known catalyst poison, as discussed above, which is studied very widely in different applications [332–334]. There exist different solutions to avoid sulfur poisoning such as addition of sulfide-forming metal or an oxide sorbent to the catalyst [55]. It is also a good strategy to avoid the materials known to be sensitive to sulfur poisoning, if possible. Examples of sulfur-tolerant materials are the noble metals (except Ru) and high oxygen mobility/storage supports such as ceria, zirconia or their mixed oxides. Gd doping has been observed to improve sulfur tolerance [335].

Emissions of pharmaceutical industry are very complicated due to the batch-type of production. It means that the composition of the emissions may change in connection of different products made. Pharmaceutical industry uses substituted organic compounds, e.g., chlorinated compounds, for example as solvents [336]. In addition to chlorinated compounds, the emissions typically contain oxygenated organic compounds, such as, acetone and ethyl acetate. In these cases, for example Pt/Al₂O₃-CeO₂ catalyst seems to be stable at least to some extent [337]. However, it is always possible that platinum is gradually volatilized by the formation of PtCl₄ [338]. As catalyst support material, Ce-Zr mixed oxides show interesting behavior against Cl-poisoning [339].

To conclude, in the cases of VOC utilization to produce chemicals, the most significant deactivation mechanism is poisoning that is more pronounced in connection of utilizing the substituted compounds. When it comes to syngas production, several deactivating phenomena exist depending on the source of the gas. If proper purification of emission before reforming is done, the major cause of deactivation at high temperature is sintering and at low temperature, the coking. Regarding the potential catalytic materials, noble metals seem to be a good choice as well as high oxygen mobility support materials.

6. Economic Issues Related to Utilization of Organic Emissions

To get an idea about economic issues related to utilization of volatile organic compounds emissions, certain subjects need to be summarized. As a starting point, the emission amounts and sources give a view what is the maximum potential of the utilization of VOCs. Assessment of the sources of the emissions can be used to evaluate the industrial sectors that could be potential users of the utilization technologies. The replacement of the emission treatment system by a process that is able to utilize the emissions is still possible in many cases. The feasibility of different options depends on the qualities of emitted compounds and the need of the products made via utilization. It has been estimated by the U.S. Department of energy that in short term, the market for the utilization of the industrial VOC emissions as the fuel is limited to industrial plants that produce and collect the volatile compounds [9].

The NMVOC emissions, reported by EEA (European Environment Agency), have decreased by 57% compared with 1990 levels in European countries. In 2011, the most significant sources of NMVOC emissions are solvent and product use (43%), commercial, institutional and households (17%), road transport (15%), and industrial processes (8%), energy production and distribution (10%) (see Figure 4). The decline in emissions since 1990 has primarily been due to reductions achieved in the road transport sector due to the introduction of catalytic converters [324].

Different emission data registers and research inventories are using different kind of classification to the industrial sectors that emit NMVOC. The European Pollutant Release and Transfer Register (E-PRTR) divides the NMVOC emissions into nine sectors:

- (1) Energy sector
- (2) Production and processing of metals
- (3) Mineral industry
- (4) Chemical industry
- (5) Waste and waste water management
- (6) Paper and wood production processing
- (7) Intensive livestock production and aquaculture
- (8) Animal and vegetable products from the food and beverage sector
- (9) Other activities

E-PRTR contains annual data reported from 28,000 industrial facilities in Europe. In year 2012 the total NMVOC amount from these facilities was 457,862 t. The biggest emitters were mineral oil and gas refineries (27.9%), surface treatment of substances, objects or products (15.6%), and industrial scale production of basic organic chemicals (14.2%) as presented in Figure 5. United Kingdom, Spain, France, Germany and Norway are the top five countries when checking the releases per country [340].

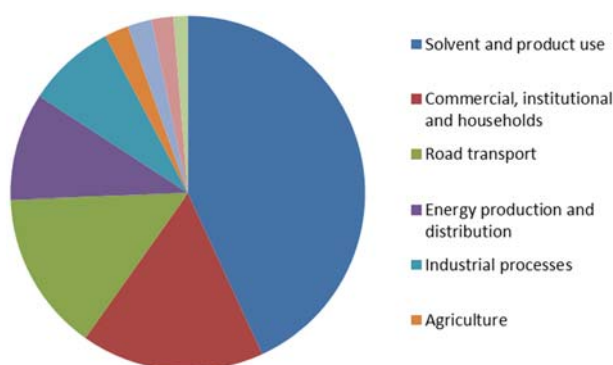


Figure 4. NMVOC emissions shares from different source categories in European countries in 2011 (Data collected from [324]).

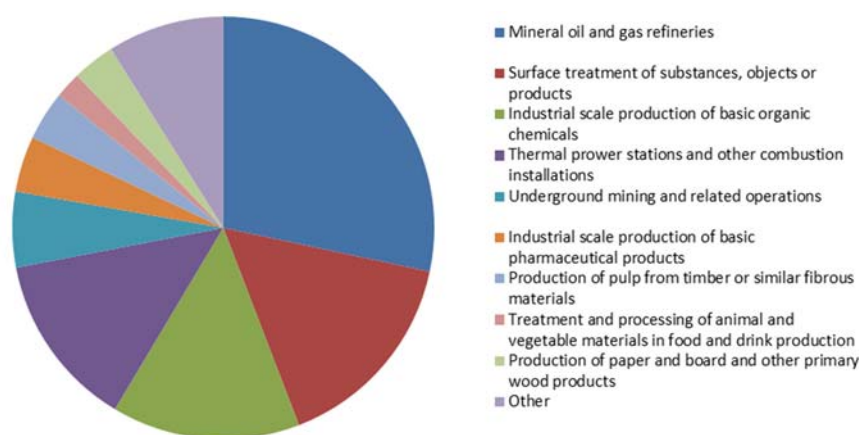


Figure 5. NMVOC (Non-Methane VOC) emission shares from European industrial facilities in 2012 (Data collected from: [341]).

When we consider different types of VOCs, as an example, Theloke *et al.* [342] have reported the share of the total VOC emissions (in Germany 1998) from four different categories; transport, solvent use, production and storage processes and combustion processes. From these sources, 33% of the VOC emissions were alkanes, 23% aromatics, 14% alcohols, 8% alkenes, 5% esters, aldehydes 4%, glycol derivates 4%, and 3% ketones. It is clear that different emissions sources have different profiles of compounds (see Table 8); for the solvent use the three biggest groups are alkanes 28%, alcohols 24% and aromatics 22%. For transport the shares for the three largest groups of compounds are 41% alkenes, 27% aromatics and 16% alkenes. For stationary combustion the three biggest are aromatics 37%, alkanes 29% and alkenes 19%. For production processes, the shares are alkanes 31%, alcohols 29%, and alkenes 15%.

Table 8. Division of emissions to substance classes (data from Germany 1998) for different emission sectors [342].

substance class	Solvent use (%)	Transport (%)	Stationary combustion (%)	Production processes (%)
alkanes	28	41	29	31
alkenes	1.3	16	19	15
alkynes	-	3	4	0.03
aromatics	22	27	37	5
alcohols	24	-	-	29
aldehydes	-	9	8	4
esters	9	-	-	-
ethers	1.3	-	-	2.4
ketones	6	1	2	0.2
glycol derivates	7	-	-	-
halogenated hydrocarbons	1.3	-	-	2.7
carbonic acids	0.1	-	-	-
not allocated	-	3	1	11

To get more global view, United States and China are important emission inventory areas as well. U.S. EPA (United States Environmental Protection Agency) categorizes the anthropogenic VOC sources to five different groups [343]:

- (1) Stationary fuel combustion
- (2) Industrial processes
- (3) Highway vehicles
- (4) Non-road mobile
- (5) Miscellaneous excluding wildfires

In the U.S. the VOC emission data is collected and estimated by the National Emission Inventory (NEI). According to NEI data, total estimated VOC emissions from anthropogenic sources was 18,169,000 t in year 2011. Compared to 1990 the decrease is 35% [343]. In 2005 the NMVOC emissions in China were estimated to be 20.1 Tg. The dominated emission sectors were industrial and domestic solvent use (28.6%), road transportation (23.4%), and biofuel combustion (18%). The estimation for year 2020 is 25.9 Tg [171,207,344].

The cost of air pollution is also a key point in this discussion whether the companies should change from current situation and to invest to utilization of VOC emissions. To compare the current situation, it is known that the costs of air pollution from the 14,325 largest polluting facilities in Europe were between 59 and 189 billion euros in 2012. 50% of these costs are result of just 191, or 2% of the facilities. Power generation sector was responsible for around 70% of the total damage costs from industry. Of the top 30 facilities causing the highest damage, 29 were power-generating facilities [345]. It shows that the efforts to find industry that could be interested in utilization of emission gases could be started with few companies. It should be interesting that the high costs caused by air pollution could be converted to incomes when converting the emissions in valuable substances.

However, it seems important that the economics of the utilization needs to be considered case by case. There are emission streams available as well as raw materials to utilization processes, but whether the economic benefits will come from energy usage or chemical production is strongly case dependent. The costs caused by the air pollution could be minimized by utilization of the gases. This should be clearly shown to the polluting industry to increase their interest towards sustainable production.

7. Utilization of VOC Emissions and Sustainability

Environmental catalysis is defined as the development of catalytic materials suitable for abatement of environmental pollutants or to be used in more sustainable and environmentally sound production processes compared with the existing ones [346]. Catalysis has been used already for around 30 years in emissions abatement, e.g., in SO_x , VOCs, automotive exhaust gas purification via converting them to less harmful compounds [347]. The new trend that has started with the CO_2 emissions is to convert the harmful compounds by catalytic processes to valuable products, chemicals, materials and fuels or fuel compounds [348]. VOC emissions that are very often just released into the air as such or after oxidation, offer an excellent starting material for these processes. An important opportunity exists in finding a process route that captures VOCs in, e.g., flue, process and exhaust gases and converts these molecules over preferably a single catalyst composition to valuable compounds [349]. There are still many opportunities for innovations and understanding of these new approaches, e.g., catalytic membranes, hybrid materials, catalytic microreactors. The design and use of catalysts for environmental protection along with their use in processing valuable compounds out of, e.g., gaseous emissions like VOCs is a challenge and a highly motivating field for scientists in the future. The parallel design of the whole process for emissions utilization with separation, purification, concentration and catalysis units or their combinations will be done in the future in a sophisticated manner and the use of catalysts for these purposes will probably show the greatest growth in demand.

Sustainability in, e.g., the chemical industry and sustainable production are the ‘creation of goods and services using processes and systems that are non-polluting, conserving of energy and natural resources, are economically efficient, safe and healthful for workers, communities, and consumers, and socially and creatively rewarding for all working people’ [350]. In sustainable production the goal is to minimize energy use, waste generation and environmental hazards, and to improve process safety [351–353]. When designing new processes or improving the existing ones it is important to guarantee that sustainability assessment is comparable and relevant. There are many ongoing approaches to develop analysis tools for assessing the sustainability of production processes and for defining common criteria

for analyzing sustainability [354,355]. Sustainable production concerns products and services, process design and operation, wellbeing of workers in, e.g., the chemical industry [356]. According to the green chemistry and engineering principles products, processes and services should be safe and ecologically sound throughout their life cycle and appropriate, designed to be durable, repairable, readily recycled, compostable, and easily biodegradable [354–356]. Development of 3D multidimensional sustainability assessment methods including environmental, economic and social sustainability aspects and criteria for processes utilizing, e.g., VOCs existing in various gas streams, *i.e.*, flue, process, exhaust gas streams is very important. Significantly improved capabilities to master and increase sustainable utilization of VOCs exist over novel catalysts and wise selection of process units.

Nanostructured catalytic materials are seen to offer excellent ways to enhance the sustainable use of gaseous emissions since they have excellent features such as better control of activity, selectivity, and deactivation of catalysts. Research in catalysis nanoscience has dealt with the research questions raising from the relationship between catalyst synthesis and active site structure on the atomic- and nanoscale, reaction mechanisms, and catalyst activity, selectivity, lifetime. The outcomes including utilization of VOC emissions will have a great impact on chemicals manufacturing in the future both from environmental, societal and economic perspectives. Process integration at the nanoscale offers as well new tools for process design [357–359].

From the traditional areas of VOCs abatement, research activities are extending to a wide range of applications including, e.g., the use of VOCs in chemicals and fuels production. In all these applications catalysis is the essential tool to enable sustainable production. Catalysis offers not only the way of abating the VOCs' odors, their atmospheric reactivity and harms in the working environment but also provides excellent options for novel and sustainable products.

8. Conclusions

As discussed in the review, the utilization of the VOC emissions is an economically interesting, environmentally sound idea that supports the sustainability of the processes. Currently, the most common way of utilization of VOC is in the energy production. Some of the organic compounds studied find also use in fuels production. If we think the future in a short term-production of synthesis gas and hydrogen seems to be the most straightforward way to utilize VOCs. The VOC emissions have high potential in that application area. In the longer term, more specific low temperature processes in the utilization of organic gases will come into the picture. For example, utilization of non-thermal plasma, photocatalysis and biocatalytic processes become more realistic especially in the case of methane. If we consider chemicals production from the VOC, the currently existing possibilities are not numerous. However, the potential of the VOCs in chemicals production is very wide—even high-value products could be made. When we consider the different emission sectors, namely solvent use, transport, stationary combustion and production processes, the emissions of aromatic compounds, alcohols and alkanes are quantitatively highest. Therefore, currently these are the most potential groups of compounds to be considered in the utilization purposes. When considering the utilization of emissions originating from certain industrial sector, it is important to keep in mind the need for the recovery and pre-treatment technologies (separation, purification, concentration). Also, the flexibility of the utilization process would be important in the situations when potential emission streams change or the markets of the certain products change.

Careful selection and development of catalytic materials and reactor technologies take an important role in this approach, especially when the emission streams contain catalyst poisons or if the utilized compound itself contains heteroatoms that may cause catalyst deactivation. The utilization of VOC is a very interesting research area and it offers wide possibilities for further studies.

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Author Contributions

Satu Ojala is the first and corresponding author of the manuscript. She designed the general contents of the manuscript and invited the other writers to join the work. All the other writers have expertise in the topical area they contributed. Satu Ojala also wrote introduction, conclusions and participated writing of VOC utilization section. She is the second supervisor of the doctoral studies of Niina Koivikko, Tiina Laitinen and Anass Mouammine. Niina Koivikko wrote the Chapter 5 and participated to the background survey for designing the contents of the manuscript. Tiina Laitinen and Anass Mouammine participated writing the VOC utilization in chemicals production. The work described here related to the VOC utilization in the chemicals production, is related to the thesis works of Niina Koivikko, Tiina Laitinen and Anass Mouammine. Prem Kumar Seelam took the complete responsibility on Chapter 3, Said Laassiri wrote the Chapter 4.1. Kaisu Ainassaari was responsible on writing the Chapter 2 and Riitta Keiski wrote the Chapter 7. Riitta Keiski is the principal supervisor of Niina Koivikko, Tiina Laitinen, Anass Mouammine and Kaisu Ainassaari. Rachid Brahmī is the supervisor of the doctoral work of Anass Mouammine.

Conflicts of Interest

The authors declare no conflict of interest.

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