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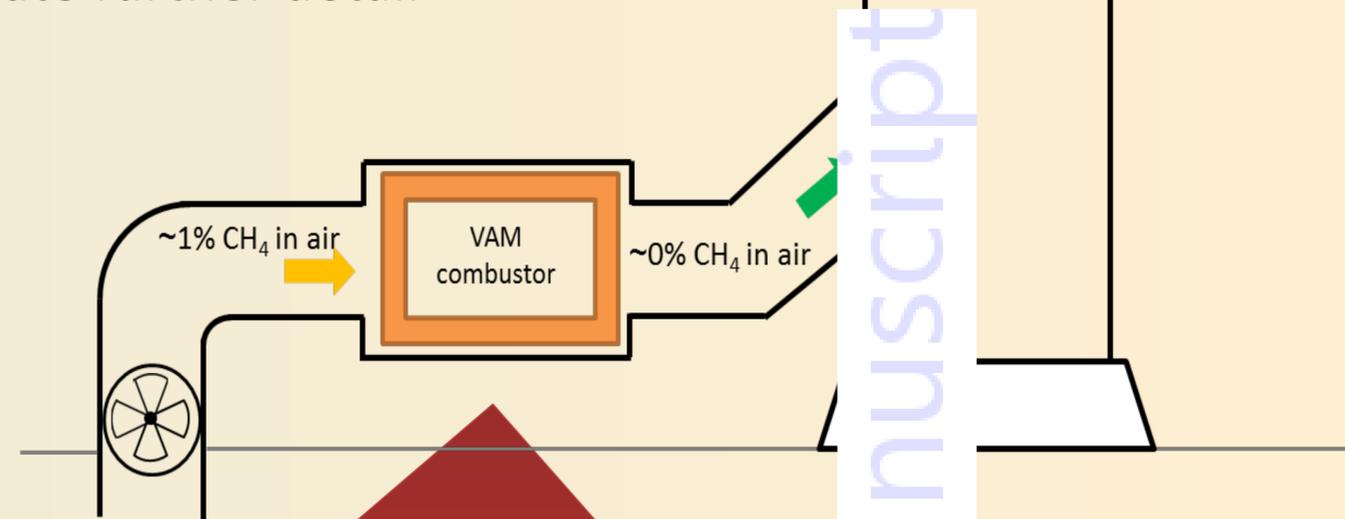
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Coal-mine methane leaks to the atmosphere and urges actions from the stakeholders to mitigate/utilize the emission. This paper reviews the challenges and opportunities of any technological options together with their benefits and drawbacks. A specific discussion is expanded on the current progress of flameless combustion technology with a few highlights on Pd-based catalyst development and important practical aspects which necessitate further detail investigation.



1 Identify: problems, opportunities, challenges

2 Survey current state of the art technological options: benefits & drawbacks

3 Develop enabling technology

4 Develop material and testing equipment

A review on the development of combustion technology for methane emitted from coal mine ventilation air systems (VAM).

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Abstract

Fugitive gas emissions from coal mining are widely known as significant contributor to the emission of alkanes, mainly methane to the receiving environment. Utilization of coal mine ventilation air methane (VAM) is a crucial mission in order to minimize methane emission in atmosphere. This paper reviews current technological option for mitigation and utilization of methane emission from coal mining. Challenges and opportunities of each technology were discussed together with their benefits/ disadvantages. Discussion on the option of technology recommends catalytic combustion technology as a more prospective option due to the low and variable concentration of methane in coal-mine ventilation air, as well as its high volumetric flow. In this review, a specific discussion is expanded on the current development of flameless combustion with a few highlights on Pd-based catalyst development. The remaining uncertainties and obstacles in development of Pd-based catalysts for VAM are discussed in detail. This paper highlights a few important practical aspects which necessitate further detail investigation such as catalyst deactivation phenomena, the stability of catalyst under humid conditions, the effect of coal dust on catalytic activity and stability. It is noteworthy that the pressure drop, heat recovery/ self-sustaining and long term deactivation are the key for a successful development of VAM catalytic combustor.

1. Introduction

Fugitive gas emissions from coal mining are a significant contributor to the emission of alkanes, mainly methane to the receiving environment. Methane has a greenhouse gas potency 25 times greater than that of CO₂ ^[1], and as such the total oxidation of methane to carbon

dioxide is seen as a technological option to reduce net greenhouse gas emissions from underground coal mining. In excess of 60% of the total coal mining-related methane emissions originate from the ventilation air system.^[2, 3] The successful development of a technology for methane mitigation and utilization would greatly reduce greenhouse gas emissions associated with coal mining.

Many research groups, including those in universities, government laboratories and industry, are assessing the technical requirements and challenges associated with treatment of ventilation air methane (VAM) streams. The technological developments for methane mitigation and utilization are described, including their benefits and drawbacks.

This review commences with the discussion on catalytic combustion in general, followed by a specific discussion on the process of methane total oxidation. Subsequently, current progresses in catalyst investigation for methane combustion are discussed, *i.e.* supported palladium catalysts, gold-based catalysts and single metal oxide catalysts.

2. Characteristic of ventilation air methane (VAM)

Developing an efficient technology for VAM utilization and mitigation requires detailed information on the characteristics of coal mining emissions. In general, coal-mine ventilation air consists of nitrogen, oxygen, methane, carbon dioxide and water vapour, where the methane concentration is below 1%.^[3-5] Traces of CO, C₂H₂ and higher hydrocarbons, He, H₂, HCN, NH₃, NO_x, H₂S, SO₂ or organic sulphur compounds, fine coal dust and CaCO₃ particles are also present.^[5, 6]

The characteristics of ventilation air methane was investigated in detail by Shi Su and co-workers at four mines located in eastern Australia.^[4] It was found that in addition to air, the mine-ventilation streams contained CH₄, H₂O, and traces of CO, H₂S and SO₂. Methane

concentration varied considerably but was below 1% while H₂S and SO₂ concentrations were less than 1 ppm. CO spikes were detected at a maximum of 28 ppm during shift changes which was attributed to diesel equipment being started. Humidity measurements suggested that the ventilation air of all mines tested varied between 70% and 100% relative saturation. It was reported also that the effect of mining activities on the concentration of methane in the ventilation air was significant. During mine production, many coal and other particles (such as calcium oxides, iron oxides, clay, quartz etc.) were detected. The dust loading was 4.47 mg m⁻³ with the maximum particle size of 0.5 mm. A low concentration of particles was observed in the VAM stream when the mine was not producing. In general, the flow rate of “gassy” mines ventilation air (VA) stream is ranging from 150 m³ s⁻¹ to 300 m³ s⁻¹ however methane concentration, temperature and flow rate is not constant, especially when mine operations are changing.

Based on the above-mentioned characteristics of VAM of the gassy mines, catalytic combustion technology would be a prospective way to mitigate the methane emission. This is due to its capability to oxidise lean methane in air mixtures, even those with fluctuating methane concentrations. A relatively low reaction temperature characteristic of this flameless combustion brings a great benefit in designing a self-sustainable system for capturing the energy and oxidising methane. Moreover, NO_x emissions can be avoided if the combustion occurs at low temperatures.

3. Technology options for utilization and mitigation of VAM

The low concentration of methane in mine ventilation air, and the presence of water vapour and solid particulates, generate challenges with respect to utilisation and mitigation. The typically high volumetric flowrates of mine ventilation air leads to significant contribution to

the world's anthropogenic methane emission (*ca.* 8%). This requires either treatment in its dilute state, or the concentration of the feed stream to levels that can be used in conventional methane-fuelled engines.^[4]

In general, mitigation and utilization technologies of VAM are classified into two categories, ancillary uses and principal uses.^[7-9] For the ancillary uses, the mine ventilation air is used as supplemental fuel, added to input air of various combustion systems. Only a fraction of VAM gas can be used with this technique, while the remainder of the methane gas is released to the atmosphere. As principal use, VAM gas is utilized as the primary fuel and oxidized in a reactor primarily with the aim of reducing net greenhouse gas (GHG) emissions, as well as producing heat or electricity. Selection of one of these options for providing the best solution for a mine depends on several factors including: (a) highest return of investment, (b) governmental policy such as carbon credit only for ventilation air methane or for all the mine methane, (c) site conditions on the mine site, and (d) mine safety requirements.^[7]

3.1. Direct combustion options

Fig. 1 illustrates the current technological options available for VAM mitigation and utilization. Some options make use of ventilation air as a combustion air for above-ground installations such as boilers, engines and turbines to provide heat or power at the mine site. Using these options, the energy recovery of the process is quantifiable, but only contributes a small percentage of the total fuel used for conventional gas turbines and gas engines.^[10] The safety aspects of the connection between the unit and mine shaft also becomes a major factor. A decoupling of the mine shaft and the above ground VAM mitigation facility is necessary. The presence of coal-dust in mine ventilation air leads to a higher cost of filtering of the dust. The impact of coal-dust can be reduced if the VAM stream is utilized in pulverized coal-fired boiler,

however it is rare that a pulverised fuel power station is in operation in close proximity to an underground coal mine. Fluctuations in the total flow rate and the concentration of methane in the mine ventilation air may negatively influence the performance of the boiler and other equipment at a power plant. For instance, a rapid drop in VA flow rate could instantly decrease the air supply for boiler and interfere the combustion process. Conversely an increase in methane concentration of mine VA can result in overheating and subsequent boiler furnace tube damage.

The use of coal mine ventilation air in hybrid waste/coal/tailings/methane combustion systems was considered as an alternative option for methane mitigation. It is anticipated that this technological approach could mitigate VAM and utilise waste coal, as well as recover waste energy for power generation. Oxidizing methane in a fluidized bed is a potential approach for the use of ventilation air methane in pulverized coal boilers. However, implementation of this technology poses considerable technological challenges such as pressure drop imposed by the fluidized bed. Additional systems/regulations are needed to control the combustion process and provide a sustainable operation.

To hybridize coal mine waste methane and waste coal, several companies have developed rotating (rotary) kilns, however maintaining the stability of the combustion process requires input gas or fuel of high and relatively constant concentration. Somewhat disappointing process performance was reported when the rotary kiln was fed with low grade solid fuels, such as anthracite culm and difficulties in relation to maintaining sustained combustion, even when large quantities of supplemental fuels were used.^[11]

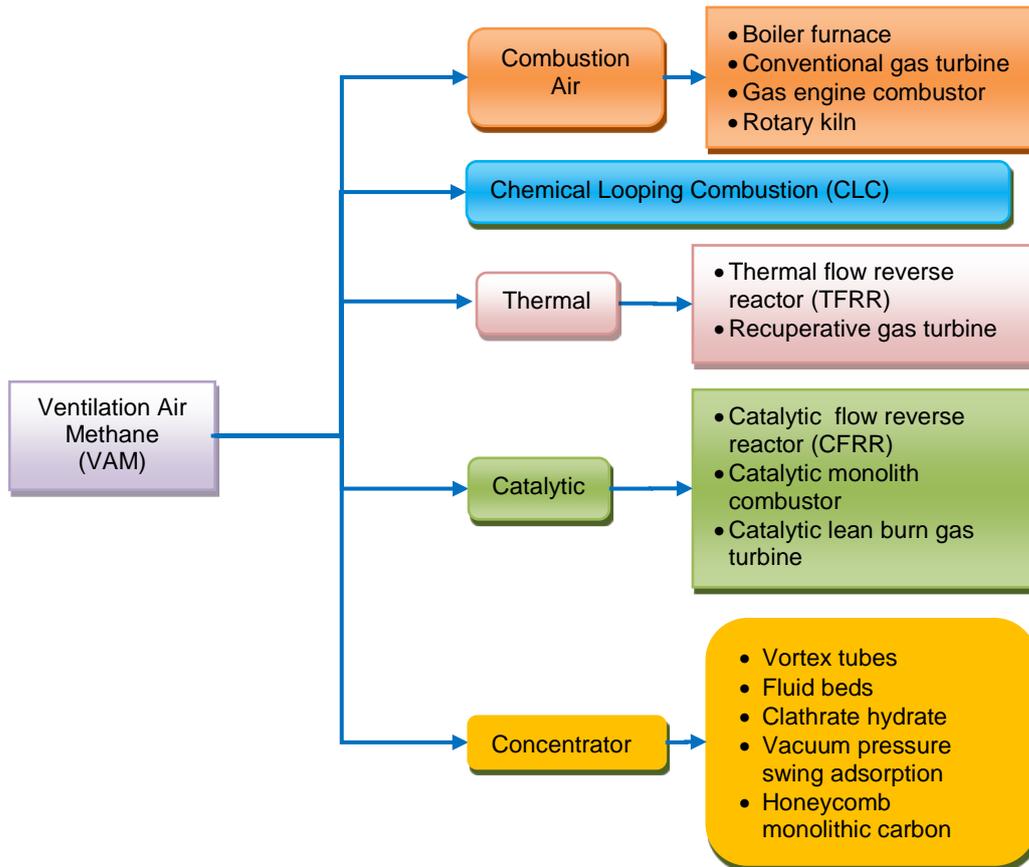


Fig. 1. Technologies for ventilation air methane

Fluidized bed technology can also be used to combust waste coal through mixing with ventilation air methane. During the combustion process in fluidized beds, solid fuels are suspended by upward-blowing jets of air, resulting in the turbulent mixing of gas and solids. The bubbling fluid provides a media for high chemical reaction rates and rates of heat transfer. The mixing action of the fluidised bed can facilitate flue gases contacting with a sulphur-absorbing chemicals, such as limestone or dolomite that has been added to the bed.^[7] This insight was reported during studies in Pennsylvania, where there are 14 circulating fluidised bed combustion (CFBC) power plants burning waste coals including anthracite culm. These power plants successfully operate using advanced CFBC technology which can directly fire unprocessed waste coal.^[12] Nevertheless, for hybrid waste coal/methane fluidized bed

combustion, more experimental studies are needed to establish that the methane can be fully combusted.

Internal combustion engines are also considered as possible option for VAM mitigation and utilization. In this technology, high methane concentration is used as the primary fuel to generate electric and the mine ventilation air is introduced to the engine as combustion air. The capital cost required is relatively low if the engines can be located near the coal mine, and thus no or minor additional costs are involved with supplying the VAM stream to the engines. However, since the combustion process takes place at high temperatures, the formation of NO_x is notable^[10] and the presence of coal-dust becomes a major concern. Although the capital cost is relatively low, only a small fraction of methane in ventilation air can be utilized in internal combustion engines. Likewise, a small percentage of methane in ventilation air can contribute to the total fuel consumed in a conventional gas turbine. Coal mine ventilation air can be used for diluting the combustion process and cooling the turbines, however it is likely that methane passes through the turbine without combustion. To deal with this problem, more complex turbine systems are required including a compressed ventilation air system.^[7]

3.2. Chemical looping systems

Combined process of thermal and catalytic oxidation systems can potentially be implemented in a chemical looping system for ancillary use of ventilation air methane. Recently, Zhang and co-workers proposed three chemical looping based systems as alternative pathway for utilization of ventilation air methane.^[13] The proposal includes (i) converting VAM to hydrogen in a dual loop chemical looping process, (ii) thermal oxidation of VAM using an integrated gasification chemical looping and (iii) utilization of VAM as oxidizing agent in chemical looping combustion of synthesis gas.

The first option was proposed to employ a Cu-based chemical loop to separate oxygen from the VAM gas and a Fe-based loop to reduce methane of oxygen depleted VAM stream as well as produce pure hydrogen.

The second proposed pathway is to oxidize methane in a novel VAM combustor (VC) system with hydrogen as supplementary fuel. The hydrogen supply is from an integrated gasification chemical looping combustion (IGCLC) of coal. Feasibility study of an integrated IGCLC-VC was performed using thermodynamics method. It was reported that the VC temperature was higher than 915 °C at methane concentration as low as 0.1%. Thermodynamically, this process is feasible, however the VAM flow rate and methane concentration are the main factors affecting the overall performance of the system.

The third option is an ancillary used of VAM gas as combustion air in chemical looping combustion of synthesis gas. It was suggested that methane is oxidized in an air reactor in the presence of iron oxide as oxygen carrier.^[14] Similar to option 2, thermodynamic simulation showed that variations in methane concentration and flow rate resulted in reactor temperature change. The progress of this technology for VAM treatment has not been demonstrated experimentally and thus is still at an early stage. There are technological barriers that must be overcome prior to installation of pilot scale plant such as a large fraction of N₂+CO₂, a decrease in CO₂ capture rate, stability of metal oxides during reduction-oxidation cycles etc.

3.3. Flow reversal reactors

Another group of technologies available for VAM mitigation and utilization is to thermally or catalytically oxidize the lean methane mixtures to CO₂. Using these options, VAM can

potentially be utilized as a primary fuel in combustion processes. However, the use of VAM will only be effective if the combustion system can operate at methane concentrations below its flammability limit. In this group of technologies, VAM gas is used as the primary feed for thermal flow reverse reactors (TFRR), catalytic flow reversal reactor (CFRR), catalytic monolith reactors, lean burn gas turbines and concentrators/membrane reactors.

Thermal flow reversal reactors (TFRR) employ the flow-reversal principal to transfer the heat of combustion initially to a solid medium then back to incoming air to increase its temperature until it reaches the auto-ignition temperature of methane.^[15] A TFRR system consists of a ceramic or silica gravel bed located in the centre of the reactor and electric heating elements as the bed pre-heater. Fig. 2 illustrates the flow-reversal process of this system. Initially, ventilation air is fed from one end to the reactor by opening valve A, and heated until the oxidation takes place close to the centre of the particle bed. When the temperature at the downstream end of reactor reaches the oxidation temperature ($> 1000\text{ }^{\circ}\text{C}$), the direction of airflow is automatically reversed, allowing the incoming VAM gas flow through valve B to encounter auto-oxidation temperatures near the centre of the bed where methane oxidation takes place. The hot gases again transfer heat to the near (cold) side of the bed and exit the reactor. Then, the process again reverses.^[3]

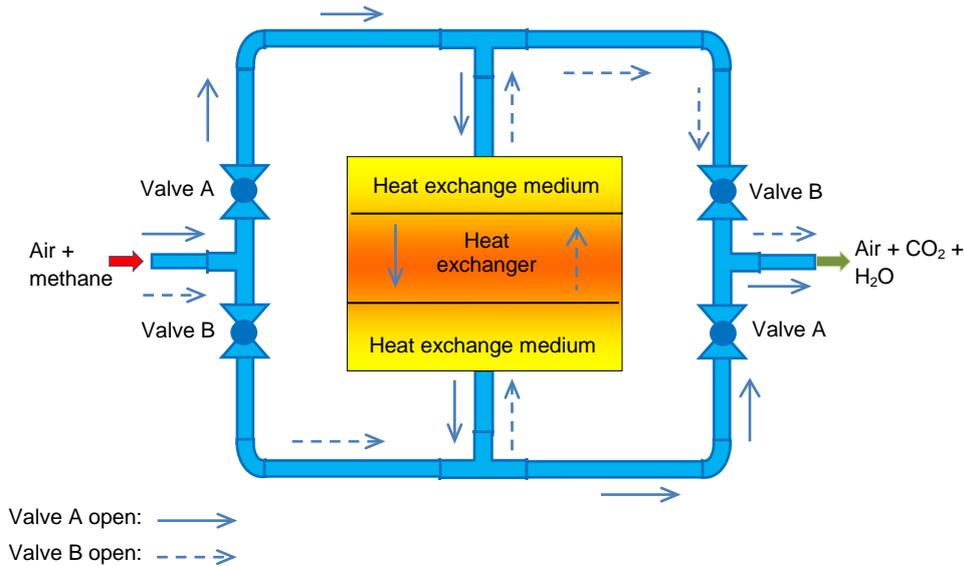


Fig. 2. Schematic of thermal flow-reversal process^[10]

The flow-reversal process is managed by a programmable logic controller to maintain the hot area of the bed in the middle of the oxidizer. This controller supports the oxidation of a constant stream of VAM over time. A technical assessment using numerical modelling suggested that TFRR can sustain operation with ventilation air containing methane concentrations as low as 0.1 percent.^[10] Unfortunately, the upper limit of bed temperature increases the likelihood of the formation of NO_x gases. The homogeneous combustion in porous medium was studied in order to support the self-maintained operation of TFRR.^[16] It was shown that the use of monolith as porous medium decreases the ignition temperature and enhances the combustion of methane. However, the stability of combustion is strongly affected by gas velocity and the pore size of monolith. A very recent assessment reported that for self-maintained operation methane concentration should be higher than 0.25%.^[17] The operational and maintenance costs of this unit is relatively high since the heater consumes energy and the presence of particulates in the VA stream^[4] may create major problems, including corrosion of the reactor.

Catalytic flow reversal reactors (CFRR) offers benefits with regard to auto-ignition temperature of methane and the absence of NO_x formation. CFRR adapts the thermal flow-reversal technology described above by using a catalyst to reduce the auto-oxidation temperature of methane to a temperature as low as $350\text{ }^\circ\text{C}$.^[3] It was reported that in order to sustain process operation, a pilot scale CFRR required the minimum methane concentration in the ventilation air to be 0.19%,^[18] however there was no information on how long the CFRR unit can be operated at this low methane concentration. The overall performance of this system depends on methane concentration, cycle time and velocity. The catalyst selection plays an important role in fixing the main operation variables in order to obtain a stable and auto-thermal operation.^[19] A recent lab-scale study of VAM combustion in a vertical CFRR suggested that this reactor was successfully operated under a wide range of operating conditions with self-sustaining operation even at methane concentration as low as 0.13 vol% resulting methane conversion of 88.16%.^[20]

3.4. Monolithic reactors

The uses of monolithic reactors for lean methane combustion were demonstrated as a potential solution for destruction of coal mine methane emission, as well as extracting the heat from the combustion reaction.^[21] Catalytic-monolith reactors (CMR) employ a honeycomb type-monolith-reactor to oxidize the methane with very low pressure drop even though the flow rate is very high. Monoliths used consists of a structure of a parallel channels with walls coated by a porous support containing catalytically active particles.^[8] Compared to the other reactor technologies, CMR units are reduced in size due to the high surface activity. However, an additional heating system is required, *i.e.* heat exchanger to pre-heat the ventilation air. To reach auto-ignition temperature, a monolith reactor should be operated above $500\text{ }^\circ\text{C}$, which is

higher compared to CFRR. An experimental study suggested that the methane concentration required for sustainable CMR operation is $\geq 0.4\%$.^[7]

3.5. Lean gas turbine

Methane emissions from VA can be treated also in a recuperative gas turbine, where the heat from the combustion process is used to preheat the air containing methane reaching the auto-ignition temperature (in the range 700–1000 °C), with the combusted gas being used to drive a turbine. Development of a lean-burn gas turbine is still in progress and primarily focuses on reducing the required limit of methane concentration in air. The combination of a lean-burn gas turbine and catalytic combustor is an effective strategy for increasing the efficiency of the system. Initially, Energy Development Limited (EDL)'s recuperative gas turbine, CSIRO lean-burn catalytic turbine and Ingersoll-Rand (IR)'s micro-turbine were developed with a catalytic combustor.^[7] It was reported that the CSIRO catalytic turbine and the IR catalytic micro-turbine can operate at a methane concentration of 1%, while EDL recuperative turbine required at least 1.6% of methane in air. Therefore, additional quantities of methane will need to be added to the VAM stream. Using a lean burn gas turbine, not only low methane concentration can be utilized, methane captured from pre and post mining may also be added as fuel.

Very recently, CSIRO has successfully developed a lean burn catalytic combustion turbine technology. A prototype ventilation air methane catalytic combustion gas turbine (VAMCAT) was constructed and tested at methane concentration as low as 0.8% generating electricity output of 19-21 kWe.^[22] The main component of the VAMCAT set-up includes a pre-burner, a catalytic combustor, a compressor, a turbine, a recuperator and a gearbox. Start-up of the unit employs a start-up motor and a pre-burner to reach a self-sustaining operational level. Indeed, this set-up requires higher initial power consumption and a high performance dust filtering

system which are the disadvantages of this technology. The experimental results suggested that the overall efficiency of a small unit VAMCAT is 11%. Therefore, this technology needs more improvement, especially on the recuperator effectiveness. Mine site trials and operation are necessary to identify the actual problems and the barriers in implementation of VAMCAT technology. Further investigation requires more evaluation of VAMCAT performance at varying methane concentration and flow rate.

3.6. Concentrator

Concentrators are an alternative solution to enrich the methane concentration in ventilation air to meet the minimum methane concentration required to operate a gas turbine, although this approach has serious technological challenges most notably that the VAM volume is very large and methane concentration in the VAM is not constant. Usually, concentrators are used to capture volatile organic compounds (VOC). Potentially, a concentrator can process ventilation air containing 0.1 – 0.9% of methane can be enriched up to 20% of methane. Vortex tubes could be a potential method for VAM utilization and mitigation as gas separation devices leading to produce a higher concentration of methane.^[23] However, effective technologies to enrich methane concentration are still under development.

A fluid bed concentrator is considered as an alternative way to increase methane concentration. This concentrator consists of an adsorber, a vessel containing adsorbent fluid with adsorbed methane, methane desorption system and a feeding system for the adsorbent medium. Activated carbon or zeolites are suitable adsorbent media which can be re-generated by increasing the temperature and results in the release of concentrated methane into a lower volume stream. After the methane desorption process (adsorbent regeneration), the adsorbent medium can be stored back to the adsorber for reuse. Unfortunately, recent experiments on this

technology have not been successful.^[7] To be considered as a viable technology for application in VAM, further development is required based on cost-effective processing of the waste methane in a variety of site/plant conditions.

Vacuum pressure swing adsorption (VPSA) system is an alternative approach to enrich methane contained in mine ventilation air, where activated carbon was used as adsorbent.^[24] Using this method, methane concentration can be increased from 0.3% to 0.75% at the adsorption pressure < 250 kPa, however 0.2% of methane was retained in the effluent gas. A lower adsorption pressure was carried out at ambient temperature to achieve the capture of 70% of the methane from a feed of VAM with an initial methane concentration of 0.2%.^[25] Alternatively, a honeycomb monolithic carbon fiber composite (HMCFC) can be utilized as an adsorbent for methane enrichment.^[26] It was reported that HMCFC increased the adsorption capacity to double that of commercially available activated carbon material. A feed gas of 0.56% methane in air mixture resulted in a final methane concentration of 0.01% at the outlet of HMCFC adsorbent, operated at ambient temperature and atmospheric pressure. Recently, a coconut shell-based carbon adsorbent was prepared and showed improved adsorption capacity compared to other adsorbents.^[27] Nevertheless, the assessment of adsorbent in VPSA or other reactors such as fluidized bed and monolithic carbon fibre composite is still in laboratory scale.

Methane enrichment using clathrate hydrate formation is another promising method for capturing methane from mine ventilation air. Earlier work illustrated a novel concept for separating CO₂ from the flue gas (post-combustion) and fuel gas (pre-combustion) of power plant using clathrate hydrate process^[28] where gas hydrates were formed in a semi-batch stirred vessel in the presence of tetrahydrofuran (THF).^[29] Later, the feasibility of this method to separate methane from the coal mine methane (CMM) gas has been investigated,^[30, 31] where

development of CMM separation process was experimentally performed through the formation of tetra-n-butyl ammonium bromide (TBAB) semiclathrate hydrate.^[31]

Basically, the concept of hydrate-based methane concentration is illustrated in Fig. 3.^[32] The potential of this procedure for lean methane containing gas stream was further studied using a statistical thermodynamic approach to predict hydrate formation as a function of reaction pressure.^[33] This theoretical study showed that enrichment of methane from VAM using the hydrate-based gas separation method is achievable. A recent experimental work by Du et al. confirmed the possibility of enriching lean methane mixtures from mine ventilation air using clathrate hydrate technique.^[34] They used tetra-butyl phosphonium bromide (TBPB) as hydrate promoter resulting 0.5 vol% of methane in air was enriched up to 3.5 times in the hydrate phase. The pressure required for reducing the hydrate is high (in the range of 1.92–18.55 MPa), and as such application in a VAM stream would present considerable practical challenges.

Recent investigations have aimed at exploring suitable and cost-effective low-dosage promoters for methane extraction. In the presence of tri-n-butyl phosphine oxide (TBPO) and TBAB at three different initial loadings (5 wt%, 15 wt%, and 26 wt%), methane extraction was examined.^[32] The results showed that higher loading of either TBPO or TBAB increases the net uptake of methane gas. TBPO has particular advantages in reducing the pressure required for hydrate formation, and enhancing methane enrichment rate. On the other hand using THF, Zhao et al. showed a decrease in separation factor as reaction pressure increased.^[35] However, this concept is relatively new. Implementation of clathrate hydrate method for capturing methane emissions from mine ventilation air poses some challenges such as the performance of the of the materials in the high volumetric flow rate of VAM stream and the presence of coal dust and other contaminants in the gas stream. These practical aspects related to commercial

implantation of the technology would need to be addressed and solved, together with safety and economic considerations.

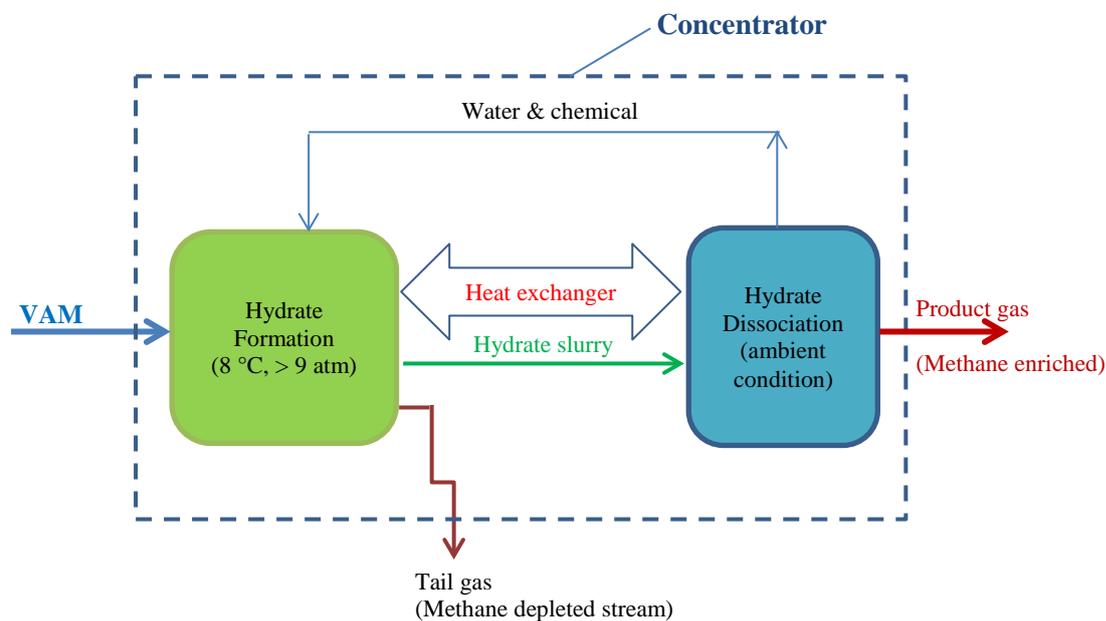


Fig. 3. Block diagram of methane enrichment process using clathrate hydrate formation ^[32]

3.7. Methanotrophs

A biological method using methanotrophs is presently considered as an option for coal mine methane emission abatement. An earlier investigation reported that using aerobic methane oxidizing bacteria (*Methylomonas methanica*) in a bio-filter can remove methane from coal mine atmosphere in 24 h.^[36] Later, Sly et al. developed a continuous biofilter using *Methylomonas fodinarum* ACM 3268 to remove 0.25-1.0 vol% methane in air.^[37] It was reported that 70% of methane was removed with a residence time of 15 min. Culture-independent molecular biological approach were used to investigate methanotroph diversity and activity in an alkaline soil environment. This environment contained a high diversity of methanotrophs including some uncultivated methanotrophs.^[38] A lab scale multi-layer reactor was developed to control the methane concentration in the coal mine.^[39] Although, removal efficiency of methane was not significant, the potential of biofilter technology for coal mine

atmosphere has been demonstrated. Very little is known about the basis of methanotroph groups and needs more investigation to understand the fundamental knowledge of methanotrophy.^[40] Development of machinery for converting VAM requires more works to address a number of aspects such as lack of suitable methanotrophic isolate, gas transfer limitation, competitive inhibition of methane monooxygenase (MMO), regeneration of reducing equivalents for MMO and product toxicity.^[41]

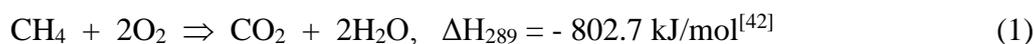
Mitigation and utilization of VAM faces significant challenges, due to the low and variable concentration of methane, as well as its high volumetric flow. To enrich methane concentration in ventilation air, concentrators are considered to be useful devices when methane concentration in ventilation air does not meet the requirement. Mine site specific conditions are the main factors to be evaluated in assessing the applicability of technology for mitigation and utilization of coal mine ventilation air at any site. It is very important to investigate safety aspects when any type of technology is connected to the mine site. Globally, the greenhouse gas effect from underground coal mine ventilation air could be reduced about 95% by using oxidation methods. On the other hand emissions from coal mining could be reduced to 67%.^[8]

Due to its low methane concentration, VAM does not support the combustion, so flaring is not feasible. Adding higher concentration of methane to the ventilation air and burning it would offer some remedy, but overall it would add to the total emission of greenhouse gases. Enrichment of methane using membrane separation or other methods (such as vortex tubes, fluid beds, clathrate hydrate, VPSA and honeycomb monolithic carbon) are also potentially feasible for methane mitigation and utilization. The enriched methane gas can be fed directly to gas turbines or reciprocating engines to produce power. Another way of using VAM is to oxidise the methane to carbon dioxide in thermal flow-reversal reactors. The challenges

associated with pressure drop and heat recovery which must be overcome if the VAM technology is to be self-sustaining. Current development in microbial biocatalysis and progress in functional genomics and proteomics of methanotrophs provide opportunity in finding a new effective strategy for VAM abatement. Flameless combustion could be more practical but the low caloric value of lean methane mixture makes self-sustaining operation difficult. Finally, recent technological developments in the catalytic oxidation of methane may be a prospective way to ease the methane emission, despite problems with catalyst deactivation during operation.

4. Catalytic combustion of Methane

The catalytic process of methane oxidation is well known and has been used since the end of the 20th century as a method of energy production from natural gas without emitting nitrogen oxides. In general the reaction process can be described by the equation:



This combustion process can produce CO₂ and CO, depending on the air fuel ratio. Oxygen enriched reaction results in the formation of CO₂ as the only carbonaceous product while partial oxidation will produce CO and CO₂. The reactions can be described as follows:



Catalysts are able to replace flame combustion and oxidize lean methane mixtures, even when the concentration of methane is less than 5%. Catalytic combustion enables the utilization of pure and low-concentration methane gases as an environmentally friendly source of energy^[5]. Although methane oxidation will produce carbon dioxide which is another greenhouse gas, CO₂ has a reduced GHG potential and is readily absorbed from the exit gas stream, whereas methane adsorption is much more challenging.

A possible mechanistic pathway of methane oxidation over noble metals has been outlined by Oh and co-workers^[43] as shown in Fig. 5. Since the O₂ adsorption occurs at a faster rate than methane adsorption, the surface of the catalyst is initially fully occupied by oxygen and subsequently chemisorption of CH₄ on the surface of catalyst takes place. The chemisorption of methane onto noble metals then cleaves the hydrogen atoms from CH₄ and produces surface methyl or methylene radicals. The adsorbed atoms subsequently react with adsorbed oxygen to produce carbon dioxide and H₂O in direct oxidation or chemisorbed formaldehyde. This chemisorbed formaldehyde is either desorbed as HCHO or decomposed as adsorbed CO and adsorbed H atoms. Subsequently, adsorbed CO and H atoms are either desorbed as CO and H₂ or reacted with adsorbed O₂ to produce CO₂ and H₂O, depending on the composition of the reactant mixture.

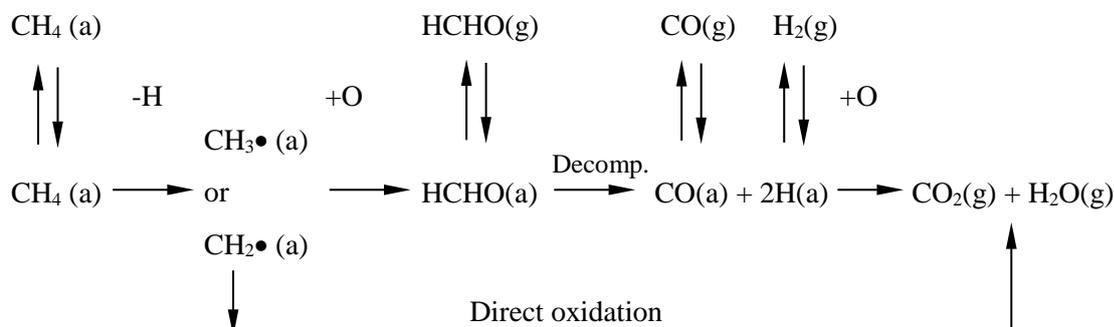


Fig. 5. A possible mechanism for catalytic oxidation of methane, (a) adsorbed, (g) gas phase^[43]

5. Progress in catalyst development for methane combustion

Methane is the most challenging of all hydrocarbons to activate. Most studies and developments in catalytic oxidation were initiated with an overarching aim of reducing hydrocarbons emissions from internal combustion engines. It was reported that reasonable catalytic activity can be achieved at temperatures below 400 °C^[44, 45]. For these applications, noble metal catalysts such as Pt or Pd on an Al₂O₃ supports were reported to be the most active

catalysts^[46]. A number of investigations were devoted to designing catalytic materials which are able to operate at high temperatures, for long periods of time, and in humid and oxygen-rich conditions. Low reaction temperatures are a distinct advantage in VAM application because: (1) the production of NO_x gases can be minimised (essentially zero), (2) a self-sustaining system of methane mitigation and utilization can be designed based on the catalyst activity. It is expected that a self-sustaining system is feasible at reaction temperatures of 200 °C because thermodynamically, the adiabatic temperature rise of complete-methane oxidation is (very approximately) 23 K per 0.1% of methane in air^[47]. Therefore, most of the recent studies are focussed on developing methane oxidation catalyst which can operate at temperatures as low as possible.

Recent developments in catalytic materials for methane oxidation enable operation at approximately 100% conversion of CH₄ to CO₂ at reaction temperatures of 320-450 °C, depending on the system and catalyst characteristics. Currently, palladium supported on alumina catalyst is identified as the most active catalyst for total methane oxidation^[48, 49]. Supported gold catalysts have also been shown as active materials, where significant conversions were observed at the temperature as low as 350 °C in catalytic oxidation of lean methane mixtures^[50-52]. Single metal oxide catalysts (such as Co₃O₄, Mn₂O₃ etc.) are also reported, mainly because of low cost and higher resistance to deactivation^[53].

5.1. Palladium-based catalysts

Supported palladium catalysts are widely used in many catalytic combustion and converter systems. The mechanism of methane oxidation over Pd-based catalyst is complex. A number of papers have been devoted to understand the oxidation behaviour and catalytic properties of

supported Pd catalysts, examining aspects as diverse as role of feed ratio, particle size and dispersion, pre-treatment effects, poisoning effect of water, chlorine and sulphur poisoning and deactivation.^[49, 54-56, 57-59] Progress on development and investigation of palladium catalysts will be reviewed in this section. The specific issues related to VAM application such as water inhibition and catalyst deactivation are explored and discussed in more detail below.

Earlier works on palladium-based catalysts were focussed on establishing the influence of O₂/CH₄ ratio during catalytic combustion of air-methane-mixtures, in order to understand the mechanism of methane oxidation. When methane is oxidised under oxygen-rich conditions over supported precious metal catalysts, carbon dioxide is the only carbonaceous compound found in the outlet gas mixture.^[60, 61] On the other hand, under oxygen-deficient oxidation, the formation of carbon monoxide was detected where the selectivity of CO has strong correlation with the reaction temperature. Under these conditions, the production of CO₂ and H₂O increases with increasing temperature until the oxygen is totally consumed, where the formation of carbon monoxide is observed thereafter.^[61] At higher temperature the selectivity to CO is increased and lower feed ratio ([O₂]/[CH₄]) also increases selectivity towards CO in favour of CO₂. Carbon dioxide in the feed stream (which can be present in VAM) has been shown little significant effect on the activity,^[62] which is an important for the VAM application as the concentration of CO₂ in VAM is often around 1%.

The influence of H₂, He and O₂ used for catalyst activation procedure were investigated for palladium supported on metal oxides catalysts.^[45, 63] It is generally agreed that catalyst pre-treatment plays an important role in controlling the activity and durability of catalysts. The necessity for pre-treatment can significantly influence its applicability for VAM combustion. Earlier studies reported that pre-treatment under hydrogen increased the activity of catalysts,

whereas O₂ pre-treatment led to a decrease in the activity of the catalyst.^[45, 64] Subsequent investigations also found that the reduced form of palladium was an important active site for the catalytic combustion reaction.^[63, 65, 66] However, some researchers have reported that reactant mixtures were also used (successfully) as pre-treatment gases^[46, 61, 67] where catalyst activation under reactant mixtures (O₂-CH₄-carrier gas) leads to catalysts being more active than those pre-treated with hydrogen.^[68, 69] It was suggested that factors which can influence catalyst activation include: (a) poisoning the active sites by the substances remaining in the catalyst from its precursor (primarily chlorine);^[45, 65, 68] (b) transformation from an initially amorphous PdO state to a crystalline state^[46, 70, 71] and (c) interactions with the support phase, especially at low Pd coverage.^[55]

Under oxygen-rich conditions, for palladium catalysts, it is suggested that PdO is formed and this phase represents the active phase for methane oxidation.^[48] Prior investigations have clearly highlighted the importance of PdO for methane combustion.^[72, 73, 74] It was suggested that the transformation of PdO ↔ Pd is reversible in presence of oxygen^[75] and metallic Pd is less active than PdO. The reactivity of oxygen chemisorbed on Pd metal and oxide ions for Pd/Al₂O₃ catalysts was compared by Burch and Urbano.^[73] The catalyst was prepared by impregnating alumina with palladium nitrate and exposed to oxidation and reduction treatment at 500 °C prior to measuring the resulting catalytic activity. Catalytic, steady-state and pulse experiments suggested that metallic Pd is not an active catalyst, while the pre-oxidized sample is active. However, time-on-stream experiments at 300 °C, over the pre-reduced sample, revealed that the oxidation commences with the rapid formation of a monolayer of oxygen, followed by a slower oxidation step which with time-on-stream lead to almost complete oxidation of palladium. It was found also that fully oxidised bulk PdO is the optimum state of

the active site for methane oxidation and the intermediate state corresponding to a layer of PdO on a Pd metal core has no greater activity compared to the bulk PdO.^[74, 76]

The presence of both PdO and Pd metal on the catalysts under reaction conditions was reported in the literature.^[71, 77] Lyubovsky and Pfefferle initially found that Pd metallic surface is formed after pre-treatment at temperatures in excess of 800 °C, followed by transformation into a highly dispersed PdO clusters during cooling cycle leading to increase in conversion with decreasing temperature.^[77] On the other hand, an investigation by Datye and co-workers proposed that the PdO to Pd transformation is initiated at the surface upon heating and causes small domains of Pd metal to form on the surface of PdO.^[71] Upon cooling step, these small domains are readily re-oxidised, which is not the case when complete transformation into Pd metal (at T in excess of 925 °C) is achieved. It was suggested that complete oxidation of the Pd metal can result in the formation of polycrystalline PdO, with a roughening of the particle surfaces. Re-activation of the Pd metal catalysts upon cooling could be associated to two possible mechanisms: (i) PdO re-formation (increase in the fraction of Pd metal particles fully re-oxidised into bulk PdO) or (ii) a reaction mechanism which involves metallic Pd.

Palladium supported on ceria-zirconium oxide catalysts was investigated by Ciuparu and Pfefferle in order to assess the influence of oxygen content in supported Pd/PdO particles on the activity in methane oxidation.^[78] The amount of metallic Pd was varied by controlled chemical reduction with methane. It was observed that catalyst activity initially increases with the degree of reduction, reaching a maximum and then decreasing continuously as the oxygen is depleted. This indicates that slight reduction results in enhanced improvement in catalytic activity compared to either fully oxidised or fully reduced metallic particles. Moreover, the

partially reduced sample was found to re-oxidise more readily than the completely reduced catalyst.

More recent investigations suggested that the surface structure of the Pd-based catalysts changes with time-on-stream under fuel-rich conditions.^[79] For this investigation, 5 wt% Pd/Al₂O₃ were used and studied under oxidation–reduction cycles (pulse reactor studies). The results showed that the initial methane combustion activity of the oxidized catalyst is much higher than that of the reduced form. The methane combustion activity of the partially reduced and oxidized catalysts is strongly influenced by the degree of PdO reduction and Pd oxidation, respectively; it decreases with increasing Pd content but increases with increasing PdO content. It was suggested that along with the relative concentration of PdO and Pd, the PdO formation pathway is also critical parameter influencing the methane combustion activity of the catalyst. Recent investigations have shown that, under controlled conditions, Pd/Al₂O₃ catalysts calcined in air and then reduced in hydrogen exhibit a lower activity at lower reaction temperatures compared to those calcined in air only. Nevertheless, at reaction temperatures higher than 290 °C, all samples exhibit similar activity.^[80] Overall, there are still uncertainties regarding the relationship between pre-treatment history and the activity of catalyst. One important question that arises from these investigations is “how to optimise the catalytic activity and what kinds of gases are suitable for a particular catalyst and its support?”

Several kinetic studies of methane combustion over supported Pd catalysts were reported in the literature.^[45, 69, 81, 82, 83] Under oxidising or stoichiometric conditions, the order of reaction over Pd/Al₂O₃ catalysts is first order with respect to methane and essentially zero order with respect to oxygen concentration. While CO₂ was suggested to have no effect on reaction rate, a strong inhibition was observed upon adding H₂O into the feed, where the order with respect

to H₂O was reported in the range of -0.6 to -1.0.^[82-84] Under dry feed conditions, apparent activation energies were ranging between 70 and 90 kJ mol⁻¹.^[69, 82, 83] whereas the activation energy increased to 151 ± 15 kJ mol⁻¹ when 2 vol% H₂O_(v) was present in the VAM feed.^[82] It can be suspected that varying the concentration of water vapour in the feed and modification of support material will influence on the nature of the active site.

Possible effects of fouling by carbon (or coke) on the activity of supported metal catalysts are important factors which need to be considered for catalytic combustion of VAM. Deactivation of supported metal catalysts by coke may occur due to chemisorption or carbide formation, even under the oxygen-rich conditions present in VAM. Coke formation may also occur due to blocking of surface sites, metal crystallite encapsulation, plugging of pores and destruction of catalyst pellets by carbon whiskers.^[85] While coking of transition metal catalysts was reported during the combustion of methane at higher concentrations^[86, 87] and reaction temperatures,^[87] a limited number of publications consider carbon deposition on palladium catalyst under lean methane conditions at low temperatures. One investigation showed that methane can be activated over Pd catalysts at temperatures as low as 180 °C.^[79] The presence of coke on Pd catalysts at this temperature could have important consequences on catalytic activity as recently reported in the literature.^[80] It was shown that carbon is formed on Pd-based catalysts even under very lean conditions (0.6 vol% CH₄ in air). By purging the coked sample in air at 320 °C, the carbide species can be converted to CO₂.

VAM streams are normally saturated with water vapor. Since it is well recognized that water strongly inhibits the activity of catalysts, the effect of water vapor on the performance (especially long term) is crucial to any technology employing low temperature conversion of VAM. Recently, it was shown that water vapour is one of the main contaminants that influence

combustion of VAM at low temperatures.^[88] The mechanism of catalyst deactivation by water vapour is still uncertain.^[89] Some earlier studies reported that the water produced by reaction significantly inhibits the activity of Pd/Al₂O₃ at lower temperatures due to competition with methane for active sites.^[62, 83, 90] Furthermore, an irreversible deactivation can possibly be induced by the presence of water where the active site (PdO) transforms into a less active site (palladium hydroxide).^[62, 83, 90, 91] The rate of Pd/Al₂O₃ catalyst deactivation in the presence of water, either present in the feed (such as the case in VAM) or produced in the reaction, is strongly dependent on reaction temperature.^[62, 91] The inhibiting effect of water is more significant at lower temperatures and becomes less apparent at temperatures higher than 450 °C.^[62] Ciuparu and co-workers suggested that the hydroxyl groups produced by reaction are bound strongly on the surface and when the external water is introduced the surface becomes saturated and the rate of desorption of water from the surface of the catalyst is inhibited due to the high concentration of water vapour in the feed and product stream.^[84] Recent work by Schwartz et al. proposes an alternative explanation regarding deactivation of palladium supported on various metal oxides.^[89, 92] Hydroxyl groups formed during the reaction accumulate on the catalyst support and inhibit the rate of exchange of oxygen between the support and PdO,^[92] which is necessary for surface reaction. This accumulation of hydroxyl groups prevents the migration of oxygen from the support to the Pd active site, as well as reducing the availability of oxygen involved in the oxidation of methane.^[89] This explanation is supported by a recent investigation where the water vapour was found to be a primary factor responsible for low temperature catalyst deactivation.^[93] Clearly the primary mechanisms leading to deactivation is still contentious, as hydroxyls form on both the Pd site and the support in high concentrations^[89] and deactivation can potentially originate from either the support or palladium.

Recently, Di Carlo and co-workers reported an improved tolerance against water poisoning in catalytic combustion of methane over palladium catalysts by using a support which inhibited or delayed the reaction between Pd and H₂O,^[94] however no long-term stability test results were reported. The application of a catalytic process for VAM abatement requires long-term evaluation of the catalyst stability and durability under humid feed condition. An extended period of time of hydrocarbon oxidation activity was reported by Yamamoto and Uchida reported over Pt and Pd supported on alumina for lean-burn natural gas engine exhausts^[95] where the total hydrocarbon conversion dropped from 80% to 50% within 2,500 h at 385 °C. More recent investigation by Liu et al.^[96] reported that during 3,200 h methane combustion experiment at 600 °C, Pd supported on Ni-modified alumina catalyst demonstrated a stability improvement. It was suggested that the stability of Pd/NiO-Al₂O₃ catalyst was improved by optimizing the Ni/Al ratio.

The long-term catalyst stability tests at reaction temperatures less than 600 °C and the effect of CO₂ in the feed for long term catalyst stability tests have been initially examined on Pd/Al₂O₃ catalyst under simulated VAM stream.^[93] Progressive deactivation was observed during 1100 h time-on-stream experiment which mainly due to the formation of palladium hydroxide. The final bed temperature after 1150 h at 90% methane conversion level was 500 °C. No effect of CO₂ addition to the feed was observed during this investigation. In addition, the effect of coal mine dust on the catalytic combustion of ventilation air methane was also examined in this investigation. It was reported that adding VAM dust into the reactor leads to severe catalyst deactivation where over 1100 h time-on-stream experiment, an average methane conversion level can be achieved only at 75% at reaction temperature below 600 °C.^[93] The humid conditions of ventilation air streams urges future investigations to focus on low temperature reactions (in the range of 200-300 °C) where the hydroxyl is the most abundant surface species

and the rate is limited by water desorption from the surface of the catalyst. Accumulation of hydroxyl species on the catalyst support can prevent the migration of oxygen from the support to the Pd active site, as well as reducing the availability of oxygen involved in the oxidation of methane. This requires more work such as kinetic and isotope experiments at different reaction conditions to clarify this argument.

The effect of Pd particle size on catalytic activity is still unclear, while most research groups have asserted that methane combustion is a structure sensitive reaction, there have been some contradictory suggestions.^[97] The effect of palladium particle size on catalytic activity were investigated to confirm the structure sensitivity of Pd during CH₄ oxidation.^[68] A more detailed study was carried-out by Baldwin and Burch where palladium was dispersed on Al₂O₃ support within an average diameter of 2-74 nm. Pd dispersion was obtained by varying the calcination temperature and tested under continuous-flow conditions of 1 vol% CH₄ in air.^[46] Unfortunately, the relationship between palladium particle size and reaction rate of methane oxidation was not clearly explained. Meanwhile, Burch and Loader reported that there was no evidence of a particle size affecting the catalytic behaviour of Pd and Pt catalysts.^[98] This suggestion was supported by Ribeiro et al. who prepared Pd catalysts supported on Al₂O₃, ZrO₂ and Si-Al₂O₃ and determined the turnover rate on the basis of Pd dispersion measured after reaction. It was concluded that the reaction was not structure-sensitive, however, some variation of the activity with the particle size was considered. A recent work on Pd load and dispersion on catalytic activity in methane combustion and on redox behaviour of Pd supported on alumina catalysts suggested that the catalyst with lower Pd loading and higher metal dispersion exhibits a lower specific catalytic activity.^[58] Therefore, more detailed investigation is needed to clearly address the relationship between the catalytic activity and the particle size, especially for the catalysts which have been operated under extremely humid conditions.

Despite considerable effort, the mechanism of catalyst deactivation is not fully understood.^[89] Deactivation can occur through chemical, mechanical and thermal processes.^[85] Thermal deactivation processes include the loss of active-site surface area as a result of particle aggregation and collapse of the support pore structure through re-crystallization. Chemical transformation can also result in the loss of active metal sites.^[85] Pd/Al₂O₃ catalyst activity can be affected by both thermal and chemical transformations.^[99]

These deactivation processes can be accelerated under high-temperature hydrothermal ageing. A study of hydrothermal ageing on methane combustion over Ce-promoted PdO/ZrO₂ catalysts highlighted the impact that ageing temperature plays on catalyst deactivation.^[100] Hydrothermal treatments for two weeks on various supported Pd catalysts at 900 °C under simulated domestic boiler exhaust gas were performed to understand the ageing mechanism in natural gas combustion.^[101] Deactivation studies were reported recently for natural-gas vehicle catalysts^[102] and diesel oxidation catalysts^[103] where significant changes in morphology and chemical poisoning were observed. A recent article reported that support phase transformation and particle sintering were found after thermal (at 900 °C in air) and stoichiometric (at 900°C, air-fuel equivalent ratio = 1) ageing over Pd/YFeO₃ three-way-catalyst.^[104]

The mechanism of catalyst deactivation has been recently investigated particularly under simulated VAM gas.^[88] It was reported that catalyst deactivation is initially caused by palladium particle migration followed by particle growth and changes in support structure. This is more prominent in the presence of water vapour. Catalyst characterization technique employed in this investigation substantiates the changes in pore structures of support material where the phase of alpha-alumina was observed after long-term time-on-stream

experiments.^[88] Particle growth and pore structure changes are varied depending on temperature and reaction conditions which are difficult to explain. In order to develop a comprehensive understanding of the deactivation phenomena, it is necessary to understand the complexity of the elementary processes. More information is required for dispersion and particle-size distribution versus time which is necessary for validating sintering models for process design/optimization and model development/validation, more statistically significant measurements of sintering rates are needed for supported metal catalysts under reaction conditions over several hundreds of hours and where possible in large scale processes. While spectroscopic tools have been used effectively during the past two decades to advance our fundamental understanding of sintering and redispersion, additional insights into atomic and molecular processes occurred during sintering and redispersion are needed to develop more realistic models.

5.2. Supported gold catalysts

Investigations focussed on low temperature catalytic oxidation over gold catalysts were pioneered by Haruta and co-workers.^[105] They developed gold supported on transition metal oxides to oxidise carbon monoxide. It was reported that this type of catalyst has been used successfully for CO oxidation at temperatures as low as -70 °C. Gold catalysts were reported to be more active in carbon monoxide oxidation compared to traditional platinum or palladium supported catalysts. The earlier studies also found that the catalysts for CO oxidation can be used to promote methane oxidation by using transition metal oxides as supports.

An earlier investigation by Waters and co-workers^[106] studied methane combustion over transition metal oxide supported gold catalysts prepared by co-precipitation. A micro-reactor

was used to observe the trend in activities of Au/Co₃O₄, Au/NiO, Au/MnO_x, Au/Fe₂O₃, and Au/CeO under operating conditions where mass and heat transfer effect were minimized. They have found that the trend in activities was Au/Co₃O₄ > Au/NiO > Au/MnO_x > Au/Fe₂O₃ >> Au/CeO_x.

Gold catalysts on metal oxide supports were prepared by Solsona et al.^[51] and tested for the total oxidation of methane, ethane and propane. The catalyst was made by several methods including co-precipitation, deposition-precipitation and impregnation. The catalysts were tested at atmospheric pressure in a fixed-bed stainless steel tubular flow reactor and analysed by online gas chromatography. They found that Au/CoO_x prepared by co-precipitation method was the most active catalyst which can complete oxidation of methane at 350 °C. Based on their activity, the order of catalysts was: Au/CoO_x > Au/MnO_x > Au/CuO > Au/Fe₂O₃ > Au/CeO₂ > Au/TiO₂. This order has the same reactivity as observed for the supports.

Gold catalysts supported on iron oxide were prepared recently by Choudhary et al. for methane oxidation experiment using different preparation methods: deposition-precipitation (DP) and homogenous deposition precipitation (HDP). Gold with different loadings was deposited on various supports such as Fe₂O₃, MnO₂, CoO_x, CeO₂, Ga₂O₃, Al₂O₃ and TiO₂. Prior to the activity measurement, each sample was heated in nitrogen at 600 °C for 1 h and then 1 vol% CH₄ in air was continuously passed through the catalyst at the flow rate of 100 ml min⁻¹.^[52] It was reported that the Au/Fe₂O₃ prepared by HDP showed higher activity compared to those prepared by DP. The transmission electron microscopy images show that an HPD method leads to catalysts with much higher Au loading and smaller Au particle size. Undertaking studies at different space velocities, the performance of Au/Fe₂O₃ (HDP) were evaluated. An increase of the gas hourly space velocity from 10,000 to 100,000 h⁻¹ increased the ignition temperature

(for 10% CH₄ conversion) from *ca.* 200 °C to 350 °C. At 500 °C (100% conversion) the time-on-stream activity of Au/Fe₂O₃ (HDP) catalyst was observed during 50 h. The catalytic activity was slightly decreased to 80% conversion but then remained constant for 50 h continuous reaction. Unfortunately, there is no explanation why this catalyst is stable once the conversion reaches 80%. In addition, during experiments there were three gold species detected: Au⁰, Au¹⁺ and Au³⁺, but none of these are claimed as an active phase of gold.

The effect of support on the catalytic performance of Au/Co₃O₄-CeO₂ catalysts for methane oxidation was reported by Liotta and co-workers.^[107] They prepared gold-based catalysts supported on Co₃O₄, CeO₂, and mixed Co₃O₄-CeO₂ using co-precipitation method. The methane oxidation experiment results show that Au/Co₃O₄ is the most active catalyst, followed by Au/Co₃O₄-CeO₂ and then by Au/CeO₂ catalyst.^[107] It was suggested that the better performance of cobalt containing support is due the presence of Co²⁺ and Co³⁺ ions, being active sites for oxygen and methane activation, respectively. On the basis of the increased reducibility of the oxides, gold is acting as the promoter for the oxygen mobility.

Nanosize AuO_x/Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ (AuO_x/CZY) catalysts were successfully produced by adopting the cetyltrimethyl ammonium bromide (CTAB)-assisted hydrothermal treatment method.^[108] The Au concentration on the solid catalyst was varied using a novel in-situ reduction method. The characterization result confirmed that the CZY and gold were nano-sized particles where the diameter is in the range of 5-50 nm and 2-20 nm, respectively. Among the catalysts investigated in this work, the 0.2% AuO_x/CZY catalyst appeared most active for methane oxidation where 100% conversion was achieved at *ca.* 640 °C. It was concluded that the catalytic performance of the CZY-supported gold catalyst is dependent to the AuO_x dispersion, Au³⁺/Au⁰ molar ratio, Au and CZY particle sizes and catalyst reducibility.

Bimetallic Au-Pt and Au-Pd supported on cobalt oxide catalysts were investigated by Miao and Deng under reactant mixture of 1 vol% CH₄ and 5 vol% O₂ in N₂.^[50] The Au-Pt/Co₃O₄ and Au-Pd/Co₃O₄ catalysts at different Au, Pt and Pd loading were prepared by co-precipitation method in order to find a better Au-containing catalyst for low oxidation temperature of methane. All samples were calcined in air at 500 °C for 5 h and then reduced in hydrogen at 400 °C for 3 h. The result showed that Au-Pt/Co₃O₄ was the highest Au-containing catalyst activity where 100% conversion was achieved at 360°C. Unfortunately, the detailed mechanism on the interaction between Au, Pt and support was not described in this report. The role of gold in promoting the methane oxidation reaction has not been addressed. It seems that the development of supported gold catalysts is still at an early stage. To improve the activity and stability of this type of catalyst, significant research activity is required to address some issues such as the active site of gold, the role of gold and its interactions with support material and the effect of water.

5.3. Unsupported metal oxide catalysts

Transition metal oxides have been considered as catalysts for total oxidation of methane due to their higher stability and lower cost when compared to noble metals.^[97] Earlier work reported the use of single-metal oxides (such as Cr₂O₃, NiO, Mn₂O₃, Co₃O₄, and CuO) and these studies evaluated the activities and deactivation phenomena during lean methane combustion.^[53] Among those tested, Co₃O₄ was the most active catalyst but was less stable compared to Mn₂O₃. Preparing different morphologies of cobalt oxide was demonstrated recently as a strategy for improving the catalytic activity.^[109] Enhanced activity and stability was reported for Co₃O₄ nanotube prepared using a morphology-directed technique.^[110] The

higher activity observed from these nanotubes catalysts was reported to be due to the prominence and exposure of the (112) crystal plane and high reactivity of the surface oxygen. The issue of catalyst stability in the presence of water vapour in the feed has not been addressed yet.

The performance of Co_3O_4 and $\text{Co}_3\text{O}_4\text{-MO}_x$ binary oxides have recently been evaluated and correlated with the synthesis methods, morphological and structural properties.^[111] Advances in the synthesis strategies and the characteristics of cobalt oxide catalysts enlighten potential application for this type of catalyst in various catalytic processes. It is highlighted that the information about relationship between reactive planes/redox properties and catalytic activity of Co_3O_4 in methane oxidation are still limited. Current investigations suggest that the activity of Co_3O_4 is related to either the reactive {112}/{110} planes or the surface oxygen species, bulk oxygen mobility, re-oxidation of cobalt species, and active oxygen vacancies of nano-sized Co_3O_4 with controlled size. The higher adsorption capacity of Co_3O_4 has been recently suggested to be one of the factors responsible for better activity in methane oxidation.^[112] A better understanding of this issue needs more investigations to be performed under different reaction conditions. Particularly for lean methane oxidation under humid conditions, as the rate limiting step and catalyst deactivation are not fully addressed.

Table 1 shows the milestone of catalyst development since 1990 where most of works were dedicated for modification of supported Pd catalysts. Information on catalyst, support and reaction conditions is briefly provided including its reference. At first, gamma-alumina, ZSM-5 and zirconia have been used as support material for Pd and Pt catalysts. Later, combination of various transition metal oxides as support for Pd catalysts was explored aiming for an increase in catalyst stability against water vapour and sulphur compounds. A few

investigations used Pd catalyst supported on high surface area material, such as zeolite which was modified with silica, titanium and cerium oxides to enhance the catalyst activity and stability. Monolithic Pd-based catalysts have also been prepared and tested using Zr-Al alloy oxide showing stable activity under humid condition. Nano-sized cobalt oxide, either as single oxide or combined with other oxides have been shown as potential catalyst. However, a limited number of investigations have been taken under reaction condition mimicking the actual VAM stream condition.

Table 1. List of catalysts developed for total oxidation of lean methane mixtures

Year	Catalyst (loadings and supports)	Reaction conditions		Ref.
		Temperature and methane conversion ranges)	Feed composition	
1990	1.95% Pt/ Al ₂ O ₃	Temperature: 280-600°C CH ₄ conversions : 0-100%	[O ₂]/[CH ₄] ratio = 4	[113]
1992	0.16% Pd/ Al ₂ O ₃	Temperature: 250-700°C CH ₄ conversions : up to 100%	[O ₂]/[CH ₄] ratio = 5	[114]
	0.14% Rh/ Al ₂ O ₃	Temperature: 370-700°C CH ₄ conversions : up to 80%		
	0.2% Pt/ Al ₂ O ₃	Temperature: 400-700°C CH ₄ conversions : up to 80%		
1993	2.18% Pd/ Al ₂ O ₃	Temperature: 250-415°C CH ₄ conversions : 6-100%	[O ₂]/[CH ₄] ratio = 4	[115]
1994	4%Pt/Al ₂ O ₃ and 4% Pd/ Al ₂ O ₃	Temperature: 300-550°C CH ₄ conversions : 1-99%	[O ₂]/[CH ₄] ratio = 5:1 (oxygen-rich);	[98]
1994	3.39 wt% Pd-ZSM-5	Temperature: 225-275°C CH ₄ conversions : 10-100%	Feed: 1% CH ₄ in air GHSV = 30,000 h ⁻¹ .	[116]
	4.19 wt% PdO/ Al ₂ O ₃	Temperature: 275-375°C CH ₄ conversions : 10-100%		
1995	4%Pd/Al ₂ O ₃	Temperature: 275-425°C CH ₄ conversions : 10-100% (for dry feed) CH ₄ conversions : 0-90% (for wet feed)	Feed: 1% CH ₄ in air	[62]
1997	Pd/Al ₂ O ₃ wash-coated onto cordierite monolith (400 cpi) PdO/ZrO ₂	Temperature: 300-450°C CH ₄ conversions : 4-98%	Feed: 500 ppm CH ₄ , 10% steam, balance air. GHSV = 60,000 h ⁻¹ .	[54]
		Temperature: ca. 250-450°C CH ₄ conversions : ca. 5-98%	Feed: 1% CH ₄ and 4% O ₂ in a helium balance	
1998	Au/MgO (0.04-15 wt% Au)	For 0.04% Au/MgO at 750 °C the conversion of CH ₄ was only 10.7% where the products were C ₂ H ₆ , C ₂ H ₄ , CO ₂ and CO.	Feed: 46% CH ₄ , 8% O ₂ , balanced with helium.	[117]

Year	Catalyst (loadings and supports)	Reaction conditions		Ref.
		Temperature and methane conversion ranges)	Feed composition	
1998	Pd/SiO ₂ (sol-gel processing)	Temperature: ca. 320-520°C CH ₄ conversions : 10-98%	Feed: 1 vol% CH ₄ , 2 vol% O ₂ , and helium (balance).	[118]
1999	1 wt% Pd/Al ₂ O ₃	Temperature: ca. 250-500°C CH ₄ conversions : 5-98%	Dry feed: 800 ppm CH ₄ , 6.5% O ₂ , and nitrogen (balance).	[91]
2000	1.9 – 2.2 wt% Pd/Al ₂ O ₃	Temperature: ca. 200-450°C CH ₄ conversions : 0-100%	Feed gas: 1% CH ₄ , 4% O ₂ , N ₂ balance GHSV: 15,000 h ⁻¹	[90]
2000	1 wt% Pd/ZrO ₂ and 1 wt% Pd/ZrO ₂ stabilized with SiO ₂	Temperature: ca. 250-430°C CH ₄ conversions : 3-98%	Feed: (O ₂ /CH ₄ = 4, 5% CH ₄) balance N ₂ .	[119]
2001	Pd/Ce _{0.67} Zr _{0.33} O ₂	Temperature: 250-500°C CH ₄ conversions : 8-100%	Feed: 1 vol% CH ₄ , 4 vol% O ₂ , balance N ₂	[120]
2001	Pd/SnO ₂ Pd/Al ₂ O ₃ -36NiO	Temperature: 325-440°C CH ₄ conversions : 10-90% Temperature: 310-460°C CH ₄ conversions : 10-90%	Feed: 1 vol% CH ₄ , 20 vol% O ₂ , 20 vol% H ₂ O, and N ₂ (balance) Space velocity = 48,000 h ⁻¹ .	[121]
2001	Co ₃ O ₄ 1.91 wt% Au/Co ₃ O ₄ 1.96 wt% Pt/Co ₃ O ₄ 1.92 wt% Pd/Co ₃ O ₄ 1.9 wt% Au-1.48 wt% Pd/Co ₃ O ₄ 1.92 wt% Au-1.63 wt% Pt/Co ₃ O ₄	Temperature: 250-420°C CH ₄ conversions : 2-100% Temperature: 241-418°C CH ₄ conversions : 2-100% Temperature: 235-385°C CH ₄ conversions : 2-100% Temperature: 224-376°C CH ₄ conversions : 2-100% Temperature: 241-388°C CH ₄ conversions : 2-100% Temperature: 218-360°C CH ₄ conversions : 2-100%	Feed: 1 vol% CH ₄ , 5 vol% O ₂ , and N ₂ balanced Hourly space velocity: 10,000 h ⁻¹	[122]
2002	0.4%Pt-0.8%Pd/Al ₂ O ₃ (Cl-free).	Temperature: 230-350 °C CH ₄ conversions : 10-100%	Feed: 1.1 vol% CH ₄ , 2.7 vol% O ₂ , balance N ₂	[123]
2003	Pt(0.1 wt%)-Pd(0.2 wt%) supported on Al ₂ O ₃ Pt (0.2wt%) - Pd (0.3 wt%) supported on TiO ₂	Temperature at 90% methane conversion level (T_{90}) = 294 °C Temperature at 90% methane conversion level (T_{90}) = 255 °C	Feed: 300 ppmv methane in air GHSV = 21,000 h ⁻¹ .	[124]
2003	Pd/SnO ₂ wash-coated on 300 cpsi ceramic monolith	Temperature range: 250 – 320 °C CH ₄ conversions : 10 - 90%	Feed: 1 vol.% CH ₄ and 99 vol.% air. GHSV = 41,000 h ⁻¹ .	[125]
2003	Co–Mn/Al-MCM-41	Temperature range: 300 – 600 °C CH ₄ conversions : 2 - 100%	Feed: 0.5 vol% CH ₄ , 8 vol% O ₂ , 5 vol% H ₂ O balance argon	[126]
2005	Pd/SiO ₂ Pd/ZrO ₂ -Y	Temperature range: 200 – 400 °C CH ₄ conversions : 0 – 95%	Feed: 5000 ppm V CH ₄ in air. WHSV = 12-60 h ⁻¹ .	[127]
2005	Pd/Sn _{0.4} Zr _{0.6} O ₂	Temperature range: 250 – 425 °C CH ₄ conversions : 5 – 100%	Feed: 1 vol% CH ₄ and 99 vol% air. GHMV = 33,000 h ⁻¹ .	[128]
2006	Pd-Pt/γ-Al ₂ O ₃	Temperature range: 350 – 550 °C CH ₄ conversions : 10-100%	Feed: 2000 vol.ppm CH ₄ , 5 vol% O ₂ (helium balance)	[129]

Year	Catalyst (loadings and supports)	Reaction conditions		Ref.
		Temperature and methane conversion ranges)	Feed composition	
	(2.12 wt% metal loading at ratio Pd/Pt = 0.93/0.07)		GHSV = 20,000 h ⁻¹ .	
2006	0.1 wt% Pd/H-beta	Temperature range: 327 – 527 °C CH ₄ conversions : 0 – 100%	Feed: 2000 vol.ppm CH ₄ , 10 vol% O ₂ , 10% water vapour (N ₂ balance)	[130]
2006	Pt-Pd-Au/CeO ₂	The most active catalyst is 2%Pt-3%Pd-0.4%Au/CeO ₂ where T ₅₀ = 252 °C and T ₉₀ = 302 °C.	1% CH ₄ and 4% O ₂ (N ₂ as carrier gas) GHSV = 15,000 h ⁻¹	[131]
2006	30 wt% Co ₃ O ₄ /CeO ₂	Temperature range: 300 – 700 °C CH ₄ conversions : 2-98%	Feed: 0.3 vol% of CH ₄ + 0.6 vol% O ₂ + 5 vol% H ₂ O in He WHSV = 60,000 mL g ⁻¹ h ⁻¹	[132]
2007	0.7 wt% Pd/Co ₃ O ₄	Temperature range: 200 – 450 °C CH ₄ conversions : 0 - 100%	Feed: 0.3 vol% of CH ₄ + 0.6 vol% O ₂ in He WHSV = 60,000 mL g ⁻¹ h ⁻¹	[133]
2007	2%Pt-3%Pd-0.4%Au/CeO ₂	Temperature range: 200 – 350 °C CH ₄ conversions : 10 - 100%	Feed: 1% CH ₄ , 10% O ₂ and 89% He	[134]
2007	Pd/LaMnO ₃	Temperature range: 250 – 500 °C CH ₄ conversions : 0 - 100%	Feed: 1 vol% CH ₄ in air.	[135]
2007	Pd/HMS	Temperature range: 200 – 450 °C CH ₄ conversions : 0 - 100%	Feed: 0.3 vol% of CH ₄ + 2.4 vol% O ₂ in He WHSV = 60,000 ml g ⁻¹ h ⁻¹	[136]
2007	Pd/ZSM-5	The best active catalyst was Pd/ZSM-5 prepared by impregnation, 0.55% Pd loading. T ₉₀ = 374 °C;	Reactant: 1% CH ₄ , 4%O ₂ , Helium balance.	[137]
2007	Cu/ZSM-5	The best catalyst was achieved the total conversion at 500 °C, it was 20%Cu/ZSM-5 sample prepared by impregnation method.	Fixed-bed quartz reactor. Reactant: 2000 ppm CH ₄ , 10% O ₂ , balanced with N ₂ . GHSV= 36,000 h ⁻¹	[138]
2007	AuOx/Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	The best performance was achieved over the 0.2% AuOx/CZY catalyst, T ₁₀₀ = 660 °C at GHSV of 50,000 h ⁻¹ .	Fixed-bed quartz reactor. Reactant: 2000 ppm CH ₄ , 4vol. % air, balanced with N ₂ . GHSV= 30,000 h ⁻¹	[139]
2007	Co ₃ O ₄ /γ-Al ₂ O ₃	Temperature range: 200–400 °C CH ₄ conversions : 5 - 100%	Feed: 1 vol% CH ₄ in air Space velocity: 15,000 h ⁻¹	[140]
2008	Pt-Pd/Al ₂ O ₃ with constant Pd loading (2%) and different Pt/Pd atomic ratio	At 350 °C the maximum CH ₄ conversion level is 80% achieved by Pt/Pd with atomic ratio of 0.10.	Reactant: 0.3 vol.% CH ₄ + 2.4 vol% O ₂ in helium.	[141]
2008	Monolithic 0.5% Pd/0.3%Co/Al ₂ O ₃	Temperature range: 250–425 °C CH ₄ conversions : 0 - 95%	Feed: 1 vol% CH ₄ in air	[142]
2008	Pd/ZrO ₂ -Ce	Temperature range: 300 –550 °C CH ₄ conversions : 10 - 90%	Feed: 5000 ppm CH ₄ in synthetic dry air	[100]
2008	Pd/ZrO ₂ -Y	Temperature range: 250- 530 °C CH ₄ conversions : 0 - 99%	Feed: 5000 ppm CH ₄ in synthetic dry air	[57]
2008	Pd-ZSM-5	Temperature range: 150- 370 °C CH ₄ conversions : 0 - 90%	Feed: 0.2% CH ₄ , 0.4%O ₂ and N ₂ balance; Space velocity: 36000 h ⁻¹	[143]

Year	Catalyst (loadings and supports)	Reaction conditions		Ref.
		Temperature and methane conversion ranges)	Feed composition	
2009	1 wt% Pd/5 wt% TiO ₂ -SiO ₂	Temperature range: 250- 550 °C CH ₄ conversions : 0 - 95%	Feed: 0.3 vol.% CH ₄ + 2.4 vol.% O ₂ + 10 vol. ppm of SO ₂ in He WHSV: 60000 ml g ⁻¹ h ⁻¹	[144]
2009	2% Pd/LaMnO ₃ -ZrO ₂	Temperature range: 350-700 °C CH ₄ conversions : 0 - 100%	Feed: 2% CH ₄ and 16% O ₂ in He GHSV: 6000 h ⁻¹	[145]
2009	Mn-Co oxide with a Co/Mn molar ratio of 5:1	Temperature range: 250-360 °C CH ₄ conversions : 2 - 100%	Feed: 1% CH ₄ , 10% O ₂ , balance N ₂ WHSV = 36,000 mL h ⁻¹ g ⁻¹	[146]
2009	1.3 wt% Pd supported on medium pore zeolites TNU-10 (Si/Al = 7.1)	Temperature range: 340-425 °C CH ₄ conversions : 20 - 90%	Feed: 1 vol.% CH ₄ and 4 vol.% O ₂ in He GHSV = 120,000 h ⁻¹	[147]
2009	Cu-Mg-AlO with Cu at% 10-20%	Temperature range: 300-500 °C CH ₄ conversions : 0-100%	Feed: 1% vol. CH ₄ in air VHSV = 20,000 h ⁻¹	[148]
2009	Co ₃ O ₄ Mn ₂ O ₂	Temperature range: 250-550 °C CH ₄ conversions : 2 - 100% Temperature range: 300-600 °C CH ₄ conversions : 0-100%	Feed: 2000 ppmV CH ₄ balance air	[53]
2010	2wt%Pd/15wt%CeO ₂ /Al ₂ O ₃	Temperature range: 230-530 °C CH ₄ conversions : 0 - 98%	Feed: 0.5% CH ₄ , 2% O ₂ , 10 ppm SO ₂ in He	[59]
2010	2 wt% Pt– 1 wt% Pd/Al ₂ O ₃	Temperature range: 300-450 °C CH ₄ conversions : 5 - 98%	Feed: 2000 ppmV CH ₄ , 10 vol% O ₂ , balance He	[149]
2010	Pd/TiO ₂ (10%)–SiO ₂	Temperature range: 200-450 °C CH ₄ conversions : 0 – 100%	Feed: 0.3 vol% CH ₄ + 2.4 vol% O ₂ + 5 vol% H ₂ O + 10 vol ppm of SO ₂ in helium WHSV: 60000 mLg ⁻¹ h ⁻¹	[94]
2010	1.25 wt%Pd/La-Al ₂ O ₃ 1.25 wt% Pd-2 wt% Co/La-Al ₂ O ₃ 1.25 wt% Pd/ 2 wt% Co/La-Al ₂ O ₃	Temperature range: 360-470 °C CH ₄ conversions : 40–100% Temperature range: 360-470 °C CH ₄ conversions : 30-100% Temperature range: 350-480 °C CH ₄ conversions : 20–100%	Feed: 630 ppm CH ₄ , 10 vol% H ₂ O, 0.4 vol% CO, 5 vol% O ₂ , 12 vol% CO ₂ , and N ₂ as balance. GHSV = 34,000 h ⁻¹	[150]
2011	Pd/SBA-15	Temperature range: 240-430 °C CH ₄ conversions : 0 – 100%	Feed: 150 ppm NO + 1500 ppm CH ₄ + 7% O ₂ in Ar. GHSV = 22,100 h ⁻¹	[151]
2011	2 wt% Pd/Co ₃ O ₄	Temperature range: 225-275 °C CH ₄ conversions : 6.8 – 98.2%	Feed: 2% CH ₄ in air GHSV = 40,000 h ⁻¹	[152]
2011	1 wt% Pd/HMS 1 wt% Pd/ 5wt% Ti-HMS 1 wt% Pd/10 wt% Ti-SBA-15	Temperature range: 200-500 °C CH ₄ conversions : 0 – 100% Temperature range: 250-550 °C CH ₄ conversions : 0 – 97% Temperature range: 200-450 °C CH ₄ conversions : 0 – 98%	Feed: 0.3 vol% CH ₄ + 2.4 vol% O ₂ + 10 vol. ppm of SO ₂ in He WHSV: 60,000 ml g ⁻¹ h ⁻¹	[153]
2011	1 wt% Pd/Zr _{0.5} Ce _{0.5} O ₂ /SiC and 1 wt% Pd/ZrO ₂ /SiC	Temperature range: 210-340 °C CH ₄ conversions : 0 – 100%	Feed: 20% O ₂ + 1% CH ₄ + 79% N ₂ Space velocity: 10,000 h ⁻¹	[154]

Year	Catalyst (loadings and supports)	Reaction conditions		Ref.
		Temperature and methane conversion ranges)	Feed composition	
2011	11.6 wt% PdO/Ce _{0.64} Zr _{0.16} Bi _{0.20} O _{1.90} /γ-Al ₂ O ₃ 7.3 wt% Pt/Ce _{0.64} Zr _{0.16} Bi _{0.20} O _{1.90} /γAl ₂ O ₃	Temperature range: 150-320 °C CH ₄ conversions : 0 – 100%	Feed: 1 vol% CH ₄ in air Space velocity: 20,000 h ⁻¹	[155]
2011	2 wt% Pd supported on β-SiC foam blocks	Temperature range: 300-500 °C CH ₄ conversions : 0 – 95%	Feed: 1724 ppm CH ₄ in air Catalyst weight = 1 g	[156]
2011	Co–Ce–O composite oxides	Temperature range: 250-600 °C CH ₄ conversions : 2–100%	Feed: 1.0 vol% CH ₄ + 4.0 vol% O ₂ in Ar WHSV: 30,000 ml g ⁻¹ h ⁻¹	[157]
2012	1 wt% Pd/H-MCM-41 1 wt% Pd/MCM-48	Temperature range: 326-550 °C CH ₄ conversions : 10–100% Temperature range: 339-550 °C CH ₄ conversions : 10–98%	Reaction gas mixture: O ₂ /CH ₄ = 4	[158]
2012	0.6 wt% Pd/NiO–Al ₂ O ₃	Temperature at 100% CH ₄ conversion (<i>T</i> ₁₀₀) = 600 °C After 3200 h time-on-stream, CH ₄ conversion remained at ca. 96%.	Feed: 0.4 vol% of CH ₄ , 4 vol% of H ₂ O and balancing air. GHSV= 80,000 h ⁻¹	[96]
2013	Co/Cr mixed oxide with Co:Cr (mol) = 1:2	Temperature range: 325-575 °C CH ₄ conversions : 5–100%	Feed: 2000 ppm CH ₄ , 10 vol% O ₂ , 10 vol% H ₂ O and balance N ₂ GHSV= 36,000 mL h ⁻¹ g ⁻¹ .	[159]
2013	3 wt% Ce - 30 wt% Cr/γ-Al ₂ O ₃ La _{0.7} Ce _{0.3} FeO ₃	Temperature range: 300-450 °C CH ₄ conversions : 5–100% Temperature range: 320-550 °C CH ₄ conversions : 7–98%	Feed: CH ₄ :O ₂ :N ₂ = 2:8:90 Feed: 0.5 vol% CH ₄ , 3 vol% O ₂ and 96.5 vol% N ₂ Space velocity: 12,000 ml gcat. ⁻¹ h ⁻¹ .	[160] [161]
2014	1 wt% Pd/SiO ₂ -TiO ₂	Temperature range: 200-400 °C CH ₄ conversions: 0–100%. After treated in 10 ppm SO ₂ at 350 °C, activity is restored.	Feed: 0.3 vol% CH ₄ + 2.4 vol% O ₂ in Ar WHSV = 60,000 mL g ⁻¹ h ⁻¹ .	[162]
2014	0.5 wt% Pd/ZrO ₂ (Support was calcined at 1000 °C for 6 h)	Temperature range: 340-500 °C CH ₄ conversions : 0–98%	Feed: 1 vol% CH ₄ , 20 vol% O ₂ , 3% H ₂ O balance N ₂ GHSV=120,000 h ⁻¹	[163]
2014	3.5 wt% Pd–SBA-15	Temperature range: 200-450 °C CH ₄ conversions : 5–100%	Feed: 150 ppm NO + 1500 ppm CH ₄ + 7% O ₂ in Ar.	[164]
2014	1.5% Pd/Zr _{0.5} Al _{0.5} O _{1.75} coated on honeycomb cordierite	Temperature range: 340-420 °C CH ₄ conversions : 46–100%	Feed: 0.075% CH ₄ , 0.10% CO, 5.0% O ₂ , 12.0% CO ₂ , 12.0% H ₂ O balance N ₂ GHSV = 50,000 h ⁻¹	[165]
2014	1.5 wt% Pd/TiO ₂ -Zr _{0.5} Al _{0.5} O _{1.75} coated on honeycomb cordierite	Temperature range: 250-320 °C CH ₄ conversions : 42–100%	Feed: 0.075% CH ₄ , 0.30% CO, 5.0% O ₂ , 12.0% CO ₂ , balance N ₂ GHSV = 30,000 h ⁻¹	[166]
2015	Co ₃ O ₄ Fe ₂ O ₃	Temperature range: 250-500 °C CH ₄ conversions : 2–100% Temperature range: 350-580 °C CH ₄ conversions : 3–100%	Feed: 6000 ppm CH ₄ balance air. GHSV = 100,000 h ⁻¹ .	[112]
2016	1.4 wt% Pd/TS-1	Temperature to achieve 90% conversion (<i>T</i> ₉₀) = 430 °C.	Feed: 7000 ppm CH ₄ , 10,000 ppm CO ₂ ,	[167]

Year	Catalyst (loadings and supports)	Reaction conditions		Ref.
		Temperature and methane conversion ranges)	Feed composition	
		After 1900 h time-on-stream, $T_{90} = 450$	3–4 vol% H ₂ O balance air GHSV = 100,000 h ⁻¹	

6. Summary

Supported palladium catalysts are the most active materials and widely used for catalytic combustion of lean methane mixtures. It is commonly agreed that PdO is the active phase. However, its sensitivity to water vapour becomes a challenge to its use as efficient catalyst for methane emissions abatement from coal mine ventilation air systems. A number of fundamental studies have been reported and have contributed to improving the understanding the reaction pathways and catalyst deactivation phenomena. However, there are remaining significant uncertainties and obstacles to explain the influence of parameters such as the pre-treatment history, palladium particle size and the presence of contaminants on the catalytic behaviour of Pd catalysts. For the VAM mitigation application, there are many important practical aspects in which further detailed investigation such as catalyst deactivation phenomena, the stability of catalyst under humid conditions, the effect of coal dust on catalytic activity and stability. The pressure drop, heat recovery/ self-sustaining and long term deactivation are the key for a successful development of VAM catalytic combustor.

Attempts to improve the catalytic activity of Pd catalysts in methane combustion are still carried-out. The intrinsic activity of PdO for the reaction could potentially be increased by increasing the degree of dispersion of PdO. However, improving the catalytic activity of Pd catalysts is not necessarily the key issue with respect to the use of these catalysts, compared to the effect of water vapour. To develop successful technology for the VAM mitigation

application, strategies to improve the catalysts resistance to water vapour rather than only improving catalytic activity need to be developed. The literature suggests that the mechanism of water vapour inhibition of Pd-based catalysts remains somewhat uncertain at this stage.

Another route for preparing efficient catalysts for VAM combustion could be improving the catalytic activity of transition metal oxide catalysts. Nano-sized cobalt oxide catalysts have drawn much attention due to its lower cost and higher stability compared to noble metal catalysts. Enhanced activity and stability reported in the literature over nano-sized cobalt oxide catalysts offers a good prospect for VAM combustion.

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