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Review Article

Application of hopcalite catalyst for controlling carbon monoxide emission at cold-start emission conditions

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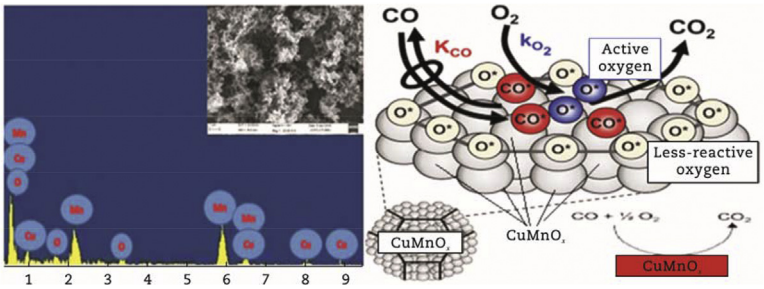
HIGHLIGHTS

- In the cold start period, the catalytic converter is entirely inactive, because the catalytic converter has not warmed up.
- The cold start phase is also depending upon the characteristics of vehicles.
- The amount of catalyst required to entrap the toxic pollutants throughout the cold-start period is usually much less than that needed in catalytic converters.
- Hopcalite ($CuMnO_x$) catalyst could work very well at the low temperature, it can overcome the problem of cold-start emissions if used in a catalytic converter.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon monoxide (CO) is a poisonous gas particularly to all leaving being present in the atmosphere. An estimate has shown that the vehicular exhaust contributes the largest source of CO pollution in developed countries. Due to the exponentially increasing number of automobile vehicles on roads, CO concentrations have reached an alarming level in urban areas. To control this vehicular exhaust pollution, the end-of-pipe-technology using catalytic converters is recommended. The catalysts operating efficiently in a catalytic

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converter are a challenging class of materials for applications in cold start of engines to maintain indoor air quality. In the cold start period, the catalytic converter was entirely inactive, because the catalytic converter had not been warmed up. The cold start phase is also depending upon the characteristics of vehicles and property of catalysts. The increasing cost of noble metals with the increasing number of vehicles motivates the investigation of material concepts to reduce the precious metal content in automotive catalysts or to find a substitute for noble metals. Hopcalite ($CuMnO_x$) catalyst could work very well at the low temperature; thus, it can overcome the problem of cold-start emissions if used in a catalytic converter. Further, low cost, easy availability and advanced synthesis methods with stabilizer, promoter, etc., advocates for the use of hopcalite as an auto exhaust purification catalyst. Although there are numerous research articles present on this topic until now, no review has been presented for demanding this issue. So there is a space in this area, and it has been made an attempt to seal this hole and progress the future scope for hopcalite catalyst for purification of exhaust gases by this review.

1. Introduction

Carbon monoxide (CO) is one of the most poisonous and also called as the unnoticed poison of the 21st century. With the increasing number of vehicles on roads, CO concentrations have reached an alarming level in urban areas. An estimate has shown that automobile exhaust contributes about 64% of CO pollution in the urbanized countries (Badr and Probert, 1995; Benjamin and Alphonse, 2016; Chen et al., 2018). In comparison with diesel engine, the petrol engine vehicles produce more CO into the environment. The CO formed in internal combustion (IC) engine is operating by the burning of fossil fuels (petrol or diesel), as an intermediate reaction during the incomplete combustion of HC (Cholakov, 2010). The air/fuel (A/F) ratio plays an important role in the efficiency of combustion process. When an IC engine gets a stoichio-metric mixture of A:F = 14.7:1, it emits a minimum amount of pollutants into the atmosphere (Chhatwal et al., 1975; Ismaila et al., 2013). The natural concentration of CO in air is around 0.2 parts per million (ppm), that amount affects not only the human beings but also vegetation by interface with plant respiration and nitrogen fixation (Kamrani, 2008). The CO is profoundly affected on the cardiovascular system of human and animal body and combined with hemoglobin present in the blood cells and converted into carboxy-hemoglobin (CoHb), which reduces the oxygen-carrying capacity of a human body (Pulkrabek, 2004). The chronic effect of CO poisoning on human health increases the pulse rate, respiration system failure, neurological reflexes, headaches and dizziness. After CO exposure, arrhythmias, angina attacks and increase in the level of cardiac enzymes would happen (Air Improvement Resource, Inc., 2005; Alfuso et al., 1993; International Council on Clean Transportation (ICCT), 2016).

The ambient temperature catalytic oxidation of CO is a very important process and is widely applied in automotive air cleaning technologies, CO detectors, gas masks for fire-fighters, mining application and selective oxidation of CO in reformer gas for fuel cell applications (Aguila et al., 1991). The performance of catalytic converter is highly depending upon the types of catalysts used. In the presence of catalyst, the rate of chemical reaction was increased; it acts like an agent that reduces the activation energy of the reactions (Faiz et al., 1996; Kramer et al., 2006). The noble metals (Pt, Pd, Rh, Au, Ag, etc.) and base metals (Cu, Mn, Cr, Co, Ni, Fe, etc.) are widely used as a catalyst in the catalytic converter. Commercial catalysts mainly applied for CO oxidation present in the exhaust gas clean-up are noble metals (Pillai and Deevi, 2006). It has a high activity and thermal stability so that it was widely used as a catalyst in a catalytic converter. Compared to noble metal catalysts, the hopcalite ($CuMnO_x$) is one of the oldest known catalysts for CO oxidation at low temperature (Royer and Duprez, 2011). The $CuMnO_x$ is broadly used for the respiratory protection systems in many types of applications like military, mining and space devices, etc. In 1920, Lamb, Bray and Frazer discovered various mixture oxides of Cu, Mn, Ag, and Co, and identified them as a group of catalysts known as hopcalite (Huang and Tsai, 2003; Zhou et al., 2014). The structure of hopcalite catalyst is also depending upon the preparation methods, drying temperature and calcination conditions of the catalyst. The oxygen species associated with copper in $CuMnO_x$ catalyst are very active and may be dominated by the low-temperature catalytic oxidation of CO (Dey et al., 2016).

The reasons for enhanced catalytic activity are the improved lattice oxygen mobility, specific surface area and pore volume of the $CuMnO_x$ catalysts. To improve the reactivity of lattice oxygen associated with Cu species as well as the mobility of lattice oxygen from Mn species (Dey et al., 2017), the Cu-oxide is found weakly active for CO oxidation, but in conjunction with Mn-oxide in appropriate proportions, very active $CuMnO_x$ catalyst system was generated (Solsona et al., 2004; Summers et al., 1993). The "cold-start" problem controlling the unwanted emissions produced before the catalytic converter reaches operational

temperatures. During cold-start phase, about 60%–80% of CO is emitted from automobile vehicle even equipped with a three-way catalyst (TWC) (Dey et al., 2017). TWC which uses noble metals is not being able to function effectively until it reaches the light-off temperature of 200 °C as the conversion efficiency depends strongly on the working temperature and is practically zero during the starting and warming up period (Singh and Prasad, 2014). Among the base metal catalysts, the hopcalite is highly active for purification of vehicular exhaust. The addition of ceria (Ce) into $CuMnO_x$ catalyst increases their performances due to their excellent oxygen storage capacity (OSC) provided by the redox couple: $2CeO_2 \leftrightarrow Ce_2O_3 + O$, making active oxygen available for the acceleration of oxidation reactions and structural improvement of metal dispersion (Cai et al., 2012). Further, gold (Au) based $CuMnO_x$ catalysts show high activity at low temperatures, good stability under moisture and resistance to sulfur poisoning (Cole et al., 2010). It is also reported that the Au is about 1000 times more active than Pt in the catalytic oxidation of CO under basic but not acidic environments. The highly dispersed gold nano-particles on suitable metal oxides show great catalytic activity in low-temperature CO oxidation (Haruta et al., 1989; Morgan et al., 2010).

By promoting Au in the hopcalite catalysts, their activity can be improved and maintained in the low temperature range for CO conversion. India has sufficient Au reserves; therefore application of Au in place of Pt would be attractive proposition for catalytic control of vehicular CO emissions under cold-start conditions (Raphulu, 2004). Several authors have investigated various catalysts for low temperature CO oxidation. The high activity is due to the formation of Cu-Mn spinel $CuMn_2O_4$ during the co-precipitation process (Dey et al., 2018). The redox reaction has been proposed to explain the $CuMnO_x$ catalyst activity, i.e., an electronic transfer between Cu and Mn cations within the spinel lattice (Choi et al., 2016). It is usually accepted that the improvement of Cu^+ and Mn^{4+} concentrations in $CuMnO_x$ catalyst ensures a deactivation of material (Tanaka et al., 2003). The high catalytic activity can be maintained at room temperature, which is the so-called "amorphous" $CuMnO_x$ in the place of spinel $CuMn_2O_4$ catalyst (Elmhamdi et al., 2017). The phase structure of $CuMnO_x$ catalysts has a major influence on the activity of CO oxidation. The success of $CuMnO_x$ catalyst has prompted a great deal of fundamental work devoted to clarifying the role played by each element and nature of active sites (Gao et al., 2016; Njagi et al., 2010). This manuscript provides a summary of published information regarding pure and substituted hopcalite catalyst, synthesized methods, properties and their application for CO emissions control.

2. Vehicular cold-start emissions control

The high tailpipe emissions (60%–80% of CO and HC) would occur from a motor vehicle even equipped with a three-way catalyst (TWC) converter within the first few minutes or approximately first few kilometers after a vehicle starts. This period is called cold-start condition and the high emissions arisen during this period is due to the following reasons.

1. Low temperature and high pressure in the engine cylinder make it difficult for fuel to vaporize. Hence, the engines require an enriched mixture to ensure that an adequate amount of fuel is vaporized to achieve combustible mixture. The fuel-rich mixture leads to incomplete combustion, resulting in partially burned fuel (CO emissions) and unburned fuel (HC emissions).
2. Cold-start requires longer engine cranking times that would be needed at higher temperature. This adds to the emission of incomplete combustion products.
3. Internal friction in the engine and drive train is greater than that at higher temperature, requiring greater power output from the engine during warm-up.
4. The catalyst is cold, hence is not effective, during the first few minutes of operation.
5. On many vehicles, air injection to the catalyst is delayed by a timer while the vehicle warms up. Air injection with high levels of unburned or incompletely burned fuel entering the catalyst (as typically occurs during warm-up of cold engines) can cause catalyst temperatures rise and possibly damage the catalyst. This delay is typically between 5 and 15 min.

The emission values of regulated pollutants, available for cold and hot phase of driving cycle, mostly depends upon the speed-time pattern. In these phases, an enrichment of air-fuel mixture is needed, which affects the catalyst conversion efficiency. The difference between emissions during the cold start and hot start phases is that under hot engine and fully operating catalyst, emission factors of CO and HC were about 3–4 times lower than those observed under warm engine conditions. During the cold start, the engine and catalytic converter are not at their optimal operating conditions, which causes highly influences various factors (Dey et al., 2019a; Dhanalakshmi and Suresh, 2018; Iodice and Senatore, 2012; Yusuf and Inambao, 2019). First, the cold engine requires a rich mixture to compensate for fuel that does not contribute to the combustion because it condenses at the cold internal parts of the engine for fuel that has not yet vaporized. Second, the catalyst has to warm up during the cold start period, thus the catalyst efficiency increases rapidly during the early moments after a cold start (E et al., 2019; Gao et al., 2019; Li et al., 2019). The fuel that is not combusted or partially combusted, passes the catalyst untreated as HC and CO. Nowadays, the catalyst improving the most important part of total emission during a vehicle running take place in cold phases. A catalytic converter, mixture control and cold start emissions play an important role in automobile exhaust pollutions (Aspromonte and Boix, 2019; Iodice and Senatore, 2016; Mirzaei et al., 2013).

The "first phase" of cold transient is characterized by the highest cold-start emissions owing to the greatest enrichment of fuel-air ratio and the lower temperatures of the engine, lubricant and catalytic converter. During the "second phase" of cold-start transient, emissions decline owing to the gradual increase of catalyst and engine temperatures and lower enrichments of the air-fuel mixture ratio. The "third phase" was

characterized by the lowest cold-start emissions because the operating temperatures are achieved and air-fuel mixture values are very near to the stoichiometric ratio (Iodice et al., 2016). In addition, at the lowest temperature of ambient air, the cold engine during the cold phase hinders the gasoline vaporization, thus increasing the formation of unburned fuel and leading to increased unburned HC emissions as a result of there being too much fuel present to achieve complete combustion. A rich fuel-air mixture produces very high amount of CO emissions (Hamedi et al., 2019; Zhu et al., 2019). The lower engine loads, corresponding to low values of constant speed, and the excessive leaning of fuel-air mixture would result in irregular operating conditions of the engine. The internal engine optimizes more accurate mixture control of fuel injection systems, allowing a better control of fuel feeding and enhancing catalyst efficiency (Li et al., 2008; Iodice and Senatore, 2013).

The emission levels depend on driving cycle, due to the differences in kinematic parameters, such as speed and acceleration. Modern vehicles are equipped with a spark ignition engine with fuel injection and electronic mixture control, and a three-way catalyst; as a result, CO and unburned HC emissions in cold conditions represent a significant share of total emissions if compared with those given off in warm conditions. The cold-start performance of vehicle engines remains a crucial phase because the thermal efficiency of last generation engines is significantly lower at cold-start than the steady-state conditions (Vasic and Weilenmann, 2006). The poor cold-start performance assigns a high fuel consumption. The steady-state performance of internal combustion engines has improved noticeably over the years, both in terms of fuel consumption and emissions quality. During the cold-start phase, as little as 9% of the energy in fuel is converted to effective work, as a result of components and fluids being below their optimal temperatures. The energy transferred to the cylinder walls causes the coolant, the metallic structure (including the block and crankshaft) and lubricant to warm up (Iodice and Senatore, 2015; Roberts et al., 2014; Ryou et al., 2019).

In energy balance, the heat sink of automobile engine found that 60% of energy was used to heat the structural parts, with approximately 20% being absorbed by the coolant and 10% by the lubricant. In the cold-start phase, the engine components are not yet at the operation conditions. In particular, the fuel can condense on the cool walls of the inlet manifold and cylinder. It is necessary to increase the supply of fuel to support combustion (Libardi et al., 2014; Hedinger et al., 2017; Ryou et al., 2019). For petrol engine vehicles equipped with a three-way catalyst, the performance of catalyst is reduced during the cold-start transient. During the engine warm-up phase, there are effectively three thermal masses interacting with each other, including main engine block, lubricant and coolant. In the early phases of warm-up when the cylinder walls are cold, most of the energy from combustion is transferred to the walls owing to the high temperature difference between them and combustion gases (Li et al., 2008; Iodice and Senatore, 2016; Iodice et al., 2016).

In this situation, the cold start emissions condition has started. At 20 °C, only 10%–30% of gasoline actually vaporizes when injected into the combustion chamber. That means 70%–90% of the fuel remains in the liquid phase. Therefore, 8–15 times the stoichiometric amount of additional fuel is injected in order to produce enough vapors for perfect ignition (Pattrick et al., 2004; Zhou et al., 2019). The non-vaporized fuel remains as a liquid till combustion. The fuel vapors are ignited by the spark plug and most of the liquid fuel vaporizes and exits the engine partially combusted, containing relatively large amounts of CO (1%–7%) and HC (0.1%–0.7%). The amount of cold-start phase is also dependent on the outside temperature and characteristics of vehicle. The catalytic converters used in automobile vehicles are capable to reach the reductions of CO, HCs and NO_x up to 95% when they are completely warmed up (Giakoumis et al., 2017; Hu et al., 2007; Weilenmann et al., 2005). An exhaustive survey of research was carried out concerning the cold start emissions is given in the report summing up research focusing on the characterization of cold start emissions as a function of the following five parameters.

(1) Technology or emission standard (FAV1/Euro-1.Euro-4).
(2) Average vehicle speed.
(3) Ambient temperature.
(4) Traveled distance.
(5) Engine stop time (also called parking time).

Their main goal was to describe the relative cold start extra emissions as a function of stop times. A stop time longer than 12 h is sufficient to cool the engine and catalyst down to ambient temperature of 20 °C–30 °C. Some researchers refer to the catalyst warm up time from almost zero efficiency at cold-start to 50% conversion efficiency as the light-off time (Andre and Joumard, 2005). Typically, with a conventional TWC converter containing noble metal catalyst, it is necessary to reach 300 °C for light-off to occur. The excess cold start emission (hatched area) of a typical vehicle is shown in Fig. 1. The emission decreases due to the

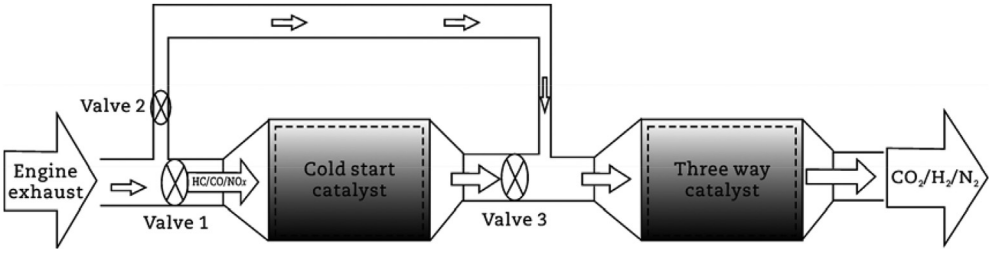

Fig. 1 – Schematic diagram of catalytic converter for solution of cold start problems.

progressive increase of temperature of engine and catalyst, followed by a stable operation when the normal engine temperature is reached at the time known as cold start period (Favez et al., 2009). Many distances driven are so short that the end of cold-start period is either not reached or just about to reach. Short journeys, mostly consisting of home to work place, home to various service units in the city such as post office and bank, home to school, home to local shops, home to doctor's chamber, have large average fuel consumption and emission values (g/km) due essentially to cold start (Bera and Hegde, 2010; Krishna et al., 2019; Sendilvelan and Bhaskar, 2016; Sothea and Oanh, 2019).

On average, the cold start distance defined as the distance necessary for cold tailpipe emissions to reach hot emission levels is typically within 5 km. This indicates that a large amount of urban driving occurs in cold conditions. This scenario is even worse at low ambient conditions. Cold-start emission of pollutant gases from vehicles is thus one of the most important problems in large cities, where the number of vehicles and daily engine starting per populated area is high (Ludykar et al., 1999; Tingvall and Pettersson, 2009). The initial low cylinder wall temperature throughout cold starting prohibited fast and full mixture preparation (mainly fuel vaporization) and led to abrupt heat release after the prolonged ignition delay, resulting in a steep cylinder pressure rise and high peak pressures (Fig. 2). The thermal status of engine played a key role with respect to combustion stability and turbocharger response. For all the examined starting tests, irrespective of coolant temperature or fuel blend, the peak cylinder pressure exhibits a continuous, uninterruptible decreasing trend during the stabilization phase. The difference in the average cylinder pressures between the 1st and 10th deciles is at least 10 bar for all cases. For all the hot-starting tests, a considerable degree of peak cylinder pressure deviation is apparent even 15 s after starting of the engine. Combustion instability was significant, particularly during cold starting. Repeatedly high differences were encountered as regards the peak cylinder pressure between the successive cycles (Blondeau and Mertens, 2019; Hedinger et al., 2017; López-Pérez et al., 2019).

Actually, the cold-starting event was characterized by a series of engine cycles with complete and incomplete combustion for several seconds after initiation of the starter. The composition of various pollutants emitted by car running at idling condition during cold start period is described in Fig. 2. Hence, minimizing emission of pollutants in the cold-start period is very critical for getting very low tailpipe emission. Therefore, in recent years, there are efforts to reduce tailpipe emission during cold-start in order to achieve low emission vehicles (Air Improvement Resource, Inc., 2005; Cholakov, 2018).

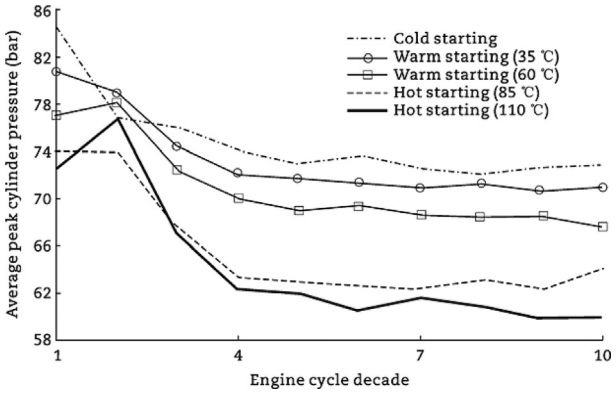

Fig. 2 – Cold start emissions of various pollutants.

2.1. *Cold start CO emission standard*

In order to achieve the low emission from vehicles during cold-start, the US, EPA CO emission standards from 2002 for light-duty vehicles (LDVs) were 3.4 g/mi at 20 °F and 4.4 g/mi at 20 °F for light-duty trucks up to 6000 GVWR. EPA tests of properly operating vehicles indicates that 90% increase in CO emissions at 20 °F occurs as compared to CO emissions at 75 °F during the cold start. The Euro III and Euro IV emission standards have included a sub-ambient cold-start test at a temperature of −7 °C, during the first 780 s of urban driving cycle, limiting HC and CO tailpipe emissions in such conditions (Quarles, 1974). It is estimated that the proposed EPA cold-temperature standards as originally defined (the original rule contained standards for light-duty trucks) would reduce CO emissions by 2.6–3.1 million tons annually by the year 2000 and 5.8–7.7 million tons when complete fleet turnover has been achieved. Application of standards will help mitigate the effect of travel growth beyond the year 2000, bringing areas into attainment and reducing CO inventories by 10%–18% (Sierra Research, Inc., 2002). Two- and three-wheelers remain important modes of transport in many Asian countries and cities now and in the future, and contribute to a large share of air pollution and traffic congestion. Most of the cities and towns in India are highly polluted, especially due to petrol and diesel-powered two- and three-wheelers as they contribute about 80% of the total number of vehicles (Sierra Research, Inc., 2003). In India there are above 18 million petrol-powered two wheelers and over 1.5 million petrol and diesel-powered three-wheelers and their population is growing at a rate about 15% per annum. It is a common sight in India and other developing countries that during traffic jams in congested areas of cities, these vehicles produce tremendous air pollution (Rajvanshi, 2002). The emission norms in India and EU are represented in Table 1.

Table 1 – Emission norms in India parallel to EU emission standards.

Norms	European	Year	CO (g/km)	HC + NO_x (g/km)
1991 norms	–	–	14.30–27.10	2.00 (Only HC)
1996 norms	–	–	8.68–12.40	3.00–4.36
1998 norms	–	–	4.34–6.20	1.50–2.18
India stage 2000 norms	Euro 1	2000	2.72	0.97
Bharat stage-II	Euro 2	2001	2.20	0.50
Bharat stage-III	Euro 3	2005	2.30	0.35
Bharat stage-IV	Euro 4	2010	1.00	0.18
Bharat stage-V	Euro 5	2017	0.63	0.10
Bharat stage-VI	Euro 6	2020	0.50	0.07

The national effort to control this automobile pollution can be traced to the 1970 Clean Air Act, which required a 90% reduction in CO, HC and NO_x emissions from automobiles. The emission standards were first adopted in 1991 and continuously upgraded since then. The first major revision occurred in 1996, the second in 2000, the third in 2005 and next in 2010 (Innovative Transport Solutions (iTrans) Pvt. Ltd., 2009). With effect from April 1st, 1996, the test as per Indian driving cycle with cold start (20 °C–30 °C) on chassis dynamometer, mass emission standards for diesel vehicles (including two- and three-wheelers) are given in Table 1. With effect from April 1st, 1998, the test as per Indian driving cycle with cold start (20 °C–30 °C) on chassis dynamometer, the standard for CO emission was 4.5 g/km for all categories of petrol driven two- and three-wheelers. The growing of environmental concerns over the past three decades has resulted in regulatory action around the globe to begin more rigorous emission standards successively (Heck and Farrauto, 2001).

2.2. *Techniques to minimize cold start emissions*

Faced with increasingly strict emission standards, automobile makers have investigated a variety of approaches to reduce cold-start emissions. Several potential techniques to minimize the cold start emissions have been developed. These can be divided into two categories. The first category based on quickly bringing the catalyst to working temperature includes (a) close-coupled catalyst, (b) electrically heated catalyst, (c) pre-heat burner, (d) partial oxidation catalyst, (e) exhaust-gas ignition, (f) combustion/chemically heated catalyst, (g) secondary air injection, (h) heat storage device and (i) cold-start spark retard or post manifold combustion. The second technique involves trapping hydrocarbons (HC) during cold-start for release after the catalyst has reached operating temperature (Ball, 1996; Bhasin et al., 1993).

2.2.1. *Close-coupled catalyst (CCC)*

Traditionally, the close-coupled or engine manifold mounted catalysts are placed in positions very near to the engine, thus reducing the time necessary for heating the engine exhaust to increase the catalyst temperature. The close-coupled catalyst technology has approached ULEV emission levels after aging at 1050 °C for 24 h. It is generally used with a chassis three-way catalyst as shown in Fig. 3. Lu and Zhang (2010) patented the preparation of TWC to be used as close-coupled catalyst for purification of exhaust gas from motor vehicle (Lu and Zhang, 2010). The catalyst active components are a mixture of noble metal, non-noble metal oxide and rare-earth oxide, wherein the noble metal is palladium and rhodium, the non-noble metal is manganese, cobalt, iron and rare-earth oxide is cerium oxide applied on the wash-coated cordierite honeycomb. The CCCs can heat up quickly but are not very effective under rich exhaust conditions of "over-fueling" or "acceleration enrichment" (Heck et al., 1995).

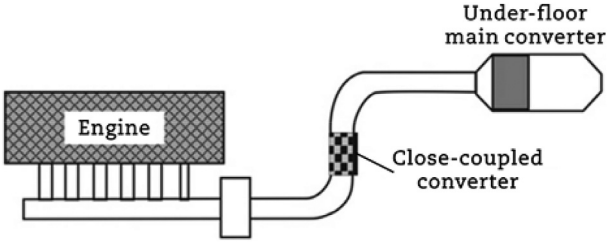

Fig. 3 – Close-coupled converter in a vehicle.

The practice of "over-fueling" or "acceleration enrichment" resulting in high HC and CO emissions has come under pressure to be reduced or eliminated. Reducing this protection combined with an increase in higher speed driving habits of the US and existing autobahn driving habits increases the engine manifold discharge temperatures to around 1050 °C especially for the four- and six-cylinder engines, thus, changing the operating envelope of the close-coupled catalyst. In fact, a technology assessment published by CARB showed the projected technologies for achieving the low emissions and close-coupled catalyst was not a viable option. The dominant technology was the electrically heated catalyst (Lu and Zhang, 2010; Summers et al., 1993).

2.2.2. *Electrically heated catalyst (EHC)*

Another approach to overcome the cold temperatures during startup is to provide heat to the exhaust gas or the catalytic surface using resistive metal and an electric source. The electric heater is placed in front of the catalyst that receives the pre-heated gases thus, provides very efficient reaction in the cold-start period, reducing the time required for catalyst light-off temperature. EHC systems use a small catalyst ahead of the main catalyst (Gottberg et al., 1986). The substrate, onto which the catalyst is deposited, is made from resistive metal filament so that, when an electric current is passing through, the filament heated up quickly (Fig. 4). This brings the catalyst to its full operating temperature in a few seconds. Substantial advances have been made in reducing the power requirements for EHC's and recent studies have shown that the extra battery can be eliminated and the EHC can be powered off by the vehicle alternator. Fig. 4 shows the cold start performance of an EHC (Bhaskar et al., 2010; Shimasaki et al., 1997). Sendilvelan and Sassykova (2019) prepared the electrically heated transition metal oxide catalyst for controlling the cold start emission from engine. The electrical energy is converted into thermal energy by increasing the heating temperature of the catalyst, which will be more effective for reducing the specific heat of the catalyst metal (Sendilvelan and Bhaskar, 2016).

Electrically heated catalysts having low mileage have been shown to achieve ULEV, however, the durability to 100,000 miles is still an open issue. Actual in-use experience is being gained on larger vehicles and these studies give the needed "on the road" experience with EHC's (Laing, 1994).

2.2.3. *Pre-heat burner*

The pre-heat burner uses the gasoline fuel in a small burner placed in front of the catalyst. The burner is turned on during cold start and heat generated warms up the catalyst so that the catalyst is warm when the cold exhaust from the manifold reaches the catalyst (Oser et al., 1994).

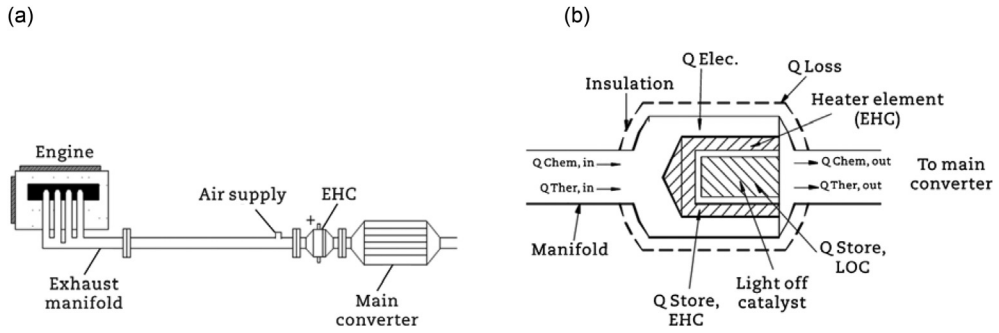

Fig. 4 – Electrically heated catalyst used in a vehicle. (a) Flow diagram of the treatment systems. (b) Schematic diagram of EHC.

2.2.4. *Partial oxidation (PO_x) catalyst*

Partial oxidation (PO_x) catalysts convert HCs to CO and H_2 under rich exhaust conditions (Eq. (1)). Careful selection of active metal catalysts may result in at least activity and selectivity to the partial oxidation of CO (based on methane studies).

$$CH_4 + O_2 \rightarrow CO + 2H_2 \quad (1)$$

A partial oxidation catalyst (Fig. 5) is interposed between an exhaust manifold and a catalytic converter in the exhaust system of an engine. The hydrogen produced is used to promote faster light-off of catalytic converter in the exhaust system. Also, HC emissions discharged into the surrounding environment are reduced during the initial period following the cold-start (Bartley, 2001).

Bartley has reported that under insufficient oxygen, a total HC reduction of 19% was realized at 24 °C and only up to 3% at −7 °C. Addition of supplemental oxygen to the exhaust during the cold-start, which was intended to simulate an adjustment in the engine calibration to less rich operation, resulted in a total HC reduction of 18% with the PO_x catalysts in place, but no benefit when the PO_x catalysts are removed. Hence, the PO_x catalyst approach can be used to reduce cold-start HC emissions from a US Tier 2 vehicle, even under sub-ambient cold-start condition of −7 °C (Bartley, 2001, 2007).

2.2.5. *Exhaust-gas ignition (EGI)*

The exhaust gas ignition involves placing an ignition source (e.g., glow plug) in between two catalysts. During cold start, the engine deliberately run rich (air/fuel ratio ≈ 9) so that large quantities of hydrogen are produced in the exhaust and small amount of air is injected to make the mixture flammable. This is ignited by a glow-plug upstream which heats the catalyst (Ma et al., 1992).

2.2.6. *Chemically/combustion heated catalyst (CHC)*

The chemically/combustion heated catalyst (CHC) uses highly reactive species, usually H_2 and oxygen (air), which are fed into the catalyst prior to the starting of engine. The exothermic hydrogen-oxygen spontaneous flameless catalytic combustion generates heat locally, right at the TWC where it is needed during cold start (Kanada et al., 1996).

2.2.7. *Secondary air injection (SAI)*

Due to "rich fuel mixture" during the cold start phase, a large quantity of un-combusted HC and CO is produced in the exhaust. To reduce the level of these pollutants, ambient secondary air is injected into the exhaust manifold directly downstream of the exhaust valve during the cold starting phase. This results in post oxidation of pollutants in the converter having highly active low temperature catalyst to form CO_2 and H_2O, therefore reducing the emissions. The

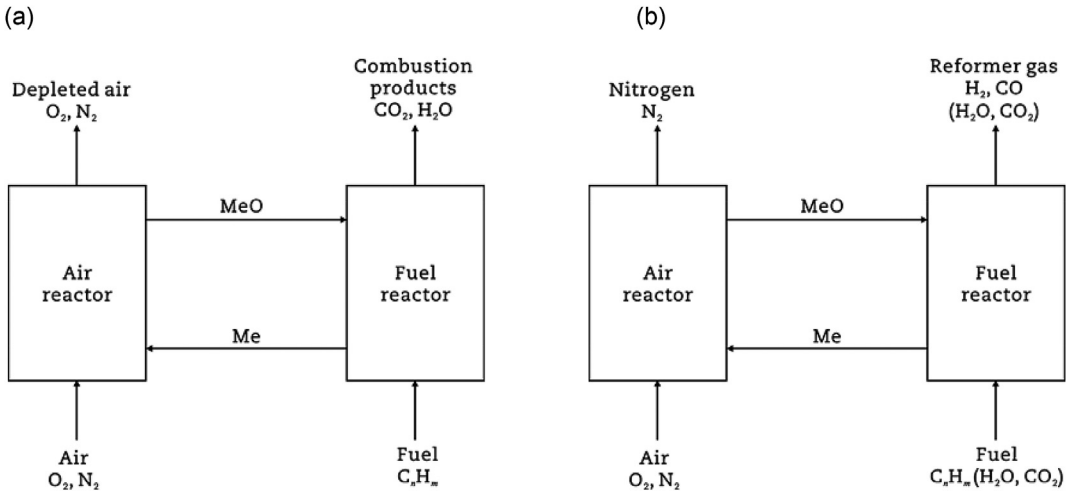

Fig. 5 – Partial oxidation catalyst reaction with pollutants. (a) Combustion products. (b) Reformer gas.

secondary air can be supplied actively or passively. In a passive system, the fluctuations in pressure of the exhaust system are utilized. The additional air is drawn in via a timed valve due to the vacuum created through the flow speed in the exhaust pipe. In an active system, the secondary air is blown by a pump. This system allows better control. The heat generated in this process additionally warms the catalytic converter greatly and reduces the start-up time for the converter, therefore improving exhaust quality during the cold start phase significantly. Among various techniques, secondary air injection (SAI) shown in (Fig. 6) received a lot of attention due to its robust and consistent performance to meet the development (Borland and Zhao, 2002).

In addition, when compared with other approaches, SAI can be implemented relatively easily with today's engine system without requiring a major design change. Lee (2010) reported that the engine operation, with relative air/fuel ratio 20% in rich of stoichiometric ratio and 100% in secondary air, yielded the fasted catalyst light-off (4.2 s). The SAI system reduced HC emissions by 46%–88% and CO emissions by 37%–93% compared with the normal conditions. In petrol engine vehicles, the secondary air injection is a useful method of reducing harmful substance emissions during the cold start periods. A petrol engine needs a "rich mixture" for reliable cold starting. The fuel-air mixture contains excess fuel. Therefore, the high quantities of CO and unburned HC are produced during the cold starting. Since the oxygen sensor emissions control and catalytic converter have not yet reached their operating temperature at the time of this phase, these harmful exhaust gas components can escape into the environment (Lee, 2010).

2.2.8. *Heat storage device/double walled exhaust pipe*

A variety of heat storage devices have also been suggested, all of which work on the principle of retaining heat from the time when the car was last shutdown until the following cold-start. The beneficial impact of reducing cold start emissions via thermal management has led to numerous improvements of the exhaust system components up stream of the converter in order to minimize the heat loss with fabrication of low heat capacity piping (Kishi et al., 1998). Manufacturers have developed ways to insulate the exhaust manifold and exhaust pipe. Attaching the CCC to a double walled, stainless steel exhaust pipe containing an air gap within the double walls is probably the most common thermal management strategy used today to heat up the catalyst quickly (Kandylas and Stamatelos, 1999).

2.2.9. *Cold-start spark retard or post manifold combustion*

Approaches aimed at reducing cold start emissions involve retarding the ignition timing so as to allowing some HC to pass through the exhaust and light off the catalyst sooner. The effect of retarded spark timing on increasing exhaust gas temperature and subsequently reducing tailpipe HC emissions was widely reported in the literature (Chan and Zhu, 1999). Heywood (1997) cites retarded spark timing as one of the more promising means of quickly raising the catalyst temperature to an active level. Research dating back to 2018 clearly shows the effect of retarded spark timing on exhaust HC, particularly as they are dependent on exhaust gas temperature (Hamedi et al., 2019; Heywood, 1997). A large body of results (Fig. 7) shows that this effect is, in fact, quite remarkably linear. Recent investigations extend earlier results to various load and speed points under cold and transient engine operating conditions. A linear relationship

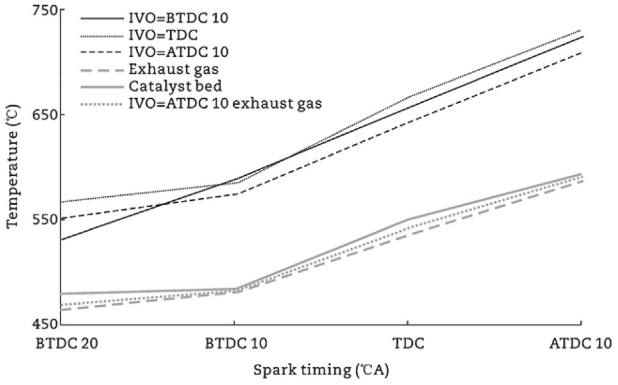

Fig. 7 – Cold-start spark retard combustion in a vehicle.

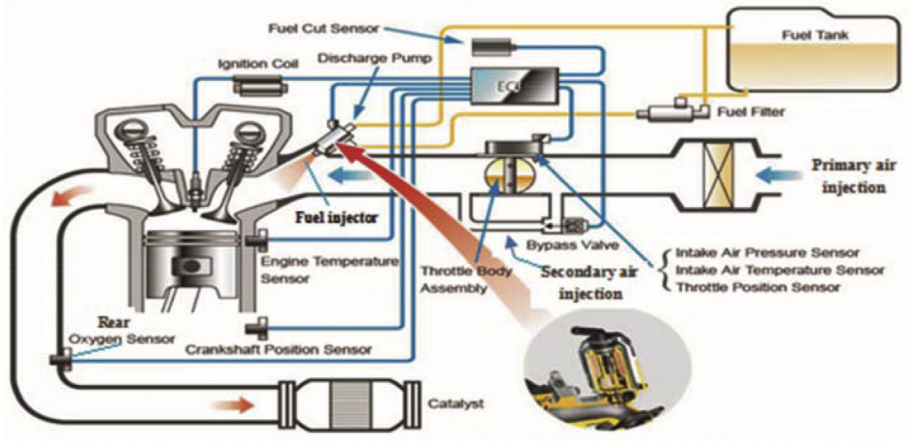

Fig. 6 – Secondary air injection in a vehicle.

between spark timing and exhaust gas temperature exists (Russ et al., 1999).

Spark assisted compression ignition (SACI) combustion is a prospective way of extending the high load limit of homogeneous charge compression ignition (HCCI) while maintaining high thermal efficiency. It provides such a mechanism, helping to control the phasing and stability of a primarily auto-igniting charge. The engine load at ambient conditions goes into the SACI regime by modulating variables such as spark timing, internal and external exhaust gas recirculation (EGR) rates, intake temperature and effective compression ratio with late intake valve closing. As the spark increases, the ratio of internal to external exhaust gas recirculation was reduced to maintain the phasing and the initial heat release rates became steadier. This effect led to an increase in overall burn period, causing both peak rates of pressure to rise and combustion stability to decrease. In colder charges, the spark advance was required to enhance the fraction of flame-based heat release in order to provide the additional compression heating to promote auto ignition (Heywood, 1997; Ueno et al., 2000).

2.2.10. *Hydrocarbon trap*

The second approach to reduce the emissions during a cold start is the HC adsorption trap in which the cold HCs are adsorbed and retained, on an adsorbent, until the catalyst reaches the light-off temperature. For an in-line HC trap system to work, the HC must be eluted from the trap at the exact time when the floor catalyst reaches a reaction temperature higher than 250 °C. The desorbed HCs are oxidized in the normal TWC catalyst (Iliyas, 2008). A typical HC trap of vehicle is shown in Fig. 8. A large number of patents disclose the broad concept of using an adsorbent material to minimize HC emissions during the cold-start engine operation. Various HC adsorbents such as activated carbons or different types of zeolites (silicalite, mordenite, Y-type, ZSM-5 and beta zeolite) have been proposed (Cullen et al., 2007).

Studies have been conducted to quantify the HC species during the vehicle driving cycle. Hydrocarbon trapping strategies using solid adsorbents have been found to effectively trap heavy components in the exhaust, e.g., aromatics, but the light HCs, e.g., C_2–C_4 fractions, desorbed from the trap before the catalyst has reached a high enough temperature for efficient combustion to occur. The main challenges lied in finding a suitable adsorbent material so that proper overlap between the HC desorption temperature and catalyst light-off temperature was achieved (Liu and Wei, 2008). A successful method to trap lighter HC molecules was shown in Fig. 8, which is often desorbed before the catalyst reached its working (light-off) temperature. The nanoporous structured ZSM-12 zeolite has non-intersecting, one-dimensional pores that are so small that molecules cannot pass by one another through the pores. Thus, even a small fraction of strongly adsorbing "blocker" molecule could effectively trap a sizeable number of lighter components (Wang et al., 2009). Further, ZSM-12 zeolite represents superior HC trapping performance in the presence of inhibiting constituents (i.e., H_2O, CO_2 and H_2O-CO_2 mixture) after the hydrothermal ageing. In this regard, Puértolas et al. (2012) designed means of molecular simulation tools and later synthesized a highly effective HC trap for the abatement of cold start HC emissions with specific adsorption sites for different molecules present in the exhaust gases. The simple solution of placing a monolith coated with a HC adsorbent (Fig. 9) upstream from the catalyst is problematic, because the thermal mass of adsorbent monolith delays the heat from engine exhaust reaching the catalyst. As the adsorbent temperature rises, the stored HC desorbs and passes over the catalyst which is still below the light-off temperature, therefore, unable to convert the hydrocarbons (Santoso and Ament, 2010).

Ideas to get around this heat management problem have often involved the use of bypass valves in the exhaust. In one recent example, a fluidic valve is used to direct the exhaust stream through a HC trap at cold-start. After the exhaust stream has become hot, gases are re-directed to the catalyst while the HC slowly desorbed from the trap. Catalyzed HC traps, in which the HC trap and catalyst are coated onto the same monolith, have also been proposed to lessen the heat management problem involved with the HC traps (Burk et al., 1995a, 1995b, 2003). Another suggestion for heat management in a HC adsorbent system is to coat a catalyst onto a heat-exchanger with two flow paths. In this system, the exhaust gas first passes through the catalyst/heat exchanger, then through the HC trap, finally, again through the same catalyst/heat exchanger. A concept which does not involve the use of an adsorbent is the storage of total exhaust stream into a collection bag underneath the car during cold-start, the contents of which are released to the catalyst after it has reached operating temperature. Some unique system designs have been proposed (Czaplewski et al., 2002). A cross-flow heat exchanger designed trap system demonstrated a 70% reduction in the non-methane cold start hydrocarbons

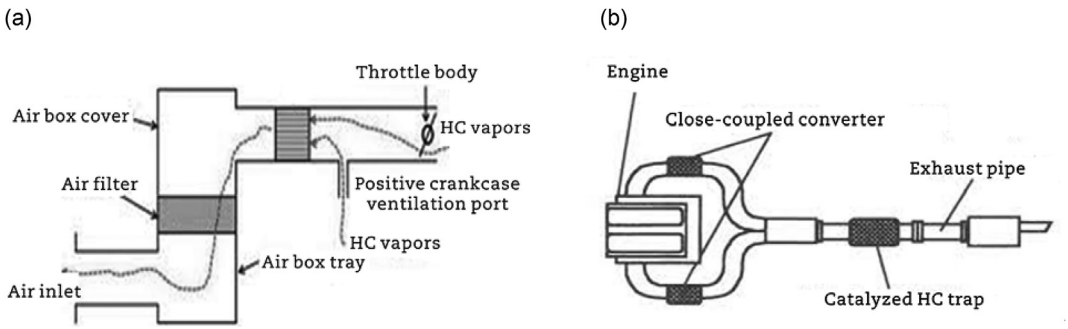

Fig. 8 – Hydrocarbon trap of vehicle. (a) Positive crankcase ventilation. (b) Close-coupled converter.

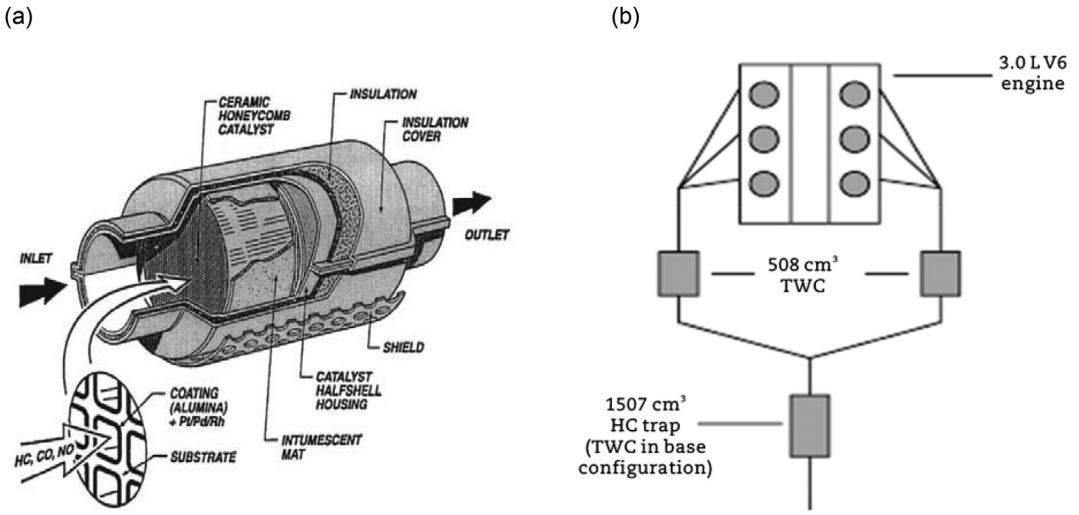

Fig. 9 – Catalytic converter. (a) Catalytic converter design. (b) Hydrocarbon trap of vehicle.

during FTP cycle #1. Another trap design utilizes a cylinder with a central hole to allow the passage of the exhaust gas (Elangovan et al., 2004). This design contains a light-off catalyst, a trap and a downstream catalyst. Air is injected in the hole during cold start to divert the majority of flow to the trap in the cylinder annulus. The small amount bypassed through the hole pre-heats the downstream catalyst (Elangovan et al., 2005).

When the light-off catalyst is functional and the downstream catalyst heats up to temperature, the air is turned off and trap desorbs the HCs. These trap designs are still under evaluation (Lafyatis et al., 1998). There will be commercial niche markets for trap systems used in combination with close-coupled catalyst or electrically heated catalysts. However, all these methods add significant complexity and cost to the emission control system. Close-coupled catalysts are located in the valuable space near the engine compartment (which is inconvenient for engine design and can result in a loss of power) and also must be robust to very high temperature exposure (Puértolas et al., 2012; Takei et al., 1993). Bulky EHCs require large amounts of power at start-up, and often require the use of a second battery. EGI systems require the complexity of implementing a glow-plug into the exhaust stream (Williams et al., 1996). Feeding hydrogen to the catalyst prior to starting the engine is inconvenient, and requires a ready source of hydrogen on-board. Heat storage devices are bulky, involving the use of expensive materials, may be difficult to fabricate. The HC trap strategies involving valves in the exhaust are unpopular due to their inherent complexity, and there are concerns about the durability of a valve in the corrosive exhaust environment (Heimrich et al., 1992; Patil et al., 1996).

Obtaining proper overlap between the HC desorption temperature and catalyst light-off temperature is difficult in catalyzed HC trap systems. The catalytic heat exchanger requires a catalyst with multi-directional flow channels, inevitably leads to a 360° turn in the exhaust pipe (Hochmuth et al., 1993). The exhaust collection bag is bulky, particularly for small vehicles. In general, most of these cold-start solutions benefit through the application of improved catalyst technology (so-called "low-light-off catalysts") shown in Fig. 10, which begin to operate at lower temperatures. Development of such high activity and durable low-light-off catalysts' is the need of present research (Burk et al., 1995a, b).

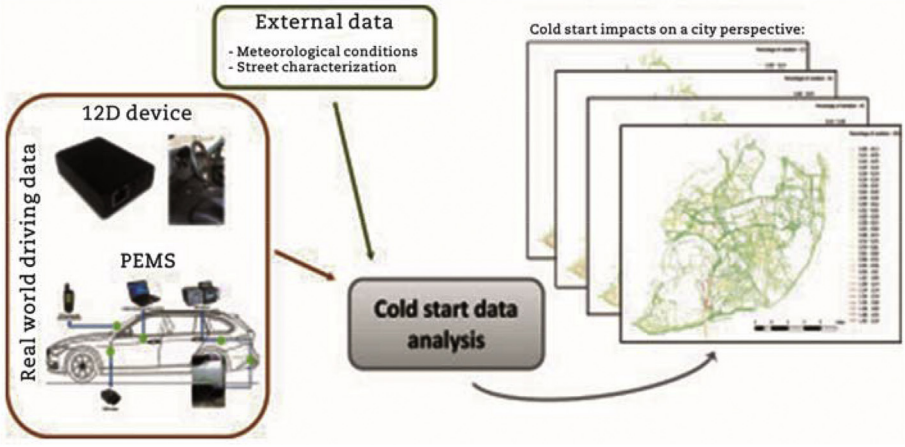

Fig. 10 – Cold start data analysis.

3. Cold start catalysts

During the cold start period, the exhaust contains relatively large amounts of CO (1%–7%), H_2 (0.5%–3%) and HC (0.1%–0.7%). It is possible to oxidize hydrogen at low temperatures (even < 0 °C) on a noble metal catalyst. CO and HC need higher temperatures before the conversion starts (Patil et al., 1998). If at least one of either CO or some HC could be converted at lower temperatures, not only would the harmful emissions be lowered, but the catalyst would also be heated up faster due to the heat generated by the exothermal chemical reactions. Various types of catalysts have been reported active at low/ambient temperatures for CO oxidation but none of them can be used to overcome the cold emissions problem due to some other reasons (Haruta and Sano, 1981).

The catalysts resistant to moisture, CO_2 and other vehicular emissions in addition to thermal sintering, as well as highly active at ambient temperatures can potentially be used in the cold start converter. The catalyst should also be resistant to the lubricating oil, which is indispensable for wear protection of the mechanical parts of engines and it has a deleterious phosphorous poisoning impact on catalyst activity. The appropriate catalysts include noble metals, base metals, semiconductors and transitional metal oxides etc. (Lisnyak et al., 2012). Various types of catalysts have been reported active at low/ambient temperatures and can potentially be used in the cold start converter to overcome the cold emissions problem. In cold start conditions, the CO proves to be the most perilous so that more attention has been focused on catalytic control of CO gas (Layla et al., 2008). The catalytic performance is strongly influenced by the oxygen coordination around their surfaces as shown in Fig. 11. The low-price and high-performance catalysts may have a high perspective to find its appliance to the catalytic reaction. The catalysts used in catalytic converter for various applications are discussed below.

(1) Hopcalite.
(2) Perovskites.
(3) Spinel.
(4) Monel.
(5) Pyrochlores.
(6) Hydrotalcite.

These catalysts have been found to be active at low temperature but deactivate rapidly. The deactivation is attributed to carbonate formation and consumption of surface oxygen that makes the particular site lose its activity. The catalyst could be effectively regenerated by light of irradiation.

3.1. *Synthesis of catalysts*

The structure of catalyst is also depending upon the preparation methods. There are various methods which have been applied for the preparation of catalyst. The property of heterogeneous catalyst is also depending upon the preparation conditions. There are three fundamental stages of catalyst preparation which may be illustrious.

(1) Synthesis of primary solid (or first precursor solid) associating all the valuable components.
(2) Processing of that primary solid to get the catalyst precursor, e.g. by heat treatment.
(3) Activation of precursor to provide the active catalyst and activation may take place instinctively at the beginning of catalytic reaction.

There are several methods used for the preparation of catalysts and each method's effect on the performance of catalyst for CO oxidation is as follows.

(1) Co-precipitation method.
(2) Sol-gel method.
(3) Impregnation method.
(4) Reactive grinding method.
(5) Hydrothermal method.
(6) Pyrolysis method.

The effect of preparation conditions, including metal ions concentration, ageing time, pH, drying temperature and calcination temperature, has highly influenced on the activity

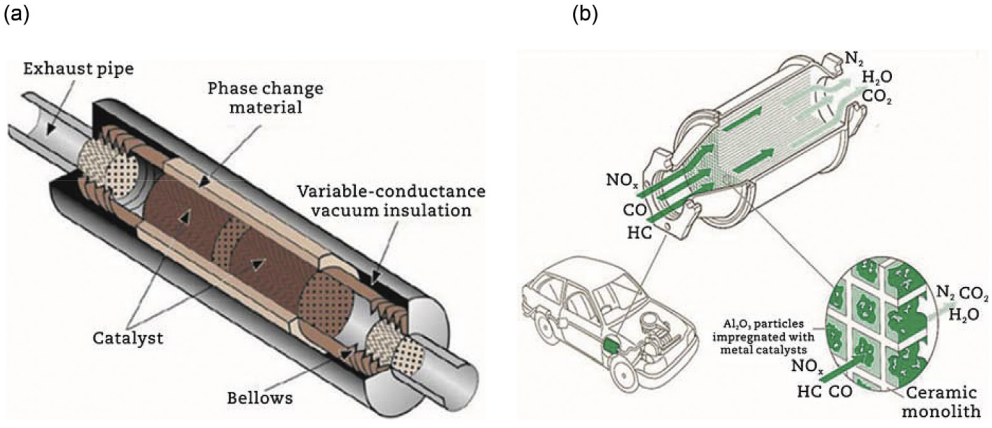

Fig. 11 – Catalyst used in a catalytic converter. (a) Operation of catalytic converter. (b) Conversion of exhaust gas.

of catalyst. The various parameters, which highly affected on the activity of resulting catalyst, include calcination temperature, reduction temperature and reduction time, etc. (Paldey et al., 2005). The calcination temperature has strong influence on the chemical composition and physico-chemical properties of the resulting catalyst. The using of different supports in catalyst improved their performance and reduced their cost for CO oxidation. The promoters are the substances that increase the activity of catalyst. They create the ideal conditions of the catalyst and even increase the life of catalyst by saving them from poison (Li et al., 2007).

3.2. *Application of hopcalite catalysts in cold start emission control*

The pioneering work of Lamb, Bray and Frazer resulted in the discovery of a new group of outstanding catalysts towards the end of World War I, which is known as hopcalite ($CuMnO_x$). Such catalysts can effectively catalyze the oxidation of dry CO even at room temperature. The hopcalite are active at temperatures as low as −20 °C and have high durability for oxidation of CO in dry conditions, but they are readily poisoned by water vapor (Cole et al., 2010; Dey et al., 2017). The recent works showed that the addition of gold in the hopcalite not only improves their activity, but also prevents the deactivation of catalyst. Kireev et al. (2009) developed a procedure for the modification of hopcalite green catalyst using CO binder to obtain new-quality moisture-resistant granules. They also reported that the exhausted catalyst can be regenerated. Such a catalyst is very useful in personal respirators/masks (e.g., for industry workers, scuba divers, fire-fighters, etc.), but it fails in catalytic converter operating at higher temperature due to sintering. This catalyst may be used in proposed device to get rid of the cold-start emissions suggested in the present treatise (Elmhamdi et al., 2017; Kireev et al., 2009). Pillai and Deevi (2006) achieved for the first time room temperature total oxidation of CO into CO_2 over unsupported copper oxide catalyst prepared by a controlled heating of precipitated copper hydroxide after activation of catalyst in a redox environment. They proposed that the active phase was a metastable non-stoichiometric form of copper oxide produced during the treatment of oxide in a redox environment (Gao et al., 2016; Pillai and Deevi, 2006). The catalyst lost its activity upon exposure to the exterior atmosphere due to absorption of moisture, yet the activity could be regained by an activation step. Gold catalysts with low-temperature activity towards CO and HC oxidation are suitable for vehicles exhaust gas treatment, especially during the cold start period. Since the pioneering work of Haruta et al. (1989), the ability of gold nano-particles (2–5 nm) to complete CO oxidation at very low temperatures (as low as −70 °C), is well known (Haruta et al., 1989; Njagi et al., 2010). In the absence of oxygen, low temperature reaction of CO, below 100 °C, is seen for Au catalysts such as $Au/CuMn_2O_4$ and Au/Co_3O_4. The huge publications on gold catalysts for low temperature oxidation of CO are available as cross references in several reviews related to automotive pollution control (Haruta and Sano, 1981).

The schematic diagram of gold supporting hopcalite catalyst is shown in Fig. 12. The four major issues of Au-catalyzed CO oxidation are based on available experimental results and computational investigations. These issues are as follows.

(1) The importance of nature of support on catalyst activity.
(2) The Au oxidation is necessary for high activity.
(3) The presence of moisture in the reaction feed the catalytic activity was maintained.
(4) Reasons for high activity were the presence of small size Au nano-particles and specific morphology.

The applications of gold-based catalysts in cold-start conditions must be protected from the overheated of the catalytic converter (as gold is very high temperature sensitive), by the action of valves that divert the hot exhaust gasses away from the catalyst under the normal operating temperature of the exhaust was reached. Thus, CO pollution essentially occurs during the first five minutes after starting the engines. The low-temperature supported AuNP catalyzed CO oxidation and obviously solved this problem (Davis and Kung, 2007). Therefore, to get rid of cold-start emissions hereby, it is necessary to propose two catalytic converters, one with cold start gold catalyst and another with usual TWC, fitted with three solenoid valves to control flow direction of engine exhaust. During the cold start, exhaust gases are made to

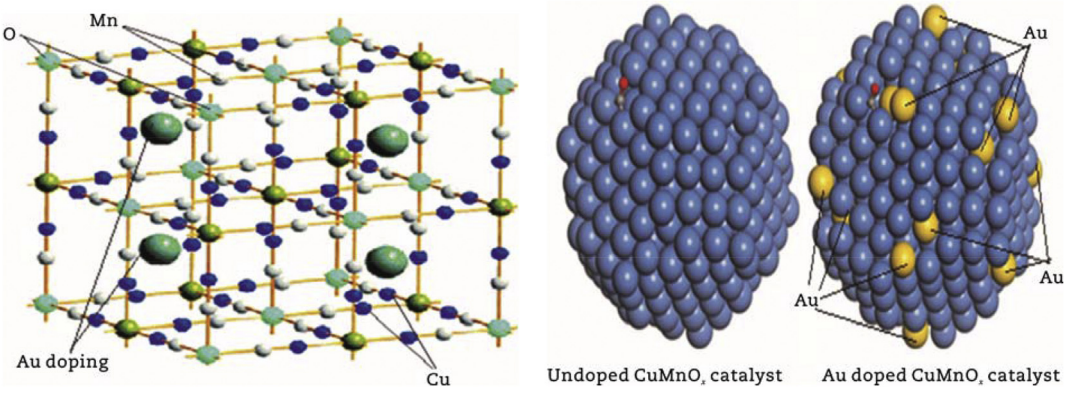

Fig. 12 – Schematic diagram of gold supporting hopcalite catalyst.

pass over the cold start catalyst by switching on solenoid valves 1 and 3, while keeping valve 2 closed. Oxidation of the exhaust pollutants will take place at low temperature over cold start catalyst, minimizing emissions as well as raising temperature (being exothermic reaction) of the cold converter effluent, which will heat the subsequent TWC converter rather rapidly (Sun and Sivashankar, 1998; Cortie and Vander, 2002).

The light-off characteristic was representing the activity of catalysts with the increasing of temperature. The characteristic temperatures T_{10}, T_{50} and T_{100} correspond to the initiation of oxidation, 50% conversion and full conversion of CO respectively. The increasing temperature increases the specific surface area and pore volume of the catalyst, thus improving the activity of catalyst (Dey et al., 2019a). At lower temperatures, the cubic spinel phase $CuMnO_x$ catalyst was obtained but it contains a significant quantity of impurities. The redox behavior of Cu and Mn species is most viable to influence the reactivity in CO oxidation. The crystallographic properties are expected due to the presence of two types of Jahn Teller ions, Mn^{3+} and Cu^{2+} (Dey et al., 2017, 2018). The distribution of metal cations amongst the tetrahedral and octahedral sites, as well as the valances of Cu and Mn ions is still weakly understood. The hopcalite represent the outstanding performance for CO oxidation created by several preparation methods such as sol-gel, supercritical anti-solvent precipitation, redox reaction and majority of cases by co-precipitation method (Libardi et al., 2014). The basic parameters such as calcination strategy and ageing time would also affect on the activity of $CuMnO_x$ catalyst for CO oxidation. The improved catalytic activity was due to an improved specific surface area, lattice oxygen mobility and pore volume of the catalysts. These all may be combined together to the overall performance of $CuMnO_x$ catalysts in CO oxidation at low temperatures (Dey et al., 2018; Sendilvelan and Sassykova, 2019). The operating parameters and activity measurements of various $CuMnO_x$ catalysts prepared by different methods are discussed in Table 2.

The activity of $CuMnO_x$ catalyst is strongly depending upon the nature of metal ions concentration and their allocation in the crystal lattice. The Mn-based catalysts are very active for CO oxidation and needed tetravalent Mn, but Mn (IV) compounds are usually unstable at the high temperature; therefore, the addition of Cu compounds increased their stability and activity also (Clarke et al., 2015). The presence of MnO_2 in a highly amorphous form is an assertion for a high surface area for contacting with the Cu atoms, which was a prerequisite for high activity of $CuMnO_x$ catalyst. In the spinel CuMn2O4 catalyst containing more than one transition metal ion per unit. The distribution and valence sites of the cations among both the tetrahedral (A sites) and octahedral (B sites) sublattices of the spinel structures (Kondrat et al., 2011). The electronic configuration of Cu(I) occupies in the $CuMn_2O_4$ spinel structure, the octahedral sites, where they are subjected to the larger extra-atomic relaxation energy. In the $CuMnO_x$ catalyst, manganese oxide is able to absorb activate oxygen and subsequently copper to improve and stabilize active phases (Qian et al., 2013; Zaki et al., 2009). The structural defects connected with the oxygen vacancies and Mn_2O_3 highly distributed on the catalytic surface facilitate the catalyst reducibility. The $CuMnO_x$ which oxide with spinel-like structures have received more consideration because of their great electrical and magnetic properties. These properties are influenced by the nature of metal ion concentrations and their allocation in the crystal lattice of $CuMnO_x$ catalyst (Hoshyar et al., 2015; Dey et al., 2016).

3.3. *Mechanism of CO oxidation over hopcalite catalyst*

The efficiency of $CuMnO_x$ catalysts for reactions with stable CO molecules is depending upon the chemisorption processes. The chemisorption of reacting gases (Fig. 13) is an important process, which increases the concentration of reactant on the catalyst surfaces and induces the adsorbed molecules processing on high energy to get easier chemical reactions. The discrete reaction mechanisms are steady with the observed kinetics. The first mechanism shows that the mostly accepted CO oxidation reaction on a $CuMnO_x$ catalyst surface involves O_2 adsorption to form the O_2^* precursors, which split on a vicinal vacancy (Zhao et al., 2015). In the second mechanism, the O_2 activation occurs via the kinetically applicable CO^*-assisted O_2 dissociation step without the specific concern of stable O_2^* precursors as represented in Fig. 13. In the CO oxidation process, the oxygen is first adsorbed on the $CuMnO_x$ catalyst surface with the energy of activation (Dey et al., 2019b).

When the temperature is high in a significant quantity so that the adsorption of oxygen reaches enough proportions, any CO passing over the catalyst surfaces either reacts directly with the adsorbed oxygen or else is initial adsorbed then reacts, after which the CO being produced was desorbed. The similar nature of $CuMnO_x$ catalyst was synthesized by the redox method and could be one of the major factors contributing to their high catalytic activity (Dey et al., 2018). A better tool for measuring the performance of $CuMnO_x$ catalyst for CO oxidation is reported with the activation energy of the process. It is significant to develop the kinetic expressions (Fig. 14) for catalytic oxidation of CO because they can be implemented into the CFD models which are useful for optimization and reactor design in cold start emission control (Dey et al., 2017).

Chemical kinetics establishes the factors, which can influence the rate of reaction under concern, provide clarification for the measured value of rate and leads to the rate equations, which are valuable in the reactor design (Dey et al., 2018). Early study indicates that the catalysts start to oxidize CO before it is oxidized by air and this is an investigation of a Mars-van Krevelen-type mechanism, which has consequently found support. A Langmuir–Hinshelwood-type mechanism between adsorbed oxygen and CO has also been proposed, and it is not clear if either of them operates independently or there is a combination of both. The amount of reactant consumed and product formed can be monitored as a function of surface composition of catalyst (Dey et al., 2017; Libardi et al., 2014).

Table 2 – The operating parameters and activity measurements of various $CuMnO_x$ catalysts prepared by different methods for cold start emission control.

Catalyst*	Catalyst preparation method	Operating parameters	Remarks	References
$CuMn_2O_4$	Co-precipitation method	The 100 mg catalyst with feed gases consisted of (5% CO in He, 5 mL/min) and O_2 (50 mL/min) at temperature 20 °C and total GHSV was 33,000 h^{-1}.	$CuMn_2O_4$ (T_{100} = 20 °C, Time = 12 h)	Hutchings et al. (1996)
$CuMn_2O_4$	Co-precipitation method	The 100 mg catalyst; usually CO (5% CO in He, 5 mL/min), O_2 (50 mL/min) and GHSV was 33,000 h^{-1}.	$CuMn_2O_4$ (T_{50} = 32 °C, T_{100} = 80 °C)	Hutchings et al. (1998)
$CuMn_2O_4$	Co-precipitation method	The 100 mg catalyst, (0.45 vol.% CO), at flow rate (20 mL/min) with CO (5% CO in He, 5 mL/min) and O_2 (50 mL/min) and GHSV was 33,000 h^{-1}.	$CuMn_2O_4$ (T_{70} = 30 °C const., Time = 30 min)	Taylor et al. (1999)
$CuMn_2O_4$	Co-precipitation method	The 100 mg catalyst in the feed gases (0.25% CO, 5% O_2 balance He) and total flow rate was 60 mL/min.	$CuMn_2O_4$ (X_{co}^{**} = 80%, at 30 °C, Time = 10 h)	Mirzaei et al. (2003)
$CuMnO_x$	Co-precipitation method	The 100 mg catalyst, with a gas mixture (1% CO, 99% dry air) was feed at a rate of 80 mL/min.	$CuMnO_x$ (T_{80} = 25 °C, Time = 10 min)	Mirzaei et al. (2013)
$Au/CuMnO_x$	Co-precipitation method	The reaction conditions: 100 mg catalyst, with total flow rate of 22.5 mL/min, molar ratio (CO: O_2: He = 1: 89: 10), reaction temperature 30 °C on a time on-line of 1000 min.	$Au/CuMnO_x$ (T_{70} = 30 °C const., Time = 1000 min)	Solsona et al. (2004)
$Cu_{1.5}Mn_{1.5}O_4$	Co-precipitation method	The total flow rate: 1000 mL/min; (4 vol.% CO; 20 vol.% O_2, balance He) and heating rate 12 °C · min^{-1}, with the weight of catalyst was 100 mg, (SV being 310,000 h^{-1}).	$Cu_{1.5}Mn_{1.5}O_4$ (T_i = 75 °C, T_{50} = 110 °C, T_{100} = 120 °C)	Paldey et al. (2005)
$CuMnO_x$	Co-precipitation method	The 250 mg catalyst with specific velocity was 45,000 h^{-1}, time was 50 min and initial concentration of CO was about 3×10^{-5} to 5×10^{-5} mol/L.	$CuMnO_x$ (T_i = 40 °C, T_{65} = 100 °C const.)	Li et al. (2007)
Co-promoted $CuMnO_x$	Co-precipitation method	The 100 mg catalyst with 5000 vppm CO in air and GHSV velocity was 33,000 h^{-1}.	Cobalt promoted $CuMnO_x$ (T_i = 80 °C, T_{50} = 120 °C, T_{65} = 160 °C const.)	Jones et al. (2008)
$CuMnO_x$	Co-precipitation method	The reaction conditions are 30 °C temperature, 5000 vppm CO in air, GHSV of 33,000 h^{-1} with weight of catalyst was 100 mg.	$CuMnO_x$ (T_i = 16 °C, T_{50} = 30 °C const., Time = 90 min)	Jones et al. (2009)
$CuMnO_x$	Redox method	The 100 mg catalyst consisted of (1% CO, 2% O_2 and 5% N_2 in He), space velocity was 35,000 mL/h/g_{cat}.	$CuMnO_x$ (T_{50} = 25 °C, T_{100} = 35 °C)	Njagi et al. (2010)
$Au/CuMnO_x$	Deposition precipitation method	The $Au/CuMnO_x$ catalysts aged for 0.5 h at 25 °C temperature, 5000 vppm CO in air, GHSV = 12,000 h^{-1}.	$Au/CuMnO_x$ (T_{100} = 50 °C, Time = 20 min)	Cole et al. (2010)

Mesoporous $CuMnO_x$	Redox method	The 100 mg catalyst in presence of (1% CO, 1% O_2, 60% H_2 balanced N_2) with a total flow rate of 50 mL/min and space velocity 35,000 mL/h/g_{cat}.	Mesoporous $CuMnO_x$ ($T_i = 4\ ^\circ C$, $T_{50} = 12\ ^\circ C$, $T_{100} = 25\ ^\circ C$)	Njagi et al. (2011)
$CuMn_2O_4$	Conventional precipitation method	The 50 mg catalyst at the temperature 25 °C with space velocity 12,000 h^{-1}, present in a premixed cylinder (5000 ppm CO in air).	$CuMn_2O_4$ ($T_{70} = 25\ ^\circ C$, Time = 40 min)	Tang et al. (2011)
$CuMnO_x$	Co-precipitation method	The 200 mg catalyst with space velocity: 20,000 mL/h/g_{cat} and feed gas composition of (1% CO, 20% O_2 and 79% N_2).	$CuMnO_x$ ($T_i = 0\ ^\circ C$, $T_{50} = 30\ ^\circ C$, $T_{100} = 50\ ^\circ C$)	Cai et al. (2012)
$CuMnO_x$ catalyst doping with Co_3O_4, CeO_2 and AgO_2	Co-precipitation method	The 0.7839 g catalyst in presence of 1% CO in air with a total flow rate of 60 mL/min.	$CuMnO_x$ ($T_{35} = 48\ ^\circ C$, Time = 120 min), $CuMnO_x - Co_3O_4$ ($T_i = 20\ ^\circ C$, $T_{50} = 30\ ^\circ C$, $T_{80} = 54\ ^\circ C$, Time = 120 min), $CuMnO_x - CeO_2$ ($T_i = 20\ ^\circ C$, $T_{50} = 46\ ^\circ C$, $T_{100} = 65\ ^\circ C$, Time = 110 min), $CuMnO_x - AgO_2$ ($T_i = 20\ ^\circ C$, $T_{50} = 30\ ^\circ C$, $T_{100} = 45\ ^\circ C$, Time = 120 min)	Rani and Prasad (2014)
$CuMnO_x$	Co-precipitation method	The 200 mg catalyst with feed gas (1% CO −20% O_2−79% N_2) and space velocity of 20,000 mL/g/h.	$CuMnO_x$ ($T_i = 13\ ^\circ C$, $T_{50} = 30\ ^\circ C$, $T_{100} = 70\ ^\circ C$)	Shi et al. (2015)
Cu supported $CeMnO_2$	Co-precipitation method	The 210 mg catalyst in feed gases composition (2% CO, 2% O_2 and 96% H_2) with space velocity 20,000 h^{-1}.	Cu/CeO_2 ($T_i = 55\ ^\circ C$, $T_{50} = 80\ ^\circ C$, $T_{100} = 130\ ^\circ C$), $Cu/Ce_{0.9}Mn_{0.1}O_2$ ($T_i = 30\ ^\circ C$, $T_{50} = 65\ ^\circ C$, $T_{100} = 120\ ^\circ C$)	Hoshyar et al. (2015)
$CuMnO_x$ addition SnO_2	Co-precipitation method	The 100 mg catalyst with feed gases composition (1% CO, 21% O_2 balanced N_2), overall flow rate of 30 mL/min and resultant space velocity was 18,000 mL/h/g_{cat}.	$CuMnO_x$ ($T_i = 30\ ^\circ C$, $T_{50} = 56\ ^\circ C$, $T_{100} = 85\ ^\circ C$), $CuMnO_x$ −10.6 wt.% SnO_2 ($T_i = 20\ ^\circ C$, $T_{50} = 30\ ^\circ C$, $T_{100} = 40\ ^\circ C$)	Clarke et al. (2015)
$Cu_xMn_{3-x}O_4$	Precipitation method	The 50 mg catalyst in presence of (0.8% CO, 20% O_2 in Ar) and heating rate 2 °C/min with a total flow rate of 1.63 mL/s.	$Cu_xMn_{3-x}O_4$ ($T_i = 25\ ^\circ C$, $T_{50} = 50\ ^\circ C$, $T_{100} = 80\ ^\circ C$)	Benjamin and Alphonse (2016)
$CuMnO_x$	Co-precipitation method	The 100 mg catalyst at temperature 25 °C with 5000 ppm CO in synthetic air.	$CuMn_2O_4$ ($X_{co} = 40\%$ at 25 °C, Time = 20 min)	Clarke et al. (2015)
$CuMnO_x$	Co-precipitation method	The 100 mg catalyst in presence of (2.5% CO in air) and heating rate 2 °C/min with a total flow rate of 60 mL/min.	$CuMnO_x$ ($T_i = 25\ ^\circ C$, $T_{50} = 42\ ^\circ C$, $T_{100} = 78\ ^\circ C$)	Dey et al. (2017)
CuO/MnO_2, $CuMnO_x$	Co-precipitation method	The 100 mg catalyst in presence of (2.5% CO in air) and heating rate 2 °C/min with a total flow rate of 60 mL/min.	CuO ($T_i = 25\ ^\circ C$, $T_{50} = 90\ ^\circ C$, $T_{100} = 150\ ^\circ C$), MnO_2 ($T_i = 25\ ^\circ C$, $T_{50} = 65\ ^\circ C$, $T_{100} = 120\ ^\circ C$), $CuMnO_x$ ($T_i = 25\ ^\circ C$, $T_{50} = 45\ ^\circ C$, $T_{100} = 80\ ^\circ C$)	Dey et al. (2018)
$Ag/CuMnO_x$	Co-precipitation method	The 100 mg catalyst in presence of (2.5% CO in air) and heating rate 2 °C/min with a total flow rate of 60 mL/min.	$CuMnO_x$ ($T_i = 25\ ^\circ C$, $T_{50} = 55\ ^\circ C$, $T_{100} = 80\ ^\circ C$), $Ag - CuMnO_x$ ($T_i = 25\ ^\circ C$, $T_{50} = 35\ ^\circ C$, $T_{100} = 55\ ^\circ C$)	Dey et al. (2019b)
$CuMnO_x$	Sol−gel method	The 100 mg catalyst with flow rate of 30,000 mL/g/h at reaction temperature 60 °C−120 °C and total flow rate was 50 mL/min.	$CuMnO_x$ ($T_i = 60\ ^\circ C$, $T_{30} = 120\ ^\circ C$ const.)	Kramer et al. (2006)

(continued on next page)

Table 2 – (*continued*)

Catalyst*	Catalyst preparation method	Operating parameters	Remarks	References
$CuMnO_x$	Sol–gel method	The (Cu/Mn = 1/2) at a flow rate: 50 mL/min with composition (1 vol.% CO, 1 vol.% O_2, 60 vol.% H_2 and balance N_2).	$CuMnO_x$ (T_i = 30 °C, T_{50} = 80 °C, T_{100} = 120 °C)	Hasegawa et al. (2009)
CuOx additives Mn_2O_3 and Cr_2O_3	Impregnation method	The 100 mg catalyst with gas mixture (1% CO, 1% O_2, 50% H_2 and balanced N_2) and overall flow rate was 60 mL/min, GHSV was 30,000 h^{-1}.	CuOx – Mn_2O_3 (T_i = 50 °C, T_{50} = 160 °C, T_{100} = 220 °C), CuOx – Cr_2O_3 (T_i = 60 °C, T_{50} = 190 °C, T_{100} = 225 °C)	Zaki et al. (2009)
CuO/MnO_2	Incipient wetness impregnation method	The 100 mg catalyst in presence of (1% CO, 99% dry air) with a feed rate 20 mL/min, and space velocity was 24,000 mL/g_{cat}/h.	CuO (T_i = 140 °C, T_{50} = 200 °C, T_{100} = 415 °C), MnO_2 (T_i = 60 °C, T_{50} = 100 °C, T_{100} = 160 °C), CuO/MnO_2 (T_i = 30 °C, T_{50} = 60 °C, T_{100} = 100 °C),	Qian et al. (2013)
$CuMnO_x$	Grinding and precipitation method	The 50 mg catalyst in presence of (5000 ppm CO in air) at a total flow rate of 22.5 mL/min.	$CuMnO_x$ (T_i = 120 °C, T_{50} = 190 °C, T_{100} = 240 °C)	Kondrat et al. (2011)
$CuMn_2O_4$	Grinding ball mill method	The 50 mg catalyst with a flow rate of 21 mL/min and GHSV was 12,000 h^{-1} at temperature 25 °C, 5000 ppm CO in air.	$CuMn_2O_4$ (X_{CO} = 40% at 25 °C, Time = 72 h)	Clarke et al. (2015)
$Cu_{1.5}Mn_{1.5}O_4$ nano-particle	Precipitation method & flame sprays pyrolysis	The 100 mg catalyst (0.67 vol.% CO, 66.00 vol.% N_2 and 33.33 vol.% O_2) at temperature 300 °C for 20 min and total gases flow rate was 100 mL/min.	$Cu_{1.5}Mn_{1.5}O_4$ nanoparticle (T_i = 25 °C, T_{50} = 50 °C, T_{100} = 110 °C)	Biemelt et al. (2015)
CuO/Ce-MnO	Urea nitrate combustion method	The 500 mg catalyst in presence of 1 vol.% CO in air with GHSV was 52,000 mL/g/h.	Ce-Mn-O (T_i = 225 °C, T_{50} = 270 °C, T_{70} = 350 °C const.), CuO/Ce-Mn-O (T_i = 100 °C, T_{50} = 120 °C, T_{100} = 160 °C)	Zhao et al. (2015)

Note: * means hopcalite catalysts and their derivatives. ** means final conversation percentages of CO at 30 °C.

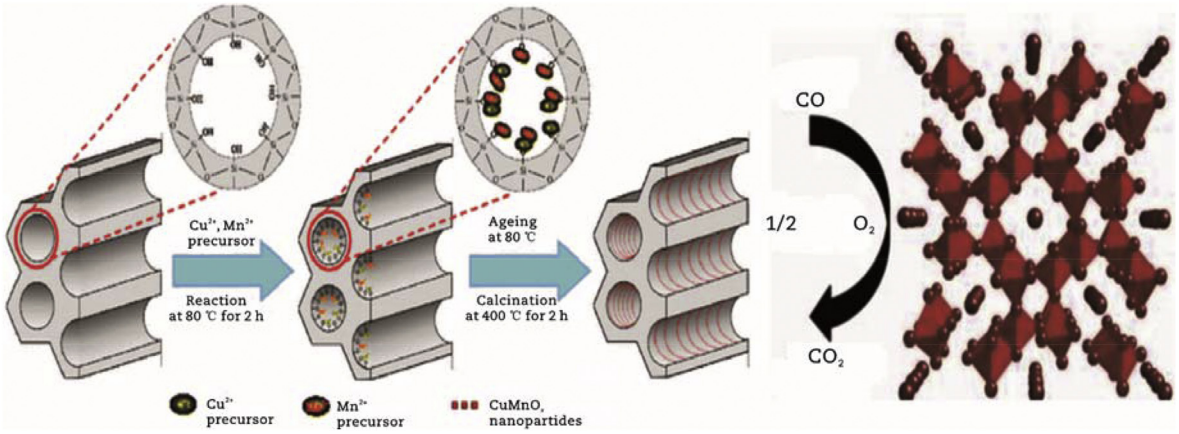

Fig. 13 – Mechanism of CO oxidation over hopcalite catalyst.

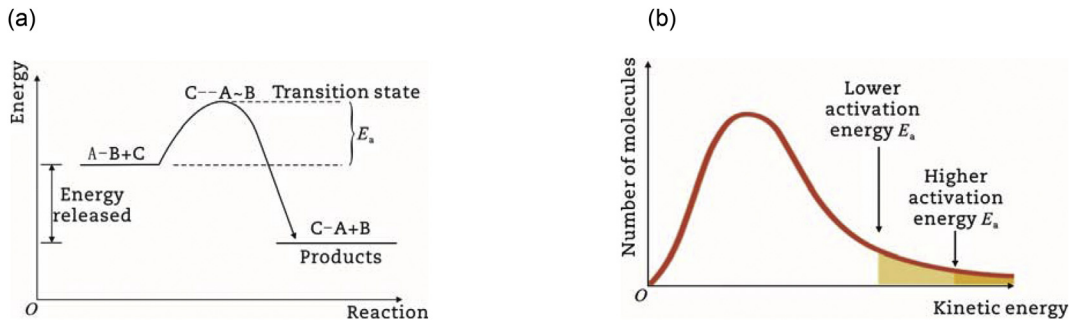

Fig. 14 – Kinetics study of hopcalite catalysts for CO oxidation. (a) Energy and reaction state of catalyst. (b) Activation energy of catalyst.

3.4. *Deactivation of hopcalite catalyst*

The activity and selectivity of hopcalite catalyst in catalytic converter are crucial for CO oxidation reaction. The catalyst's deactivation and loss over time in a catalytic activity is shown in Fig. 15. The catalyst's deactivation can be divided into the six different types: (1) poisoning, (2) thermal degradation, (3) fouling, (4) vapor compound formation, (5) solid-solid and/or vapor-solid reactions and (6) crushing/abrasion. The main cause of catalyst's deactivation is mainly divided into three parts: chemically, mechanically and thermally (Min and Friend, 2007). The lead, sulphur poisoning, carbon formation

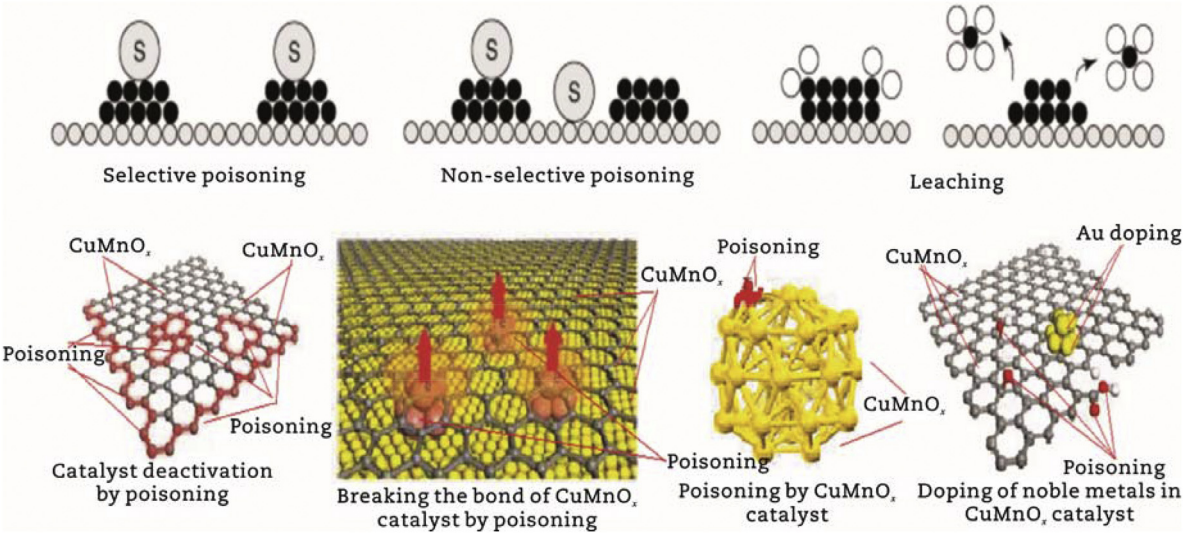

Fig. 15 – Deactivation of hopcalite catalyst.

and sintering are the main causes of catalyst's deactivation. The $CuMnO_x$ catalyst is easily deactivated by a trace amount of moisture present in the catalyst. To reduce the deactivation of catalyst, a small amount of Fe, Au and Ni can be added into the $CuMnO_x$ catalyst, which also increases the lifetime of $CuMnO_x$ catalyst. In addition, to increase the rate of CO oxidation, a further improvement is made by incorporating Au into the $CuMnO_x$ catalyst; thus, lower levels of deactivation are observed (Comotti et al., 2006; Romero-Sarria et al., 2014; Kam and Hughes, 1979).

The regeneration of deactivated hopcalite catalysts is highly depending on the chemical, economic and environmental factors. As time goes on, the temperature of engine exhaust will reach the light-off temperature of the TWC. Then the engine exhaust will be diverted or bypassed the cold start catalyst by switching off solenoid valves 1 and 3 and subsequently opening solenoid valve 2, which could prevent the cold start catalyst from deactivation (sintering) and make high-temperature catalyst operational for purification of the exhaust emissions (Romero-Sarria et al., 2014; Kam and Hughes, 1979). When catalysts are operated at higher temperatures, any impurity can be burnt off. Under practical conditions, the $CuMnO_x$ catalysts may be deactivated by various impurities present in air or occasionally by the accumulation of reaction products on their surface. Although the catalysts can be regenerated by heat treatment in presence of oxygen, the heating temperature is strictly limited below that of calcinations (Veprek et al., 1986). It is unrealistic to use a heater or furnace for regenerating catalysts in a residential environment. $Au/CuMnO_x$ catalysts, which are used for cleaning living atmosphere at ambient temperatures, can be regenerated by photo irradiation. Poisoning of gold catalysts via carbonate deposition by interaction with atmospheric CO_2 can be avoided by storing the catalysts in a closed canister at room temperature. These catalysts can keep their activity for two years under these conditions (Roozbehani et al., 2013).

4. Conclusions

The cold-start emission of CO from automobile vehicles is one of the serious problems in large cities, where the number of vehicles and daily engine starting per populated area is high. Various techniques have been employed to deal with the cold-start emission problem of the vehicles. Most of these cold-start solutions benefit through the application of low-light-off catalysts which begin to operate at ambient temperatures. Due to the ever-rising number of vehicles on roads, the choice of appropriate catalyst for catalytic converters is a fundamental step to control the hazard of vehicular pollution, in terms of activity, selectivity, durability, availability and cost. The stability of a catalyst is a more desirable characteristic than its activity for application in the catalytic converter. The use of noble metals has stringent effects on the commercial cost of the catalyst, thus a great interest has recently been turned to oxide-based catalysts. The hopcalite is one of the best and most promising non-noble metal oxide catalyst for low temperature CO oxidation, thus it is a very good candidate for vehicle exhaust gas treatment, especially during the cold start period. The hopcalite is more tolerant to poison than other base metal catalysts, so it could be better used for oxidation catalysts of automobile emission control. The modification of hopcalite catalyst with the addition of suitable support, promoter, pretreatment and advanced synthesis methods would lead to the desirable performance of hopcalite in converter in the near future. Although hopcalite is a well-studied catalytic material, further research is still required in order to develop this catalyst following newer routes based on the oxide catalysts, which are suitable for vehicular exhaust catalytic converter.

Conflict of interest

The authors do not have any conflict of interest with other entities or researchers.

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REFERENCES

Aguila, J., Chan, N., Courtis, J., 1991. Proposed Regulations for California Phase 2 Reformulated Gasoline. Technical Support Document. California Air Resources Board, Sacramento.

Air Improvement Resource, Inc., 2005. Examination of Temperature and RVP Effects on CO Emissions in EPA's Certification Database. Final Report CRC Project No. E-74a. Coordinating Research Council, Inc., Alpharetta.

Alfuso, S., Aurlemma, M., Police, G., et al., 1993. The Effect of Methyl-Ester of Rapeseed Oil on Combustion and Emissions of Di-diesel Engines. Technical Paper 932801. SAE, Warrendale.

Andre, J.M., Joumard, R., 2005. Modeling of Cold Start Excess Emissions for Passenger Cars. INRETS Report No. LTE 0509. INRETS, Bron.

Aspromonte, S.G., Boix, A.V., 2019. Improving of cold-start and combustion emissions in lean NO conditions with active and selective AgAl mesoporous catalysts. Journal of Environmental Chemical Engineering 7 (2), 102995.

Badr, O., Probert, S.D., 1995. Carbon monoxide concentration in the earth's atmosphere. Fuel and Energy Abstracts 36 (1), 47.

Ball, D., 1996. A Warm-up and Under Floor Converter Parametric Study. Technical Paper 932765. SAE, Warrendale.

Bartley, G.J.J., 2001. Method for Reducing Cold-Start Hydrocarbon Emissions in a Gasoline, Natural Gas, or Propane Fueled Engine. US Patent 6244044. United States Patent and Trademark Office, Washington DC.

Bartley, G.J.J., 2007. Sub-ambient cold-start emissions reduction using SwRI®POx catalyst technology. Topics of Catalysis 42 (1–4), 345–349.

Benjamin, B.F.F., Alphonse, P., 2016. Co-Mn-oxide spinel catalysts for CO and propane oxidation at mild temperature. Applied Catalysis B: Environmental 180, 715–724.

Bera, P., Hegde, M.S., 2010. Recent advances in auto exhaust catalysis. Journal Indian Institute of Science 90, 299–325.

Bhasin, M., Nagaki, D., Koradi, P., et al., 1993. Novel Catalyst System for Treating Exhaust Gases from Internal

Combustion and Stationary Source Engines. Technical Paper 930254. SAE, Warrendale.
Bhaskar, K., Nagarajan, G., Sampath, S., 2010. Experimental investigation of cold start emissions using electrically heated catalysts in a spark ignition engine. International Journal of Automotive and Mechanical Engineering 2 (1), 105–118.
Biemelt, T., Wegner, K., Trichert, J., et al., 2015. Hopcalite nanoparticle catalysts with high water vapor stability for catalytic oxidation of carbon monoxide. Applied Catalysis B: Environmental 184, 208–215.
Blondeau, J., Mertens, J., 2019. Impact of intermittent renewable energy production on specific CO_2 and NOx emissions from large scale gas-fired combined cycles. Journal of Cleaner Production 221, 261–270.
Borland, M., Zhao, F., 2002. Application of secondary air injection for simultaneously reducing converter-in emissions and improving catalyst light-off performance. In: SAE Powertrain & Fluid Conference & Exhibition, Washington DC, 2002.
Burk, P.L., Hochmuth, J.K., Anderson, D.R., et al., 1995a. Cold start hydrocarbon emissions control via admixing three way conversion catalysts with heat exchange and hydrocarbon adsorption phenomena. Studies in Surface Science and Catalysis 96, 919–930.
Burk, P.L., Hochmuth, J.K., Anderson, D.R., et al., 1995b. Cold Start Hydrocarbon Emissions Control. Technical Paper 950410. SAE, Warrendale.
Burk, N.R., Trimm, D.L., Howe, R.F., 2003. The effect of silica: alumina ratio and hydrothermal ageing on the adsorption characteristics of BEA zeolites for cold start emission control. Applied Catalysis B: Environmental 46 (1), 97104.
Cai, L., Guo, Y., Lu, A., et al., 2012. The choice of precipitant and precursor in the co-precipitation synthesis of copper manganese oxide for maximizing carbon monoxide oxidation. Journal of Molecular Catalysis A: Chemical 360, 35–41.
Chan, S.H., Zhu, J., 1999. The Significance of High Value of Ignition Retard Control on the Catalyst Light-Off. Technical Paper 962077. SAE, Warrendale.
Chen, Y., Ma, J., Han, B., et al., 2018. Emissions of automobiles fueled with alternative fuels based on engine technology: a review. Journal of Traffic and Transportation Engineering (English Edition) 5 (4), 318–334.
Chhatwal, G.R., Mehra, M.C., Sataka, M., et al., 1975. In Environmental Air Pollution and its Control. Anmol Publications, New Delhi.
Choi, K., Lee, D., Kim, H., et al., 2016. Reaction characteristics of precious-metal-free ternary Mn–Cu–M (M = Ce, Co, Cr and Fe) oxide catalysts for low-temperature CO oxidation. Industrial and Engineering Chemistry Research 55 (16), 4443–4450.
Cholakov, G.S., 2010. Control of exhaust emissions from internal combustion engine vehicles. Pollution Control Technologies 3, 1–8.
Cholakov, G.S., 2018. Catalytic converters and other emission control devices. Pollution Control Technologies 3, 11–18.
Clarke, T.J., Davies, T.E., Kondrat, S.A., et al., 2015. Mechano-chemical synthesis of copper manganese oxide for the ambient temperature oxidation of carbon monoxide. Applied catalysis B: Environmental 165, 222–231.
Cole, K.J., Carley, A.F., Crudace, M.J., et al., 2010. Copper manganese oxide catalysts modified by gold deposition: the influence on activity for ambient temperature carbon monoxide oxidation. Catalysis Letters 138 (3), 143–147.
Comotti, M., Li, W., Spliethoff, B., et al., 2006. Support effect in high activity gold catalysts for CO oxidation. Journal of American Chemical Society 128 (3), 917–924.
Cortie, M.B., Vander, L.E., 2002. Catalytic gold nano-particles. Materials Forum 26, 1–14.
Cullen, M.J., Rollinger, J., Kapolnek, M., et al., 2007. Cold Start Emission Reduction Monitoring System and Meilthod. US 2007/0283682 A1. United States Patent and Trademark Office, Washington DC.
Czaplewski, K.F., Reitz, T.L., Kim, Y.J., et al., 2002. One-dimensional zeolites as hydrocarbon traps. Microporous and Mesoporous Materials 56 (1), 55–64.
Davis, R.J., Kung, M.C., 2007. Understanding Au-catalyzed low-temperature CO oxidation. In: AlChE Annual Meeting, Salt Lake City, 2007.
Dey, S., Dhal, G.C., Mohan, D., et al., 2017. Study of hopcalite ($CuMnO_x$) catalysts prepared through a novel route for the oxidation of carbon monoxide at low temperature. Bulletin of Chemical Reaction Engineering & Catalysis 12 (3), 393–407.
Dey, S., Dhal, G.C., Mohan, D., et al., 2018. Effect of various metal oxides phases present in $CuMnO_x$ catalyst for selective CO oxidation. Materials Discovery 12, 3–71.
Dey, S., Dhal, G.C., Mohan, D., et al., 2019a. Ambient temperature complete oxidation of carbon monoxide using hopcalite catalysts for fire escape mask applications. Advanced Composites and Hybrid Materials 2 (6), 1–19.
Dey, S., Dhal, G.C., Mohan, D., et al., 2019b. Synthesis of the silver promoted $CuMnO_x$ catalyst for ambient temperature oxidation of carbon monoxides. Journal of Science: Advanced Materials and Devices 4 (1), 47–56.
Dey, S., Dhal, G.C., Prasad, R., et al., 2016. Effect of nitrate metal (Ce, Cu, Mn and Co) precursors for the total oxidation of carbon monoxide. Resource-Efficient Technologies 3 (3), 293–302.
Dhanalakshmi, A., Suresh, M., 2018. Experimental investigation of emission control using Ag catalytic converter in a four stoke diesel engine. International Journal of Mechanical Engineering and Technology 9 (13), 199–202.
E, J., Liu, G., Zhang, Z., et al., 2019. Effect analysis on cold starting performance enhancement of a diesel engine fueled with biodiesel fuel based on an improved thermodynamic model. Applied Energy 243, 321–335.
Elangovan, S.P., Ogura, M., Davis, M.E., et al., 2004. SSZ-33: a promising material for use as a hydrocarbon trap. Journal of Physical Chemistry B 108 (35), 13059–13061.
Elangovan, S.P., Ogura, M., Zhang, Y., et al., 2005. Silicoalumino phosphate molecular sieves as a hydrocarbon trap. Applied Catalysis B: Environmental 57 (1), 31–36.
Elmhamdi, A., Pascual, L., Nahdi, K., et al., 2017. Structure/redox/activity relationships in $CeO_2/CuMn_2O_4$ CO-PROX catalysts. Applied Catalysis B: Environmental 217, 1–11.
Faiz, A., Weaver, C.S., Walsh, M.P., 1996. Air Pollution from Motor Vehicles, Standards and Technologies for Controlling Emissions. The World Bank Reconstruction and Development, Washington DC.
Favez, J.Y., Weilenmann, M., Stilli, J., 2009. Cold start extra emissions as a function of engine stop time: evolution over the last 10 years. Atmospheric Environment 43 (5), 996–1007.
Gao, J., Jia, C., Zhang, L., et al., 2016. Tuning chemical bonding of MnO_2 through transition-metal doping for enhanced CO oxidation. Journal of Catalysis 341, 82–90.
Gao, J., Tian, G., Sorniotti, A., et al., 2019. Review of thermal management of catalytic converters to decrease engine emissions during cold start and warm up. Applied Thermal Engineering 147, 177–187.
Giakoumis, E.G., Dimaratos, A.M., Rakopoulos, C.D., et al., 2017. Combustion instability during starting of turbocharged diesel engine including biofuel effects. Journal of Energy Engineering 143 (2), 04016047.
Gottberg, I., Rydquist, J., Backlund, J., et al., 1986. New Potential Exhaust Gas after Treatment Technologies for "Clean Car" Legislation. Technical Paper 910840. SAE, Warrendale.

Hamedi, M.R., Doustdara, O., Tsolakis, A., et al., 2019. Thermal energy storage system for efficient diesel exhaust after treatment at low temperatures. Applied Energy 235, 874–887.
Haruta, M., Sano, H., 1981. Catalytic combustion of hydrogen I – its role in hydrogen utilization system and screening of catalyst materials. International Journal of Hydrogen Energy 6 (6), 601–608.
Haruta, M., Yamada, N., Kobayashi, T., et al., 1989. Gold catalysts prepared by co-precipitation for low-temperature oxidation of hydrogen and of carbon monoxide. Journal of Catalysis 115 (2), 301–309.
Hasegawa, Y., Maki, R., Sano, M., et al., 2009. Preferential oxidation of CO on copper-containing manganese oxides. Applied Catalysis A: General 371 (1–2), 67–72.
Heck, R.M., Farrauto, R.J., 2001. Automobile exhaust catalysts. Applied Catalysis A: General 221 (1–2), 443–457.
Heck, R.M., Hu, Z., Smaling, R., et al., 1995. Close Coupled Catalyst System Design and ULEV Performance after 1050°C Aging. Technical Paper 952415. SAE, Warrendale.
Hedinger, R., Elbert, P., Onder, C., 2017. Optimal cold-start control of a gasoline engine. Energies 10 (10), 1–17, 1548.
Heimrich, M.J., Smith, L.R., Kitowski, J., 1992. Cold-start Hydrocarbon Collection for Advanced Exhaust Emission Control. Technical Paper 920847. SAE, Warrendale.
Heywood, J.B., 1997. Motor vehicle emissions control: past achievements, future prospects. In: Handbook of Air Pollution Form Internal Combustion Engines. Academic Dress, Salt Lake City, pp. 3–23.
Hochmuth, J.K., Burk, P.L., Tolentino, C., et al., 1993. Hydrocarbon Traps for Controlling Cold Start Emissions. Technical Paper 930739. SAE, Warrendale.
Hoshyar, N., Irankhak, A., Jafari, M., 2015. Copper catalysts supported on $CeMnO_2$ for CO oxidation in hydrogen rich gas streams. Iranian Journal of Chemical Engineering 12 (3), 3–14.
Hu, T., Wei, Y., Liu, S., et al., 2007. Improvement of spark-ignition (SI) engine combustion and emission during cold-start, fueled with methanol/gasoline 1820 blends. Energy Fuels 21 (1), 171–178.
Huang, T., Tsai, D., 2003. CO oxidation behavior of copper and copper oxides. Catalysis Letters 87 (3–4), 173–178.
Hutchings, G.J., Mirzaei, A.A., Joyner, R.W., et al., 1996. Ambient temperature CO oxidation using copper manganese oxide catalysts prepared by co-precipitation: effect of ageing on catalyst performance. Catalysis Letters 42 (1–2), 21–24.
Hutchings, G.J., Mirzaei, A.A., Joynerb, R.W., et al., 1998. Effect of preparation conditions on the catalytic performance of copper manganese oxide catalysts for CO oxidation. Applied Catalysis A: General 166 (1), 143–152.
Iliyas, A., 2008. One-dimensional Molecular Sieves for Hydrocarbon Cold-Start Emission Control (PhD thesis). The University of New Brunswick, Fredericton.
Innovative Transport Solutions (iTrans) Pvt. Ltd., 2009. Final Report for International Council for Clean Transportation (ICCT) & the Institute for Transport and Development Policy (ITDP). TBIU, New Delhi.
International Council on Clean Transportation (ICCT), 2016. India Bharat Stage VI Emission Standards. Policy Update. ICCT, New Delhi.
Iodice, P., Senatore, A., 2012. Analysis of a Scooter Emission Behavior in Cold and Hot Conditions: Modelling and Experimental Investigations. Technical Paper 2012-01-0881. SAE, Warrendale.
Iodice, P., Senatore, A., 2013. Road transport emission inventory in a regional area by using experimental two-wheelers emission factors. In: World Congress on Engineering, London, 2013.
Iodice, P., Senatore, A., 2015. Appraisal of pollutant emissions and air quality state in a critical Italian region: methods and results. Environmental Progress & Sustainable Energy 34 (5), 1497–1505.
Iodice, P., Senatore, A., 2016. A numerical-experimental approach to assess emission performance of new generation engines during the cold transient. International Journal of Automotive and Mechanical Engineering 13 (3), 3599–3612.
Iodice, P., Senatore, A., Langella, G., et al., 2016. Effect of ethanol–gasoline blends on CO and HC emissions in last generation SI engines within the cold-start transient: an experimental investigation. Applied Energy 179, 182–190.
Ismaila, S.O., Bolaji, B.O., Adetunji, O.R., et al., 2013. On vehicular emissions of petrol and diesel engines. International Journal of Engineering 1584, 178–180.
Jones, C., Cole, K.J., Taylor, S.H., et al., 2009. Copper manganese oxide catalysts for ambient temperature carbon monoxide oxidation: effect of calcination on activity. Molecular Catalysis A: Chemical 305 (1–2), 121–124.
Jones, C., Taylor, S.H., Burrows, A., et al., 2008. Cobalt promoted copper manganese oxide catalysts for ambient temperature carbon monoxide oxidation. Chemical Communication 1707, 1–7.
Kam, E.K.T., Hughes, R., 1979. The effect of catalyst fouling on the performance of adiabatic packed-bed reactors – a theoretical study. Chemical Engineering Journal 18 (1), 93–102.
Kamrani, E., 2008. Adaptive fuzzy control for air-fuel ratio of automobile spark ignition engine. World Journal of Engineering and Technology 2 (12), 196–204.
Kanada, Y., Hayashi, M., Akaki, M., et al., 1996. Hydrogen Added After-Burner System. Technical Paper 960346. SAE, Warrendale.
Kandylas, I.P., Stamatelos, A.M., 1999. Engines exhaust system design based on heat transfer computation. Energy Conversion & Management 40 (10), 1057–1072.
Kireev, A.S., Mukhin, V.M., Kireev, S.G., et al., 2009. Preparation and properties of modified hopcalite. Russian Journal of Applied Chemistry 82 (1), 169–171.
Kishi, N., Hashimoto, H., Fujimori, K., et al., 1998. Development of the Ultra Low Heat Capacity and Highly Insulating (ULOC) Exhaust Manifold for ULEV. Technical Paper 980937. SAE, Warrendale.
Kondrat, S.A., Davies, T.E., Zu, Z., et al., 2011. The effect of heat treatment on phase formation of copper manganese oxide: influence on catalytic activity for ambient temperature carbon monoxide oxidation. Journal of Catalysis 281 (2), 279–289.
Kramer, M., Schmidt, T., Stowe, K., et al., 2006. Structural and catalytic aspects of sol–gel derived copper manganese oxides as low-temperature CO oxidation catalyst. Applied Catalysis A: General 302, 257–263.
Krishna, S.M., Salam, P.A., Tongroon, M., et al., 2019. Performance and emission assessment of optimally blended biodiesel-diesel-ethanol in diesel engine generator. Applied Thermal Engineering 155, 525–533.
Lafyatis, D.S., Ansell, G.P., Bennett, S.C., et al., 1998. Ambient temperature light-off for automobile emission control. Applied Catalysis B: Environmental 18 (1–2), 123–135.
Laing, P., 1994. Development of an Alternator-Powered Electrically-Heated Catalyst System. Technical Paper 941042. SAE, Warrendale.
Layla, A., Azim, M., Ali, K.A., et al., 2008. Effects of excess cobalt oxide nanocrystallites on $LaCoO_3$ catalyst on lowering the light off temperature of CO and hydrocarbons oxidation. Iranian Journal of Chemical Engineering 27, 71–77.
Lee, D., 2010. Effects of Secondary Air Injection during Cold Start of SI Engines (PhD thesis). Massachusetts Institute of Technology, Boston.

Li, H., Andrews, G.E., Savvidis, D., et al., 2008. Study of thermal characteristics and emissions during cold start using an on-board measuring method for modern SI car real world urban driving. SAE International Journal of Engines 1, 804–819.
Li, L., Wang, S., Wang, G., et al., 2019. Effect of clamping stress on cold start performance of PEMFC. Energy Procedia 158, 1744–1749.
Li, M., Wang, D., Shi, X., et al., 2007. Kinetics of catalytic oxidation of CO over copper-manganese oxide catalyst. Separation and Purification Technology 57 (1), 147–151.
Libardi, S.H., Skibsted, L.H., Cardoso, D.R., 2014. Oxidation of carbon monoxide by perferrylmyoglobin. Journal of Agricultural and Food Chemistry 62 (8), 1950–1955.
Lisnyak, V.V., Safonova, V.V., Ischenko, E.V., et al., 2012. Preparation and activity of Pt (Pd)/WP2O7 catalysts for H_2 oxidation. Research Journal of Chemical Sciences 2 (6), 50–54.
Liu, X., Wei, X., 2008. Hydrothermally Stable Ag-Zeolite Traps for Small Olefin Hydrocarbon Molecules. US Patent 20080253950. United States Patent and Trademarks Office, Washington DC.
López-Pérez, E., Hermosilla, T., Carot-Sierra, J.M., et al., 2019. Spatial determination of traffic CO emissions within street canyons using inverse modeling. Atmospheric Pollution Research 1–8, https://doi.org/10.1016/j.apr.2019.01.019.
Lu, G.Y., Zhang, Z.G., 2010. Close Coupled Catalyst for Purification of Exhaust Gas and the Preparation Thereof. US Patent 20100048383. United States Patent and Trademark Office, Washington DC.
Ludykar, D., Westerholm, R., Almen, J., 1999. Cold start emissions at +22, −7 and −20°C ambient temperatures from a three-way catalyst (TWC) car: regulated and unregulated exhaust components. The Science of Total Environment 235 (1–3), 65–69.
Ma, T., Collings, N., Hands, T., 1992. Exhaust Gas Ignition (EGI) – a New Concept for Rapid Light-off of Automotive Exhaust Catalyst. Technical Paper 920400. SAE, Warrendale.
Min, B.K., Friend, C.M., 2007. Heterogeneous gold-based catalysis for green chemistry: low-temperature CO oxidation and propane oxidation. Chemical Reviews 107 (6), 2709–2724.
Mirzaei, A.A., Shaterian, R.H., Habibi, M., et al., 2003. Characterization of copper-manganese oxide catalysts: effect of precipitate ageing upon the structure and morphology of precursors and catalysts. Applied Catalysis A: General 253 (2), 499–508.
Mirzaei, A.A., Shaterian, H.R., Joyner, R.W., et al., 2013. Ambient temperature carbon monoxide oxidation using copper manganese oxide catalysts: effect of residual Na^+ acting as catalyst poison. Catalysis Communication 4, 17–20.
Morgan, K., Cole, K.J., Goguet, A., et al., 2010. TAP studies of CO oxidation over $CuMnO_x$ and $Au/CuMnO_x$ catalysts. Journal of Catalysis 276, 38–48.
Njagi, E.C., Chen, C., Genuino, H., et al., 2010. Total oxidation of CO at ambient temperature using copper manganese oxide catalysts prepared by a redox method. Applied Catalysis B: Environmental 99 (1–2), 103–110.
Njagi, E.C., Genuino, H.C., Kingondu, C.K., et al., 2011. Preferential oxidation of CO in H_2 rich feeds over mesoporous copper manganese oxide synthesized by a redox method. International Journal of Hydrogen Energy 36 (11), 6768–6779.
Oser, P., Mueller, E., Hartel, G., et al., 1994. Novel Emission Technologies with Emphasis on Catalyst Cold Start Improvements Status Report on VW-Pierburg Burnerl Catalyst Systems. Technical Paper 940474. SAE, Warrendale.
Paldey, S., Gedevanishvili, S., Zhang, W., et al., 2005. Evaluation of a spinel based pigment systems as a CO oxidation catalyst. Applied Catalysis B: Environmental 56 (3), 241–250.
Patil, M.D., Hertl, W., Williams, J.L., et al., 1996. In-line Hydrocarbon Adsorber System for ULEV. Technical Paper 960348. SAE, Warrendale.
Patil, M.D., Peng, Y.L., Morse, K.E., 1998. Airless In-Line Adsorber System for Reducing Cold Start HC Emissions. Technical Paper 980419. SAE, Warrendale.
Pattrick, G., Vander Lingen, E., Corti, C.W., et al., 2004. The potential for use of gold in automotive pollution control technologies: a short review. Topics in Catalysis 30 (1–4), 273–279.
Pillai, U.R., Deevi, S., 2006. Room temperature oxidation of carbon monoxide over copper oxide catalyst. Applied Catalysis B: Environmental 64 (1–2), 146–151.
Puértolas, B., Navlani-Garcıá, M., López, J.M., et al., 2012. Molecular simulation design of a multisite solid for the abatement of cold start emissions. Chemical Communications 48 (52), 6571–6573.
Pulkrabek, W.W., 2004. Engineering Fundamentals of the Internal Combustion Engine. Pearson Prentice Hall, Upper Saddle River.
Qian, K., Qian, Z., Hua, Q., et al., 2013. Structure activity relationship of CuO/MnO_2 catalysts in CO oxidation. Applied Surface Science 273, 357–363.
Quarles, J., 1974. Control of air pollution from new motor vehicles and new motor vehicle engines. Federal Register of United States 39 (204), 38250–38271.
Rajvanshi, A.K., 2002. Electric and improved cycle rickshaw as a sustainable transport system for India. Current Science 83 (6), 1–6.
Rani, R., Prasad, R., 2014. Studies of carbon monoxide oxidation at ambient conditions. Recent Research in Science and Technology 6, 89–92.
Raphulu, M.C., 2004. Catalytic Oxidation of Carbon Monoxide and Methane with Gold Based Catalysts (PhD thesis). University of the Witwatersrand, Johannesburg.
Roberts, A., Brooks, R., Shipway, P., 2014. Internal combustion engine cold-start efficiency: a review of the problem, causes and potential solutions. Energy Conversion and Management 82, 327–350.
Romero-Sarria, F., Plata, J.J., Laguna, O.H., et al., 2014. Surface oxygen vacancies in gold based catalysts for CO oxidation. RSC Advances 4 (25), 13145–13152.
Roozbehani, B., Houshmand, D., Badakhshan, A., 2013. Thermal and catalytic degradation of polystyrene with a novel catalyst. Science International 25 (4), 819.
Royer, S., Duprez, D., 2011. Catalytic oxidation of carbon monoxide over transition metal oxides. Chemcatchem 3, 24–65.
Russ, S., Thiel, M., Lavoie, G., 1999. SI Engine Operation with Retarded Ignition: Part 2 – HC Emissions and Oxidation. Technical Paper 993507. SAE, Warrendale.
Ryou, Y.S., Lee, J., Kim, Y., et al., 2019. Effect of reduction treatments (H_2 vs. CO) on the NO adsorption ability and the physicochemical properties of Pd/SSZ-13 passive NOx adsorber for cold start application. Applied Catalysis A: General 569, 28–34.
Santoso, H.G., Ament, F., 2010. Cold Start Emission Strategy for Hybrid Vehicles. US 7778767. United States Patent and Trademark Office, Washington DC.
Sendilvelan, S., Bhaskar, K., 2016. Electrically heated transition metal oxide catalyst for cold start emission reduction from gasoline engine. Indian Journal of Environmental Protection 36 (12), 986–992.
Sendilvelan, S., Sassykova, L., 2019. Chemically heated catalytic converter design options and performance using heated metal oxides. Journal of Chemical Technology and Metallurgy 54 (3), 571–577.

Shi, L., Hu, Z., Deng, G., et al., 2015. Carbon monoxide oxidation on copper manganese oxides prepared by selective etching with ammonia. Chinese Journal of Catalysis 36 (11), 1920–1927.
Shimasaki, Y., Kato, H., Abe, F., et al., 1997. Development of Extruded Electrically Heated Catalyst System for ULEV Standards. Technical Paper 971031. SAE, Warrendale.
Sierra Research, Inc, 2002. Review of CO Compliance Status in Selected Western Areas. SR02-09-04. Sierra Research, Inc., Mountain View.
Sierra Research, Inc, 2003. Review of Current and Future CO Emissions from On-Road Vehicles in Selected Western Areas. SR03-01-01. Sierra Research, Inc., Mountain View.
Singh, P., Prasad, R., 2014. Catalytic abatement of cold start vehicular CO emissions. Catalysis Industry 6 (2), 122–127.
Solsona, B., Hutchings, G.J., Garcia, T., et al., 2004. Improvement of the catalytic performance of $CuMnO_x$ catalysts for CO oxidation by the addition of Au. New Journal of Chemistry 28, 708–711.
Sothea, K., Oanh, N.T.K., 2019. Characterization of emissions from diesel backup generators in Cambodia. Atmospheric Pollution Research 10, 345–354.
Summers, J., Skowron, J., Miller, M., 1993. Use of Light-off Catalysts to Meet the California LEV/ULEV Standards. Technical Paper 930386. SAE, Warrendale.
Sun, J., Sivashankar, N., 1998. Issues in cold start emission control for automotive IC engines. In: The American Control Conference, Philadelphia, 1998.
Takei, Y., Hirohiko, H., Okada, M., et al., 1993. Effect of Gasoline Components on Exhaust Hydrocarbon Components. Technical Paper 932670. SAE, Warrendale.
Tanaka, Y., Utaka, T., Kikuchi, R., et al., 2003. Water gas shift reaction for the reformed fuels over Cu/MnO catalysts prepared via spinel-type oxide. Journal of Catalysis 215 (2), 271–278.
Tang, Z.R., Kondrat, S.A., Dickinson, C., et al., 2011. Synthesis of high surface area $CuMn_2O_4$ by supercritical anti-solvent precipitation for the oxidation of CO at ambient temperature. Catalysis Science & Technology 1 (5), 740–746.
Taylor, S.H., Hutchings, G.J., Mirzaei, A.A., 1999. Copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation. Chemical Communications 15, 1373–1374.
Tingvall, B., Pettersson, E., 2009. Demonstration of Multi Gas Exhaust Measurements during Cold Start Conditions. Luleå University of Technology, Luleå.
Ueno, M., Akazaki, S., Yasui, Y., et al., 2000. A Quick Warm-Up System during Engine Start-Up Period Using Adaptive Control of Intake Air and Ignition Timing. Technical Paper 000551. SAE, Warrendale.
Vasic, A.M., Weilenmann, M., 2006. Comparison of real-world emissions from two wheelers and passenger cars. Environmental Science & Technology 40 (1), 149–154.
Veprek, S., Cocke, D.L., Kehl, S., et al., 1986. Mechanism of the deactivation of hopcalite catalysts studied by XPS, ES and other techniques. Journal of Catalysis 100 (1), 250–263.
Wang, W., Lahti, J.L., Gillanders, C.A., et al., 2009. Method for On-board Diagnosis of Cold Start Emissions Reduction Control Strategy. US 7630826. United States Patent and Trademark Office, Washington DC.
Weilenmann, M., Soltic, P., Saxer, C., et al., 2005. Regulated and nonregulated diesel and gasoline cold-start emissions at different temperatures. Atmospheric Environment 39 (13), 2433–2441.
Williams, J.L., Patil, M.D., Hertl, W., 1996. By-pass Hydrocarbon Adsorber System for ULEV. Technical Paper 960343. SAE, Warrendale.
Yusuf, A.A., Inambao, F.L., 2019. Effect of cold start emissions from gasoline-fueled engines of light-duty vehicles at low and high ambient temperatures: recent trends. Case Studies in Thermal Engineering 14, 100417.
Zaki, M.I., Hasan, M.A., Pasupulety, L., 2009. Influence of CuOx additives on CO oxidation activity and related surface and bulk behaviors of Mn_2O_3, Cr_2O_3 and WO_3 catalysts. Applied Catalysis A: General 198, 247–259.
Zhao, F., Gong, M., Zhang, G., et al., 2015. Effect of the loading content of CuO on the activity and structure of CuO/Ce-Mn-O catalysts for CO oxidation. Journal of Rare Earths 33 (6), 604–610.
Zhou, L., Hua, J., Wei, H., et al., 2019. An experimental investigation on low load combustion stability and cold-firing capacity of a gasoline compression ignition engine. Engineering 5 (3), 558–567.
Zhou, Y., Wang, Z., Liu, C., 2014. Perspective on CO oxidation over Pd-based catalysts. Catalysis Science and Technology 1, 69–81.
Zhu, M., Xie, X., Wu, K., et al., 2019. Experimental investigation of the effect of membrane water content on PEM fuel cell cold start. Energy Procedia 158, 1724–1729.

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