MATEC Web of Conferences 87, 02020 (2017) DOI: 10.1051/matecconf/20178702020
ENCON 2016

Advanced Catalytic Converter in Gasoline Enginer Emission Control: A Review

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Abstract. Exhaust emission from automobile source has become a major contributor to the air pollution and environmental problem. Catalytic converter is found to be one of the most effective tools to reduce the overwhelming exhaust pollutants in our environment. The development of sustainable catalytic converter still remains a critical issue due to the stringent exhaust emission regulations. Another issue such as price and availability of the precious metal were also forced the automotive industry to investigate the alternatives for producing a better replacement for the material used in catalytic converter. This paper aims at reviewing the present development and improvement on the catalytic converter used on the reduction of exhaust emission in order to meet the regulations and market demand. The use of new catalyst such as to replace the noble metal material of Platinum (Pt), Palladium (Pd) and Rhodium (Rh) has been reviewed. Material such as zeolite, nickel oxide and metal oxide has been found to effectively reduce the emission than the commercial converter. The preparation method of the catalyst has also evolved through the years as it is to ensure a good characteristic of a good monolith catalyst. Ultrasonic treatment with combination of electroplating technique, citrate method and Plasma Electrolytic Oxidation (PEO) has been found as the latest novel preparation method on producing an effective catalyst in reducing the exhaust emission.

1 Introduction

Air pollution in Malaysia is reaching a critical level as witnessed during haze and El Nino crisis. Automobile source has been found contributed nearly 82% to the air pollution [1]. Since in the earlier 1940 and 1950s the air quality problem that engulfing some developing cities has been caused by the increasing number of vehicles [2].According to the Annual Report of the Road Transport Department of Malaysia [3], the number of registered road vehicles had increased from approximately 6.8 million in 1995 to 12.2 million in March 2003. Figure 1 shows the number of registered vehicles in Malaysia as of 1987-2002.

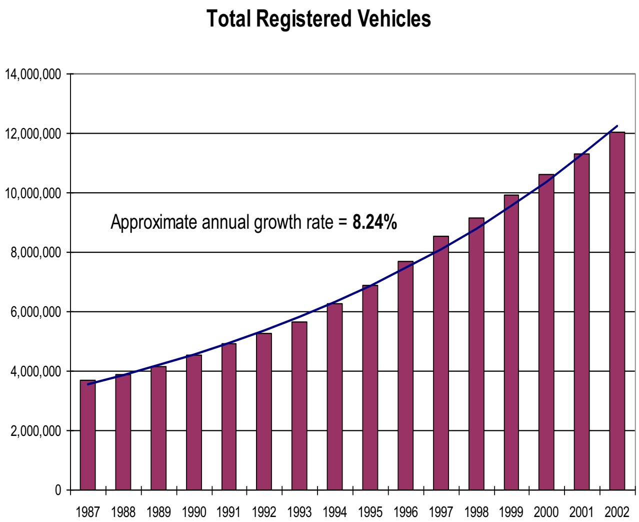

Figure 1 : Analysis of total registered vehicles in 1987 -2002 [3]

Emission by gasoline has known as a major source of air pollution along urban traffic routes especially in developed countries. In Malaysia, it can be estimated that nearly 51% from 12 millions of registered vehicles using gasoline engine [4].Gasoline engines which are also known as internal combustion engine (ICE) where initiation of the combustion process of air–fuel mixture is ignited within the combustion chamber and the ignition is done either by spark ignition (SI) or compression ignition (CI) [5]. Emission from gasoline engine can be reduced with an improvement in engine design, combustion conditions and catalytic after treatment devices [6]. Since the introduction in the middle of 1970s, catalytic converter has been found to be the best option out of various existing technologies for the control of vehicle exhaust emission. These gases are eliminated by the basic reactions occur inside a catalytic converter through oxidation for Carbon Monoxide(CO), Hydrocarbon(HC) and reduction for Nitrogen Oxide (NO_x).

Over the recent years, automotive exhaust after-treatment processes a range of advanced technologies based on oxidation and three-way catalyst, adsorption, storage and filtration processes. This enables the reduction of CO, HC, NO_x and particulate emissions (PM) from a gasoline or diesel engine in order to meet the demands of current and future exhaust emission regulations. In this paper, the advanced approach on the catalyst material and preparation of the catalyst were highlighted in order to identify the most suitable type of catalyst on to fulfill the requirements and market demand in automotive industry.

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 DOI: 10.1051/matecconf/20178702020

2 Three-Way Catalytic Converter

In the earlier 1980s, the automotive manufacturer has to include exhaust after treatment control system for four-stroke passenger car gasoline engines by three-way catalytic converter, which is capable of simultaneously reducing hydrocarbons, carbon monoxide and nitrogen oxides emissions [7]. This catalytic converter normally is placed after the exhaust manifold in-line with the exhaust system in order to be used to bring a desirable chemical reaction to take place in the exhaust flow [8].

The conventional Three-way catalyst (TWC) converters control CO, HC, and NOx effectively (80 to 90%) efficiency at or close to the stoichiometric air/fuel ratio which is normally used in the spark ignition engines [9] as shown in Figure 2. Three-way catalysts operate in a closed-loop system including a lambda or oxygen sensor to regulate the air: fuel ratio on gasoline engines [10].

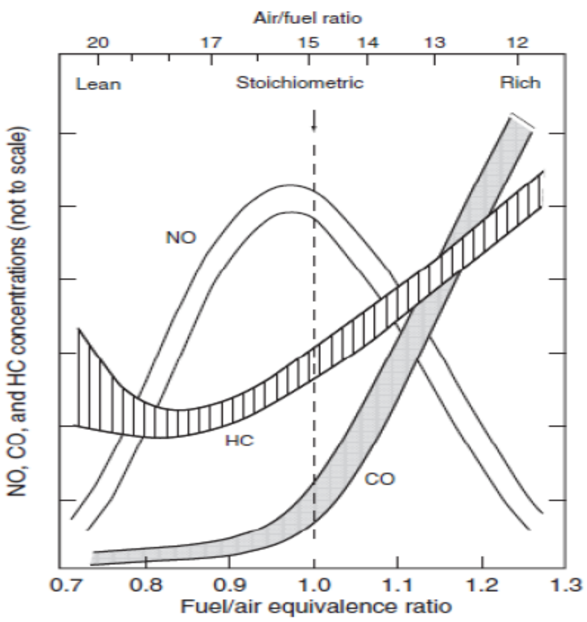

Figure 2 .Air-fuel-ratio for exhaust SI gasoline emission

3 Advanced Catalytic Materials

In the last few years, the most dominant catalyst for gasoline vehicles has been the monolith or honeycomb structure catalyst. This catalyst consists of a cordierite skeleton coated with a highly porous washcoat of about 90% γ-Al_2O_3 and a mixture of alkaline-earth metals, oxides etc and last the noble metals (Platinum (Pt), Palladium(Pd) and Rhodium(Rh) which are fixed in the washcoat surface as shown in Figure 3.

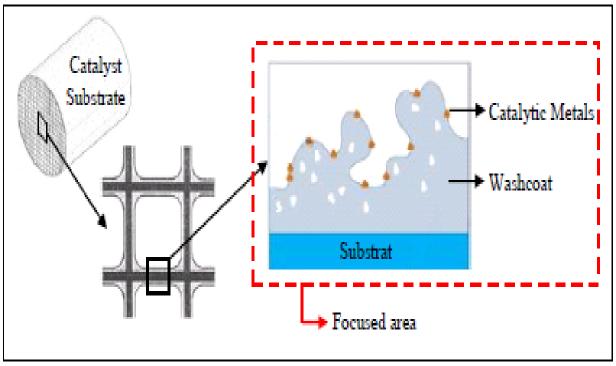

Figure 3. Washcoat and catalyst development focused area in catalytic converter [12].

The development in catalyst material was driven by the quest for the replacement of precious metal that limited in supply and higher cost. The noble metal catalytic converter has been found to cause several type of problems such as converter meltdown, carbon deposit, catalyst fracture and poisoning [13]. Amin and Rathod [14] have stated that the metal-base is more readily available and substantially cost effective than precious metal. Figure 4 shows the parameters that could affect the performance of the catalyst of precious metal [15].

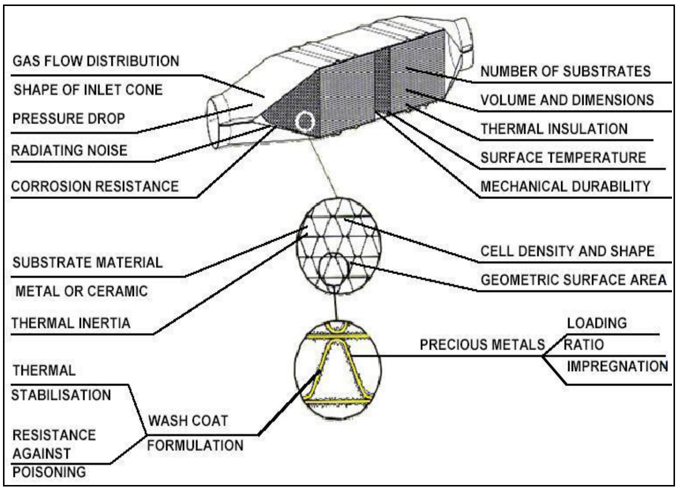

Figure 4 .Parameters affecting the catalyst performance [15]

3.1. Zeolite

Zeolites in natural and synthetic form have been found on the removal of NOx pollutant. The combination of zeolites with vanadia/titania can produce a catalyst that is more resistant to deactivation with a wide DeNOx operating window [16]. Latest study by Karthikeyan [17] has presented the use of zeolite as a catalyst in catalytic reduction of S.I engine emission. Zeolites may be produced by the conversion of fly ash as shown in. This low cost fly ash based zeolites has gained new research

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interest among the automotive industry manufactures due to their unique properties in several applications such as ion-exchange, molecular sieves, adsorbents and catalyst. The result revealed that the CO and HC emissions were significantly reduced at all levels of load conditions. It is also observed that the trends for percent reduction in HC and CO are almost similar in speed test. This proves that the In-house made metal doped zeolite converter performs better than that of commercial converter. Figure 5 and 6 shows the variation of HC and CO conversion efficiency with brake power of the engine.

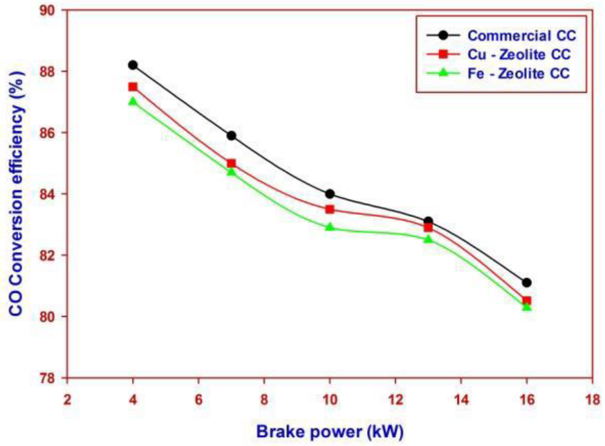

Figure 5. Hydrocarbon against Brake Power[17]

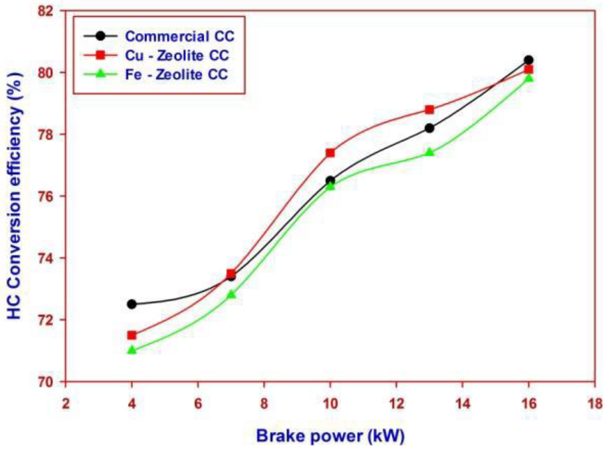

Figure 6 . Carbon Monoxide against Brake Power[17]

3.2 Nickel Oxide

Sebayang et al.,[18] had studied the preparation of NiO catalyst on FeCrAl substrate. FeCrAl is known as metallic substrate due to their advantages of high temperature corrosion resistance. Nickel oxide (NiO) exhibited high activity and selectivity of methane due to the ability of NiO to undergo reduction process owing to the presence of defect sites of the surface. Despite of the fast catalyst deactivation and carbon deposition, NiO catalyst was favorable due to its high thermal stability and low price. Previous study by Kester et al.,[19] which investigates the structure, texture and reducibility of co-precipitated NiO-Al_2O_3 catalyst which is influenced by nickel oxide loading and temperature of heat treatment has found that interactions in co-precipitated NiO-Al_2O_3 system are intensive. Therefore, nickel oxide can be considered as the best catalyst material for catalytic converter. Nickel oxide application is also effectively for the NOx absorber catalyst in order to reduce the emissions of hydrogen sulfide (H_2S) during desulfation [20]

3.3 Titanium Dioxide

Ranganathan [21] in his study invstigate the performance of several type of converters which are the metal oxide such as titanium dioxide (TiO_2), cerium oxide (CeO_2) and copper nitrate ($Cu(NO_3)_2$) , Zirconium dioxide (ZiO_2) with wire mesh substrate. Both the catalyst material used in this are inexpensive in comparison with conventional catalyst such as noble metals like Platinum (Pt), Palladium (Pd) and Rhodium (Rh). The study show a positive results that is the new two catalyst catalytic converters are effective than the present conventional catalytic converter manufacture. The emission from exhaust is rectified up to 20% than the OEM fitted values. Figure 7 shows the titanium based catalytic converter.

Figure 7. Titanium based catalytic converter [21]

4 Advances Preparation of Novel Catalyst

Preparation technologies for the manufacture a catalyst have evolved through the years. The characteristics of a good monolith catalyst should be met by managing preparation procedures.

4.1. Ultrasonic Treatment

Putrasari [22] investigates the new approach of coating technique using a combination of nickel electroplating, ultrasonic treatment and oxidation process. This research

DOI: 10.1051/matecconf/20178702020

discovered the preparation of NiO catalyst on FeCrAl substrate using various nickel electroplating process based on the weight gain during oxidation. The ultrasonic treatment is the power which has been converted to frequency by the transducer which generates a high cavitations bubble in a liquid system. This will result in the production of an intense shock out wave which flow through the liquid and strike out the material. The ultrasonic treatment prior to nickel electroplating was shown in Figure 8.

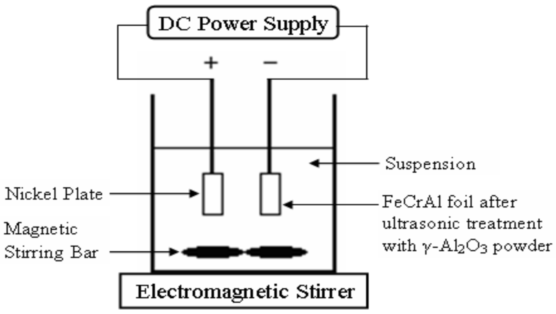

Figure 8 . Schematic diagram of electroplating process [22].

This novel electroplating process was found to improved the high temperature oxidation resistance and the best method to adhere NiO on FeCrAl substrate.

4.2. Citrate Method

Benadda et al., [23] investigated the effect of the preparation method on the structural and catalytic properties of MnOx-CeO2 Manganese Cerium Mixed Oxides. The catalyst of MnOx-CeO2 was prepared by a-Carbonate route [MnCe-CPC] and b-Citrate route [MnCe- Cit]. The citrate method leads to the formation of a solid with smaller surface area, pore volume and average pore diameter as shown in Figure 9 and Figure 10.

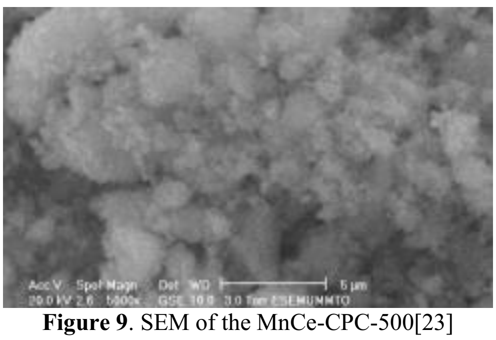

Figure 9. SEM of the MnCe-CPC-500[23]

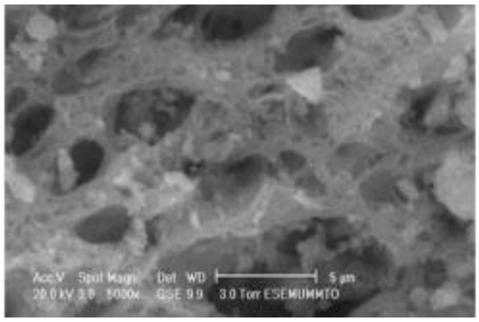

Figure 10. SEM of the MnCe-CIT-500[23]

The result shows that MnOx-CeO_2 mixed oxides prepared by the co-precipitation and citrate methods promotes to a good catalytic activity. This proves that the preparation method is strongly affect the textural properties and catalytic behavior of these oxides. The citrate method was found to form the solid with the best catalytic performance, a strong interaction between cerium and manganese and the small particle size seem to be at the origin of this performance.

4.3. Plasma Electrolytic Oxidation (PEO)

PEO is a novel method that being used in surface engineering technology. It has been considered as one of the methods that provide advantages in term of cost-effectiveness and environmentally friendly in which it can improve the corrosion and wear resistance of magnesium and magnesium alloys [24-26]. The coating layer that produced by PEO has a complex mechanism due to the combination of electro-, thermal-, and plasma-chemical reactions in the electrolyte [27].

Hussein et al. [28] conduct PEO process to form the ceramic coatings. During the process, the ceramic coating simultaneously grows inwards towards the alloy substrate and outwards towards the surface of the coating. The coating growth that been produced involved three processes including electrochemical reactions, the plasma chemical reactions and thermal diffusion. Figure 11 shows the schematic diagram of the coating process for PEO treatment.

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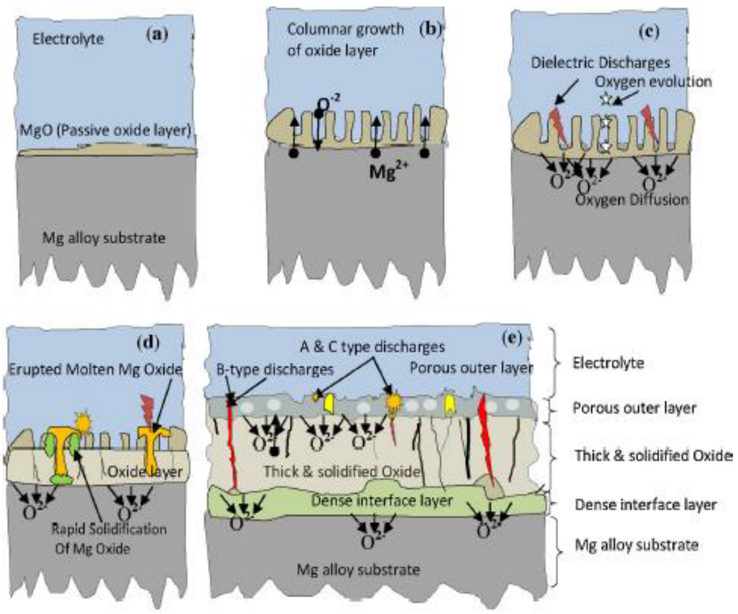

Figure 11 .Schematic diagram of the coating process for PEO treatment [29]

Yang et al., [30] proposed the method of a process as shown in Figure 12 to form aluminium oxide on FeCrAl surface. This new approach of PEO use electric energy prior to oxidation time to formed the oxide particle .It was found that Al and O contents increased and Al oxide area was observed when applied energy increased because of enhancement of reactivity between insulating oxide and micro-charging in an electrolyte. The study presents a possibility of aluminium oxide formation by electro-chemical coating process without any pre-treatment of FeCrAl.

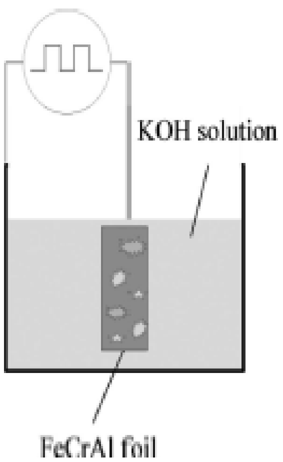

Figure 12 . Schematic diagram of the plasma electrolytic oxidation process [30]

5 Conclusions

A list of new technologies was developed by the researchers to reduce exhaust emission and catalytic exhaust after treatment has been reviewed. As to meet the stringent exhaust emission regulations, research was centred around the material developed and the preparation method for the best replacement of the precious noble metal. Continuous improvement in materials modification technologies, as part of an integrated system comprising control of exhaust emission allows meeting more and more stringent combustion engines emissions legislations.

Acknowlegement

The authors would like to thank the Ministry of Education and Universiti Tun Hussein Onn Malaysia (UTHM) through the funding supported FRGS grant under no Vot. 1216 and Centre for Graduate Studies-UTHM.

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