

CHEMICALLY HEATED CATALYTIC CONVERTER DESIGN OPTIONS AND PERFORMANCE USING HEATED METAL OXIDES

Subramanian Sendilvelan¹, Larissa Sassykova²

¹Department of Mechanical Engineering
Dr. M.G.R Educational and Research Institute, University
Chennai-600 095, India

E-mail: sendilvelan.mech@drmgrdu.ac.in

²Faculty of Chemistry and Chemical Technology
Al-Farabi Kazakh National University
71, Al-Farabi str., 050040, Almaty, Kazakhstan

E-mail: larissa.rav@mail.ru

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ABSTRACT

A chemically heated and electrically initiated catalyst in combination with a traditional converter can achieve the Low and Ultra Low Emission Vehicle (ULEV) standards. Experiments are conducted to investigate the impact of the various heating strategies and the system design parameters aiming emission decrease. An attempt is also made to reduce the cold-start emission of a multi-cylinder SI engine using Chemically Heated Catalytic (CHC) converter of a different volume of CHC filled with different oxides acting as a catalyst. It is found that CHC reduces cold-start hydrocarbon and carbon monoxide emission when used with the existing catalytic converter. The maximum CO and HC reduction is achieved with the catalytic converter with copper oxide as a catalyst over nickel oxides filled with CHC after the cold start of the engine.

Keywords: chemically heated catalyst, emission control, petrol engine, cold start emission.

INTRODUCTION

Automotive emission standards are becoming a major issue in India due to the highly polluted environment in the metros. As we know that Euro-IV is already applied in the national capital region and very shortly Euro-II will be implemented. Very soon Euro-V and Euro-VI have to be implemented in order to follow the clean air norms. Euro-III and Euro-IV norms could be met by using a multi-point injection system and a catalytic converter appropriately designed to meet them. However, Euro-III and Euro-IV pose considerable problems referring particularly to the start-up [1].

According to the Environmental Protection Agency (EPA) the current technology vehicles emit the majority of tailpipe HC and CO emissions during the first minute or two of operation from the cold start [2]. Two factors

contribute to the high emission at the start up. First, the catalyst does not begin to oxidize HC and CO until; it can take the exhaust gas between one to two minutes to raise the catalyst temperature to the light off level [3]. Secondly, most engines generally run a little rich during the initial warm up [4].

The quick catalyst light off is a key part of decreasing HC and CO emissions to Low Emission Vehicle (LEV) levels [5]. The catalyst light off can be quickly achieved by heating the catalyst to an effective temperature as quickly as possible while providing a near stoichiometric exhaust air-fuel ratio [6]. Using chemical and electrical energy to quickly heat a catalyst substrate is an effective means of reducing cold start HC and CO emissions. Batteries are used to pre-heat CHC prior to the engine starts using power levels of 5 kW and above [7]. Tremendous improvements are made in the past couple of years to

decrease the power consumption to 2 kW - 3 kW level aiming to obtain a lower battery impact. However, even a 2 kW power requirement has a substantial impact on the battery life [8]. Also, providing 2 kW to 3 kW from a 12-volt battery requires large wire diameters. Besides, the sophisticated power switching mechanism has a very considerable effect on the battery life [9]. Recent CHC activities have focused the efforts on the electrical energy and emission reductions. This work addresses both of these CHC technology themes [10].

EXPERIMENTAL

An electrically heated catalytic converter

The CHC consists of the heater element, the Light-Off Converter (LOC) and the main catalytic converter (MC). The heater element should initiate CO and HC oxidation in the subsequent LOC as quickly as possible due to the effect of the chemical heating. Together with the enthalpy of the exhaust gas and additional electrical energy, the main catalytic converter is very quickly brought to its operating temperature. To achieve large reductions of the cold start emissions it is necessary to have CHC and light off catalyst bed temperature above the light off temperature, which is the temperature where 50 % emission reduction is achieved after the engine start up. It is important to maintain this temperature at which near maximum conversion efficiency is achieved. The minimization of the heater energy requirements require to maximize the battery life, to reduce the overall cost, and to minimize any mileage penalties. It is reported that CHC and the main converter temperature affect significantly the effectiveness of CHC systems.

Eqs. 1 and 2 present the relationship between the time, the temperature and the electrical energy supplied:

$$E_{\text{Elec}} = MC (T_{\text{CHC}} - 25^{\circ}\text{C}) \quad (1)$$

$$E_{\text{Elec}} = V^2/R \text{ xt} \quad (2)$$

Eq.1 shows that the minimization of the heater mass, M, will maximize the heater temperature for a given amount of electrical energy. According to Eq. 2 the electrical energy supplied is dependent on V, R and t. Furthermore, the minimization of the time requires the resistance decrease or the voltage increase. The reducing of the resistance much below 0.032 ohms is not

considered desirable because of the increasing electrical energy losses in the batteries and the associated connections. The variation of the voltage is more desirable since doubling the voltage results in 1/4 the time to supply the same electrical energy. Therefore, a 24-volt battery system is chosen for these experiments.

The electrical energy is changed to thermal energy as defined by Eq. 2. The latter assumes little heat loss to the environment during the heat-up and no exhausts gas passing through CHC during the heating. For a given electrical energy level, it is desirable to maximize the heater temperature as the catalyst will be more effective. The reduction of the specific heat of the metal or the mass of the heater can maximize the heater temperature. By optimizing the heated mass, it is possible to greatly increase the rate of the temperature rise. Thus, by heating only a small volume of the catalyst, it is possible to reach very rapidly the temperature at which the catalyst starts acting. Once the exothermic reaction begins, an abundance of chemical energy is released which acts to heat up the main converter. The energy balance of this system is shown schematically in Fig. 1. It is evident that the chemical and the thermal energy come out of CHC. The energy balance is described by Eq. (3):

$$Q_{\text{Chem,out}} + Q_{\text{Ther,out}} = Q_{\text{Chem,in}} + Q_{\text{Ther,in}} + Q_{\text{Elec}} - Q_{\text{Store,CHC}} - Q_{\text{Store,LOC}} - Q_{\text{Loss}} \quad (3)$$

Eq. (3) is a modified form developed by L. S. Socha et al. [11]. The heat loss to the ambient is included because it reduces the thermal energy coming out of CHC as it is significant. The main converter attains more rapidly its operating temperature, mainly due to the energy released by the homogeneous catalytically activated gas

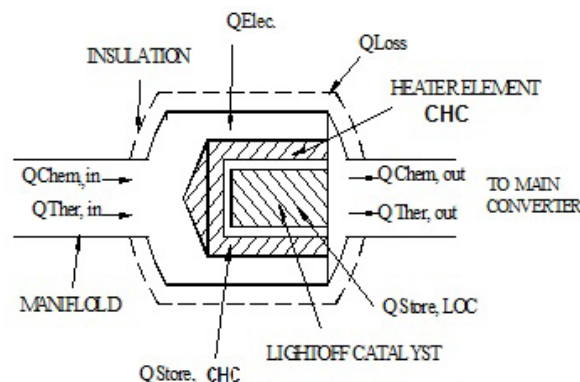


Fig. 1. Energy balance of CHC.

reaction. Using this analysis as a guide, experiments are incorporated in the test plan to quantify the impact of the heat-up time, the heater mass, the heater temperature, and the energy requirement on the cold start emissions.

Air injection

During the cold-start phase the engines must be run with fuel mixtures of a composition richer than the stoichiometric one in order to ensure smooth operation. The chemical reactions occurring in CHC refer to the oxidation of the hydrocarbon and the oxidation of carbon monoxide. The principal equations of the reactions are:

$$2\text{HC} + 5/2 \text{O}_2 \longrightarrow 2\text{CO}_2 + \text{H}_2\text{O} \quad (4)$$

$$\text{CO} + 1/2 \text{O}_2 \longrightarrow \text{CO}_2 \quad (5)$$

If the air-fuel ratio is rich, there is insufficient oxygen in the exhaust stream in the case of the maximum conversion of HC and CO [12]. The lack of oxygen in the catalytic converter during this period provides only partial oxidation of CO and HC, thus resulting in higher exhaust gas emissions [13 - 15]. This problem is handled by injecting secondary air after the exhaust valves of the engine. The air is supplied from a compressor at constant pressure through a nozzle at the leading side of CHC in the exhaust pipe. A regulator and a rotameter are used to regulate and measure the air supply. The injected air can react with the hot exhaust gas, thus providing an initial oxidation of CO and HC in the exhaust piping [16 - 18]. The heat produced by the oxidation reactions increases the exhaust gas temperature, resulting in a fast catalyst light-off. Air calibration tests are carried out to determine the optimum rate and duration of the air injection. The data indicates that air injection is required only 40 seconds after starting the engine from cold-start and at the rate of 90 liters per minute.

Assembly of CHC and an experimental setup

The experiments are conducted on a multi-cylinder, vertical, water-cooled, four stroke, spark ignition engine coupled to a hydraulic dynamometer. They are carried out at 1,750 rpm with 50 % of the maximum load after an idling period of 20 s. The Electrically Heated Catalytic Converter is placed before the main catalytic converter on the exhaust pipe. The main converter used refers to a commercially available converter exposed to approximately 5,000 km of a vehicle operation. The CHC housing is made of stainless steel insulated by a thick

layer of asbestos rope to prevent heat loss. The substrate is made of stainless steel mesh. The concentric surface of the mesh is filled with different oxides namely, copper oxide, chromium oxide, nickel oxide and silver oxide as catalysts in case of three different volumes of 145 cc, 271 cc and 387 cc. The mesh is heated by 1.5 kW band type electrical heater. The inner cylinder is also filled with these catalysts, which act as a light-off catalyst. Fresh catalysts are used for this test. The CHC is placed before the main catalytic converter on the exhaust pipe.

The inlet, the bed, and the outlet temperature of CHC is measured by three chromel-alumel thermocouples. The sensor signal is used to control the electrical heating to avoid excessive energy supply. A data logger system is used to analyze the temperature variation. All thermocouples are connected to the data logger. The latter used here refers to 8-channel 12-bit data logger. The gas analyzer (Crypton 285 OIML II- SPEC) is used for the measurement of HC and CO in the exhaust gases. The response time of the gas analyzer is 10 seconds.

RESULTS AND DISCUSSION

The experiments are conducted with chemically heated electrically initiated catalytic converter attached with the main catalytic converter in a four-stroke SI engine. The discussions on the results are given below. Fig. 2 shows the brake power in kW for the different volume of CHC of 145cc, 271cc and 378cc versus the specific fuel consumption in kg/kW h. Initially, all four-oxide catalysts are tested but only the values for copper oxide is reported here because it shows desirable SFC.

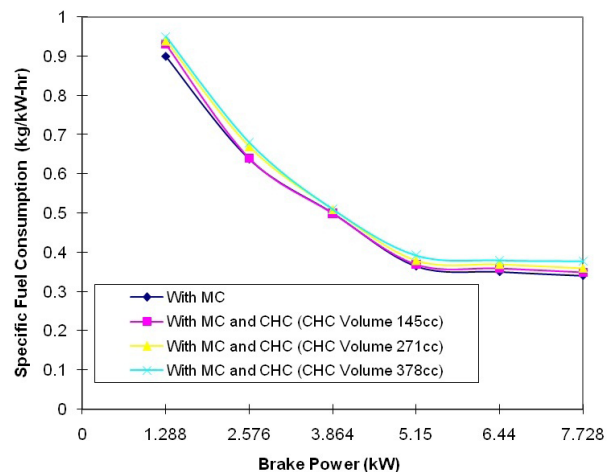


Fig. 2. SFC vs Brake Power for three different volumes of CHC.

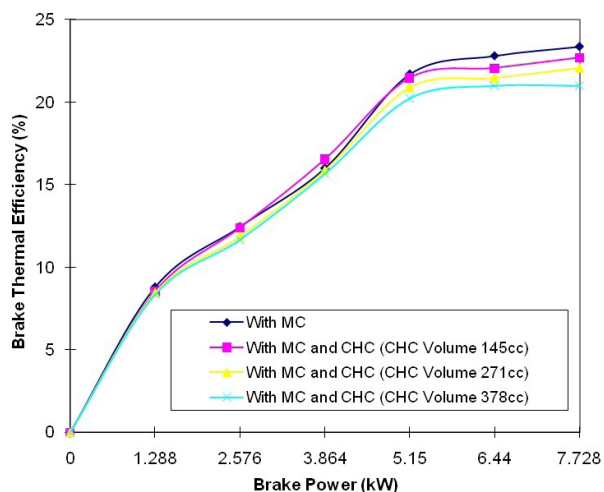


Fig. 3. Brake Thermal Efficiency vs Brake Power for three different volumes of CHC.

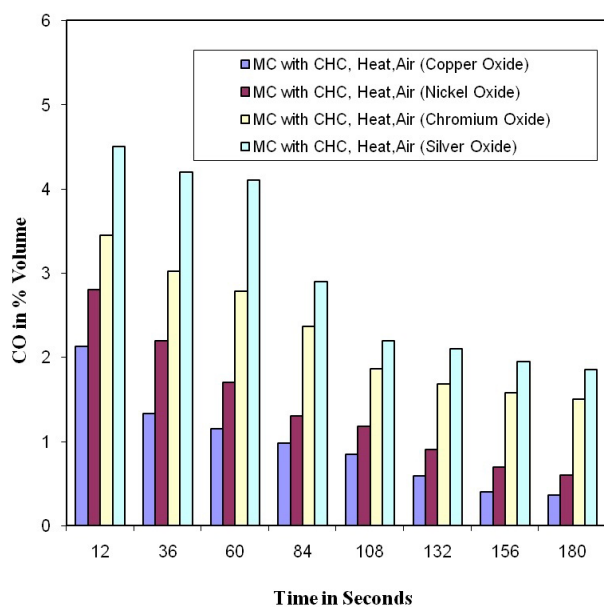


Fig. 4. CO vs time for 145 cc volume of CHC with 90 lpm air injection for 40 Seconds.

The reason for the back pressure could be due to the high volume of CHC.

Fig. 3 shows the brake power in kW for CHC of 145cc, 271cc and 378cc versus the brake thermal efficiency. Initially, all four-oxide catalysts are tested but only the values for copper oxide is reported here because it shows desirable high Brake thermal efficiency in the case of all volumes studied. The reason for the back pressure could be due to the high volume of CHC. The brake thermal efficiency is almost comparable with MC configuration with 145cc volume of CHC. The back

pressure tested for CHC of 145cc, 271cc and 378cc also clearly indicates that less back pressure is observed in the case of a volume of 145cc. That is why this volume is used in the tests carried out to optimize the design.

Fig. 4 shows the variations of CO versus time in seconds from the cold start of the engine. The latter is with a main catalytic converter with CHC of 145cc volume, different oxides as catalysts and 90l pm air injection for 40 s. It is seen that the content of CO decreases with time. It is higher for chromium, silver and nickel oxide. The decrease of CO is 2.13 vol. % in 12 s. It gradually decreases and reaches 0.36 vol. % at 180 s in case of the main converter with 145cc volume CHC and copper oxide as a catalyst and 90l pm air injection for 40 s. The decrease of CO content amounts to 2.8 vol. % in 12 s and decreases further to 0.6 vol. % for 180 s under identical conditions in presence of nickel oxides. The decrease of CO content amounts to 3.45 vol. % in 12 s and gradually decreases to reach 1.5 vol. % for 180 s under identical conditions in presence of chromium oxide. The decrease of CO content amounts to 4.5 vol. % in 12 s and gradually decreases to reach 1.85 vol. % for 180 sec. under identical conditions in presence of silver oxide as a catalyst. This clearly shows that not only the performance with less back pressure copper oxide gives a high brake thermal efficiency and low specific fuel consumption with reduced CO emission.

CHC with copper oxide as a catalyst decreases significantly the cold-start HC and CO emissions in case of all configurations tested. The latter are successful, because they initiate quickly the catalytic reaction. The preheating of CHC needs power to heat the metal catalyst. After engine starting, the power can be provided by the alternator. But this will slightly reduce the efficiency of the engine in view of the pollution created during cold start. The efficiency can be increased by many ways like turbocharges, exhaust gas recirculation and engine management systems etc. The oxides used in this work are not expensive as the conventional catalytic converter. The latter uses precious metals, which are costlier than other metals. Those used here refer to stainless steel mesh coated with different metal oxides which are cheap and easy to produce by an electroplating method. So, there is no need to work with inefficient oxides like those of chromium, nickel and silver aiming properties improvement. Copper oxide is found the best for the purpose. Its reproduction over the metal mesh is easy.

Theoretical investigation - multiple regression analysis

The advantage of using this technique is that no initial assumption on the form of the correlation is needed. The procedure is tested using the experimental data. Regression is a procedure applied to find the form of the best fitting correlation as well as the constants in it. Genetic programming offers a way to carry it out. The correlations obtained on the ground of the experimental data are commonly used to estimate the heat rate in thermal components. Most often this reduction of the experimental data to correlations is based on the initial choosing a specific functional form of the correlation for which the constants are then determined.

The performance of CHC, CO conversion rate, depends on the temperature of the exhaust before the CHC, the temperature of the MC and the time from the cold start of the engine which are treated as independent variables to correlate the emission performance of CHC. The data gathered from the test run with 1.5kW heating and 90 lpm air supply leads to:

$$\text{CO (Conversion rate)} = 51.87132 - 0.24151 t - 0.0009 T_{in} + 0.173323 T_{mc} \tag{6}$$

where t is the time from cold start of the engine in s, T_{in} is the temperature of the exhaust before CHC in °C, while T_{mc} is the surface temperature of the main converter in °C.

This equation is a valuable engineering tool to estimate CHC performance under the given conditions. Among the different volume of CHC tested, that of 145 cc gives lower CO and HC emissions compared with

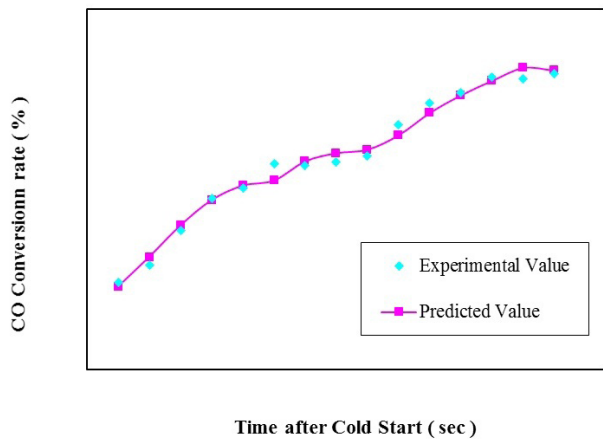


Fig. 5. Variation of CO conversion rate with time after cold start.

those of 271 cm³ and 378 cm³. The largest reductions of the cold start HC and CO emissions are obtained by combining a resistance heating of the catalyst with a secondary air injection. Among the different air injections tested, that of 90 l/min shows better reductions than those of 80 l/min and 100 l/min. Among the different durations of the air injection tested, that referring to 40 s from the cold start of the engine shows better reductions than that of 20 s. The maximum reduction is achieved when CHC of a volume of 145cc is filled with copper oxide catalyst and 90 lpm of air injection is provided during the first 40 s after the cold start of the engine. The generalized equation presented here using multiple regression analysis can be used with confidence to analyze the emission performance. Figs. 5, 6 and 7 show the time variation from the cold start (in s) of the predicted and the experimental CO conversion rate, the

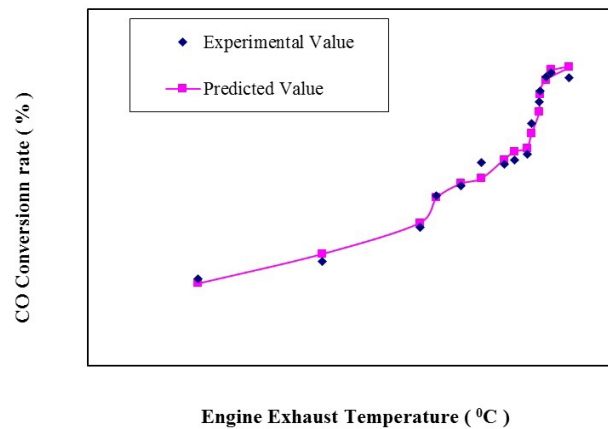


Fig. 6. Variation of CO conversion rate with Engine Exhaust Temperature.

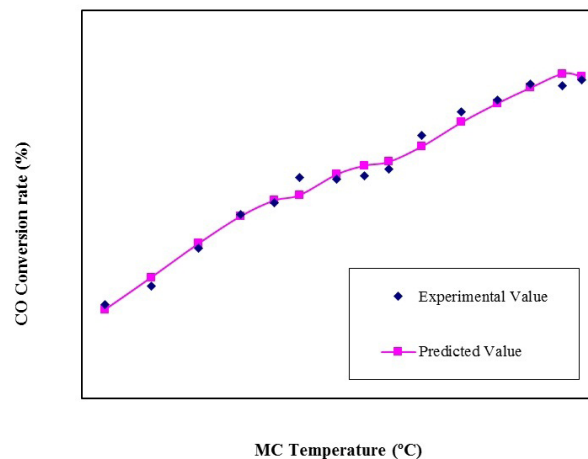


Fig. 7. Variation of CO conversion rate with MC temperature.

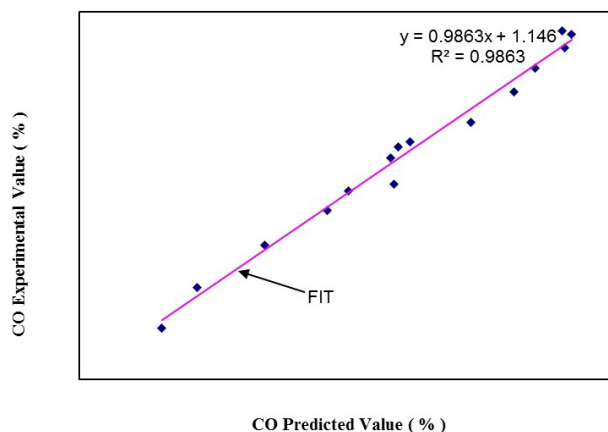


Fig. 8. Variation of CO experimental value with CO predicted value.

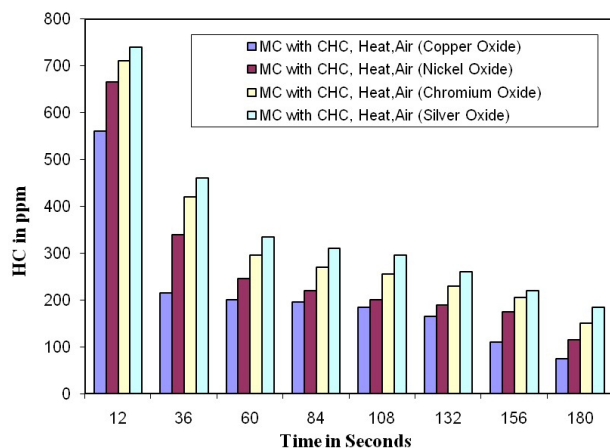


Fig. 9. HC vs time for 145 cc volume of CHC with 90 lpm air injection for 40 seconds.

engine exhaust temperature before CHC, and the temperature of the main catalytic converter, respectively. The figures show that any two independent variables can be predicted by fixing the third independent variable and the corresponding CO conversion rate. It is also seen that the predicted values and the experimental data are in close agreement with each other.

Fig. 8 shows the predicted and the experimental values of CO conversion rate. A review of the test-data indicates that the predicted values are in close agreement with the experimental values. Therefore the equation developed can be used with confidence to analyze the emission performance. Fig. 9 presents the variations of HC in ppm versus the time in s from the cold start of the engine with CHC of 145 cc volume containing different oxides as catalysts with 90 lpm air injection within 40

s. It is seen that HC values are initially higher and decrease further to 180 s for all conditions of the catalytic converter with CHC with air injection. The maximum decrease is achieved with a catalytic converter and 145 cc volume CHC filled with copper oxide. The air injection in this case is 560 ppm within 12 s after the cold-start and decrease further to 75 ppm after 180 s. But the other oxides show the higher value of HC than copper oxide.

CONCLUSIONS

Based on the experimental investigation on a four-stroke SI engine with copper oxide, chromium oxide, silver oxide and chromium oxide catalysts, it is concluded that there is a significant reduction in CO and HC emission by the use of CHC with air injection, due to complete oxidation in the presence of high temperature air. From the preceding paragraphs, it is found that CHC filled with copper oxide gives the better results and CHC volume of 145cc shows favorable results. Further in the case of CHC with 1.5kW heat and with air injection of 90lpm during the first 40 seconds after starting the engine reaches light off temperature very quickly than other configuration. The maximum reduction in CO % by vol. is 2.13 in 12 sec. and gradually decreases and reaches 0.36 at 180 sec. in case of CHC with copper oxide as catalyst. The silver oxide shows poor performance among all oxides tested.

REFERENCES

1. G.P. Macey, R. Breech, M. Chernaik, C. Cox, D. Larson, D. Thomas et al., Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study, *Env. Heal.*, 13, 2014, 82.
2. C.S. Raj, S. Arul, S. Sendilvelan, C.G.Saravanan, A comparative assessment on performance and emissions characteristics of a diesel engine fumigating with methanol, methyl ethyl ketone, and liquefied petroleum gas, *Energy Sources Part a-Recovery Util Environ. Eff.*, 32, 2010, 1603-1613.
3. N. Nithyanandan, S. Sendilvelan, K. Bhaskar, N. Balaji, S. Mohanamurugan, Exposed area influence for light off of catalyst to reducing hc/co emission from automobile SI engine exhaust by using low mass electrically heated metal catalyst, *Int. J. Appl.*

- Eng. Res., 5, 2010, 441-448.
4. S. Sendilvelan, K. Jeyachandran, K. Bhaskar, Pollution studies on gasoline engine with electrically heated catalyst, Am. Soc. Mech. Eng. Int. Combust. Engine Div. ICE, 36, 2001.
 5. L.R.Sassykova, A.Ussenov, A.T.Massenova, Sh.A.Gil'mundinov, K.S.Rakhmetova, V.N.Bunin, Zh.T. Basheva and M.K.Kalykberdiyev, Creation of high effective nano-structured catalysts on base of Pt, Pd for neutralization of motor transport exhaust, Int. J. Chem. Sci., 14, 1, 2016, 206-212.
 6. K. Bhaskar, L.R.Sassykova, M. Prabhakar, S. Sendilvelan, Effect of dimethoxy-methane (C₃H₈O₂) additive on emission characteristics of a diesel engine fueled with biodiesel, International Journal of Mechanical and Production Engineering Research and Development, 8, 1, 2018, 399-406.
 7. L.R. Sassykova, A. Nalibayeva, Sh.A. Gil'mundinov, Development of technology of synthesis of catalysts for neutralization of emissions of the industry and motor transport, Bulg. Chem. Comm., 49, 3, 2017, 583-588.
 8. M. Presti, L. Pace, L. Poggio, V. Rossi, Cold start thermal management with electrically heated catalyst: a way to lower fuel consumption, SAE Int., 8, 2013.
 9. S. Ye, Y.H. Yap, S.T. Kolaczowski, K. Robinson, D. Lukyanov, Catalyst "light-off" experiments on a diesel oxidation catalyst connected to a diesel engine - Methodology and techniques, Chem. Eng. Res. Des., 90, 2012, 834-845.
 10. L. Pace, M. Presti, An alternative way to reduce fuel consumption during cold start: The electrically heated catalyst, SAE Tech. Pap., 2011.
 11. L.S. Socha, D.F. Thompson, D.K. Smith, P.A. Weber, Emissions performance of extruded electrically heated catalysts in several vehicle applications, 1995.
 12. E. Zervas, X. Montagne, J. Lahaye, Emissions of regulated pollutants from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio, Environ. Sci. Technol., 37, 2003, 3232-3238.
 13. I.A. Reşitoğlu, K. Altinişik, A. Keskin, The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems, Clean Technol. Environ. Policy, 17, 2014, 15-27.
 14. V.Y. Prikhodko, S.J. Curran, J.E. Parks, R.M. Wagner, Effectiveness of diesel oxidation catalyst in reducing HC and CO emissions from reactivity controlled compression ignition, SAE 2013; 2013-01-05, 329-335.
 15. M. Kamijo, M. Kamikubo, H. Akama, K. Matsu-shita, Study of an oxidation catalyst system for diesel emission control utilizing HC adsorption, JSAE Rev., 22, 2001, 277-280.
 16. Y.A. Aubakirov, L.R. Sassykova, A.M. Nalibayeva, K. Dossumov, Z.K. Tashmukhambetova, A.S. Zhumakanova, A.K. Zhussupova, N.K. Zhakirova, Synthesis and testing of catalysts for decrease of toxic emissions of vehicles, Orient. J. Chem., 33, 6, 2017, 3130-3137.
 17. K. Bhaskar, S. Sendilvelan, L.R. Sassykova, Effect of premix and exhaust gas recirculation on the emission characteristics of biodiesel fueled engine, News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 428, 2, 2018.
 18. L. Sassykova, V. Bunin, A. Nalibayeva, M. Nurakhmetova, Synthesis of catalysts on the metal block carriers and testing their effectiveness in the real conditions of operation, J. Chem. Technol. Metall., 53, 3, 2018, 537-542.