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AUTOMOTIVE EMISSION ABATEMENT: STUDIES ON THE EFFECT OF TiO_2-Co BASED CATALYTIC CONVERTER

KU HALIM KU HAMID & MUHD. HAIRUL AZMAN ABAS
Department of Chemical Engineering, Faculty of Mechanical Engineering,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

ABSTRACT

Emissions from automotive exhausts can be reduced by catalytic converters located in the exhaust system. Automobile exhaust converters were introduced in 1975 to oxidize the unburned CO and HC to carbon dioxide (CO_2) and water (H_2O) respectively. A second-generation converter was introduced in the U.S. in 1981 which catalyzed the oxidation reactions and simultaneously reduced nitrogen oxides to nitrogen. These three-way converters (TWC) have been used in all new vehicles since then. A newly designed catalytic converter system was established in this study to investigate the effectiveness of the catalytic reaction. Pieces of stainless steel wire mesh supported with Co/TiO_2 were arranged linearly inside the exhaust chamber to increase the reaction area of the gases to catalytically transform into relatively benign ones. The wire mesh was rearranged in order to replace the role of conventional ceramic honeycomb monolith, which made of cordierite and coated with washcoat to support the catalytic material. Application of the stainless steel wire mesh as a basic design could provide a low cost and competitive catalytic material supporter. Each pieces was placed closed to each other before it was impregnated with TiO_2 and Cobalt. The effectiveness of the catalyst was determined by analyzing the exhaust emission before and after it was passed through the cat-co. The result shows that the amount of toxic gases level in the exhaust emission decreased as closed to the commercial cat-co capacity.

Key words: *Stainless steel, wire mesh, catalytic material, Cobalt, TiO_2*

INTRODUCTION

Petrol engine emissions are a source of environmental pollution possible health risks. Carbon monoxide (CO), nitrogen oxides (NO_x) and particulate matter emissions are the main problems since very small particles carrying various suspected mutagenic hydrocarbons can penetrate deeply into the lungs, while NO_x compounds contribute to both acid rain and photochemical smog. Other pollutant emissions (unburnt hydrocarbons and CO) also contribute to these problems, which may lead to serious respiratory systems failure. Present and near future environmental regulations concerning petrol engines will focus on both fuel composition and emission control, the most plausible approach being after-treatment techniques like the combination of traps, reduction and oxidation catalysts to eliminate particulate matter and hazardous gases. Since the temperature range of typical exhausts is 200–400°C, a potentially useful catalyst has to operate efficiently in that temperature range and be thermally stable (1).

Catalytic materials in automobile converters are generally supported on a ceramic honeycomb monolith. The honeycomb, made of cordierite, contains 300 to 400 square channels per square inch, and is coated with an activated high surface area alumina layer called the washcoat. A five to one ratio of Pt to Rh (totaling between 20 – 40 g/ft^3) is highly dispersed on the washcoat (3). The design of the support material and the application of highly precious metals however will increase the trade value of TWC and thus affecting the automobile prices in the market. Therefore, there are demands for a low cost and comparable cat-co as an alternative to substitute current cat-co, hence reducing the cost affected and the price of automobiles, which now faced mostly by third world countries.

The reactions for the TWC catalyst are shown in Table 1 (3). There are two simple principles reaction occurs in the cat-co; oxidation and reduction process. Nowadays, automobile manufacturers had turn to used three-way cat-co (TWC) instead of two-way cat-co. If two-way cat-co only considering oxidation process which put more concern on unburned hydrocarbon (HC) and carbon monoxide (CO) only, TWC includes reduction reaction within the cat-co involving conversion of nitrogen particulates (NO and NOx) besides retaining the oxidation reaction.

Table 1. Three-way converter (TWC) reactions.

$CN_n + (1 + n/4)\ O_2$	→	$CO_2 + n/2\ H_2O$
$CO + ½\ O_2$	→	CO_2
$NO + CO$	→	$½\ N_2 + CO_2$
$NO + H_2$	→	$½\ N_2 + H_2O$
$(2 + n/2)\ NO + CH_n$	→	$(1 + n/4)\ N_2 + CO_2 + n/2\ H_2O$
$CO + H_2O$	→	$CO_2 + H_2$
$CH_n + H_2O$	→	$CO + (1 + n/2)\ H_2$

Co supported on TiO_2 is active for oxidations reactions and is stable at high temperature, but it has not been tested extensively as an alternative catalyst for particulate matter combustion. When fresh, the carrier is made up of two crystal structures: anatase and rutile. Catalytically, the anatase form is the most important in that it has the highest surface area (50-80 m^2/g) and is thermally stable up to about 500°C. The rutile structure has a low surface area (< 10 m^2/g), and it forms at about 550°C (1).

Installation of activated carbon layer in the cat-co chamber could help in promoting gas adsorption, especially when the engine just started (cold start). Employment of stainless steel wire mesh, as a carrier support is an advantage since it could adsorb high temperature, thus activating the catalysts to react. However, the role of Co, TiO_2 and activated carbon are not fully understood. Objective of this research is to report on the performance of Co/TiO_2 in reducing hazardous gases into less harmful ones, regarding its structure and properties.

MATERIALS AND METHODS

Catalyst preparation: 0.20 x 0.20 mm stainless steel wire mesh with 80.0 mm dia. was arranged linearly using a steel rod as its core as shown by Figure 1. The wire mesh then impregnated with 2M Co/4M TiO_2 solutions. The stainless steel wire mesh was dipped in the solution for 8 h. After the impregnation, the catalysts were dried at 120°C for 2 h before calcined at 500°C for 4 h. The process was repeated for three times to ensure the distribution of carrier solution evenly.

Cat-co engine testing: The catalysts performance testing was conducted using ICE 1.6 L, in-line 4-cylinder provided by Proton Berhad. The gas concentration was measured using gas analyzer (Kane-May Quintox). Experiment were carried out using few set of cat-co. Firstly, stainless steel wire mesh and activated carbon (AC), referred as CC1. Secondly, CC2 that was developed from standard stainless steel impregnated with TiO_2 with cobalt catalyst and AC. Thirdly, stainless steel doped with TiO_2 together with AC, indicated as CC3. Finally, CC4 was fitted with stainless steel doped with cobalt and AC. Both CC3 and CC4 were used to monitor the significant of TiO_2 and Co as catalysts.

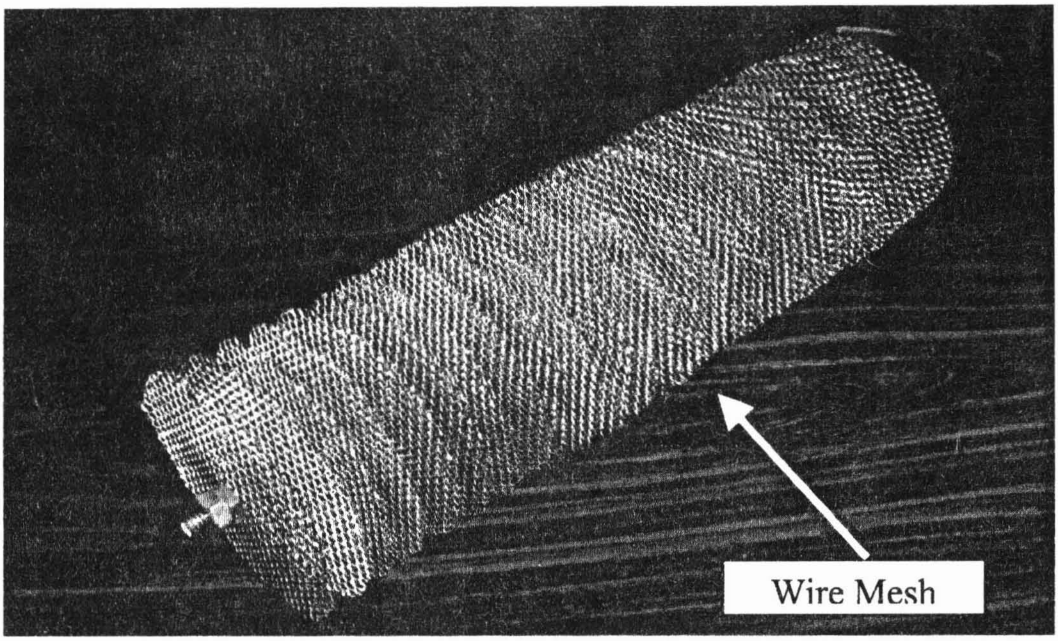

Figure 1. Arrangement of stainless steel wire mesh to develop cat-co design.

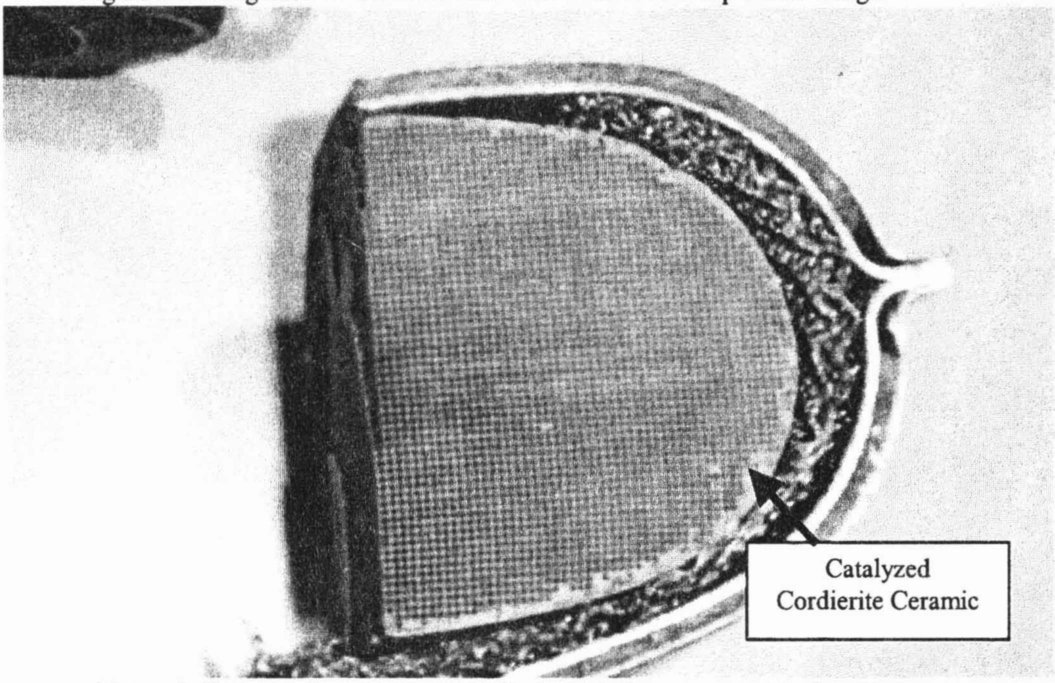

Figure 2. Cross-section of commercialized catalytic converter (standard).

RESULT AND DISCUSSION

The new design of cat-co in this study is totally different from the currently available cat-co. The design comprises of two major objectives which are retention time (t_R) of the gases in the cat-co i.e. reduction and oxidation of the gas and adsorption of the combustion emission gas by activated carbon before the catalyst being activated.

Figure 3 shows the results of CO_2 level for the different cat-co used in this work. It can be seen that the percentage of CO_2 level increased as compared to standard cat-co. The effect of AC and cobalt to CO_2 resulting the level of CO_2 increase to nearly 50 percent; which closed to the standard cat-co. From Figure 3, CC4 shows the main role of cobalt solely as oxidation agent when the results indicate the conversion of CO_2 level is 46.63 percent, compared to 76.21%, 61.41%, 63.39% and 44.14% for standard cat-co, CC1, CC2 and CC3 respectively. Combination of Co with TiO_2 in CC2 shows a better conversion when the CO_2 level increase to 83 percent compared with standard cat-co.

Reactivity of the catalysts also presented by O_2 level as shown by Figure 4. The figure shows the reduction of O_2 level due to the oxidation activities in the cat-co chamber. Oxygen present in the combustion chamber in excess in order to achieve nearly completes combustion of fuel and it is released through tailpipe as exhaust emission. High temperature generated by combustion process activates the catalysts to react. CO reacts with oxygen present in the exhaust emission to form CO_2. CC2 indicates 19.19% reduction, slightly different from standard cat-co, which have 19.96% reduction. While CC3 and CC4 show almost similar readings, varying from 9 percent to 16 percent respectively. Association of O_2 molecules with HC and CO resulted in increment of CO_2 level. The oxidation reaction, which promoted by Co, could be simplified by these equations:

$$4HC + 5O_2 \rightarrow 2H_2O + 4CO_2 \quad \text{eq. 1}$$
$$2CO + O_2 \rightarrow 2CO_2 \quad \text{eq. 2}$$

However, the reactions give maximum conversion of all components if it occurs near the stoichiometric of air to fuel ratio and at high temperature (3).

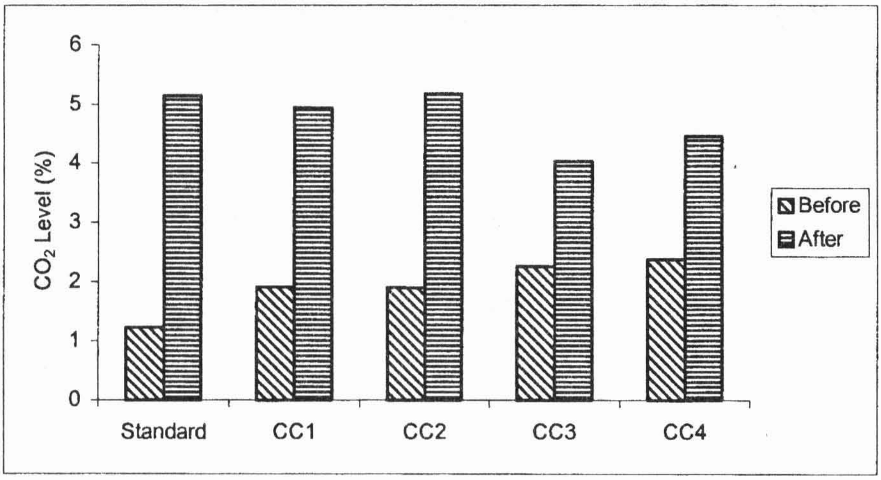

Figure 3. Comparison of CO_2 level between standard cat-co with various designs of catalysts.

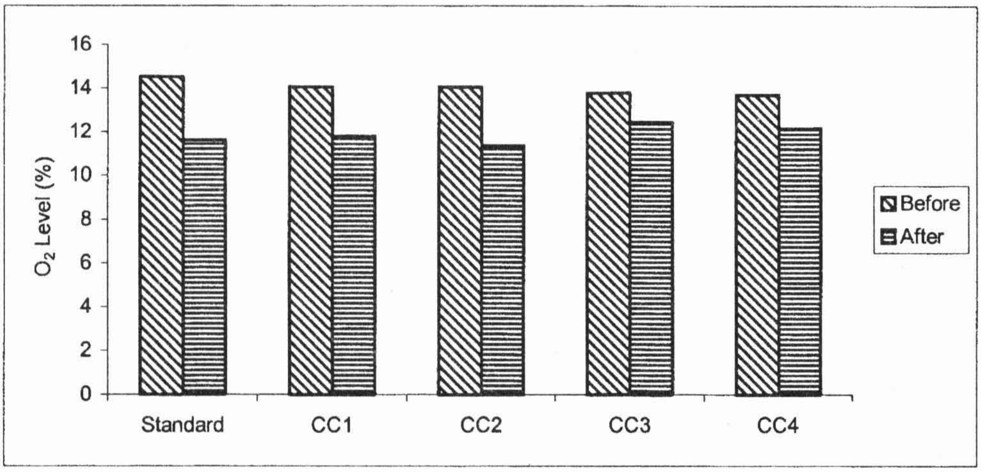

Figure 4. Comparison of O_2 level between standard cat-co with various designs of catalysts.

Effect of oxidation reaction also shows a reduction of CO level. Despite being oxidized to carbon dioxide (CO_2), CO also undergone a reduction reaction whereby CO dissociated with NO molecules and forms CO_2 and nitrogen gas.

$$2CO + 2NO \rightarrow N_2 + 2CO_2 \qquad \text{eq. 3}$$

TiO_2 plays an important role as a reduction agent in this reaction. However, the effective role of TiO_2 in this research is not fully understood since the reduction of CO is too low compared with 68.83% reduction by the standard cat-co. As shown by Figure 5, CC2 reduction is 25.44% followed by CC1, CC4 and CC3, with 14.98%, 10.08% and 7.36% reduction respectively. The low conversion of CO in reduction reaction probably due to the distribution of TiO_2 on the wire mesh. Uniformity of washcoat on the support material is important since it provides place for Co attachment. The distribution of TiO_2 will determine the surface area available for catalytic reaction, thus effecting the redox reaction and efficiency of cat-co.

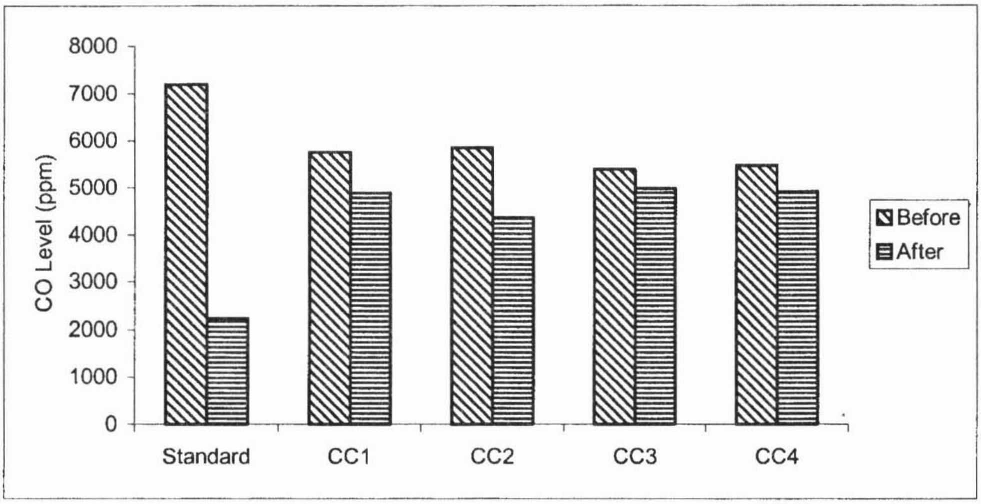

Figure 5. Comparison of CO level between standard cat-co with various designs of catalysts.

Reaction of NO and NOx with CO and hydrocarbon as well as H_2 in this study however is not fully understood. The conversion of these gases is slightly lower compared to the standard cat-co. Based on Figure 6, standard cat-co shows 73.62% reduction while CC1 indicates only 12.90% conversion. The maximum reduction recorded was 23.00%, indicates by CC2. CC3 and CC4 only recorded 4.17% and 9.62% respectively. Although TiO_2 is the most preferred carrier in selective reduction of NO and NOx, but the effectiveness still depends on its surface area and inertness.

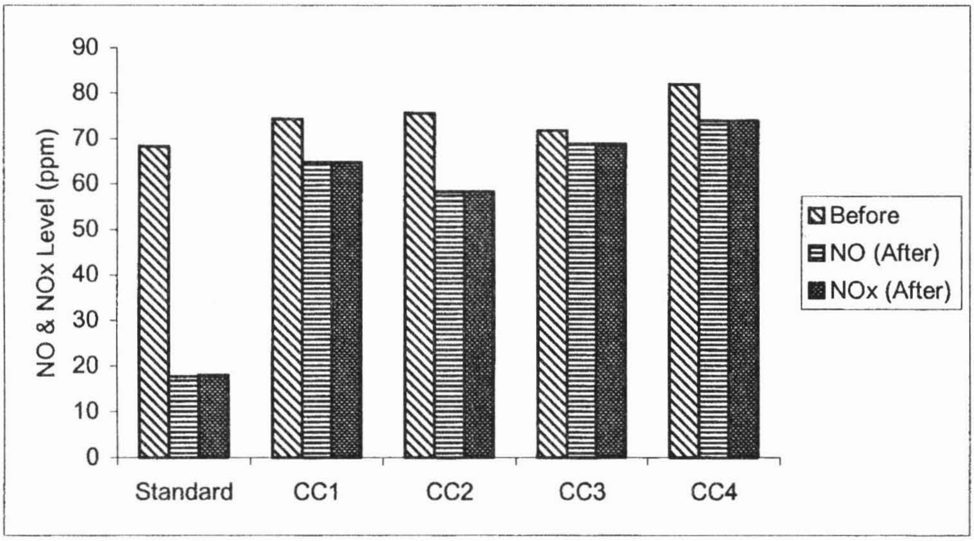

Figure 6. Comparison of NO and NO_x level between standard cat-co with various designs of catalysts.

The low performance of the designed cat-co is due to lower external surface area, i.e. 208 inch square, while the area available for standard cat-co ranges between 300 to 400 square channels per square inch. Besides that, the insulated standard cat-co as shown by Figure 2 could reduce the heat loss, which is significant in catalytic reaction.

CONCLUSION

Results of the designed Co/TiO_2-based cat-co show a similar pattern as the standard cat-co. Co/TiO_2 has a potential to be used in cat-co to control automotive emission since its shows a good oxidation and reduction reaction. The reduction of carbon monoxide (CO) was obtained 25.44 % while the reduction of nitrogen compound (NO and NOx) was obtained 23.00 %. Further research should be carried out to analyze and characterize the surface of Co/TiO_2, increase the available catalytic reaction area and identification of suitable insulator.

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