

Development of Base Metal Catalyst and Its Compatibility Study for Motorcycle Applications

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ABSTRACT

We developed a copper catalyst using zero Platinum group metals (hereafter PGMs) to fit motorcycle specific emission gas environment. Though many research reports to develop catalyst without using PGMs that are precious and costly resources are available, no reports had proven Base Metal Catalyst development to meet actual emission regulation equivalent to PGM catalysts. Compared to conventional PGM catalysts, higher temperature is required to keep high catalytic conversion efficiency by utilizing properties of this Base Metal Catalyst. Thus, this Base Metal Catalyst is located in cross coupling position, though it is rare case in motorcycle. This catalyst location could cause negative impacts on engine knocking, engine performance and drivability. This time, to overcome such negative impacts we optimized whole exhaust system, including parts around catalyst. In this paper, we report our vehicle development with Base Metal Catalyst to fit current emission regulation, while meeting required features for real vehicle, including vehicle appearance, and noise regulation.

CITATION: Ueno, K., Horimura, H., Iwasa, A., Kurasawa, Y. et al., "Development of Base Metal Catalyst and Its Compatibility Study for Motorcycle Applications," *SAE Int. J. Engines* 9(4):2016, doi:10.4271/2016-32-0071.

INTRODUCTION

Motorcycles are one of the major modes of transportation globally, and further expansion of motorcycle demand and usage is expected to continue because of population growth and individual income increase, in particular in developing countries. At the same time, challenges to environmental issues, such as air pollution, are becoming more important. With this trend, emission regulations are getting more stringent globally for motorcycles as well. In accordance with this, the efforts to minimize the impact on air pollution become important to respond to social needs for environment conservation, while maintaining features of motorcycles, such as driving characteristics, convenience, and price attractiveness. In this paper, focusing on catalysts for purification of motorcycle exhaust gas that is one of the prevention devises from the air pollutions, we will describe the compatibility of newly developed Base Metal Catalyst in applications to motorcycles. Platinum Group Metals (hereafter PGMs), such as platinum, palladium and rhodium, are commonly used for automotive and motorcycle catalysts. Since PGMs are precious and costly resources, many research results have been reported on the developments of catalysts without using PGMs [1]. However, issues on emission performance, durability and anti-poisoning have not been solved yet. Therefore, using Base Metal Catalyst, any example of practical application that meets actual emission regulations has not been reported [1, 2]. In these circumstances, we investigated various issues including productivity in mass production and eventually completed the development of a

new copper based catalyst that satisfies specific requirements for motorcycle emissions and established a method to utilize this catalyst effectively for models in Indian market that is one of the biggest motorcycle markets. Consequently a motorcycle that meets emission regulations was successfully developed without sacrificing features as an attractive vehicle.

AIM OF DEVELOPMENT

Overview of Base Metal Catalyst

Currently, normal motorcycle catalysts use costly PGMs to meet the vehicle emission regulation. Base Metal Catalyst is a catalyst that does not contain PGMs, and many base metals have been studied in the past for automotive emission control, such as Cu, Co, Fe, Ni, and Mn, etc. The main concern for a Base Metal Catalyst in vehicle emission control has been that it is thermally less stable and prone to S poison. As more stable support materials and cleaner fuels become available, use of a Base Metal Catalyst for emission control should be revisited. In this work, Cu and Mn were selected as active ingredients for the high activity toward CO and hydrocarbon oxidation. A stabilized alumina (Al_2O_3) together with an appropriate amount of CeO_2 was used to support Cu and Mn. Preparation of the Base Metal Catalyst is similar to that of a PGM catalyst, and the active components, Cu and Mn, were highly dispersed on the supports which then were slurried, and was coated to a metal monolith.

Reaction of Base Metal Catalyst

In general, challenge of PGM catalyst is NOx reduction, and it is same as Base Metal Catalyst as well. Since Cu^{2+} does not have a function of NOx reduction, Cu^+ or Cu form is necessary for NOx reduction. Under oxygen atmosphere, Cu remains CuO form and does not change to Cu^+ form. Under atmosphere with very low-oxygen partial pressure, reduction reaction occurs (major example is $\text{CO} + 2\text{CuO} \rightarrow \text{CO}_2 + \text{Cu}_2\text{O}$) and Cu^{2+} changes to Cu^+ form. NOx reduction in exhaust gas proceeds, as follows: $2\text{NO} + \text{Cu}_2\text{O} \rightarrow \text{N}_2 + 2\text{CuO}$. During this reaction, Cu^+ form returns to Cu^{2+} . In this way the reaction Cu valences change [3, 4, 5]. Due to several reasons, feedback control of motorcycle is slightly rich side, so that this reductive reaction occurs and as a result, NOx is cleaned up.

Performance of Base Metal Catalyst

Figure 1 shows the results of Model Gas Reactor Light-off testing ($20^\circ\text{C}/\text{min}$) with $\text{A/F} = 14.5$. CO performance of Base Metal Catalyst showed the equivalent results with PGM catalyst. On the other hand, to achieve the equivalent results of HC and NO as well as CO, Base Metal Catalyst requires more than 400°C at least (e.g. 250°C higher than PGM catalyst case). NO conversion achieved 98%, while HC conversion rate was slow and achieved less than 90% at 500°C , though the reaction started with lower temperature. PGM catalyst starts reaction from around 200°C for all three elements (CO, HC, and NO), and Light-off of Base Metal Catalyst was inferior to PGM catalyst, except for CO.

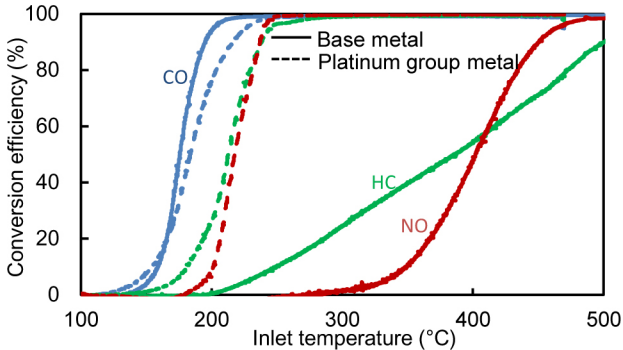


Figure 1. Light-off of Base Metal Catalyst and PGM catalyst in rich

Performance of Base Metal Catalyst

Figure 2 shows A/F characteristics at 350°C for Base Metal Catalyst and PGM catalyst with fresh condition. In general, Base Metal Catalyst own equivalent A/F characteristics with PGM catalyst, and this indicates that Base Metal Catalyst has a function as three way catalyst. Based on these results, we confirmed this Base Metal Catalyst can be applied for real vehicle as three-way catalyst though some of the characteristics are still inferior to PGM catalyst. To apply Base Metal Catalyst, further optimization is necessary, for example, usage condition such as temperature and location.

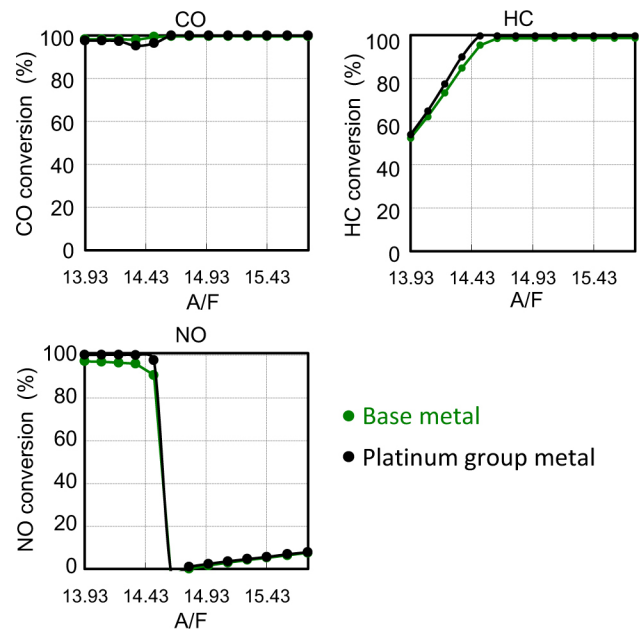


Figure 2. A/F characteristics of Base Metal Catalyst and PGM catalyst in fresh

CHALLENGE ITEMS FOR COMPATIBILITY STUDY

Selection for Target Region

There are 2 categories for motorcycles, 1) big displacement vehicles where main market is developed countries, and 2) commuters, that have relatively small size engine vehicle where main market is developing countries. From market size point of view, more than 95% of motorcycle sales are commuter segment. Recently, India market has become the largest motorcycle market, while China was the largest in the past, and we expect this trend will continue for the moment. We selected India market as our target since we can maximize our contribution for PGM resource saving by Base Metal Catalyst.

Compatibility for Indian Vehicle and Characteristics of India Emission Regulation

Since India customers have a strong request for fuel economy, air-fuel ratio of Indian motorcycles has set up lean condition. Needless to say, better fuel economy contributes to CO_2 emission reduction. Thus, we examined the light-off performance ($20^\circ\text{C}/\text{min}$) by Model Gas Reactor with lean condition ($\text{A/F} = 15.8$) as shown in Figure 3. In this lean condition, CO performance of Base Metal Catalyst was better than PGM catalyst. For HC conversion, we found Base Metal Catalyst achieved 98% at 300°C . Under lean condition Base Metal Catalyst showed equivalent performance with PGM catalyst for CO and HC when temperature increases. Based on these results, we concluded that Base Metal Catalyst can be applied for Indian market vehicles if we set up appropriate condition of Base Metal Catalyst to utilize its performance effectively. The target emission regulation in India is BSIII and BSIV. CO and HC+NOx are

control subjects for BS III, while CO, HC+NOx and NOx are control subjects for BS IV (BS IV will be applied for new model vehicles from April 2016, and for existing mode from April 2017). And BSIII includes durability degradation rule, while BSIV does not.

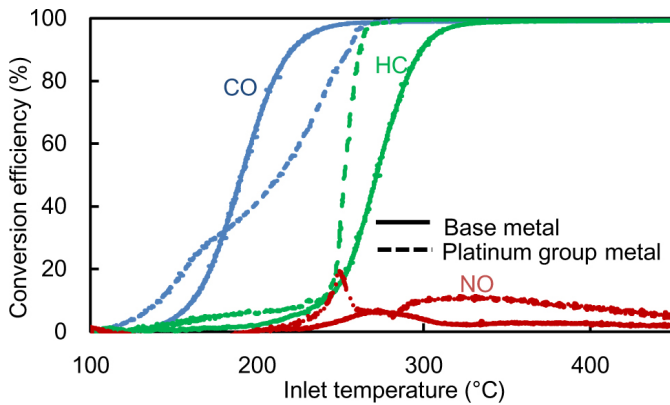


Figure 3. Light-off of Base Metal Catalyst and PGM catalyst in lean

Aging Impact on Base Metal Catalyst

Figure 4 shows the light-off results (T50, i.e. the temperature at which the conversion efficiency rate reaches 50%) for PGM catalyst and Base Metal Catalyst. In the figure, the graphs are shown only for CO and HC, as they have the values of T50 under lean burn conditions. At fresh CO performance of Base Metal Catalyst was same or better than PGM catalyst, while HC performance of Base Metal Catalyst was slightly inferior to PGM catalyst. After 900°C aged (900°C x 4 h in Air), CO Light-off performance of Base Metal Catalyst was equivalent or better than PGM catalyst, while HC light-off performance was clearly inferior to PGM catalyst.

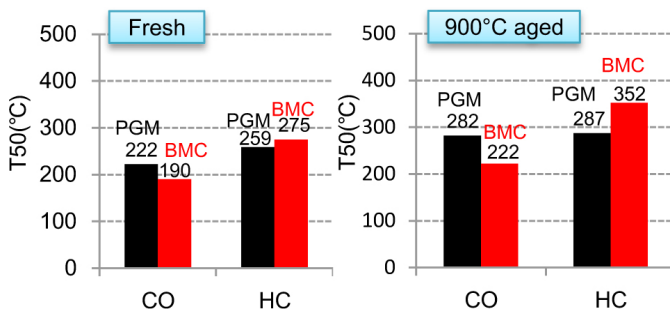


Figure 4. T50 of Base Metal Catalyst fresh and after aging

Figure 5 shows XRD (X-ray diffraction) pattern. At fresh, clear peaks of active ingredients Cu and Mn were not detected, and these are expected to exist as fine oxide. On the other hand, after 900°C and higher temperature aged, we found that activated species easily forms spinel complex oxide (CuAl_2O_4) with Al_2O_3 . Moreover, after 1100°C aged (1100°C x 4 h in Air), sharper peak was detected in XRD pattern and it indicates the grain growth, though there is no structural change in activated species. In addition, very minor $\alpha\text{-Al}_2\text{O}_3$ peak was detected.

Figure 6 shows EPMA (Electron Probe Micro Analyzer) image of Base Metal Catalyst layer section. In fresh, it can be confirmed that Cu and Mn are highly distributed in the layer. After 1100°C aged, though Cu is distributed in whole layer, Cu particles became bigger clearly, while Mn particles show similar distribution and size with fresh. Judging from XRD and EPMA, Base Metal Catalyst should not be used at 1100°C aged level.

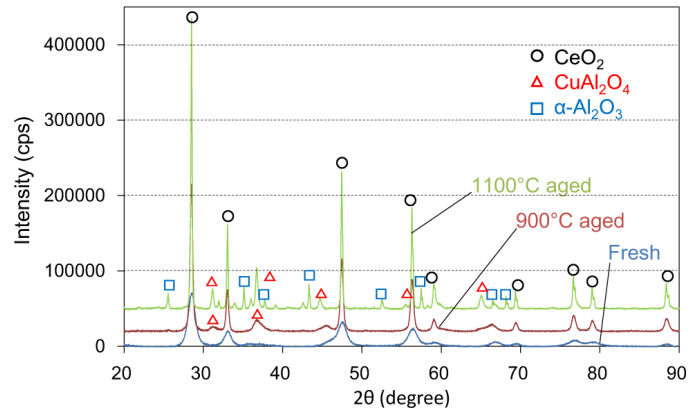


Figure 5. XRD pattern of Base Metal Catalyst-fresh and after aging

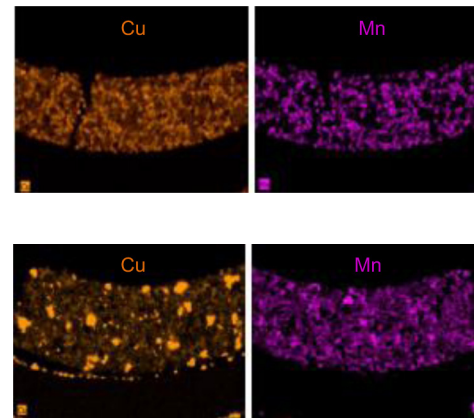


Figure 6. EPMA of Base Metal Catalyst at fresh and after aging

Influence of Poisoning

It is commonly known that the sulfur in gasoline poison cause PGM catalyst poisoning. We investigated the sulfur poisoning effect on emission performance of Base Metal Catalyst. As poisoning condition, Base Metal Catalyst was applied under N_2 atmosphere flow contains 5ppm SO_2 , 5% H_2O and 10% O_2 at 400°C for 4 hours. Figure 7 shows that the light-off performance results of the treated sample. As a result, sulfur poisoning negatively impacted on the performance both for PGM catalyst and Base Metal Catalyst. In this testing condition, the influence was equal or less compared to PGM catalyst, so that we concluded special measures against sulfur poisoning is not necessary.