

## ADDITIVE CATALYSTS FOR AN AUTOMOTIVE PHOTOCATALYST SYSTEM

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**ABSTRACT**—As a promising catalyst reducing cold start emissions of automobiles, a photocatalyst system has been studied. Since the photocatalyst is only activated by UV wavelength light, it needs no heat energy like a conventional TWC, therefore no light-off time. However, as a cold temperature catalyst to treat cold start emissions of a vehicle, previous studies on characteristics of photocatalyst have room for improvement in terms of performance and durability subject to aging conditions and exhaust gas conditions. In this study, additive catalysts for photocatalyst have been investigated from the viewpoints of performance and durability improvement. Eleven different coating samples were prepared with the combination of six kinds of additives and two kinds of photocatalyst materials. Then these samples were aged with a hydrothermal aging process. The performance of these samples was measured on a model gas apparatus with simulated exhaust gases. The durability was also analyzed with X-ray diffraction meter.

**KEY WORDS** : Photocatalyst, Cold Start Emission, Additive Catalysts, Conversion, Durability

### 1. INTRODUCTION

As emission regulations become more and more stringent, the needs for reducing cold start emissions are becoming increasingly important. The most promising technology being studied and applied today is the use of a warm-up converter using precious metal catalyst. Warm-up converter should be positioned close to the engine for fast light off.

The system is extremely efficient for reducing HC, CO and NO<sub>x</sub> after light-off. However, more than 80% of all emissions from a vehicle during the FTP75 (Federal Test Procedure) modes come out within the couple of minutes after starting the engine (Williamson *et al.*, 1999). The main reason is the inherent characteristics of precious metal catalysts that can only be activated at high temperature. Therefore, as long as a precious metal catalyst is used for the emission reduction, a certain length of time to elevate the temperature of a catalyst for proper reaction can not be avoided.

To overcome this shortage of a precious metal catalyst, lots of studies have been performed. As a result, a photocatalyst system was suggested to reduce cold start emissions (Son *et al.*, 1999a; Son *et al.*, 1999b). Photocatalyst could be activated under proper light condition as soon as the light is on. Therefore, it needs no time to activate. Photocatalyst has been studied to purify wastewater and

VOC (Volatile Organic Compounds) in atmosphere in industrial applications. As a light source UV (Ultra Violet) lamp or sunlight was used to supply proper wavelengths in those systems (Martin *et al.*, 1996). However a UV lamp has some disadvantage in maintenance due to its short lifetime. To be applied on a vehicle system, it should meet 120,000 miles of durability requirement and needs little maintenance under hydrothermal and poisoning conditions. Even though sunlight is very cost effective, UV in sunlight is too weak to apply to the systems of high concentration gases and high gas flow. The photocatalyst system suggested in this study is composed of a warm-up converter, a photocatalyst converter and a plasma system as a light source that penetrates cells of ceramic honeycomb (Son *et al.*, 1999a). In the system, warm up converter plays a main role to reduce emission after its light-off while photocatalyst converter does a supplementary role only to reduce cold start emission for the first one or two minutes. The photocatalyst converter is located 2.5m downstream from engine to be protected from high temperature exposure. Even though this system needs to be improved a lot as a whole system, it shows a high possibility of reducing cold start emission.

In this study, additive catalysts for photocatalyst were investigated from the viewpoints of performance and durability improvement. Six different kinds of additives were coated on the two different kinds of photocatalyst. The additive catalysts were considered to improve surface area, electron mobility and adsorption capacity. The

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samples were aged with a hydrothermal aging process. The performance of these samples was measured on a model gas apparatus with simulated exhausted gases. The durability was also analyzed with XRD (X-Ray Diffraction Meter).

## 2. THEORETICAL BACKGROUND

As a photocatalyst, TiO<sub>2</sub> takes three crystal structures. The first one is rutile, which tends to be more stable at high temperature. The second one is anatase, which tends to be more stable at lower temperature. The third one is brookite, which is usually found only in the form of minerals. The anatase TiO<sub>2</sub> shows a higher photoactivity than other structures of TiO<sub>2</sub>. One of the reasons may be the differences in their band gap energy that is the minimum energy of light required to get the electrons excited enough to get out. For anatase TiO<sub>2</sub> this energy is 3.2 eV, which corresponds to that of UV light, while the energy for rutile type is 3.0 eV, corresponding to that of violet light. The VB (Valence Band) energies for anatase and rutile are both similar, which is very low in the energy diagram. For both structures, the VB holes have great oxidizing capability. The CB (Conduction Band) energy of anatase is higher than that of rutile. The CB energy level of anatase includes electrolytic reduction of molecular oxygen to superoxide as well as electric reducing water to hydrogen (Fujishima *et al.*, 1999a). This means that anatase structure is more active in breaking organic compounds.

The photocatalytic reaction starts with the exposure of TiO<sub>2</sub> to light. Equation (1) shows the reaction (Fujishima *et al.*, 1999b).



After exposure to light, two reaction starters are generated; one is electron ( $e^-$ ) and the other is positive electron hole ( $h^+$ ). One of the notable characteristics of TiO<sub>2</sub> is that the oxidizing power of the holes is greater than the reducing power of the excited electrons. If there is water in the gas stream like exhaust gas, the TiO<sub>2</sub> adsorbs the water on the surface. The electron holes oxidize the adsorbed water molecules and generate hydroxyl radicals, which have strong oxidation capacity. In this reaction, TiO<sub>2</sub> is regenerated to original form. This is represented in Figure 1 and Equation (2).



The hydroxyl radicals can then react with organic compounds like HCs in exhaust gas, initially producing free radicals that have one unpaired electron. Meanwhile, the electrons are used to reduce oxygen in the flow and form the superoxide radical anion. Because oxygen is

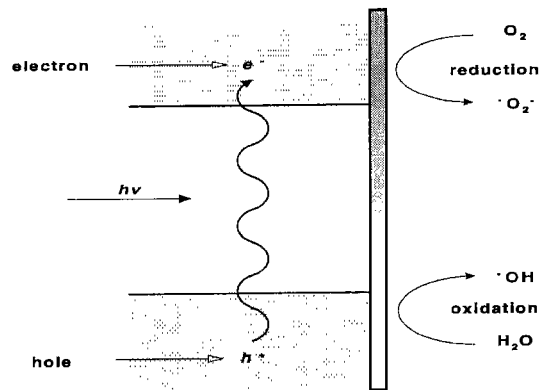


Figure 1. Reaction mechanism on TiO<sub>2</sub>.

easier to reduce than water, it will tend to be reduced, producing the superoxide radical anion. This is represented in Equation (3).



Oxygen that obtained electrons and hydrogen that lost electrons make hydrogen peroxide. The hydrogen peroxide reacts with adjacent electrons and ionized hydrogen and produces H<sub>2</sub>O<sub>2</sub>. The resulting unstable mid-products and products can decompose organic compounds to produce a carbon dioxide and water. This reaction mechanism occurs within a very short time period and makes a chain reaction in the gas stream. These reactions are illustrated in Equation (4)~(6).

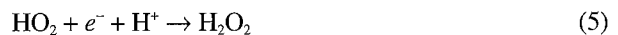


Table 1. Sample specifications.

Sample ID	Photocatalyst Material	Additive Catalyst
S1	P1	none
S2	P1	A1
S3	P1	A1 + A2
S4	P1	A1 + A3
S5	P1	A1 + A4
S6	P1	A1 + A5
S7	P1	A1 + A6
S8	P2	none
S9	P2	A1
S10	P2	A1 + A2
S11	P2	A1 + A6

### 3. THEORETICAL BACKGROUND

#### 3.1. Sample Preparation

Physical property of P1 sample was changed by changing law materials and named as P2. Based on these fundamental  $\text{TiO}_2$  catalysts, 6 kinds of additive catalyst were added to improve durability and performance. A1 additive catalyst was considered to increase active sites by offering large surface area. A2~A5 additive catalysts were considered to increase electron mobility in photocatalyst material (Harada and Naoi, 1996; Fu *et al.*, 1996). A6 additive catalyst was considered to increase surface adsorption of target gas components. A1~A5 additive catalysts were metal catalyst and A6 was molecular sieve material.

#### 3.2. Durability Test

Micro electric furnace was used to aging the samples. During the aging process, the air flow was provided that contained  $60^\circ\text{C}$  vapor pressure water. Flow rate of air was 2 L/min. Temperature was elevated with  $10^\circ\text{C}/\text{min}$  rates. The set value had  $100^\circ\text{C}$  intervals from ambient temperature to  $900^\circ\text{C}$  temperature. At the set value, temperature was retained for 4 hours and then decreased to ambient temperature with  $10^\circ\text{C}/\text{min}$  rates. After the aging, phase of samples was analyzed with XRD.

#### 3.3. Conversion Test

Figure 2 shows the diagram of a model gas test apparatus. To simulate exhaust gases of automobile, synthetic gases were supplied through a water bubbling system. Table 2 shows the simulated gases used in conversion test. The

balance gas was nitrogen and was controlled to meet 110,000 1/hr SV condition. The water bubbling system was set to temperature that can supply 10% water. The whole gas line was heated to prevent condensing vapor to water. The concentration of supplied gases was controlled with mass flow controllers that can control the gas concentration by 1 ppm. For the HCs, propane was supplied because propane is very difficult to be oxidized on the photocatalyst. Usually low carbon HCs show a little tendency to adsorb on the catalyst surface. The sample temperature was measured with a k-type thermocouple that was located at outlet of the sample. For the experimental convenience, a UV lamp that has the same wavelengths with the non-thermal plasma was used.

The propane concentration was analyzed with a GC (Gas Chromatography) equipped FID (Flame Ionization Detector). Table 3 shows operating conditions of the GC. Including gas concentrations and temperature, all test

Table 2. Supplied gases for model gas test.

Gas	Concentration
$\text{C}_3\text{H}_8$	500 ppm
CO	1%
NO	500 ppm
$\text{O}_2$	0.84, 2, 5, 10, 20.0%
$\text{H}_2\text{O}$	10%
$\text{N}_2$	Balance Gas
SV	110,000 1/hr

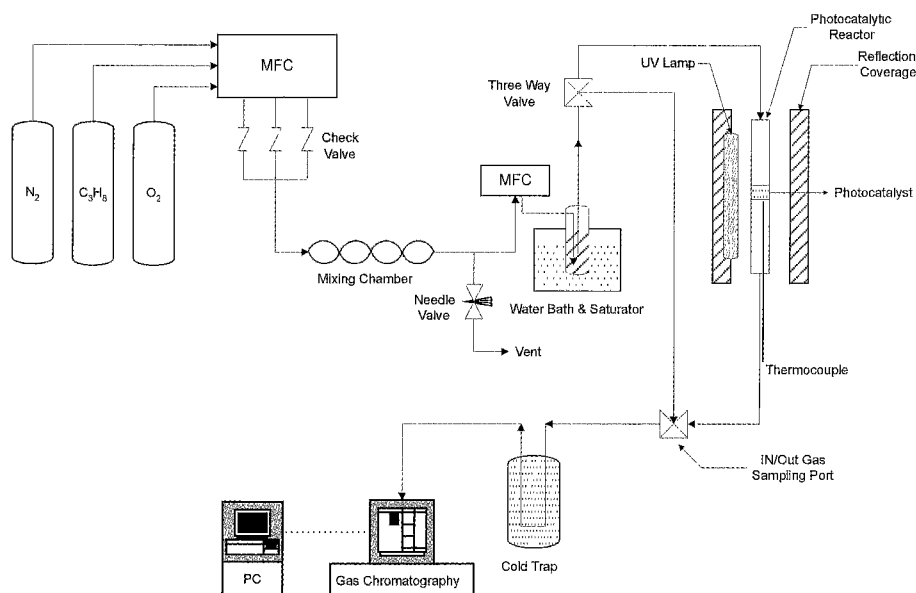


Figure 2. Schematic diagram of model gas test for photocatalytic oxidation to set value.

Table 3. Analysis conditions of GC.

Column	1/8" gamma alumina packed column
Detector Temp.	FID, 200°C
Injector Temp.	100°C
Oven Temp.	150°C isotherm
Carrier Gas	He, 30 cc/min
Sampling Part	6-port valve, interval 2 min

results were saved on a PC with a data logger.

## 4. RESULTS AND DISCUSSION

### 4.1. Hydrothermal Durability

Figure 3 shows XRD patterns of S1 sample according to hydrothermal aging temperatures. S1 sample that has no additive catalyst on P1 shows phase transformation from anatase to rutile at 600°C temperature. The anatase phase was totally transformed to rutile phase at over 700°C temperature. This means that performance capability of TiO<sub>2</sub> catalyst will be dropped by energy decreasing of photoreaction from 3.2 eV to 3.0 eV.

Figure 4 shows XRD patterns of S8 sample according to hydrothermal aging temperatures. S8 sample that has no additive catalyst on P2 shows no phase transformation from anatase to rutile until 900°C temperature. This means that P2 TiO<sub>2</sub> material is superior to P1 material in hydrothermal aging condition.

The summary of phase transformation tests of the samples was summarized in Table 4. Additive catalyst A1, added to increase surface area, shows positive effects on P1 material durability. Other additive catalysts except A2 additive show no effect on P1 material durability.

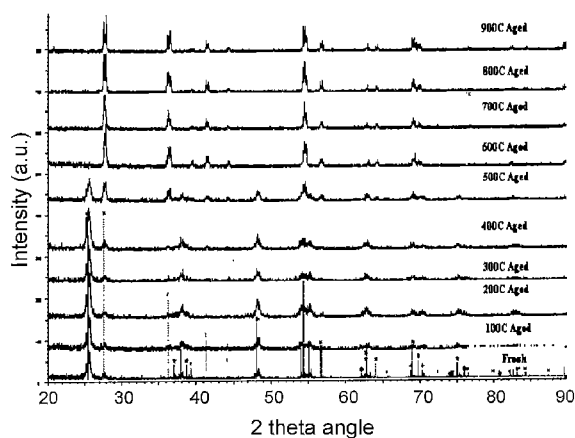


Figure 3. XRD patterns of S1 sample after hydrothermal aging for 4 hours.

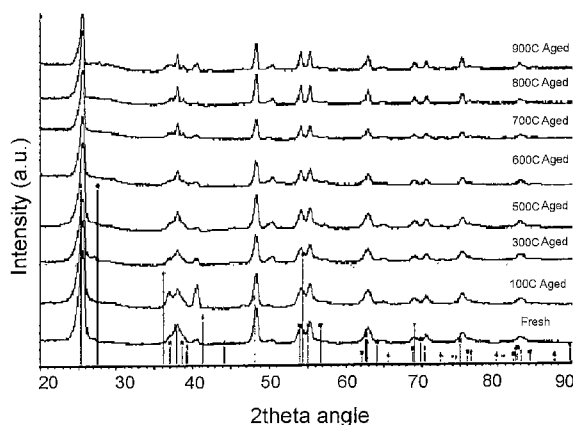


Figure 4. XRD patterns of S8 sample after hydrothermal aging for 4 hours.

Table 4. Summary of phase transformation temperatures of the samples after hydrothermal aging for 4 hours.

Sample ID	Photocat. Material	Additive Catalyst	Max. Temperature before Phase Transformation, °C
S1	P1	none	500
S2	P1	A1	700
S3	P1	A1 + A2	600
S4	P1	A1 + A3	700
S5	P1	A1 + A4	700
S6	P1	A1 + A5	700
S7	P1	A1 + A6	700
S8	P2	none	900
S9	P2	A1	800
S10	P2	A1 + A2	800
S11	P2	A1 + A6	800

Additive catalyst A2 shows negative effects on P1 material durability. In case of P2 TiO<sub>2</sub> material, A1 additive catalyst shows negative effects on hydrothermal durability. This means that additive catalysts have to be carefully chosen according to the characteristics of base material. The other additive catalysts show no effect on hydrothermal durability. It means that electron mobility is not an important factor for hydrothermal durability of photocatalyst P1 and P2.

### 4.2. Conversion Performance

Figure 5 shows propane conversion efficiency of S1 sample according to hydrothermal aging temperature. The sample was aged for 4 hours at each aging temperatures. For the experiment, only propane 500 ppm, and

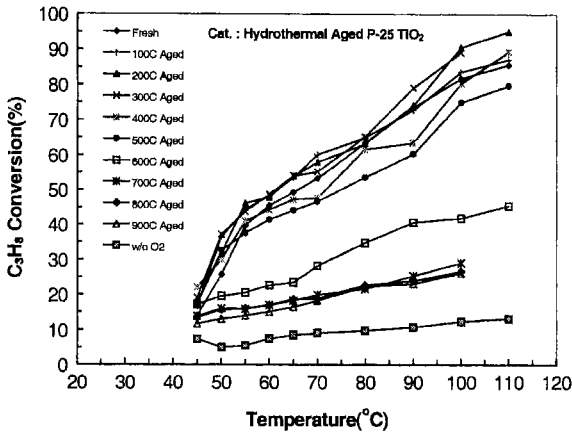


Figure 5. Propane conversion according to hydrothermal aging temperature of S1 sample.

oxygen 5% were supplied without other gases to check performance drop by phase transformation of TiO<sub>2</sub> material. As the aging temperature is increasing, the propane conversion is decreasing gradually by small gap to 500°C aging temperature, while the conversion efficiency drops rapidly at 600°C aging temperature. This coincides with the phase transformation result of Figure 3. At the temperatures over 700°C where only rutile phase exists, the conversion efficiency decreases to 25%. This means that rutile TiO<sub>2</sub> performance is about a quarter of anatase TiO<sub>2</sub>.

Figure 6 shows propane conversion of S2 sample according to oxygen concentration after hydrothermal aging at 900°C temperature. The gas compositions are illustrated in Table 2. As the oxygen concentration increases, the propane conversion is shown to be increasing. Even though it shows conversion increasing according to oxygen level, the conversion efficiency is

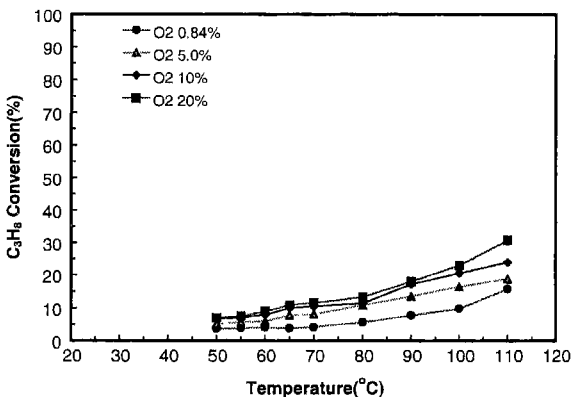


Figure 6. Propane conversion of S2 sample according to oxygen concentration after aging at 900°C hydrothermal aging.

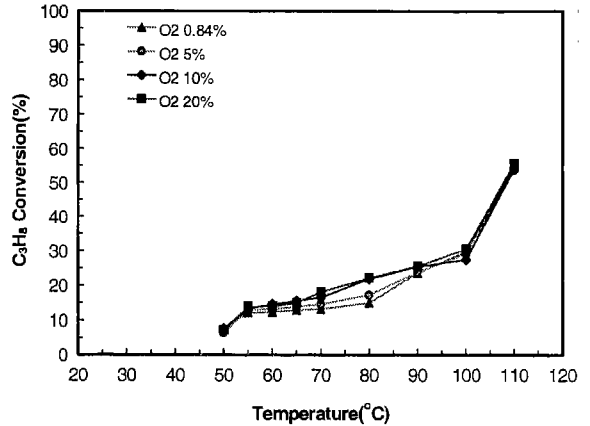


Figure 7. Propane conversion of S7 sample according to oxygen concentration after aging at 900°C hydrothermal aging.

too low to be applied to the vehicle aftertreatment system. Because the phase transformation, anatase to rutile of S2 sample is completed at 800°C aging temperature, the propane conversion is similar to that of 900°C aging results of S1 sample in Figure 5. This means that A1 additive catalyst does not play a role to increase propane conversion after 900°C hydrothermal aging even though it does play a role to retard phase transformation under hydrothermal aging.

Figure 7 shows propane conversion of S7 sample according to oxygen concentration after hydrothermal aging at 900°C temperature. The gas compositions are illustrated in Table 2. The conversion is independent of oxygen concentration, unlike S2 sample. The maximum conversion is much higher than that of S2 sample even

Table 5. Summary of conversion performances of the samples after hydrothermal aging for 4 hours.

Sample ID	Photocatalyst Material	Additive Catalyst	Conversion Efficiency at 110°C, %
S1	P1	none	31
S2	P1	A1	31
S3	P1	A1 + A2	22
S4	P1	A1 + A3	27
S5	P1	A1 + A4	21
S6	P1	A1 + A5	9
S7	P1	A1 + A6	62
S8	P2	none	25
S9	P2	A1	19
S10	P2	A1 + A2	39
S11	P2	A1 + A6	60

though it is aged at 900°C temperature. It may come from the characteristics of A6 additive catalyst that has much higher adsorption capacity. Because the photocatalyst reaction is a surface reaction, the more adsorption on catalyst surface means the higher conversion on catalysts.

Table 5 shows the summary of conversion tests at 110°C outlet temperature. P1 photocatalyst shows higher conversion than that of P2 photocatalyst though it shows poorer durability on hydrothermal aging. A1 additive catalyst has positive effects on only P1 material in durability and conversion performance. On the contrary, A1 additive catalyst has negative effects on P2 material in durability and conversion performance. Except A6 additive catalyst, the other additive catalysts (A2~A5) show negative effect on both P1 and P2 material in conversion performance. It means that the considered additive catalysts to increase electron mobility in photocatalyst material are not effective. Conversely, it seems to elevate recombination rate of electrons and positive holes. Only A6 additive catalyst shows positive effect on both P1 and P2 material in conversion performance. A6 additive catalyst (case of S7 and S11) increased the conversion efficiency about two times compared with P1 and P2 alone material (case of S1 and S8) even though it is aged at 900°C temperature. At this temperature, there is no anatase phase catalyst. If the catalyst is exposed to lower temperature shown in Table 4, anatase phase will still exist and the conversion performance will be much higher than that of Table 5, like the conversion of Figure 5. This means that if the photocatalyst system is located on the position where the maximum exhaust temperature does not exceed the temperature of Table 4, the conversion performance will be sufficient to reduce the cold start HC emissions and to meet emission regulations by complimenting the performance of warm-up converter.

## 5. CONCLUSIONS

Additive catalysts for an automobile photocatalyst system were investigated from the viewpoints of performance and durability improvement. Six kinds of additive were coated with two kinds of photocatalyst and the samples were aged with a hydrothermal aging process. The performance of these samples was measured on a model gas apparatus with simulated exhausted gases. The durability was also analyzed with XRD. Through these tests the following results are obtained;

(1) The maximum temperature of phase transformation from anatase to rutile can be improved by addition of appropriate additive catalysts. The most important factor to enhance hydrothermal durability is the surface area of additive catalyst. However, it is noted that the additive

catalyst has to be chosen to match with the characteristics of photocatalyst materials.

(2) Phase transformation from anatase to rutile means conversion efficiency drop by reducing band gap energy of TiO<sub>2</sub> material.

(3) Adding of appropriate additive catalysts can compensate the conversion drop due to phase transformation. In this study, the adsorption characteristic is found to be the most important factor to get higher conversion.

(4) If the photocatalyst system is used as a supplementary system for the conventional precious metal catalyst system to reduce cold start emissions, it shows the potential to clear more stringent emission regulations.

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