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# Catalytic Combustion of Diesel Soot over Perovskite-Type Catalyst: Potassium Titanates[1]

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**Abstract**—Potassium titanates with a high crystallinity were successfully prepared by the sol–gel method and characterized by XRD, SEM, and BET surface area measurements. $K_6Ti_4O_{11}$, $K_2Ti_2O_5$, $K_2Ti_4O_9$ were found to have better soot oxidation performance compared with $Pt/TiO_2$ and $CeO_2$ based catalysts. $K_2Ti_2O_5$ may be an excellent candidate for soot oxidation due to its high oxidation activity, water-stability, resistance to sulfur poisoning and economical advantages. Certain amount of $NO_x$ can contribute to the catalytic combustion of diesel over potassium titanates, implying that $K_2TiO_5$ may be a kind of catalyst for simultaneous removal of $NO_x$ and soot.

*Keywords*: potassium titanates, diesel soot, soot oxidation, $NO_x$

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## 1. INTRODUCTION

The emission of the various pollutants from the exhaust gases leads to a serous atmospheric pollution and climate change [1, 2]. Particulate matter (PM) and $NO_x$ are the main pollutants in diesel engine emissions. The increasing demand of the diesel engines in the heavy-duty engine sector will lead a large amount of soot particulate matter and $NO_x$ emission [3]. Increasingly stringent environmental legislations on the reduction of $NO_x$ and soot from the various sources of exhaust gases require the devices and technology that can abate these pollutants [4]. For the removal of $NO_x$ the selective catalytic reduction (SCR) and $NO_x$ storage—reduction (NSR) are currently the most favored technologies, while for the elimination of soot diesel, particulate filters (DPFs) are usually taken into consideration [5]. However direct oxidation of these soot particulates takes place at temperatures of 825–875 K, while the temperature of diesel exhaust is typically 450–675 K, and when the engine is fitted with non-catalytic traps frequent high temperature regeneration are required [6, 7]. These regenerations are usually inefficient and inconvenient. The high temperature regeneration of the uncatalyzed filter is generally carried out injecting a diesel fuel into the exhaust stream. This strategy leads to an uncontrolled exothermic heat release, which can destroy a filter. In this case, a catalyzed soot is the good way to decrease the soot burn-off temperature in a controlled fashion, and in tis way to increase the overall fuel efficiency of the diesel engine.

Pt-based catalyst is always designed as a multifunctional reactor that functions not only as $NO_2$ generator but also as soot filter [8]. However, precious metal catalysts are expensive, so that it is desirable to develop cheap and efficient candidate catalysts. So far, a large number of papers reported that perovskite-type oxides [9, 10], $CeO_2$ based oxides [11–13] and some other systems showed soot oxidation activities, but the oxidation temperature was not low enough for practical application. We recently synthesized a new type of potassium titanate catalysts as a promising substitute for Pt-based catalysts for NO oxidation, and these catalysts showed a higher activity for the NO oxidation to $NO_2$ and better resistance to the inhibitory effects of $NO_2$ and $SO_2$ [14–18]. However, the soot oxidation performances of potassium titanates have not been investigated in detail.

The goal of the current study is to systematically screen a series of new potential potassium titanates on their catalytic activity for soot oxidation by $O_2$. The tight contact between catalyst and soot was achieved by grinding in an agate mortar in order to define an intrinsic catalytic activity under optimal conditions. The loose contact was made shaking gently the reactor tube that contains the catalyst-soot mixture up and down for 20 s. The soot oxidation activities are correlated with the content of K and Ti in potassium titanates.

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[1] The article is published in the original.

## 2. EXPERIMENTAL

### 2.1. Catalyst Synthesis

Potassium titanates $K_6Ti_4O_{11}$, $K_2Ti_2O_5$, $K_2Ti_4O_9$ were prepared by sol-gel method. The starting materials were $KNO_3$ (Shinyo Pure Chemical Co., Ltd, purity 99.5%), $Ti(OC_2H_5)_4$ (Sigma-Aldrich, purity 99%) and citric acid anhydrous (Sigma-Aldrich, purity 99.5%). The citric acid anhydrous solution was prepared using ethylene glycol as solvent, and then the calculated amount of $Ti(OC_2H_5)_4$ was added to above citric acid anhydrous solution under stirring, and then $KNO_3$ in light excess dissolved in ethylene glycol was added to the above reacting mixture. The mole ratio of citric acid: total metal ions were controlled to be around 1.5 : 1. The competition between hydrolysis and the condensation reactions was controlled with an excess of distilled water and a desired volume of $NH_3$–$H_2O$, which sets PH of the reacting mixture to 6. Stirring at 40°C with the evaporation of water was used to secure the adherence of hydrolyzed and condensed alkoxide solution (“Sol”). The gel was then heated at 120–150°C for several hours to make a primary powder, which was calcined at desired temperature to obtain the powder with a final composition.

### 2.2. Catalyst Characterization

The BET specific surface areas were calculated from the adsorption isotherms of $N_2$ at 77 K by means of Micrometrics ASAP 2010 sorption analyzer. The samples were degassed at 300°C in vacuum for 5 h before adsorption measurements. X-ray diffraction patterns were obtained using an X-ray analyzer (XRD, M18XHF, Mac Science Co., Japan). Ni-filtered Cu$K_\alpha$ radiation ($\lambda = 0.15415$ nm) was used with an X-ray gun operated at 40 kV and 200 mA. The samples were scanned over the $2\theta = 10°–80°$ range of with a rate of 0.02° per step. The morphology of catalysts was investigated by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4200).

### 2.3. Soot Oxidation Activity Tests

Soot oxidation activity tests were performed in a flow-reactor, consisting of a packed-bed made of quartz tube (10 mm internal diameter). The reactor temperature was controlled by a proportional-integral-derivative (PID) temperature controller (Han Kook electronic Co.) and measured by a K-type thermocouple (0.5 mm outer diameter). The feed gas was composed of $NO_x$ and $O_2$ balanced with He. The $NO_x$ from the reactor outlet were continuously determined by means of an $NO_x$ analyzer (Chemiluminescence NO–$NO_2$–$NO_x$ analyzer, Model 42C, high level, Thermo Environmental Instruments Inc.), and the $CO_2$ concentration was analyzed by 41C High Level Gas Filter Correlation Analyzer (Thermo Environmental Instruments Inc.).

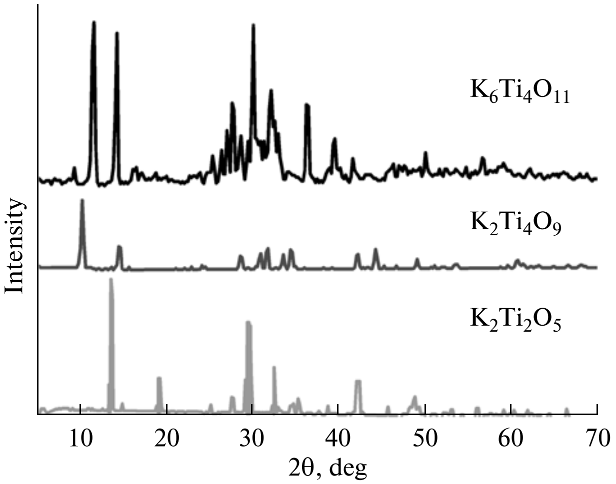

**Fig. 1.** XRD diffraction patterns of potassium titanates catalysts.

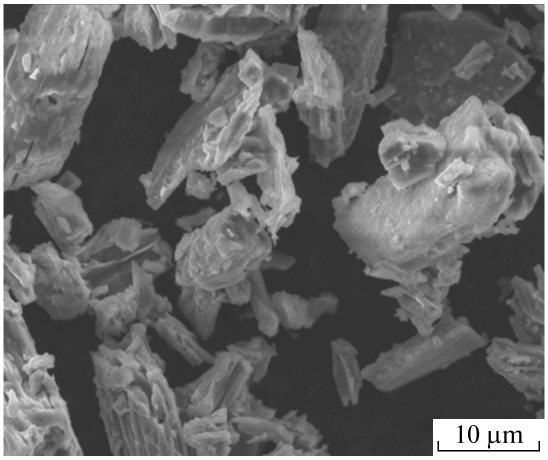

**Fig. 2.** SEM images of synthesized $K_2Ti_2O_5$.

## 3. RESULTS AND DISCUSSION

### 3.1. Catalyst Characterization

The X-ray diffraction patterns of potassium titanates catalysts are showed in Fig. 1. From the diffractograms it can be seen that all potassium titanates catalysts prepared are high crystalline materials and their characteristics are consistent with the reference data ($K_6Ti_4O_{11}$ PDF 41-0491, $K_2Ti_2O_5$ PDF 13-0448, $K_2Ti_4O_9$ PDF 32-0681).

SEM images of $K_2Ti_2O_5$ are shown in Fig. 2. It can be seen that $K_2Ti_2O_5$ sample is composed of irregular flat plate-like particles with the average particle size ranging from several-micrometers to several-tenths of the micrometer both in width and length.

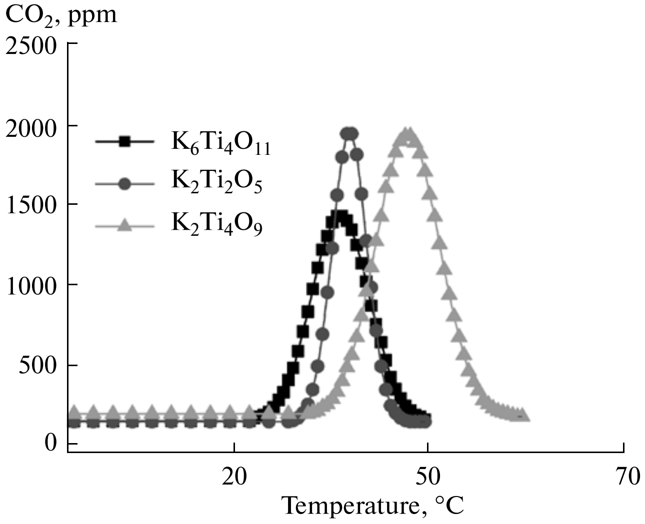

**Fig. 3.** Soot temperature programmed oxidation (TPO) with $O_2$ over selected catalysts. (Reaction conditions: 0.9 g of catalyst and 0.1 g soot mixture, total flow rate 100 mL/min, He balance, heating rate 2°/min).

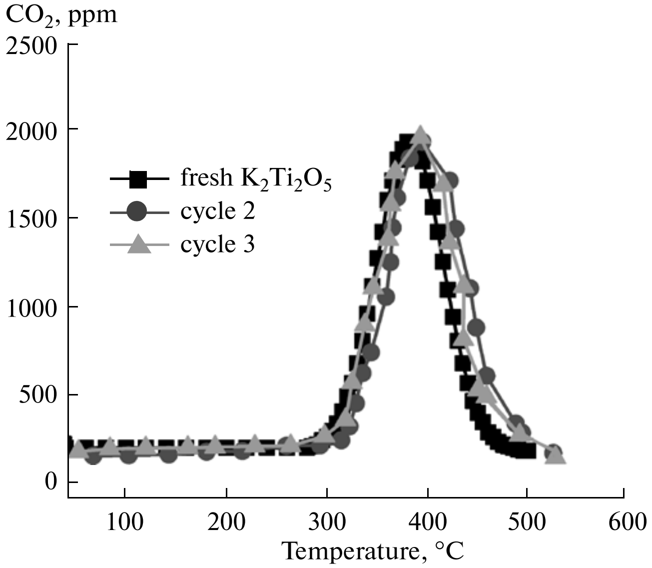

**Fig. 4.** Stability of $K_2Ti_2O_5$ in soot temperature programmed oxidation (TPO) with $O_2$. (Reaction conditions: 0.9 g of catalyst and 0.1 g soot mixture, total flow rate 100 mL/min, He balance, heating rate 2°/min).

### *3.2. Soot Oxidation Activity and Stability of Potassium Titanates with $O_2$*

The influence of the catalysts in loose contact mode is very limited and ambiguous due to uncertainties of catalyst soot mixing. The soot activity test of different catalyst, therefore, is studied in the tight contact mode. Figure 3 shows the results of the soot temperature programmed oxidation (TPO) activity test in $O_2$ for catalyst-soot mixtures in tight contact mode. The onset soot oxidation temperature $T_{10}$, temperature at soot conversion 10%, is 270, 295, 335°C for $K_6Ti_4O_{11}$, $K_2Ti_2O_5$, $K_2Ti_4O_9$, respectively. The temperature corresponding to the maximum reaction rate of soot oxidation ($T_p$) increases in the following order: $K_6Ti_4O_{11}$ (312°C) < $K_2Ti_2O_5$ (322°C) < $K_2Ti_4O_9$ (382°C). Among these catalysts, $K_6Ti_4O_{11}$ showed superior performance followed by $K_2Ti_2O_5$. The reason may be higher contents K and O in $K_6Ti_4O_{11}$.

In the present work, the stability of $K_2Ti_2O_5$ in the soot oxidation was also evaluated by comparing the performances of the fresh samples and used samples. When the temperature programmed oxidation test was finished the used catalyst was brought to test again in tight contact mode as shown in Fig. 4. For $K_2Ti_2O_5$ catalyst, no appreciable deactivation was observed, even after three cycles, thereby providing further evidence that this catalyst is highly stable.

### *3.3. Influence of K/Ti and O/Ti*

It is generally accepted that oxygen-containing species play a key role in the catalytic activity of alkali metal compounds during carbon gasification. All potassium titanates $K_6Ti_4O_{11}$, $K_2Ti_2O_5$, $K_2Ti_4O_9$ have good soot oxidation performance according to our present results. Figure 5 shows $T_p$ values as functions of K/Ti and O/Ti in potassium titanates. The soot oxidation peak temperature moves to lower temperature with increasing ratio of potassium to titanium (K/Ti). The ratio of oxygen to titanium (O/Ti) has also a positive impact on the soot oxidation performances of potassium titanates. It is widely accepted that K is the most active catalyst for soot oxidation, based on which many K-doped catalysts with high soot oxidation activities have been developed. Eleonora Aneggi and other authors [19] investigated the soot oxidation activity of $CeO_2$ with different amount of K, and stated that 10 wt %. K-doped $CeO_2$ shows the best performance. Moreover they indicated that the presence of potassium stabilizes the activity of the calcined $CeO_2$.

### *3.4. Effect of Contact Mode*

Loose contact conditions are better approximation of real operating conditions while the tight contact mode is helpful to get insight into the intrinsic characteristics of the catalysts. So the soot oxidation activities of both contact modes were chosen for comparison in Fig. 6. The onset soot oxidation temperatures $T_{10}$ (temperature at 10% soot conversion) in tight contact mode is similar to that in loose contact mode, while, the $T_{max}$ (temperature at maximum soot oxidation reaction rate) in loose contact is about 70°C higher than that in tight contact mode. In tight contact, the soot is thoroughly oxidized by $O_2$ in the temperature range from 260 to 380°C, and $T_{max}$ is located at about 340°C, indicating that the oxidation reaction rate was relatively high. In the case of loose contact, however, soot oxidation temperature range is from 260 to 468°C and $T_{max}$ is shifted to values around 390°C. The soot particles are well dispersed on the catalyst surface in tight contact, but in the case of loose contact, only small amount of soot was closely contacting the catalyst surface. Occurrence of the same soot on the catalyst surfaces can be the reason to the similarity of $T_{10}$ values whereas a different dispersion state of soot can account for considerable differences in $T_{max}$ for loose and tight contacts.

### *3.5. Soot Oxidation with $NO_x$*

The $NO_x$ can influence the soot oxidation activity of $K_2Ti_2O_5$ sincet $NO_x$ molecule is small enough to gain a free access to all the catalytic sites of potassium titanates. Figure 7 shows the soot oxidation activity with $NO_x + O_2$ observed under tight contact conditions. The results show that certain amount of $NO_x$ has a positive influence on the performance of $K_2Ti_2O_5$, which is consistent with the results reported for the $Fe_2O_3$ catalyst [20]. Both $T_{max}$ and $T_{10}$ move to high temperatures with decreasing $NO_x$ concentration. With the reaction mixture containing 1% $NO_2$ a value of $T_{max}$ is near 290°C, which is about 100°C lower than that found for the 10% $O_2$ mixture in the absence of $NO_2$. It appears that $K_2Ti_2O_5$ may be a kind of catalyst for simultaneous removal of $NO_x$ and soot. Conversely, the lower $NO_x$ concentration at 1000 ppm has a negative influence on the soot catalytic combustion performance of $K_2Ti_2O_5$ and NO has a greater impact than that of $NO_2$. The underline reason may be that $K_2Ti_2O_5$ can adsorb and storage NO, and further decrease the soot oxidation activity of $K_2Ti_2O_5$.

### *3.6. Influence of $O_2$ Concentration*

The effect of $O_2$ on the soot oxidation activity of $K_2Ti_2O_5$ is shown in Fig. 8. The results show that the $O_2$ concentration has only a moderate impact on $T_{10}$, and $T_{max}$ decreases with enhancing $O_2$ concentration, implying that the soot oxidation reaction is only controlled by thermodynamics.

### *3.7. Influence of $H_2O$ and NO*

In practice, certain amounts of $H_2O$ exist in the diesel engine emissions. It was therefore of interest to investigate the influence of $H_2O$ and NO on the soot oxidation activity. Figure 9 shows the effect of $H_2O$ + NO on the oxidation activity of $K_2Ti_2O_5$ at different $H_2O$ concentration and constant NO concentration. The results show that both the onset oxidation temperature $T_{10}$ and the soot oxidation peak temperature ($T_{max}$) are not influenced by the concentration of $H_2O$, implying that $K_2Ti_2O_5$ is a kind of water-stable soot oxidation catalyst.

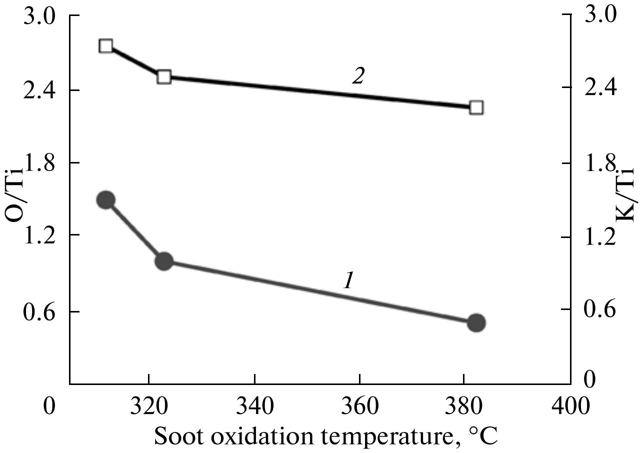

**Fig. 5.** Correlation between soot oxidation peak temperature and K/Ti, O/Ti.

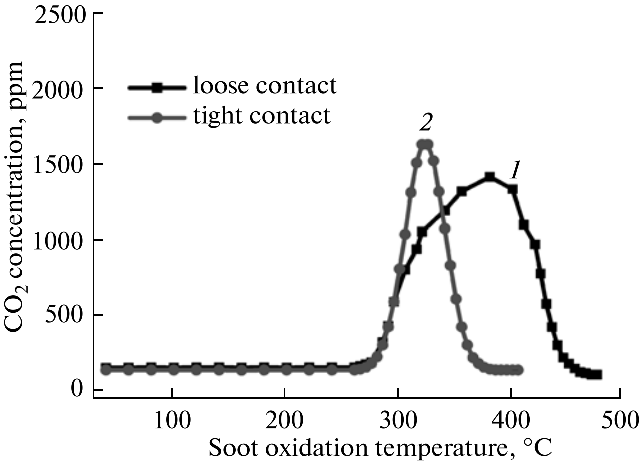

**Fig. 6.** Temperature programmed oxidation (TPO) of $K_2Ti_2O_5$ in loose and tight contact.

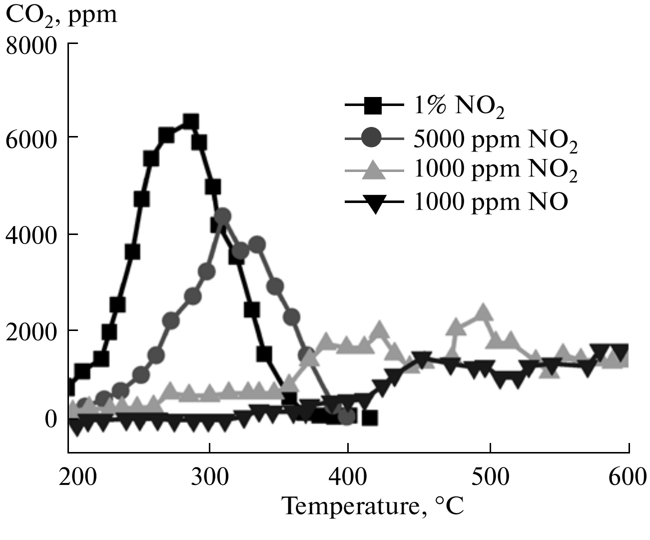

**Fig. 7.** Effect of $NO_x$ on temperature programmed oxidation (TPO) of $K_2Ti_2O_5$. (Reaction conditions: 0.9 g of catalyst and 0.1 g soot mixture, total flow rate 100 mL/min, He balance, heating rate 2°/min).

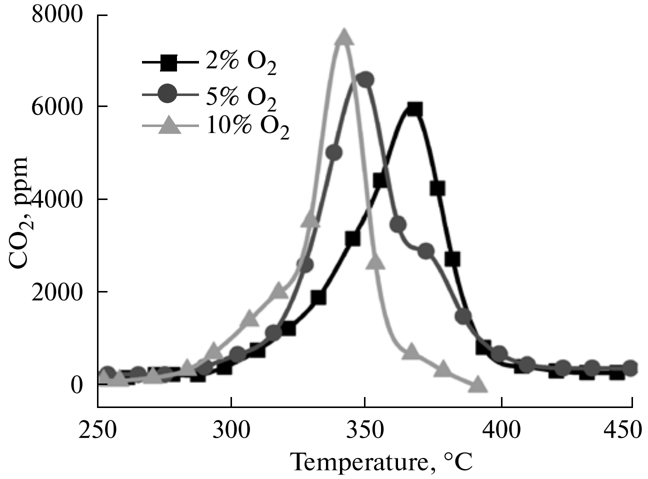

**Fig. 8.** Effect of $O_2$ on soot oxidation activity of $K_2Ti_2O_5$. (Reaction conditions: 0.9 g of catalyst and 0.1 g soot mixture, total flow rate 100 mL/min, He balance, heating rate 2°/min).

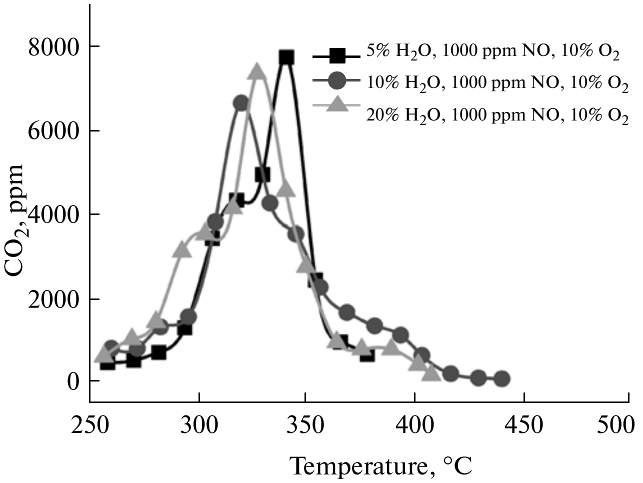

**Fig. 9.** Effect of $H_2O$ on soot oxidation activity of $K_2Ti_2O_5$. (Reaction conditions; 0.9 g of catalyst and 0.1 g soot mixture, total flow rate 100 mL/min, He balance, heating rate 2°/min).

## 4. CONCLUSIONS

Potassium titanates prepared by sol–gel method have better soot oxidation activity compared with Pt based catalysts, $CeO_2$ based catalysts, and perovskite. The order of increasing activity of potassium titanates in soot oxidation corresponds to the increasing K/Ti and O/Ti values: $K_6Ti_4O_{11} < K_2Ti_2O_5 < K_2Ti_4O_9$. Certain amount of $NO_x$ has a positive influence on the performance of potassium titanates, suggesting that $K_2Ti_2O_5$ may be a kind of catalyst for simultaneous removal of $NO_x$ and soot. The $O_2$ concentration has only a moderate impact on the soot oxidation activity of potassium titanates. $K_2Ti_2O_5$ is a kind of water-stable soot oxidation catalyst, since its activity is not affected by the presence of $H_2O$. With high oxidation activity, water-stability and economical advantages over Pt-based catalysts, $K_2Ti_2O_5$ may be an excellent candidate for removal soot from exhaust gases.

## ACKNOWLEDGMENTS

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