# K-supported catalysts for diesel soot combustion: Making a balance between activity and stability

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## ARTICLE INFO

## ABSTRACT

Two typical K-supported oxides ($K/Al_2O_3$ and $K/TiO_2$) were selected as catalysts for diesel soot combustion in order to evaluate the relationship between activity and stability. The surface species were first characterized by X-ray powder diffraction (XRD), X-ray absorption fine-structure (XAFS), infrared analysis (IR), X-ray photoelectron spectroscopy (XPS), in situ IR of $CO_2$ adsorption and temperature-programmed desorption of $CO_2$ ($CO_2$-TPD). Then the activity was studied by temperature-programmed oxidation (TPO), temperature-programmed reduction with soot (Soot-TPR) and in situ IR of soot combustion reactions. Lastly, the stability of the catalyst was checked by washing with water and analysis for K. This showed that $K/TiO_2$ displayed negligible activity due to the immobilization of K$^+$ ions in $TiO_2$ to form $K_2Ti_6O_{13}$. However, $K/Al_2O_3$ exhibited superior activity owing to the presence of active free K$^+$ ions on the surface. The downside is the leaching of K$^+$ ions into the effluent containing some water vapor, resulting in its poor stability – the other side of the coin for the highly active free K species. One of the suggested strategies for making a balance between activity and stability is encapsulating active K species in the channel of the catalyst as demonstrated by the tunneled cryptomelane.

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## 1. Introduction

Soot (black carbon) from diesel engines exerts harmful effects on the environment and human health [1–3]. In particular China has suffered severe haze problems (PM2.5) since 2013 [4]. Soot particulates from diesel engines are important sources of PM2.5. The use of a Diesel Particulate Filter (DPF) is the most effective control technology for diesel soot emissions [5]. However, DPFs must be regenerated by combustion of the accumulated soot [6], whereas catalytic technology is the most effective and economical technique [7]. Now the main objective is the development of highly active catalysts [8–11].

Catalysts containing potassium (K) have attracted increasing attentions owing to their high activity for soot combustion [12–18]. Many groups [19–23] have done pioneering and extensive studies for this kind of catalyst system, including evaluation and screening of various catalytic materials, the effects of the soot-catalyst contact and mobility of catalysts, as well as the influence of supports, etc. Generally, K is thought to act as a molten salt with the ability of improving catalyst (solid)-soot (solid) contact by increasing surface mobility. However the deactivation of this kind of catalysts is unavoidable resulting from the loss of K either by sublimation at high temperatures [24,25] or dissolution of the K$^+$ ions in the diesel exhaust, which typically contains water vapor [26]. Neyertz et al. clearly found that the $K/Ce_{0.65}Zr_{0.35}O_2$ catalysts were deactivated after the severe aging treatment due to K volatility [24]. An et al. also attributed the degradation of K-containing catalysts to the sublimation of K during the soot combustion process [25]. More importantly, it is known that diesel exhaust typically contains 5–7% water vapor at temperatures of 250–600 °C. Besides, condensed water is also present in the cases of cold start or long traffic-jam in winter [26]. Such K-containing catalysts can be readily degraded due to the leaching of active free K species [13,18]. Consequently great efforts have been made by many researchers to enhance the stability of K-containing catalysts. Incorporating K$^+$ ions into oxides has a great potential to effectively stabilize K$^+$ ions [27–29]. However, once K$^+$ ions were immobilized in the lattice of the oxides, lower activity and higher soot oxidation temperatures were observed [25,30].

Thus, we aimed at deeply studying the relationship between activity and stability for catalysts containing potassium. K-supported single oxides were chosen in this work. In order to

fabricate different kinds of K species with various mobility or stability, it is needed to choose supports with different acidity. By this way, various degrees of interaction between K and supports can be controlled, leading to the difference of the stability for these K-supported catalysts. From this point of view, two typical oxides, $Al_2O_3$ and $TiO_2$ were selected in consideration of their wide applications in acidic supports. It is well known that $TiO_2$ is more acidic than $Al_2O_3$. Higher stability for $K/TiO_2$ can be obtained than that for $K/Al_2O_3$, leading to their differences in activities for catalytic soot combustion. Based on these ideas, the existential states of K species on $K/Al_2O_3$ and $K/TiO_2$ were elucidated at first by conventional and especially state-of-the-art characterization techniques. Then, the active sites and their contributions to the catalytic activity, as well as the reaction mechanism for K-containing catalysts were clarified. It is found that activity and stability are two sides of the coin that need to be balanced. One promising strategy is finally suggested for K-containing catalysts, which is to encapsulate active K species in the channel of the catalyst, as demonstrated by the tunneled cryptomelane.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared by impregnating single oxides ($Al_2O_3$ and $TiO_2$) with an aqueous solution of $K_2CO_3$. $Al_2O_3$ and $TiO_2$ are supplied by Xinmeiyu Alumina Co., Ltd. of China and Sinopharm Chemical Reagent Co., Ltd. of China, respectively. Prior to the preparation, the oxides were heat-treated at 850 °C in air for 2 h. By characterization by XRD (Fig. 1), it can be seen that $Al_2O_3$ consists of $\xi$-$Al_2O_3$ and $\delta$-$Al_2O_3$. While for $TiO_2$, both anatase and rutile are present. Then suspensions of the oxides in aqueous solutions of potassium carbonate were evaporated while being stirred at 90 °C until a paste was achieved which was then dried at 120 °C overnight and calcined at 850 °C in air for 2 h. These prepared catalysts were designated as $K/Al_2O_3$ and $K/TiO_2$. According to our previous work [31], the theoretical weight loading amount of K is determined as 8 wt.%.

The as-prepared samples are also referred to as fresh catalysts and the weight loading amounts of K were measured by ICP and XRF, as listed in Table S1. It can be seen that almost all of the supported K can be maintained even after calcination at 850 °C. The fresh samples after washing by water were denoted as $K/Al_2O_3$-w and $K/TiO_2$-w, respectively, which were obtained by stirring the suspension of the fresh catalysts in deionized water at room temperature for 24 h, then filtering, drying at 120 °C overnight and calcination at 850 °C in air for 2 h.

### 2.2. Catalyst characterization

Powder X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-rc diffractometer.

Surface area and pore size distribution were determined by $N_2$ adsorption–desorption at 77 K using the BET method with a Micromeritics ASAP 2020 instrument after off gassing at 300 °C for 5 h prior to analysis.

X-ray absorption fine-structure (XAFS) measurements for the K K-edge were performed on the XAFS station of Beijing synchrotron radiation facility (BSRF, Beijing, China). K K-edge (3608 eV) data were collected at the 4B7A beam line of the spectra in the fluorescence mode with a Si (Li) detector.

IR experiments were carried out using a FTIR spectrometer (Bruker Tensor 27) over the range 400–4000 $cm^{-1}$ with 32 scans at a resolution of 4 $cm^{-1}$. The samples were diluted with KBr in a ratio of 1:100.



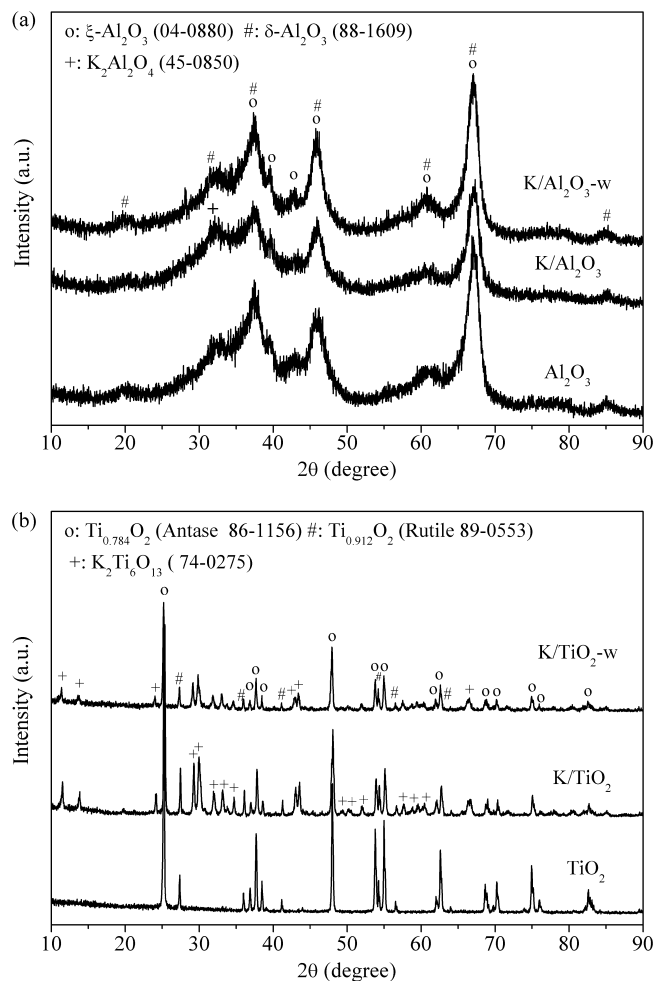**Fig. 1.** XRD patterns of supports, fresh catalysts and those after water-washing treatment: (a) $K/Al_2O_3$; (b) $K/TiO_2$.

X-ray photoelectron spectroscopy (XPS) data were obtained on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K$\alpha$ radiation (225 W, 15 mA and 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C 1s hydrocarbon peak at 284.80 eV.

X-ray fluorescence (XRF) experiments were performed on a ZSX Primus II instrument from Rigaku.

Inductively coupled plasma-atomic emission spectrometer (ICP-AES) experiments were carried out on an IRIS Intrepid IIXSP instrument from Thermo Elemental.

Temperature-programmed desorption of $CO_2$ ($CO_2$-TPD) experiments were carried out in a fixed bed micro-reactor consisting of a quartz tube (6 mm i.d.). A 50 mg catalyst was pretreated in He (100 mL/min) at 850 °C for 1 h and then cooled to 250 °C in He. When the temperature stabilized at 250 °C, 3976 ppm $CO_2$ in He (100 mL/min) was introduced. After saturation, the flow was switched to He (100 mL/min) to flush the sample to remove the weakly adsorbed species at 250 °C and then cooled to 150 °C. Desorption was then conducted by heating the catalyst from 150 to 850 °C at a temperature ramp of 10 °C/min in He (100 mL/min). The sample was held at 850 °C until the completion of $CO_2$ desorption. The desorbed $CO_2$ was detected by a quadruple mass spectrometer (MS, OminiStar 200, Balzers). The amount of $CO_2$ adsorbed at 250 °C was calculated by the integration of the $CO_2$ desorption peaks.