A nanorod-like KTi$_8$O$_{16}$ catalyst for soot combustion

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Abstract. A nanorod-like KTi$_8$O$_{16}$ catalyst was successfully prepared by combustion method and applied for removing hazardous diesel soot. The cryptomelane structure of KTi$_8$O$_{16}$ is confirmed by X-ray powder diffraction (XRD). The straight and smooth crystalline nanorods with the diameter of 180 nm are identified by transmission electron microscopy (TEM) and (200) facet is observed to be preferentially exposed. K cations are not freely present in cryptomelane structure of KTi$_8$O$_{16}$ derived from X-ray absorption fine-structure (XAFS) results, possibly due to the confinement or interaction of K with Ti element. By temperature-programmed oxidation (TPO) experiments, its catalytic soot combustion performance was evaluated, with $T_{10}$ and $T_{m}$ of 435°C and 511°C, which are decreased by 19°C and 45°C respectively compared with pure anatase TiO$_2$. K$^+$ species are deduced to serve as the active sites in the catalytic soot oxidation reaction, which are confined in the channels of the nanorod-like KTi$_8$O$_{16}$.

1. Introduction
Diesel soot posed detriment effects on environment and human bodies[1]. To remove this hazardous matter, catalytic combustion becomes one of the most efficient ways[2, 3]. The key issue is developing excellent catalyst to sharply decrease soot oxidation temperatures. Many kinds of catalytic components have been applied for this reaction, such as, transition metals, noble metals, alkali metals. Among these, alkali metals, especially K-containing catalysts displayed high soot combustion activity and thus raised increasing concerns in the recent studies.

Most reporters attributed the function of K to the improvement of contact efficiency between soot and catalyst owing to its low melting point, or to the enhanced redox properties of the transition metal components by oxygen vacancies induced by introduction of K. As a matter of fact, K was approved to be able to act as the independent active sites and exhibited outstanding activity for catalytic soot oxidation[4-6]. In view of this mechanistic point, the redox abilities of other components in the K-containing materials become no longer necessary for the superior catalytic soot combustion activity.

The layered K$_2$Ti$_2$O$_5$ has been reported for catalytic soot combustion[7]. Also, the irregular flat plate-like K$_2$Ti$_2$O$_5$, K$_2$Ti$_4$O$_9$ and K$_2$Ti$_6$O$_13$ have been applied for other oxidation reactions[8]. In order
to improve the water resistance stability, K$_{1.35}$Ti$_8$O$_{16}$ with quasi free K cations confined in hollandite-type tunnels has been reported for catalytic soot combustion in our previous work[6]. However, as the amount of K increased, enhanced soot combustion activity was observed[6], implying the excessive K possibly on the top site of the tunnel. As inspired by these, KTi$_8$O$_{16}$ with the least amount of K for the hollandite K$_y$Ti$_8$O$_{16}$ ($y=1.0$-$2.0$) was prepared by combustion method to ensure that K ions are exactly controlled in the tunnel as best as possible and thus mechanistic studies can be carried out. Moreover, considering the shape-dependent effects of the catalysts on their oxidation activities, the nanorod-like material may have advantages for holding up soot emitted from diesel exhaust. Thus, a nanorod-like KTi$_8$O$_{16}$ with the cryptomelane structure was prepared in this work. Much higher catalytic activity was obtained for soot combustion compared with pure TiO$_2$, attributing to the function of K$^+$ confined in the channels of KTi$_8$O$_{16}$.

2. Experimental

2.1. Catalyst Preparation

KTi$_8$O$_{16}$ was prepared by combustion method. TiO$_2$, KCl and NP-9 were mixed in an atomic ratio of 1:20:3 for 2 h and then calcined at 800°C for 20 h under air atmosphere. Then, the as-prepared product was dispersed in the distilled water to remove the impurity, then filtered and dried at 100°C to obtain the desired catalyst.

For comparison, anatase TiO$_2$ was synthesized by precipitation method. Typically, NH$_3$$\cdot$H$_2$O solution (25%) was dropped into a solution of Ti(SO$_4$)$_2$ under vigorous agitation until pH=10. The resultant precipitates were filtered and thoroughly washed with distilled water, then dried at 100°C overnight and calcined at 500°C for 5 h in air.

2.2. Catalyst Characterization

XRD patterns were recorded on a Rigaku D/max-rc diffractometer. TEM images with selected area electron diffraction (SAED) were obtained with a JEOL JEM-2010 microscope. XAFS experiments were performed by Beijing synchrotron radiation facility (BSRF) in China. Infrared spectrum (IR) was recorded by a FTIR spectrometer (Bruker Tensor 27) during 400-4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. The sample was diluted by KBr in a weight ratio of 1:100.

2.3. Activity Measurement

Temperature-programmed oxidation (TPO) experiments are performed on the fixed bed micro-reactor. Printex–U purchased from Degussa is selected as the model soot. The model soot was mixed with the catalyst in an agate mortar with a mass ratio of 1:9 for 0.5 h to realize a tight contact between them. The as-obtained mixture of 50 mg was pretreated at 200°C in He atmosphere (50 mL/min) for 1 h to eliminate the adsorbed species on the surface. After cooling to 50°C, a flow of 5 vol.% O$_2$ balanced with He (100 mL/min) was passed over and then the TPO reaction began at an increasing rate of 5°C/min. CO$_2$ and CO productions were obtained on-line by a gas chromatograph (SP–6890) produced by Shandong Lunan Ruihong Chemical Instrument Corporation in China. The gas chromatograph was fixed with a flame ionization detector (FID), which can detect methane converted from CO$_2$ and CO over a Ni catalyst at 360°C after separation of CO$_2$ and CO over a Porapak Q column. Three parameters were chosen from TPO results to evaluate the performance of catalysts: the temperature when 10% of soot can be burnt off ($T_{10}$), the temperature where the maximum soot combustion rate ($T_m$) was reached, the selectivity to CO$_2$ formation ($S_{CO2}$) which was defined as the amount of CO$_2$ divided by the total CO$_x$ (CO$_2$ and CO) amounts.

3. Results and Discussion

XRD patterns show that the as-prepared sample is indexed to the cryptomelane structure of KTi$_8$O$_{16}$ (JCPDS 41-1097) (Figure 1). Anatase TiO$_2$ was also successfully synthesized (Figure 1).
As shown in Figure 2a and Figure 2b, it can be observed that the as-prepared KTi₈O₁₆ involves the straight and smooth crystalline nanorods with the diameter of 180 nm, as well as some small particles. These nanorods are monocrytals deduced by SAED (Figure 2b). It can also be seen that these nanorods display lattice fringes with the interplaner spacing of 0.53 nm (Figure 2c), which can be ascribed to (200) facet of KTi₈O₁₆[9]. It is also consistent with XRD results after referring to the XRD standard cards (JCPDS 41-1097). Thus, it can be deduced that the (200) facet of KTi₈O₁₆ are preferentially exposed for the nanorod-like KTi₈O₁₆ catalyst.

Figure 1  XRD patterns of KTi₈O₁₆ and TiO₂

Figure 2  TEM images of KTi₈O₁₆: (a) low-resolution image; (b) representative image and SAED of a single nanorod; (c) high-resolution image
For KTi$_8$O$_{16}$ and TiO$_2$, the IR peaks in the region of 400-800 cm$^{-1}$ were attributed to the stretching vibrational mode of the Ti-O bonds\cite{10, 11} (Figure 3). For example, the peaks at 784, 605 and 497 cm$^{-1}$ are typical vibrations of octahedral TiO$_6$ skeleton in a cryptomelane structure. It is noticeable that the spectral features do not display a significant contribution from the K$^+$, suggesting the absence of surface K species. K ions were deduced to exist in the channels of KTi$_8$O$_{16}$.

The environment of Ti in KTi$_8$O$_{16}$ was detected by XAFS (Figure 4). Figure 4a and Figure 4b displayed the normalized absorption and Fourier transform spectra of Ti K-edge for KTi$_8$O$_{16}$ and TiO$_2$. For KTi$_8$O$_{16}$, different adsorption peaks from those of TiO$_2$ were observed (Figure 4a). For TiO$_2$, the first peak at 0.155 nm in the Fourier transform spectra can be assigned to Ti-O bond. The other two peaks at 0.254 and 0.303 nm are attributed to Ti-Ti bonds with the single and multiple scattering paths of Ti atoms, respectively (Figure 4b)\cite{12}. For KTi$_8$O$_{16}$, the peaks at 0.141, 0.244 and 0.385 nm can be ascribed to the Ti-O coordination shell, as well as the edge-shared and corner-shared Ti-Ti coordination shell in octahedral TiO$_6$. These results implied that interaction of K with Ti may exist, thus local conditions of Ti were influenced by the existent K species. Furthermore, it can be observed that normalized absorption of K K-edge for KTi$_8$O$_{16}$ are totally different from those of KCl, KOH and K$_2$CO$_3$ (Figure 5). It can be suggested that K cations are not freely present in the tunnel of cryptomelane, possibly due to the confinement or interaction of K with Ti.
Figure 5  Normalized absorption of K K-edge for KTi₈O₁₆ and standard samples

In order to evaluate the catalytic performance of the nanorod-like KTi₈O₁₆ catalyst, O₂-TPO experiments were performed, the results of which were displayed in Figure 6. KTi₈O₁₆ catalysts showed superior soot combustion activity, with $T_{10}$ and $T_m$ of 435°C and 511°C, which are decreased by 19°C and 45°C compared with pure TiO₂, respectively. The selectivity to CO₂ formation was also increased slightly from 75.4% to 78.9%. The enhancement of catalytic performance for KTi₈O₁₆ can be ascribed to the presence of active K⁺ species in the channels of the cryptomelane structure. Besides, it can be found that the nanorod-like KTi₈O₁₆ displayed considerable catalytic activity to K₁.₃₅Ti₈O₁₆ particles with higher K contents reported in our previous work[6], implying that the nanorod-like structure of KTi₈O₁₆ may increase the contact efficiency of soot and catalyst and thus leads to the further improvement of the catalytic performance for soot oxidation.

Figure 6  TPO patterns for KTi₈O₁₆, TiO₂ and uncatalyzed reaction

4. Conclusion

KTi₈O₁₆ catalyst was successfully synthesized by combustion method and characterized as nanorod-like material by TEM. Its unique structure leads to the superior catalytic soot combustion activity, with $T_{10}$ and $S_{CO_2}$ of 435°C and 78.9%, respectively. The confined K ions in the channels of KTi₈O₁₆ were deduced to serve as the active sites by comparing with TiO₂ possessing poor activity.
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