Promoted Soot Oxidation by Doped $K_2Ti_2O_5$ Catalysts and NO Oxidation Catalysts

Qiang Wang, Jong Shik Chung, and Zhanhu Guo

School of Environmental Science and Engineering, POSTECH, Pohang, 790-784, Republic of Korea
Department of Chemical Engineering, POSTECH, Pohang 790-784, Republic of Korea
Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, Texas 77710, United States

ABSTRACT: In the present work, the promotion effects by doping metals on $K_2Ti_2O_5$ or by combining an additional NO oxidation catalyst are studied in detail for soot oxidation. The synthesized catalysts are characterized by X-ray diffraction. The promoting effects of NO and NO$_2$ on soot oxidation were examined on both $K_2Ti_2O_5$ and metal-doped $K_2Ti_2O_5$ catalysts. With pure $K_2Ti_2O_5$ catalyst, NO has a negligible promotion effect, because of the fact that $K_2Ti_2O_5$, different from Pt catalysts, is unable to oxidize NO to NO$_2$. Compared to the pure $K_2Ti_2O_5$ catalyst, all the doped metals somehow enhance soot oxidation by decreasing the peak temperature ($T_p$). The activity follows the order of Pt/$K_2Ti_2O_5$ (324 °C) > Co/$K_2Ti_2O_5$ (331 °C) > Cu/$K_2Ti_2O_5$ (331 °C) > Ce/$K_2Ti_2O_5$ (335 °C) > $K_2Ti_2O_5$ (352 °C). With NO$_2$, soot starts to be oxidized at temperatures as low as 250 °C, even with pure $K_2Ti_2O_5$. When $K_2Ti_2O_5$ is combined with a NO oxidation catalyst (Co/$K_2Ti_2O_5$), both the starting temperature ($T_s$) and $T_p$ were greatly decreased, from 295 °C to 240 °C and from 352 °C to 326 °C, respectively. Therefore, the combination of $K_2Ti_2O_5$ with a NO oxidation catalyst can enhance the soot oxidation activity significantly.

1. INTRODUCTION

Because of their high efficiency, reliability, and durability, the sales of diesel-engine cars have been increasing significantly since the mid-1990s. The main pollutants emitted from diesel engines are nitrogen oxides (NO$_x$) and particulate matter (PM). Unfortunately, the PM in the nanoscale, which is classified as a carcinogen, can penetrate into the lung and cause severe bronchial troubles. As a result, the legislation levels of the emitted pollutants from diesel engines are becoming more and more stringent. However, these emission standards cannot be met anymore by only modifying the diesel engines and fuel additives. Thus, the development of after-treatment technologies to treat the diesel emissions is essential.

The most promising technique for the PM abatement is the diesel particulate filter trap (DPF). The PM compounds are first trapped on the filter and then are oxidized by O$_2$ or NO$_2$. In this system, some catalysts are highly required to reduce the soot ignition temperature. The critical issue of the DPF is the development of an effective and economical catalyst. Currently, most of the oxidation catalysts used in the international markets are noble-metal-based materials. Because of the high cost of noble metals, many attempts have been made to develop noble-metal-free catalysts. During the last decades, several types of noble-metal-free catalysts have been developed, including perovskite-type oxides (such as La$_{1-x}$K$_x$MO$_3$ (M = Fe, Co, Cu, or Mn)), spinel type oxides (such as Cu$_{1-x}$Fe$_x$O$_4$), alkaline or heavy-metal oxides (such as CuO, V$_2$O$_5$, and K/ CeO$_2$), and the mixtures of halides with vanadates or molybdates (such as Cs$_2$O·V$_2$O$_5$). In addition to the catalytic activity, several other characteristics such as thermal stability and sulfur poisoning have also been taken into account. Normally, the temperature of the emitted gases could be very high. The majority of the catalysts used in the real vehicles cannot survive the operating conditions and become sintered. In addition, the sulfur in the emitted gases can cause a permanent loss in activity by reacting with the active components.

It is widely accepted that potassium is the most active catalyst for soot oxidation, based on which many K-doped catalysts with high soot oxidation activities have been developed. However, the high mobility and low evaporation temperature of potassium limit their applications. To obtain an active soot oxidation catalyst with superior thermal stability, potassium-containing compounds can be one of the solutions. Okubo et al. have reported that potassium-enriched nepheline group materials exhibit excellent soot oxidation activity and have claimed that the highly improved oxidation activity is attributed to the K species that exist on the surface of nepheline group materials. Recently, we discovered that soot combustion could be catalyzed by several potassium titanate compounds including $K_2Ti_3O_8$, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$, which were prepared by solid-state reaction between $K_2CO_3$ and TiO$_2$ at temperatures of 850–1100 °C. $K_2Ti_3O_8$ is observed to possess the highest activity for soot combustion. It is well-known that platinum, cobalt, cerium, and copper are active catalysts for soot oxidation. Therefore, in order to further increase the soot oxidation activity of $K_2Ti_3O_8$, some metal catalysts including palladium, cobalt, or cerium were doped on $K_2Ti_3O_8$. The synergetic effects between $K_2Ti_3O_8$ and the supported metals for soot oxidation activities have not been reported yet.

Received: April 4, 2011
Accepted: May 18, 2011
Revised: May 14, 2011
Published: May 18, 2011
In the present work, the promotion effect of the doping metals such as copper, platinum, cerium, and cobalt on K₂Ti₂O₅ for soot combustion was investigated. Besides the direct promoted soot combustion by the doping metals, the indirect promotion by oxidizing NO to NO₂ by combining with one more NO oxidation catalyst, Co/K₂Ti₂O₅, was also investigated.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation and Characterization. K₂Ti₂O₅ was prepared from a stoichiometric amount of K₂CO₃ and TiO₂ precursors at 850 °C using a solid-state reaction method. Briefly, 6.91 g of K₂CO₃ (Yakuri Pure Chemical Co., Ltd.) was mixed with 7.99 g of TiO₂ (Hombikat UV 100) by ball milling for 24 h, followed by calcination at 850 °C for 10 h in air to obtain K₂Ti₂O₅.

K₂Ti₂O₅ catalysts doped with metals such as copper, platinum, cerium, or cobalt (denoted as M/K₂Ti₂O₅) are prepared following the same incipient wetness impregnation process. Cu(NO₃)₂·3H₂O, H₂PtCl₆·7H₂O, Ce(NO₃)₃·6H₂O, and Co(NO₃)₂·6H₂O are used as metal precursors. Copper, cerium, or cobalt (5 wt % for each), and 2 wt % Pt were loaded for the corresponding samples. The dried complexes were then calcinated at 850 °C for 5 h in air.

K₂Ti₂O₅ and metal-doped K₂Ti₂O₅ were analyzed by X-ray diffraction (M18XHF, Mac Science Co., Ltd., Yokohama, Japan) in order to assess their purity and crystalline structures. Nickel-filtered Cu Kα radiation (λ = 1.5415 Å) was used with an X-ray gun operated at 40 kV and 200 mA. Diffraction patterns were obtained within the range of 2θ = 10°–70° with a step size of 0.02°.

2.2. Catalytic Activity Test. Temperature-programmed oxidation (TPO) tests were carried out to evaluate the soot oxidation activities. Reaction tests were performed in a flow-reaction equipment, consisting of a packed bed made of quartz tubes (with an internal diameter of 2 mm). For a typical test, the gas flow rate was adjusted at 100 mL/min. The temperature ramping rate was 10 °C/min at 0–200 °C, and then 1 °C/min at 200–400 °C. The mixture of the catalyst (0.1 g) and the soot (0.01 g) was chosen to yield a space velocity of 40 000 h⁻¹. The contact between catalyst and soot was achieved by grinding in an agate mortar. The reactor was introduced into an electric furnace (Han Kook Electronic Co.). The outlet CO₂ concentration was recorded by a CO₂ analyzer (Chemiluminescence CO₂ analyzer, Model 41C, high level, Thermo Environmental Instruments, Inc.).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalysts Doped with Different Metals. Figure 1 shows the XRD profiles of the as-synthesized Pt/K₂Ti₂O₅, Cu/K₂Ti₂O₅, Ce/K₂Ti₂O₅, and Co/K₂Ti₂O₅. After comparing with the standard XRD patterns, the supported metals are in the forms of Pt, CuO, CeO₂, and Co₃O₄, respectively. The characteristic peaks of Pt are observed at 39.7°, 46.2°, and 67.5° 2θ (JCPDS Powder Diffraction File Card No. 04-0802), CuO at 35.3° and 38.5° (JCPDS Powder Diffraction File Card No. 44-0706), CeO₂ at 28.5° and 33.1° (JCPDS Powder Diffraction File Card No. 43-1002), and Co₃O₄ at 31.3°, 36.8°, and 65.2° (JCPDS Powder Diffraction File Card No. 43-1003), respectively. All the other peaks match well with those of the as-synthesized K₂Ti₂O₅. The inset shows the chemical structure of K₂Ti₂O₅, which possesses a special configuration of layered structure, in which K atom between the layers has an interesting asymmetrical linkage with eight oxygen anions.

3.2. Effects of NO and NO₂ on Soot Oxidation. It is well-known that NO and NO₂ are helpful for soot combustion, especially for Pt-based catalysts. In the presence of Pt, NO can be oxidized to NO₂, which is a more oxidative reagent than O₂. Therefore, both the effects of NO and NO₂ on soot oxidation were first investigated on K₂Ti₂O₅, and the results are shown in Figures 2 and 3. A negligible promotion effect is noticed when NO is added to O₂, indicating that K₂Ti₂O₅, different from Pt catalyst, is not able to oxidize NO to NO₂. With 5000 ppm of NO, the peak temperature is only decreased by 12 °C (see Figure 2). However, NO₂ is observed to be much more effective than O₂ for soot oxidation, as shown in Figure 3. With only 700 ppm NO₂, two CO₂ desorption peaks, located at 280 and 360 °C, were observed during the TPO measurements. By further increasing the concentration of NO₂ to 1200 ppm, the
intensity of the lower-temperature peak is increased, while that of the higher-temperature peak is weakened. Meanwhile, the temperature for the high-temperature peak shifts to a lower value. When the concentration of NO₂ reaches 2500 and 5000 ppm, the high-temperature peak completely disappeared. This result indicates that the low-temperature soot oxidation is attributed to NO₂, while the high-temperature soot oxidation is attributed to K₂Ti₂O₅. It is interesting to note that the soot can be easily oxidized in the presence of NO₂ at ∼1000 ppm and at temperatures as low as 300 °C.

3.3. Effects of the Doping Metals on Soot Oxidation. Figure 4 shows soot oxidation over K₂Ti₂O₅ catalysts doped with different metals. In the O₂ system, the doping metals (except platinum) are observed to have negligible promotion effects on soot oxidation. For Cu/K₂Ti₂O₅, Co/K₂Ti₂O₅, and Ce/K₂Ti₂O₅, both the starting temperature (Tₛ) and the peak temperature (Tₚ) remain the same as those of the pure K₂Ti₂O₅. However, for Pt/K₂Ti₂O₅, the Tₚ value (335 °C) is much lower than that of the pure K₂Ti₂O₅ (360 °C). The promotion effect of Pt/K₂Ti₂O₅ is mainly due to the high oxidative activity of the supported platinum metal, which has already been considered to be the best catalyst for soot oxidation.38,39

The practical vehicle emissions normally contain a certain amount of NOₓ (∼1000 ppm, over 80% is NO). According to recent investigations, the preoxidation of NO to NO₂ will greatly help soot oxidation and decreases the combustion temperature.34−36,40 The promotion effect by the doped metals in the NO (1000 ppm) and O₂ system was investigated. The results are shown in Figure 5. Compared to the pure K₂Ti₂O₅, all the catalysts doped with metals somehow enhance soot oxidation by decreasing the Tₚ value, and the activity follows the order of Pt/K₂Ti₂O₅ (324 °C) > Co/K₂Ti₂O₅ (331 °C) = Cu/K₂Ti₂O₅ (331 °C) > Ce/K₂Ti₂O₅ (335 °C) > K₂Ti₂O₅ (352 °C). However, similar to that in the O₂ system, Tₛ (ca. 300 °C) still remain very high, which is similar to that (300 °C) of K₂Ti₂O₅. This indicates that the supported metals on K₂Ti₂O₅ also have a poor NO oxidation activity in the low-temperature range. Based on this observation, we believe that the soot oxidation activity of K₂Ti₂O₅ should be increased by combination with an active NO oxidation catalyst.

3.4. Promotion Effect of the Addition of NO Oxidation Catalyst Co/K₂Ti₂O₅. Recently, we have reported a novel and highly efficient NO oxidation catalyst Co/K₂Ti₂O₅ which can convert over 80% of NO to NO₂ at ∼280 °C (see Figure 6). The existence of a maximum NO conversion is due to the thermo-dynamic equilibrium given in eq 1. Please note that, at temperatures of 250−300 °C, a larger amount of NO₂ can be achieved.
with a conversion rate of 25%–75%. The produced NO2 can directly oxidize soot to CO2 at this low-temperature range:

$$\text{NO}_2 \leftrightarrow \text{NO} + \frac{1}{2} \text{O}_2$$

Figure 7 shows the TPO results over the mixture of Co/ K2Ti2O5 and K2Ti2O5 (1:1 in weight ratio), and K2Ti2O5 alone catalysts with NO content of 1000 ppm in the flow gas. By combining a NO oxidation catalyst, both the $T_d$ and $T_p$ values were greatly decreased, from 295 °C to 240 °C and from 352 °C to 326 °C, respectively. It is worthwhile to notice that almost no CO2 was generated from the pure K2Ti2O5 catalyst at 300 °C; however, a significant amount of CO2 was produced by combining Co/K2Ti2O5 NO oxidation catalyst at the same temperature. It is easy to understand that the promoted soot oxidation activity is due to the produced NO2 by Co/K2Ti2O5.

4. CONCLUSIONS

Pure K2Ti2O5 catalysts and K2Ti2O5 catalysts doped with metals (M/K2Ti2O5, where M = Pt, Cu, Ce, and Co) were synthesized and characterized for soot combustion. XRD analysis indicated that the doped metals were in the forms of Pt, CuO, CeO2, and Co3O4, respectively. Both the effects of NO and NO2 on soot combustion were investigated over these catalysts. NO is observed to have limited effects on soot oxidation, even with the catalysts doped with metals. Only Pt/K2Ti2O5 catalysts decreased the $T_d$ value, by 25 °C, with a NO content of 1000 ppm. However, NO2 is observed to greatly enhance soot oxidation over both K2Ti2O5 and M/K2Ti2O5 catalysts. The effect of combining an additional NO oxidation catalyst (1:1 in weight ratio) was also studied, and it showed that the $T_p$ value was greatly decreased, to as low as 326 °C, arising from the NO2 that was produced by oxidizing NO over a Co/K2Ti2O5 catalyst.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail addresses: wang_qiang@ices.a-star.edu.sg (Q.W.), zhanhu.guo@lamar.edu (Z.G.).

Present Addresses
1) Institute of Chemical and Engineering Sciences, A*STAR, 1 Pesek Road, Jurong Island, 627833, Singapore.

REFERENCES

(2) Atria, I.; Such- Basañez, I.; Bueno-López, A.; García-García, A. Comparison of the catalytic activity of MO3 (M = Ti, Zr, Ce) for soot oxidation under $\text{NO}/\text{O}_2$. J. Catal. 2007, 250, 75.


