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Diesel soot oxidation catalyzed by Co-Ba-K catalysts: Evaluation of the performance of the catalysts

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ABSTRACT

The Co-Ba-K catalysts supported on alumina ceramic substrates were prepared. All the catalysts were characterized by X-ray diffraction and thermogravimetry/differential scanning calorimetry. The catalytic activities were evaluated by a soot oxidation reaction using the temperature-programmed reaction system. The catalytic activities of Co_3O_4, $Ba(NO_3)_2$, Co-Ba, and Co-Ba-K catalysts were studied, and the effect of the contact mode on the soot onset ignition temperature and soot oxidation rate was also discussed. The soot onset ignition temperature is 373 °C for Co-Ba catalysts with molar ratios of 1:2, 1:1 and 2:1, which is the same as that of pure Co_3O_4. The Co-Ba catalysts containing KNO_3 can greatly lower the soot onset ignition temperature value. The catalytic activity of pure Co_3O_4 and $Ba(NO_3)_2$ is affected by catalyst–soot contact intensity. The soot onset ignition temperature is not affected by contact intensity for the catalysts with proper Co-Ba-K ratios. The soot oxidation rate is greatly accelerated when the Co-Ba-K catalysts and soot are in the tight contact mode.

1. Introduction

Diesel engines are more popular due to the relatively high thermal efficiency and fuel economy versus that of gasoline engines. However, particulate matter and NO_x emissions are the main problems since very small particles carrying various suspectedly mutagenic hydrocarbons can penetrate deeply into the lungs. So diesel engine emissions are a source of environmental pollution and possible health risks. Present and near future environmental regulations concerning diesel fuels will focus on both fuel composition and emission control, the most plausible approach being after-treatment techniques like the combination of traps and oxidation catalysts to eliminate soot particles [1]. Since the temperature range of typical exhausts is 200–400 °C, a potentially useful catalyst has to operate efficiently in that temperature range and be thermally stable. A large number of catalysts have been studied for soot oxidation. Simple metal oxides (e.g., Co_3O_4, Cr_2O_3, CuO, Fe_2O_3, V_2O_5, MoO_3, and PbO) only operate satisfactorily at high temperatures (>500 °C) [2,3], but a combination of metal oxide and an alkali impregnated on different supports notably improves their performance [1,2–6]. Catalysts of supported KNO_3 are active for the combustion reaction of particulate matter [7]. As can be seen from all of the above, alkali-metal-doped catalysts have been studied widely, especially those containing potassium. There is still some research about potassium reported claiming the ability to improve the activity of catalysts for carbon oxidation [8–21]. The catalysts containing Co have been studied widely [1–3,5]. The catalytic activity is very slow when the alkaline earth metal oxide and soot are in loose contact condition. For example, T_{comb} is 599 °C when CaO and soot are loose contact condition [22]. The catalysts containing Ba can lower the soot ignition temperature 100–150 °C when the catalysts and soot are in tight contact condition [23]. Here, we explore Co-Ba and Co-Ba-K catalysts for soot oxidation. The effect of the catalyst–soot contact mode on catalytic activity is investigated in detail, and the probable catalytic mechanisms are discussed.

2. Experimental

2.1. Catalyst preparation

Analytical pure Co_3O_4, $Ba(NO_3)_2$, and KNO_3 were obtained as commercial products. The Co-Ba catalysts with $Co_3O_4/Ba(NO_3)_2$ molar ratios of 1:2, 1:1, and 2:1 and the Co-Ba-K catalysts with $Co_3O_4/Ba(NO_3)_2/KNO_3$ molar ratios of 0.5:0.25:2, 0.5:0.5:2, and 0.5:1:2 were prepared. The powders (about 200 mg) were mixed together by grinding in an agate mortar for 15 min at predetermined molar ratios. The fine powders were then mixed with a kind of organic binder solution by grinding to achieve a paintlike mixture. The porous α-alumina substrates (dimension

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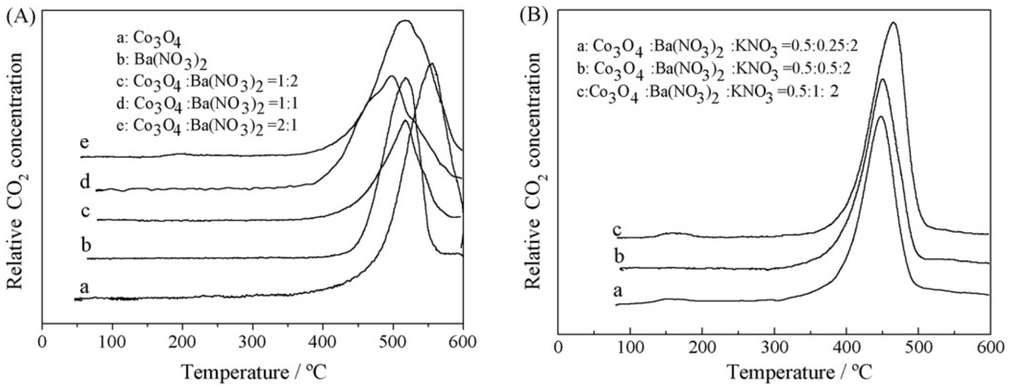

Fig. 1. TPR curves of (A) Co-Ba catalysts and (B) Co-Ba-K catalysts.

20 mm × 15 mm × 1 mm, porosity 25%) were impregnated with the paintlike mixture to get coating layers of the precursor chemicals and then dried in an oven at 50 °C for 10 h. After being dried, the mixture-coated substrates were calcined in a furnace at 600 °C for 3 h to obtain the catalyst-coated substrate.

2.2. *Catalytic oxidation activity characterization*

The temperature-programmed reaction (TPR) system [24] was used to characterize the catalytic activities of the prepared catalysts. Before TPR testing, the supported catalysts were fumed above the burning diesel oil to be coated with a layer of soot. During TPR testing, the CO_2-removed air was inlet into the furnace at a flow rate of 1 L/min with simultaneous detection of the CO_2 concentration in the outlet gas. T_o is defined as the soot onset ignition temperature, and T_p is the peak temperature of TPR or differential scanning calorimetry (DSC) curves. In addition, ΔT ($\Delta T = T_p - T_o$) was used to evaluate the reaction rate of soot. So T_o and ΔT were used to evaluate the catalytic activities of the catalysts for soot oxidation. During the TPR test, the tube furnace was heated from room temperature to 600 °C at a heating rate of 10 °C/min with the CO_2-removed air fed into the furnace at a flow rate of 1 L/min.

2.3. *Catalyst structure characterization*

The crystalline phase of the catalyst materials was identified by powder X-ray diffraction (XRD; Rigaku D/max-rA, Rigaku, Japan) equipped with a Cu Kα radiation source. The precursor chemicals were mixed together by grinding in an agate mortar for 15 min at predetermined molar ratios. The fine powders were then mixed with a kind of organic binder solution by grinding to achieve a paintlike mixture, then dried in an oven at 50 °C for 10 h and calcined in a furnace at 600 °C for 3 h. The obtained powders were used in the XRD experiment. Thermogravimetry/differential scanning calorimetry (TG-DSC; STA 449C, Netzsch, Germany) was used to study the soot onset ignition temperature (T_o) when the obtained catalysts and soot were in the tight contact mode. The preparation method of the catalysts used in the TG-DSC experiment was the same as that in the XRD experiment. The soot used in the TG-DSC experiment was collected using glassware above the burning diesel oil, which is the same method as that in the TPR experiment. For the sample used in the TG-DSC experiment, the catalysts and soot were mixed in a weight ratio of 3:1 and ground in an agate mortar to achieve a tight contact condition. The thermal analyses were carried out at a heating rate of 10 °C/min from room temperature to 650 °C in the air.

3. Results and discussion

The TPR curves of soot combustion in the CO_2-removed airflow for the catalysts supported on α-alumina substrates are plotted in Fig. 1. T_o, T_p, and ΔT are presented in Table 1.

As can be seen from Fig. 1A and Table 1, T_o is 370 °C for pure Co_3O_4, which is lower than $Ba(NO_3)_2$, whose T_o is 424 °C. But the soot oxidation rate based on $Ba(NO_3)_2$ is more rapid than that of Co_3O_4. ΔT is 184 and 94 °C for Co_3O_4 and $Ba(NO_3)_2$, respectively. T_o is 373 °C for the Co-Ba catalysts with molar ratios of 1:2, 1:1 and 2:1, and T_p for the Co-Ba catalyst with a molar ratio of 2:1 is almost the same as that of the Co-Ba catalyst with a molar ratio of 1:2. The T_p is 124 °C for Co-Ba catalyst with a molar ratio of 1:2, which is the lowest among the three Co-Ba catalysts. Fig. 1B shows the TPR curves of Co-Ba-K catalysts. T_o is 310 °C for the Co-Ba-K catalysts with molar ratios of 0.5:0.25:2 and 05:05:2, and ΔT is almost the same for above two catalysts. T_o is lowered 63 °C for the Co-Ba-K catalyst with a molar ratio of 0.5:0.25:2 versus that of the Co-Ba catalyst with a molar ratio of 2:1.

Fig. 2 shows the XRD patterns of the prepared catalysts. As can be seen from Fig. 2, the main crystalline phases are Co_3O_4 and $BaCoO_3$ for the Co-Ba catalysts with molar ratios of 1:1 and 2:1. It can be seen from Fig. 1A and Table 1, the T_o for above two Co-Ba catalysts is almost identical with pure Co_3O_4, but the ΔT is accelerated greatly at the cooperation of Co_3O_4 and $BaCoO_3$. As can be seen from Fig. 2, with the increase of Co_3O_4 content, the peak intensity of $BaCoO_3$ phase is weakened for the Co-Ba catalyst. It can be seen from Table 1, the ΔT for the Co-Ba catalysts with a molar ratio of 1:1 is more rapidly than the Co-Ba catalysts with a molar ratio of 2:1, which shows that the Co-Ba catalyst has the optimal catalytic activity when Co_3O_4 and $BaCoO_3$ phases have the appropriate ratios. The main crystalline phases are KNO_3, Co_3O_4 and Ba_3CoO_5 for the Co_3O_4-Ba-K catalyst with a molar ratio of 0.5:0.25:2. T_o is lowered greatly at the cooperation of the three phases than that of Co_3O_4

Table 1
The soot onset ignition temperature and Soot oxidation rate of catalysts on TPR curves

Catalyst	T_o (°C)	T_p (°C)	ΔT (°C)
Pure Co_3O_4	370	554	184
Pure $Ba(NO_3)_2$	424	518	94
Co_3O_4:Ba = 1:2	373	517	144
Co_3O_4:Ba = 1:1	373	497	124
Co_3O_4:Ba = 2:1	373	518	145
Co_3O_4:Ba:K = 0.5:0.25:2	310	447	137
Co_3O_4:Ba:K = 0.5:0.5:2	310	450	140
Co_3O_4:Ba:K = 0.5:1:2	352	467	114

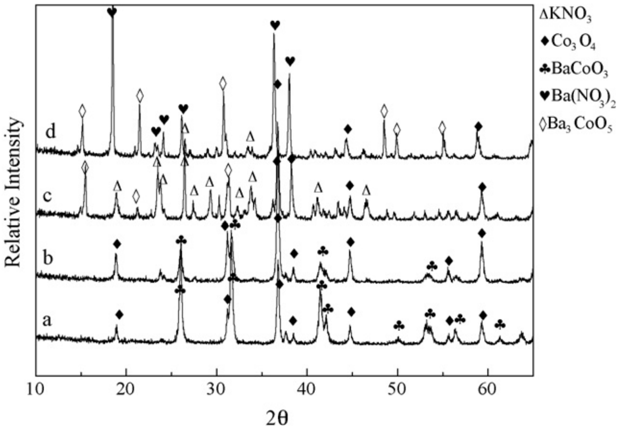

Fig. 2. XRD patterns of catalysts. (a) Co_3O_4:Ba = 1:1, (b) Co_3O_4:Ba = 2:1, (c) Co_3O_4:Ba:K = 0.5:0.25:2, and (d) Co_3O_4:Ba:K = 0.5:1:2.

and $BaCO_3$. However, the ΔT is slightly slower than the Co-Ba catalysts with molar ratios of 1:1. The introduction of KNO_3 evidently lowered the soot ignition temperature. Some research [13,16,17,25] shows the formation of low-temperature eutectics that melt at the operating temperature, which enables one to obtain a good contact between the active phase and the carbon particles. The drop of T_o cannot be attributed to the melting of KNO_3, as the melting temperature of KNO_3 is 330 °C, while T_o is 310 °C for the Co-Ba-K catalyst with a molar ratio of 0.5:0.25:2. T_o is above 350 °C on the action of a single KNO_3 phase, so the fall of T_o by the introduction of KNO_3 is not caused by a single KNO_3 phase but by the cooperation among KNO_3, Co_3O_4 and Ba_3CoO_5. The Co_3O_4-Ba-K catalyst with a molar ratio of 0.5:1:2 contains the KNO_3, Co_3O_4, Ba_3CoO_5 and $Ba(NO_3)_2$ phases. At the cooperation of the four phases, the T_o is 352 °C, and ΔT is 114 °C. The T_o is elevated and T_p is accelerated at above four phases than that of KNO_3, Co_3O_4 and Ba_3CoO_5, which illustrated further that the appearance of $Ba(NO_3)_2$ phases can accelerate the soot oxidation rate.

Fig. 3 shows the TG-DSC curves of prepared catalysts and soot mixtures in tight contact condition. The weight loss should be 25% on the TG curves for all the catalysts, as the catalysts and soot were mixed in a weight ratio of 3:1. However, the weight loss has a deviation of 25% more or less, as the amounts of the catalyst and soot used were only 6 and 2 mg, respectively, in the TG-DSC experiment. So the error was produced during weighing and grinding of the sample. The exothermic peaks are presented on DSC curves for all the catalysts in Fig. 3, which shows that the soot combustion belongs to an exothermic reaction. As can be seen from Fig. 3, T_o is only 343 °C on the TG-DSC curve, which is lowered 27 °C versus that on the TPR curve for pure Co_3O_4. There are two peaks on its DSC curve, which means that the soot oxidation reaction includes two steps for the pure Co_3O_4. The soot onset ignition temperature is lowered, and the soot oxidation rate is greatly accelerated for pure Co_3O_4 in the tight contact mode versus that for the loose contact mode. In other words, the catalytic activity of Co_3O_4 is affected by contact intensity between the soot and Co_3O_4. Co_3O_4 can provide active oxygen through redox, and bulk CoO is known to transform into Co_3O_4 upon heating in the air in the temperature range of 400–500 °C, and CoO has been observed to be mainly converted to Co_3O_4 by 450 °C on alumina [2,26,27]. So the catalytic mechanism of Co_3O_4 for soot oxidation should be as follows:

$$2Co_3O_4 + C \rightarrow 6CoO + CO_2$$

$$6CoO + O_2 \rightarrow 2Co_3O_4$$

The effect of contact intensity on the soot onset ignition temperature of $Ba(NO_3)_2$ is the same as that of Co_3O_4, as the T_o is lowered 46 °C on the TG-DSC curve versus that on the TPR curve for the pure $Ba(NO_3)_2$. As seen from Fig. 3, there are two peaks at 437 and 580 °C on the DSC curve of the $Ba(NO_3)_2$-soot mixture, so the soot oxidation reaction may be divided into two steps. In addition, the second loss weight step may still include the decom-

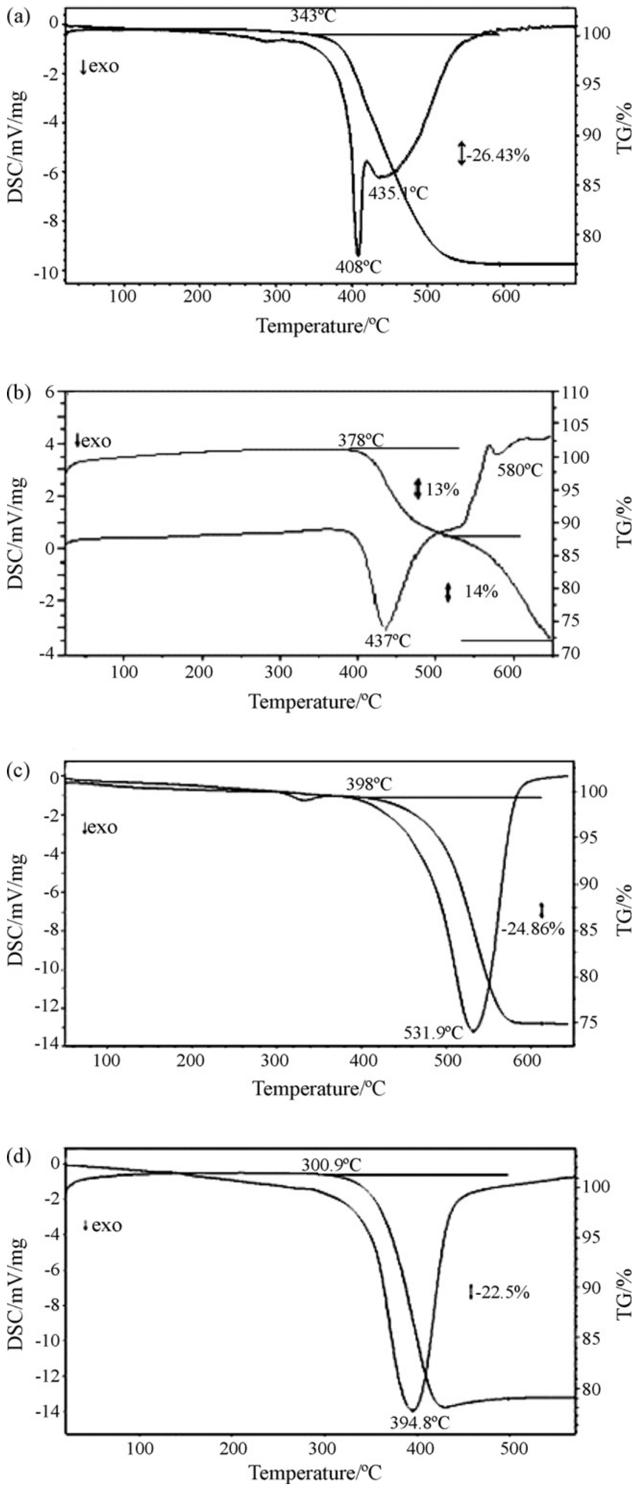

Fig. 3. TG-DSC curves of Co-Ba-K catalysts and soot mixtures. (a) Co_3O_4, (b) $Ba(NO_3)_2$, (c) Co:Ba = 1:1, and (d) Co:Ba:K = 0.5:0.25:2.

position of $Ba(NO_3)_2$, as $Ba(NO_3)_2$ can be decomposed at about 600 °C. It can be seen from Table 1, ΔT is 184 °C on the TPR curve and is only 65/92.1 °C on the TG-DSC curve for Co_3O_4, whereas ΔT is 94 °C on the TPR curve and is 59/202 °C on the TG-DSC curve for $Ba(NO_3)_2$. Thus, it can be concluded that the soot oxidation rate is less affected by contact intensity for $Ba(NO_3)_2$ than by Co_3O_4. It is obvious that only in the tight contact mode can the adsorbed oxygen atom and soot just react with catalysts. So the contact mode is an important parameter in the above mechanism. The T_o value on TG-DSC curve is high versus that on TPR curves for Co-Ba catalysts with a molar ratio of 1:1 and that on TG-DSC curve for pure $Ba(NO_3)_2$. It shows that the catalytic activity of Co_3O_4 and $BaCoO_3$ phases in tight contact condition is worse than in loose contact condition. The reason may be the catalytic activity of pure Co_3O_4 in tight contact condition is good, but the catalytic activity of $BaCoO_3$ is worse than Co_3O_4. It can be speculated that the influence of $BaCoO_3$ on the T_o in the tight contact mode is more serious than that in the loose contact mode, which leads the T_o to be higher at the cooperation of Co_3O_4 and $BaCoO_3$. T_o is 300.9 °C and ΔT is 93.9 °C on the TG-DSC curve which is lowered 9.1 °C and is accelerated 43.1 °C versus that on TPR curve for the Co-Ba-K catalyst with a molar ratio of 0.5:0.25:2. For the Co-Ba-K catalyst with a molar ratio of 0.5:0.25:2, T_o is little affected and Tp is greatly affected by contact intensity. Although the melting of KNO_3 can enhance the contact between catalysts and soot, this contact is different with the tight contact made in TG-DSC test. As the contact mode is a major problem, which inhibits its application in diesel exhaust treatment, the introduction of an appropriate $Ba(NO_3)_2$ ratio can reduce the impact of contact intensity on the soot oxidation rate for Co_3O_4. The T_o on the DSC curve is as much as that on the TPR curves, which means that contact intensity has little effect on the soot onset ignition temperature for the Co-Ba-K catalyst with a molar ratio of 0.5:0.25:2. Thus, it can be seen that the KNO_3 content has an important effect on the soot onset ignition temperature whether in the tight contact or loose contact mode. The melting temperature of KNO_3 is 330 °C, so the Co-Ba-K catalyst–soot contact intensity is greatly increased, which also improved the soot oxidation rate further above 330 °C. Querini et al. [3] explained that potassium played an important role in Co,K/MgO catalysts: (i) it increases the catalyst–soot contact by increasing surface mobility; (ii) it preserves the reducibility and dispersion of cobalt by improving stability against thermal treatments, and (iii) it favors the oxidation of soot by consuming the carbon to form carbonate species during soot combustion. In addition, Carrascull et al. [7] have explained that KNO_3 plays an important role during soot oxidation in KNO_3/ZrO_2 catalysts; on the one hand, the molten potassium nitrate makes it possible to obtain good contact between the catalyst and diesel soot; on the other hand, a probable mechanism is that one in which the nitrate is reduced to nitrite by reaction with carbon and the oxygen or the nitrogen oxide oxidize the nitrite again to nitrate.

$$2KNO_3 + C \rightarrow 2KNO_2 + CO_2$$

$$2KNO_2 + O_2 \rightarrow 2KNO_3$$

Our results are consistent with their studies.

4. Conclusions

The soot onset ignition temperature is 373 °C for Co-Ba catalysts with molar ratios of 1:2, 1:1, 2:1, which is the same as that of pure Co_3O_4. The introduction of KNO_3 into Co-Ba catalysts can greatly lower the soot onset ignition temperature. The catalytic activities of pure Co_3O_4 and $Ba(NO_3)_2$ are affected by the catalyst–soot contact intensity. The reason is that only in the tight contact mode can the adsorbed oxygen atom and soot just react with catalysts. The soot onset ignition temperature is not affected by contact intensity for the catalysts with a proper Co-Ba-K ratio, which shows that the cooperation of Co_3O_4, Ba_3CoO_5, $Ba(NO_3)_2$, and KNO_3 can lower the soot onset ignition temperature whether in the tight contact mode or in the loose contact mode. The soot oxidation rate is greatly accelerated when the Co-Ba-K catalysts and soot are in the tight contact mode. On the one hand, KNO_3 has a lower melting point (about 330 °C), and the Co-Ba-K catalyst–soot contact intensity is greatly increased above 330 °C; on the other hand, KNO_3 can improve the dispersion degree of Co_3O_4 and $Ba(NO_3)_2$, and the soot oxidation rate is greatly quickened. The introduction of KNO_3 is aimed at lowering the soot onset ignition temperature, but its melting point is very low, which results in the loss of activity. Co_3O_4, which is also a kind of oxidant, is added to moderate the loss of potassium and the effect of the catalyst–soot contact mode on catalytic activity.

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