Enhancement of Soot Combustion with Alkaline Salts through Melting Process

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Abstract: Molten salts are attractive materials as a reaction media for environmental processes in order to decompose toxic substances. In this work, some experiments based on the temperature-programmed oxidation were carried out to investigate the soot combustion activities of several alkaline salts (Li₂CO₃, LiCl, LiNO₃, K₂CO₃, KCl, KNO₃ and NaNO₃) and their mixture (LiNO₃+KNO₃). For the investigations, the comparison of soot combustion activity was made among basic alkaline salts with various melting points. Without alkaline salts, the soot combustion occurred around 723 K, while the soot combustion with alkaline carbonate and chloride was promoted around 650 K. Nitrates group showed higher activity due to the formation of molten phases.

Keywords: Soot Combustion, Molten salt, Alkaline Salts

1. INTRODUCTION

The soot combustion has attracted considerable attention because of their environmental impacts. Molten alkaline salts are considered as a potential reaction media for the soot combustion due to the unique properties such as high stability at high temperatures [1], ability for particle collection [2] and high reactivity [3]. Several molten salts are mentioned for this purpose: Molybdenum, vanadium, and cesium oxide or sulphate based molten salts are considered as good candidates for soot oxidation media [4]. Nitrates and carbonates based molten salts are considered as good candidates for soot oxidation media [5]. On the other hand, LiNO₃, NaNO₃ and KNO₃ showed high performance and good stability around 823 K [6]. These promotion activities for soot combustion have been found to depend markedly on the melting temperature of salts. However, very few studies have been reported on promotion properties of salts mixtures. The mixing of salts would offer advantages for the reduction of melting temperatures of alkaline salts.

As a fundamental study, activities of LiNO₃, Li₂CO₃, LiCl, KNO₃, K₂CO₃, KCl, NaNO₃ and LiNO₃-KNO₃ for the soot combustion were investigated. In order to evaluate the activity for the soot combustion, the soot oxidation rate was calculated from the amount of CO and CO₂. Soot oxidation rate was defined as following the equation:

\[ \text{Soot oxidation rate} \left[ \text{s}^{-1} \right] = \frac{(\text{CO formation rate} [\text{g/s}]) + (\text{CO₂ formation rate} [\text{g/s}] )}{(\text{Initial weight of soot [g]})} \]

TG/DTA equipment (RIGAKU, Thermo plus TG 8120) was employed for the thermal analysis. Each alkaline salt was loaded 22–25 mg into the alumina cell and heated at 1 K/min under the static air condition.

2. EXPERIMENTAL

As alkaline salts, reagents of LiNO₃, Li₂CO₃, LiCl, KNO₃, K₂CO₃, KCl and NaNO₃ (Wako Pure Chemicals Industries, Ltd., 120-01231, 12-113, 125-01161, 160-04035, 160-03491, 163-03545 and 160-03491) were used. The activated carbon was used as the simulated soot (Wako Pure Chemicals Industries, Ltd., LiNO₃-KNO₃ was prepared by mixing LiNO₃ and KNO₃ (Li:K = 42.5:57.5 molar ratio) in mortar.

Sample salts were ground with simulated soot (2:1) and then dried. The obtained sample was carefully mixed with alumina powder (d = 75-212 μm) with a spatula at a ratio of 3: 20. This alumina powder was to avoid the pressure loss and fluxion of molten salts. The soot combustion was achieved by employing a temperature programmed oxidation (TPO) method with a conventional fixed-bed reactor. 460 mg of the mixture was loaded into the U-type quartz reactor (8 mm in diameter; ca. 15 mm bed height). For soot combustion experiments, the reactor temperature was elevated at 0.6 K/min from 400 to 800 K. An O₂/He gas flow (O₂: 10 vol%, He: balance) was fed into the reactor at a constant rate of 200 ml/min. The outlet gas from the reactor was analyzed by an FID gas chromatograph (Shimadzu, GC 8APF) with a methanizer (GL science, MT 221) to measure amounts of CO and CO₂. Soot oxidation rate was defined as following the equation:

\[ \text{(Soot oxidation rate) [s⁻¹]} = \frac{(\text{CO formation rate [g/s]}) + (\text{CO₂ formation rate [g/s]})}{(\text{Initial weight of soot [g]})} \]

3. RESULTS AND DISCUSSION

Fig.1 shows the soot oxidation rate without the alkaline salt as a function of temperature. Upon heating the soot combustion started around 600 K followed by a rapid increase with the oxidation rate. The oxidation rate reached a maximum value at T=723 K and then decreased. This indicates the soot combustion requires the high temperature and high activation energy in order to be decomposed.

Fig.2 shows soot oxidation curves for LiCl, KCl, Li₂CO₃ and K₂CO₃. When alkaline salts packed with
soot, the oxidation behaviors were obviously changed due to the promotion by alkaline salts. The peaks of oxidation rate were sifted to lower temperatures than that without the alkaline salt, and the maximum rates were obtained at 633, 689, 671 and 677 K for LiCl, KCl, Li2CO3 and K2CO3, respectively. This promotion effect may be explained by the catalytic effect of salts powder, however, in the soot oxidation, contacts of solid-solid interaction are not tight and are depended on the condition of preparation. Indeed, the behavior of oxidation rates were depending on the kind of alkaline salts, and were complicated function of temperature. In the case of Li2CO3, the main peak had a shoulder peak at the higher temperature (767 K), indicating that Li2CO3 seemed to have no relation to combustion.

Fig. 3 displays the soot oxidation behavior with alkaline nitrates (LiNO3, KNO3 and NaNO3) and the mixture of nitrates (LiNO3+KNO3). Obtained results showed that peaks of the oxidation rate were observed at 649, 647 and 653 K for LiNO3 KNO3 and NaNO3, respectively. The mixture of nitrates showed the maximum rate at 645 K. Thus, note that the nitrates had almost the same behavior each other above 600 K, whereas LiNO3 and its mixture with KNO3 showed a different behavior below 600 K. LiNO3 had a secondary peak (583 K) because of a significant acceleration of the soot combustion at lower temperature. Similar peak was also shown in the results of the mixture of nitrates (LiNO3+KNO3). This peak was observed at the near temperature (592 K) of the secondary peak of pure LiNO3.

On the other hand, DTA curves of alkaline nitrates (LiNO3, KNO3 and NaNO3) and the mixture of nitrates (LiNO3+KNO3) are also shown in Fig. 3. As seen in curves, for the nitrate group, we can find clear peaks assigned to the melting. The obtained melting points of LiNO3, KNO3 and NaNO3 were 526, 606 and 579 K, respectively, and the mixture of LiNO3 and KNO3 was found to melt at extremely lower temperature than that of pure nitrates (406 K).

There are two possible explanations for the promotion of the soot combustion at lower temperatures. One is explained by the carbon contribution to the reaction system.

Alkaline metal nitrate decomposes into nitrite with releasing oxygen in the high temperature region (>873 K):

\[
\text{MNO}_3 \xrightarrow{\text{MNO}_2 + 1/2 \text{O}_2} \quad (1)
\]

where M represents alkaline metals (M=Li, K, Na). When soot (C) is involved in the system, following reaction proceeds at low temperatures (<700 K):

\[
\text{MNO}_3 + 1/2\text{C} \xrightarrow{\text{MNO}_2 + 1/2\text{CO}_2} \quad (2)
\]

Thermodynamically, nitrite converted by above equations, (1) and (2) is unstable at lower temperatures, so that the nitrate is reproduced as follows:

\[
\text{MNO}_2 + 1/2\text{O}_2 \xrightarrow{\text{MNO}_3} \quad (3)
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Accordingly, a nitrate-nitrite cycle can be made in the temperature region from 500-700 K.

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Another explanation is kinetic effects by the liquid phase in the reaction system. As shown in Fig 3, LiNO₃, KNO₃ and NaNO₃ appeared to involve in the combustion as a liquid phase. Note that almost the same oxidation curves were observed for any nitrates above 600 K. These behaviors can be explained by assuming the high contact of liquid phase with the soot: the soot oxidation with liquid-solid interaction proceeds rapidly and uniformly with the increase of liquid phase. This may imply the significant reduction of the activation energy in the soot combustion (mentioned above as eq. (2)). Particularly, LiNO₃ and its mixture with KNO₃ showed the high oxidation rate at lower temperatures (<600 K). Melting temperatures of these nitrates were substantially smaller than those observed for other nitrates. Therefore, the lower melting temperature, the higher oxidation rates were observed at low temperatures.

Because of the toxicity and hazardousness for environments, the loss of nitrates is unfavorable. Our results revealed that the nitrates had higher activities at lower temperatures. Such mild conditions lead to prevent from vaporizing of nitrates due to their low vapor pressures. However, more careful studies are necessary to clarify the details of phase transition behaviors of this system and the nitrates stabilities especially at higher temperatures.

4. CONCLUSIONS

Promotion effects of alkaline salts (Li₂CO₃, LiCl, LiNO₃, K₂CO₃, KCl, KNO₃ and NaNO₃) and their mixture (LiNO₃+KNO₃) for the soot oxidation were investigated. The soot oxidation was enhanced by the addition of alkaline salts, however the oxidation curves showed a quite different behavior depended on the physical properties of salts. When carbonates and chlorides were used, the oxidation started without melting in the higher temperature range around 650 K. The behavior of oxidation rates were depending on the kind of alkaline salts, and were complicated function of temperature. On the other hand, the molten nitrates showed enhancements of the soot oxidation at 583-590 K and at 649-653 K. These promotion effects towards the soot oxidation may be explained by carbon contribution to the reaction system, and by kinetic effects of liquid phases that has the well contact with the soot particles.

REFERENCES