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The catalytic activities and thermal stabilities of Li/Na/K carbonates for diesel soot oxidation

Yongheng Zhang [a,b,*], Xiaoting Zou [a]

[a] College of Materials and Environmental Science, Qingdao University of Science and Technology, 53 Zheng-Zhou Road, Qingdao 266042, China
[b] Key Laboratory of Rubber and Plastics, Ministry of Education, Qingdao University of Science and Technology,
53 Zheng-Zhou Road, Qingdao 266042, China

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Abstract

The alkali carbonates displayed a good catalytic activity for soot oxidation and their catalytic performances follow the order $K_2CO_3 > Na_2CO_3 > Li_2CO_3$ with soot ignition onset temperatures (IOTs) of 310 °C, 320 °C and 320 °C respectively. Na/K and Li/Na/K carbonate catalysts produced by combinations of the three alkali carbonates displayed the lowest IOT of about 320 °C that was higher than that of pure K_2CO_3. It was found that the variation of Li:Na:K molar ratios has very limited effect on the catalytic activity, but considerable effect on the thermal stability of the catalysts.Thermal treatment at 700 °C caused a limited change of IOT, but the deterioration of catalytic performance. In the Li/Na/K catalyst system, the formation of crystalline phases with low melting temperature was observed.

Keywords: Alkali carbonate; Diesel soot oxidation; Catalytic activity; Thermal stability

1. Introduction

Precious metals [1,2] and transition metal oxides/salts, such as Co–Ni [3], Cu–Fe [4], K–Cu, K–Co [5], Co–Ba–K [6], Cu–K–Mo [7], Cu–V–K [8], Cs–Fe–V [9] and other vanadate-based catalysts [10–13] have been studied for diesel soot oxidation. Rare earth metal oxides such as Ce–La [14], La–Cr [15], Pr–Cr [16], La–K [17], La–K–Cr [18], La–K–Mn–O [19], La–K–Cu–V [20], Co–Ce [21], Ce–Co–K [22] and Sm–K [23] have also been widely studied because of their redox properties. The past studies have shown the important role of alkali metallic or alkaline-earth metallic elements on the catalytic activity enhancement of the catalysts [24–26]. A detailed study carried out by An et al. [27] showed that the catalytic activity of Fe_2O_3 based catalyst could be significantly improved by doping alkali metallic elements. However, these elements were mostly added into metal oxides or salts in the form of nitrates, chlorides and hydrates. There are few reports on using single or mixed alkali carbonates as catalysts for soot oxidation [24]. Miyazaki et al [28,29] has reported the catalytic combustion of coal using K_2CO_3. In this work, the catalysts based on K_2CO_3, Na_2CO_3 and Li_2CO_3 were loaded on porous ceramic substrate and their catalytic activity for soot oxidation and thermal stability was investigated.

2. Experimental materials and methods

2.1. Catalyst preparation and characterization

Analytical grade Na_2CO_3, K_2CO_3 and Li_2CO_3 were used to prepare the catalysts with variable Na:K and Li:Na:K molar ratios according to the method described elsewhere [31]. The precursor chemicals (about 100 mg)

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[*] Corresponding author. Address: College of Materials and Environmental Science, Qingdao University of Science and Technology, 53 Zheng-Zhou Road, Qingdao 266042, China. Tel.: +86 532 84022831; fax: +86 532 84022814.

E-mail address: yonghengzhang@yahoo.com (Y. Zhang).

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supported on porous alumina ceramics prepared by tape-casting [30] (dimension 20 × 15 × 1 mm, porosity 25%) were calcined at 600 °C or 700 °C for 3 h to produce the catalysts for catalytic activity measurement. The un-supported catalysts were also characterized by thermogravimetry (TG, TG209, Netzsch, Germany) and differential scanning calorimetry (DSC, DSC204F1, Netzsch, Germany) at a heating rate of 10 °C/min from room temperature to 500 °C or 850 °C in N_2. Some samples have been characterized by using X-ray diffraction (XRD, Rigaku D/max-rA, Rigaku, Japan).

2.2. Reaction tests

The purpose-built temperature-programmed reaction (TPR) system [31] was used to characterize the catalytic activities of the prepared catalysts. Before testing, the supported catalysts were fumed over the burning diesel to coat 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 CO_2 concentration in the outlet gas. The soot ignition onset temperature (IOT) defined as the temperature where the CO_2 was detected, was used to assess the catalytic activities of the catalysts. In order to determine the CO_2 absorption capability of the catalyst systems, the raw samples (contacting air for over 8 h) without coating soot were put into TPR run, to obtain the TPR curves (blank testing) and to eliminate the effect of absorbed CO_2 on the ignition temperature identification, as for V/K based catalysts studied previously by present authors [31]. Subsequently, the samples were taken out from the furnace and coated with soot, immediately followed by putting the samples into the hot furnace (temperature about 300 °C). The furnace was cooled to about 100 °C with flowing of the CO_2-removed air followed by the second TPR run of the catalyst with soot coating.

3. Results and discussions

It is well known that the addition of alkali metal elements in the forms of nitrates, halides or hydrates into various oxides would significantly promote the catalytic activity of the oxides for soot oxidation [27,32,33]. In this exploration, the alkali carbonates Na_2CO_3, Li_2CO_3 and K_2CO_3 were studied as the soot oxidation catalysts in the form of various combinations, considering the advantage of their anti-degradation property by CO_2 and high thermal stability. These compounds have much higher melting points (Table 1) than those of their corresponding nitrates and chlorides and are decomposed only when the temperature is higher than the melting points. Hence, these compounds are thermally stable when the diesel exhaust temperature is under their melting temperatures.

Table 1
The melting points of various types of alkali salts

Potassium salts		Sodium salts		Lithium salts	
Type	Melting point (°C)	Type	Melting point (°C)	Type	Melting point (°C)
K_2CO_3	891	Na_2CO_3	851	Li_2CO_3	723
KCl	771	NaCl	800	LiCl	608
KNO_3	334	$NaNO_3$	308	$LiNO_3$	255

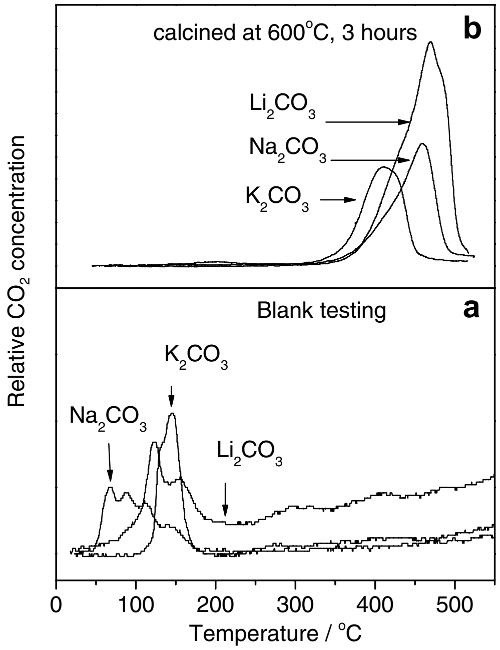

Fig. 1. The intrinsic catalytic activities and CO_2 production characteristics of Na_2CO_3, K_2CO_3 and Li_2CO_3 loaded on alumina ceramic substrate and calcined at 600 °C for 3 h: (a) the CO_2 production characteristics (blank testing), (b) the catalytic activity.

The TPR runs of these compounds without soot coating (blank testing), shown in Fig. 1a, revealed the CO_2 evolution processes at the temperature ranges of 100–180 °C, 50–160 °C and 70–100 °C for K_2CO_3, Na_2CO_3 and Li_2CO_3, respectively. Obviously, the CO_2 production processes were attributable to the formation of bicarbonates according to the following reactions:

$$K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3 \tag{1}$$

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2 \tag{2}$$

The TPR run results obtained instantly after the blank testing are shown in Fig. 1b. It can be seen from this figure that K_2CO_3 displayed the highest intrinsic catalytic activity with an IOT of about 310 °C, but Na_2CO_3 and Li_2CO_3 showed a comparable IOT of about 320 °C.

The blank testing results of Na/K catalysts, shown in Fig. 2a, displayed the CO_2 production process with peak temperatures positioned at 90 °C, 150 °C and 200 °C. The former two peaks were most likely caused by the decompositions of Na and K bicarbonate species respectively, because similar phenomena were also observed for the pure compounds. The peak, centered at 200 °C was attributed to the decompositions of Na/K bicarbonate species. XRD analyses have confirmed that the $NaKCO_3$ was formed in