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Carbonate-Promoted Catalytic Activity of Potassium Cations for Soot Combustion by Gaseous Oxygen

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The possible mechanism of soot combustion catalyzed by potassium carbonate loaded on aluminosilicate was elucidated to understand the surface reaction in solid–solid–gas triphasic catalysis. Potassium species on aluminosilicate showed high catalytic performance for the oxidation of carbon black by gaseous oxygen. Aluminosilicate helped in stabilizing the alkali cation on the surface. The carbonate ion played a critical role in enhancing the catalytic performance by acting as a supplier of active electrons to gaseous oxygen. To the best of our knowledge, this is the first report on the essential role of carbonate on the catalytic activity of an alkali cation for an oxidation reaction, although carbonate (carbon dioxide) is widely recognized to hinder the catalytic performance of the alkali compound for base-catalyzed reactions.

Despite the increasing demand for electric cars, automobiles with an internal combustion system continue to be the preferred mode of transportation because of the high energy density of liquefied fuel. Because of its high energy-conversion efficiency, the diesel-engine combustion system may contribute to the reduction of CO₂ emission per unit travel distance. More than 70% of the new automobiles sold in European markets are based on diesel engines. The combustion mechanism entails the inhalation of a large quantity of air into the engine and the release of a high concentration of oxygen in the exhaust. Therefore, installation of a three-way catalyst (TWC) in the emission suppression system for NO_x emission control in the presence of an excess amount of oxygen is difficult.^[1] In addition, reducing particulate matter (PM) emission is also important for diesel-emission management.^[2,3] Installation of a diesel particulate filter (DPF), which comprises a semiplugged ceramic honeycomb with a wall-flow system on the partitioned

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porous wall of the honeycomb, in the emission system of diesel automobiles is an efficient means of removing more than 95% of the emitted PM.^[4] However, to avoid frequent regeneration or replacement of such filters, a catalyst that eliminates carbonaceous PM by combustion is required.^[5] In the continuously regenerating trap (CRT) system, developed by the Johnson Matthey Company, NO is oxidized by the first catalyst with a large amount of Pt to obtain NO₂, which in turn catalyzes PM oxidation at approximately 300 °C; this corresponds to the emission temperature in the diesel combustion system. The DPF is installed in the second stage of the catalyst system, where PM is captured and oxidized by NO₂ generated in the first stage. A third catalyst is required to remove NO that is used as NO₂ for the oxidant of the PM, in which urea is necessary as the reductant of NO.

Gaseous oxygen is not used as the oxidant for PM because of the high temperatures (exceeding 600 °C) required. To promote the oxidation of PM by oxygen present in diesel emission, many researchers have tried to find catalysts that require a temperature as low as the emission temperature. Although potassium species are promising candidates for catalyst components,^[6] they have several disadvantages: potassium is volatile at the temperatures required for carbon oxidation and easily dissolves in water to afford a highly alkaline solution that can damage the ceramic honeycomb. We found that potassium carbonate stabilized on a tectoaluminosilicate such as sodalite zeolite or a nepheline mineral shows excellent catalytic performance, which is similar to that of bulk potassium carbonate and is durable against rinsing in water.^[7-9]

In this study, we elucidated the mechanism of carbon oxidation by gaseous oxygen on potassium carbonate species with/ without loading on a nepheline surface, with the aim of identifying the active catalytic centers. To the best of our knowledge, this is the first attempt at clarifying the overall catalysis mechanism by considering the role of the carbonate anion in the oxidation reaction.

Catalytic performance of bulk alkali carbonates

Figure 1 a shows the typical CO_2 elution curves detected by a mass spectrometer (m/z = 44) during carbon black (CB) combustion in air. CO_2 is generated during the combustion without any formation of CO, and the temperature at which the curve starts to steepen correlates well with the catalytic activity. Alkali carbonates catalyzed this reaction at a low temperature upon mixing CB in the so-called tight contact state. Upon performing the combustion with various alkali metal carbonates,



Figure 1. a) CO₂ detected at m/z=44 by mass spectrometry during CB combustion on different alkali carbonates under an air stream. b) DRIFT spectra of each alkali carbonate.

the combustion initiation temperature decreased in the order sodium > potassium > rubidium > cesium; this implies that the catalytic activity increased with the atomic weight of the alkali metal. Furthermore, the higher the basicity of the alkali element, the higher the catalytic performance for carbon combustion by oxygen. Given that alkali metal oxides are generally basic, acidic CO₂ hinders their basic catalytic performance.^[10] In contrast, alkali metal carbonates are not pyrolyzed into oxides in the temperature range tested for the combustion reaction, and this indicates that the catalytic activity originated from each carbonate. The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the carbonates are illustrated in Figure 1 b. The broad absorption band at 1600–1400 cm⁻¹ could be assigned to the asymmetric vibration of the carbonate species for each carbonate, whereas the sharp band at 1800 cm⁻¹ corresponds to the symmetric vibration of carbonate. Interestingly, the broad band split into two or three bands upon changing the alkali element carbonate from sodium to cesium. The vibration mode of the carbonate is affected by alkalinity/ basicity, which can be referred to as a polarizing effect.^[11] Given that strong basicity favors electron donation, the high catalytic activity of the strongly basic alkali carbonate could be due to the activation of oxygen by the donated electron(s).

Performance of alkali carbonates on crystalline aluminosilicate

Basically, the catalytic performance of alkali carbonate on sodalite corresponds to that of the bulk alkali carbonate. Sodalite showed very low activity for CB combustion with gaseous oxygen, as previously reported.^[6] An excess amount of sodium on the surface of sodalite might lead to the formation of sodium carbonate by reaction with ambient CO₂ to afford Na₂CO₃/Na-sodalite, which showed high catalytic activity for the reaction. Further, as mentioned in our previous report, potassium carbonate loaded sodalite underwent a phase change to a nepheline group upon heating at high temperatures of approximately 800 °C^[7] and the exact phase was determined by the amount of potassium loaded on sodalite prior to heat treatment. The formed nepheline held sodium carbonate on the surface through solid ion exchange during the treatment. The catalytic performance of the nepheline was compared with that of sodium and potassium carbonates, as summarized in Figure 2, by measuring the activation energy for CB oxida-



Figure 2. Activation energy for CB combustion in air with and without a catalyst (Na_2CO_3 , K_2CO_3 , and K_2CO_3 -loaded Na-nepheline).

tion as a function of carbon conversion. To speculate the active species on the surface of the calcined nepheline, the apparent activation energy of soot oxidation was determined by using the Ozawa method^[12] and Equation (1):

$$\frac{d\log\beta}{d\left(\frac{1}{\tau_a}\right)} = 0.4567 \frac{E}{R} \tag{1}$$

in which β represents the heating rate; T_{α} is the temperature corresponding to a carbon conversion of α %, as calculated from the thermogravimetric curve; and *E* is the apparent activation energy in kJ mol⁻¹. *E* can be estimated from the slope of the least-squares straight-line fit of the log β versus $1/T_{\alpha}$ plot. The measured *E* values, 100–120 kJ mol⁻¹, were much lower than those obtained without using a catalyst, 140–150 kJ mol⁻¹. A high *E* was necessitated at a higher conversion

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of CB on alkali carbonates; this indicates that combustion of the residual carbon during the last stage of the reaction is difficult. On the contrary, there was no notable conversion dependence on the nepheline catalyst, which showed the characteristics of both sodium and potassium carbonates. Nevertheless, we can conclude that the carbonate species on the surface of the nepheline grains acted as the catalytically active sites. Notably, the IR spectra of the carbonate on nepheline, as displayed in Figure 3, differed from those of the bulk carbonate. As compared with the carbonate species in sodium carbonate, the band assignable to carbonate was shifted to a lower frequency, which is indicative of further donation of electron(s) or an increase in the basicity of sodium/ potassium carbonate on nepheline. The enhanced catalytic activity observed upon potassium carbonate loading on aluminosilicates compared with that on sodium carbonate also supports this observation.

Notably, other potassium salts such as sulfates and nitrates on crystalline aluminosilicate showed a high catalytic performance, which was comparable to that of potassium carbonate. Interestingly, only carbonate remained on the surface after the combustion (results not shown). Raman spectroscopic studies revealed that the nitrate anion was pyrolyzed, whereas the sulfate anion remained in trace amounts and car-

bonate was the major anion. Legutko et al. also suggested that K_2CO_3 was the best precursor for PM oxidation among KOH, K_2CO_3 , KNO₃, CH₃COOK, and K_2SO_4 .^[20]

Effect of contact with carbon grains on the performance of carbonate catalysts

Silver^[13] or platinum^[14] on ceria shows high catalytic activity for soot combustion by gaseous oxygen through a solid-solid-gas triphasic reaction. Effective contact between the catalyst surface and CB is important for this type of reaction. Unlike the previously mentioned tight contact mode, the loose contact, observed in the case of the typical Ag catalyst for PM combustion, Ag/CeO₂, and also in the typical Pt automobile catalyst, Pt/CeO₂-ZrO₂ with CB resulted in a CO₂ elution curve much broader than that resulting in the case of the potassium catalyst, as shown in Figure 4. On Ag/CeO₂ and Pt/CeO₂-ZrO₂, active oxygen generated from bulk CeO₂ moves to the surface of silver or platinum to react with CB only if it is adjacent to the surface oxygen species. In other words, the active oxygen species never flies into the gaseous phase, which could be the main reason for the need for the tight-contact mode for this type of triphasic catalysis. Upon using a potassium catalyst, on the contrary, the contact mode used does not critically affect the catalytic performance, which raises the possibility that the active species probably flies into the gaseous phase.

The catalytic performances of platinum and potassium species for CB oxidation in a helium stream are demonstrated in Figure 5. Even though gaseous oxygen was absent, CO_2 was detected for the platinum catalyst at 250, 500, and 700 °C, at



Figure 3. DRIFT spectra of Na_2CO_3 , Na-nepheline, K_2CO_3 -loaded Na-nepheline, and calcined one.



Figure 4. CB combustion on Ag/CeO₂, Pt/CeO_2 –ZrO₂, and K₂CO₃-loaded Na–nepheline for different mixing modes.

which point the lattice oxygen of the CeO_2 - ZrO_2 support started to desorb. This finding indicated that the active oxygen was derived from the platinum support, as the lattice oxygen could easily desorb at such low temperatures. Cobalt(II,III)

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Figure 5. CB oxidation under He stream on Pt/CeO_2-ZrO_2 , K_2CO_3 -loaded Co_3O_4 , and K_2CO_3 -loaded Na–nepheline.

oxide (Co₃O₄) is known to catalyze the oxidation of carbon monoxide by using the lattice oxygen present in Co₃O₄.^[15] The work function of the catalyst was lowered by the addition of potassium,^[16] and this resulted in higher catalytic activity for the oxidation reaction. Distinct bands for CO₂ generated by CB oxidation on K/Co $_3O_4$ were seen at 580 and 750 $^\circ$ C, and even at higher temperatures. On the contrary, potassium-containing nepheline did not show catalytic activity at a low temperature of approximately 300 °C under the conditions used in the present study. Therefore, potassium on nepheline uses oxygen in the gas phase to catalyze CB oxidation; that is, the active oxygen for this reaction is derived from the gas phase and it flies back to the gas phase to attack carbon. Nevertheless, we should consider the possibility that the potassium species may also fly; potassium may be vaporized at a high temperature, which decreases the catalytic performance. During the laboratory-scale tests to 800 °C, which were repeated 10 times, the catalytic activity of potassium carbonate on nepheline remained unchanged, and the decrease in the amount of potassium was negligible.

Mechanism for carbon oxidation catalyzed by potassium carbonate

We then attempted to investigate how gaseous oxygen was activated. For the oxidation of a carbonaceous compound, oxygen should be reduced to gain nucleophilicity. Two different mechanisms have been considered for the reaction: electron donation to carbon and oxygen transfer to carbon.^[17] In the latter case, for example, transition metals that show redox capacity or oxygen-storage capacity, such as CeO₂, act as catalytically active centers, whereas such a redox mechanism might be difficult in the case of the potassium carbonate catalyst. Only the carbonate can act as the electron donor for oxygen. As indicated by the IR spectra in Figure 1 b, the electron density of the carbonate increased with the atomic weight of the alkali metal, and the band corresponding to the carbonate shifted to a lower frequency with an increase in the

electron density of the carbonate. Interestingly, the frequency was further decreased if the carbonate was located on the nepheline surface. The intrinsic catalytic activity of potassium carbonate increased if it was supported on the surface of crystalline aluminosilicate, and this is indicative of the vital role of the carbonate ion in the activation of gaseous oxygen.

The results of investigations performed thus far on coal gasification and carbon oxidation by oxygen and by potassium suggest that an electron is transferred from carbon to gaseous oxygen through potassium.^[17–19] Direct removal of the electron from its orbital electron requires very high energy; therefore, it is reasonable to propose that the alkali species aids the process by forming a conjugated orbital with the carbonate. Thus, we can conclude from Figure 6a that an active electron is lo-



Figure 6. a) Possible mechanism for carbon combustion with gaseous oxygen on an alkaline carbonate supported aluminosilicate surface. b) The electron structure of potassium carbonate on the aluminosilicate surface. The balloon shown in the figure indicates the SOMO of potassium carbonate.

cated at the carbonate site and that this electron is released from the carbonate through potassium for the generation of a nucleophilic oxygen species. Here, the alkali aluminosilicate plays an indirect role in stabilizing such a carbonate species. Potassium shows high catalytic activity for carbon oxidation, because it allows better contact with carbon owing to its elution.^[17] Although potassium might be volatilized during the oxidation of carbon, it is electrostatically stabilized on aluminosilicate, as also suggested by Su and McGinn.^[21] The high-energy active electron in the singly occupied molecular orbital (SOMO) of potassium carbonate located on nepheline (Figure 6b) can attack an oxygen molecule and reduce it to a more active oxygen species.

We also found that oxygen activated by potassium carbonate on sodalite/nepheline never catalyzed the oxidation of hydrocarbons and carbon monoxide and that its oxidation ability was uniquely selective to carbon oxidation. The oxygen species generated through this mechanism might be less nucleophilic than O^{2-} , which can attack C–H and C–O species; this results in complete oxidation into carbon dioxide and water molecules.

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Finally, we focus on a base catalyst derived from alkali ion exchanged zeolites such as potassium zeolites. Ambient carbon dioxide adheres strongly on the surface of the alkali ion on a zeolite, which thus prevents the adsorption of other molecules on the active basic oxygen adjacent to the alkali cation, and this results in carbonate formation on the surface.^[11] Researchers have reported that in base catalysis, deactivation occurs by the adhesion of CO_2 , and hence, the catalyst must be pretreated at temperatures as high as 800 to 900 °C. However, CO_2 elimination or carbonate decomposition at such high temperatures may cause sintering of the catalyst. However, the "cumbersome" carbonate, as an oxidation catalyst, plays an important role as an electron pool and electron donor to promote the activation of gaseous oxygen.

Experimental Section

Catalyst preparation

Sodalite was synthesized according to the procedure reported in the literature.^[6] An impregnation method was used to load potassium carbonate onto the sodalite. Potassium carbonate (16 wt%) was added to a sodalite slurry in distilled water. The obtained slurry was vigorously stirred for 24 h at 80 °C and was subsequently dried at 100 °C, which resulted in the physical deposition of potassium carbonate onto the support. The potassium-carbonate-supported sodalite was thermally treated by using an electric muffle furnace, by heating to 800 °C at 10 Kmin⁻¹ and by maintaining at 800 °C for 5 h in a stream of air. The obtained samples were washed with water at room temperature. Each gram of thermally treated K₂CO₃/sodalite was suspended in distilled water (80 mL) in a polypropylene bottle, and the suspension was vigorously stirred for 24 h at room temperature. The obtained samples were filtered and dried at 60 °C.

Characterization of catalysts

Powder X-ray diffraction (XRD) patterns were recorded to confirm the formation of the active component "nepheline" by using a M03X-HF diffractometer, Bruker AXS, Germany, with CuK_a radiation ($\lambda = 1.54$ Å) at 40 kV and 30 mA. The 2 θ values ranged from 5 to 45°. IR spectra were recorded by using an FTIR-4100 singlebeam FTIR, (JASCO, Japan) that was connected to a diffuse-reflectance IR cell by using a KBr diluent. The spectra were generated at a resolution of 4 cm⁻¹. Raman spectroscopy was performed at room temperature by using a NR-1800, JASCO, with a $\lambda = 532$ nm green laser. The measurement was performed at cumulated twice and the exposure time was 60 s. The chemical composition of the solid or liquid samples was characterized by using an inductively coupled plasma atomic emission spectrometer, P4010, Hitachi, Japan.

Ab initio quantum chemistry calculations were performed by using DFT. The B3LYP hybrid function and the 3-21G basis set were used for the calculations.

Catalytic activity test

The catalytic activity of the samples used for soot combustion was evaluated by using temperature-programmed oxidation (TPO) on a thermogravimetric/differential thermal analyzer (Thermoplus TG-8120, Rigaku, Japan) directly connected to a mass spectroscope M- QA200TS, Anelva Japan. Carbon black #2600 (CB, Mitsubishi Chemicals Co.) particles with a diameter of 13 nm were used as a reference for the carbonaceous soot found in diesel exhaust. Laboratory-scale examination of the catalytic activity was conducted on two types of contacts: one is "loose contact", for which the soot is mixed with the catalyst by using a spatula, and the other is "tight contact", for which the soot and catalyst are mixed in an agate motor. It has long been known that the "loose-contact" scenario is more reflective of DPF under practical conditions. In this research, the catalysts and carbon black were simply mixed together with a spatula to achieve a loose contact, which was similar to that observed under pseudopractical conditions. The CB/catalyst mixtures had weight ratios of approximately 1:10, so that the possible mass and heat transfer limitation described in the literature could be prevented. The mixtures were heated to 800 °C at 10 K min⁻¹ in a flow of 10% oxygen in helium. The catalytic activity for CB combustion was typically evaluated on the basis of the temperature, the point at which the CO_2 (m/z=44) elution curve starts to appear. A weight loss and an exothermic peak attributed to the combustion of CB and to the generation of CO₂ were simultaneously detected by using thermogravimetry-differential thermal analysis (TG-DTA) and mass spectrometry, respectively. The weight of the sample decreased and evidence for CO₂ elution were simultaneously observed in the mass spectrum. An exothermic peak in the DTA measurements was clearly visible after a slight delay from the time of CO₂ elution. Therefore, the catalytic activity for carbon combustion could be evaluated on the basis of temperature.

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