CATALYTIC ACTIVITIES OF K_2CO_3 SUPPORTED ON PEROVSKITES FOR COMBUSTION OF COAL CHARS

Young-Kwang Kim, LiFang Hao, Jin Miyawaki, Isao Mochida, Seong-Ho Yoon*

Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 816-8580, Japan

Introduction

Effective energy-saving combustion and gasification of solid carbon such as coal, char and particulate matters (PMs) are most important subjects for the environmental protection to reduce PMs exhausted from diesel engine and industries as well as for the low-temperature combustion and conversion of coals.

Alkali metal salts have been reported as the best catalyst for the combustion and gasification of carbon, although their activity strongly depends on the type of salts, of which the reaction mechanisms are believed to be activated through their reduction to the metallic state, staying on the carbon surface or vaporizing from surface due to the sublimation pressure at the reaction temperature.

The alkali metal carbonates supported on perovskite type oxide showed higher catalytic activity in carbon combustion than those supported on γ-Al_2O_3 or perovskite type oxide itself.[1] This result is given by synergy effect of K_2CO_3 and perovskite type oxide. The unique role of perovskite is to hold the catalytically active species in the reaction zone drastically to increase the catalytic turnover. However, the mechanism of K_2CO_3 activation from perovskite support and the reason for the ability of perovskite to hold K_2CO_3 are not cleared yet.

In the present study, we have investigated the mechanism of catalytic activation of K_2CO_3 in the carbon combustion from K_2CO_3 supported on $LaMn_{1-x}Cu_xO_3$ system.

Experimental

Perovskite-type oxides, $LaMn_{1-x}Cu_xO_3$ (LMC), were prepared by the citric acid-aided Sol-Gel process, and the conventional evaporation-to-dryness process. K_2CO_3 (10 wt%) was deposited on perovskite support through immersing in K_2CO_3-ethanol/H_2O and removed the solvent by drying at 110 °C[2] , namely, wet impregnation (WI) method.

The specific surface areas were calculated by BET method from the N_2 adsorption isotherms at 77 K. Powder X-ray diffraction (XRD) patterns of the LMC samples were recorded using a X-ray diffractometer (RINT III, Rigaku, Cu Kα radiation). The step scans were taken over the range of 2θ angles from 10 to 89.98° in the step of 0.01°, and intensity data for each step was collected for every 5s. FT-IR spectra of catalyst samples were obtained using a JASCO FT/IR-6000 infrared spectrometer at an ambient temperature and atmosphere.

Combustion experiments were performed by TG analysis (NII TG/DTA 6300) of carbon and catalyst mixture (ca. 10 mg, 50:50 wt %) up to 1000 °C with heating rate of 2 °C min^{-1} under N_2/O_2 flows (90:10 ml min^{-1}).

Results and Discussion

Various kinds of compositions of crystallized $LaMn_{1-x}Cu_xO_3$ were carefully synthesized by Sol-Gel process. $LaMnO_3$ (LM) exhibited the largest surface area of 9.6 m^2g^{-1}. As for the substitution ratios of Mn to Cu, specific surface area decreased until x = 0.4 (LMC64). The surface area of x = 0.5 carried an appearance of new structure, as will be discussed below.
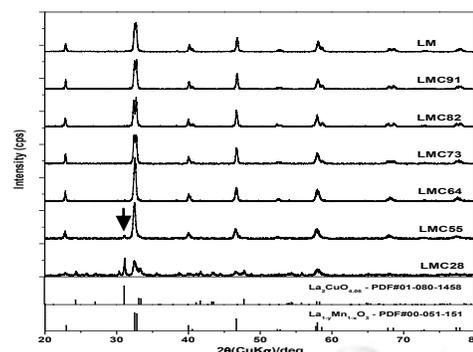

Fig. 1 XRD patterns of $LaMn_{1-x}Cu_xO_3$

Figure 1 shows the X-ray diffraction patterns of $LaMn_{1-x}Cu_xO_3$ calcined at 750 °C. For comparison purpose, the bar patterns of rombohedral $La_{1-y}Mn_{1-x}O_3$ (PDF#00-051-151), and tetragonal $La_2CuO_{4.05}$ (PDF#01-080-1458) phases are also included. It can be seen that the samples of the Mn/Cu ratio from 10/0 to 6/4, namely from LM to LMC64, have single-phase perovskite structure. LMC55 showed new phase appearance as tetrahedral La_2CuO_4 (marked with an arrow), and the sample composed of higher Cu ratio, LMC28, was tetrahedral dominated form. A careful inspection of the diffraction profile for the substituted perovskites reveals that partially distorted form coexists with the regular crystal structure. Thus, x = 0.1-0.3 seems better to fit to the rhombohedral $La_{1-y}Mn_{1-x}O_3$ structure, because of the presence of a faint splitting at 33° and 57°; for x = 0.4 , the diffraction profiles are cubic structure. The structure corresponds to the cubic $LaMnO_3$ with some modification that gives it a structure with rhombohedral geometry [3]. As shown in Figure 1, x = 0.2, LMC82, experiences the largest distortion. The diffraction peak of catalysts impregnated 10 wt% K_2CO_3 cannot found any difference with bare perovskite catalysts.

In Figure 2, FT-IR spectra of K_2CO_3 and a series of K_2CO_3 loaded $LaMn_{1-x}Cu_xO_3$ samples (loading amount 10, 20, 0r 30 wt%) are compared. 10 wt% K_2CO_3 / $LaMn_{1-x}Cu_xO_3$ samples gave new peaks at 1653, 1541, 1492, and 1101 cm^{-1}, in addition to the absorption bands of bulk K_2CO_3 at 1696, 1627, 1395, and 1366 cm^{-1} that can be assigned to monodentate or bidentate carbonate. Thus, it is clear that the states of CO_3^{2-} in bulk K_2CO_3 and in supported K_2CO_3 are different. The dissociative adsorption of K_2CO_3 on the support surface has been reported for K_2CO_3 supported on alumina[4] as shown in Figure 3.
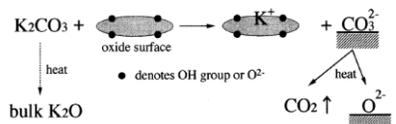
Fig. 3 Scheme for dissociated ions of K_2CO_3 on oxide surface[4].

On oxide surface of support, K_2CO_3 exists in dissociated form. The dissociation was remarkable at the 10 wt% K_2CO_3 / $LaMn_{1-x}Cu_xO_3$.
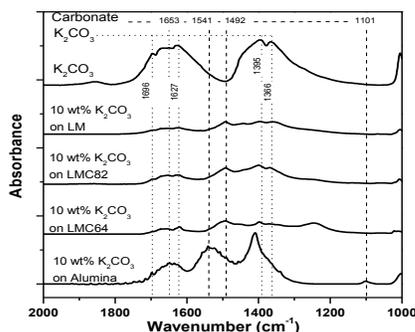

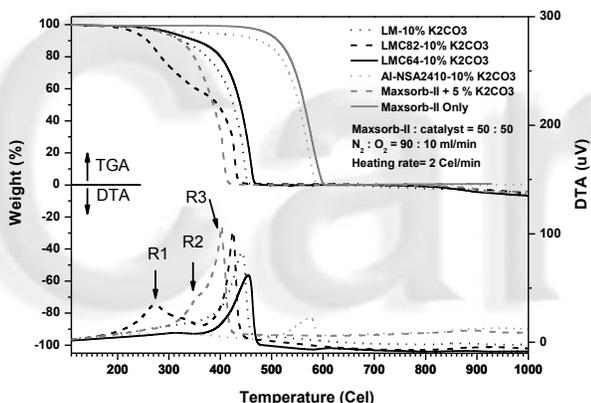**Fig. 2** FT-IR spectra of K_2CO_3, and 10-30 wt% K_2CO_3 / $LaMn_{0.8}Cu_{0.2}O_3$

Fig. 4 Comparison of catalytic activity for char oxidation over 10 wt% K_2CO_3 / $LaMn_{1-x}Cu_xO_3$ catalysts

Figure 4 shows TG combustion profiles of microporous activated carbon, Maxsorb-II, which has a similar to porous character with coal chars with 10 wt% K_2CO_3 / $LaMn_{1-x}Cu_xO_3$ catalysts. In the catalytic combustion with catalysts supported on LMC82, the profile showed two large weight losses at around 280 and 420 °C. The other small weight loss at above 700 °C was also found, which might be due to the potassium loss from catalyst, because potassium has high mobility over this temperature.

The different exothermal peaks suggest different reaction at each of combustion of which reason is conjectured from the different K_2CO_3 activity by the effect of supports. Especially, LMC82 that has a large distortion, as shown in Figure 1, enables to activate K_2CO_3 at lower temperature.
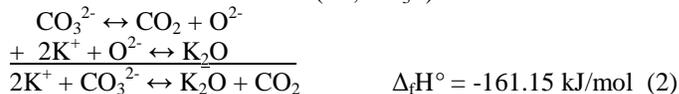
The activation of K_2CO_3 is believed to be initiated by the reduction of itself with carbon or reductive functional groups on the carbon. Reactions 1-6 are presumed to be related to the activation.

Decomposition
$$K_2CO_3 \leftrightarrow K_2O + CO_2 \qquad \Delta_fH° = +394.107 \text{ kJ/mol} \quad (1)$$

Reaction of dissociated ions (K^+, CO_3^{2-})
$$CO_3^{2-} \leftrightarrow CO_2 + O^{2-}$$
$$\underline{+ \; 2K^+ + O^{2-} \leftrightarrow K_2O}$$
$$2K^+ + CO_3^{2-} \leftrightarrow K_2O + CO_2 \qquad \Delta_fH° = -161.15 \text{ kJ/mol} \quad (2)$$

Carbothermic reduction
$$K_2CO_3 + 3C + O_2 \leftrightarrow K_2O + 4CO \quad \Delta_fH° = +240.48 \text{ kJ/mol} \quad (3)$$

Metal formation & metal oxidation & carbonate formation
$$K_2O + 3C + O_2 \leftrightarrow 2K + 3CO \qquad \Delta_fH° = -49.80 \text{ kJ/mol} \quad (4)$$
$$2K + C + O_2 \leftrightarrow K_2O + CO \qquad \Delta_fH° = -498.69 \text{ kJ/mol} \quad (5)$$
$$K_2O + C + O_2 \leftrightarrow K_2CO_3 \qquad \Delta_fH° = -788.48 \text{ kJ/mol} \quad (6)$$

From the thermodynamic view, we can expect that K_2CO_3 activation with carbon (R2, reaction 3) occurs in the lower temperature region than decomposition of K_2CO_3 itself (reaction 1). Then, reaction will be more activated with the chain reaction by K_2O formation (R3, reaction 4 and 5). In addition, K_2CO_3 supported on LMC82 showed another activation of K_2CO_3 below 300 °C (R1). This reaction is presumed to be related to dissociated ions of K_2CO_3 (K^+, CO_3^{2-}) on the surface of LMC82 (reaction 2). Other perovskite oxides (LM and LMC64) and alumina supporter also show the dissociated ion activation of K_2CO_3 in low temperature region, even if the amount is a little.

Consequently, perovskite oxides can more help K_2CO_3 to be activated than alumina supports at low temperature region. It means that perovskite oxides have the strong surface activity for dissociation of K_2CO_3 to K^+ and CO_3^{2-} (reaction 2). Especially, LMC82 showed the best activity of K_2CO_3 of which the reason might be due to the defect sites from the large structure distortion of LMC82.

References
[1] Miyazaki T, Tokubuchi N, Arita M, Inoue M, Mochida I. Catalytic Combustion of Carbon by Alkali Metal Carbonates Supported on Perovskite-Type Oxide. Energy & Fuels. 1997;11(4):832-6.
[2] Miyazaki T, Tokubuchi N, Inoue M, Arita M, Mochida I. Catalytic Activities of K_2CO_3 Supported on Several Oxides for Carbon Combustion. Energy & Fuels. 1998;12(5):870-4.
[3] Pecchi G, Campos C, Pe O, Cadus LE. Structural, magnetic and catalytic properties of perovskite-type mixed oxides $LaMn_{1-y}Co_yO_3$ (y=0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0). Journal of Molecular Catalysis A: Chemical. 2008;282(1-2):158-66.
[4] Yamaguchi T, Wang Y, Komatsu M, Ookawa M. Preparation of New Solid Bases Derived from Supported Metal Nitrates and Carbonates. Catalysis Surveys from Japan. 2002;5(2):81-9.