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Peroxide Anions as Possible Active Species in Oxidative Coupling of Methane

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Oxidative coupling of CH_4 forming C_2H_6 and C_2H_4 proceeded smoothly upon contact with Na_2O_2, BaO_2, and SrO_2 at low temperatures below 673 K. This indicates that O_2^{2-} ions are very reactive for activation of CH_4. O_2^- ions contained in the peroxides did not activate CH_4.

Partial oxidation of methane into higher hydrocarbons is one of the most challenging problems in heterogeneous catalysis. Since Keller and Bhasin[1)] reported the possibility of synthesis of C_2-hydrocarbons (C_2H_4 + C_2H_6) by oxidative coupling of methane over metal oxides, many groups[2-7)] are beginning to work in this area and there is increasing industrial activity.[8)] However, only a few fundamental work has reported concerning the oxygen species which are responsible for the catalytic activation of methane over metal oxides.

It is believed that oxidative coupling of methane is initiated by the abstraction of H from CH_4 to form $CH_3\cdot$ radicals.[3,9)] A coupling of two $CH_3\cdot$ radicals produces C_2H_6. Subsequent oxidative dehydrogenation of C_2H_6 produces C_2H_4. Lunsford and coworkers[3,9,10)] have suggested that the oxygen species responsible for the abstraction of H from CH_4 over MgO and Li-promoted MgO are the oxygen ions O^- and $[Li^+O^-]$, respectively. They also suggested O_2^- ions as active oxygen species over La_2O_3.[11)] Recent work in our laboratory has demonstrated that Sm_2O_3 in the presence of O_2 has high activity and selectivity for the synthesis of C_2-hydrocarbons from CH_4.[4f)] Kinetic studies on the reaction suggested that the active oxygen species responsible for the activation of CH_4 is not monoatomic oxygen species but diatomic ones such as O_2, O_2^-, or O_2^{2-} on the surface of Sm_2O_3.[4g)] In this communication we describe the reaction between CH_4 and the peroxide anions O_2^{2-} of Na_2O_2, BaO_2, and SrO_2 in order to get information about the active oxygen species responsible for oxidative coupling of CH_4.

The Na_2O_2, BaO_2, and SrO_2 powders used were obtained from Wako Pure Chemical Company. The purity of the metals in each peroxide was >99%. The experiments were carried out using a conventional closed gas-circulation apparatus. A conventional microcatalytic method using a gas-flow system (He carrier) was also applied for the test of the reactions.

Before each run of reaction, the metal peroxides were treated in a vacuum or in a stream of helium at the reaction temperatures. Evolution of oxygen from the oxides was observed during this pretreatment. The reaction of CH_4 with the peroxides was carried out by introducing pure methane into the reaction system after the evolution of oxygen ceased. For the microcatalytic experiments, a volume of methane 1.2 ml STP was introduced into the helium stream (40 ml STP min^{-1}) upstream from the peroxides (0.60 g). The conversion of CH_4 and the yields of products were calculated on the basis of carbon number of CH_4 reacted.

Table 1 shows the effects of temperatures and the pressure of oxygen on the conversion of methane and the yields of C_2H_6 and C_2H_4 observed for the reaction between Na_2O_2 [$(Na^+)_2O_2^{2-}$] and CH_4 using the microcatalytic method. Formation of C_2H_6 was clearly observed at the temperatures above 573 K. The yield of C_2-compounds reached to 11.2% at 673 K. These observations show that the oxygen species in Na_2O_2 are reactive for the oxidative coupling of CH_4 even at the temperatures below 673 K. It is to be noted that the reaction products observed were only C_2H_6 and C_2H_4. The quantity of C_2-compounds produced corresponds to 18 to 56% of that of CH_4 reacted on the basis of carbon balance. The absence of CO, CO_2, and H_2O in the gas phase indicates that these compounds are captured by Na_2O_2. Actually, separate experiments showed that H_2O, CO and CO_2 were irreversibly captured by Na_2O_2 at 573 K.

The presence of oxygen in the gas phase decreased the yield of coupling products (Table 1). This observation suggests that the active oxygen species capable to break C-H bond of CH_4 can not be created from the oxygen in the gas phase.

Table 1. Oxidative coupling of CH_4 by Na_2O_2

Reaction temp. /K	Pressure of O_2 in a pulse /kPa	% Conversion of CH_4	% Yields C_2H_6	% Yields C_2H_4
523	0	0	0	0
553	0	<1	trace	0
573^a	0	<1	0.10	0
573^a	10	0	0	0
573^a	20	0	0	0
598	0	<1	0.44	0
623^a	0	7.8	2.20	0
623^a	10	6.5	1.77	0
623^a	20	6.3	1.09	0
653	0	25.5	6.07	0.17
673	0	62.4	11.02	0.18

Pressure of CH_4 in a pulse was 101 kPa. a) Pressure of CH_4 was 50 kPa.

Figure 1 shows the ESR spectra of the oxygen species observed at 77 K for the Na_2O_2 samples treated under different conditions as follows:
(a), Fresh Na_2O_2 sample degassed at room temperature for 30 min. Strong signal due to O_2^- was observed;[12] (b), Sample (a) was degassed for 30 min at 573 K.

The signal due to O_2^- disappeared after this treatment; (c), Sample (b) was contacted with oxygen at 13.3 kPa and 573 K. The signal due to O_2^- reappeared, but the intensity was two orders of magnitude lower than that of sample (a). The products from CH_4 were measured by microcatalytic method during that the temperature of fresh Na_2O_2 (sample (a)) was gradually increased up to 423 K. Conversion of CH_4 did not occur at all during this procedure. Reactivity of sample (b) for the oxidation of CH_4 was greater than that of sample (c), which was examined at 573 and 623 K. These observations strongly suggest that the O_2^- ions would not contribute to C-H bond activation.

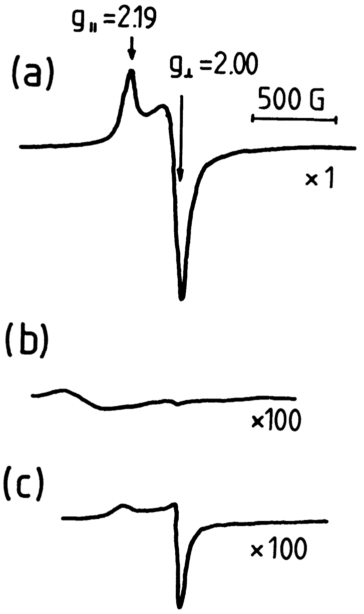

Fig. 1. ESR spectra of the oxygen species in the Na_2O_2 sample.

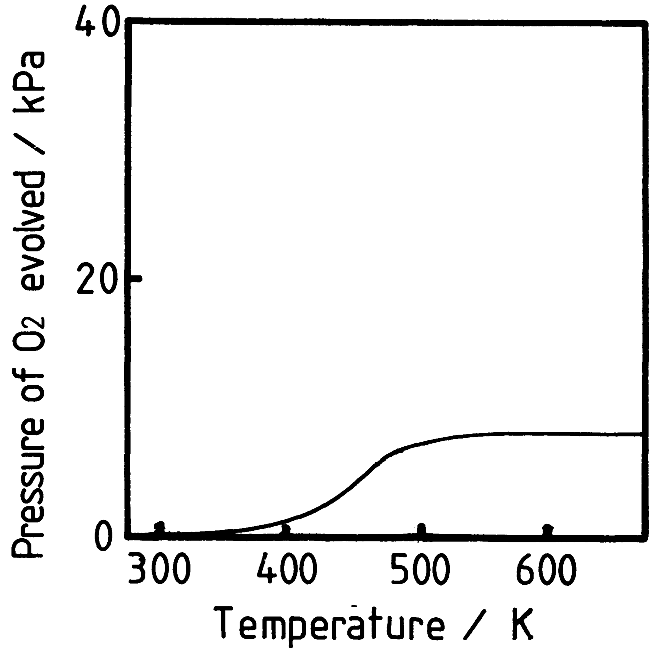

Fig. 2. Oxygen evolution from the Na_2O_2 sample with raising temperatures.

Figure 2 shows the pressure of oxygen evolved from the fresh Na_2O_2 sample (0.50 g) with increasing temperature of the oxide at a rate of 5 K/min. The experiment was carried out using closed system of 118 ml volume. As can be seen in Fig. 2, oxygen evolved at the temperature range 373-523 K. The evolution of oxygen was completed at 523 K, because no further desorption observed at 523 - 673 K. Evacuation of oxygen in the gas phase did not cause any further desorption of oxygen at 598 K. The evolution of oxygen can be ascribed to the decomposition of NaO_2 ($Na^+O_2^-$) contained as an impurity in the original Na_2O_2 sample. The NaO_2 is responsible for the ESR spectra for sample (a) in Fig. 1. The decomposition of NaO_2 may be written as follows,

$$2NaO_2 \longrightarrow Na_2O_2 + O_2 \qquad (1)$$

The total amount of oxygen evolved at the temperatures up to 623 K corresponded to about 9% of the amount of oxygen in the original sample.

The maximum amount of C_2-compounds produced at 598 K over Na_2O_2 was 3.5×10^{-5}

mol/g-Na_2O_2. Since two oxygen atoms per C_2H_6 molecule are needed, the oxygen atoms used for synthesizing C_2-hydrocarbons were 7.0×10^{-5} mol/g-Na_2O_2. The surface area of the Na_2O_2 sample measured by BET method using N_2-adsorption was 0.73 m^2/g. Assuming that the number of Na_2O_2 units on the surface is roughly 3×10^{18} m^{-2} on the basis of lattice parameters of the oxide, the number of oxygen atoms needed for synthesizing C_2-compounds is 9 times greater than the number of surface oxygen atoms. Thus, it is almost certain that the lattice oxygens of Na_2O_2 on the surface as well as in the bulk would contribute to the oxidative coupling of CH_4.

BaO_2 and SrO_2 were also effective in oxidative coupling of CH_4 at >623 and >473 K, respectively. Since oxidative coupling of CH_4 usually needed higher temperatures than 873 K,[1-7)] the results in this work show that the peroxides are specifically active in C-H bond breaking of CH_4. Thus, it is clear that O_2^{2-} ions are very reactive oxygen species for converting CH_4 into C_2-hydrocarbons.

In conclusion, we suggest that peroxide anions O_2^{2-} could be the oxygen species responsible for activation of methane in partial oxidations over rare earth metal oxides and alkali metal promoted oxides.

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