Effect of Oxidants on the Oxidative Coupling of Methane over a Lead Oxide Catalyst

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Oxidative coupling of methane was studied over a PbO/MgO catalyst using a variety of oxidants such as N_2O, NO, CO_2, and SO_2. While N_2O showed both high activity and selectivity for the title reaction, NO produced CO_2, exclusively. The coupling reaction was assumed to proceed via the redox cycle of Pb and PbO on each oxidant mentioned above. Carbon dioxide produced small amounts of C_2 hydrocarbons and CO, while SO_2, was inactive for the reaction. Oxygen, N_2O, CO_2 could oxidize the Pb/MgO which had been formed by the reaction of PbO/MgO with methane at 1023 K. Thus-prepared PbO/MgO produced C_2 hydrocarbons from methane. Even NO, which gave no C_2 hydrocarbons in the CH_4–NO cofeed reaction, converted the Pb/MgO to PbO/MgO and the PbO/MgO gave C_2 hydrocarbons exclusively upon reacting with CH_4. NO seems to oxidize the methyl radical, which is an intermediate of the coupling reaction to CO_2. The ineffectiveness of SO_2 as an oxidant was attributed to the formation of PbS, which is inactive in the methane activation.

Since the pioneering work by Keller and Bashin,1) a great number of catalysts have been found to be effective for the title reaction. The reaction systems reported so far are classified into 4 groups:

(A) Metal oxides, which exhibit abilities to change the oxidation state easily under reaction conditions, such as PbO,2,3) MnO,5) Bi_2O_3,6) NiO,7) and Tl_2O_3.8)

(B) Alkaline earth metal oxides, such as MgO and CaO, which are undoped9,10) or doped with Li^+,11–14) Na^+,15) K^+,16) alkaline earth metal halide17,18) or rare earth oxides.19)

(C) Rare earth oxides, which are undoped20) or doped with alkali metal compounds.21)

(D) Noncatalyzed gas-phase reaction.22,23)

Active oxygen species for the catalysts which belong to group (A) have been claimed to be bulk oxygen in metal oxides,7,24) while the surface oxide ion or adsorbed oxygen has been proposed for the catalysts of group (B) and group (C).12,25,26)

Oxidants other than O_2, such as N_2O or CO_2, have been applied to the methane coupling reaction. Ito et al. compared the reactivity of dinitrogen monoxide to methane with O_2 over a lithium promoted magnesium oxide catalyst and concluded that dinitrogen monoxide is not a preferable oxidant.12) Otsuka et al. studied the effect of N_2O oxidation over a series of rare earth oxides and confirmed that N_2O gave a lower conversion of methane but a higher selectivity for C_2 hydrocarbons than O_2.27) Meng et al. examined methane activation by N_2O over lead oxide catalysts supported on γ-Al_2O_3 and NaY zeolite to find that C_2 hydrocarbons were formed with a selectivity of 40%.28) Hutching et al. found that on a Li/MgO catalyst N_2O promoted CH_4 coupling but NO inhibited the reaction while giving CO_2, exclusively and claimed the presence of two oxidizing species on the catalyst.29) We have reported that in the noncatalyzed gas-phase system N_2O gave a higher selectivity than O_2 for the formation of C_2 hydrocarbons from CH_4, whereas NO was inactive for the reaction.22) We also reported that methane reacted with CO_2 to form C_2 hydrocarbons and CO over a PbO/MgO catalyst.30) Aika and Nishiyama also reported a promotional effect of added CO_2 on the CH_4–O_2 cofeed reaction over PbO/MgO.31)

In this study the effects of a series of oxidants such as O_2, N_2O, NO, SO_2 and CO_2 were examined systematically over a PbO/MgO catalyst in order to clarify how each oxidant activates methane and the active oxygen species for the coupling reaction.

Experimental

The catalyst used was 20 wt%-PbO/MgO, prepared by impregnating commercially available magnesium with lead(2) nitrate from aqueous solution and then calcining it at 800 °C.10) Methane oxidation reactions were conducted with a fixed-bed flow-type reaction apparatus under atmospheric pressure; the catalyst charge was 1 g. The reactor was a quartz tube with an inner diameter of 10 mm, in which another quqartz tube (6 mm o. d.) was inserted as a thermocouple holder. Methane conversions were performed according to the following two procedures: One was a CH_4–oxidant cofeed reaction and another was a periodic oxidation–reduction reaction. The reaction conditions of the cofeed reaction were 650—800 °C, W/F=1 g h mol^{-1}, $P(CH_4)$=14 kPa, P(oxidant)=1—4 kPa, and helium balance. In the case of CO_2, the composition of the reactant was CH_4:CO_2=1:1 and W/F was 5 g h mol^{-1}.

A periodic reaction was conducted along the following flow module: Air oxidation⟶N_2 purge(5 min)⟶CH_4 reaction(20 min) N_2 purge(20 min)⟶Oxidation(10 min). The cycle of the CH_4 reaction and oxidation was repeated at least 2 times. The procedure of the periodic reaction has

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been described elsewhere.[24] However, the first activation of the catalyst was performed by oxygen (air); then the second and the third activations were performed by each oxidant. All of the reactions and products were analyzed by gas chromatography. The separation columns used were Porapak R for dinitrogen monoxide and sulfur dioxide and MS-13 X for nitrogen monoxide, respectively. The analysis methods for other reactants and produucts have been described elsewhere.[24] A Toshiba-Beckmann 951 NO/NO_x meter was also used for the analysis of nitrogen monoxide. X-Ray diffraction (XRD) measurements of the catalysts were recorded with a Rigaku Denki Ru-200 diffractometer with Ni-filtered Cu-K radiation.

Results and Discussion

Thermodynamic Consideration. The free-energy changes of ethane formation from methane with these oxidants are shown in Table 1. From a thermodynamic perspective, oxygen and nitrogen oxides are favorable oxidants for a coupling reaction ($G°_f<0$), whereas sulfur dioxide and carbon dioxide are unfavorable ($G°_f>0$). However, the equilibrium conversion of methane by CO_2 oxidation is about 10% under the conditions of 750 °C, $CH_4/CO_2=1$, and normal pressure.

CH_4-Oxidant Cofeed Reaction. In Fig. 1 are shown the space-time yields (STY) of the reaction products obtained by various cofeed reactions at 750 °C over a 20 wt%-PbO/MgO catalyst. The partial pressure of dinitrogen monoxide and nitrogen monoxide in the feed gas was set to be about twice that of oxygen in order to adjust the CH_4–O stoichiometry. In the case of the CH_4–CO_2 reaction, $P(CO_2)$ and the modified residence time (W/F) were 50 kPa and 5 g h mol^{-1}, respepctively, because of the low reaction rate.

(a) N_2O. Dinitrogen monoxide gave a similar STY of CH_4 oxidation (12.8 mmol g^{-1}h^{-1}) to that obtained by O_2 (11.6 mmol g^{-1} h^{-1}), the values of which correspond to CH_4 conversions of 8.5 and 8.1%, respepctively (Fig. 1). The product distribution was also similar to that of the CH_4–O_2 reaction, except for the lack of CO. The temperature dependence of the reaction using N_2O revealed that a higher temperature is favored for making C_2 hydrocarbons (Fig. 2), which is also similar to the case of O_2 oxidation.[10] We have reported that N_2O is effective to make C_2 hydrocarbons in a noncatalyzed system[22] while giving a higher selectivity (88%). However, the production rate was lower by about two orders of magnitude than that in the

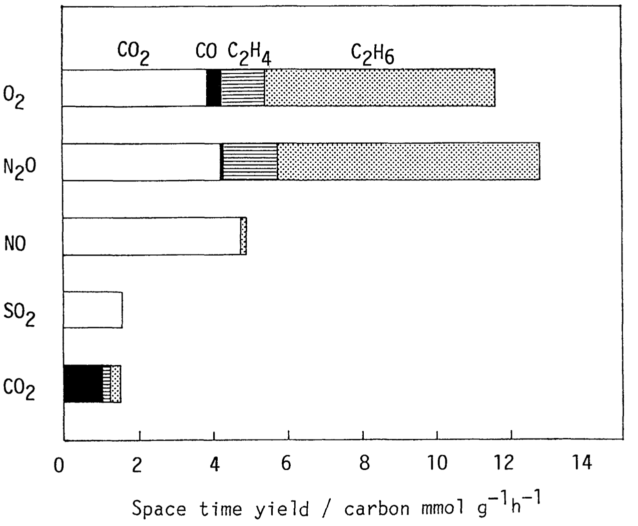

Fig. 1. Effect of oxidant on oxidative coupling of methane. Cat.; 20 wt%-PbO/MgO, 750 °C, $W/F=$ 1.0 g h mol^{-1}, $P(CH_4)=14$ kPa, P(oxidant)=1.6 kPa (for O_2, N_2O, NO, SO_2), $W/F=5.0$ g h mol^{-1}, $P(CH_4)=$ 5 kPa, $P(CO_2)=5$ kPa, (for CO_2).

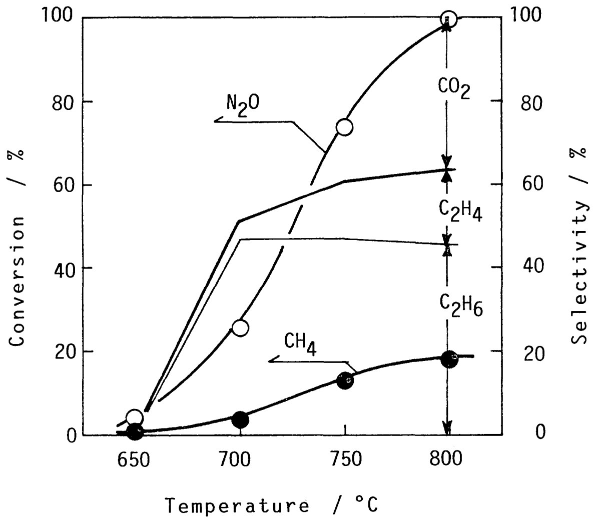

Fig. 2. Effect of temperature on the oxidative coupling of methane with N_2O as oxidant. Cat.; 20 wt%-PbO/MgO, 1.0 g h mol^{-1}, CH_4:N_2O:He= 10:4:86.

Table 1. Changes in Gibbs Free Energy in Oxidative Coupling of Methane with Various Oxidants

Reaction		$\Delta G_f°$/kcal mol^{-1}		
		700 °C	750 °C	800 °C
$2CH_4+1/2O_2 \rightarrow C_2H_6+H_2O$	(1)	−28.9	−28.1	−27.3
$2CH_4+N_2O \rightarrow C_2H_6+H_2O+N_2$	(2)	−66.2	−66.5	−66.7
$2CH_4+1/2NO \rightarrow C_2H_6+H_2O+1/2N_2$	(3)	−47.7	−46.8	−45.9
$2CH_4+1/2SO_2 \rightarrow C_2H_6+H_2O+S$	(4)	7.2	7.9	8.7
$2CH_4+1/3SO_2 \rightarrow C_2H_6+2/3H_2O+1/3H_2S$	(5)	6.2	6.6	7.0
$2CH_4+CO_2 \rightarrow C_2H_6+H_2O+CO$	(6)	17.8	17.4	16.9

present case, indicating that the reaction in the present system proceeds mainly on the catalyst surface.

The oxidative coupling of CH_4 over PbO/MgO has been clarified to be consist of a redox cycle between Pb and PbO; that is, a methane conversion into C_2 hydrocarbons by PbO (Eq. 7) and a reoxidation of metallic Pb with dioxygen (Eq. 8):

$$2\,CH_4 + PbO \longrightarrow C_2H_6 + H_2O + Pb, \tag{7}$$

and

$$Pb + 1/2O_2 \longrightarrow PbO. \tag{8}$$

The Gibbs free energy changes for the oxidation of Pb by N_2O oxidants shows as listed in Table 2 that the N_2O reaction with PbO (Eq. 9) is also thermodynamically favorable, as well as O_2. Therefore, the mechanism for the formation of C_2 hydrocarbons by N_2O is believed to be the same as that by O_2; namely, the reaction of CH_4 with PbO (Eq. 7) and the reoxidation reaction of reduced lead by N_2O (Eq. 9). We have confirmed that N_2O was completely decomposed to N_2 and O_2 on the PbO/MgO catalyst at 750 °C. Therefore, it is not clear whether N_2O reacts directly with Pb or after being converted to O_2.

(b) NO. Although a methane oxidation with NO is thermodynamically favorable (Table 1), the yield of C_2 hydrocarbons in the CH_4–NO reaction was much lower than those in the O_2–or N_2O– oxidation on the PbO/MgO catalyst, as indicated in Fig. 1. As shown in Table 3, CO_2 was formed exclusively (selectivity; >97%) under all reaction conditions. However, NO exhibited a strong oxidative ability of Pb; the oxidized Pb by NO gave C_2 hydrocarbons as well as N_2O or O_2 (Table 4). Therefore, the extremely low selectivity of C_2 hydrocarbons in a cofeed reaction might be interpreted in terms of the two prossible reasons given below.

[1] surface oxygen species derived from NO is active only for a complete oxidation of methane. The species would be an adsorbed one on PbO (PbO–O_x), since such a species derived from O_2 is considered to be active regarding the formation of carbon oxides.[24]

[2] NO inhibits a coupling reaction; thus molecular NO attacks the methyl radical, which is formed by the reaction of CH_4 with PbO, in the gas phase to form CH_3NO. It is then finally decomposed to CO_2. It is well-known that nitrogen monoxide is a radical inhibitor.[32] The fact that NO oxidized Pb to PbO and PbO oxidized CH_4 to C_2H_6 by periodic oxidation (Table 4 and Fig. 4) suggests that concept [2] is more plausible.

(c) SO_2. When sulfur dioxide was used as an oxidant, CO_2 was produced exclusively, as shown in Fig. 1. Though other by-products (not shown) were carbonyl sulfide and elemental sulfur, neither hydrogen sulfide nor methane thiol was formed. Further consideration is presented later.

(d) CO_2. It is noticeable that the oxidative coupling of methane proceeded to some extent by utilizing CO_2 as an oxidant (Fig. 1). The product distribution is explained by assuming the following reaction stoichiometry (Eq. 14—16):

$$CO_2 \longrightarrow CO + (O), \tag{14}$$

$$2\,CH_4 + (O) \longrightarrow C_2H_6 + H_2O, \tag{15}$$

Table 2. Changes in Gibbs Free Energy in Oxidation of Lead with Various Oxidants

Reaction		$\Delta G_f°$/kcal mol^{-1}		
		700 °C	750 °C	800 °C
$Pb+1/2O_2 \rightarrow PbO$	(8)	−29.6	−28.5	−27.4
$Pb+N_2O \rightarrow PbO+N_2$	(9)	−67.0	−66.9	−66.8
$Pb+NO \rightarrow PbO+1/2N_2$	(10)	−48.4	−47.2	−46.0
$Pb+1/2SO_2 \rightarrow PbO+1/2S$	(11)	6.4	7.5	8.6
$Pb+CO_2 \rightarrow PbO+CO$	(12)	17.0	16.9	16.8
$Pb+S \rightarrow PbS$	(13)	−22.5	−22.4	−22.4

Table 3. Methane Conversion by NO over 20 wt%-PbO/MgO Catalyst. W/F=1.0 g h mol^{-1}, He Balance

	Concentration/mol%				
CH_4	11.5	16.0	12.1	13.1	12.7
NO	1.5	3.7	7.5	3.7	3.7
Temperature/°C	750	750	750	800	700
Conversion/mol%					
CH_4	2.0	3.3	4.0	5.6	2.1
NO	6.3	7.2	19.4	24.5	3.5
Selectivity/C-mol%					
C_2H_6	1.7	1.0	0	2.5	0
CO_2	98.3	98.9	100	97.5	100

Table 4. Characterization of PbO Catalyst by XRD.[a] Same Experiments Shown in Figs. 3 to 6

	Oxidant	XRD peak		
		PbO	Pb	PbS
After oxidation	O_2	VS	—	—
	N_2O	VS	—	—
	NO	VS	—	—
	SO_2	W	—	S
	CO_2	VS	—	—
After CH_4 conversion	O_2	VW	VS	—
	N_2O	VW	VS	—
	NO	VW	VS	—
	SO_2	—	W	S
	CO_2	VW	VS	—

a) Peak intensity: VS; very strong, S; strong, W; weak, VW; very weak, —; not detected.

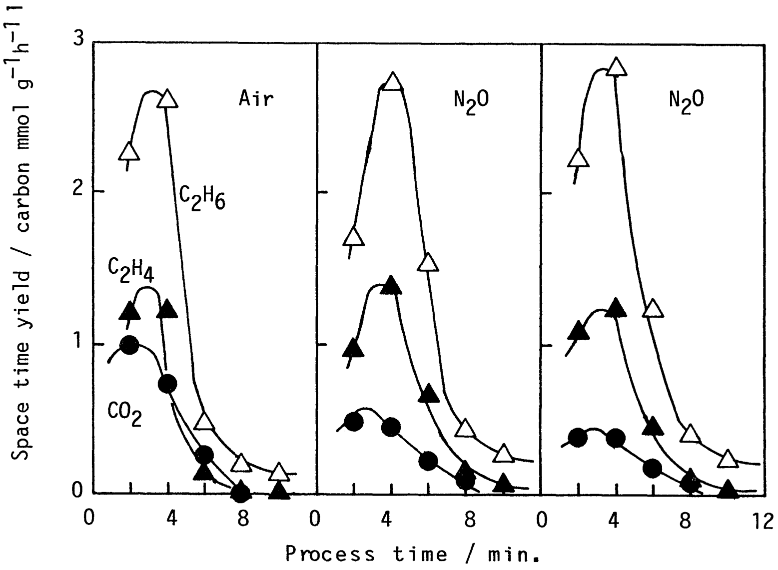

Fig. 3. Transient response of periodic CH_4 conversion: Effect of N_2O reoxidation. Cat.; 20 wt%-PbO/MgO, 750 °C, 4.3 g h mol^{-1}.

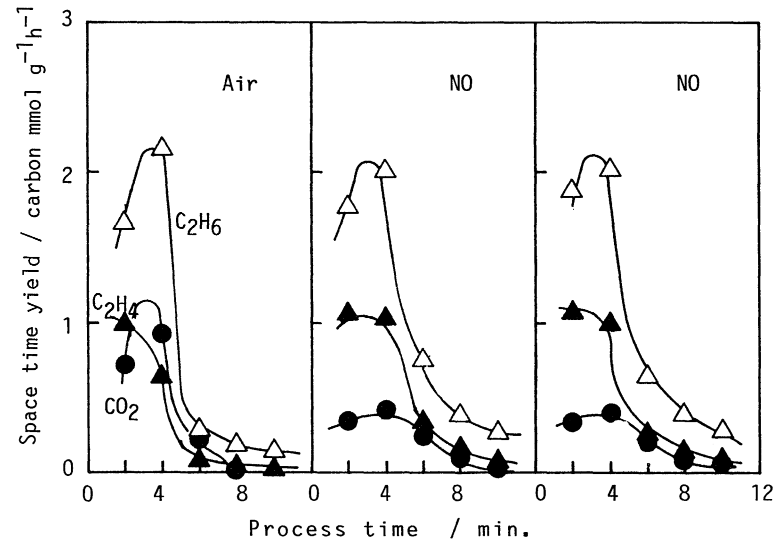

Fig. 4. Transient response of periodic CH_4 conversion: Effect of NO reoxidation. Cat.; 20 wt%-PbO/MgO, 750 °C, 4.3 g h mol^{-1}.

and

$$2\,CH_4 + 2\,(O) \longrightarrow C_2H_4 + 2H_2O. \qquad (16)$$

Carbon dioxide is dissociated to carbon monoxide and a reactive surface oxygen species (O) (Eq. 14), which may react with methane to form ethane (Eq. 15) and ethylene (Eq. 16). In fact, CO_2 oxidized Pb to PbO and PbO oxidized CH_4 to C_2H_6 (Table 4 and Fig. 5). However, the amount of CO formed was larger than the amount calculated from reactions (14)—(16). Thus, reaction (17) should be accounted for. Reactions (14) and (17) are converted to the reaction stoichiometry shown in Eq. 18, which means that one fourth of the CO was formed from CH_4.

$$CH_4 + 3\,(O) \longrightarrow CO + 2\,H_2O \qquad (17)$$

$$C^*H_4 + 3\,CO_2 \longrightarrow C^*O + 3\,CO + 2\,H_2O \qquad (18)$$

The product distribution is shown as Fig. 1. Even at 800 °C the selectivity of C_2 hydrocarbons was not high. Thus low selectivity might be attributed to the formation of surface $MgCO_3$, which is not a favorable

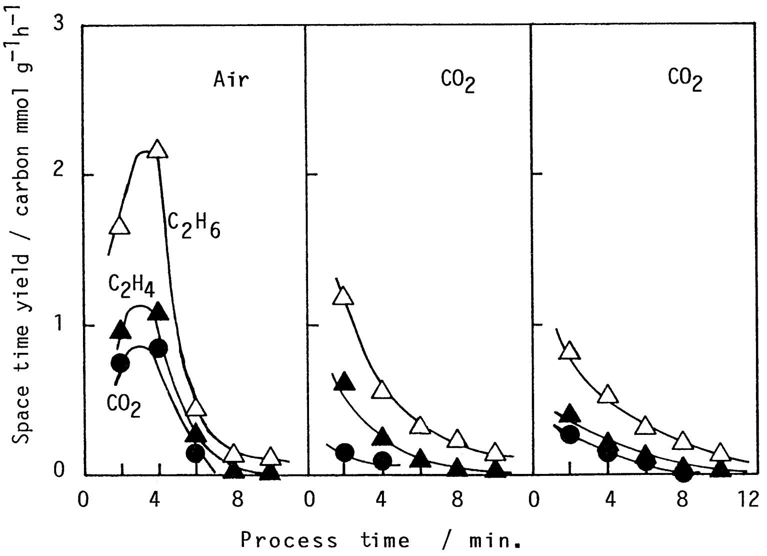

Fig. 5. Transient response of periodic CH_4 conversion: Effect of CO_2 reoxidation. Cat.; 20 wt%-PbO/MgO, 750 °C, 4.3 g h mol^{-1}.

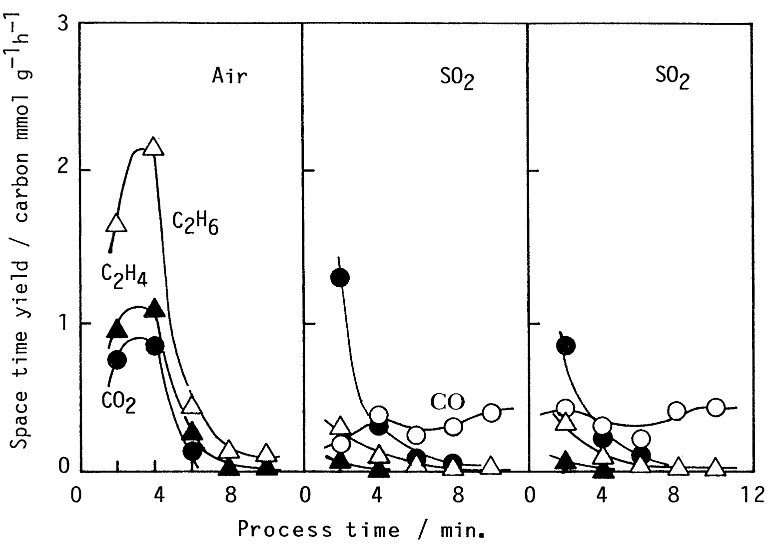

Fig. 6. Transient response of periodic CH_4 conversion: Effect of SO_2 reoxidation. Cat.; 20 wt%-PbO/MgO, 750 °C, 4.3 g h mol^{-1}.

support material. This subject will be discussed later.

Periodic Oxidation-Reduction Reaction. In the case of the CH_4-oxidant cofeed reaction, O_2 and N_2O exhibited excellent performance in the formation of C_2 hydrocarbons, similar to that of O_2, whereas other oxidants (NO, SO_2, and CO_2) did not produce the desired products selectively (as described above). However, a periodic oxidation-reduction reaction gave different results, as shown in Figs. 3 to 6. Also, the lead species identified after each reaction are shown in Table 4.

(a) N_2O, NO, and CO_2. Dinitrogen monoxide gave a similar result to that of the cofeed reaction containing O_2. Also, the periodic reaction gave C_2H_6 selectively over a catalyst which was oxidized by N_2O as demonstrated in Fig. 3. These facts correspond to that regarding O_2, which suggests that the oxidation state of lead oxidized by N_2O is similar to that oxidized by O_2 (Table 2).

Although little C_2 hydrocarbons were formed in a cofeed reaction containing NO (Fig. 1), they were formed with high selectivity in the CH_4-NO periodic reaction (Fig. 4). It was also clarified that NO has an ability to oxidize metallic Pb to PbO, and PbO gave C_2

hydrocarbons upon a reaction with CH_4, as demonstrated in Table 4. This means that although the redox cycle is possible in the CH_4–NO cofeed reaction system, NO inhibits the coupling reaction, probably because it reacts with the methyl radical to form CO_2. C_2 hydrocarbons were formed selectively at a comparable rate in a periodic CH_4–CO_2 operation (Fig. 5), while the rate of C_2 formation in a cofeed reaction was much lower than that in the O_2-containing cofeed reaction (Fig. 1). However, the amount of C_2 hydrocarbons formed in the second treatment was slightly smaller and the amount of CO formed was slightly larger than that obtained in the first treatment. This observation might be attributed to the formation of a surface carbonate species of carrier material of the catalyst (MgO) which is unfavorable for the coupling reaction.[24)]

(b) SO_2. When sulfur dioxide was used as an oxidant, a small amount of C_2 hydrocarbons was formed in the periodic reaction (Fig. 6), although no C_2 hydrocarbons were formed at all in the cofeed reaction. The low CH_4 selectivity even in a periodic reaction, should be attribuuted to the formation of PbS according to Eqs. 11 and 13 during a reaction with SO_2 (Table 4), since PbS is never reduced by a reaction with CH_4. It is thus concluded that the redox cycle expressed as reactions (7) and (11) is inhibited by the formation of PbS.

Conclusion

Methane activation with a MgO-supported PbO catalyst was studied by using a variety of oxidants such as O_2, N_2O, NO, SO_2, and CO_2 resulting in the following conclusion:

1) In a CH_4–oxidant cofeed reaction, N_2O exhibited excellent activity and selectivity for the formation of C_2 hydrocarbons as well as O_2, whereas NO and CO_2 gave only small amounts of the desired product and SO_2 made no C_2 hydrocarbons.

2) Not only O_2 and N_2O, but also NO and CO_2, showed high selectivity for the formation of C_2 hydrocarbons in a periodic oxidation–reduction operation. This was because of the formation of PbO, which gave C_2 hydrocarbons upon a reaction with CH_4, with the reaction of a reduced catalyst and these oxidants as well as O_2 and N_2O. However, NO or CO_2 seems to have some inhibiting effect on the coupling reaction.

3) When SO_2 was used as an oxidant for methane conversion, lead sulfide was formed, which impeded the coupling reaction in either the cofeed reaction or the periodic reaction.

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