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Selective Oxidative Coupling of Methane over Supported Lead Oxide Catalyst

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It was found that lead oxide catalysts supported on basic materials such as MgO and β''-Al_2O_3 were excellent catalysts for the oxidative coupling of methane to C_2 hydrocarbons. For example, PbO/MgO catalyst gave 11.1 mmol/g·h of C_2 STY and 87% of C_2 selectivity under the conditions of 750 °C, W/F=1.0 g·h/mol, $P(CH_4)$=61 kPa, $P(O_2)$=1.6 kPa and atmospheric pressure.

Methane is a main constituent of natural gas of which proved reserve is very large. The largest part of the current use for methane is that as fuel. In chemical meaning methane is most inactive and , therefore, it has been used largely for the production of synthesis gas by steam reforming. Recently, keen attention is being paid to oxidative coupling reaction of methane to C_2 hydrocarbons as chemical raw material. Supported PbO catalysts have been reported to be active for this reaction by Keller et al.1) and Hinsen et al.2) However, the selectivity to C_2 hydrocarbons was poor (<58%) on γ-Al_2O_3-supported catalyst, and C_2 STY was low (0.75 mmol/g·h) on SiO_2-supported catalyst. Hinsen et al. also pointed out that alkali addition to PbO/γ-Al_2O_3 catalyst gave increased selectivity for C_2.2) The other catalysts which are reported to be active for this reaction such as rare earth metal oxides3) and Li/MgO4) have basic character. On the other hand, C_2 hydrocarbons were scarecely obtained on acidic catalysts such as H-ZSM5, using dioxygen as the oxidant.5) In view of the above, acidity or basicity of catalysts are significant to this reaction.

In the present work, a number of supported PbO catalysts have been prepared and tested proving that basic carriers such as MgO or β''-Al_2O_3 are excellent materials for producing C_2 hydrocarbons from methane. Some of the catalytic properties of PbO/MgO have been also studied.

All the catalysts used were prepared by impregnating supports with aqueous solution of $Pb(NO_3)_2$ by a dry-up method, followed by drying in air at 120 °C for 12 h. PbO loading was 20 wt%. They were activated in flowing air at 750 °C for 0.5-1 h in situ. All the supports were used after calcination in air at 800 °C for 2 h before impregnation. The size of the catalysts was 20-40 mesh. Activity tests were performed with a flow type reaction apparatus. The reactor was a quartz tube with 10 mm inner diameter. The standard reaction conditions were 750

^{o}C, 1.0 g·h/mol, atmospheric pressure, P(CH_4)=14 kPa, and P(O_2)=1.6 kPa and the balance was nitrogen gas. Catalyst loaded was 1.0 g in weight. All the reactants and products were analysed by gas chromatography.

Table 1 shows the experimental results obtained over PbO catalysts on various supports. All data were taken when the activities reached steady state (4-5 h) except for MgO and β''-Al_2O_3 (24 h). The yield in the table is conversion of methane to each product. Although oxygen conversions were fairly high (40-100%) on acidic carriers such as γ-Al_2O_3 and SiO_2-Al_2O_3, carbon oxides were formed predominantly over C_2 hydrocarbons. Even in the case of PbO/γ-Al_2O_3, which has been reported to be active for this reaction,2) the selectivity to C_2 hydrocarbons

Table 1. Effect of carrier material on PbO catalyst

Carrier	Conversion /%		Yield /%				Selectivity /%			
	O_2	CH_4	C_2H_6	C_2H_4	CO	CO_2	C_2H_6	C_2H_4	CO	CO_2
γ-Al_2O_3	100	7.8	1.24	1.19	0.10	5.20	16.1	15.4	1.3	67.2
SiO_2-Al_2O_3a)	52.9	3.3	0.03	0.05	2.33	0.82	0.8	1.5	72.3	25.5
SiO_2-Al_2O_3b)	42.4	2.4	0.06	0.05	1.46	0.92	2.5	1.8	58.8	36.9
SiO_2c)	29.9	2.4	1.11	0.18	0	1.13	45.8	7.5	0	46.6
SiO_2d)	0.5	0.1	0.09	0	0	0	100	0	0	0
α-Al_2O_3	1.8	0.1	0.10	0	0	0	100	0	0	0
SiC	1.4	0.1	0.05	0	0	0	100	0	0	0
TiO_2	23.0	3.0	1.10	0.09	0	0.87	53.3	4.4	0	42.4
ZrO_2	9.1	1.1	0.46	0.04	0	0.60	41.9	3.4	0	54.7
ZnO	36.2	3.5	1.19	0.15	0	2.15	34.1	4.2	0	61.7
Nb_2O_5	9.6	0.9	0.12	0.10	0	0.67	13.7	0	10.9	75.4
CuO	23.5	1.2	0.13	0	0	1.10	10.6	0	0	89.4
SnO_2	46.2	4.6	1.99	0.36	0	2.21	43.6	7.9	0	48.5
BeO	79.5	5.8	2.39	0.31	0	3.14	48.9	5.3	0	53.8
MgO	84.3	10.0	5.29	1.30	0.25	3.21	52.6	12.9	2.4	32.0
CaO	100	10.1	3.02	0.48	0	5.31	34.3	5.5	0.1	60.2
SrO	16.5	1.7	0.67	0.08	0	0.95	39.4	4.9	0	55.7
BaO	14.8	1.5	0.54	0.03	0	0.95	35.8	1.9	0	62.3
$CaCO_3$	81.4	7.4	2.70	0.57	0	4.28	35.8	7.6	0	56.7
$SrCO_3$	52.5	3.9	1.37	0.22	0	2.29	35.2	5.8	0	59.0
$BaCO_3$	49.3	3.0	0.95	0.07	0	1.95	31.9	2.4	0	65.7
β''-Al_2O_3	88.6	10.1	5.19	1.25	0	3.64	51.5	12.4	0	36.1
La_2O_3	97.8	7.9	2.37	0.41	0	5.10	30.1	5.2	0	64.8

a)SiO_2/Al_2O_3=4.9. b)SiO_2/Al_2O_3=11.2. c)after 0.5 h. d)after 4 h
PbO loading;20 wt%, Reaction conditions;Temp 750 ^{o}C, W/F=1.0 g·h/mol, P(CH_4)=14 kPa, P(O_2)=1.6 kPa.

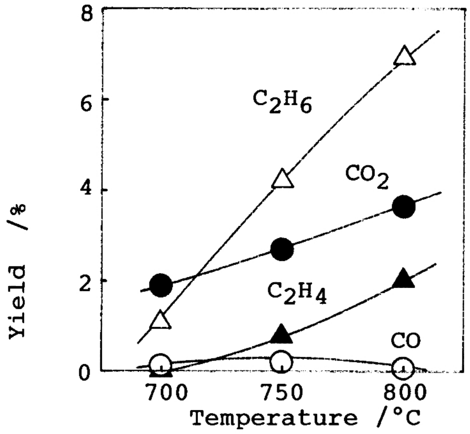

Fig. 1. The effect of temperature cat. PbO/MgO, W/F=1.0 g·h/mol, $P(CH_4)$=14 kPa, $P(O_2)$=1.6 kPa.

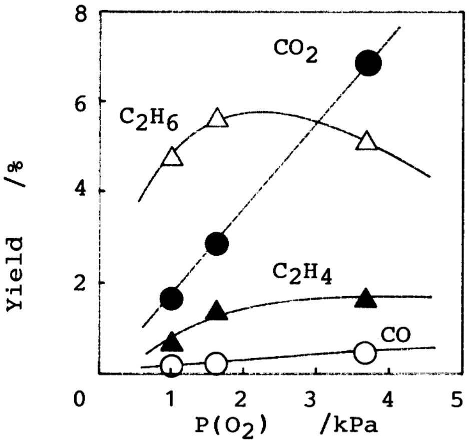

Fig. 2. The effect of $P(O_2)$ cat. PbO/MgO, Temp 750 °C, W/F=1.0 g·h/mol, $P(CH_4)$=14 kPa.

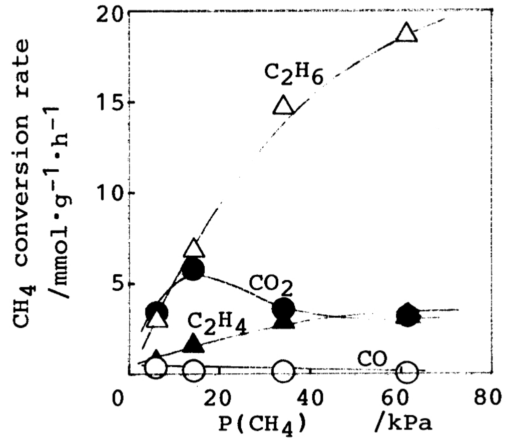

Fig. 3. The effect of $P(CH_4)$ cat. PbO/MgO, Temp 750 °C, W/F=1.0 g·h/mol, $P(O_2)$=1.6 kPa.

was 32% or less. Neutral supports such as SiO_2, α-Al_2O_3, and SiC showed poor O_2 conversions. In the case of SiO_2 deactivation was very fast, that is the O_2 conversion was 30% at 0.5 h of process time, and after 4 h O_2 conversion decreased to 0.5%. This observation coincides with that has been already reported[2]. It seems that PbO reacted with SiO_2 to form an inactive compound. As only ethane was detected from the initial period on α-Al_2O_3- or SiC-supported catalysts, apparent selectivity to C_2 hydrocarbons was nearly 100%. Over the PbO supported on the carriers weakly acidic or basic such as TiO_2, ZrO_2, and ZnO, oxygen conversions were not so high (9-36%) but the yields of C_2 hydrocarbons were fairly high (0.53-1.34%), and the CO_2 formation was relatively small. Thus the selectivity of C_2 hydrocarbons reached 40-60%. On the catalysts supported on basic materials such as oxides or carbonates of alkaline earth, β''-Al_2O_3, and La_2O_3, oxygen conversions (49.3-97.8%) and the yields of C_2 hydrocarbons (1-7%) were fairly high. The exceptional low activities of SrO- and BaO-supported catalysts might be attributed to their low surface area. Because their parent materials have exceptionally low melting points ($Sr(OH)_2$;375 °C and $Ba(OH)_2$; 408 °C) and thus melted during the calcination at 800 °C. Among these catalysts, MgO- and β''-Al_2O_3-supported catalysts showed outstanding yields and selectivities to C_2 hydrocarbons which were higher than 6% and 60%, respectively.

As MgO-supported catalyst showed the highest activity and selectivity for C_2 hydrocarbon formation, its catalytic performances were studied. Fig. 1 shows the dependence on reaction temperature under the standard conditions. With the increase in temperature, the increase in ethane and ethylene was larger than CO and CO_2, so that the selectivity to C_2 hydrocarbons increased from 38.5% to 70.8% as the temperature was raised from 700 °C to 800 °C. Experimental results obtained by changing partial pressure of O_2 in the feed gas from 1.0 kPa to 3.6 kPa while keeping $P(CH_4)$ at 14 kPa are shown in Fig. 2. Ethane yield increased with increasing $P(O_2)$ up to 1.6 kPa and then decreased. The yields of CO and CO_2 increased linearly, and ethylene yield slightly increased with increasing $P(O_2)$. Therefore, selectivity to C_2 hydrocarbons was decreased from 75.6% to 48.2%. The effects of $P(CH_4)$ on the reaction was also examined as demonstrated in Fig. 3. While the formations of CO and CO_2 increased with increasing $P(CH_4)$ up to 15 kPa and decreased above the pressure, those of ethane and ethylene were increased monotonously. Particularly, ethane production at 60 kPa was six times higher than that at 6.4 kPa and space time yield (STY) of C_2 hydrocarbons reached to 11.1 mmol/g·h. The value is comparable to those shown in the literature (Table 2). Moreover, at the pressure above 34 kPa, C_3 hydrocarbons (propane and propylene) were formed.

In conclusion, basic materials are effective as a carrier of PbO catalyst for oxidative coupling of methane, and the reaction is favored at higher temperature, lower $P(O_2)$, and higher $P(CH_4)$.

Table 2. Catalytic activity for oxidative coupling of methane

Catalyst	C_2 STY $mmol \cdot g^{-1} \cdot h^{-1}$	C_2 sel. %	Temp °C	$P(CH_4)$ kPa	$P(CH_4)/P(O_2)$	Ref. No.
PbO/SiO_2	0.75	71.4	740	70	10	2
Sm_2O_3	0.79	92.8	700	18.2	45	3
Li/MgO	0.25	50.3	720	7.9	2.0	4
Li/Sm_2O_3	1.41	57	750	5.1	2.5	6
$LaAlO_3$	8.31	48.4	710	50	5.0	7
PbO/MgO	11.10	85.3	750	61.3	37.8	This work

References

1) G.E. Keller and M.M. Bhasin, J. Catal., 73, 9(1982).
2) W. Hinsen, W. Bytyn, and M. Baerns, Proc. 8th Int. Congr. Catal., 3, 581(1984).
3) K. Otsuka, K. Jinno, and A. Morikawa, Chem. Lett., 1985, 499.
4) T. Ito, Ji-Xiang Wang, Chiu-Hsun Lin, and J.H. Lunsford, J. Am. Chem. Soc., 107, 5062(1985).
5) J.R. Anderson and P. Tsai, Appl. Catal., 19, 141(1985).
6) K. Otsuka, Q. Liu, M. Hatano, and A. Morikawa, Chem. Lett., 1986, 467.
7) H. Imai and T. Tagawa, J. Chem. Soc., Chem. Commun., 1986, 53.

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