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Active and Selective Catalysts for the Synthesis of C_2H_4 and C_2H_6 via Oxidative Coupling of Methane

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Active and selective catalysts for oxidative coupling of methane were tested over many metal oxides (30 oxides) under the experimental conditions chosen (T = 973 K, P_{O_2} = 0.4 kPa, P_{CH_4} = 18.2 kPa, P_{He} = 82.7 kPa). In general, the oxides of rare earth elements showed higher C_2-selectivity (C_2H_6 + C_2H_4) than 80%. Among the various metal oxides tested, Sm_2O_3 was the most active and selective catalyst in the formation of C_2-hydrocarbons (selectivity 93%). No appreciable decrease in activity and selectivity was observed after the experiments for 180 h at 973 K. The kinetic studies on the reaction over Sm_2O_3 were carried out under different experimental conditions. Relative rates of reactions of CH_4, C_2H_6, and C_2H_4 suggest that the overall reaction of CH_4 proceeds as follows:

$$\begin{tikzcd}
CH_4 \arrow[rr, "\mathrm{I}"] \arrow[dr, "\mathrm{III}"'] & & C_2H_6 \arrow[r, "\mathrm{II}"] \arrow[dl, "\mathrm{V}"] & C_2H_4 \\
& CO_2 + CO & &
\end{tikzcd}$$

The apparent activation energies for each path can be put in order as $E_{II} > E_I > E_V > E_{III}$. Therefore, the C_2-selectivity and the ratio of C_2H_4/C_2H_6 increase as the reaction temperatures were raised. The pressure effects on the rate of reaction observed showed that the C_2-selectivity becomes better when P_{O_2}/P_{CH_4} decreases. For example, at 18.2 kPa of P_{CH_4}, the C_2-selectivity approached 100% when the mole percentage of oxygen in reactants decreased to 1.6%.

INTRODUCTION

Methane is the most abundant component of natural gas, usually containing over 90 mol% of the hydrocarbon fraction of the gas. Oxidative dehydrogenation and subsequent coupling of methane to ethane and ethylene ($CH_4 \overset{O_2}{\rightarrow} C_2H_4, C_2H_6$) is an attractive attempt on the basis of the use of natural gas as a raw material for the synthesis of ethylene. Because of the high molecular stability of methane, its use as a raw material for the synthesis of higher hydrocarbons is very limited.

Keller and Bhasin (*1*) reported that the catalysts containing the oxides of Pb, Bi, Sn, Tl, Cd, or Mn were the most active catalysts for the formation of C_2-hydrocarbons (C_2H_4 + C_2H_6) with selectivities of ca. 50%. The selectivity is defined as the percentage of converted methane reacted to C_2H_6 and C_2H_4. Hinsen and Baerns (*2, 3*) reported that PbO on SiO_2 carrier was the best with respect to the C_2-selectivity approaching 72%, but its catalytic activity was low. As far as we know, this was the highest C_2-selectivity ever reported. Very recently, Ito and Lunsford reported that lithium-doped magnesium oxide in the presence of O_2 has high activity for converting methane to C_2-compounds (*4*).

Here we will describe the results of screening for the catalysts which exhibit better catalytic activity and selectivity of

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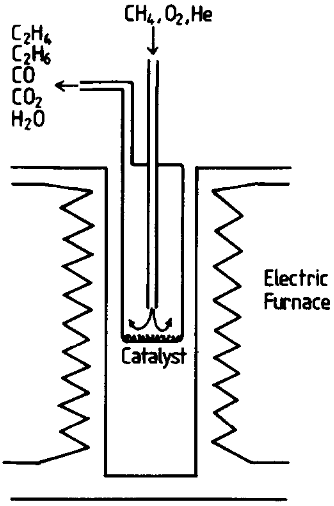

FIG. 1. Illustration of the reactor.

C_2-hydrocarbons (5). The reaction paths for the reaction over the best catalyst will also be discussed.

EXPERIMENTAL

The catalysts used were all reagent grade metal oxides (purity >99%) in the form of powder obtained from Asahi Chemical Industry Company and Wako Pure Chemical Company. Surface areas of the catalysts after the test for their catalytic efficiencies, were measured by means of BET method using nitrogen at 77 K. The apparatus for testing the various catalysts was a conventional gas flowing system for methane, oxygen, and helium, and the analytical equipment.

The catalysts (3–1000 mg) without dilution with inert bare supports were placed at the bottom of the quartz reactor. Internal diameter and length of the reactor were 2 and 10 cm, respectively (Fig. 1). Reactants were fed via a helium carrier over the catalysts. Since the space velocity at the reactor was very small (60–30 h^{-1}), the complete mixing of the gases by diffusion and convection in the reactor can be expected. In fact, the conversions of oxygen and methane observed for the outlet gas from the reactor were proportional to V/F.

The conditions for testing the various catalysts were chosen as follows: weight of catalyst = 500 mg, T = 973 K, $P^0_{CH_4}$ (pressure of methane at the entrance of the reactor) = 18.2 kPa, $P^0_{O_2}$ = 0.4 kPa, P^0_{He} = 82.7 kPa.

RESULTS AND DISCUSSION

Catalytic Efficiencies of the Metal Oxides

Catalytic activities and selectivities for the formations of C_2H_6, C_2H_4, and CO_2 have been tested for various rare earth metal oxides, PbO, Bi_2O_3, SnO_2, Ga_2O_3, GeO_2, In_2O_3, ZnO, CdO, CaO, and MgO at 973 K. The products were only C_2H_6, C_2H_4, CO, CO_2, and H_2O. The catalytic activities (rates per surface area of the catalysts) for the formations of C_2H_6 and C_2H_4 are shown in Fig. 2. Filled triangles in the figure indicate the activities for C_2-hydrocarbons (C_2H_4 + C_2H_6). The activities of the metal oxides which were reported to be good catalysts for the oxidative coupling of methane (*1–3*) are shown on the right side in Fig. 2. The catalytic activities for the rare earth metal oxides are plotted on the left. Figure 2 shows that the specific activ-

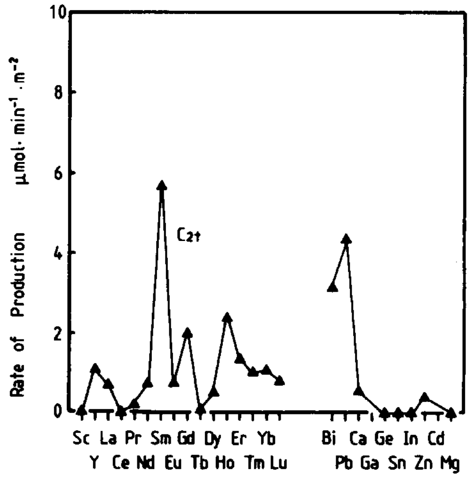

FIG. 2. Comparison of the catalytic activities of metal oxides. The metal elements of the oxides tested are shown on the abscissa. See text for experimental conditions.

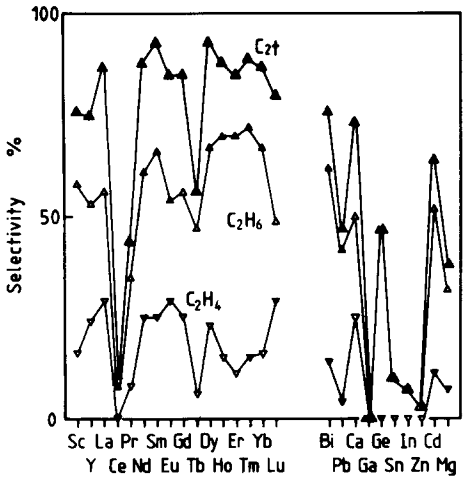

FIG. 3. Selectivities of C_2H_6, C_2H_4, and the sum of C_2-hydrocarbons (C_{2t}).

ity in the formation of C_2-hydrocarbons is the largest for Sm_2O_3.

The selectivities of C_2H_6 and C_2H_4 are plotted in Fig. 3. This figure shows that the oxides giving higher C_2-selectivity (C_2H_6 + C_2H_4, denoted by C_{2t}) than 70% are the rare earth metal oxides (except for the oxides of Ce, Pr, and Tb), Bi_2O_3, and CaO. Except for the oxides of Ce, Pr, and Tb, the lanthanide oxides, including lanthanum, showed particularly high C_2-selectivity (>80%). The selectivities for the Sm_2O_3 and Dy_2O_3 reached 93% which is the highest value ever reported. The acidic oxides such as HY, ZSM-5, $SiO_2 \cdot Al_2O_3$, or Al_2O_3 showed high catalytic activity for burning but low C_2-selectivity of less than 3%. The oxides in Fig. 3 are believed to have basic or amphoteric properties as their chemical nature. Generally, the latter oxides show high selectivity for the formation of C_2-hydrocarbons. These observations imply that basic sites on the surface of the catalysts play an important role in oxidative coupling of methane.

As described above, the highest selectivity and catalytic activity in the formation of C_2-hydrocarbons observed for Sm_2O_3 suggest that this oxide is the most promising catalyst among the metal oxides tested in this work. No appreciable decrease in activity and selectivity was observed for Sm_2O_3 after the operation of the experiments for 180 h at 973 K. Sm_2O_3 was a very stable catalyst for the reaction. Thus, we chose Sm_2O_3 and we will describe the catalytic efficiency of this oxide and as well as the kinetic studies on the reaction.

Catalytic Efficiency of Sm_2O_3 for Oxidative Coupling of Methane

Table 1 shows the effects of pressure of oxygen on the conversions of CH_4 and O_2 as well as on the selectivities of the products. The experiments were carried out at 973 and 1023 K at $P_{CH_4} = 18.2$ kPa and $P_{O_2} = 0.059$–3.50 kPa using 1.00 g Sm_2O_3. The formation of CO was observed at high oxygen pressure. However, under low oxygen pressure, all the CO formed must have been oxidized to CO_2.

The C_2-selectivity at 973 K increased from 85.9 to 98.5% when the pressure of oxygen decreased from 0.88 to 0.059 kPa. The C_2-selectivity observed at the lowest oxygen pressure was extremely high. The conversions of oxygen shown in the table are considerably high (62–77%) except for the case of the lowest oxygen pressure. The ratio of $[C_2H_4]/[C_2H_6]$ in the products increases as the ratio of $[O_2]/[CH_4]$ in the reactants increases. The selectivity of C_2H_4 exceeded that of C_2H_6 at 1023 K when P_{O_2} was raised above 1.37 kPa. In general, higher C_2-selectivity than 82% is observed when the fraction of oxygen in the reactants is less than 6% at both temperatures.

Temperature Effect on the Reaction

Temperature effects on the rates of formation of products and selectivities of the products are plotted in Fig. 4 as functions of temperature. The experiments were carried out at $P_{CH_4} = 18.2$ kPa and $P_{O_2} = 0.93$ kPa with a gas mixture flow rate of 37.5 ml min^{-1} using a small amount of Sm_2O_3 (3.3 mg) in order to control the O_2-conversion below 5% at temperatures under 973 K.

TABLE 1

Effects of P_{O_2} on the Conversion and Selectivity

Reaction temperature (K)	P_{O_2} (kPa)	Conversion (%)		Selectivity (%)				
		CH_4	O_2	CO_2	CO	C_2H_4	C_2H_6	C_{2t}
	0.059	0.88	33.0	1.5	0	16.2	82.3	98.5
	0.298	2.71	62.0	5.5	0	27.1	67.3	94.5
973	0.466	3.53	63.0	7.2	0	30.3	62.5	92.8
	0.684	4.40	66.4	10.3	0.8	32.3	56.6	88.9
	0.878	5.41	66.9	12.7	1.4	33.3	52.6	85.9
	0.455	3.85	77.1	11.1	0	36.2	52.7	88.9
	0.672	4.70	76.6	13.8	0	38.8	47.4	86.2
1023	1.06	6.36	75.9	18.0	0	40.2	41.8	82.0
	1.37	7.79	76.5	21.4	0	40.5	38.1	78.6
	3.50	15.1	77.4	37.1	2.3	37.2	23.4	60.6

Note. P_{CH_4} = 18.2 kPa, flow rate = 25 ml min^{-1}, Sm_2O_3 = 1.00 g.

The O_2-conversion at 1023 K, however, increased up to 9.8%. Under the experimental conditions described above, the amount of CO formed was comparable to that of CO_2 at any temperature. The smaller amount of the catalyst used (3.3 mg) compared to that used in the experiments of Table 1 (1.00 g) is the cause for the incomplete burning of CO. The selectivities for each product are shown in Fig. 5. This figure shows that the C_2-selectivity (C_{2t}) increases from 37% (823 K) to 89% (1023 K) as the temperature is raised. The fraction of C_2H_4 in the C_2-hydrocarbons also increases with temperature.

Reaction Paths

Table 2 shows the partial pressures of the reactants and products in the effluent gas

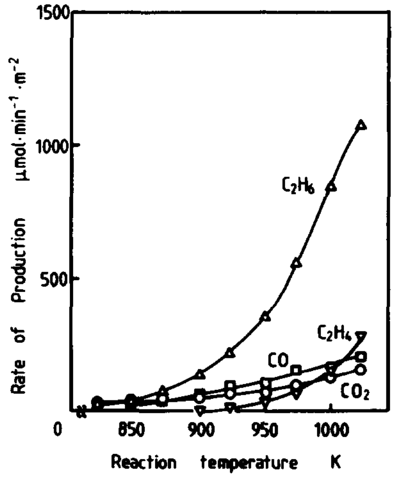

FIG. 4. Temperature effect on the reaction rates. Conditions: P_{CH_4} = 18.2 kPa, P_{O_2} = 0.98 kPa, Sm_2O_3 = 3.3 mg.

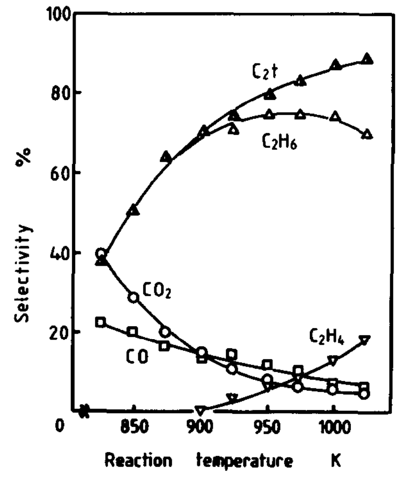

FIG. 5. Temperature effect on the selectivities of the products.

TABLE 2

Partial Pressures of the Reactants and Products

Experiment No.	Partial pressures (kPa)					
	O_2	CH_4	C_2H_6	C_2H_4	CO_2	CO
1	9.2×10^{-1}	7.7	1.2×10^{-2}	1.6×10^{-4}	1.1×10^{-2}	9.2×10^{-3}
2	9.2×10^{-1}	0	1.3×10^{-2}	2.0×10^{-4}	9.5×10^{-4}	2.4×10^{-4}
3	9.2×10^{-1}	0	0	2.0×10^{-4}	6.4×10^{-6}	0

Note. T = 883 K, flow rate = 37.5 ml min^{-1}, Sm_2O_3 = 3.3 mg.

from the reactor using different hydrocarbons, i.e., CH_4, C_2H_6, and C_2H_4 as the starting reactants. The experiments were carried out at 883 K under a flow rate of reactants of 37.5 ml min^{-1}. Experiment No. 1 in Table 2 indicates the results using 7.7 kPa of CH_4 and 0.92 kPa of O_2 as reactants. The partial pressures of the products in the effluent gas measured are indicated on the same line at the right side. Experiment 2 shows the results using C_2H_6 as the starting reactant. The partial pressure of C_2H_6 was controlled to be nearly the same as that of C_2H_6 observed in experiment 1. Comparing the partial pressures of C_2H_4 in experiments 1 and 2, we notice that nearly the same amounts of C_2H_4 were formed in both experiments. However, there is much difference in the rates of formations of CO and CO_2 between experiments 1 and 2. The summed rate of formations of CO and CO_2 in experiment 1 is 17 times faster than that in experiment 2. These observations suggest that, for the general reaction path shown in Fig. 6A, C_2H_4 is formed stepwise, i.e., through paths I and II, and not directly from CH_4, i.e., path VI. Moreover, the rate of path III is much faster than those of paths V and IV. In other words, CO and CO_2 are produced mainly from methane. Experiment 3 in Table 2 shows the results of experiments using C_2H_4 as the starting reactant. The pressure of C_2H_4 was adjusted to be nearly the same as in experiments 1 and 2. The rates of formations of CO and CO_2 are extremely slow compared to those observed in experiments 1 and 2. This observation shows that path IV can be neglected as a possible route when the reaction is started from methane. In conclusion, the results in Table 2 indicate that the overall reaction scheme can be written as B in Fig. 6.

Activation Energies

As described above, the rate of C_2H_6 formation (path I) was much faster than those of C_2H_4 formation (path II) and the burning of C_2H_6 (path V). Therefore, the rate of path I can be approximated by the rate of C_2H_6 formation. The temperature effect on this rate (from Fig. 4) is shown in Fig. 7 (filled triangles). The straight line in the temperature range 873–999 K gives 135 kJ mol^{-1} as the apparent activation energy of C_2H_6 formation. The temperature effect on the summed rate of CO_2 and CO formations (circles in Fig. 7) gave much smaller activation energy (66 kJ mol^{-1}) than that of C_2H_6 formation. The large difference in the activation energies between paths I and III (Fig. 6) shows that the higher the temperatures the better for the selectivities of C_2-

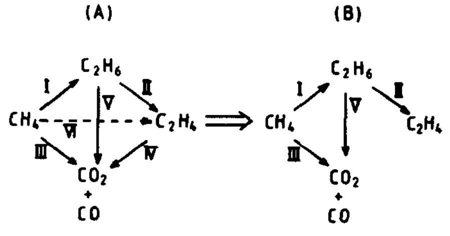

FIG. 6. Reaction paths.

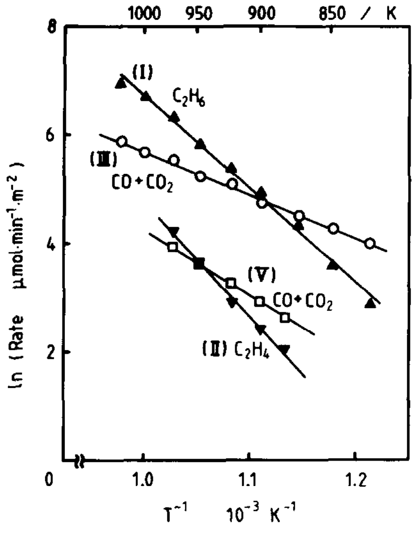

FIG. 7. Activation energy for each path. Logarithm rate of C_2H_6, CO_2 + CO, or C_2H_4 formation is plotted vs $1/T$. See text for experimental conditions. Rate of formation from CH_4: (▲) C_2H_6 formation, (○) CO_2 + CO formation. Rate of formation from C_2H_6: (▼) C_2H_4 formation, (□) CO_2 + CO formation.

hydrocarbons. The rate of formation of C_2H_4 and the summed rates of formations of CO_2 and CO were measured at different temperatures using C_2H_6 as the starting hydrocarbon ($P_{C_2H_6}$ = 0.042 kPa, P_{O_2} = 0.94 kPa). The rates measured are also plotted in Fig. 7 (▼ and □). The activation energies estimated from the plots are 173 and 94 kJ mol^{-1} for steps II and V, respectively. The large difference in the activation energies between steps II and V shows that the rate of oxidative-dehydrogenation of C_2H_6 (step II) overcomes the rate of burning of C_2H_6 (step V) at high temperatures (>950 K). The activation energies for each path in Fig. 6B are put in order as II > I > V > III. Thus, we can appreciate that the C_2-selectivity and the ratio of $[C_2H_4]/[C_2H_6]$ become favorable as the reaction temperature increases (Fig. 5).

Pressure Effects on the Rate and Selectivity

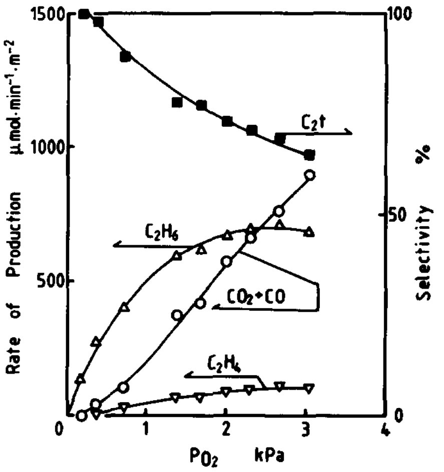

FIG. 8. P_{O_2} effects on the rates and C_2-selectivity. Conditions: P_{CH_4} = 18.2 kPa, T = 973 K, Sm_2O_3 = 2.4 mg.

Figure 8 shows the rates of formations of products and the C_2-selectivity as functions of oxygen pressure when a small amount of Sm_2O_3 (2.4 mg) is used in order to keep the oxygen conversion below 5%. The experiments were carried out at 973 K under 18.2 kPa of CH_4. The rate of C_2H_6 formation shows a maximum around an oxygen pressure of 2.7 kPa. The C_2-selectivity increases steadily with decreasing oxygen pressure. The selectivity approaches 100% at the oxygen pressure of 0.3 kPa. Figure 9

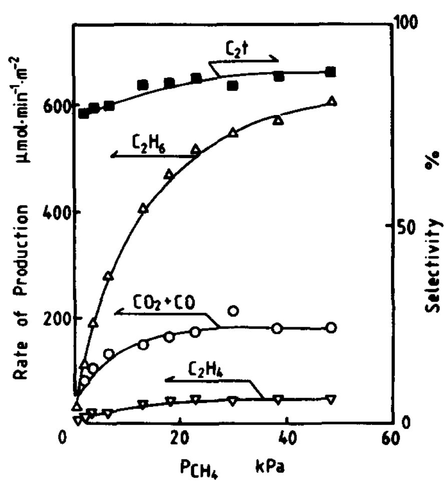

FIG. 9. P_{CH_4} effects on the rates and C_2-selectivity. Conditions: P_{O_2} = 0.98 kPa, T = 973 K, Sm_2O_3 = 2.4 mg.

shows the effect of pressure of CH_4. The experiments were carried out at 973 K under 0.98 kPa of oxygen. Both rate and selectivity increase as raising the pressure of CH_4. The results in Figs. 8 and 9 indicate that the C_2-selectivity increases with a decreasing P_{O_2}/P_{CH_4} ratio. Detailed kinetic studies on each path in Fig. 6B are needed to explain the results in Figs. 8 and 9. The rate equation for each path may enable us to elucidate the reaction mechanism for oxidative coupling of methane. Thus, we are carrying out the further kinetic studies under various reaction conditions. These results will be published soon.

A tentative reaction scheme for path I in Fig. 6 which we have in mind is written as follows:

$$Sm^{3+}V^- + \tfrac{1}{2}O_2 \rightarrow Sm^{3+}O^- \quad (1)$$

$$Sm^{3+}O^- + CH_4 \rightarrow Sm^{3+}OH^- + CH_3\cdot \quad (2)$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \quad (3)$$

where O^- ions produced on oxygen vacancy sites or basic sites (V^-) (Eq. (1)) may abstract hydrogen from methane, forming CH_3 radicals (Eq. (2)) (*4*, *6*). CH_3 radicals on the surface of Sm_2O_3 or in the gas phase may couple to form C_2H_6. The basic catalysts must be effective for the formation of O^- ions, which explains the observation that the basic or amphoteric oxides are selective catalysts for the formation of C_2-hydrocarbons.

Deep oxidation of CH_4 (path III) may be caused by surface O^{2-} or by the oxygen adsorbed (atomic or diatomic oxygen).

$$CH_4 + O^{2-} \text{ (O(a) or } O_2\text{(a))} \rightarrow \rightarrow \rightarrow CO, CO_2 \quad (4)$$

Large difference in the activation energies of path I and III supports the idea that the reaction intermediates or the oxygen species responsible for paths I and III are different. Further studies are needed to clarify these points.

ACKNOWLEDGMENT

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