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THE EFFECT OF ALKALI PROMOTERS IN OXIDATIVE COUPLING OF METHANE WITH Mn-OXIDE CATALYSTS

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Abstract—The catalytic oxidative coupling of methane to ethylene and ethane with manganese oxide catalysts promoted with alkali metal and alkali metallic-chloride has been studied at atmospheric pressure in a fixed bed flow reactor.

The main studies of reaction were carried out over maganese oxide catalysts promoted with sodium chloride and the structure and surface morphology of these catalysts was characterized by an X-ray diffraction and a scanning electron microscope. The powdered MnO_2 was changed into Mn_2O_3, and MnO_2 containing alkali metallic-chlorides was not changed to new ternary oxides but changed into Mn_3O_4 and/or Mn_2O_3 at higher calcination temperature(above 780°C).

The optimum content of NaCl promoted was 10-20wt%, an in over 10wt%, the conversion and the selectivity were kept constant. The main factor on deactivation of catalysts was the loss of the promoter(NaCl).

The addition of alkali metal salts to manganese oxide catalyst has enhanced $C_2(C_2H_4+C_2H_6)$ selectivity due to neutralizing acid sites more than the electronic factor. It was confirmed that chlorine in alkali metallic-chloride has enhanced the formation of C_2H_4, resulting in a good C_2-yield (up to 25.7%).

INTRODUCTION

The production of natural gas is increasing year by year and the reserves of natural gas are located all over the world. Methane is the most abundant component of natural gas, generally containing over 90 mole% of the hydrocarbon fraction of the gas, and it is mostly used as an energy source. The utilization of methane as feedstocks for the production of chemicals is limited due to it's high molecular stability. However, the some extent of methane is first converted into synthesis gas in a steam reforming process which then is converted into methanol by a catalytic process and subsequently into light olefins and higher hydrocarbons [1].

The steam reforming process requires intense energy as well as capital. Recently much attention is being paid to a direct conversion of methane into olefins and higher hydrocarbons.

The oxidative coupling of methane to $C_2(C_2H_4+C_2H_6$, particulary C_2H_4 is an important chemical feedstock) is of great significance because the methane included in natural gas can be used as an alternative source of hydrocarbons to cope with a predicted shortage in the supply of crude oil.

Since the oxidative coupling of methane is thermodynamically favorable to total oxidation, studies on suppressing total oxidation and enhancing the selectivity for C_2H_4 or C_2H_6 are required. Keller and Bhasin [2] reported a technique that was used to feed methane and oxygen over metal oxide catalysts alternately, so that it became correspondingly reduced or oxidized in pioneering work on the oxidative coupling of methane. Hinsen et al. [3] used the conventional flow system to study the oxidative coupling of methane with supported PbO catalysts and reported the effect of the support, alkali promoters and loading ratio of PbO. Lunsford et al. [4] reported that Li/MgO, which was an irreducible metal oxide, was very active and selective. Otsuka et al. [5] reported that rare earth metal oxides also have high activity. Although several works [6-8] in this field have been published, the fundamental and supplemental researches involving catalyst design with high yield are necessary. Jones et al. [9] have shown that supported manganese oxide is active, but bulk manganese oxide is less active. However, in the present study, the role of alkali promoters in the oxidative coupling of methane has been examined by promoting the bulk manganese oxide with various alkalis and comparing the catalytic behavior of the

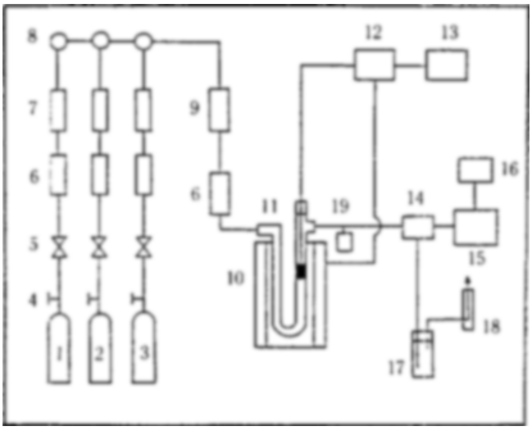


Fig. 1. Schematic diagram of experimental apparatus.

1. N_2 cylinder
2. O_2 cylinder
3. CH_4 cylinder
4. Pressure regulator
5. Needle valve
6. Silica trap
7. Capillary flow meter
8. Three way cock
9. Mixing chamber
10. Electric furnace
11. Reactor
12. Temperature controller
13. Temperature recorder
14. Gas sampler
15. G.C
16. Data processor
17. Bubble trap
18. Soap flow meter
19. $AgNO_3$ trap

resulting materials.

EXPERIMENTAL

1. Catalyst preparation

The Mn-Oxide promoted with alkali were prepared with powered MnO_2 and KNO_3, or $NaNO_3$, or Li_2CO_3, or KCl, or NaCl, and/or LiCl. Those were extra pure grades. Alkali precursors and MnO_2 were mixed together in deionized water. The resulting slurry was heated by stirring to evaporate excess water until a thick paste remained. The thick paste was then dried at 125°C in an oven for 14 hours, and was calcined in air at 400°C for 2 hours, subsequently at 780-1050°C for 6 hours; thereafter it was powdered.

2. Apparatus and methods

The schematic diagram of the experimental apparatus which employed a conventional fixed bed flow reactor system is shown in Fig. 1. The dimension of a reactor in the shape of a U is 1.1 cm I.D. and 38 cm long in inlet and 0.5 cm I.D. and 29 cm long in outlet. The catalyst(0.5g) was mechanically mixed with seasand(3g) as diluent before being packed in the reactor, because the dispersion of the catalyst increased the total yields of hydrocarbons and distributed the catalyst bed temperature uniformly. The catalyst was held in place by a small plug of quartz wool. The reactor was heated in a tubular furnace to a desirable temperature and the temperature was controlled within an accuracy of ±1.0°C by a temperature controller (Eunsuk Co., Korea).

Partial pressures of CH_4 and O_2 were 0.08 atm and 0.04 atm respectively, in all experiments, and CH_4/O_2 molar ratio was 2 that was stochiometric ratio. The total flow rate was maintained at 50 cc/min. The gaseous reactants were completely mixed in a mixing chamber which was packed with Raschig rings after being purified by passing through purifiers. They contained blue silica gel and molecular sieves. The effluent gases were analyzed by the on line G.C. (model 3BT, Shimadzu Co., Japan) system, using the Porapak Q column(3 mmϕ, 3 m long, 60-80 mesh, 90°C) for methane, carbon dioxide, ethylene, ethane and water, and the Molecular sieve 5A column (3 mmϕ, 3m long, 60-80 mesh, 90°C) for hydrogen, oxygen and carbon monoxide.

A quick determination of the basicity of catalysts was made by measuring the pH of the result suspension [10], which was mixed with 0.2g of a fresh catalyst in 40 mL of deionized water, with pH meter (model 501, Orion Research Co., U.S.A.). The structure and morphology of catalysts were studied by X-ray powder diffraction (Geigerflex, Rigaku, Japan) and by a scanning electron microscope (JSM-35C, Jeol, Japan). The BET surface areas were determined by nitrogen physisorption at −196°C using a Micromeritics 2300II system.

RESULTS AND DISCUSSION

The activity of the catalyst was discussed with three terms which are defined below.

% conversion(x) = [(moles of converted methane)/(moles of methane input)] × 100

% selectivity(s) = [(moles of converted methane into the ith component products)/(moles of converted methane)] × 100

% yield(y) = [(moles of converted methane into the desired product) /(moles of methane input)] × 100

Fig. 2 shows the effect of the calcination temperature of NaCl/Mn-Oxides on the conversion as well as on the selectivity. Since the melting point of NaCl is in the vicinity of 800°C [11], three calcination tem-

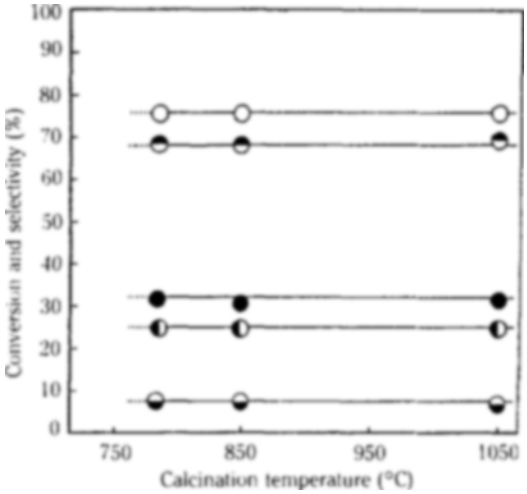


Fig. 2. Effect of calcination temperature over NaCl (20 wt%)/Mn-Oxide catalyst.
Reaction temperature = 750°C, Conversion: CH_4 (●), Selectivity: C_2 (○), C_2H_4 (◓), C_2H_6 (◒), $CO+CO_2$ (◐).

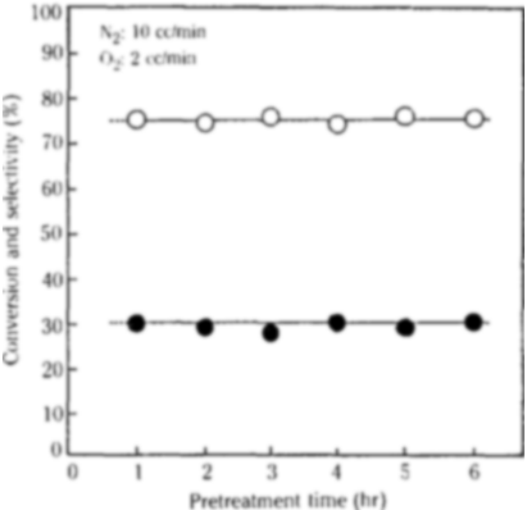


Fig. 3. Effect of pretreatment time over NaCl(20 wt%)/Mn-Oxide catalyst.
Reaction temperature = 750°C, Conversion: CH_4 (●), Selectivity: C_2 (○).

peratures were tested but no change was observed on the catalytic activity. Therefore, although it is prospected that the catalyst should be agglomerated more due to coagulation of NaCl than it was before its calcination, the above result means that the degree of agglomeration does not have any effect on the catalytic activity.

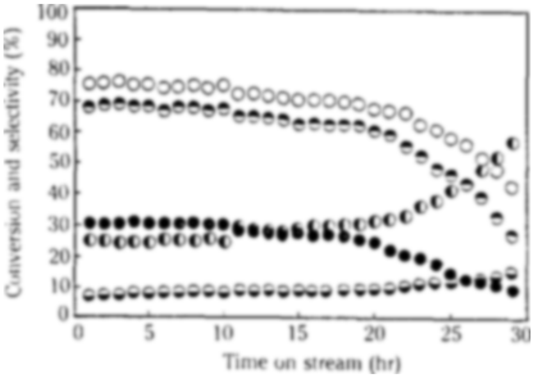


Fig. 4. Effect of reaction time over NaCl(10 wt%)/Mn-Oxide catalyst.
Reaction temperature = 750°C, Conversion: CH_4 (●), Selectivity: C_2 (○), C_2H_4 (◓), C_2H_6 (◒), $CO+CO_2$ (◐).

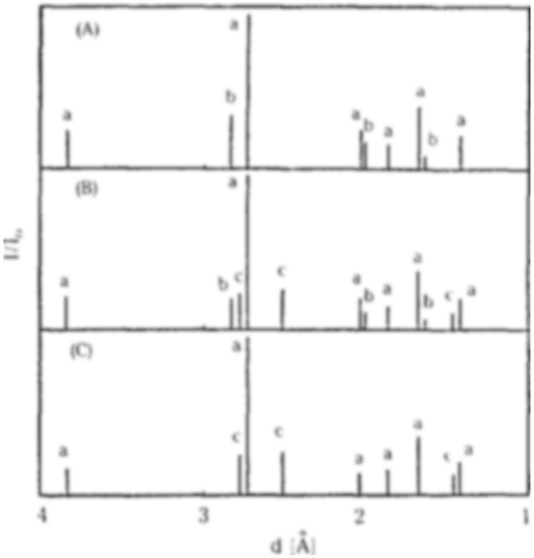


Fig. 5. XRD patterns of NaCl (10 wt%)/Mn-Oxide catalyst with reaction time.
(A) before reaction, (B) 10 hrs after reaction, (C) 30 hrs after reaction, a: Mn_2O_3, b: NaCl, c: Mn_3O_4.

Fig. 3 shows the effect of pretreatment time on the conversion and the selectivity under the mixing gas of N_2(10 cc/min) and O_2(2 cc/min). At an interval of 1 hr, the catalyst was pretreated for 6 hrs, and it does not show any meaningful change between the catalytic activity and the pretreatment time. Therefore, all experiments were carried out with the catalysts pretreated at 750°C for 1 hour.

Fig. 4 shows that the conversion and the selectivity

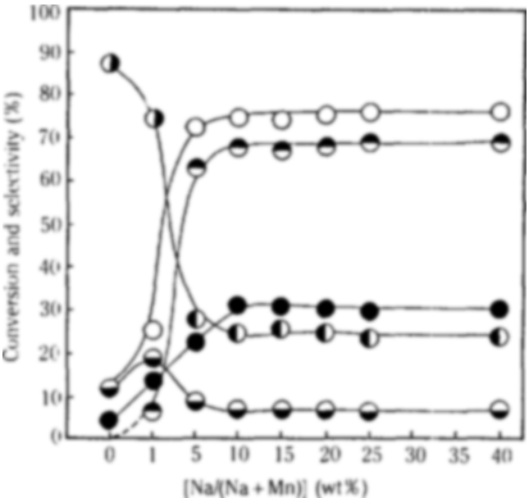


Fig. 6. Effect of NaCl content in NaCl/Mn-Oxide catalyst.
Reaction temperature = 750°C, Conversion: CH_4 (●), Selectivity: C_2 (○), C_2H_4 (◓), C_2H_6 (◒), CO_2 (◑), $CO+CO_2$ (◐).

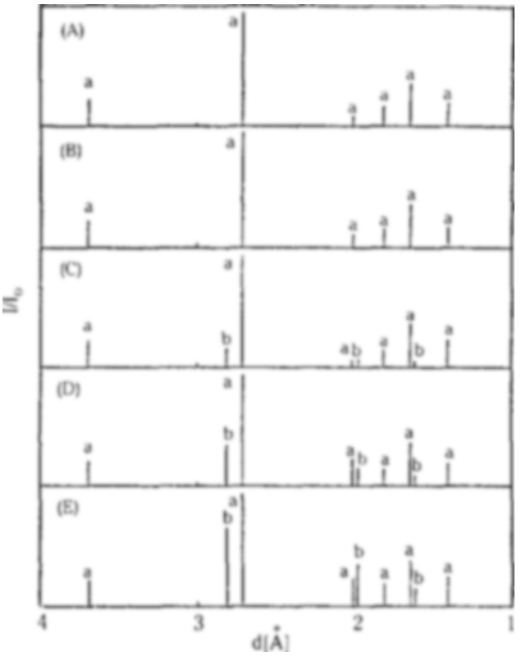


Fig. 7. XRD patterns of NaCl promoted Mn-Oxide catalysts.
(A) Mn-Oxide only, (B) NaCl (1 wt%)/Mn-Oxide, (C) NaCl (5 wt%)/Mn-Oxide, (D) NaCl (10 wt%)/Mn-Oxide, (E) NaCl (20 wt%)/Mn-Oxide,
a: Mn_2O_3, b: NaCl.

were varied with the reaction period over Mn-Oxide catalysts promoted with NaCl. Until the first 10 hours after the reaction started, the conversion and the selectivity did not vary, but the conversion and C_2 ($C_2H_4+C_2H_6$) selectivity decreased gradually after 10 hours and steeply after 18 hours; however, C_2H_6 selectivity increased somewhat. The selectivity of CO and CO_2 did not vary either till 10 hours after the reaction started, but thereafter it increased. Since it was found from Fig. 4 that the conversion and the selectivity were kept constant till 10 hours after the reaction started, the data for the conversion and the selectivity within 10 hours will be chosen later to discuss the catalytic activity.

Results of the XRD analysis of catalysts are shown in Fig. 5, which shows the origin of the catalyst deactivation. The fresh catalysts consist of NaCl and Mn_2O_3. The intensity of NaCl peaks were decreasing as reaction time went by, and after 30 hours NaCl peaks disappeared completely. New Mn_3O_4 peaks appeared in equal intensity at both 10 hours and 30 hours of usage of the catalysts. Consequently, it is supposed that the main factor on the deactivation of catalysts was due to the loss of promoters.

To examine the effect of the promoter NaCl content, runs were carried out at 750°C over Mn-Oxide catalysts promoted with various NaCl content. Fig. 6 shows that the activity increases in proportion to the increase of the NaCl content, however, catalysts

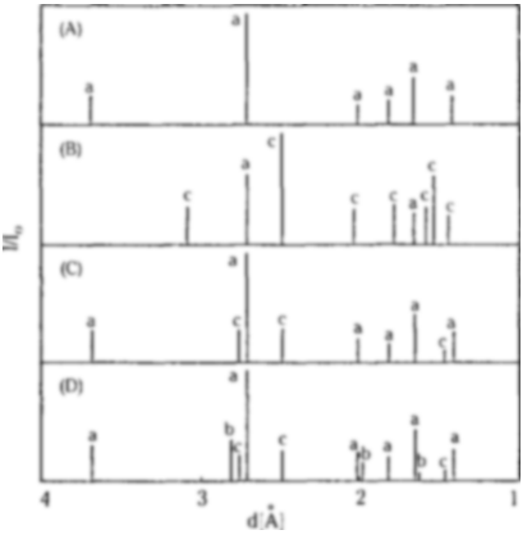
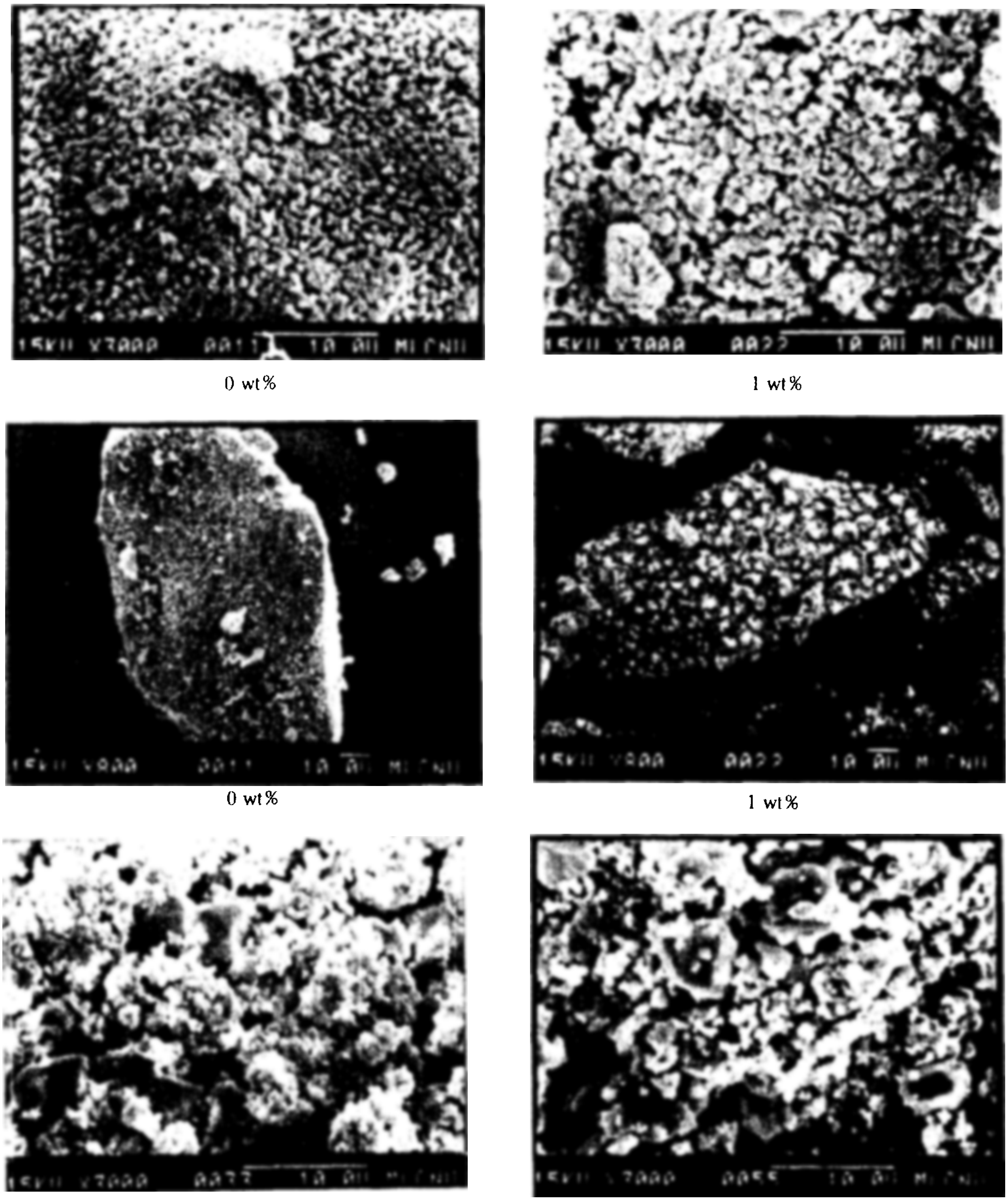


Fig. 8. XRD patterns of Mn-Oxide catalysts promoted with NaCl after reaction.
(A) Mn-Oxide only, (B) NaCl (1 wt%)/Mn-Oxide, (C) NaCl (5 wt%)/Mn-Oxide, (D) NaCl (20 wt%)/Mn-Oxide, a: Mn_2O_3, b: NaCl, c: Mn_3O_4.



0 wt% 1 wt%

0 wt% 1 wt%

5 wt% 20 wt%

Fig. 9. Scanning electron microscope graphs of Mn-Oxide catalysts with different NaCl content.

over 10 wt% maintain constant activities. Catalysts under 10 wt% NaCl content show that the formation ratio of C_2H_4 to C_2H_6, increases steeply, while the maximum conversion of CH_4 and the formation ratio of C_2H_4 to C_2H_6, 31% and 9.5, respectively, were achieved with catalysts over 10 wt% of NaCl content. This also implies that the catalysts over 10 wt% of NaCl content have a predominant activity to produce C_2H_4 which is a more favorable chemical feedstock than C_2H_6.

Fig. 7 shows XRD patterns of Mn-Oxide catalysts promoted with various NaCl content. NaCl peaks did not appear in 1 wt% of NaCl promoted catalyst due to the very small quantity of NaCl, but a good dispersion of NaCl is expected [13]. The intensity of NaCl peaks increases as the NaCl content increases. A point to be considered, having in mind a result of catalytic activities, as mentioned above, is the supposition that the effective active sites which are needed in reaction are increased up to 10 wt% of NaCl content. However, the catalysts promoted with 25 wt% and over NaCl content showed rapid deactivation after a run of 8 hours, and it is believed that this phenomenon is due to severe sintering of the catalyst.

Fig. 8 shows XRD patterns of 10 hours used Mn-Oxide catalysts promoted with various NaCl content. Mn_2O_3 peaks appeared uniquely in the fresh and used Mn-Oxide catalyst, but among the catalysts promoted with various NaCl content, the NaCl (1 wt%)/Mn-Oxide catalyst showed the largest change of Mn_2O_3 into Mn_3O_4.

Fig. 9 shows SEM photographs of Mn-Oxide catalysts promoted with 0, 1, 5, 20 wt% concentrations of NaCl. NaCl(1 wt%)/Mn-Oxide as well as Mn-Oxide show relatively uniform particle size. Both NaCl(5 wt%)/Mn-Oxide and NaCl(20 wt%)/Mn-Oxide show the shape of agglomeration of NaCl with Mn-Oxide. In the SEM photograph of NaCl(1 wt%)/Mn-Oxide catalyst, white spots, maybe NaCl, are uniformly dispersed on the surface and the clusters of metal oxide and NaCl are formed with cracks in centering around white spots. It is believed that NaCl which is uniformly dispersed in NaCl(1 wt%)/Mn-Oxide caused the increase of the negative charge of adsorption oxygen and the control of the amount of oxygen [14] concerning the oxidative coupling of methane, and consequently Mn_2O_3 was changed mainly into Mn_3O_4. This Mn_3O_4 did not show any activity.

Fig. 10 shows the effect of reaction temperature on the conversion and the selectivity of each product, which were measured over an NaCl(20 wt%)/Mn-Oxide catalyst. The maximum selectivity for C_2H_4 is observed at around 750°C, however, the selectivity for C_2H_6 keeps on decreasing as the reaction temperature increases. It is suspected that the dehydrogenation of produced C_2H_6 results in this sequence.

In most heterogeneous oxidation catalysis, the selectivity decreases as conversion increases, but this study shows maximum points of $C_2(C_2H_4+C_2H_6)$ selectivity. Therefore, this phenomenon can be interpreted by two primary reaction pathways for the CH_3 radicals which are known as the intermediate of oxidative coupling reaction of CH_4 [8,15]. One is the C_2H_4 formation reaction through the dehydrogenation of C_2H_6 which is the result product of two CH_3 radicals coupling, and another is the CO or CO_2 formation reaction through the surface methoxide ions or methyl peroxy radicals as the result products between CH_3 radicals and the oxide surface or gas oxygen, respectively [8, 15, 16]. The slopes of these two reaction pathways determine the maximum points of C_2 selectivity.

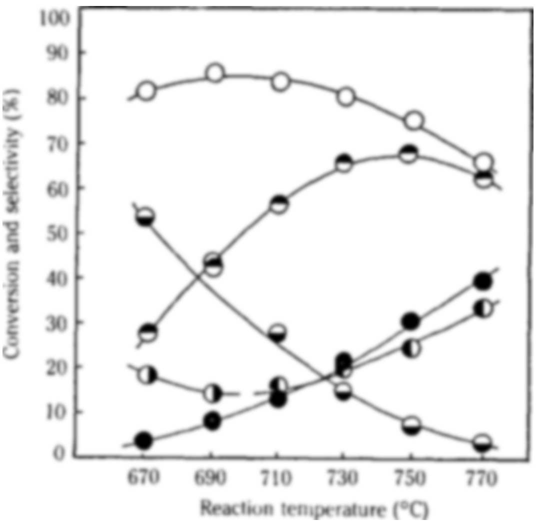


Fig. 10. Effect of reaction temperature on conversion and selectivity over NaCl (20 wt%)/Mn-Oxide catalyst.
Conversion: CH_4 (●), Selectivity: C_2 (○), C_2H_4 (◓), C_2H_6 (◒), CO_2 (◑), CO + CO_2 (◐).

In metal oxide catalysis, the increments of C_2 selectivity and yield by addition of alkali metal have been interpreted with two mechanisms. The electron donating effect of alkali metal can increase the reactivity of oxygen in M=O bond [17] and alkali metal neutralizes acid sites which are believed to be total oxidation site [18]. If such an electronic contribution of alkali-promoting were important, we would expect an increment in the activity of the reaction in the order K>Na>Li. However, in Table 1, the significant difference in the conversion and selectivity was not observed between various alkali promoters. Thus, it is believed that this electronic factor of alkali addition may not play an important role in this reaction. On the other hand, since Mn-oxide is the weak acid oxide, it is considered that the increment of C_2 selectivity is due to neutralization of acid sites by alkali promoters. According to Table 1, the fact of remarkable increment in pH of Mn-Oxide catalyst confirmed the above consideration.

By the way, in case of using KCl or NaCl or LiCl as promoters, the catalytic activity increased significantly,

Table 1. The effect of various alkali promoters on Mn-Oxide catalysts

Catalyst	S_{BET} (m^2/g)	pH	Conversion (%)		Selectivity (%)				Yield (%)
			CH_4	O_2	C_2H_4	C_2H_6	CO	CO_2	C_2
Mn-Oxide	1.3	6.69 ± 0.04	4.5	33	—	12	—	88	0.5
KNO_3/Mn-Oxide	—	10.05 ± 0.04	4.3	25	7.0	32	14	50	1.6
$NaNO_3$/Mn-Oxide	—	11.07 ± 0.04	4.7	20	8.0	30	15	47	1.7
Li_2CO_3/Mn-Oxide	—	10.75 ± 0.04	6.0	32	11	30	8.0	51	2.4
KCl/Mn-Oxide	<1	6.82 ± 0.02	29	65	64	10	11	15	21.4
NaCl/Mn-Oxide	<1	6.71 ± 0.02	31	83	69	7.0	12	12	23.5
LiCl/Mn-Oxide	1.8	6.55 ± 0.02	33	100	72	6.0	12	10	25.7

Reaction condition: Catalyst = 0.5 gr., Total flow rate = 50 cc/min, Reaction temperature = 750°C.

while an insignificant difference in pH was observed. KCl, NaCl and LiCl were not changed on Mn-oxide, not forming alkali manganese compounds and it was certified by XRD. It is observed that there is no particular difference in BET surface areas between Mn-Oxide catalysts and alkali metallic-halides promoted Mn-Oxide catalysts.

At a high temperature, it was known that the chlorine radicals act as a catalyst to form the C_2H_4 from CH_4 in the gas phases [19], and it was reported that the formation of C_2H_4 increased with the increasing of the formation CH_3Cl over the LiCl/NiO catalyst [18]. In this experiment, it was observed that AgCl precipitated in an aqueous $AgNO_3$ trap at the reactor outlet. From the above result, it was indirectly confirmed that chlorine species was present in the gas phase through the reaction. Therefore, when the various alkali metallic-chlorides are used as promoters, the reason to increase the C_2 yield significantly is supposed to occur as follows. Once the metal oxide and alkali metallic-chlorides formed the ternary oxides, they stabilized the alkali phases [20]. However, by XRD analysis on the catalysts, it became clear that the species of NaCl, KCl, LiCl, Mn_2O_3 and Mn_3O_4 existed as a crystal in the catalyst. Therefore, the affinities between Cl^- and Na^+ or K^+ or Li^+ may be weakened on metal oxide [21]; then Cl radicals may be released from alkali metallic-chlorides. The dramatic improvement of the C_2 selectivity can be interpreted as the role of these Cl radicals through the reaction.

Consequently, the following proposed reaction mechanism [18,19] could be adopted as a quite accurate path to increase the conversion of CH_4 and to form C_2H_4 over a Mn-Oxide catalyst.

$$XCl + CH_4 + (1/2)O_2 \rightarrow XOH + CH_3Cl\cdot$$
$$CH_3Cl\cdot \rightarrow Cl\cdot + CH_3\cdot$$
$$2CH_3\cdot \rightarrow C_2H_6$$
$$Cl\cdot + C_2H_6 \rightarrow HCl + C_2H_5\cdot$$
$$C_2H_5\cdot \rightarrow H\cdot + C_2H_4$$

where, X is Na or K or Li.

CONCLUSION

In spite of the addition of alkali metallic-chlorides, ternary oxides were not formed, only metal oxides (Mn_2O_3 and/or Mn_3O_4) and alkali metallic-chlorides phases were present. Mn_3O_4 appeared after the reaction had no effect on the reaction in NaCl/Mn-Oxide catalysts.

The optimum content of NaCl promoted was 10-20 wt% in NaCl/Mn-Oxide catalysts and the main factor on deactivation of catalysts was the loss of the promoter with time on stream. The addition of alkali metal salts to Mn-Oxide has enhanced $C_2(C_2H_4 + C_2H_6)$ selectivity due to neutralizing acid sites, and it was confirmed that chlorine in alkali metallic-chlorides has enhanced the formation of C_2H_4, resulting in a good C_2 yield (up to 25.7%).

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