## CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Effect of Various Primary Components

In this study, Li, Mg, V, Fe and Cu were used as the primary catalytic components prepared by doping on zinc oxide support. The prepared catalysts were classified into two groups as alkali metal group, i.e., Li and Mg components, and transition metal group, i.e., V, Fe and Cu components.

Figure 4-1 showed the conversion of methane and oxygen at reaction temperature of $450°C$ on various the prepared catalysts. Results showed that, the consumption of feeding oxygen of transition elements catalysts were higher than those of alkali elements catalysts while the methane conversion of both groups were the same low quantity. This results occured in the same route on the reducing and oxidizing form of catalysts. The products distribution of methane and oxygen conversion on various the catalysts as in Figure 4-1 were shown in Table 4-1. At this reaction temperature, i.e., $450°C$, C_2-hydrocarbons were observed only for the oxidizing form of Mg/ZnO catalyst, however, its quantity was considerable small. In reducing form of the prepared catalysts, one fourth of

the products distribution was carbon dioxide and the others were hydrogen and water. It can be said that one fourth part of the oxidation reaction of methane was the complete oxidation which represented by CO_2 and the others were the partial oxidations which represented by the amount of H_2 leaving. The complete oxidation reaction is the undesirable route, therefore, the feed composition was prepared in the form which has less of the oxygen concentration or CH_4/O_2 mole ratio higher than those of the complete oxidation mole ratio. According to the stoichiometric equation of complete oxidation of CH_4 and O_2 as showed in equation(4.1),

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad (4.1)$$
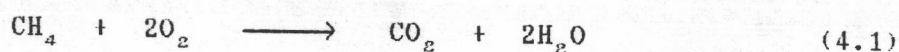
the mole ratio of $CH_4 : O_2 = 0.5$. Figure 4-2 also showed the conversions of methane and oxygen on the same catalysts, however, at the elevated reaction temperature, i.e., $600°C$. At this higher temperature, the conversion of methane on alkali elements catalysts were considerable increased several times as compared with at $450°C$ and also higher than those of the increasing of the transition elements catalysts. Furthermore, according to the increasing rate of methane conversion related to the increasing rate of oxygen conversion for those of alkali elements; an increasing rate of oxygen from ca. 20% to ca. 60% or 3 times while methane conversion increased from ca. 0.5% to ca. 4% or 8 times. And transition elements; an increasing rate of oxygen conversion from ca. 50% to 70% or 1.4 times while methane conversion increased from ca. 0.5% to 2%
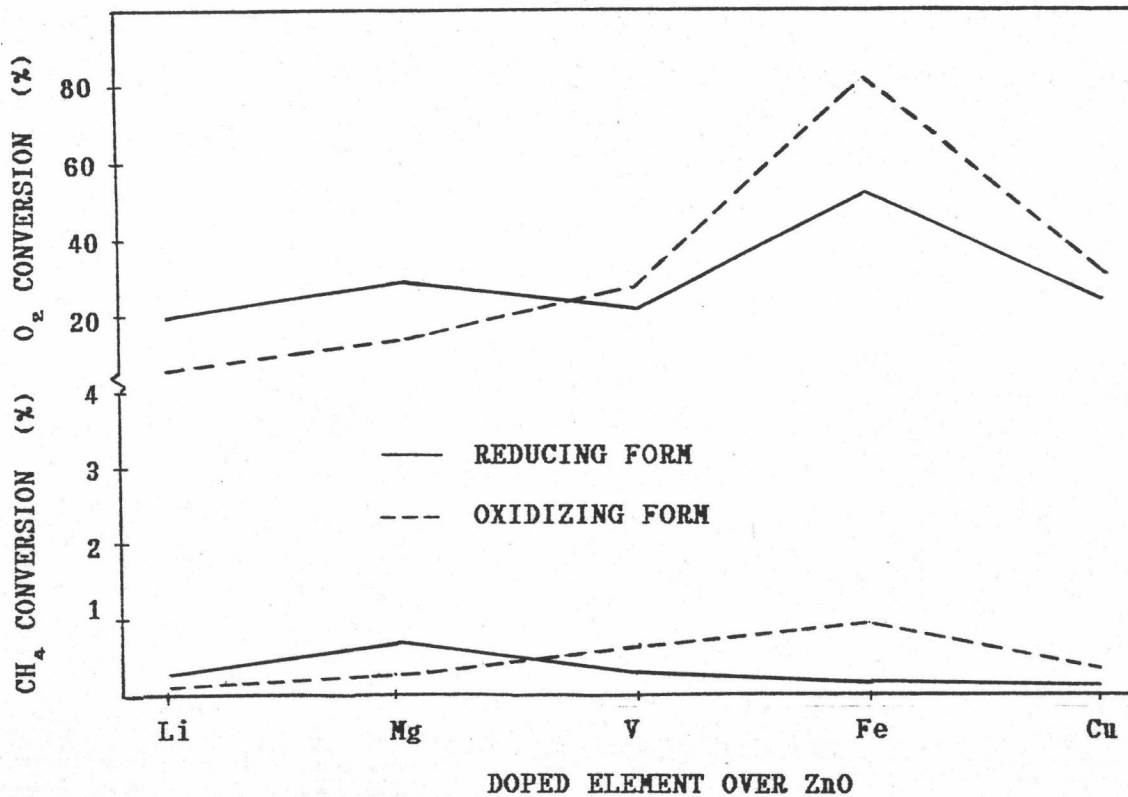
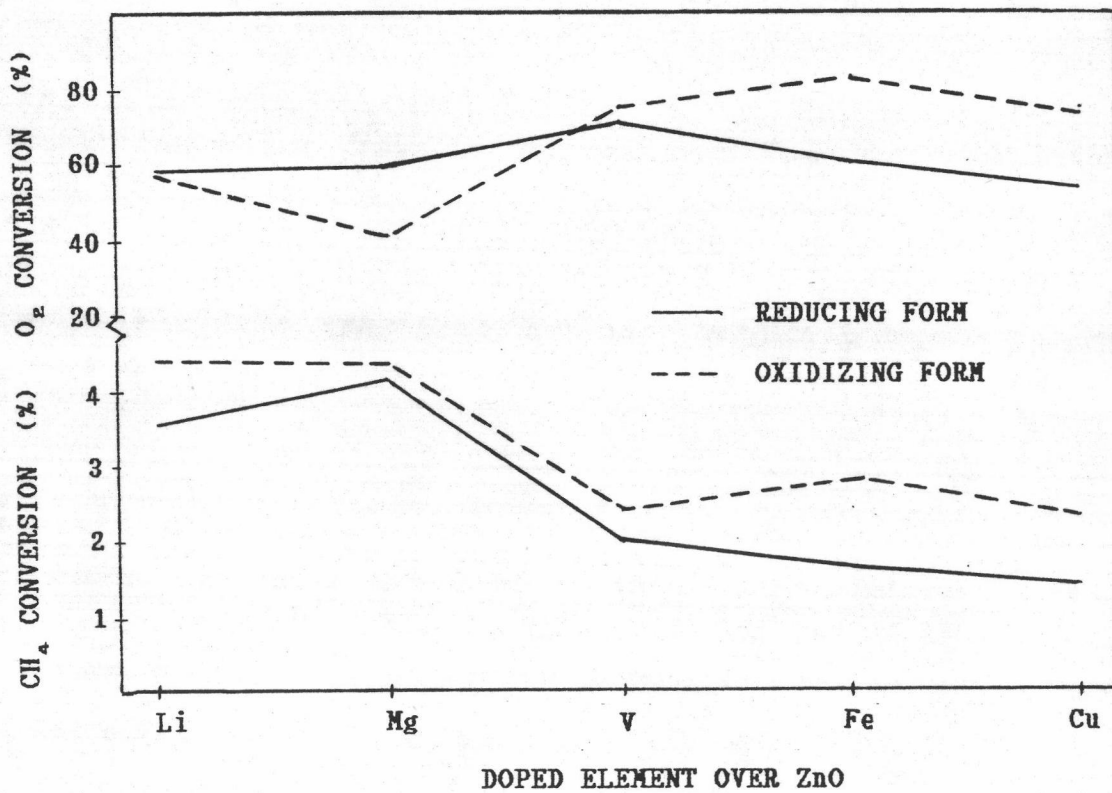Figure 4-1   Conversion of methane and oxygen

on various catalysts at 450 °C

Figure 4-2   Conversion of methane and oxygen

on various catalysts at 600 °C

TABLE 4-1 PRODUCTS DISTRIBUTION OF CH_4 OXIDATIVE COUPING ON

VARIOUS METALS DOPED ZnO CATALYSTS AT 450 ^{o} C [a]

CATALYST	PRODUCT DISTRIBUTION (% mole)			
	H_2	CO_2	C_2H_6	H_2O
REDUCING FORM				
Li	25.14	20.28	---	54.58
Mg	35.63	24.43	0.53	39.40
V	9.70	20.27	---	70.03
Fe	61.74	17.78	---	20.47
Cu	12.79	25.31	---	61.90
OXIDIZING FORM				
Li	24.53	11.05	---	64.42
Mg	42.20	26.78	---	28.02
V	---	18.79	---	81.21
Fe	---	6.04	---	93.96
Cu	---	100.00	---	---

[a] REACTION CONDITIONS : ATMOSPHERIC PRESSURE, FEED COMPOSITION

$CH_4:O_2:N_2$ = 10:1:11, ADDED METAL ION

= 0.9% BY WEIGHT OF CATALYST, AND WHSV

= 0.52 hr^{-1}

or 4 times. This may mean that the ability of oxygen adsorption in catalytic reaction depend on the nature of used primary component of catalyst and temperature. As the results showed in both figures, transition elements had a high oxygen conversion or oxygen adsorption rate at low temperature therefore the increasing of temperature made a little increasing rate of oxygen adsorption rate and methane conversion. Alkali elements had a low oxygen conversion at low temperature therefore the increasing of temperature made a lot of oxygen and methane conversion.

Table 4-2 showed the products distribution of conversion of methane and oxygen on various the catalyst at 600°C. The higher temperature, i.e., 600°C, C_2 compounds remarkably increased in both elemental groups. however, the increasing of C_2 products for alkali group was considerably higher than those of transition group. Addition with the higher methane conversion of alkali group therefore, the used primary component of catalyst, alkali elements was better than transition elements. Furthermore, as the results showed in Table 4-2, the higher the temperature increases complete oxidation which is represented by the increasing of CO_2. However, CO_2 and H_2O still remained the main products of all catalysts as in the products distribution at 450° C. Furthermore, Li/ZnO oxidizing form catalyst was the maximum C_2-hydrocarbons production. The carbon compounds in products distribution such as CO, CO_2, C_2H_4 and C_2H_6 were represented as the carbon compounds selectivity which is showed in Table 4-3. This term was used to

TABLE 4-2   PRODUCTS DISTRIBUTION OF CH_4 OXIDATIVE COUPLING ON

VARIOUS METALS DOPED ZnO CATALYSTS AT $600°C$ [a]

CATALYST	PRODUCT DISTRIBUTION (% mole)				
	H_2	CO_2	C_2H_4	C_2H_6	H_2O
REDUCING FORM					
Li	3.29	57.78	0.47	3.93	34.54
Mg	3.84	41.94	1.46	3.47	49.29
V	1.98	49.04	0.43	1.25	47.31
Fe	36.74	26.63	0.25	1.36	35.01
Cu	1.30	53.96	0.58	3.01	41.15
OXIDIZING FORM					
Li	18.22	48.89	1.15	8.08	23.66
Mg	2.58	59.91	1.08	4.15	32.28
V	1.66	41.43	0.96	0.63	55.82
Fe	1.90	35.79	---	1.92	60.41
Cu	1.40	34.75	0.60	2.09	61.15

[a] REACTION CONDITIONS : ATMOSPHERIC PRESSURE, FEED COMPOSITION

$CH_4 : O_2 : N_2$ = 10:1:11, ADDED METAL ION

= 0.9% BY WEIGHT OF CATALYST, AND WHSV

= 0.52 hr^{-1}

indicate the performance of catalyst in changing of carbon atom from methane via the catalytic reaction into carbon compound products. As the results in Table 4-3, carbon dioxide was the major product of the reactions, this indicate that the pathway of complete oxidation was the main route. The total C_2 selectivity from carbon compounds selectivity (ethane plus ethylene) at $600^\circ C$ was shown in Figure 4-3. The alkali group gave the higher C_2 selectivity than the transition ones. Therefore, the multiplication of methane conversion and total C_2 selectivity as the total C_2 yield in Figure 4-4 showed that the alkili elements had total C_2 yield higher than transition elements several times.

The considerable difference in catalytic activity between the alkali and transition metals are the methane conversion and C_2 selectivity. Alkali metals have an efficiency to produce C_2 hydrocarbons greater than transition metals on both reducing form and oxidizing form of catalysts. This behaviour has presented in previous chapter (chapter II) in the scopeline of the active catalyst for oxidative coupling of methane to produce C_2 hydrocarbons. It mentioned the capability of forming peroxide and superoxide from adsorbed oxygen and ability in chemisorption with the involved compounds in the reaction. For the further understanding of the reason, let us reconsider in Table 2-1. According to the table, the transition metals used in these experiments were classified as group A and B_3 which have a strong

TABLE 4-3 CARBON COMPOUNDS DISTRIBUTION AND C_2 HYDROCARBONS YIELDS OF CH_4 OXIDATIVE COUPLING ON VARIOUS METALS DOPED ZnO CATALYST AT 600°C

CATALYST	CARBON COMPOUNDS SELECTIVITY (%) [a]			$C_2^=/C_2$ [b]	YIELD (%) [c]	
	CO_2	C_2H_4	C_2H_6		C_2H_4	C_2H_6
REDUCING FORM						
Li	86.79	1.41	11.88	0.120	0.05	0.42
Mg	80.98	5.63	13.39	0.421	0.23	0.55
V	93.61	1.63	4.76	0.344	0.04	0.11
Fe	89.19	1.68	9.13	0.184	0.05	0.26
Cu	88.26	1.89	9.85	0.192	0.04	0.23
OXIDIZING FORM						
Li	72.58	3.42	24.00	0.142	0.15	1.04
Mg	85.15	3.06	11.79	0.260	0.13	0.51
V	95.00	2.12	2.88	0.736	0.04	0.06
Fe	90.37	--	9.63	--	--	0.17
Cu	86.58	3.01	10.42	0.289	0.05	0.16

a. CARBON COMPOUNDS DISTRIBUTION =

(NUMBER OF CARBON ATOM*PRODUCED MOLES)/(REACCTED MOLES OF CH_4)

b. $C_2^=/C_2$ = C_2H_4:C_2H_6 RATIO IN a.

c. YIELD = (2*PRODUCED MOLES OF C_2)/(MOLES CH_4 IN THE FEED)
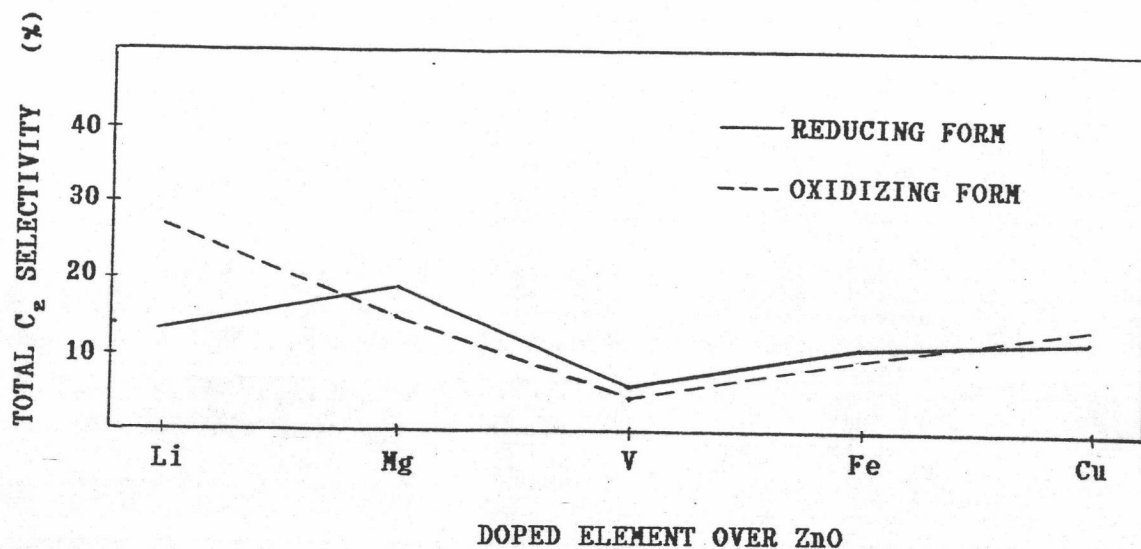
Figure 4-3 Total C_2 selectivity basis on carbon compound products at 600°C.
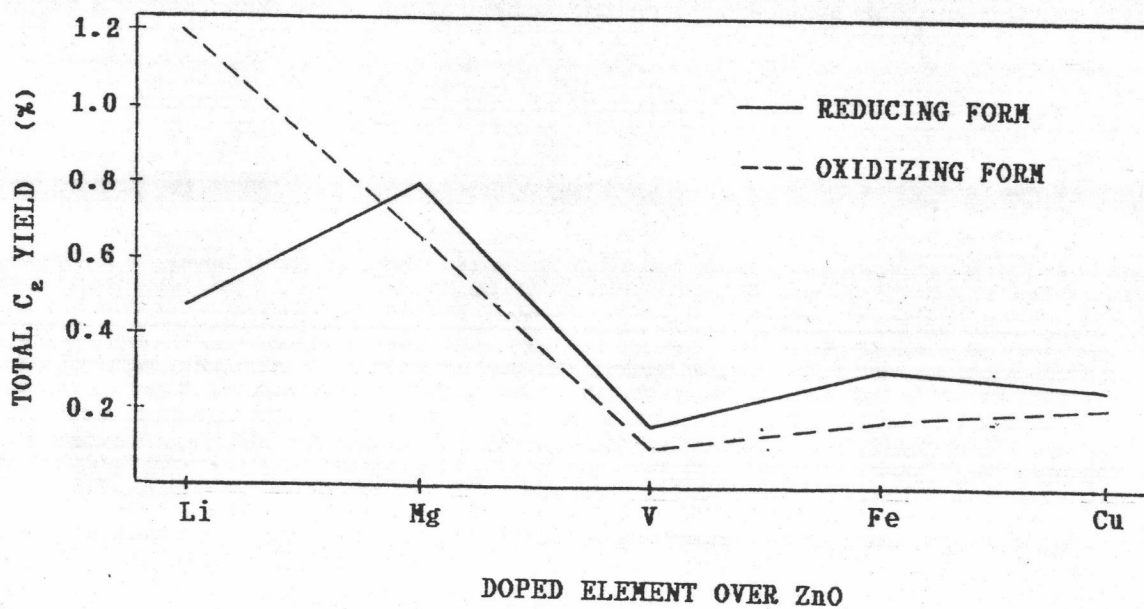

Figure 4-4 Total C_2 yield at 600 °C

chemisorption with the unwanted compounds as C_2H_4, CO, H_2, CO_2 and N_2. The alkaline metals were classified as group D and E which have a strong chemisorption with O_2 only. According to the Figure 2-2. The transition metals used in these experiments have no the capability of forming peroxide and superoxide from adsorbed oxygen. The alkali metals used in these experiments have the capability of forming peroxide from adsorbed oxygen. This capability is necessary to generate the active site of catalyst in arc-fusion technique. Therefore, transition metals have no activity in methyl radicals promotion. Consequentially, transition metals have less respondsibility to the formation of C_2 hydrocarbons products.

The essential demonstration is a role of typical alkali metals such as Li and Mg that why they have different efficiency. Therefore, each element must separately present to their different characters. It is neccessary to summarize the important factors about the relationship between doped metal and support in term of the catalysts activity for oxidative coupling reaction showed in Table 4-4.

As for factor 1, the decreasing of surface area is not unexpected as it is well-know that many oxides sinter when doped with alkali metal [1:60]. This may be observed from the photographs of catalyst surface by SEM which will be presented when Li- and Mg-doped ZnO are discussed. However, zinc oxide surface before catalyst preparation, after oxygen treatment (oxidizing form) and after

Table 4-4 The important factors of catalyst activity for oxidative
coupling reaction.

No	Factor	Effective result	Cause	Ref.
1	- Sintering of metal oxide.	- Reduction of catalyst surface.	- Type of doped element and support. - Doped amount.	[1]
2	- Adsorption: Chemisorption of reatants and product gases.	- Reduction of active site. - Order of oxidation state.	- Type of doped metal.	[5]
3	- Arc-fusion: Ionic radius of both doped element and support cation.	- Solubility or fusion of doped cation into the support lattice.	- Matching of doped element and support.	[1, 2,3]
4	- Formation of active center: Ability of forming O^- ions.	- Active site for generation of methyl radicals.	- Type of doped element.	[5]

hydrogen treatment (reducing form) are shown in Figure 4-5. The zinc oxide particles size after catalyst preparation seemed to be the same as before catalyst preparation. The reason may be that zinc oxide has a melting point at $1978^{\circ}C$ [6], therefore, the treatment of catalyst at $600^{\circ}C$ is too low to affect the sintering of the zinc oxide particles.

Factor 2 is a normal factor in heterogeneous catalytic reaction that a moderate chemisorption give the best activity than either strong or weak chemisorption [5: 24]. Each metal has a different ability of this factor. Table 2-1 is a good reference for the oxidative coupling reaction of methane that metals in Group A to Group C should be the non-active catalytic elements because they have a strong chemisorption with CO, H_2, CO_2 and N_2.

Factor 3 and 4 are the major important factors to indicate active catalyst in oxidative coupling reaction which have been accepted in many researchs. These factors are the ability of the catalyst to generate the methyl radical via the abstraction of hydrogen atom from methane by O^- ions. This means that the active catalyst must be able to produce the active center of metal and oxygen atom as $[MO^-]$. This center can be formed by arc-fusion technique and the reaction of gaseous oxygen which have been explained previously in chapter II. The cation of doped metal must have a smaller size than or be near the size of ionic radius of the

cation in the support lattice. For example, Li doped over MgO, the ionic radius of Mg^{2+} is 0.66 Å and that of Li^+ is 0.68 Å, therefore, the substitution between Mg^{2+} and Li^+ is available. The support lattice must have one oxidation state higher than doped element; for example, the substitution of a monovalent cation into a divalent site [2:5064]. According to the stoichiometric consideration, this aspect makes an excess of cation in support lattice and oxygen vacancies. Then gaseous oxygen react with cation of doped metal element on the support and the resulting oxygen form would be deposited on the oxygen vacancy positions. This phenomena usually occur at high temperature which result to form O^{2-} ions and holes which are formed to active center [M^+O^-]. In later step, the ability of forming O^{2-} ions occurs on the monovalent and divalent of alkali metals which can be found in Figure 2-2.

Zinc oxide is a bitter-tasting, while to gray powder that is insoluble in water, melts at 1978 °C. The oxidation state of zinc ion is +2 [6]. However, even zinc has two electrons at outermost valency but it can be state at +1 charge while magnesium and calcium have no +1 oxidation state [7]. This means that zinc oxide has a propensity to be an active catalyst because it can change the state of oxygen ion from O^{-2} to O^- which O^- ion is the active site of the methyl radical formation from methane. The ionic radius of these two ions are Zn^+ = 0.88 Å and Zn^{2+} = 0.74 Å [7]. Because of oxidation state of zinc ion in zinc oxide is +2 change therefore Zn^{2+} = 0.74 Å is used for the discussion in arc-fusion technique.
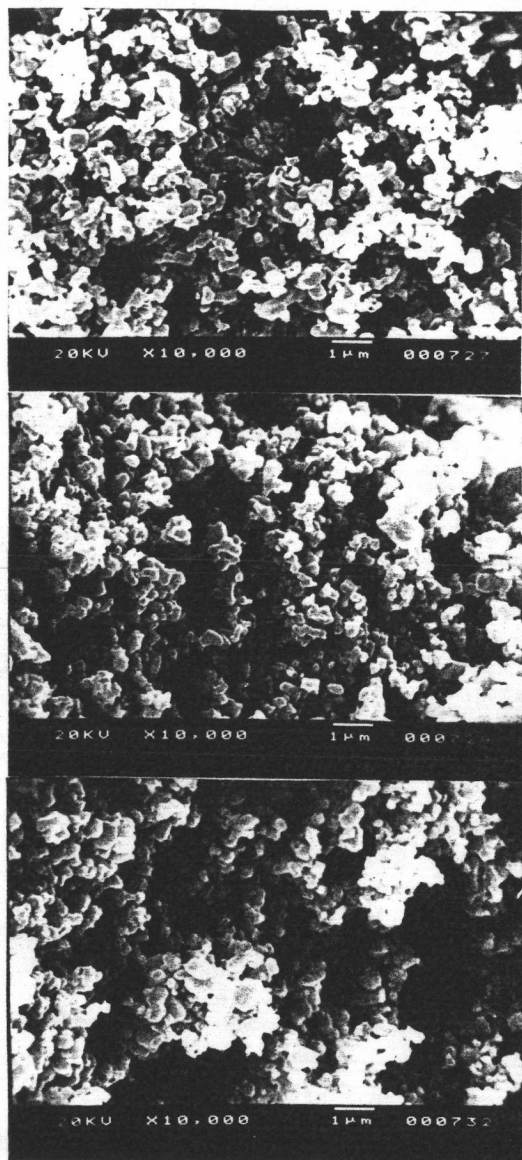
A : Before catalyst preparation

B : After treated with oxygen at 600°C

(oxidizing form)

C : After B treated with hydrogen

at 600°C (reducing form)

Figure 4-5   Scanning electron microscope photographs of

zinc oxide at various preparation steps.

1. Lithium versus Zinc Oxide

Li$^+$ ions are smaller than Zn^{2+} ion, therefore, they can easily substitute for Zn^{2+} ions in ZnO lattice. For every two Li$^+$ ions leaving carbonate phase, only one Zn^{2+} enters. Because of the near cation size of these two cations, it is available for one-by-one substitution (a proposal model of arc-fusion process of Li$_2$CO$_3$ and ZnO was shown on Figure 4-6). This cause an excess of cation Li$^+$ in the ZnO matrix which suggests the formation of oxygen vacancies those may exist on the surface. Later gaseous oxygen molecules immediately react with the vacancies at high temperature

Li$_2$CO$_3$ bulk

Li$^+$ = 0.68 Å [7] ⟶ ZnCO$_3$

Zn^{2+} = 0.74 Å [7] ⟶ LiO
⟶ Li$^+$

ZnO bulk

Li$_2$CO$_3$
m. p. = 700°C[6]
decompose=1200°C[8]
ZnCO$_3$
decompose= 300°C[8]

ZnO
m. p. =1978°C[6]
LiO
m. p. =1427°C[8]
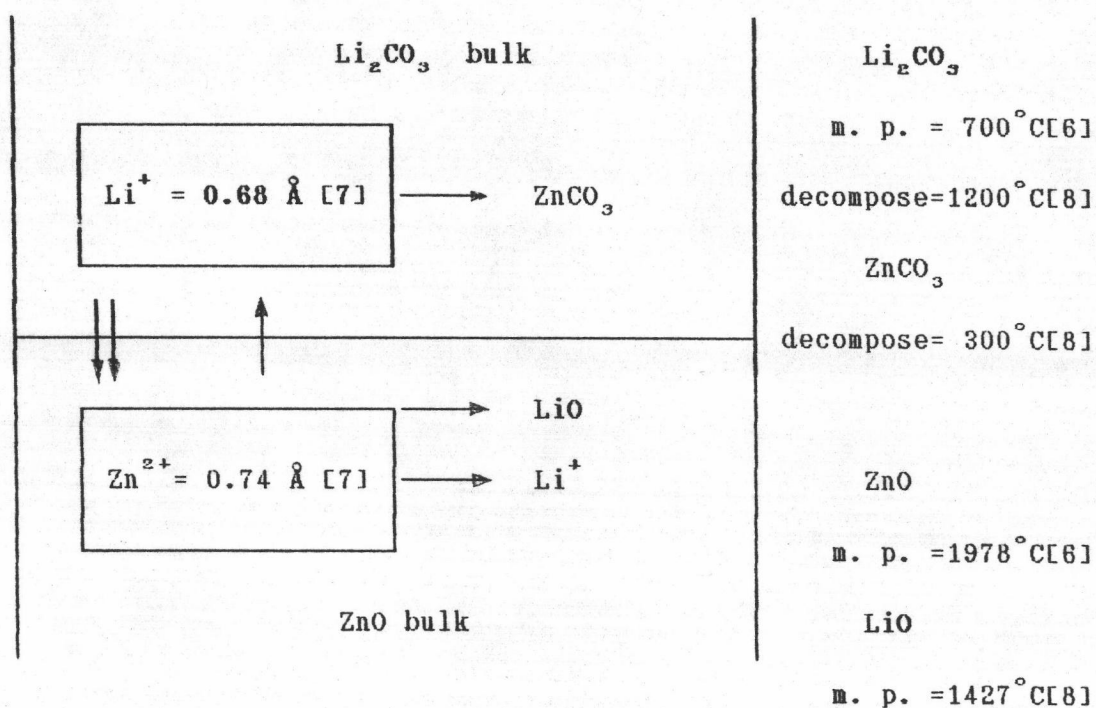
Figure 4-6 A proposal model of arc-fusion process of
Li$_2$CO$_3$ and ZnO

resulting in O^{2-} ions and holes. These holes being trapped at O^{2-} ions which are adjacent to Li^+ ions to be the active $[Li^+ O^-]$ centers. These O^- ions will react with methane to become the methyl radicals. Zn^{2+} ions which enter the carbonate phase to form $ZnCO_3$ and decompose by evolving carbon dioxide at $300°C$ to be ZnO.

Figure 4-7 showed the scanning electron microscope photographs of the surface of zinc oxide powder before catalyst preparation and after dopping with Li component. It seemed that the partical size of catalyst becomes larger in photoes B and C. The question is that did Li_2CO_3 decompose during heat treament and Li^+ in Li_2CO_3 completely substitute with Zn^{2+} ions in ZnO support. The answer is that Li_2CO_3 did not decompose at $600°C$ (decomposition temperature is $1200°C$) and the amount of Lithium in ZnO by the arc-fusion is not included on the scope of this work, however, should be very low because the treatment temperature was low, for an example of Li-doped MgO, the solubility of lithium ions in a MgO lattice is also small. The actual concentration of lithium in single crystals of MgO, which were grown by an arc-fusion technique using MgO powder doped with Li_2CO_3 to a concentration of about 5% by weight at $770°C$, was only 0.03 to 0.05 atom %[2 :5064]. Therefore, this ability, however, is an interesting topic for next step of research.

To confirm this carbonate phase, the infrared spectra of Li-doped ZnO which prepared and used in these experiments were carried
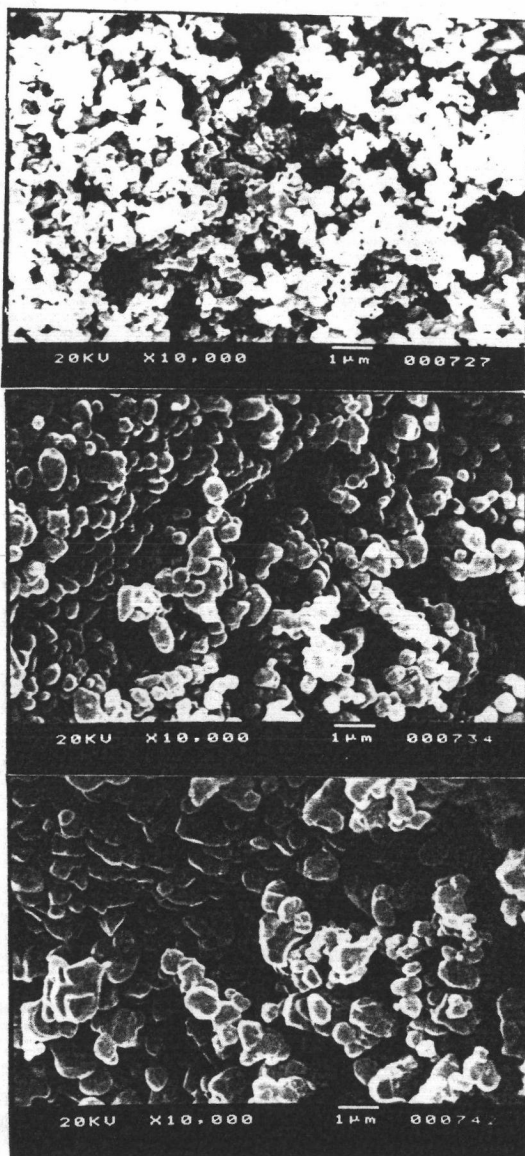
A : Zinc oxide powder
    before catalyst preparation

B : Li-doped zinc oxide after
    treated with oxygen at 600°C
    (oxidizing form)

C : B after treated with hydrogen
    at 600°C (reducing form)

Figure 4-7   Scanning electron microscope photographs of
             the surface of Li-doped zinc oxide catalysts.

out and showed in Figure 4-8. For the best discussion, the standard infrared spectra of ZnO, Li_2CO_3, and lithium oxide (plus carbonate impurity) which have been adjusted to the same scale to Figure 4-8 are also presented in Figure 4-9. On Figure 4-8, there were the spectra of carbonate group after adding Li_2CO_3 to zinc oxide at about 860, 1080 and 1440 wave number (cm^{-1}). These are able to comfirmed exactly by Figure 4-9 that spectra of ZnO (pattern A, Figure 4-9) have no signal in the range of 600-1550 wave number while the spectra of carbonate compound showed four signals in this range on pattern B and C. This also happens in other researchs, for an example, Driscoll and co-worker [1:60] tested the used catalyst, which doped MgO with Li_2CO_3, by X-Ray diffraction and recorded two phases of Li_2CO_3 and MgO (Li_2CO_3 and MgO are crystalline compounds while Li_2O is not crystalline compound [6,8]). Furthermore, they had tested and showed that Li_2CO_3 had no activity for methyl radical formation.

Figure 4-10 showed the scanning electron microscope photographs of the surface of Li-doped zinc oxide catalysts after used in the reaction test experiments. On these photoes, there was the coke on the catalyst bulk as a black layer area covered on the catalyst particles in both oxidizing and reducing forms. Deposition of coke may somewhat affect the catalytic performance such as activity and life-time of the catalysts.
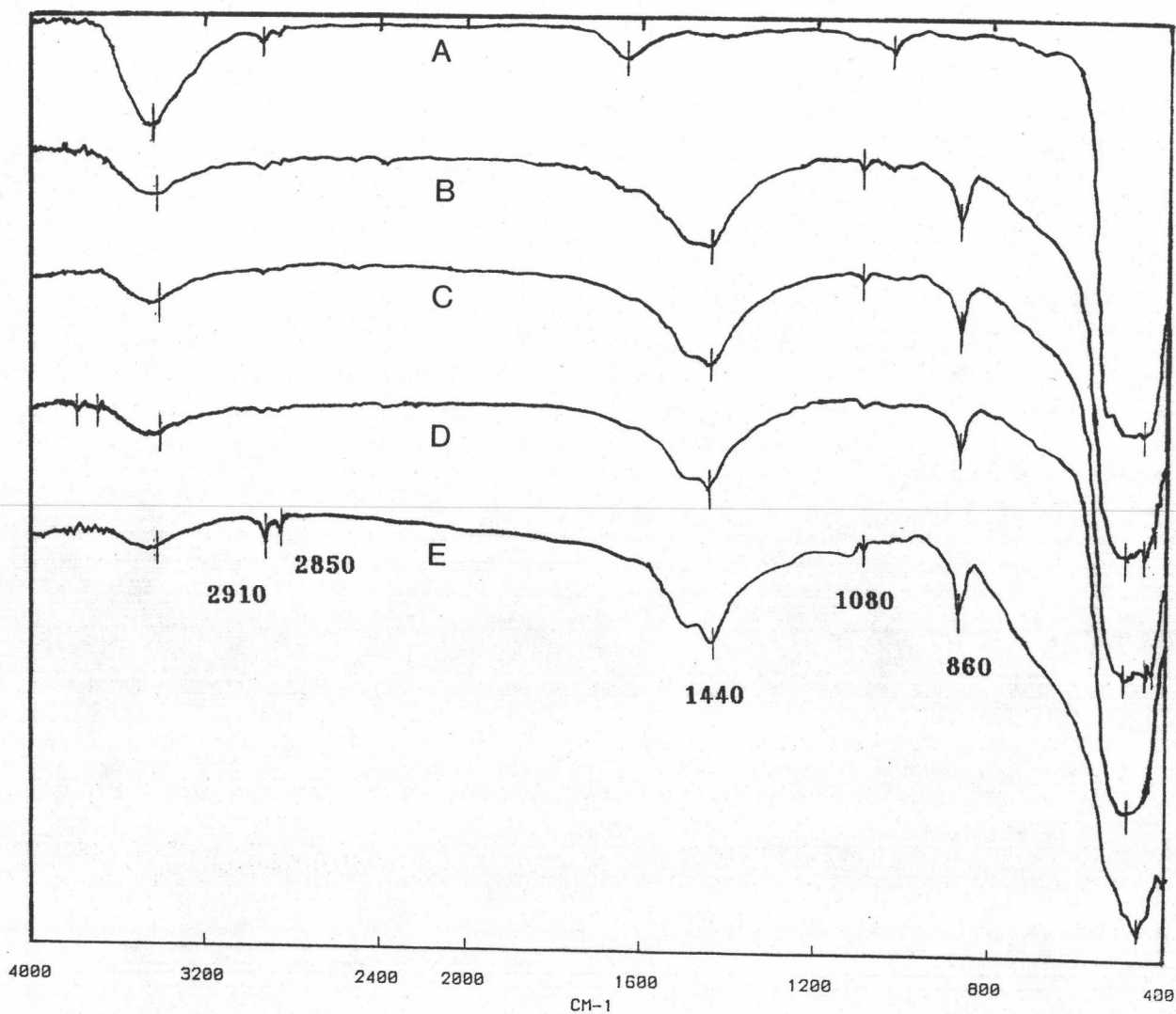
Figure 4-8 Infrared spectra of various Li-doped

zinc oxide catalysts.

A = ZnO powder before catalyt preparation.

B = ZnO after adding Li_2CO_3 and oxygen treatment (oxidizing form).

C = Li/ZnO in B after reaction.

D = Li/ZnO in B after hydrogen treatment (reducing form).
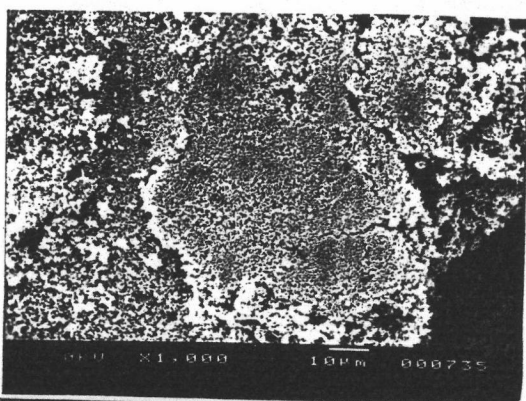
E = Li/ZnO in D after reaction.
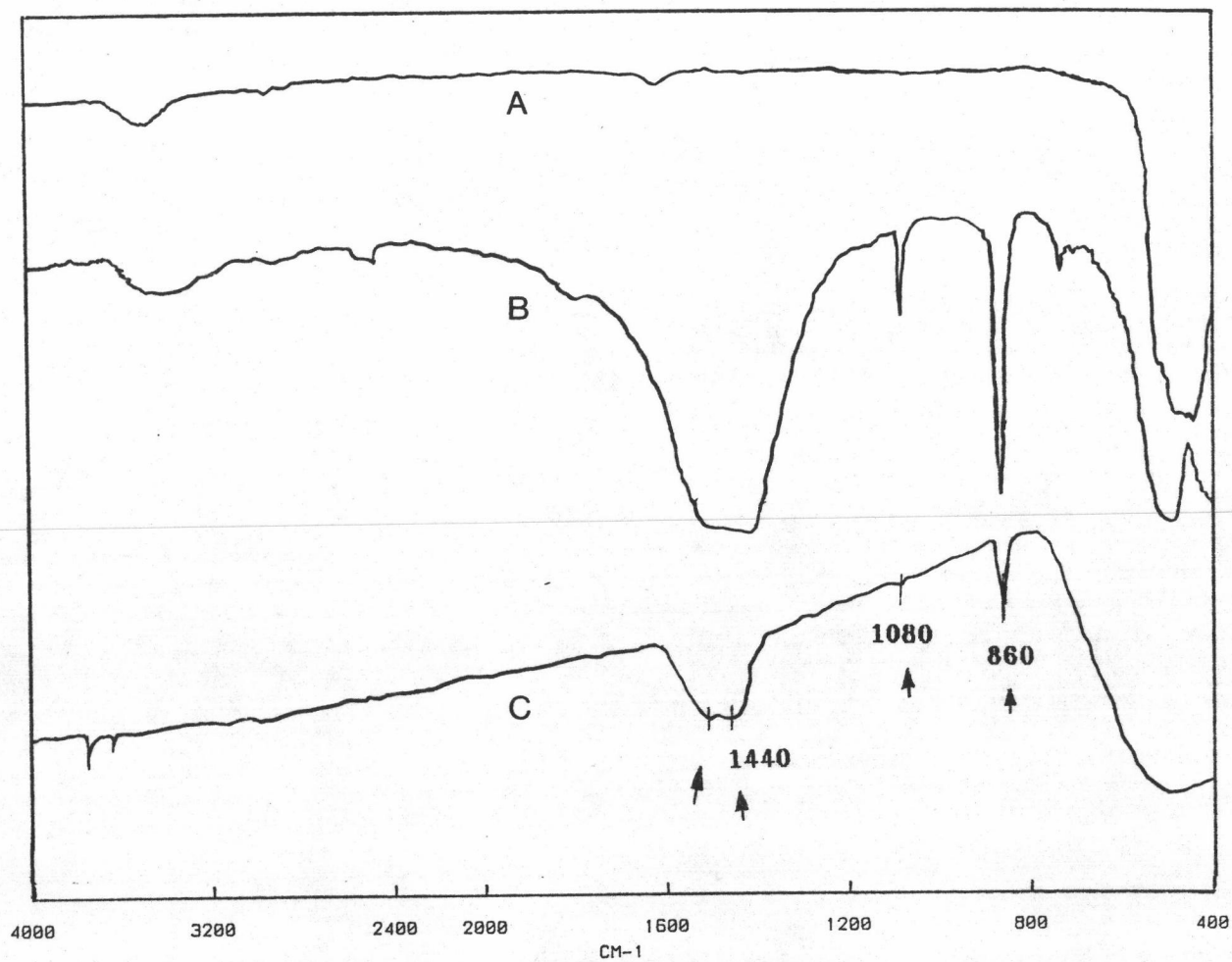
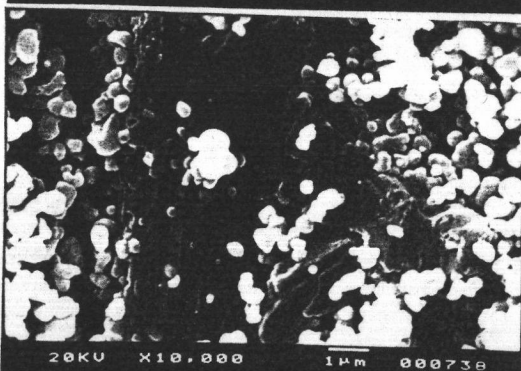Figure 4-9   Infrared spectra of reference materials.

A = ZnO [9]

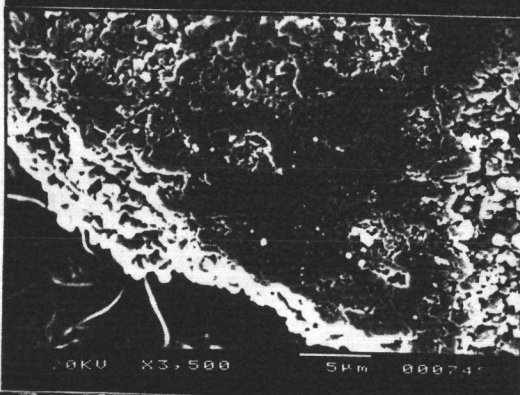B = Li$_2$CO$_3$ [10]

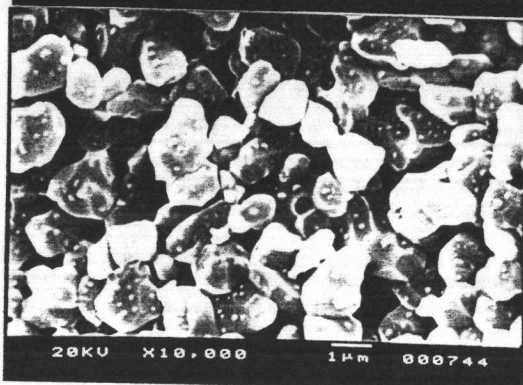C = Li$_2$O (plus carbonate impurity)

   the arrows indicate the location of the

   impurity peaks. [11]

A : Li-doped zinc oxide

(oxidizing form, figure 4-8 : B)

after reaction.

B : Magnified photo of A :

C : Li-doped zinc oxide

(reducing form, figure 4-8 : C)

after reaction.

D : Magnified photo of C :

Figure 4-10   Scanning electron microscope photographs of

the surface of Li-doped zinc oxide catalysts

after reaction at 600°C.

This coke has been exactly confirmed by infrared spectra of the Li-doped ZnO catalysts after reaction in Figure 4-8 that they had the symmetry CH_2 stretching at 2850 cm^{-1} [12]. This coke, however, is a site of the activity of Li-doped zinc oxide catalyst to convert methane to higher hydrocarbons.

2. Magnesium versus Zinc Oxide

The previous discussion has explained the arc-fusion technique that the substitution of a monovalent cation such as Li, in a divalent site of ZnO. This different electron charge make an excess of cation in ZnO lattice and oxygen vacancies, but in magnesium-doped zinc oxide, both magnesium and zinc are divalent cation. Therefore, an one-by-one substitution will occur in arc-fusion process and no excess of cation in ZnO lattice and oxygen vacancies. Figure 4-11 is a proposal of an arc-fusion process of these two divalent cations.

It has been supposed that Mg-doped zinc oxide will not be effective catalyst even the ionic radius of these two cations are available to substitute in arc-fusion. $MgCO_3$ was decomposed to be MgO at 350 $^\circ$C and MgO remain in the zinc oxide bulk. Magnesium has only one oxidation state at +2 charge, therefore, oxygen atom which bonds to magnesium must has an oxidation state at -2 charge. This O^{2-} ion is not active to generate methyl radicals. This may be the
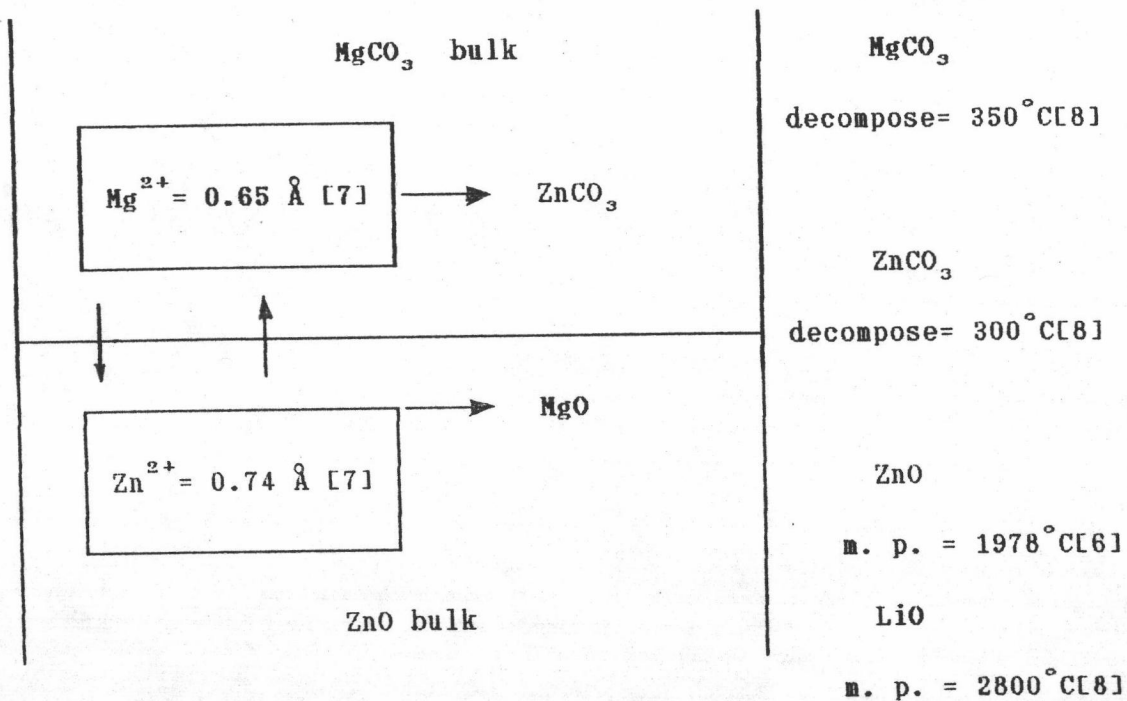
$MgCO_3$ bulk

$Mg^{2+}= 0.65$ Å [7] $\longrightarrow$ $ZnCO_3$

$Zn^{2+}= 0.74$ Å [7] $\longrightarrow$ MgO

ZnO bulk

$MgCO_3$

decompose= $350°C$[8]

$ZnCO_3$

decompose= $300°C$[8]

ZnO

m. p. = $1978°C$[6]

LiO

m. p. = $2800°C$[8]

Figure 4-11 A proposal model of arc-fusion process of

$MgCO_3$ and ZnO

reason concerning the lower catalytic abilities of Mg/ZnO than Li/ZnO. Figure 4-12 showed the scanning electron microscope photographs of the surface of Mg-doped ZnO catalysts before and after used in the reaction test experiments.
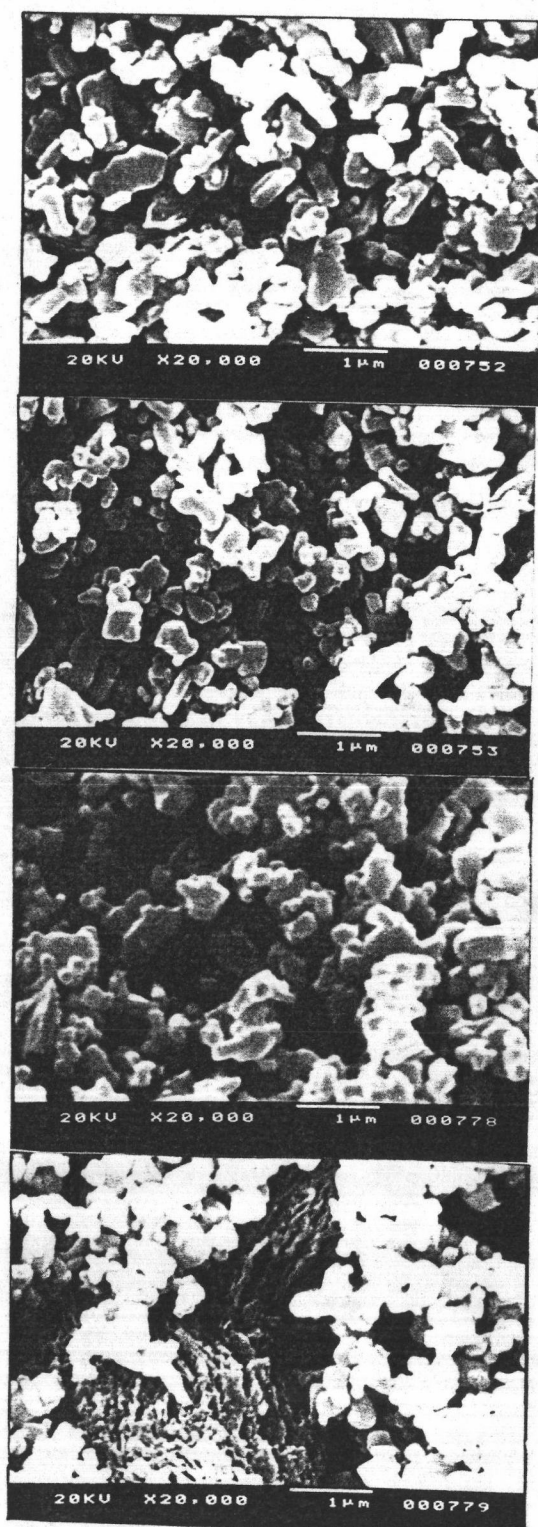
A : Mg-doped zinc oxide after
    treated with oxygen at 600°C
    (oxidizing form)

B : Mg-doped zinc oxide of A
    (oxidizing form)
    after reaction.

C : Mg-doped zinc oxide of A after
    treated with hydrogen at 600°C
    (reducing form)

D : Mg-doped zinc oxide of C
    (reducing form)
    after reaction.

Figure 4-12   Scanning electron microscope photographs of
              the surface of Mg-doped zinc oxide catalysts
              before and after reaction at 600°C.

4.2 Effect of Supports

In the present work, four types of supports, namely, ZnO, Al_2O_3, SiO_2, and zeolite were used in the investigation. The zeolite was the finished powder which compose of SiO_2 77.3 wt%, Al_2O_3 21.8 wt% and Na_2O 0.14 wt%; SiO_2/Al_2O_3 mole ratio = 6.0. The primary components doped on these supports were Li and Mg. These catlysts were prepared into two forms of catalysts, i.e., oxiding and reducing forms. The investigations were carried out at two points of reaction temperatures as $450°C$ and $600°C$. The others reaction conditions such as methane/oxygen mole ratio, pressure and space velocity were retained at the same as the previous study.

Table 4-5 showed the conversion of methane and oxygen and the products distribution for Li doped on various supports at $450°C$. As the results, there were no C_2-hydrocarbons and carbon monoxide formation, or there were only complete oxidation which represented by the carbon dioxide formation. However, the complete oxidation did not follow the stoichiometric equation that the mole of water produced must be 2 times more than those of carbon dioxide. The non-stoichiometric reaction was presented by the amount of H_2 leaving. It could be remarkable that the amount of hydrogen product increased as the amount of water product decreased whereas the amount of carbon dioxide product slightly changed. Methane conversion of these catalysts were the same low quantity as the previous catalysts which studied at reaction temperature $450°C$.

TABLE 4-5   PRODUCTS DISTRIBUTION AND CONVERSION OF CH_4 AND O_2

OF Li-DOPED OVER VARIOUS SUPPORTS AT 450°C

SUPPORT	PRODUCTS DISTRIBUTIONS (% mole)				CONVERSION (%)	
	H_2	CO_2	C_2H_6	H_2O	CH_4	O_2
REDUCING FORM						
Zinc Oxide	25.14	20.28	---	54.58	0.23	19.62
Alumina	69.66	22.87	---	7.47	0.29	92.52
Silica	18.03	22.81	---	59.11	0.36	60.44
Zeolite	49.37	8.13	---	42.50	0.21	100.00
OXIDIZING FORM						
Zinc Oxide	24.53	11.05	---	64.42	0.03	5.35
Alumina	38.35	15.31	---	46.34	0.09	14.02
Silica	---	7.17	---	92.83	0.00	56.77
Zeolite	---	9.68	---	90.32	0.05	3.58

REACTION CONDITIONS : ATMOSPHERIC PRESSURE, FEED COMPOSITION

$CH_4:O_2:N_2$ = 10:1:11, ADDED METAL ION

= 0.9% BY WEIGHT OF CATALYST, AND WHSV

= 0.52 hr^{-1}

TABLE 4-6   PRODUCTS DISTRIBUTION AND CONVERSION OF CH_4 AND O_2

OF Mg-DOPED OVER VARIOUS SUPPORTS AT $450^\circ C$

SUPPORT	PRODUCTS DISTRIBUTIONS (% mole)				CONVERSION (%)	
	H_2	CO_2	C_2H_6	H_2O	CH_4	O_2
REDUCING FORM						
Zinc Oxide	35.63	24.43	0.53	39.40	0.63	29.91
Alumina	79.74	12.28	---	7.99	0.17	94.63
Silica	9.43	32.26	---	58.31	0.60	66.79
Zeolite	48.95	12.58	---	38.47	0.22	100.00
OXIDIZING FORM						
Zinc Oxide	45.20	26.78	---	28.02	0.27	14.90
Alumina	8.41	5.47	---	86.12	0.19	17.33
Silica	---	27.80	---	72.20	0.07	27.73
Zeolite	0.57	1.44	---	97.99	0.03	23.35

REACTION CONDITIONS : ATMOSPHERIC PRESSURE, FEED COMPOSITION

$CH_4:O_2:N_2$ = 10:1:11, ADDED METAL ION

= 0.9% BY WEIGHT OF CATALYST, AND WHSV

= 0.52 hr^{-1}

Table 4-6 also showed the conversion and the products distribution at 450°C, however, for Mg doped on various supports. There was little ethane produced on Mg/ZnO catalyst. The results of these catalysts seemed to be the same as the results of doping with Li, i.e., the formation ratio of hydrogen, carbon dioxide, water and the consumption of oxygen. It is proposed that these performances resulted from the chemical nature of the supports.

Figure 4-13 and 4-14 showed the conversion of methane and oxygen on various Li- and Mg-doped supports both of reducing and oxidizing forms at reaction temperature 600°C. The experiments were performed at the same operating condition, i.e., atmospheric pressure, $CH_4:O_2$ = 10:1, and WHSV = 0.52 hr^{-1}. Results obtained were methane conversions of all prepared catalysts were considerably increased several times as compared with at 450°C. The highest methane conversion was found for ZnO supports of all of doped metals species and both of oxidizing and reducing forms. The difference in the activities of various supports in turn affect the products distribution which are presented in Figure 4-15. At higher reaction temperature, i.e., 600°C, C_2 hydrocarbons have formed on all of investigated catalysts, however, ZnO support really stand out with the maximum total C_2 amount compared to the same doped metal and oxidizing or reducing form. Especially, there was CO formation on zeolite support while the others showed none, and hydrogen formation considerlably decreased for all of these catalysts. However, CO_2 and H_2O also remained as the major components on products distribution.
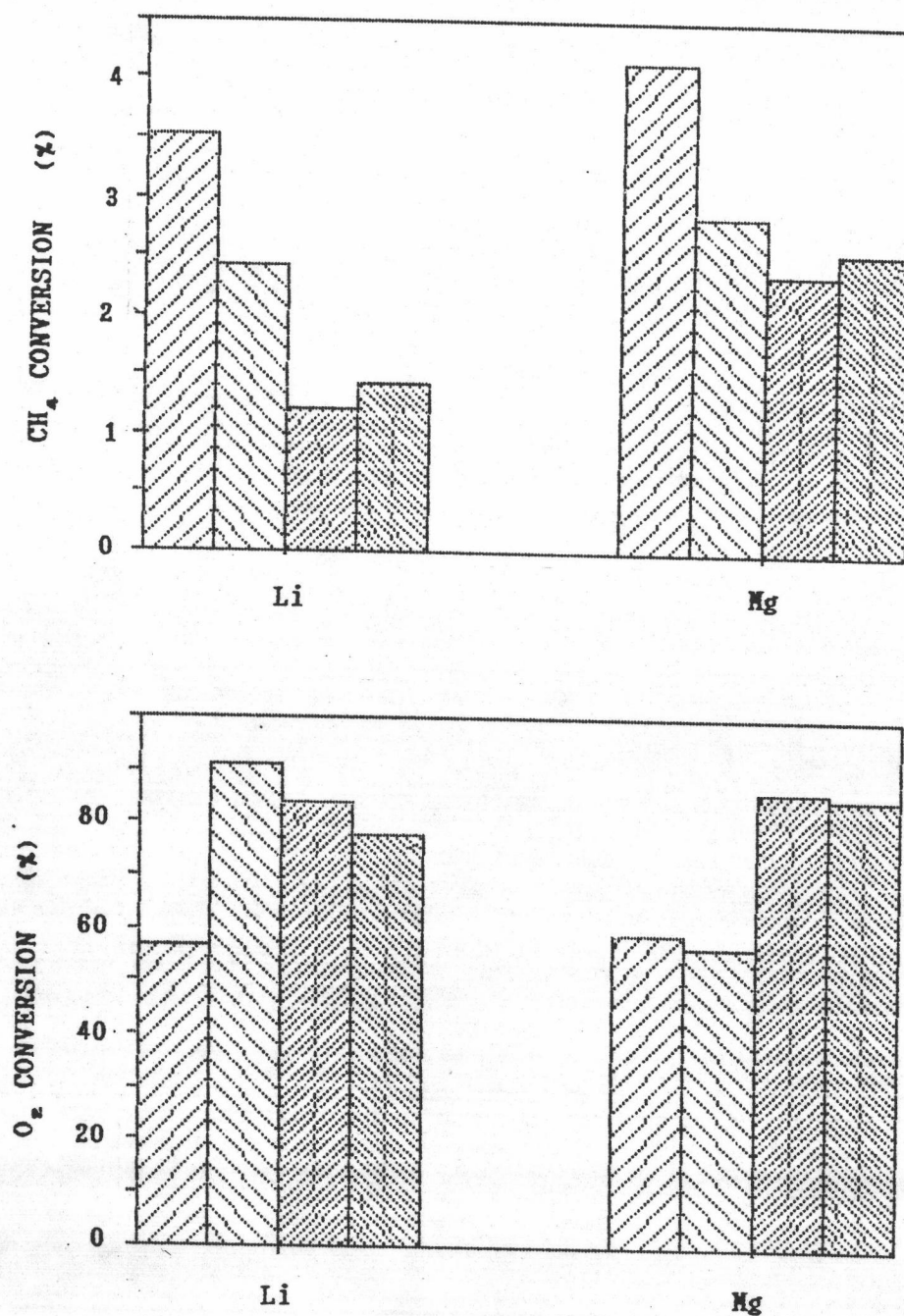
Figure 4-13 Methane and oxygen conversion of Li and Mg

doped on various supports in reducing form.
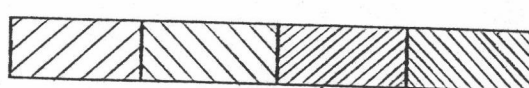
ZINC   ALUMINA SILICA ZEOLITE
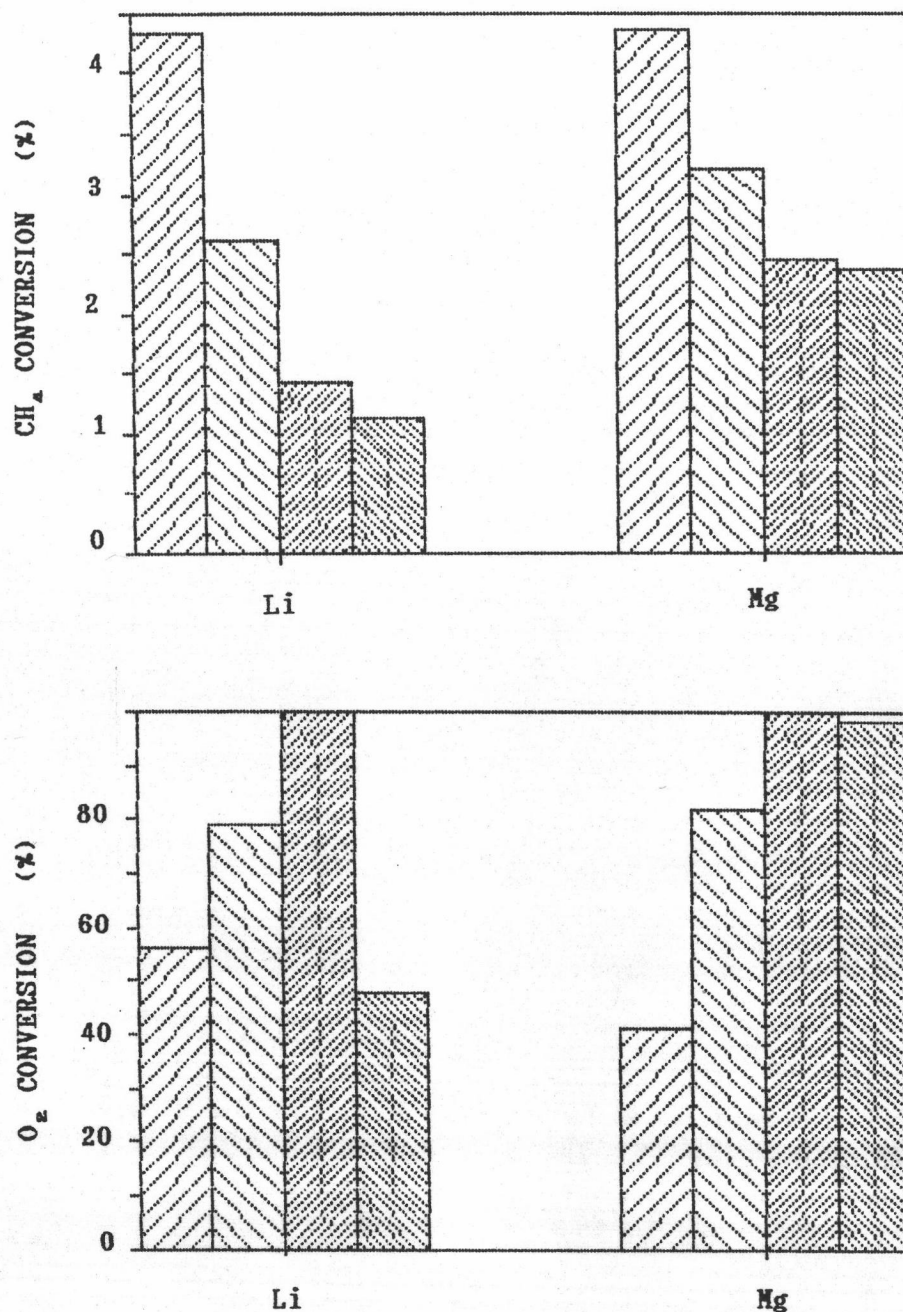
Figure 4-14   Methane and oxygen conversion of Li and Mg

doped on various supports in oxidizing form.
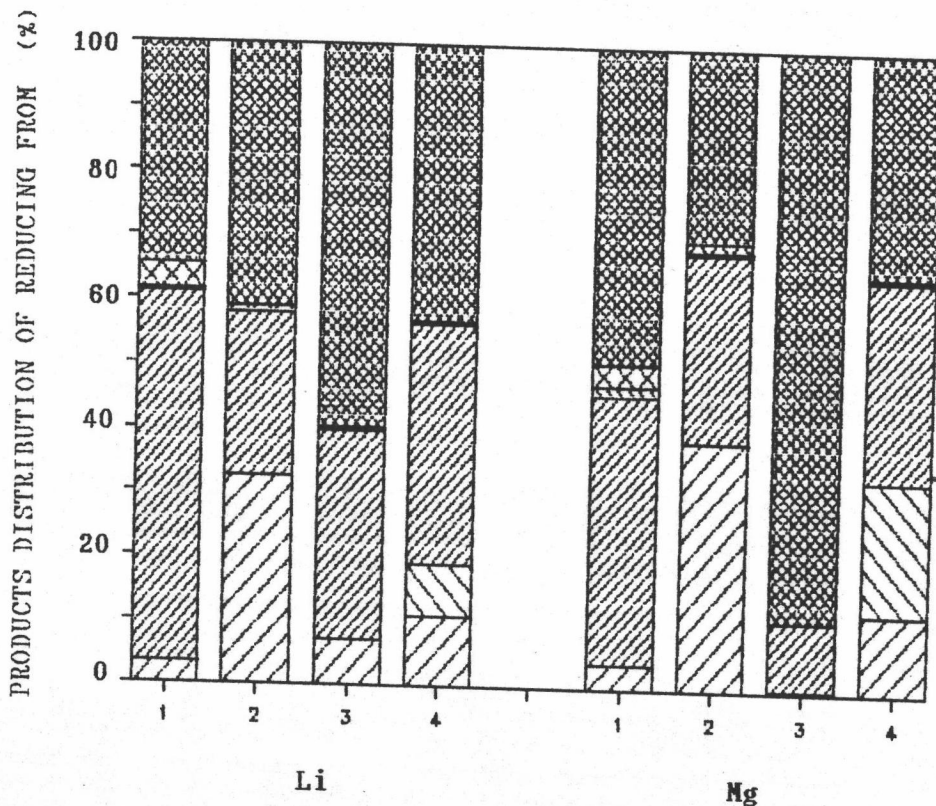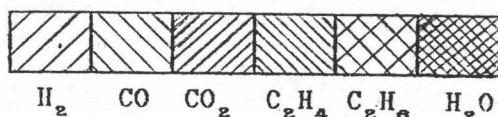
ZINC   ALUMINA   SILICA ZEOLITE
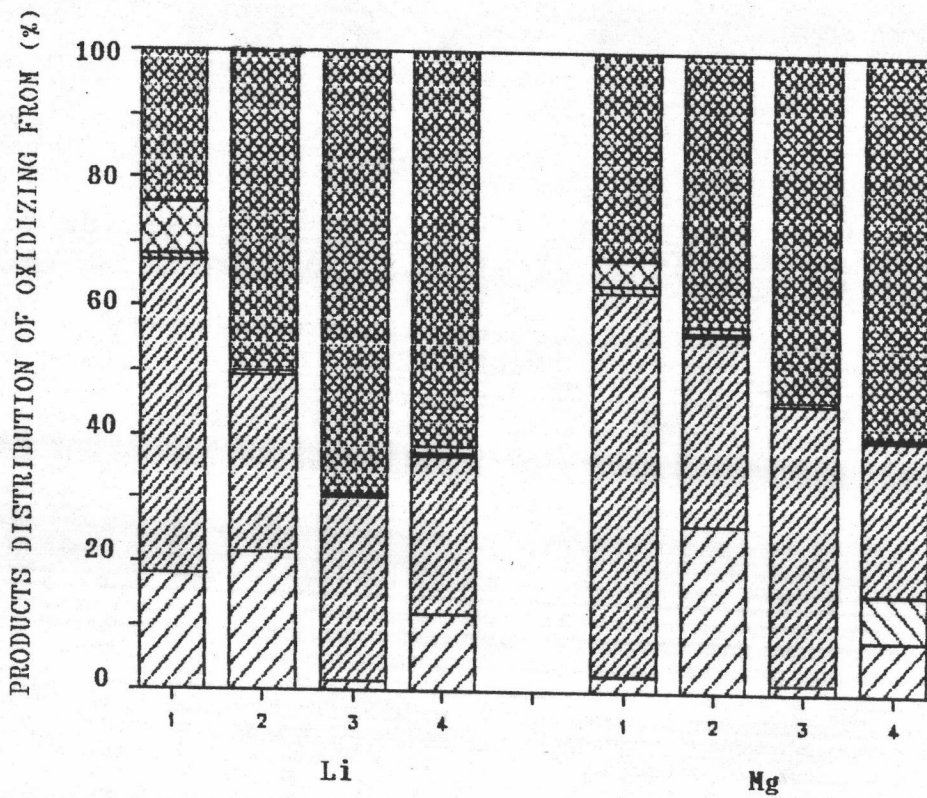
Figure 4-15 Products distribution of Li, and Mg doped on various supports in oxidizing and reducing form.

1 = ZINC OXIDE   3 = SILICA

2 = ALUMINA   4 = ZEOLITE

Concerning the C_2 hydrocarbons, the products distribution of ethane and ethylene were respresented as the carbon compounds selectivity on Figure 4-16. From these results, the important observation of C_2 formation was that C_2 were either ethane or ethane plus ethylene, or there were no ethylene formation without ethane formation. This phenomena agree with the previous hypothesis in chapter II that the path way of ethylene formation started from the partial oxidizing reaction of the produced ethane.

As all those results in the investigation of supports, ZnO support had the activity which really stand out to generate C_2 hydrocarbons while the other supports had less significant abilities. Therefore the discussion will be done on these results. According to the previous discussion concerning the effect of primary compounds in 4.1, there was the co-operation between the doped metal and support lattice namely the arc-fusion process. This means that the chemical activity of effective catalyst due to the support did not come from the high surface area only. Therefore, the effect of support will be discussed by basis on three factors concerning the chemical nature and character of supports, i.e., the arc-fusion, the catalytic abilities on its chemical nature, and the surface area of the prepared supports.

Firstly, the arc-fusion will be considered. Li^+ and Mg^{2+} ions which were used as the primary component had the ionic radius, i.e., $0.68\overset{\circ}{A}$ and $0.65\overset{\circ}{A}$ respectively. According to the previous discussion
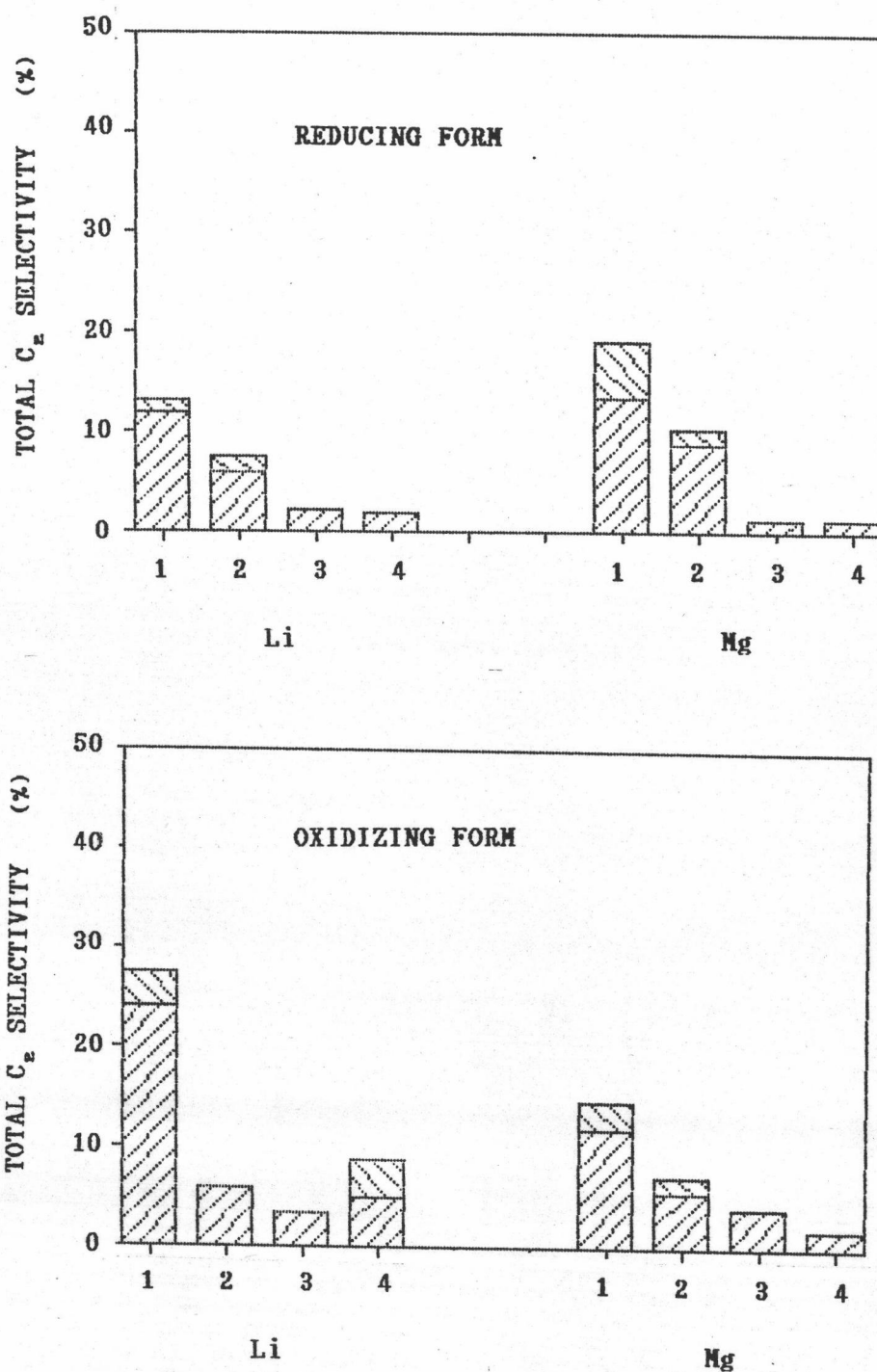
Figure 4-16 Total C$_2$ selectivity basis on carbon compound

products of Li and Mg doped on various supports.

1 = ZINC OXIDE

2 = ALUMINA

3 = SILICA

4 = ZEOLITE

ETHYLENE

ETHANE

in 4.1, the arc-fusion process of both Li^+ and Mg^{2+} ions with Zn^{2+} ions are avialable because the ionic radius of Zn^{2+} ions in ZnO which was $0.74\overset{\circ}{A}$ were bigger than those doped metals. However the arc-fusion in Li/ZnO was effective to generate the active site of oxygen ions while Mg/ZnO was not. The ionic raduis of Al^{3+} and Si^{4+} ions were $0.50\overset{\circ}{A}$ and $0.41\overset{\circ}{A}$ respectively, therefore, the arc-fusion between doped metal such as Li^+ and Mg^{2+} ions and the support lattice such as Al_2O_3, SiO_2, and Zeolite did not occur because Li^+ and Mg^{2+} ions are too large to substitute for Al^{3+} and Si^{4+} ions. Consequently, the prepared catalysts which were used for the investigation of supporting effect, according to arc-fusion process, had only the Li/ZnO catalyst which had this advantage in catalyst activity.

The later consideration was the chemical nature of each support related to the catalytic abilities. According to the classification of solids into groups depending on their catalytic abilities of heterogeneous catalysts by G.C. Bond [5:13], the used supports in this study are able to classify as shown in Table 4-7. These oxides such as alumina, silica, and magnesia, which do not interact much with oxygen are poor oxidation catalysts, but they easily adsorb water and thus may be used for catalyst dehydration [5:14]. One of the useful catalytic properties of zeolite hinges on the presence of strongly acidic hydroxyl groups which can initiate carbonium-ion reaction, and zeolite containing rare-earth ions are employed on an industrial scale in the petroleum industry

Table 4-7   The classification of the supports

| Support	Class	Function
ZnO	semiconducting oxides	oxidation dehydrogenation desulphurization
Al_2O_3, SiO_2	insulator oxides	dehydration
Zeolite $(SiO_2-Al_2O_3)$	acids	polymerization isomerization cranking alkylation

for hydrocarbon cracking. According to the previous mechanism of the oxidative coupling of methane in chapter II that the ethane formed by dimerization of methyl radicals generated from methane by the oxygen ions in metallic oxide center. Therefore the catalytic properties of zeolite do not match with the required active oxidant to produce methyl radicals from methane, cracking and oxidation. On the other hand, Al_2O_3 and SiO_2 are also not good for oxidative coupling of methane, dehydration and oxidation. ZnO was classified to be a semiconducting oxide. This type of

oxide is in turn subdivided on the basis of whether it gains or loses oxygen when heated in air. The terms of oxygen excess or deficiency leads to p- or n-type semiconducting respectively. Zinc oxide becomes oxygen-deficient on heating in air, therefore it is the n-type semiconductivity [5:31]. p-Type oxides are generally better catalysts for oxidation reactions than n-type oxides, because adsorbed oxygen species are more reactive than lattice oxide ions. This means ZnO is considered to be a proper metal oxide to oxidative coupling reaction of methane or partial oxidation because the more reactive adsorbed oxygen species make the more deep or continuously oxidize methane to be CO and CO_2 whereas the oxygen in lattice oxide ions partially oxidizes methane to be methyl radicals.

The last factor concerning the results in the investigation of supports is surface area of each type. Figure 4-17 and 4-18 showed the character of morphology of ZnO, Al_2O_3 and SiO_2. Zeolite respectively. ZnO and zeolite were porous bulk while Al_2O_3 and SiO_2 were not, therefore, the catalyst surface of ZnO and Zeolite were greater than the others. However, the methane conversion and C_2 selectivity of zeolite were several time less than zinc oxide. These may be used to support the previous discussion concerning the less significant activity of zeolite by the chemical nature.
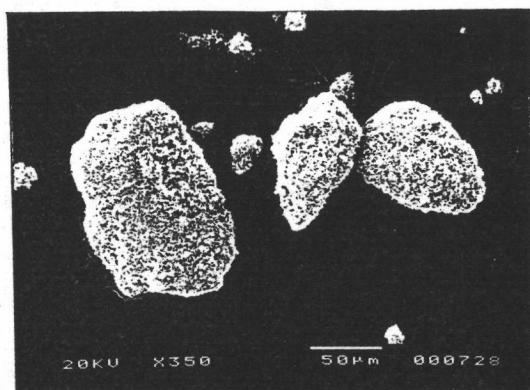
A : Zinc oxide
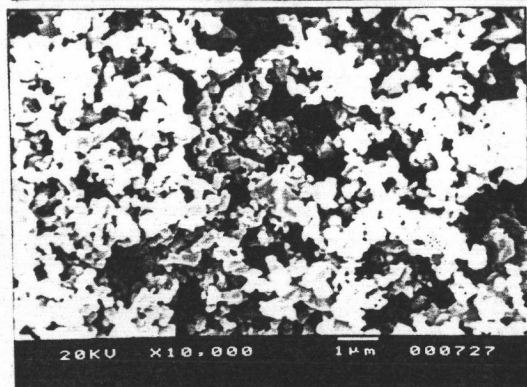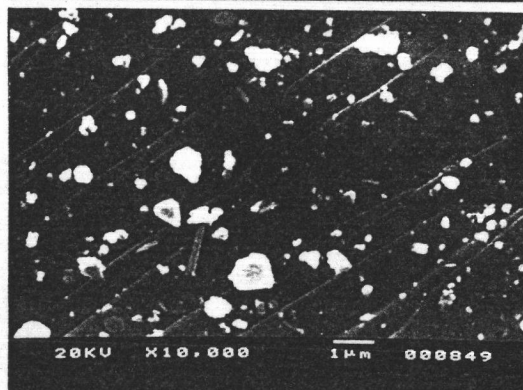
B : Magnified picture of A
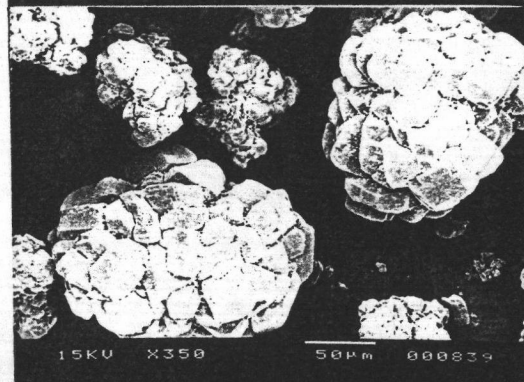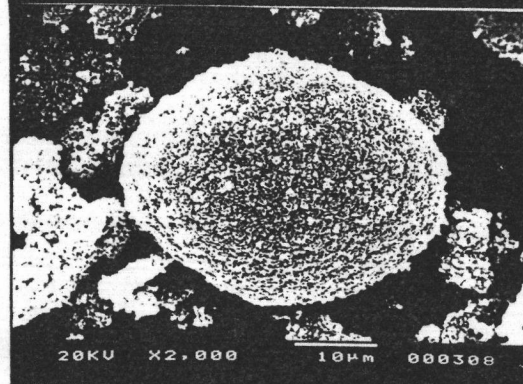
C : Alumina
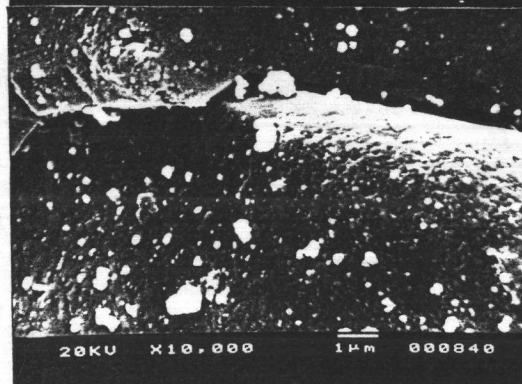
D : Magnified picture of C

Figure 4-17   Surface and morphology characteristic of
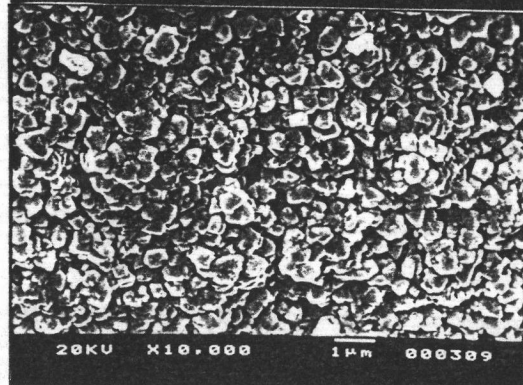
zinc oxide and alumina supports.
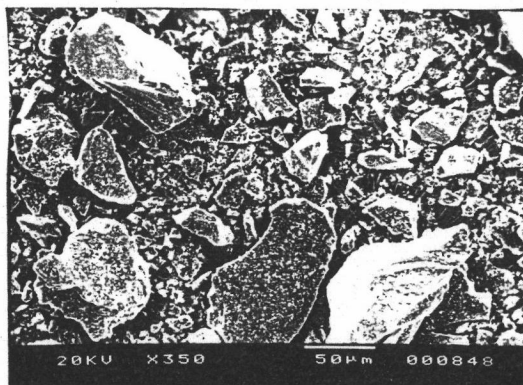
A : Silica

B : Magnified picture of A

C : Zeolite

D : Magnified picture of C

Figure 4-18   Surface and morphology characteristic of

silica and zeolite supports.

4.3 Effect of Methane/Oxygen Mole Ratio

In this study, the effect of methane/oxygen mole ratio or the concentration of oxygen in the feed gas on the catalytic performances such as the methane conversion and the products selectivity were investigated. The ratios were varied from 5:1 to 50:1 while the other conditions were kept constant at atmospheric pressure, temperature=$600^{\circ}C$ and WHSV=0.52 hr^{-1}. This investigation have been done on various catalysts as follows:

i) The various primary components such as alkali metals (Li and Mg) and transition metals(V, Fe and Cu) are doped on ZnO support.

Figure 4-19 are the plots of the methane conversion and the total C_2 selectivity versus $CH_4:O_2$ on Li- and Mg-doped ZnO catalysts. The overall products distribution of these catalysts are shown in Figure 4-21. As the results in both figures showed, when methane/oxygen mole ratio increased (oxygen concentration decreased) the conversion of fed methane decreased and C_2 hydrocarbons selectivity increased for both catalysts. However, the decreasing of methane conversion on Mg catalyst was much more than on Li catalyst. On the other hand, the increasing of C_2 selectivity on Li catalyst is much more than on Mg catalyst. As the results, there were no CO formation on these catalysts, therefore, the carbon compounds formed were CO_2, C_2H_4, and C_2H_6. As for carbon dioxide, it was
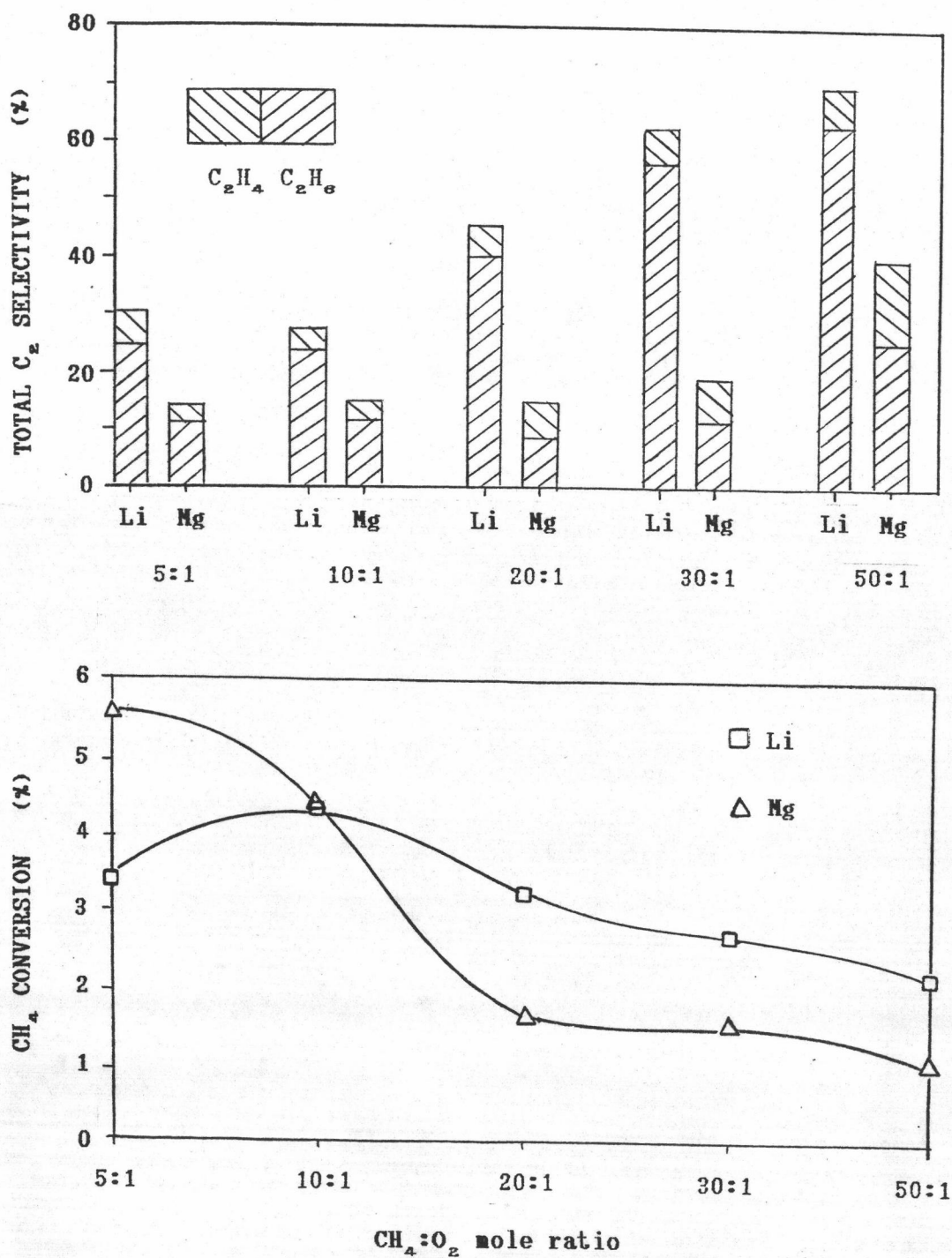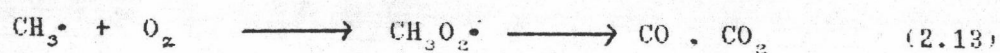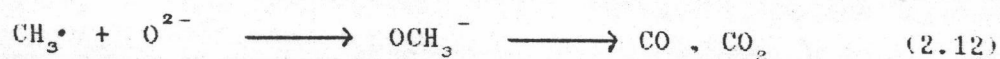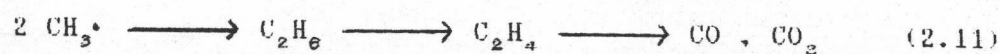
Figure 4-19 Total C$_2$ selectivity basis on carbon compound products and methane conversion of Li and Mg doped on ZnO support versus CH$_4$:O$_2$ mole ratio.

attributed to the complete oxidation while C_2 hydrocarbons were attributed to the partial oxidation character (via oxidative coupling). Therefore, this means the reducing of oxygen concentration decreased the deep oxidation reaction state. This is the required route because it means the high efficiency of changing carbon atom from methane to the valuable hydrocarbon products such as ethane and ethylene. For example, as the results in Figure 4-19 showed there was ca. 70% efficiency of changing methane carbon atom to C_2 hydrocarbons atom. The reason of this phenomenon may be explained by using the previous discussion concerning the three pathways of CO and CO_2 in chapter II as follows:

$$2\ CH_3\cdot \longrightarrow C_2H_6 \longrightarrow C_2H_4 \longrightarrow CO\ ,\ CO_2 \qquad (2.11)$$

$$CH_3\cdot + O^{2-} \longrightarrow OCH_3^- \longrightarrow CO\ ,\ CO_2 \qquad (2.12)$$

$$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot \longrightarrow CO\ ,\ CO_2 \qquad (2.13)$$

Pathway (2.11) was not a major route, pathway (2.12) should be related to the surface area of catalyst and pathway (2.13) should depend on the O_2 pressure [2:5067]. Because the results of these study were from the same catalyst, therefore, the change of CO_2 formation due to the catalyst surface in pathway (2.12) should not have much effect. Pathway (2.13) was a gas phase reaction between methyl radical and gaseous oxygen. Therefore, the decreasing of oxygen concentration in feed gas should decrease the formation of carbon dioxide formation.
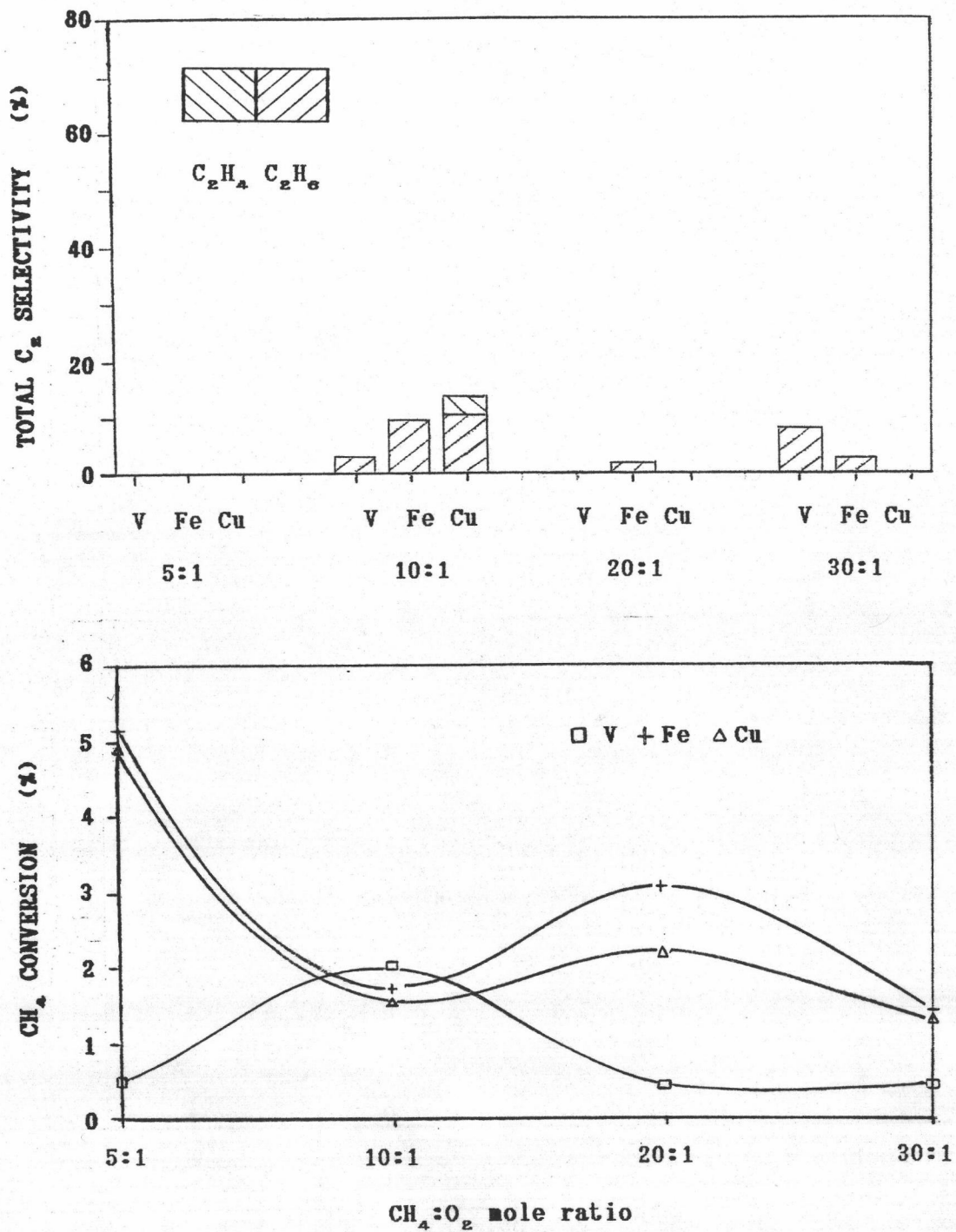
Figure 4-20 Total C_2 selectivity basis on carbon compound products and methane conversion of V, Fe and Cu doped on ZnO support versus $CH_4:O_2$ mole ratio.
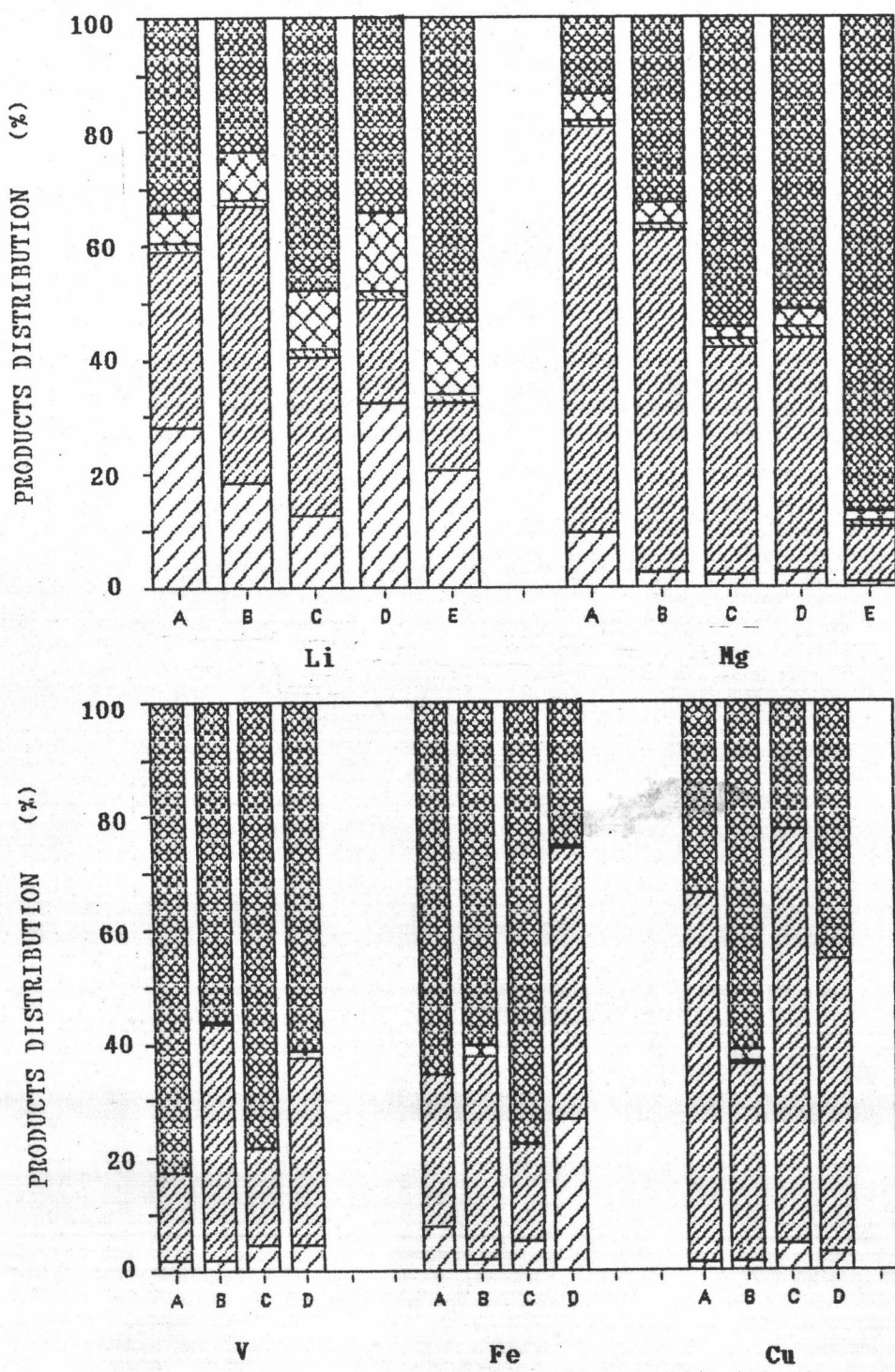
Figure 4-21 Products distribution of various elements

doped on zinc oxide versus $CH_4 : O_2$ ratio.

H_2 CO CO_2 C_2H_4 C_2H_6 H_2O

A = 5:1

B = 10:1

C = 20:1

D = 30:1

E = 50:1

Figure 4-20 showed the methane conversion and the total C_2 selectivity of V-, Fe- and Cu-doped ZnO catalysts. The products distribution of these catalysts were shown in Figure 4-21. Results showed that the reaction products were mostly CO_2 and H_2O, or there were almost complete oxidation. These confirmed the previous discussion that the doped transition metals were not the active catalyst for oxidative coupling of methane.

ii) The various supports such as ZnO, Al_2O_3, SiO_2 and zeolite were doped by Li components.

Methane and oxygen conversions are shown in Figure 4-22 and the products distribution are shown in Figure 4-23. The results from methane conversion signify that the more oxygen concentration obtained the more methane conversion. However, as for the oxygen conversion, it was affected not only by methane/oxygen mole ratio but also by the nature of support. C_2 formation was found only for zinc oxide support and the products distribution seemed to be sensitive to methane/oxygen mole ratio and the nature of support. By combining these results with those results of the transition-metal doped (V, Fe and Cu) ZnO catalysts, it seem that the oxygen concentration have no effect on these non-active catalysts while the active catalysts i.e., alkali-doped ZnO had large effect of the oxygen concentration on the products selectivity of C_2 hydrocarbons.
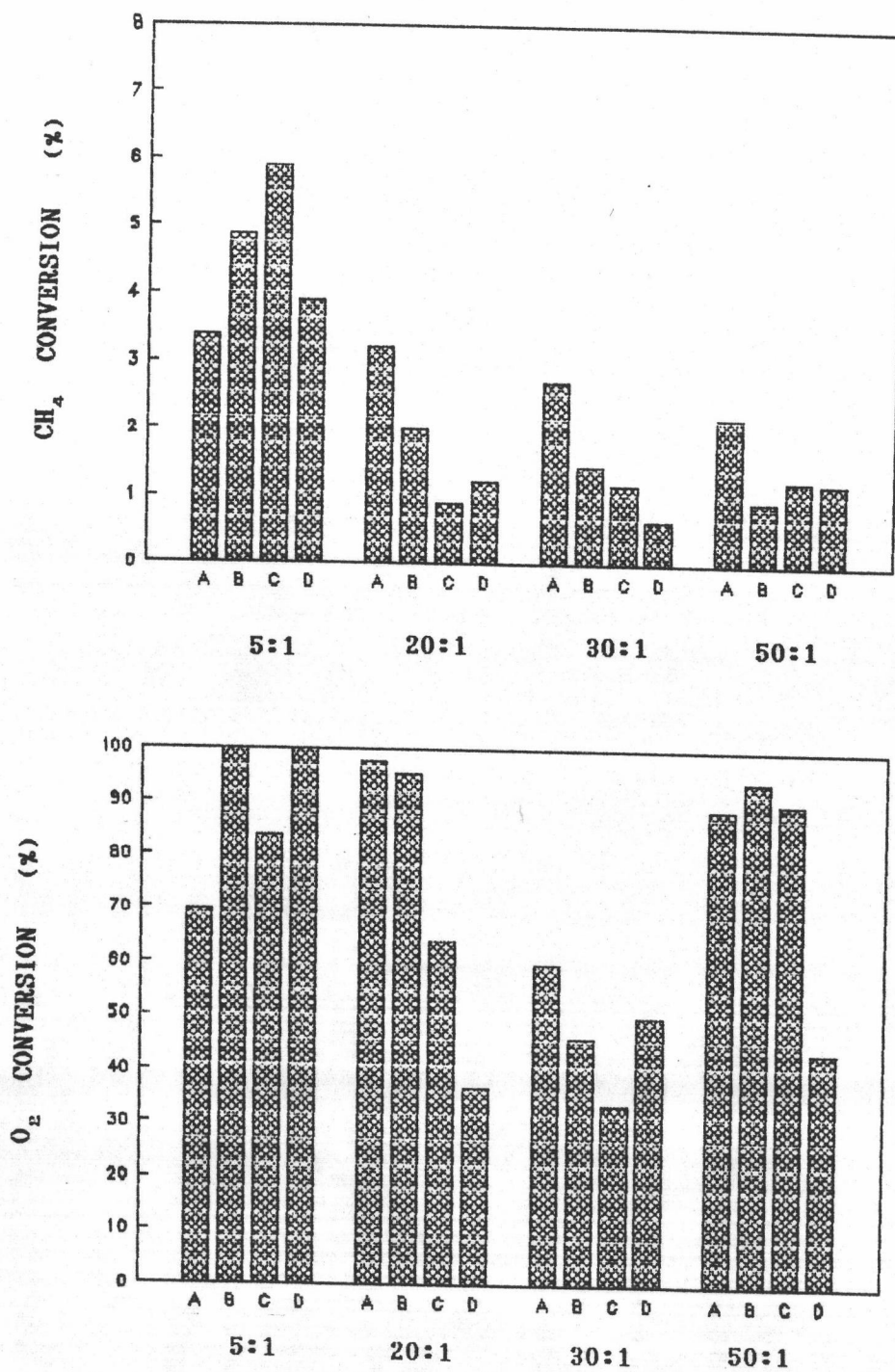
Figure 4-22 Methane and oxygen conversion of Li-doped on

various supports versus $CH_4:O_2$ mole ratio.
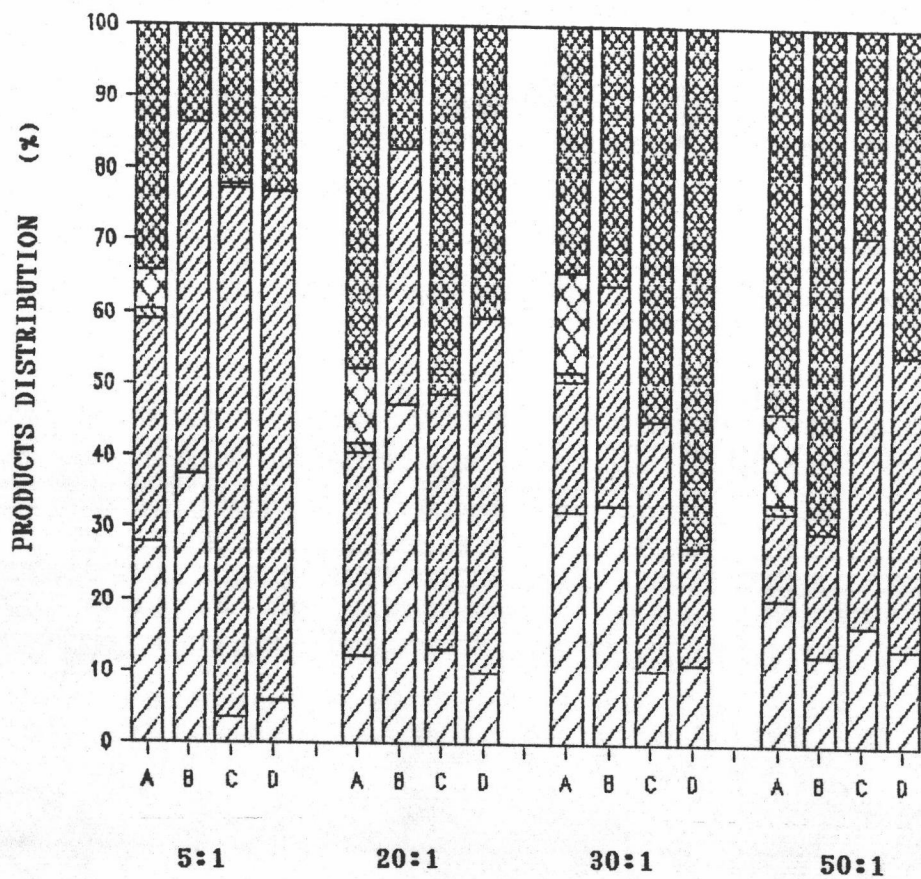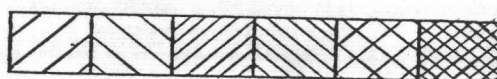

A = Zinc oxide B = Alumina C = Silica D = Zeolite

Figure 4-23   Products distribution of Li-doped on

various supports versus $CH_4:O_2$ mole ratio.

A = Zinc oxide B = Alumina C = Silica D = Zeolite

H_2 CO CO_2 C_2H_4 C_2H_6 H_2O

4.4 Effect of Temperature

This is the study of the effect of reaction temperature on the chemical reactivities such as the methane conversion and the products selectivity. The temperature was varied from 450°C to 650°C by 50 celsius interval while the other conditions were kept constant at atmospheric pressure, temperature = 600°C and WHSV = 0.52 hr^{-1}. This investigation have been done on alkali-doped zinc oxide i.e., Li- and Mg-ZnO. Methane conversion and total C_2 selectivity of Li- and Mg-doped ZnO were shown on Figure 4-24 and the products distribution of both catalysts were shown on Figure 4-25.

As for the results of Li/ZnO, both methane conversion and total C_2 selectivity greatly rose with the increasing of temperature. At 450°C and 500°C, there were no observable C_2-hydrocarbons, however, there could be found a little at 550°C. These may indicate that temperature is an important factor for reaction operating condition in oxidative coupling of methane. Therefore, the high temperature reaction is required because it results in the increasing of both CH_4 conversion and C_2 selectivity while methane/oxygen mole ratio gave opposing results, i.e., at high methane/oxygen mole ratio, CH_4 conversion decreased while C_2 selectivity increased.

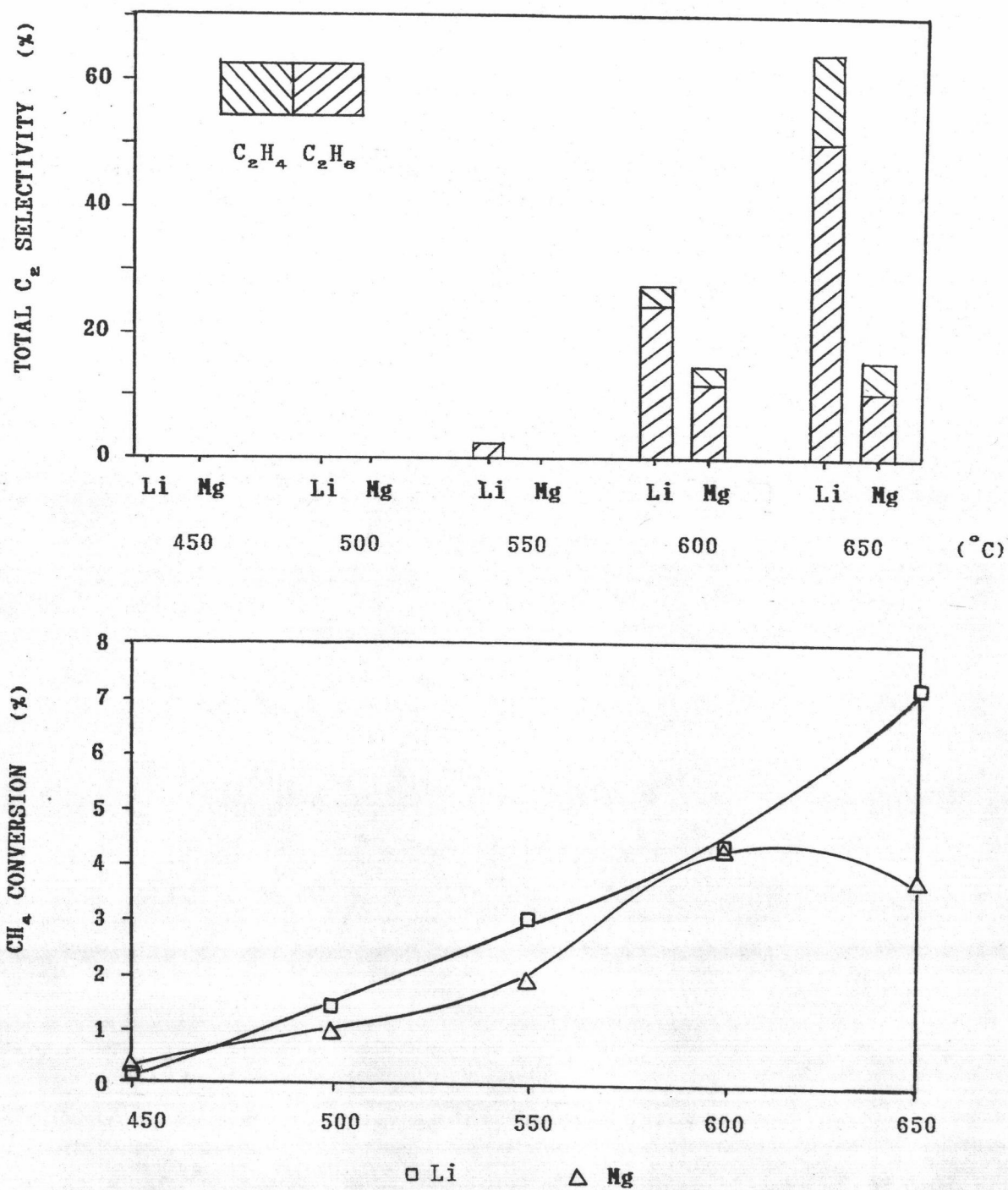As the results of Mg/ZnO, the C_2 selectivity also increase

Figure 4-24 Total C_2 selectivity basis on carbon compound
products and methane conversion of Li and Mg
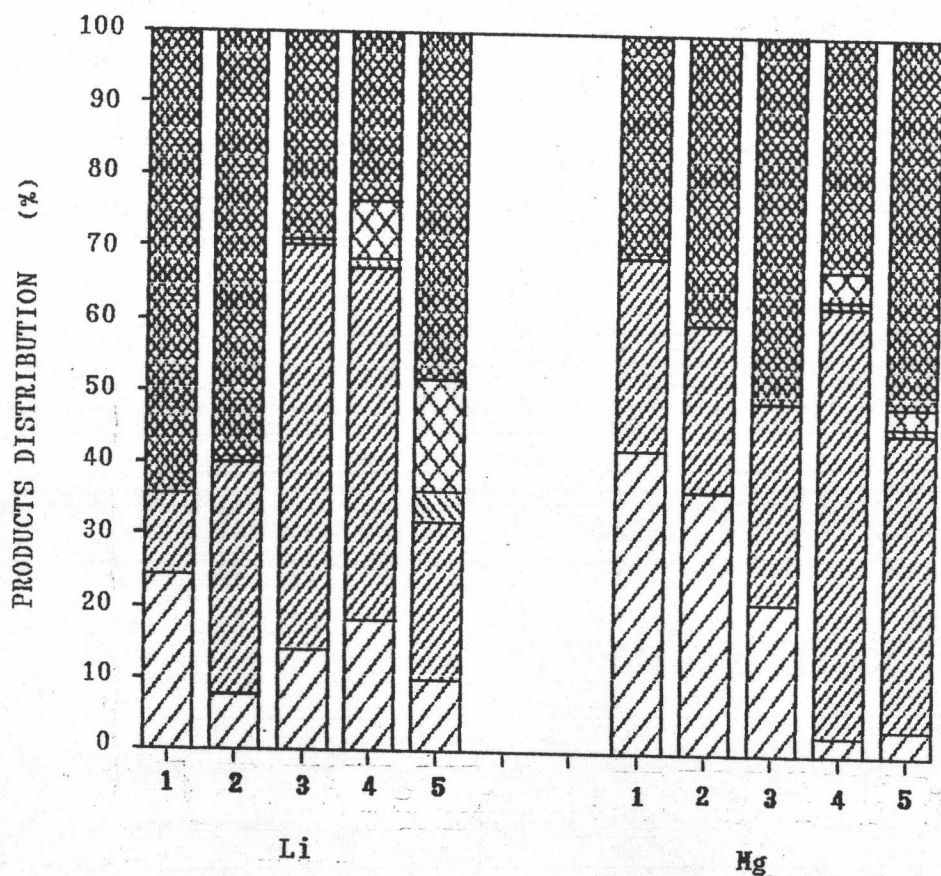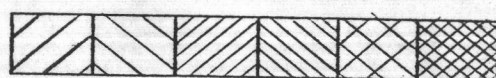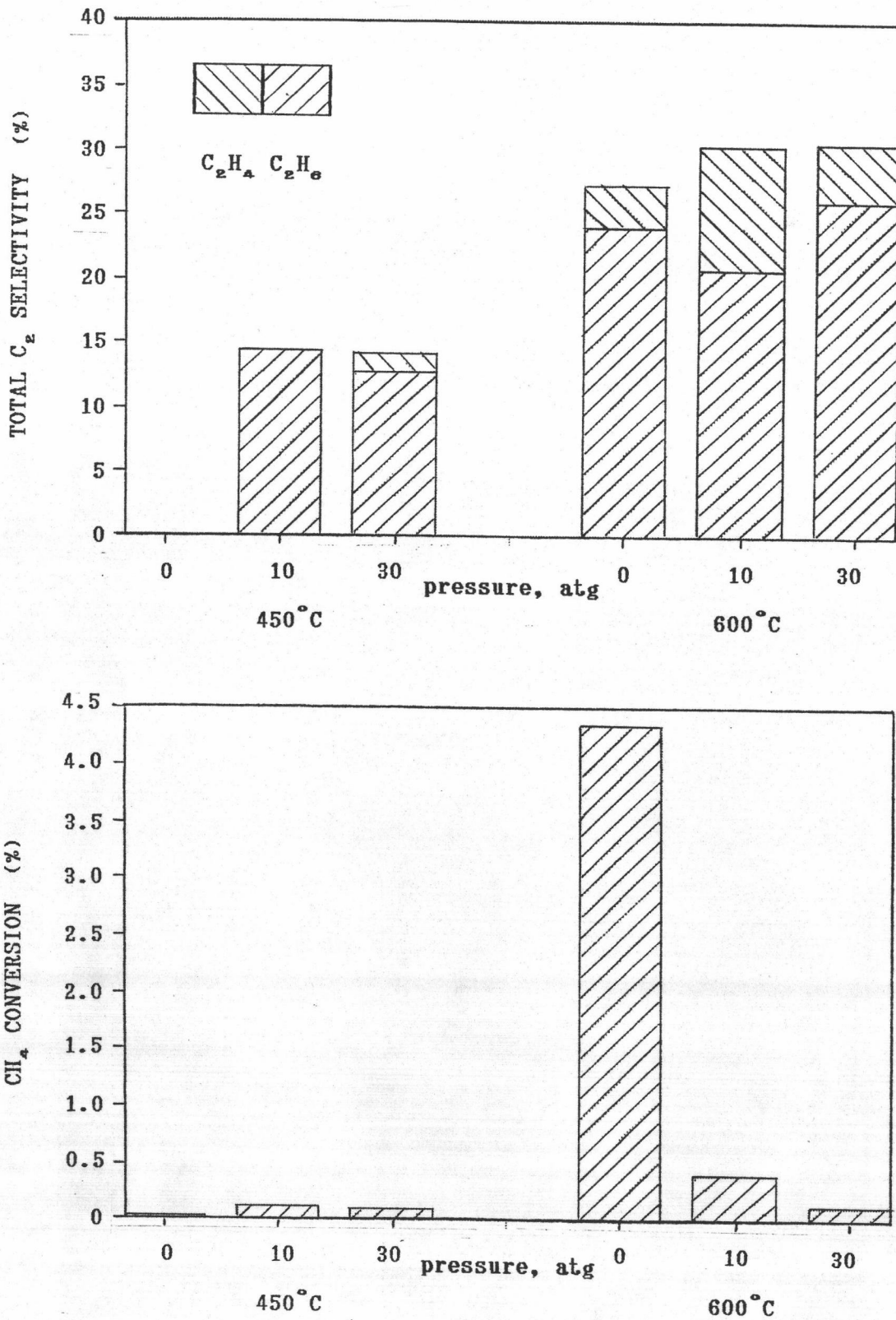doped on ZnO support versus temperature.

Figure 4-25   Products distribution of Li and Mg doped on ZnO support versus temperature.

H_2 CO CO_2 C_2H_4 C_2H_6 H_2O

1 = 450 °C
2 = 500
3 = 550
4 = 600
5 = 650

with temperature but CH_4 conversion had a change of slope at 600 °C. This occurred in Mg while Li had not this behaviour and the total C_2 selectivity was lower and slightly increased with temperature when compared with Li. These may be used to confirm the previous discussion that Li/ZnO was more active more than Mg/ZnO. The great difference of catalytic activity of these two doped metal may come from the ability of forming O^- ions which increased with temperature. Li/ZnO had this formation of O^- ions by arc-fusion while Mg/ZnO had not.

4.5 Effect of Pressure

Only Li-doped zinc oxide was selected for use in studying the effect of pressure. The experiments were done at the same feed flow rate, 1 ml/s, methane/oxygen ratio = 10 : 1 and two points of temperatures, namely, 450°C and 600°C. Pressure was varied from atmospheric pressure (0 atg.) to 30 atg. The experimental results as a bar chart were presented in Figure 4-26 for CH_4 conversion and total C_2 selectivity and Figure 4-27 for products distribution respectively. In Figure 4-26, pressure had not much effect on the C_2 carbon compounds selectivity at both temperatures, however, at 600°C methane conversion decreased. As the results in Figure 4-27, water formation decreased with increasing pressure and there was a CO formation at 30 atg. These behaviours were also found at both temperatures.

The increasing of pressure while the volumetric feed flow rate was kept constantly resulted the entrance mole of methane increased while using the same amount of catalyst. Therefore, methane conversion decreased with increasing of pressure. On the other hand, the catalyst has a limited capacity. This may be found in Figure 4-28 which showed the Space Time Yield of C_2 formation did not change with pressure. For Li-doped ZnO catalyst, the ability of this catalyst to produce C_2 was ca. 4 E-4 mole atom per hour per gram of catalyst.

Figure 4-26 Total C_2 selectivity basis on carbon compound products and methane conversion of Li doped on ZnO support versus pressure at $450°C$ and $600°C$.
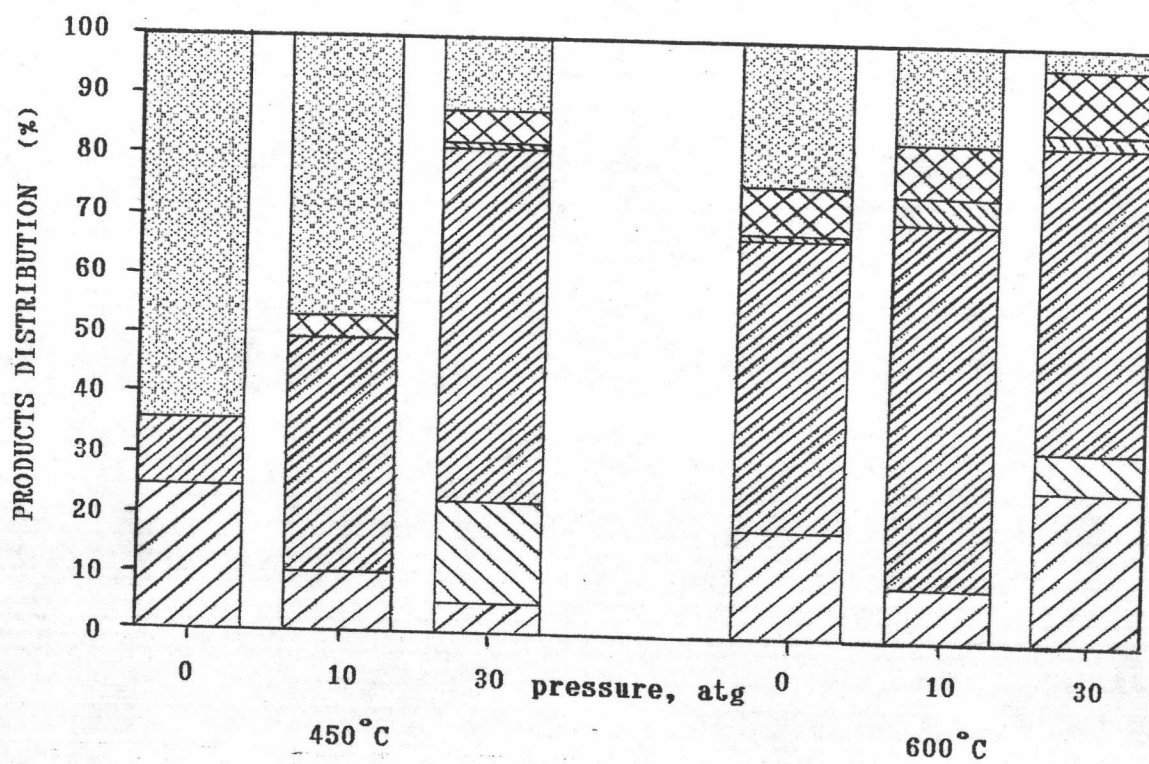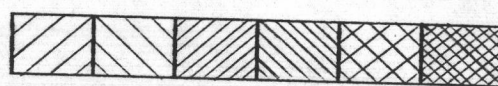
Figure 4-27 Products distribution of Li doped on zinc oxide
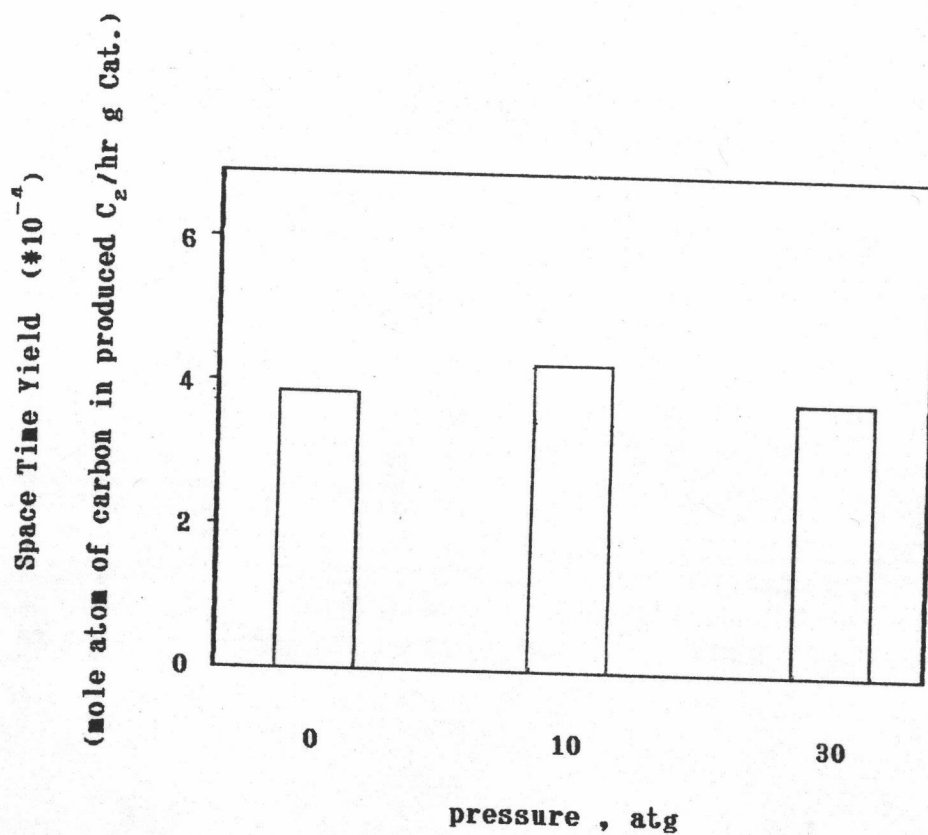versus pressure at 450 °C and 600 °C

Figure 4-28   Space Time Yield of C_2 formation on Li-doped
ZnO catalyst versus pressure at 600°C.