

SHORT COMMUNICATION

## THE EFFECT OF ALKALI METAL SALTS PROMOTED MgO CATALYSTS FOR THE OXIDATIVE COUPLING OF METHANE

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**Abstract**—Catalytic activities of the alkali metal salts are discussed based on experimental observations in a fixed bed flow reactor at atmospheric condition and instrumental analysis. LiCl (30 wt%) and NaCl (30 wt%) promoted MgO catalyst showed superior activity to mono alkali metal salts promoted MgO catalysts based on the C<sub>2</sub> yield. This suggests that the bi-alkali metal salts neutralize the nonselective acid sites due to synergistic effect. Moreover, it is estimated that the active sites is O<sup>-</sup> ions.

**Key words:** Oxidative Coupling of Methane, Alkali Metal Salts, MgO

### INTRODUCTION

Conversion of methane is an actively studied process to C<sub>2</sub> hydrocarbons [Amenomiya et al., 1990; Ito et al., 1985; Otsuka, 1987]. Methane is one of alternative energy sources for petroleum. So far, C<sub>2</sub> hydrocarbons have mainly been produced by MTG process, which is a gasoline production from methanol using ZSM-5 catalyst. The methanol is produced from syngas which is obtained from the steam reforming process of methane or produced Fisher-Tropsch process. Therefore, MTG process is rather inefficient process considering the high capital cost for production of syngas. The fact that OCM can directly produce more C<sub>2</sub> hydrocarbons from methane than the intricate MTG process has attracted a focus. However, it is thermodynamically difficult to convert methane directly to C<sub>2</sub> hydrocarbons because methane molecular is a stable compound which high C-H bond dissociation energy, 104 kcal/mole. In order to overcome this difficulty, Gibbs free energy should be lowered using oxidants such as O<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub> etc. Moreover, to get both conversion as high as 35% and C<sub>2</sub> selectivity more than 88% [Joseph, 1993], control problem of the selectivity between C<sub>2</sub> hydrocarbons and CO<sub>x</sub> should be overcome. Therefore, development of superior catalysts is essential. It has been known that many metal oxides have catalytic activity [Lee and Oyama, 1988] for OCM since Keller and Bhasin [1982] have published on oxidative coupling of methane to C<sub>2</sub> hydrocarbons over metal oxide catalysts for the first time in 1982.

This study tries to look into the active site of catalysts and catalytic activities of alkali metal salts promoted MgO catalysts by means of both reaction experiments at atmospheric condition in a fixed bed flow reactor and instrumental analyses such as FT-IR, SEM, BET, etc.

### EXPERIMENTAL

#### 1. Catalyst Preparation

The catalysts used in this study were magnesium oxide catalysts impregnated with NaCl, LiCl, KCl by Slurry method [Lin

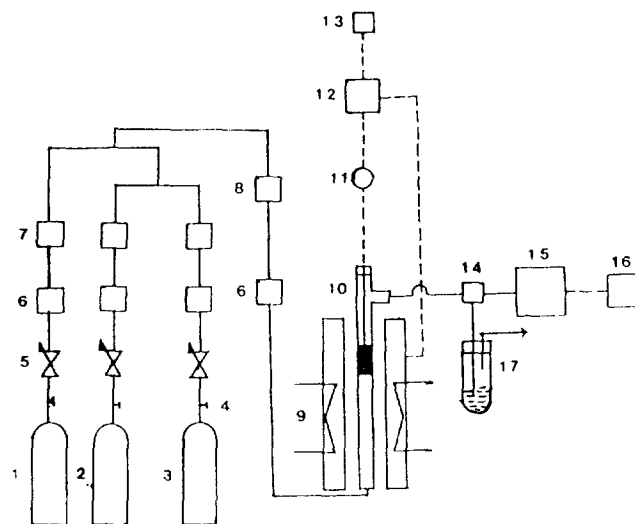


Fig. 1. Schematic diagram of experimental apparatus.

- |                             |                            |
|-----------------------------|----------------------------|
| 1. O <sub>2</sub> cylinder  | 10. Reactor                |
| 2. CH <sub>4</sub> cylinder | 11. Thermocouple           |
| 3. N <sub>2</sub> cylinder  | 12. Temperature controller |
| 4. Pressure regulator       | 13. Temperature recorder   |
| 5. Needle valve             | 14. Gas sampler            |
| 6. Silica trap              | 15. G.C.                   |
| 7. Capillary flow meter     | 16. Data processor         |
| 8. Mixing chamber           | 17. Bubble trap            |
| 9. Electric furnace         |                            |

et al., 1988]. Reagents were extra pure grades. Alkali salts and MgO were mixed into deionized water homogeneously by stirring. The slurry was heated until all the water was evaporated. The thick paste was then completely dried at 125°C in an oven for 24 hours, followed by the calcination in the electric furnace (K. K. Sanyo, Japan) under air for 6 hours at 900°C. Subsequently, it was grinded into the size of between 170 and 200 mesh.

#### 2. Apparatus and Methods

A schematic diagram of the experimental apparatus is shown-

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**Table 1. Effect of alkali metal promoters on catalytic activity**

Catalyst	Conversion (%)		Selectivity (%)					Yield (%)			
	CH <sub>4</sub>	C <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO	CO <sub>2</sub>
MgO	3.79	35.60	7.48	28.12	9.95	54.45	1.35	0.28	1.07	0.38	2.06
LiCl (30 wt%)/MgO	32.33	55.84	49.51	6.32	9.39	34.77	18.05	16.01	2.04	3.04	11.24
NaCl (30 wt%)/MgO	20.32	61.12	47.26	13.87	16.78	22.10	12.42	9.60	2.82	3.41	4.49
NaCl (60 wt%)/MgO	13.01	63.63	42.31	21.33	15.76	20.60	8.28	5.50	2.77	2.05	2.68
[LiCl (30 wt%)+NaCl (30 wt%)]/MgO	30.30	61.37	54.20	7.17	12.76	25.87	18.60	16.42	2.17	3.87	7.84
KCl (30 wt%)/MgO	18.28	55.49	32.40	23.09	1.63	42.88	10.14	5.92	4.22	0.30	7.84

Reaction Condition: Reaction Temp.=730°C, CH<sub>4</sub>/O<sub>2</sub> molar ratio=2 mol CH<sub>4</sub>/mol O<sub>2</sub>, W/F=1.7×10<sup>-4</sup> g-cat·hr/ml.

ed in Fig. 1. The reactor has an I.D. of 11 mm and length of 400 mm. It is made of stainless steel. The reactor was maintained at a certain desired temperature with an accuracy of ±1°C by a K-type thermocouple and P-controller (Eunsuk Co., Model CIS-021, Korea). The temperature was recorded. Sea sand was mechanically mixed with catalysts as a diluent before being packed in the reactor, which not only distributes the catalyst bed temperature uniformly, but also reduces the pressure drop through the packed bed. Reactant used in this way are methane (Daiho San Gyo Co., Japan), oxygen (Sin-il gas Co., Korea), and nitrogen (Sin-il gas Co., Korea). All of them have purity of 99.99%. The composition of gaseous reactants was controlled using a pressure regulator attached to each gas cylinder. The reactant can be mixed completely in mixing chamber after passing through a silica trap. Effluent was analyzed with an on line G.C. (Shimadzu Co., Model 8AT, Japan) in which Porapak Q and Molecular sieve 5A column were linked in parallel. Total flow rate was maintained at 50 ml/min. Partial pressure of methane and oxygen was 0.16 atm and 0.08 atm respectively in all experiments and CH<sub>4</sub>/O<sub>2</sub> molar ratio was stoichiometric. The instruments used to analyze the characteristics of catalysts were FT-IR (Mattson, Polaris/Icon, USA), SEM (Jeol Co., JSM-35C, Japan) and BET (AVSA, ASAP 2000, Micromeritics).

## RESULTS AND DISCUSSION

The conversion, selectivity and yield is defined to analysis activity of the catalysts as follows.

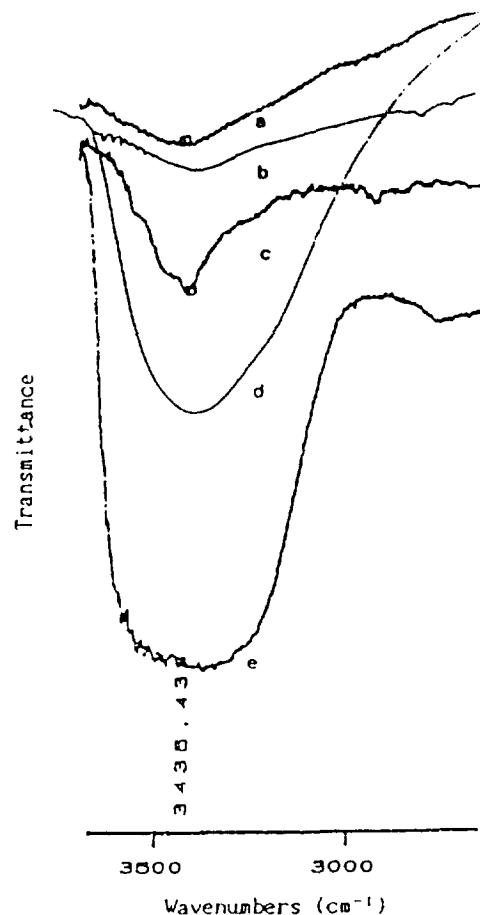
% Conversion of methane=(converted moles of methane to product/input moles of methane)×100

% Selectivity of product=(moles of desired product/converted moles of methane to product)×100

% Yield=(moles of desired product/input moles of methane)×100

Table 1 shows the activity of magnesium oxide impregnated alkali metal salts. The carrier of magnesium oxide produces mainly carbon dioxide. But magnesium oxide catalysts promoted with alkali metal salts increase the formation of C<sub>2</sub> hydrocarbons. The highest conversion to C<sub>2</sub> hydrocarbons was obtained with magnesium oxide impregnated alkali promoter, NaCl (30 wt%) mixed with LiCl (30 wt%), among the catalysts. The increase in the formation of C<sub>2</sub> hydrocarbons strongly suggests that acid sites are neutralized due to the addition of alkali metal salts, proposed by Parida et al. [1991] and Maitra et al. [1992].

Fig. 2 shows the result of FT-IR analysis, and thickness of pellets were made same. The amount of Brönsted acid site, shown

**Fig. 2. FT-IR spectra of various catalysts.**

a: MgO, b: NaCl (60 wt%)/MgO, c: NaCl (30 wt%)/MgO, d: LiCl (60 wt%)/MgO, e: [LiCl (30 wt%)+NaCl (30 wt%)]/MgO

in FT-IR spectrum, -OH absorption peak at 3435.43 cm<sup>-1</sup>, is well consistent with [LiCl(30 wt%)+NaCl(30 wt%)]/MgO>NaCl (30 wt%)/MgO>MgO based on the C<sub>2</sub> hydrocarbons yield. It seems that the yield of C<sub>2</sub> hydrocarbons increased because the many base sites of O<sup>-</sup> ions were produced on the catalytic surface as the proton, H<sup>+</sup>, was eliminated from -OH. Ruckenstein et al. [1993] suggested that the synergic effect by superbasicity formed by addition of alkali metal salts increased the formation of selective C<sub>2</sub> hydrocarbons based on XPS analysis and experiment. Roos et al. [1989] proposed that this active sites be responsible for producing CH<sub>3</sub>· radicals.

Fig. 3 shows morphology of the catalyst surface taken by SEM.

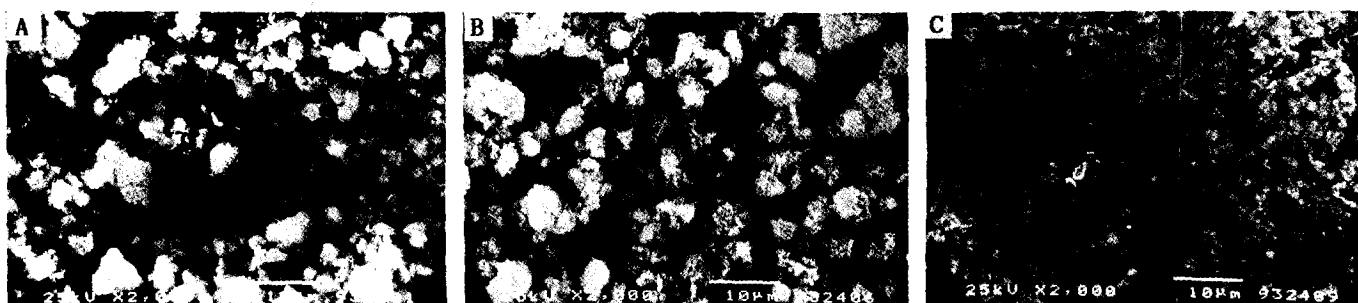


Fig. 3. SEM photographs of MgO catalysts with different promoters.

A: MgO, B: NaCl (30 wt%)/MgO, c: [LiCl (30 wt%)+NaCl (30 wt%)]/MgO

Table 2. Some physicochemical characteristics of the MgO supported alkali metal compounds after 6hr's calcination at 900°C

Catalyst	Surface area (m <sup>2</sup> /g)	Alkali metal compounds loading ratio (wt%)
MgO	3.8931±0.0709	-
NaCl/MgO	1.3529±0.0510	30
[LiCl+NaCl]/MgO	7.1421±0.1755	30+30

In comparison to magnesium oxide carrier and magnesium oxide catalyst promoted NaCl (30 wt%), the magnesium oxide catalyst promoted bialkali metal salts, NaCl (30 wt%) mixed with LiCl (30 wt%) is shown to have smaller and spherical particles uniformly distributed on the surface of catalyst. Moreover, the bialkali metal salts promoted magnesium oxide catalyst seems to be composed of amorphous crystals.

The bialkali metal salts promoted magnesium oxide catalyst seemed to increase C<sub>2</sub> selectivity because distorted lattices [Iwamatsu et al., 1988] and substituting Mg<sup>2+</sup> in lattice with Li<sup>+</sup> ion [Ito et al., 1985] would bear many basicity of O<sup>-</sup> and/or O<sup>2-</sup> [Jun, 1992] on the catalytic surface. These particles and crystals seems to act as effective active sites.

BET surface areas are listed Table 2. It seems that the surface area has no effect on the activity of catalyst.

#### NOMENCLATURE

C<sub>2</sub> : C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>  
 CO<sub>x</sub> : CO and/or CO<sub>2</sub>  
 OCM : oxidative coupling of methane

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