

CHAPTER IV

EXPERIMENT

4.1 Preparation of the catalysts

The catalysts were classified as follows :

1. Mn/Al/Li/nM and Mg/Al/Li/nM, where n was the atomic ratio of M (M = Ce, Pr, Sm)
2. Mn/Li/nM or Mg/Li/nM
3. Mn/Li/Al or Mg/Li/Al

Where LiOH.H₂O, MgO, MnO₂, and Al₂O₃ were used as the starting materials for Li, Mg, Mn, and Al, respectively. For lanthanide group metal, Ce(NO₃)₃.6H₂O, Pr(NO₃)₃.6H₂O, and Sm(NO₃)₃.6H₂O were used as the starting materials for Ce, Pr, and Sm, respectively.

The first type of catalysts were prepared by adding Al, Mg or Mn, and Li into a flask and mixing well. Then the solution of Ce, or Pr, or Sm in distilled water was added to the mixture and stirred the slurry until it was mixed well. The slurry was placed at room temperature for 3 hours, then dried at 110 °C for 12 hours. The solid product then was calcined at 500 °C for 3 hours in air.

The second type of catalysts were prepared similar to the first type, but the second type has no alumina in the catalyst systems.

The third type of catalysts were prepared by mixing Mg, Al, and Li or Mn, Al, and Li, and then calcined in air as the first and the second type ones. This type was not dried because the ternary mixed oxides be a solid.

4.2 Oxidative coupling reaction

Oxidative coupling of methane was carried out by using a conventional fixed-bed reactor at atmospheric pressure. Catalyst powder (0.2 g) was placed in the center of the quartz reactor (I.D. = 9 mm, length = 350 mm) with quartz wool at both ends of catalyst in the reactor. Using co-feed of methane and oxygen, the molar ratios of methane/oxygen was 1, 2, 3, 4, and 5 respectively. The flowrates of co-feed was calculated from space velocity, temperature and the volumes of catalysts. The space velocities were 2000, 4000, 6000, and 8000 h⁻¹ and the reaction temperatures were in the range of 600 - 750 °C. The reactor was heated to a reaction temperature within 1 hour using an electric furnace. Each reaction temperature was maintained for 5 min. before sampling the reaction product for analysis. The product analysis was done by using gas chromatograph (Gow Mac and Shimadzu GC-8A). The hydrocarbon products with carbon number higher than 2 were here in defined as C₂+ hydrocarbon.

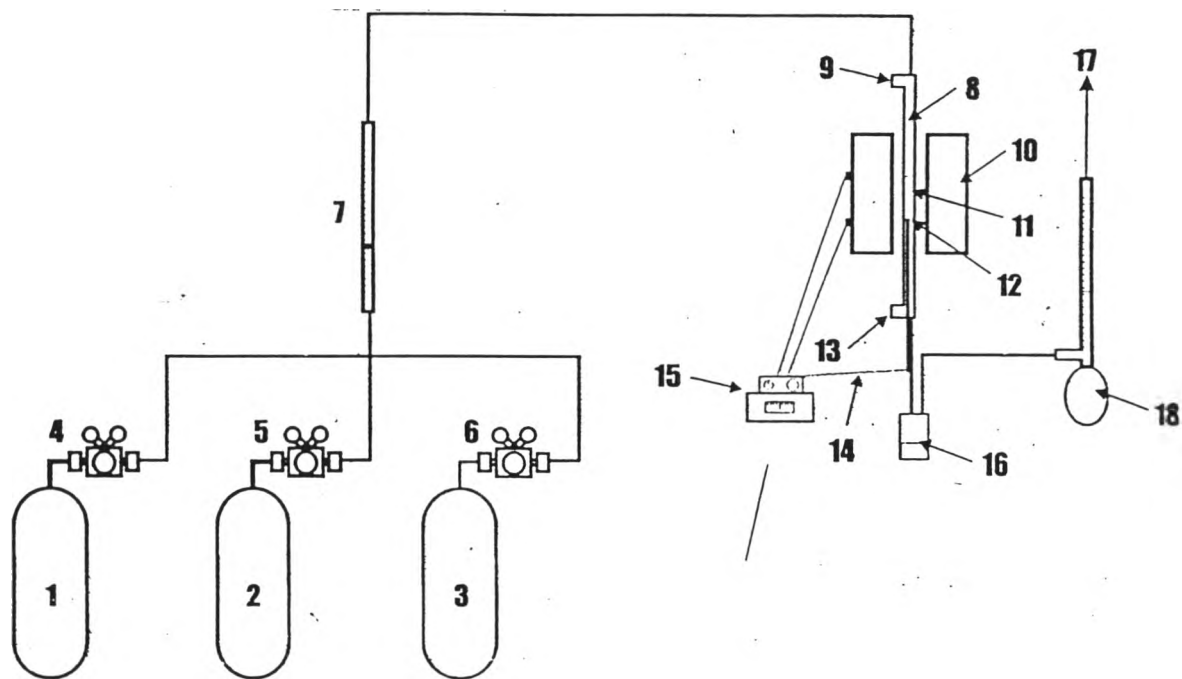


Fig Schematic diagram of the reaction apparatus for the oxidative coupling of methane

- | | |
|----------------------------------|-----------------------------------|
| 1 Ar gas cylinder | 10 electric furnace |
| 2 CH ₄ gas cylinder | 11 catalyst bed |
| 3 O ₂ gas cylinder | 12 quartz wool |
| 4 Ar gas controller | 13 product port for sampling |
| 5 CH ₄ gas controller | 14 thermocouple control reactor |
| 6 O ₂ gas controller | 15 reactor temperature controller |
| 7 flow indicator | 16 product receiver |
| 8 quartz reactor | 17 vent out line |
| 9 feed port for sampling | 18 outlet gas flow meter |

4.3 Characterization of catalysts

4.3.1. BET surface area

BET surface area of catalysts was measured by N₂ adsorption with the continuous flow method using the gas chromatograph at liquid nitrogen temperature. Helium was used as the carrier gas. The flow rate of helium was set at ca. 28 ml/min. The oven temperature of detector was set at 80 °C, and the current was set at 80 mA. Nitrogen gas was introduced to the line of flowing helium and the partial pressure of nitrogen was set at 0.3. The samples were heated from room temperature to 150 °C and kept at that temperature for 1 hour, then cooled to the temperature of liquid nitrogen and the amount of nitrogen adsorbed was measured. The BET surface area of the catalysts can be calculated by one point method.

Summary report from BET

	surface area (sq.m/g)	pore volume (cc/g)	pore size (Å)
Mg/Al/Li/0.2Ce	30.7640	0.1321	171.8038
Mg/Al/Li/0.2Pr	27.3521	0.1348	197.1733
Mg/Al/Li/0.2Sm	18.4243	0.0905	196.5642
Mg/Li/0.3Pr	6.1482	0.0129	83.9761

4.3.2. ICP for quantitative analysis of Mg, Mn, Al, Li, Ce Pr and Sm

0.100 g of catalyst powder was dissolved in 4 ml. of 36 % HCl and 1 ml. of HNO₃ and then heated by the electric heater. To the solution, the distilled water was added to volume of 50 ml. The solutions were measured by Inductively Coupled Plasma Emission Spectrometer (Model Perkin-Elmer PLASMA-1000)

Summary of quantitative analysis of metal elements of catalysta which be measured by ICP were compared in moles ratios as :

	Mg	Al	Li	Mn	Ce	Pr	Sm
Mg/Al/Li/0.05Pr	1.0	0.8	0.8	-		0.06	-
Mg/Al/Li/0.1Pr	1.0	0.8	1.0	-	-	0.1	-
Mg/Al/Li/0.2Pr	1.0	0.8	0.9	-		0.2	-
Mg/Al/Li/0.3Pr	1.0	0.8	1.0	-		0.3	-
Mg/Al/Li/0.2Ce	1.0	0.7	0.9	-	0.1	-	-
Mg/Al/Li/0.2Sm	1.0	0.8	0.9	-		-	0.2
Mg/Li/0.3Pr	1.0	-	0.9	-		0.3	-
Mn/Al/Li/0.2Pr		0.8	1.0	1.0		0.2	-

The mole ratios of alpha-alumina from ICP measurement were less than the weighing because of the process of preparing the solution for ICP measurement. This process used 70 % HNO₃, 36 % HCl and distilled water as the solvents, and alumina could not dissolve completely in this solvents.

