

Catalyst Screening for CO₂ Oxidative Coupling of Methane to C₂ Hydrocarbons

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Abstract

Basic metal oxides are suitable catalysts for the selective oxidative coupling of methane reaction using CO₂ as an oxidant known as CO₂ OCM hereafter. Catalysts screening for CO₂ OCM was performed using CeO₂- and MgO-based catalysts. The performance of the catalysts was tested in a fixed-bed quartz reactor. The CeO₂ support was combined with alkaline earth metal oxide (CaO) and transition metal oxide (WO₃ or MnO) to form a ternary metal oxide catalyst. The other catalyst tested was MgO doped with Li₂O. The addition of WO₃ to the CeO₂ catalyst is able to enhance the C₂ hydrocarbon selectivity, while the addition of MnO doping was able to increase the C₂ hydrocarbons yield and CH₄ conversion. The Li₂O/MgO catalyst is a more promising catalyst for CO₂ OCM rather than CeO₂-based catalyst. The C₂ hydrocarbon yield of 5.7 % and selectivity of 92.7 % were obtained over Li₂O/MgO catalyst. Raman spectroscopy was employed to characterize the catalysts.

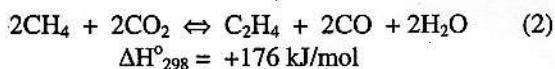
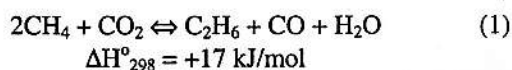
Keywords:

CO₂ Oxidative Coupling of Methane, CH₄-CO₂ Utilization, Catalysts Screening, MgO- and CeO₂-based Catalysts, Raman Spectroscopy

Introduction

It is known that natural gas in many areas, like Natuna's natural gas, contains CO₂ in large quantity other than methane and lower alkanes [1]. The direct synthesis of ethane, ethylene and acetylene (C₂ hydrocarbons) from methane is one of the most attractive methods for the efficient use of natural gas as a chemical resource. Recently, much attention has been focused on the conversion of natural gas using CO₂ as an oxidant [2,3,4,5,6,7,8]. It will be highly desirable to utilize such low value natural gas without emitting CO₂ and convert both methane and carbon dioxide from natural gas into higher value-added chemicals. Based on the fact that oxygen can induce gas-phase radicals in the gas phase, it is necessary to find an alternative oxidant which suppressed the radical induction [2]. Carbon dioxide could avoid such problem based on the fact that it will not induce gas-phase radical reactions [2,3]. More important, the reaction of CH₄ and CO₂ to produce C₂ hydrocarbons should mainly be controlled by heterogeneous catalyst. Therefore, it is highly desirable to develop catalysts which are active towards achieving high selectivity and high yield of C₂ hydrocarbons.

Thermodynamic calculations for the overall reaction of CO₂ OCM showed that the equilibrium yields of C₂H₆ and C₂H₄ formed by the reaction of CH₄ and CO₂ were 15 and 25 %, respectively, at temperature $\geq 800^\circ\text{C}$ for CO₂/CH₄ ratio of 2 [7]. In another study, the equilibrium conversion of CH₄ to C₂ hydrocarbons could reach 12 % (6 % for C₂H₆ and 6% for C₂H₄ formation) at temperature of 600°C with CO₂/CH₄ ratio of 2 [4]. Concerning the reaction pathway of the CO₂ OCM to C₂ hydrocarbons, two main reaction schemes have been proposed [2]: one is the methane-carbon dioxide reaction for producing C₂H₆ (Eq. 1) and the other is the methane-carbon dioxide reaction for producing C₂H₄ (Eq. 2). Carbon monoxide and water are also produced in this reaction.



Only a few researchers have attempted to study the oxidative coupling of methane using carbon dioxide as an oxidant. Aika and coworkers [4] reported that carbon dioxide showed a positive role in the formation of C₂ hydrocarbons in the oxidative coupling of methane over a PbO-MgO catalyst. Among 30 metal oxides studied for the reaction of CO₂ OCM to produce C₂ hydrocarbons, praseodymium and terbium oxides showed potential catalysts [2,3,4]. A series of binary metal oxides catalysts based on CaO-CeO₂ [4], CaO-ZnO [6] and La₂O₃-ZnO were developed, but the catalytic performance was not satisfactory. The modification of binary metal oxide system was also developed by combining MnO₂ with alkaline earth (CaO, SrO and BaO), while Cr₂O₃, CeO₂ and ZnO were also used to replace MnO₂ [7], but the catalytic performance was also not satisfactory. Recent development over Mn-SrCO₃ catalyst by Cai et al. [8], C₂ hydrocarbons selectivity approached 79.1 % with a C₂ hydrocarbons yield of 4.5 %. These results closely resemble the results indicated by Wang et al. [4,6,7].

It is reported that the surface basicity of the catalysts, especially for intermediate and strong basic sites, contributes to better C₂ hydrocarbon selectivity by the synergistic effect [6,9]. CeO₂ catalyst is known as having the properties of high reducibility, high oxygen storage capacity and ability to the formation of defect sites such as oxygen vacancies [6]. The oxidation activity, oxygen mobility and ionic

conductivity of CeO₂-based catalyst can be increased by doping CeO₂ with transition metal oxide, while the C₂ hydrocarbons selectivity can be increased by doping CeO₂ with alkaline earth metal oxide (CaO) [4,5,6]. The lithium-doped magnesium oxide catalyst, Li/MgO, is one of the most extensively studied catalysts for methane oxidative coupling by oxygen [9,10]. The active sites for the initial abstraction of hydrogen from methane were believed to be Li⁺O⁻ species formed by the substitution of Li⁺ at lattice sites normally occupied by Mg²⁺ [11,12]. The Li⁺-ions was incorporated in the MgO lattice as substitutional ions on magnesium sites, with oxygen vacancies for charge compensation.

This paper reports the development of a more effective catalyst system for C₂ hydrocarbons formation from methane and carbon dioxide reaction. CeO₂- and MgO-based catalysts were screened in search of the best catalyst for CO₂ OCM to produce C₂ hydrocarbons. It is expected that methyl radicals are produced by a reaction between CH₄ and O⁻ centers that formed by CO₂ adsorption and activation in the catalyst surface. The improvement in the catalytic activity with increasing number of oxygen vacancies suggests that in the oxidative coupling of methane is activated by oxygen trapped in an anion vacancy.

Materials and Methods

Catalyst Preparation

All binary and ternary metal oxide catalysts used in this study were prepared by the conventional wet-impregnation method. CeO₂ (MERCK) or MgO (97%, MERCK) powder are used as catalyst supports, while LiNO₃ (99.995%, MERCK), (NH₄)₆W₁₂O₄₀.xH₂O (85%, FLUKA), Mn(NO₃)₂.4H₂O (98.5%, FLUKA) and/or Ca(NO₃)₂.4H₂O (99%, ALDRICH) are used as precursors. Powdery CeO₂ and MgO were first immersed into an aqueous solution of M(NO₃)_n.xH₂O (M=Ca, Li, Mn,) or (NH₄)₆W₁₂O₄₀.xH₂O for 6 h at ambient temperature. The water was then evaporated in an oven (MEMMERT) at 120°C overnight. The powder was then calcined at 850°C in a muffle furnace (CARBOLITE) for 4 h and then crushed into the desired size (42-62 mesh).

Catalytic Reaction

Each run was performed using a conventional fixed-bed quartz reactor. The schematic diagram of the experimental set-up is shown in Figure 1. Before reaction, the catalyst loaded into the reactor was recalcined at 850°C in air flow (100 ml min⁻¹) for 1 h and flushed with high purity nitrogen (>99.999%, 100 ml min⁻¹) at 850°C for another 1 h. The reaction was initiated by introducing the feed gas of CH₄ (>99.999%) and CO₂ (>99.995%) to the reactor. The following inlet conditions were usually used for the reaction at catalyst screening step: T (temperature) = 850°C,

CH₄/CO₂=1/2, F (total flow rate) = 100 ml min⁻¹, W (catalyst loaded) = 2 g for CeO₂-based catalyst and 0.5 g for MgO-based catalyst. Gas flow rates were measured and controlled by the volumetric flow controllers (Alicat Scientific, Inc.). The products and unreacted gases were analyzed by an online gas chromatography (AGILENT 6890 series) equipped with a thermal conductivity (TCD) detector and PORAPAK N packed-column. The online gas chromatography was controlled by Hewlett-Packard (HP) computer equipped with Chemstation software.

Accordingly, the data processing concerning the calculation of conversion, selectivity and yield calculation was conducted based on the work reported by Asami and Wang [2,3,4,5,6,7]. Gas chromatographic data were processed on the following assumptions: the carbon in carbon dioxide was only converted into carbon monoxide and the carbon or hydrogen in methane was converted into ethane, ethylene, acetylene and carbon monoxide, or hydrogen and water, respectively. Conversion, selectivity and yield of C₂ hydrocarbon are expressed on the basis of carbon in methane, which are defined in Equations (3, 5 and 6), respectively [2,3,5]. The selectivity of carbon monoxide is calculated on the basis of carbon in methane and carbon dioxide which is defined in Equation (4).

$$\text{CH}_4 \text{ conv.} = \frac{\text{mole of CH}_4 \text{ (in)} - \text{mole of CH}_4 \text{ (out)}}{\text{mole of CH}_4 \text{ (in)}} \times 100\% \quad (3)$$

$$\text{CO select.} = \frac{\text{mole of C atom in C}_2 \text{ produced}}{\text{mole of C atom reacted from CH}_4 \text{ \& CO}_2} \times 100\% \quad (4)$$

$$\text{C}_2 \text{ select.} = \frac{\text{mole of C atom in C}_2 \text{ produced}}{\text{mole of C atom reacted from CH}_4} \times 100\% \quad (5)$$

$$\text{C}_2 \text{ yield} = \text{CH}_4 \text{ Conversion} \times \text{C}_2 \text{ Selectivity} \times 100\% \quad (6)$$

Catalyst Characterization

The vibrational and molecular characteristic of catalysts before and after reaction was characterized using Raman spectroscopy to detect the presence of crystalline phase and molecular structure of the metal oxides catalysts. The Raman spectroscopy is predominantly applicable to the qualitative and quantitative analysis of covalently bonded molecules rather than ionic structures. The Raman spectroscopy can provide information about the lattice structure of ionic molecules in the crystalline state and the internal covalent structure of complex ions as well as the ligand structure of coordination compound in the solid states. Laser Raman spectroscopy was conducted using a Perkin Elmer Spectrum GX NIR FT-Raman apparatus equipped with a Nd:YAG laser source. The powder catalyst sample was pressed into the sample holder. The excitation line was at 514.4 nm. The excitation power is constant at 350 mW for each sample, except the power for Mn-based samples is conducted in the range of 25-500 mW. The Raman spectra were measured with 2 cm⁻¹ spectral resolution with an absolute accuracy of

$\pm 0.1 \text{ cm}^{-1}$. The Raman shift band of this sample was initially performed in the range of 4000 cm^{-1} up to 100 cm^{-1} , depending on the metal oxide catalyst.

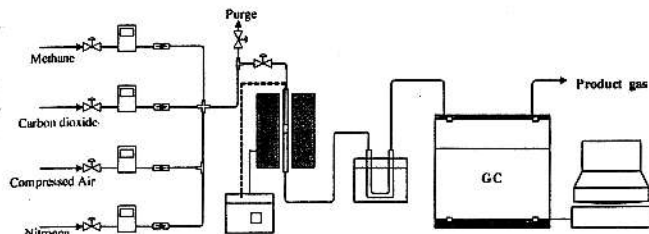


Figure 1 - Schematic Diagram of Experimental Set-Up

Results

Catalyst Performance Testing

The performances of the selected binary and ternary metal oxide catalysts for CO_2 OCM are given in Tables 1 and 2, while the performances of all catalysts tested are given graphically in Figures 2-7. According to Table 1, the order of methane conversion among MgO-based catalysts are $\text{MnO/MgO} > \text{Li}_2\text{O-WO}_3/\text{MgO} > \text{Li}_2\text{O-MnO/MgO} > \text{Li}_2\text{O/MgO} > \text{MgO}$, while the order of C_2 hydrocarbons yield are $\text{Li}_2\text{O/MgO} > \text{MgO} > \text{Li}_2\text{O-MnO/MgO} \approx \text{MnO/MgO} > \text{Li}_2\text{O-WO}_3/\text{MgO}$. The order of C_2 hydrocarbons selectivity of CeO_2 -based catalysts are $\text{CaO-WO}_3/\text{CeO}_2 > \text{CaO-MnO/CeO}_2 > \text{CaO/CeO}_2 > \text{CeO}_2 > \text{MnO/CeO}_2$. The result in Table 2 showed the order of CH_4 conversion among CeO_2 -based catalysts are $\text{MnO/CeO}_2 > \text{CeO}_2 > \text{CaO/CeO}_2 > \text{CaO-MnO/CeO}_2 > \text{CaO-WO}_3/\text{CeO}_2$, while the order of C_2 hydrocarbons yield are $\text{CaO-MnO/CeO}_2 > \text{CeO}_2 > \text{CaO-WO}_3/\text{CeO}_2 \approx \text{CaO/CeO}_2 > \text{MnO/CeO}_2$.

Table 1: Performances of MgO-based Catalysts

Catalysts	CH_4 Conv. (%)	CO Select. (%)	C_2 Hydrocarbons	
			Select. (%)	Yield (%)
MgO	6.1	47.0	53.0	3.4
2% $\text{Li}_2\text{O/MgO}$	8.2	7.3	92.7	5.7
5% $\text{Li}_2\text{O/MgO}$	7.7	6.8	98.2	3.8
5% MnO/MgO	20.1	82.6	22.4	1.7
5% $\text{Li}_2\text{O-5%MnO/MgO}$	9.8	29.1	75.9	1.7
1% $\text{Li}_2\text{O-3%WO}_3/\text{MgO}$	15.0	30.6	69.4	1.1

Table 2 - Performances of CeO_2 -based Catalysts

Catalysts	CH_4 Conv. (%)	CO Select. (%)	C_2 Hydrocarbons	
			Select. (%)	Yield (%)
CeO_2	13.5	94.8	12.3	1.7
5% MnO/CeO_2	13.9	98.3	1.7	0.2
15% CaO/CeO_2	10.3	47.6	52.4	1.3
15% CaO-5%MnO/CeO_2	9.2	42.4	62.6	2.5
15% $\text{CaO-3%WO}_3/\text{CeO}_2$	4.8	25.4	74.6	1.3

Table 3 - Catalyst Performance Results from Previous Researchers

Catalysts	CH_4 Conv. (%)	CO Select. (%)	C_2 Hydrocarbons		Ref.
			Select. (%)	Yield (%)	
CeO_2	12	-	0.5	0.1	[5]
CaO-CeO_2 (Ca/Ce=0.1)	5.1	-	46	2.3	[5]
CaO-CeO_2 (Ca/Ce=0.2)	4.9	-	55	2.7	[5]
CaO-CeO_2 (Ca/Ce=0.5)	5	-	62	3.2	[5]
CaO-CeO_2 (Ca/Ce=1)	3.4	-	46	1.6	[5]
CaO	0.3	-	36	0.1	[5]
CaO-ZnO (Ca/Zn=0.5)	3.4	18	82	2.8	[6]
CaO-MnO (Ca/Mn=1)	3.9	32	68	2.7	[7]
SrO-MnO (Sr/Mn=1)	3.9	15	85	3.3	[7]

BaO-MnO (Ba/Mn=0.5)	3.8	33	67	2.6	[7]
BaO-MnO (Ba/Mn=1)	2.3	15	85	1.9	[7]
MnO-SrCO ₃ (Mn/Sr=0.2)	5.7	79.1	20.9	4.5	[8]
MnO-SrCO ₃ (Mn/Sr=0.1)	4.9	87.9	12.1	4.3	[8]

The catalyst screening results pertaining to CO₂ OCM is also depicted in Figures 2-4 and Figures 5-7 for MgO- and CeO₂-based catalysts, respectively. The screening results are also compared to the results reported by previous researchers listed in Table 3 [5,6,7,8]. Majority of the catalysts gave lower CH₄ conversion and smaller C₂ yield if carbon dioxide is the oxidant for oxidative coupling of methane instead of oxygen. Li-doped MgO catalyst showed potential in catalyzing CO₂ OCM, although previously most researchers used it for OCM by oxygen. In brief, these MgO- and CeO₂-based catalysts showed unique performances for C₂ hydrocarbons formation from methane and carbon dioxide. The other advantage is the process also contributed to a reduction in greenhouse gas emission.

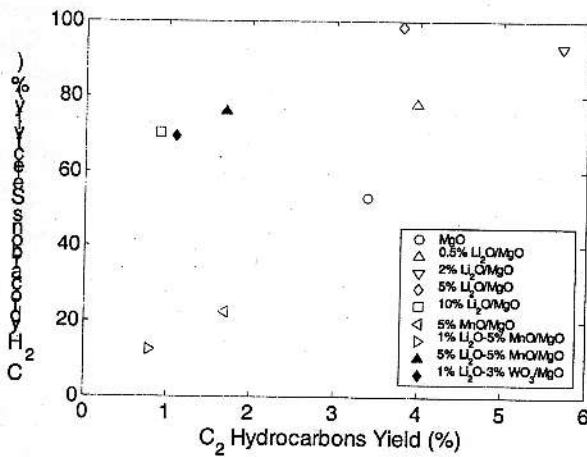


Figure 2 - MgO-Based Catalyst Screening with Respect to C₂ Yield vs C₂ Selectivity

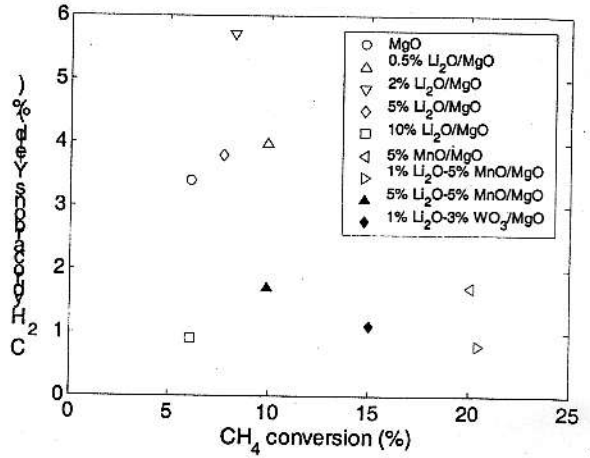


Figure 3 - MgO-Based Catalyst Screening with Respect to CH₄ Conversion vs C₂ Yield

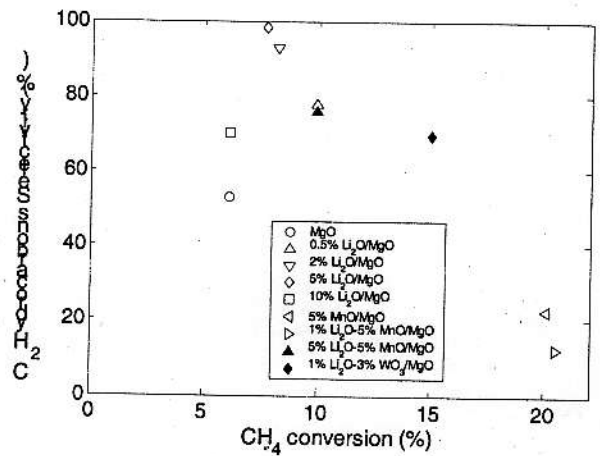


Figure 4 - MgO-Based Catalyst Screening with Respect to CH₄ Conversion vs C₂ Selectivity

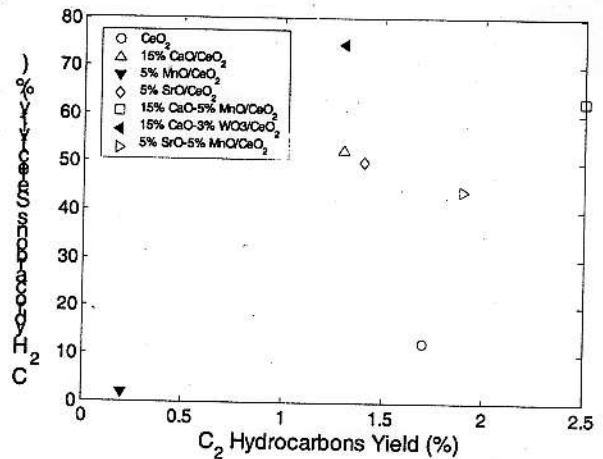


Figure 5 - :CeO₂-Based Catalyst Screening with Respect to C₂ Yield Conversion vs C₂ Selectivity

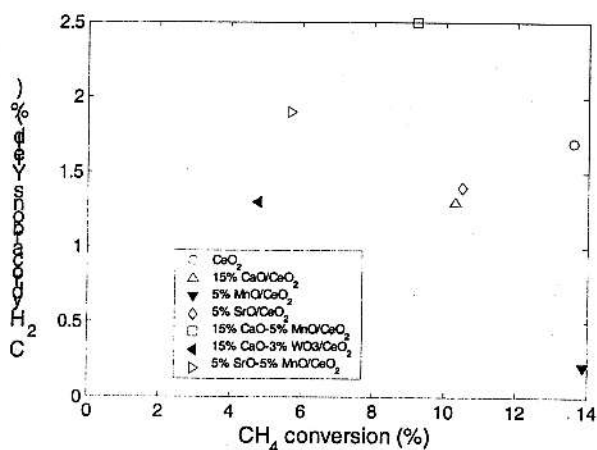


Figure 6 - CeO₂-Based Catalyst Screening with Respect to CH₄ Conversion vs C₂ Yield

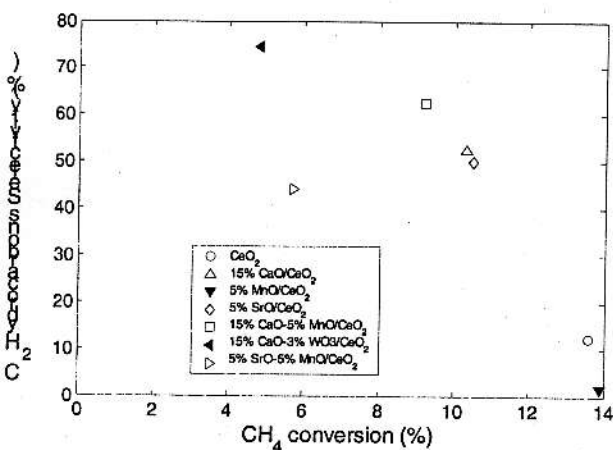


Figure 7 - CeO₂-Based Catalyst Screening with Respect to CH₄ Conversion vs C₂ Selectivity

Catalyst Characterization

The Raman spectra of CeO₂- and MgO-based catalyst are presented in Figures 8-9 and Figures 10-11, respectively. The Raman spectra of the CeO₂, CaO and WO₃ crystalline are presented in Figure 8 for pure CeO₂, CaO-CeO₂ and CaO-WO₃/CeO₂ catalysts.

The Raman characterizations of pure CeO₂, MnO/CeO₂ and CaO-MnO/CeO₂ catalysts are depicted in Figure 9. However, it is difficult to characterize the Mn-based catalysts by Raman scattering, as these catalysts samples are dark; believed to be manganese oxide, physically. The photon energy from laser power may be either absorbed or scattered elastically, but cannot be scattered inelastically (Raman), depending on the MnO-based samples. However, FT-IR spectroscopy which is more sensitive may be able to characterize them and complements the Raman scattering.

Raman spectra of the fresh and used Li₂O/MgO catalyst as well as pure MgO in the band region of 200-1200 cm⁻¹ are given in Figure 10. These spectra are also compared to the result of fresh and used tungsten oxide-doped Li₂O/MgO catalyst as presented in Figure 11 in order to investigate the effect and the role of WO₃ doping on the catalyst structure.

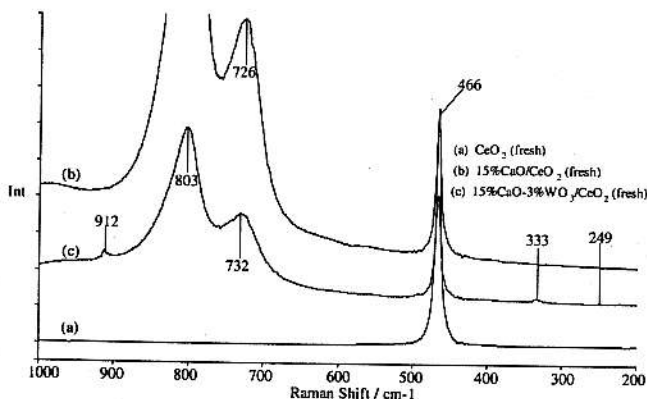


Figure 8 - Raman Spectra of Fresh CeO₂, CaO/CeO₂ and CaO-WO₃/CeO₂ Catalysts

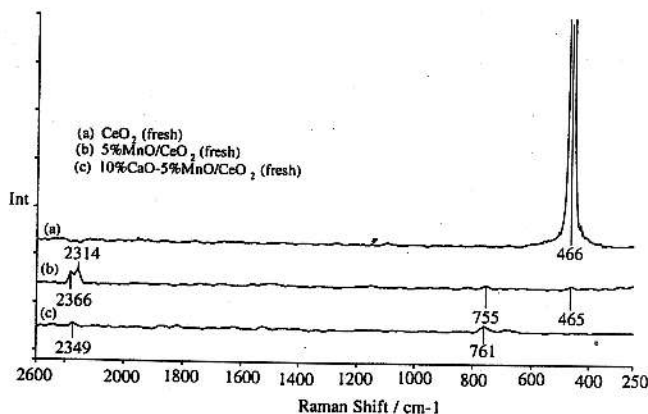


Figure 9 - Raman Spectra of Fresh CeO₂, MnO/CeO₂ and CaO-MnO/CeO₂ Catalysts

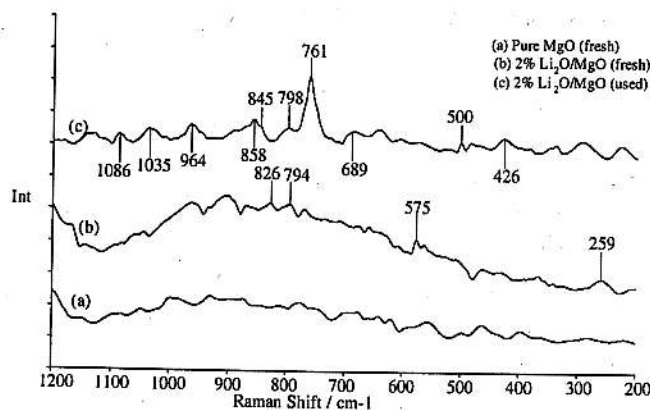


Figure 10 - Raman spectra of MgO, Li₂O/MgO

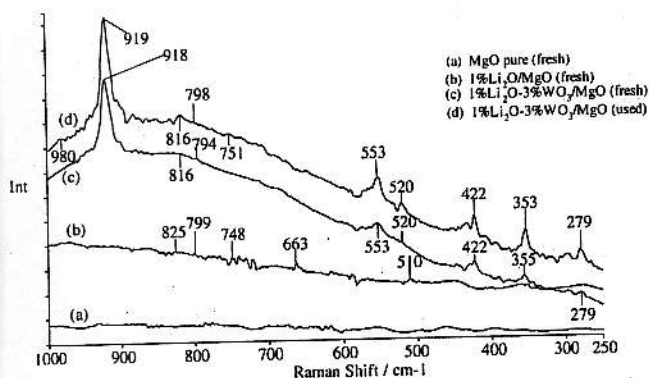


Figure 11 - :Raman Spectra of MgO, Li₂O/MgO and Li₂O-WO₃/MgO

Discussion

Catalyst Screening Suitable for CO₂ OCM

The screening of the various catalysts over MgO-based catalyst for C₂ hydrocarbons yield and selectivity is depicted in Figure 2. The results showed that the 2 wt.% Li₂O/MgO catalyst gave the best performance for CO₂ oxidative coupling of methane. As Li₂O content increased in gamut of 2-5 wt.%, the C₂ hydrocarbons selectivity increased, but unfortunately, their yield decreased. Based on the CH₄ conversion, C₂ yield and selectivity as depicted in Figures 2 and 3, it is shown that 2 wt.% Li₂O/MgO catalyst demonstrated the best catalyst performance for CO₂ OCM. The addition of transition metal oxide, such as tungsten oxide in 1 wt.% Li₂O-3 wt.% WO₃/MgO catalyst, increased methane conversion but the C₂ selectivity and yield decreased as revealed in Figure 4. 1 wt.% Li₂O-5 wt.% MnO/MgO catalyst gave the highest CH₄ conversion, but showed the lowest C₂ selectivity. For MgO-based catalyst, it is concluded that 2 wt.% Li₂O/MgO catalyst is more potential for carbon dioxide oxidative coupling of methane to produce C₂ hydrocarbons in comparison with other MgO-modified catalyst.

For the CeO₂-based catalyst, the screening results of the various catalyst compositions with respect to C₂ hydrocarbons yield and selectivity is revealed in Figures 5-7. The catalyst with 15 wt.% CaO-5 wt.% MnO/CeO₂ gave the best performance for carbon dioxide oxidative coupling of methane. This catalyst gave methane conversion of 9.2 %, C₂ yield and selectivity of 2.5 and 62.6 %, respectively. The WO₃ doping on the CaO/CeO₂ catalyst increased the C₂ hydrocarbons selectivity from 52.4 % to 74.6 %, but did not improve the C₂ hydrocarbons yield significantly. The CeO₂ and CeO₂-doped MnO catalyst gave high methane conversion and carbon monoxide selectivity, but low C₂ selectivity. The MnO doping to the CeO₂ pure catalyst decreased C₂ hydrocarbons yield and selectivity significantly, but increased methane conversion slightly. The addition of CaO (alkaline earth) increased the catalyst

basicity and led to increase the C₂ hydrocarbon selectivity and yield [5]. The addition of MnO to the 15 wt.% CaO/CeO₂ catalyst increased C₂ yield and selectivity significantly, but decreased methane conversion slightly.

Catalyst Characterization by Raman Spectroscopy

Raman scattering provides much more information on a material than just the molecular vibrations. Information can also be obtained for about the electronic nature of the material under study, e.g. defect centers like reduced transition metals [13]. Raman spectroscopy can provide information on lattice vibrations as well as internal vibrations; it can be used to determine the kinds of Li phase present over MgO catalyst after calcinations and used. In addition, Raman and IR spectroscopies are able to detect the characteristic vibrations of specific functional groups of the surface metal oxide species, functional groups bonded on the surface of catalyst and provide direct insight into their molecular structures.

The Raman spectra from Figure 8(a) showed the strong peak CeO₂ presence at band of 466 cm⁻¹, which is assigned as a fluorite type structure according to the literature [11,14]. Raman spectra of CeO₂ exhibited a most intense band between 400-500 cm⁻¹ range centered at 466 cm⁻¹, which is ascribed the characteristic of crystalline CeO₂ (Figure 8a). The Raman spectra of Ca-based crystalline visualized a most intense band at 700-850 cm⁻¹. The characteristic bands at 726, 732 and 803 cm⁻¹ are ascribed to the crystalline CaO oxide. The Raman band at 912 and 333 cm⁻¹ are due to symmetric W-O stretching and W-O bending vibrations [14], while the slight band at 248 cm⁻¹ corresponds to W-O-W deformation vibration [15]. Consequently, the stretching band at 912 and 333 cm⁻¹ are commonly used to characterize [WO₄] tetrahedral species, while the slight band at 248 cm⁻¹ is ascribed to crystalline WO₃ [14]. The position of the highest Raman band is observed at a higher wavenumber in the case of tetrahedral [WO₄] groups (912 cm⁻¹) than that of octahedral WO₆ units (804 cm⁻¹). In general, the position of the W-O stretching frequency vibration varied according to the W-O bond length (W-O bond order) [14]. However, the position of the highest W-O stretching Raman band could not be considered as a fingerprint to specify the nature of polyhedral structure especially in the case of supported materials. Monotungstate compounds, made up of [WO₄] tetrahedra, indicated bands in the range of 910-1061 cm⁻¹ (W-O symmetric stretching) and in the range of 300-830 cm⁻¹ (antisymmetric stretching and bending modes). Isopolytungstate compounds, consisting of WO₆ octahedra, are possessing bands in the range of 740-980 cm⁻¹ (W-O symmetric and W-O-W antisymmetric stretching frequencies) and in the range of 200-550 cm⁻¹ (W-O-W symmetric stretching and bending modes). The absence of Raman spectra of WO₃ band at 807 cm⁻¹ revealed that tungsten species may exist in tetrahedral of [WO₄] groups [16].

Concerning $\text{Li}_2\text{O}/\text{MgO}$ catalyst, it is believed that the active species on the $\text{Li}_2\text{O}/\text{MgO}$ catalyst to be O_2^{2-} . Since the O-O stretching mode is Raman active, Raman spectroscopy is particularly suitable to this type of investigation. The slight Raman band at 1086 cm^{-1} and strong band at 761 cm^{-1} (Figure 10c) are attributed to Li_2CO_3 . The Raman band at 1086 cm^{-1} is assigned to the symmetric stretching of the carbonate ions, while the band at 761 cm^{-1} is attributed to antisymmetric bending mode. The corresponding peak at 689 cm^{-1} in Figure 10(c) is assigned to the symmetric stretching mode of the carbonate ion, which is indicated that the crystalline Li_2CO_3 may be present on this catalyst (Figure 10c) after exposing the catalyst to reactant gas (CH_4 and CO_2).

For $\text{Li}_2\text{O}/\text{MgO}$ catalyst, the active species on this catalyst was believed to be O^- centers, but it was suggested that a diatomic species, peroxide ion, O_2^{2-} , was also the active species on this catalyst [17]. It is therefore interested to investigate by Raman spectroscopy whether peroxide ions are indeed present on the fresh and used catalyst. The Raman spectrum of Li_2O_2 is characterized at bands range of $794\text{--}860\text{ cm}^{-1}$ and broad band at about 259 cm^{-1} shown in Figure 10 [11]. The band at $794\text{--}860\text{ cm}^{-1}$ is attributed to the internal O-O stretching mode of the peroxide species O_2^{2-} and that at 259 cm^{-1} is attributed to an external lattice vibration. The Raman spectra in the bands of 500 and 426 cm^{-1} for the used catalyst (Figure 10c) are ascribed to the presence of Li_2O [11]. The disappearance of the peaks at about 259 and 826 cm^{-1} indicated the decomposition of Li_2O_2 . The new peaks at 500 and 426 cm^{-1} are attributed to Li_2O formed by the decomposition of Li_2O_2 .

The Raman characterization depicted in Figure 11 was conducted to investigate the effect and properties of 1 wt.% $\text{Li}_2\text{O}/\text{MgO}$ catalyst due to 3 wt.% WO_3 doping. The Raman spectra of the fresh 1 wt.% Li_2O - 3 wt.% WO_3/MgO catalyst were compared to both 1 wt.% $\text{Li}_2\text{O}/\text{MgO}$ and MgO catalyst. In addition, the fresh and used 1 wt.% Li_2O - 3 wt.% WO_3/MgO catalysts were also compared. The Raman spectrum of Li_2O_2 was characterized at slight peak of 798 cm^{-1} and stronger peak at 816 cm^{-1} which showed the active species of O_2^{2-} of the catalyst [11]. The presence of Li_2O in the catalyst is detected in Raman spectra of 422 , 509 and 520 cm^{-1} . The Li_2CO_3 may be present on the used catalyst (Figure 11d) which is described at Raman spectrum of about 751 cm^{-1} due to the reaction with CO_2 . The strong Raman band at 918 cm^{-1} is due to symmetric W-O stretching vibration [14] that revealed the presence of $[\text{WO}_4]$ tetrahedral species, while the slight band at about 279 cm^{-1} shows W-O-W deformation that attributed to the crystalline WO_3 . The Raman band at 553 cm^{-1} and shoulder at about 980 cm^{-1} show W-O-W deformation and W=O stretching, respectively, that attributed to the two dimensional WO_6 unit [14]. The weak peak at 980 cm^{-1} also attributed to W-O stretching that may be assigned to the crystalline MgWO_4 . The W-O bending vibration detected at about 353 cm^{-1} is probably due to the distortion of the $[\text{WO}_4]$ structure. It is

well known that a slight distortion of the ideal tetrahedron $[\text{WO}_4]$ unit led to a shift position which is ascribed to the modification of bond orders [14]. The Raman spectrum at about 816 cm^{-1} is assigned to W-O stretching vibration mode attributed to tetrahedral $[\text{WO}_4]$ unit.

Conclusion

Basic metal oxides are suitable catalysts for the selective oxidative coupling of methane reaction using carbon dioxide as an oxidant known as CO_2 OCM. The ternary metal oxides of CeO_2 -based catalyst, $\text{CaO-WO}_3/\text{CeO}_2$ or $\text{CaO-MnO}/\text{CeO}_2$, showed better performance for C_2 hydrocarbons production than that of their binary metal oxide CeO_2 -based catalyst. The CH_4 conversion, C_2 yield and selectivity for 15% CaO -5% MnO/CeO_2 catalyst are 9.2, 62.6 and 2.5 %, respectively, while for 15% CaO -3% WO_3/CeO_2 catalyst are 4.8, 74.6 and 1.3 %, respectively. WO_3 doping to the CeO_2 catalyst enhances the selectivity to C_2 hydrocarbon, while MnO doping enhances the C_2 hydrocarbons yield and CH_4 conversion. The $\text{Li}_2\text{O}/\text{MgO}$ catalyst shows a better performance to catalyze the CO_2 OCM than CeO_2 -based catalyst in which the C_2 hydrocarbons yield and selectivity are 5.7 % and 92.7 %, respectively. The catalyst characterization by Raman spectroscopy provides more information about the presence of metal doped in the surface as well as the structure based on molecular vibration. The Raman spectroscopy of catalyst can give more information about the changing of molecular structure on the surface of fresh and used catalyst.

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References

- [1] Suhartanto, T., York, A.P.E., Hanif, A., Al-Megren, H. and Green, M.L.H. 2001. Potential Utilisation of Indonesia's Natuna Natural Gas Field via Methane Dry Reforming to Synthesis Gas. *Catalysis Letters* 71(1-2): 49-54
- [2] Asami, K., Fujita, T., Kusakabe, K., Nishiyama, Y. and Ohtsuka, Y. 1995. Conversion of Methane with Carbon Dioxide into C_2 Hydrocarbons over Metal Oxides. *Applied catalysis A: General* 126: 245-255

- [3] Asami, K., Kusakabe, K., Ashi, N. and Ohtsuka, Y. 1997. Synthesis of Ethane and Ethylene from Methane and Carbon Dioxide over Praseodymium Oxide Catalysts. *Applied catalysis A: General* 156: 43-56
- [4] Wang, Y., Takahashi, Y. and Ohtsuka, Y. 1998. Carbon Dioxide-Induced Selective Conversion of Methane to C₂ Hydrocarbons on CeO₂ Modified with CaO. *Applied Catalysis A: General* 172:L203-L206
- [5] Wang, Y., Takahashi, Y. and Ohtsuka, Y. 1999. Carbon Dioxide as Oxidant for the Conversion of Methane to Ethane and Ethylene Using Modified CeO₂ Catalyst. *Journal of Catalysis* 186:160-168
- [6] Wang, Y. and Ohtsuka, Y. 2000. CaO-ZnO Catalyst for Selective Conversion of Methane to C₂ Hydrocarbons Using Carbon Dioxide as the Oxidant. *Journal of Catalysis* 192: 252-255
- [7] Wang, Y. and Ohtsuka, Y. 2001. Mn-based Binary Oxides as Catalyst for the Conversion of Methane to C₂ Hydrocarbon with Carbon Dioxide as an Oxidant. *Applied Catalysis A: General* 219: 183-193
- [8] Cai, Y., Chou, L., Li, S., Zhang, B. and Zhao, J. 2003. Selective Conversion of Methane to C₂ Hydrocarbons Using Carbon Dioxide over Mn-SrCO₃ Catalysts. *Catalysis Letters* 86 (4): 191-195
- [9] Choudhary, V.R., Mulla, S.A.R. and Uphade, B.S. 1999. Oxidative Coupling of Methane over Alkaline Earth Oxides Deposited on Commercial Support Precoated with Rare Earth Oxides. *Fuel* 78: 427-437
- [10] Johnson, M.A., Stefanovich, E.V. and Truong, T.N. 1997. An *ab initio* Study on the Oxidative Coupling of Methane over a Lithium-Doped MgO Catalyst: Surface Defects and Mechanism. *Journal of Physical Chemistry:B*. 101: 3196-3201
- [11] Yang, X. 1995. A Spectroscopic Study of Methane Oxidative Coupling Catalysts. *PhD Dissertation*. Texas A&M University
- [12] Gellings, P.J. and Bouwmeester, H.J.M. 2000. Solid State Aspects of Oxidation Catalysis. *Catalysis Today*. 58: 1-53
- [13] Mestl, G. 2000. In Situ Raman Spectroscopy – A Valuable Tool to Understand Operating Catalysts. *Journal of Molecular Catalysis A: Chemical*. 158: 45-65
- [14] Bigey, C., Hilaire, L., and Maire, G. 2001. WO₃-CeO₂ and Pd/WO₃-CeO₂ as Potential Catalysts for Reforming Applications: I. Physicochemical Characterization Study. *Journal of Catalysis* 198: 208–222
- [15] Chen, Y. and Wach, I.E. 2003. Tantalum Oxide-supported Metal Oxide (Re₂O₇, CrO₃, MoO₃, WO₃, V₂O₅, and Nb₂O₅) Catalysts: Synthesis, Raman Characterization and Chemically Probed by Methanol Oxidation. *Journal of Catalysis*. In press.
- [16] Valigi, M.; Gazzoli, D.; Pettiti, I.; Mattei, G.; Colonna, S.; de Rossi, S; and Ferraris, G. 2002. WO_x/ZrO₂ Catalysts: I. Preparation, Bulk and Surface Characterization. *Applied Catalysis A: General* 231: 159-172
- [17] Bothe-Almquist, C.L., Ettireddy, R.P., Bobst, A. and Smirniotis, P.G. 2000. An XRD, XPS, and EPR Study of Li/MgO Catalysts: Case of The Oxidative Methylation of Acetonitrile to Acrylonitrile with CH₄. *Journal of Catalysis* 192: 174-184.