

## Activation of Methane to C<sub>2</sub> Hydrocarbons over Unpromoted Calcium Oxide Catalysts

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The oxidative coupling of methane has received a great deal of attention for the last twenty five years because the reaction has been understood as a promising route for the C<sub>2</sub>-hydrocarbon production from natural gas.<sup>1,2</sup> To identify suitable catalysts giving high C<sub>2</sub>-yield, a lot of catalysts have been examined for the oxidative coupling of methane. It has been reported that high surface basicity of a catalyst is necessary to enhance the C<sub>2</sub> selectivity in the reaction.<sup>3</sup> Alkali metal oxides and alkaline earth metal oxides are strong bases so that they have catalytic activities for the oxidative coupling of methane. Alkali metal oxides seem to be unsuitable catalysts for the reaction because they form liquid phase of metal hydroxide in the presence of water vapor under reaction conditions,<sup>4</sup> while alkaline earth metal oxides are suitable catalysts because they are easily dehydrated under reaction conditions.

When alkali metal ion such as Li<sup>+</sup> or Na<sup>+</sup> is incorporated into MgO or CaO catalyst, its catalytic activity and selectivity for the oxidative coupling of methane can be enhanced.<sup>4-8</sup> However, the incorporation of alkali ions into CaO or MgO is not quite favorable. CaO itself is so basic that it has good catalytic activity for the oxidative coupling of methane but deactivated due to the formation of carbon solids or carbonate during the reaction. Nevertheless, CaO is still an attractive one in developing the catalyst for the oxidative coupling of methane because it has additional advantages of low cost and widespread availability. Recently, we have examined a series of CaO-based catalysts for the oxidative coupling of methane and have found that CaO fully-coated silica particles showed appreciable selectivity and durability for the oxidative coupling of methane. This paper reports catalytic behaviors and photoluminescence results of the CaO fully-coated silica particles.

### Experimental

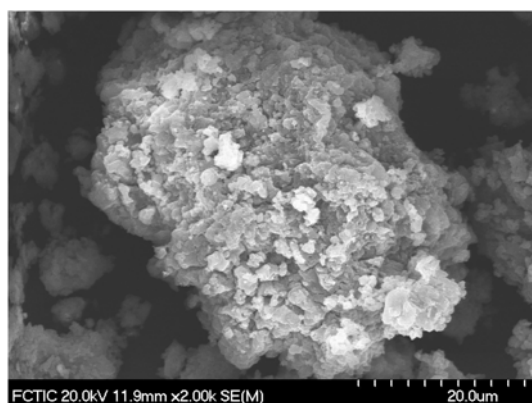
CaO powder, 30 wt.% CaO/silica, and CaO fully-coated silica particles were prepared to examine as catalysts for the oxidative coupling of methane. CaO powder was prepared by decomposition of calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 99.99%, Aldrich) at 700 °C in air. Silica powder (99.8%, Aldrich, surface area of *ca.* 200 m<sup>2</sup>/g) was calcined at 1000 °C and passed through a sieve to get the particles with sizes of ≤ 25 μm for its use as a catalyst support. The 30 wt.% CaO/silica was prepared by impregnating the silica powder with

aqueous solution of calcium nitrate at 80 °C, followed by drying in air at 110 °C, and calcined at 750 °C in air. To prepare the CaO fully-coated silica particles, the calcined silica powder and calcium nitrate were weighed to give the mole ratio of Si:Ca=1:3. The silica powder was impregnated with aqueous solution of calcium nitrate at 80 °C, followed by drying at 110 °C, and calcined at 750 °C in air. The resulting powder was passed through standard sieves to gather the particles with sizes of 45-75 μm. Photoluminescence analysis was performed for both the CaO powder and the CaO fully-coated silica particles in order to get information on the surface states of catalysts. Photoexcitation spectra with 395 nm wavelength and luminescence spectra excited at 250 nm wavelength were recorded at 25 °C with a Hitachi F-2500 fluorescence spectrophotometer.

The catalytic tests were performed in a fixed-bed continuous flow reactor operated at atmospheric pressure. The catalyst was loaded over fused silica bed placed in the middle of the reactor which was made of quartz tubing with 0.8 cm inner diameter and 20 cm length. In a typical experiment, 200 mg of catalyst was loaded into the reactor and the feed flow rate of reaction mixture was CH<sub>4</sub>/O<sub>2</sub>/He = 8/2/10 cm<sup>3</sup>/min. The purity of gases was greater than 99.99% and the gases were dehydrated and purified with suitable filters. Gaseous products were analyzed using on-line gas chromatography equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The methane conversion and product selectivities were typically compared after 1 h time-on-stream. Blank test showed 3-5% conversion of methane to carbon oxides in the temperature range of 600-800 °C. The details of kinetic experiment were described in the previous paper.<sup>9</sup>

### Results and Discussion

Figure 1 shows the SEM photograph of the CaO fully-coated silica particle, exhibiting that the surface of silica particle was entirely coated with CaO. X-ray powder diffraction (XRD) analysis was performed for the CaO powder, the 30 wt.% CaO/silica, and the CaO fully-coated silica particles. The samples were calcined at 900 °C for 3 h in air before the XRD measurement. Figure 2 showed the XRD results, in which the XRD pattern of 30 wt.% CaO/silica is significantly different from that of the CaO fully-coated silica. As shown in Figure 2(B), the 30 wt.% CaO/silica

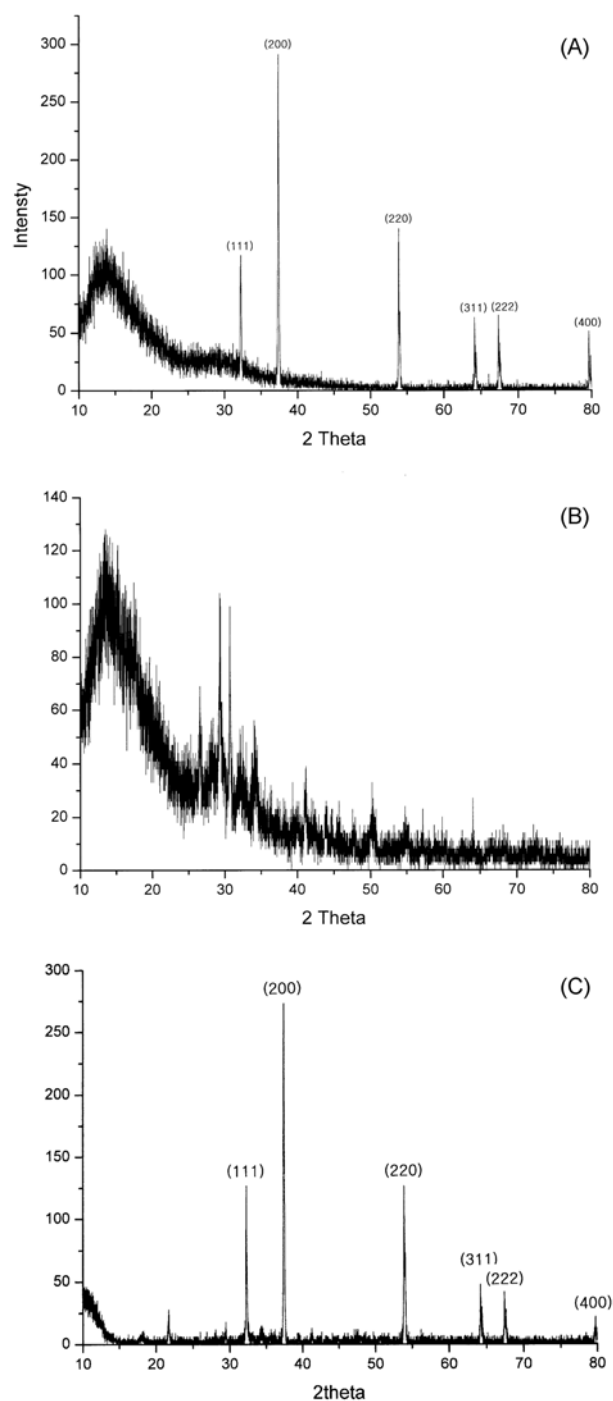


**Figure 1.** Scanning electron microphotograph of CaO fully-coated silica particle calcined at 900 °C for 3 h in air.

showed XRD peaks due to calcium silicates which were formed during the calcination at 900 °C in air. On the other hand, the CaO fully-coated silica particles showed only the XRD peaks due to CaO crystallites, indicating that the surface of particles was entirely and thickly covered with CaO.

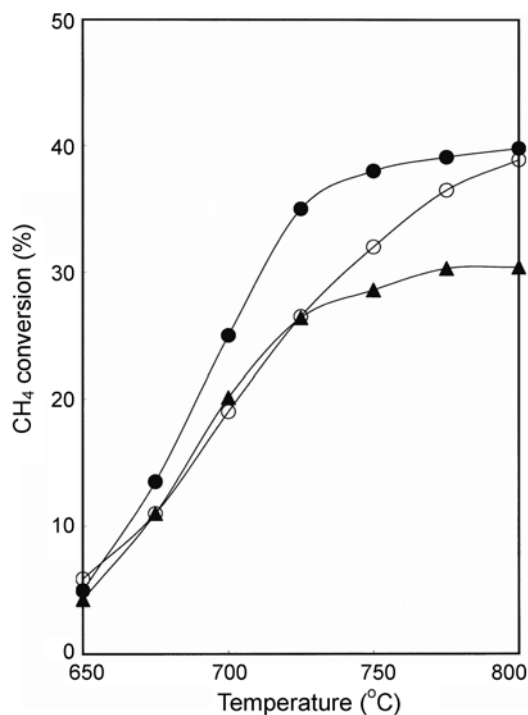
The catalysts prepared in this work showed activity for the oxidative coupling of methane and the major products were CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> in the temperature range of 650–800 °C. Figures 3 and 4 exhibit variations of CH<sub>4</sub> conversion and C<sub>2</sub> selectivity with temperature, respectively, for the present catalysts in the temperature range of 650–800 °C. There was no remarkable difference in the methane conversion between the CaO powder and the CaO fully-coated silica particles. However, the CaO fully-coated silica particles showed higher C<sub>2</sub>-selectivity than the CaO powder catalyst as shown in Figure 4. At 750 °C, the CaO fully-coated silica particles showed the C<sub>2</sub> yield of 26% with a selectivity of 68%, which is appreciable.

It is generally accepted for the oxidative coupling of methane catalyzed by metal oxides that oxygen species adsorbed on oxygen vacancy sites or basic sites activate methane to generate methyl radicals and the resulting methyl radicals are coupled to form ethane in gas phase. Various investigations have suggested that weakly adsorbed molecular oxygen such as O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>2-</sup> favors the formations of carbon oxides, while less electrophilic oxygen species such as O<sup>-</sup> and O<sup>2-</sup> enhance the formation of methyl radicals leading to C<sub>2</sub> hydrocarbons.<sup>3</sup> The stability of less electrophilic oxygen species is known to depend on the basicity of catalyst and the existence of suitable sites.<sup>10</sup> Several investigators have found that the presence of coordinatively unsaturated sites on CaO surface forms the photoluminescence spectra and the unsaturated surface sites are responsible for the catalytic activity of CaO.<sup>11–14</sup> For instance, highly unsaturated sites on CaO surface are extremely active for N<sub>2</sub>O decomposition but readily poisoned with oxygen.<sup>13,14</sup> The unsaturated sites are so basic that gaseous oxygen can be dissociatively chemisorbed on the sites to form active oxygen ions which can act as adsorption sites for methane. In order to confirm the existence of surface unsaturated sites

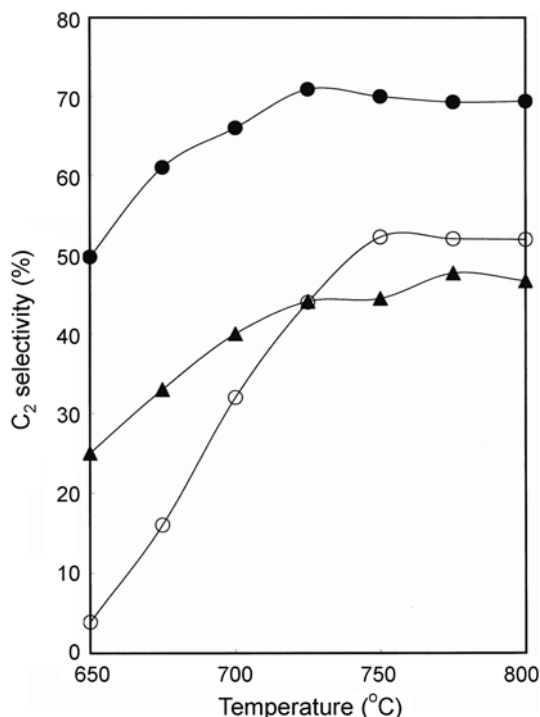


**Figure 2.** X-ray powder diffraction patterns of (A) CaO powder prepared from calcium nitrate, (B) 30 wt.% CaO/silica, and (C) CaO fully-coated silica particles. The samples were calcined at 900 °C for 3 h in air. CaO: JCPDS file No. 04-0777.

on the CaO surface, the photoluminescence analysis was performed for both the CaO powder and the CaO fully-coated silica particles. Figure 5 shows the photoluminescence emission spectra excited with 250 nm wavelength at 25 °C, in which the emission bands centered at around 395 nm are observed. Figure 6 shows the photoexcitation spectra recorded with the emission band of 395 nm wavelength at 25 °C. As shown in Figure 6, both the samples gave the

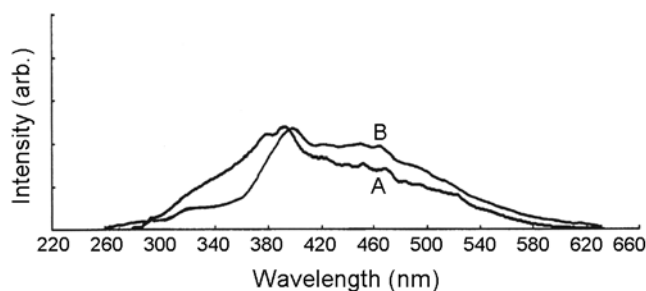


**Figure 3.** Variations of methane conversion with temperature for the oxidative coupling of methane over (●) CaO fully-coated silica particles, (▲) 30 wt.% CaO/silica, and (○) CaO powder. The flow rate of reaction mixture: CH<sub>4</sub>/O<sub>2</sub>/He = 8/2/10 cm<sup>3</sup>/min.

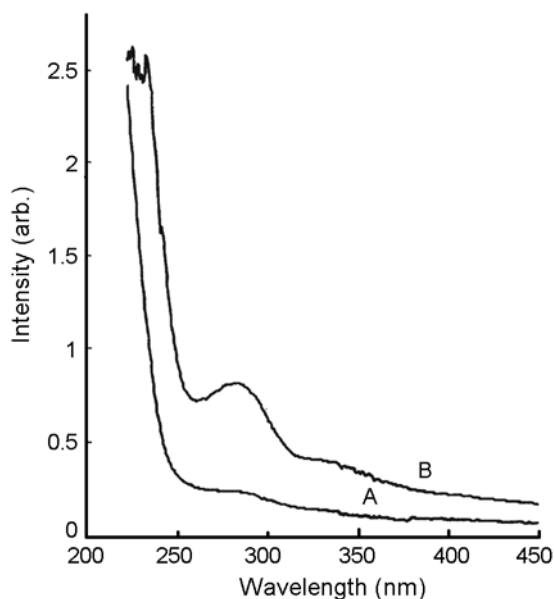


**Figure 4.** Variations of C<sub>2</sub> selectivity with temperature for the oxidative coupling of methane over (●) CaO fully-coated silica particles, (▲) 30 wt.% CaO/silica, and (○) CaO powder. The flow rate of reaction mixture: CH<sub>4</sub>/O<sub>2</sub>/He = 8/2/10 cm<sup>3</sup>/min.

excitation spectra at longer wavelength, indicating the excitation to occur at lower energy region. The excitation maximum was observed at around 286 nm for the samples



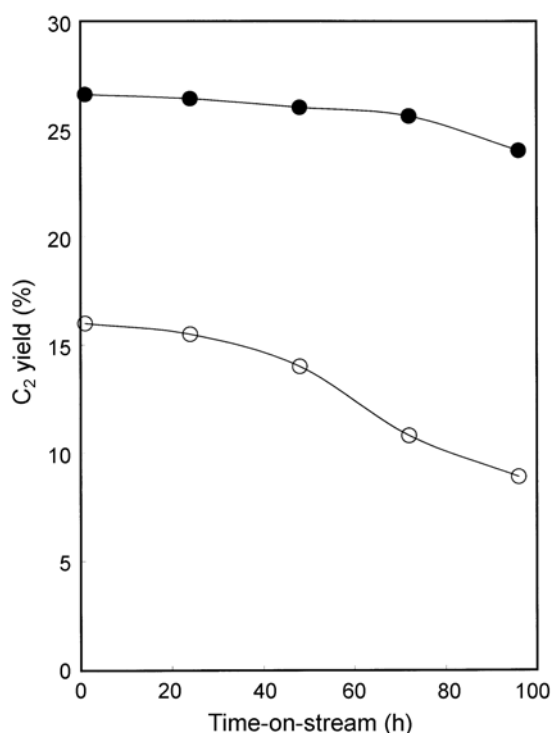
**Figure 5.** Photoluminescence spectra excited at  $\lambda = 250$  nm at 25 °C for (A) CaO powder and (B) CaO fully-coated silica particles.



**Figure 6.** Photoexcitation spectra with  $\lambda = 395$  nm at 25 °C for (A) CaO powder and (B) CaO fully-coated silica particles.

and the maximum was more noticeable in the excitation spectrum of the CaO fully-coated silica particles.

In general, the photoexcitation spectra of CaO are characterized by broad absorption bands extending from about 300 nm to shorter wavelengths as shown in Figure 6. The excitation spectra observed at lower energy region are attributed to the surface unsaturated sites having coordination number of less than 5.<sup>13-17</sup> That is, the lower excitation energy of photoluminescence is due to the surface absorption bands associated with electronic transitions in surface oxygen ions in states of low coordination. The photoluminescence spectra of Figure 6 indicate that unsaturated oxygen sites exist on the catalyst surface as suggested by other investigators.<sup>13-17</sup> In this work, BET surface areas measured by nitrogen adsorption were 18.8 m<sup>2</sup>/g and 8.5 m<sup>2</sup>/g for the CaO powder the CaO fully-coated silica particles, respectively, which enables us to consider that the catalytic activity of CaO is more sensitive to surface geometry rather than surface area. Namely, the activity of CaO seems to be strongly dependent on some structural difference in CaO crystallites. Coordinatively unsaturated sites existing on the surface of CaO crystallite can be divided into three types:



**Figure 7.** Variations of C<sub>2</sub> yield with time-on-stream for oxidative coupling of methane over (○) CaO powder and (●) CaO fully-coated silica particles at 750 °C. The flow rate of reaction mixture: CH<sub>4</sub>/O<sub>2</sub>/He = 8/2/10 cm<sup>3</sup>/min.

corner site (O<sub>3C</sub><sup>2-</sup>), plane site (O<sub>5C</sub><sup>2-</sup>), and edge site (O<sub>4C</sub><sup>2-</sup>). It has been reported that highly unsaturated sites like corner sites are responsible for the high catalytic activity of CaO in the early reaction stage, while lower unsaturated sites such as plane sites and edge sites contribute to the durability of CaO activity.<sup>13,14</sup> Figure 7 shows variations of C<sub>2</sub> yield over the catalysts with time-on-stream for the oxidative coupling of methane at 750 °C, in which the CaO fully-coated silica particles shows more stable catalytic activity than the CaO powder over the extended reaction period, implying that the catalytic activity of CaO catalyst is sensitive to the surface structure. It has been known that CaO catalyst is active for the oxidative coupling of methane but shows deactivating effect either by carbonate formation or carbon deposition during the reaction. The highly unsaturated sites are related to the high activity in the initial reaction stage, while the moderately and poorly unsaturated sites are related to the

activity in the steady state.<sup>14</sup> It is believed that the lower unsaturated sites such as O<sub>5C</sub><sup>2-</sup> or O<sub>4C</sub><sup>2-</sup> are more abundant on the CaO fully-coated silica particles than the CaO powder.

In conclusion, the CaO fully-coated silica particles shows higher catalytic stability and C<sub>2</sub> selectivity in the oxidative coupling of methane compared to the CaO powder catalyst. Although the origin of CaO coating effect on its catalytic performance is required further study to be understood, the surface geometric structure seems to be closely related to the catalytic activity and stability. Since the photoluminescent unsaturated sites on CaO are related to the formation of active oxygen ions being able to act as adsorption sites for methane, in order to maximize the catalytic efficiency, the catalytic behaviors of CaO coated catalysts are being investigated in conjunction with detailed photoluminescence studies including picosecond spectroscopies.

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