

## The Effect of Pressure on the Surface Structure of MgO/BaCO<sub>3</sub> Catalyst for Oxidative Coupling of Methane

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The effect of pressure on oxidative coupling of methane (OCM) over MgO/BaCO<sub>3</sub> catalyst was studied at the range of 0.1~1.1MPa at 1053 K. Deactivation of the MgO/BaCO<sub>3</sub> catalyst at elevated pressure was attributed to the migration of BaCO<sub>3</sub> from bulk to the surface of the catalyst.

The oxidative coupling of methane (OCM) to produce ethylene has attracted worldwide attention since Keller and Bhasin's pioneer report.<sup>1</sup> Most of the research has focused mainly on the oxidative coupling of methane at atmospheric pressure over various alkali or alkaline earth oxide catalysts, such as MgO based catalysts.<sup>2-5</sup> For commercial applications, it is also necessary to perform the oxidative coupling of methane at elevated pressure, which is economically favoring the separation of the products and saving the energy consumption. It has been established that the oxidative coupling of methane happens to be a homogeneous-heterogeneous reaction. The methyl radicals are produced on the surface of a catalyst, released and coupled in the gas phase. Currently, Ekstrom et al.<sup>6,7</sup> studied the effect of pressure on the homogeneous and heterogeneous reaction of the oxidative coupling. They reported that the gas phase reaction could be reduced by using high linear velocity at elevated pressure, however, the increase of pressure depressed the C<sub>2</sub><sup>+</sup> selectivities and methane conversion over Li/MgO, Sm<sub>2</sub>O<sub>3</sub> and SrCO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub> catalysts. This is also consistent with theoretical analysis of Labinger<sup>8</sup> and the recent results of Yu.<sup>9</sup> Nevertheless, no detailed work appeared to investigate the reason why the C<sub>2</sub><sup>+</sup> selectivities and methane conversion were depressed at an elevated pressure over the related catalysts. The present work was undertaken to explore the reason from the aspects of the catalyst surface characterization over a typical bi-alkaline earth composite catalyst<sup>3/4</sup> MgO/BaCO<sub>3</sub> for OCM, which exhibited good CH<sub>4</sub> conversion and C<sub>2</sub><sup>+</sup> selectivity during a 500 h stability test.<sup>10</sup>

The preparation method of the 39 mol% MgO/BaCO<sub>3</sub> catalyst has been described elsewhere.<sup>10</sup> The experiments were carried out in a quartz tube with an I.D. of 7mm. The quartz reactor was sleeved in a stainless-steel tube for protection. In all experiments methane and oxygen were co-fed and their flow rates were controlled by mass flow controllers (Model D07-11/ZM, Beijing Jian Zhong Machinery Factory). 0.5 g MgO/BaCO<sub>3</sub> catalyst was placed in the hottest part of the reactor and quartz chips were placed above and below the catalyst bed to minimize any noncatalytic reaction. X-ray diffraction (XRD) analyses were performed on a D-MAX-RB diffractometer with Cu K $\alpha$  radiation. areas were measured on a Carlo ERBA Soaptomatic surface area analyzer. Surface analyses were performed using a VG ESCALAB 210 X-ray photoelectron spectrometer with 300W Mg K $\alpha$  radiation. Binding energies were reference to the carbon 1s peak of adventitious carbon at 284.6eV.

**Table 1.** Surface and bulk concentration (atom%) and related binding energy<sup>10,13,14</sup> of the fresh and deactivated MgO/BaCO<sub>3</sub> catalysts

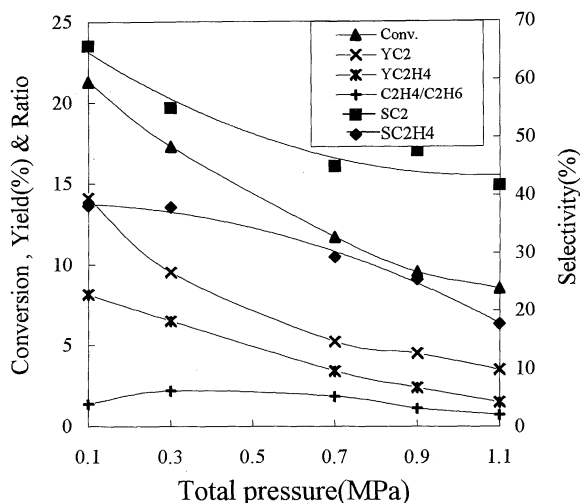
	O1s		C1s		Ba3d <sub>5/2</sub>	Mg2p	S.A. <sup>a</sup>	
BE(ev)	531.1	529.2	289.3	284.6	779.6	48.8	(m <sup>2</sup> /g)	
Assign.	O <sub>2</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	O <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	A.C. <sup>b</sup>	Ba <sup>2+</sup>	Mg <sup>2+</sup>	
Fresh	1.0	30.9	28.1	10.3	8.8	11.2	9.6	6.3
Etched <sup>c</sup>	0.9	33.9	25.5	11.3	5.6	12.1	10.7	
Deact.	0	42.9	17.0	14.3	8.2	14.6	3.6	2.1
Etched <sup>c</sup>	0	22.2	42.9	7.4	5.9	6.8	15.8	

<sup>a</sup> Surface area, <sup>b</sup> Adventitious carbon, <sup>c</sup> Etching conditions: 5kV Energy,  $\phi$  6mm, 1.5x10<sup>-6</sup> mbar Ar for 5 min.

The effect of pressure (0.1~1.1MPa) on oxidative coupling of methane over MgO/BaCO<sub>3</sub> catalyst was depicted in Figure 1. As may be seen, the conversion of CH<sub>4</sub> and selectivity to C<sub>2</sub><sup>+</sup> were simultaneously reduced with increasing pressure from 21% and 67% at atmospheric pressure to 9% and 42% at 1.1MPa respectively. It was also observed that the ratio of C<sub>2</sub>H<sub>4</sub> to C<sub>2</sub>H<sub>6</sub> and selectivity to ethylene dropped gradually with increasing pressure.

Surprisingly, when the pressure was dropped to atmospheric pressure after the experiment at 1.1MPa over the MgO/BaCO<sub>3</sub> catalyst, the conversion of CH<sub>4</sub> and the C<sub>2</sub><sup>+</sup> selectivity were merely 11% and 45% respectively, i.e., they couldn't be restored to the initial results (21% and 67% respectively). It indicates that the MgO/BaCO<sub>3</sub> catalyst gradually lost its activity at elevated pressure. It is possible that the surface structure of MgO/BaCO<sub>3</sub> catalyst is changed. The XRD patterns showed that a new MgCO<sub>3</sub> peak was formed in the deactivated catalyst. From the previous results<sup>10</sup> of our group, MgO is an active component for methane activation. It is evident that the active MgO was partially changed into MgCO<sub>3</sub> by reaction with CO<sub>2</sub> at elevated pressure. Nevertheless, the decomposition temperature of MgCO<sub>3</sub> is only 813 K which is much lower than the reaction temperature (1053 K), i.e. the deactivated MgO/BaCO<sub>3</sub> catalyst should be regenerated by the decomposition of MgCO<sub>3</sub> at atmosphere. This implied that the formation of MgCO<sub>3</sub> was only one of the reasons which led to the deactivation of the catalyst.

Furthermore, in order to explore the effect of pressure on the surface composition of the catalyst and elucidated the reason of deactivation, X ray photoelectron spectra of the catalysts were taken (Table 1). It can be seen that the near surface compositions of the fresh catalyst are 9.6 AT%<sup>11</sup> Mg and 11.2 AT% Ba, whereas, those of the deactivated one are 3.6 AT% Mg and 14.6 AT% Ba. On the contrary, the surface concentrations of Mg and Ba after etching are 15.8 and 6.8 AT% respectively in the



**Figure 1.** The effect of pressure on oxidative coupling of methane using  $\text{MgO}/\text{BaCO}_3$  (0.5 g) as a catalyst at 1053 K,  $\text{CH}_4:\text{O}_2=4:1$ , total flow rate of 150ml/min.

deactivated one. Moreover, the surface  $\text{CO}_3^{2-}$  peak of deactivated catalyst increased simultaneously with the enrichment of Ba. By comparison with the net increase of near surface concentration of Ba and  $\text{CO}_3^{2-}$  (Table 1), the near surface concentration of  $\text{CO}_3^{2-}$  increased from 10.3AT% to 14.2AT%, whereas, that of Ba increased from 11.2AT% to 14.7AT%. Since these changes are in agreement with stoichiometric  $\text{BaCO}_3$ . It is inferred that  $\text{MgO}$  was partially covered by  $\text{BaCO}_3$ . This suggestion was also in agreement with the result of surface area. As shown in Table 1, the surface area decreased from  $6.3 \text{ m}^2/\text{g}$  of the fresh  $\text{MgO}/\text{BaCO}_3$  catalyst to  $2.1 \text{ m}^2/\text{g}$  of the deactivated one. As the surface area of pure  $\text{BaCO}_3$ <sup>12</sup> was lower than  $2 \text{ m}^2/\text{g}$ , this reduction of surface area of  $\text{MgO}/\text{BaCO}_3$  indicates that  $\text{MgO}$  surface was partially covered by  $\text{BaCO}_3$ .

Based on the above results, the formation of  $\text{MgCO}_3$  was not the dominant reason of the deactivation. The migration of  $\text{BaCO}_3$  from bulk to the surface changed the concentration ratio between  $\text{MgO}$  and  $\text{BaCO}_3$ ,  $\text{MgO}$  surface was partially covered by  $\text{BaCO}_3$ , which maybe the dominant reason of the deactivation of the  $\text{MgO}/\text{BaCO}_3$  catalyst.

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