The Effect of Pressure on the Surface Structure of $MgO/BaCO_3$ Catalyst for Oxidative Coupling of Methane

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The effect of pressure on oxidative coupling of methane (OCM) over $MgO/BaCO_3$ catalyst was studied at the range of 0.1~1.1MPa at 1053 K. Deactivation of the $MgO/BaCO_3$ catalyst at elevated pressure was attributed to the migration of $BaCO_3$ 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.[1] 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.[2-5] 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.[6,7] 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_2^+ selectivities and methane conversion over Li/MgO, Sm_2O_3 and $SrCO_3/Sm_2O_3$ catalysts. This is also consistent with theoretical analysis of Labinger[8] and the recent results of Yu.[9] Nevertheless, no detailed work appeared to investigate the reason why the C_2^+ 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 catalyst¾ $MgO/BaCO_3$ for OCM, which exhibited good CH_4 conversion and C_2^+ selectivity during a 500 h stability test.[10]

The preparation method of the 39 mol% $MgO/BaCO_3$ catalyst has been described elsewhere.[10] 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 $MgO/BaCO_3$ 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 Ka 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 Kα 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[10,13,14] of the fresh and deactivated $MgO/BaCO_3$ catalysts

	O1s			C1s		$Ba3d_{5/2}$	Mg2p	S.A.[a]
BE(ev)	531.1		529.2	289.3	284.6	779.6	48.8	(m^2/g)
Assign.	O_2^{2-}	CO_3^{2-}	O^{2-}	CO_3^{2-}	A.C.[b]	Ba^{2+}	Mg^{2+}	
Fresh	1.0	30.9	28.1	10.3	8.8	11.2	9.6	6.3
Etched[c]	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[c]	0	22.2	42.9	7.4	5.9	6.8	15.8	

[a] Surface area, [b] Adventitious carbon, [c] Etching conditions: 5kV Energy, ϕ 6mm, $1.5x10^{-6}$ mbar Ar for 5 min.

The effect of pressure (0.1~1.1Mpa) on oxidative coupling of methane over $MgO/BaCO_3$ catalyst was depicted in Figure 1. As may be seen, the conversion of CH_4 and selectivity to C_2^+ were simultaneously reduced with increasing pressure from 21% and 67% at atmopheric pressure to 9% and 42% at 1.1Mpa respectively. It was also observed that the ratio of C_2H_4 to C_2H_6 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 $MgO/BaCO_3$ catalyst, the conversion of CH_4 and the C_{2+} 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 $MgO/BaCO_3$ catalyst gradually lost its activity at elevated pressure. It is possible that the surface structure of $MgO/BaCO_3$ catalyst is changed. The XRD patterns showed that a new $MgCO_3$ peak was formed in the deactivated catalyst. From the previous results[10] of our group, MgO is an active component for methane activation. It is evident that the active MgO was partially changed into $MgCO_3$ by reaction with CO_2 at elevated pressure. Nevertheless, the decomposition temperature of $MgCO_3$ is only 813 K which is much lower than the reaction temperature (1053 K), i.e. the deactivated $MgO/BaCO_3$ catalyst should be regenerated by the decomposition of $MgCO_3$ at atmosphere. This implied that the formation of $MgCO_3$ 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%[11] 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

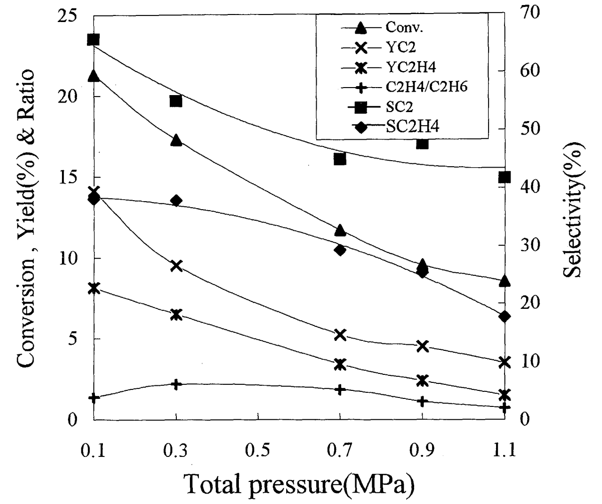

Figure 1. The effect of pressure on oxidative coupling of methane using MgO/$BaCO_3$ (0.5 g) as a catalyst at 1053 K, CH_4:O_2=4:1, total flow rate of 150ml/min.

deactivated one. Moreover, the surface 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 CO_3^{2-} (Table 1), the near surface concentration of 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 $BaCO_3$. It is inferred that MgO was partially covered by $BaCO_3$. This suggestion was also in agreement with the result of surface area. As shown in Table 1, the surface area decreased from 6.3 m^2/g of the fresh MgO/$BaCO_3$ catalyst to 2.1 m^2/g of the deactivated one. As the surface area of pure $BaCO_3$[12] was lower than 2 m^2/g, this reduction of surface area of MgO/$BaCO_3$ indicates that MgO surface was partially covered by $BaCO_3$.

Based on the above results, the formation of $MgCO_3$ was not the dominant reason of the deactivation. The migration of $BaCO_3$ from bulk to the surface changed the concentration ratio between MgO and $BaCO_3$, MgO surface was partially covered by $BaCO_3$, which maybe the dominant reason of the deactivation of the MgO/$BaCO_3$ catalyst.

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