

## DOCTORAL THESIS

### The oxidative coupling of methane over BaX<sub>2</sub>/La<sub>2</sub>O<sub>3</sub>, LaOX, and BaCO<sub>3</sub>/LaOX (X=halogen) catalysts

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THE OXIDATIVE COUPLING OF  
METHANE OVER  $\text{BaX}_2/\text{La}_2\text{O}_3$ ,  $\text{LaOX}$ , AND  
 $\text{BaCO}_3/\text{LaOX}$  (X = HALOGEN) CATALYSTS

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## ABSTRACT

The oxidative coupling of methane (OCM) reaction has been investigated over  $\text{BaX}_2/\text{La}_2\text{O}_3$ ,  $\text{LaOX}$ , and  $\text{BaCO}_3/\text{LaOX}$  ( $X = \text{halogen}$ ) catalysts. The addition of suitable amount of halogen improves the performance of the catalysts. The specific surface area of the catalysts was measured by BET method. XRD, XPS, Raman, and TGA were employed to characterize the catalysts. The interaction between oxygen and catalyst surface was investigated by means of  $^{18}\text{O}/^{16}\text{O}$  isotope exchange and  $\text{O}_2$ -TPD.  $\text{CO}_2$  adsorption and  $\text{CO}_2$ -TPD were used to study the surface basicity of the catalysts.

The 10mol% $\text{BaBr}_2/\text{La}_2\text{O}_3$  catalyst is superior to the 10mol% $\text{BaF}_2/\text{La}_2\text{O}_3$  one in  $\text{CH}_4$  conversion but slightly inferior in  $\text{C}_2$  selectivity. At 750 °C, the former had a  $\text{CH}_4$  conversion of 44.7% and a  $\text{C}_2$  selectivity of 40.5% ( $\text{C}_2$  yield = 18.1%); whereas the latter had a  $\text{CH}_4$  conversion of 27.0% and a  $\text{C}_2$  selectivity of 43.7% ( $\text{C}_2$  yield = 11.8%). It was found that  $\text{CH}_4$  conversion reached a maximum when the  $\text{BaBr}_2$  loading was 10mol%, coinciding with the loading for maximum  $\text{CO}_2$  adsorption and  $\text{La}_2\text{O}_2\text{CO}_3$  formation. It is suggested that the presence and delocalization of the  $\text{Br}^-$  electron have enhanced the basicity of surface  $\text{O}^{2-}$ , consequently increasing the H-abstraction ability and  $\text{CO}_2$  adsorption capability of the catalyst. Influenced by the presence of  $\text{Br}^-$  ions, the  $\text{La}_2\text{O}_2\text{CO}_3$  formed in OCM reaction decomposed at 690 °C instead of 790 °C which is the decomposition temperature for pure  $\text{La}_2\text{O}_2\text{CO}_3$ . During OCM reaction above 690 °C, decomposition and formation of  $\text{CO}_3^{2-}$  occur simultaneously and randomly within the crystal frame of hexagonal  $\text{La}_2\text{O}_2\text{CO}_3$ , creating  $\text{O}^{2-}$  sites suitable for methane activation.

Rhombohedral  $\text{LaOF}$  is a better catalyst than  $\text{La}_2\text{O}_3$  for OCM reaction. When 10mol%  $\text{BaCO}_3$  was loaded on  $\text{LaOF}$ , the methane conversion,  $\text{C}_2$  selectivity, and  $\text{C}_2$  yield were enhanced to 36.1, 45.3, and 16.4% respectively at 800 °C. The results of  $\text{CO}_2$ -TPD showed that there were surface  $\text{BaCO}_3$  and well-dispersed  $\text{BaO}$  on the surface of these catalysts. During OCM reaction, the well-dispersed  $\text{BaO}$  could adsorb  $\text{CO}_2$  to form surface  $\text{BaCO}_3$ . The decomposition of surface  $\text{BaCO}_3$  generated active sites for methane activation.

With contact time equal to 0.2 g s ml<sup>-1</sup> and  $\text{CH}_4:\text{O}_2:\text{N}_2 = 1:1:12$ , a  $\text{C}_2$  yield of 26.3% with a  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  ratio of 4.3 could be achieved over the 50mol% $\text{BaCO}_3/\text{LaOBr}$  catalyst at 800 °C. When the  $\text{CH}_4:\text{O}_2:\text{N}_2$  ratio was 0.5:1:12 and the contact time was 0.6 g s ml<sup>-1</sup>, the  $\text{C}_2$  yield became 18.9% and  $\text{C}_2\text{H}_4$  was the sole  $\text{C}_2$  product. The studies of  $\text{CD}_4/\text{CH}_4$  isotope exchange showed that  $\text{CD}_2\text{H}_2$  formation over the 30mol% $\text{BaCO}_3/\text{LaOBr}$  catalyst was relatively higher than over  $\text{LaOF}$  and  $\text{LaOBr}$ , implying that carbene generation was more feasible over the former. Raman studies showed that the  $\text{LaOBr}$  and 10mol% $\text{BaCO}_3/\text{LaOBr}$  catalysts were capable of forming  $\text{O}_2^{2-}$  and  $\text{O}_2^{n-}$  ( $1 < n < 2$ ) species during OCM reaction, while  $\text{LaOF}$  could form  $\text{O}_2^{n-}$  and  $\text{O}^{2-}$  species. It is concluded that the direct interaction of  $\text{CH}_4$  with  $\text{O}_2^{2-}$  is an efficient way of producing carbene, and

the coupling of carbene, rather than methyl radical, is the major step for  $C_2H_4$  generation over these highly  $C_2H_4$  selective  $BaCO_3/LaOBr$  catalysts.

The  $BaCO_3/LaOCl$  catalysts performed well ( $C_2$  yield > 19%) in OCM reaction within a wide range (10 to 70mol%) of  $BaCO_3$  loading.  $CH_4$  conversion of ca. 40% and a  $C_2$  yield of ca. 22% were obtained over the 50mol% $BaCO_3/LaOCl$  catalyst. The studies of  $CO_2$ -TPD showed that due to the presence of  $Cl^-$ , the decomposition temperature of  $BaCO_3$  was lowered from 990 to ca. 790 °C. It is proposed that the decomposition of  $BaCO_3$  under OCM conditions could create  $Cl^-$ -modified  $O^{2-}$  sites responsible for  $O_2$  and  $CH_4$  activation.

The catalytic performance of  $BaCl_2/La_2O_3$  and  $BaI_2/La_2O_3$  were also investigated. The  $BaCl_2$  loading for optimum  $BaCl_2/La_2O_3$  performance was 10mol%. The low activity of  $BaI_2/La_2O_3$  catalysts is due to iodine loss.

Correlation could be drawn between electrical conductivity and  $C_2$  selectivity over  $LaF_3/La_2O_3$  and  $BaCO_3/LaOF$  catalysts. The  $C_2$  selectivities observed over catalysts were found to distribute widely in the area between the lines:  $S = 17.5\log\sigma + 140$  and  $S = 13.0\log\sigma + 81$ . It is suggested that electrical conductivity of OCM catalysts is one of the influencing factors on  $C_2$  selectivity.

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