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The catalytic performance and characterization of BaO- and BaX2(X=F, Cl, Br)-promoted Ln2O3(Ln=Y, Er, Nd) catalysts for the oxidative coupling of methane

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Date of Award:
1998

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The Catalytic Performance and Characterization of BaO- and BaX_2(X =F, Cl, Br)-Promoted Ln_2O_3 (Ln = Y, Er, Nd) Catalysts for the Oxidative Coupling of Methane

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A thesis submitted in partial fulfilment of the requirements

for the degree of

Doctor of Philosophy

July 1998

Hong Kong Baptist University

ABSTRACT

In this work, the catalytic performances of BaO- and BaX_2(X=F, Cl, Br)-promoted Ln_2O_3 (Ln=Y, Er, Nd) catalysts have been investigated systematically for the oxidative coupling of methane (OCM). The bulk composition, crystal structure, surface composition, surface area, surface active oxygen species of the catalysts, and the activity of various oxygen species were examined by techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), temperature programmed reduction (TPR), CH_4- and O_2-pulsing experiments, Raman spectrometry, and electron paramagnetic resonance (EPR).

The performances of the 30 mol% MO/Y_2O_3 (M = Mg, Ca, Sr, Ba) catalysts for the OCM reaction have been explored. The BaO-promoted catalysts showed the best activity. When BaX_2 (X= F, Cl, Br) was used instead of BaO for the modification of Y_2O_3, the reactivities could be improved significantly, especially in C_2 selectivity and C_2H_4/C_2H_6 ratio. The 30 mol% $BaCl_2/Y_2O_3$ catalysts showed a C_2 yield of 22.3% at 800°C with $CH_4 : O_2 : N_2 = 2.47 : 1 : 11.4$, total flow rate = 50 mL min^{-1}, contact time = 0.6 g s mL^{-1}, and catalyst weight = 0.5 g. The XRD results revealed that the addition of 10-50 mol% of BaO or $BaCl_2$ could greatly alter the surface and bulk natures of Y_2O_3. The cubic Y_2O_3 lattices in BaO- and $BaCl_2$-promoted Y_2O_3 catalysts were found to have undergone

expansion which resulted from ionic substitution between Ba^{2+} and Y^{3+} ions. The reactivity of the 30 mol% $BaCl_2/Y_2O_3$ catalyst was stable within 40 h of reaction at 750°C. Although the analysis of chlorine content indicated that there was leaching of Cl^- ions, XPS results revealed no change in surface chlorine concentration. O_2-TPD and reduction studies of the fresh 30 mol% BaO- and $BaCl_2$-promoted catalysts showed that the amount of active oxygen in the former was at least 4 times that in the latter. It was apparent that the presence of Ba^{2+} ions could enhance the amount of surface oxygen species, while the presence of Cl^- could inhibit the deep oxidation reactions.

The BaF_2-promoted Y_2O_3 catalysts also exhibited good performance. A conversion of 36.1% and a selectivity of 62.1% were achieved at 750°C over the 95 mol% BaF_2/Y_2O_3 catalyst, the corresponding yield was 22.4%. The XRD results showed that the cubic Y_2O_3 lattice expanded slightly while the cubic BaF_2 lattice contracted. It is suggested that there were substitutions between the Ba^{2+} and Y^{3+} ions as well as the F^- and O^{2-} ions. Such ionic substitutions could result in the generation of active lattice defects such as anion vacancies, trapped electrons, and charge-deficient oxygen species. The EPR experiments confirmed the generation of trapped electrons in the 95 mol% BaF_2/Y_2O_3 catalyst. After H_2 reduction between 500 and 700°C, a kind of trapped electrons with EPR signal centered at 2.0871 was detected. H_2 reduction above 700°C could result in the generation of another type of trapped electrons with EPR signal centered at

2.0087. The 2.0871 signal showed doublet superhyperfine structure while the 2.0087 one was symmetrical. The former was interpreted as being due to trapped electrons interacting with the Y^{3+} ions, whereas the latter was due to trapped electrons shared among the orbitals of the surrounding cations. The 2.0871 trapped electrons spread throughout the sample, while the 2.0087 ones existed only on the surface. The involvement of surface-trapped electrons in activating O_2 was observed at 25°C, while above 500°C, trapped electrons in the bulk were also involved. According to the results, we concluded that in the OCM reaction, the BaF_2/Y_2O_3 catalysts were reduced by hydrogen dissociated from methane and trapped electrons were generated. These trapped electrons could serve as active sites for O_2 activation.

The BaO- and BaX_2-promoted Er_2O_3 catalysts have also been investigated for the OCM reaction. The $BaCl_2$-promoted Er_2O_3 catalysts showed very good performance. At 750°C with CH_4/O_2 = 2.2, the 30 mol% $BaCl_2/Er_2O_3$ catalyst showed the highest yield of 26.2%. The highest C_2H_4/C_2H_6 ratio was 20.6 at 800°C with CH_4/O_2 = 2.47. On the basis of XRD, XPS, Raman, and TPR results, one can conclude that the Ba^{2+} and X^- ions were involved in promoting Er_2O_3. According to the chemical analysis results, the stability of halide ions in the catalysts followed the sequence of $F^->Cl^->Br^-$. The F^- ions tend to diffuse into the bulk whereas the Cl^- and Br^- ions migrate to the surface of the catalyst. Although losses of Cl^- and Br^- ions occurred during the reaction, XPS studies indicated no changes in the surface concentrations of Cl^- and Br^- ions. The Raman results

showed that no dioxygen species existed on the surface of undoped Er_2O_3 while there were dioxygen species such as O_2^{2-}, O_2^{n-}, O_2^-, and $O_2^{\delta-}$ on the BaO- and BaX_2-promoted catalysts. The formation of dioxygen species on the surfaces was due to the interaction of lattice defects with gaseous O_2. Based on the Raman and TPR results, we conclude that the reducible oxygen species in these catalysts were composed of both dioxygen and mono-oxygen species. The presence of dioxygen inhibits the deep oxidation of hydrocarbons, causing the C_2 selectivity and C_2H_4/C_2H_6 ratio to increase.

The 30 mol% BaO- and 30 mol% BaX_2-promoted Nd_2O_3 catalysts performed better than the undoped Nd_2O_3 catalyst. This is due to the fact that the addition of BaO and BaX_2 to Nd_2O_3 caused the formation of lattice defects which facilitates the production of active oxygen adspecies such as O_2^{2-}, O_2^{n-}, O_2^-, and $O_2^{\delta-}$ on the surfaces. The TPR results suggested that besides the dioxygen adspecies, there was mono-oxygen on the surfaces. The CH_4-pulsing and Raman experiments demonstrated that both the mono-oxygen and dioxygen adspecies could activate CH_4 at higher temperatures but the former was more active than the latter in the deep oxidation of hydrocarbons.

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