

審査の結果の要旨

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The thesis written by Vibin Vargheese concerns the subject of methane partial oxidation by a mixture of NO and O₂ over different oxide supported Pt catalysts. During this reaction the NO+O₂ mixture reacts readily to form NO₂, the strong oxidant NO₂ then partially oxidizes the CH₄ to form oxygenates. Hence during this reaction NO and NO₂ are acting as an oxygen atom shuttle for the primary oxidant O₂.

First, a series of different oxide supported Pt catalysts were studied for the methane partial oxidation by the NO/NO₂ oxygen atom shuttle in a conventional packed-bed reactor (PBR). For the successful utilization of the NO/NO₂ shuttle mechanism, it is important that NO/NO₂ does not get reduced to form N₂. Second, the Pt/Y₂O₃ catalyst was tested for the partial oxidation of CH₄ to dimethyl ether (DME) and an in situ Fourier transform infrared spectroscopy (FTIR) measurement was used to study the adsorbed species on the catalyst. Third, a new one-pot method for the synthesis of the bimetallic catalyst was developed, and the catalysts were tested for the CH₄ partial oxidation reaction.

Chapter 1 introduces the different catalytic systems previously studied for the CH₄ partial oxidation reaction and a brief background of the different methods for the synthesis of bimetallic catalysts.

Chapter 2 deals with the screening of different Pt supported catalysts for the CH₄ partial oxidation reaction using the NO+O₂ mixture. The activity tests were conducted in a conventional packed-bed reactor (PBR), over a temperature range of 275-375 °C at 0.1 MPa. During catalyst screening, the Pt/Y₂O₃ catalyst gave selectivity for DME at all the temperatures and during this reaction, NO and NO₂ were not reduced to N₂. The activity test using O₂, NO+O₂, and NO₂ as the oxidant showed that NO₂ formed in the NO+O₂ mixture was responsible for the partial oxidation of CH₄. Hence over the Pt/Y₂O₃ catalyst the NO and NO₂ were acting as an oxygen atom shuttle for the ultimate oxidant O₂.

Chapter 3 describes the studies conducted for the partial oxidation of CH₄ to DME over Pt/Y₂O₃. Use was made of different spectroscopic techniques to understand the structure of the catalyst and to study the reactivity of adsorbed species on the Pt/Y₃O₃ catalyst. The activity test for the partial oxidation of CH₄ over the Y₂O₃ support and the Pt/Y₂O₃ catalyst, using O₂ and NO+O₂ as the oxidant showed that DME was formed only on Pt/Y₂O₃ with NO+O₂. During this reaction, NO and NO₂ were the only nitrogen-containing products observed and a contact time study showed that DME was a

primary product. An X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) analysis of Pt/Y₂O₃ showed that Pt had, small particle size and strong interactions with the Y₂O₃ support. An in situ FTIR study showed the formation of different surface nitrate species on Y₂O₃ and Pt/Y₂O₃. The reaction of nitrate species on the Pt/Y₂O₃ catalyst with CH₄ revealed the presence of a reactive bridged nitrate species at 1003 cm⁻¹. During the reaction with CH₄, the bridged nitrate species at 1003 cm⁻¹ disappeared at around 300 °C. The in situ FTIR measurements of the adsorbed CO on Pt and the adsorbed nitrate species on Pt/Y₂O₃ showed that the reactive nitrate species were formed on Y₂O₃ close to the Pt sites. Based on the in situ FTIR and catalyst activity studies it was concluded that the CH₄ activated on the Pt sites reacted with the nitrate species formed on the Y₂O₃ sites. Hence the partial oxidation of CH₄ on Pt/Y₂O₃ followed a dual-site reaction.

Chapter 4 describes a new one-pot method for the synthesis of the silica-supported bimetallic catalysts by means of differences in the reduction potentials of two metals. A series of NiPt, CuPt, FePt, and CoPt catalysts were synthesized using this method. The motivation behind the use of bimetallic catalysts was to have a catalyst with two different metal sites for the activation of oxidant and CH₄. In the proposed redox formation mechanism, a non-nobel metal (Ni, Cu, Fe, Co) acts as sacrificial seed metal atoms to reduce Pt. The fraction of non-nobel metal lost and the extent of bimetallic mixing was found to be strong functions of the amount of non-nobel metals available to reduce Pt. Evidence for the alloy formation was obtained from XRD patterns, and this was supported by TPR, XPS and CO uptake results. The XRD patterns showed the formation of single-phase alloys. Conversely, multiphase species were present in the reference silica-supported NiPt and CuPt catalysts prepared by incipient wetness impregnation. These catalysts were tested for the CH₄ partial oxidation reaction. The activity test results did not show the formation of oxygenates and only CO₂ was observed during the reaction.

Chapter 5 describes the general conclusion of the study and future visions of the use of NO/NO₂ shuttle mechanism for CH₄ partial oxidation.

The collection of papers meets the requirements for the doctoral degree in engineering and can be judged to contribute to the development of chemical systems engineering.