

Syngas Generation from Partial Oxidation of CH₄ over Rh/Al₂O₃: an In Situ IR/MS Study

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Introduction

Direct partial oxidation of methane (CH₄/O₂) over Rh is an attractive approach to produce synthesis gas. However, the reaction produces CO₂ and H₂O as major byproducts. Further improvement of the catalyst selectivity toward syngas requires a better understanding of the reaction pathway and the nature of the active site. The objective of this study is to investigate the mechanism of CH₄/O₂ reaction on Rh/Al₂O₃ by in situ infrared (IR) spectroscopy coupled with mass spectrometry (MS) analyses.

Materials and Methods

Rh/Al₂O₃ was prepared by incipient wetness impregnation method using an aqueous solution of RhCl₃·2H₂O onto γ -Al₂O₃ [1]. Transient and steady state experiments were performed by the step switch and pulse input techniques. The change in the nature and concentration of adsorbates on the catalyst surface was monitored by DRIFTS (Diffused Reflectance Infrared Fourier transform Spectroscopy) while the gaseous responses of the effluent was observed on the mass spectrometer. The catalysts are characterized by TEM and XRD.

Results and Discussion

Figure 1a,b,c summarize the IR and MS results of O₂ pulsing (1 cm³) into steady-state CH₄/Ar flow over reduced Rh/Al₂O₃ at 773K. Four single O₂ pulses followed by 24 rapid fire pulses of O₂ were performed. The intensities of MS profiles prior to O₂ pulsing represent the steady state concentration profiles of the reactant and products. O₂ pulses caused formation of CO, H₂, CO₂ and CH₄ as indicated by the positive peaks within their profiles. The evolution of CH₄ after pulsing of O₂ can be due to hydrogenation of CH_x species originating from (i) the decomposition of CH₄ on the catalyst surface and (ii) dissociation of CO to produce C species which can undergo hydrogenation. All of the O₂ pulses were completely consumed, as evidenced by the flat O₂ profile.

Significant increase in the formation of CO, H₂ and CO₂ and substantial consumption of CH₄ occurred after exposure of the catalyst to four single pulses and four pulses in the rapid fire section. The catalyst reached an optimum level of reduced and oxidized site to trigger the partial and total oxidation. Oxygen balance calculation suggests that most Rh surface atoms (entire monolayer) have been oxidized. Continuing oxygen pulses led to a rapid rise in CO and H₂ formation with a gradual increase in CO₂ formation, indicating that CO and H₂ is directly produced from partial oxidation of CH₄ instead of the CH₄ reforming with H₂O/CO₂ (total oxidation products). Infrared spectra show the intensity of adsorbed CO on Rh⁰ sites at 2025 and 2065 cm⁻¹ decreased with the number of oxygen pulses, further confirming the oxidation of the Rh⁰ to oxidized Rh. The gradual change in product formation with respect to change in Rh oxidation state was also observed in step transient studies.

This paper will present infrared and mass spec results of both pulse and step transient studies and will also discuss the dynamic behavior of adsorbed species, the reaction pathway, and the nature of active sites for partial and total oxidation of CH₄.

Significance

The reaction pathway and the nature of active sites for both partial and total oxidation of CH₄ can be elucidated from the dynamic behavior of adsorbed species and gaseous products determined by IR/MS.

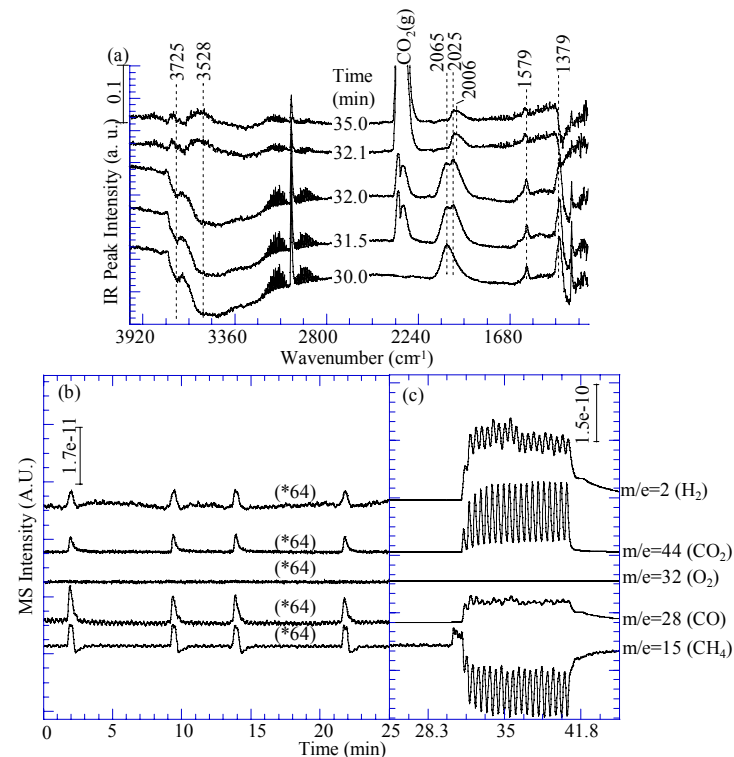


Figure 1. O₂ pulse (1 cm³) into steady state CH₄/Ar (2/38 cm³/min) flow over Rh/Al₂O₃ at 500 °C analyzed by (a) DRIFTS, (b) and (c) mass spectrometry. All of the MS profiles in Figure 1 (b) were multiplied by a factor of 64.

References

- 1 Stevens Jr., R. W., Chuang, S.S.C., J. Phys. Chem. B 108, 696 (2004).