Pulse studies of \( \text{CH}_4 \) interaction with \( \text{NiO}/\text{Al}_2\text{O}_3 \) catalysts

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Pulse studies of the interaction of \( \text{CH}_4 \) and \( \text{NiO}/\text{Al}_2\text{O}_3 \) catalysts at 500\(^\circ\)C indicate that \( \text{CH}_4 \) adsorption on reduced nickel sites is a key step for \( \text{CH}_4 \) oxidative conversion. On an oxygen-rich surface, \( \text{CH}_4 \) conversion is low and the selectivity of \( \text{CO}_2 \) is higher than that of \( \text{CO} \). With the consumption of surface oxygen, \( \text{CO} \) selectivity increases while the \( \text{CO}_2 \) selectivity falls. The conversion of \( \text{CH}_4 \) is small at 500\(^\circ\)C when a pulse of \( \text{CH}_4]/\text{O}_2 \) (\( \text{CH}_4 \) : \( \text{O}_2 = 2 : 1 \)) is introduced to the partially reduced catalyst, indicating that \( \text{CH}_4 \) and \( \text{O}_2 \) adsorption are competitive steps and the adsorption of \( \text{O}_2 \) is more favorable than \( \text{CH}_4 \) adsorption.

**Keywords:** pulse reaction; \( \text{NiO}/\text{Al}_2\text{O}_3 \) catalysts; methane activation

1. Introduction

During the last decade or so, a considerable amount of efforts have been devoted to the conversion of methane to transportable and/or value added products [1–4]. Besides the well-known methane oxidative coupling process, partial oxidation of methane to syngas has recently been found to be promising. High selectivities to \( \text{CO} \) and \( \text{H}_2 \) with excellent methane conversion have been reported over a number of supported transition metal catalysts, particularly the Ni catalysts [4–8].

The activation of methane on Ni single-crystal surfaces and model thin films of \( \text{NiO} \) had been studied by a number of researchers, using techniques such as molecular beam [9], Auger electron spectroscopy [10,11], and theoretical calculations [12]. However, for practical supported nickel catalysts, the \( \text{CH}_4]/\text{O}_2 \) to syngas reaction was investigated mainly using continuous flow microreactor systems. Data concerning activity and selectivity of the catalysts were obtained, but a very limited

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amount of information about the interaction of methane with the catalysts is made available. Moreover, Lunsford and coworkers [13] found that during the catalytic oxidation of CH$_4$ to syngas over Ni/Yb$_2$O$_3$ catalysts in the continuous flow reaction system and at high space velocities, the exothermic reaction gave rise to large temperature gradation, resulting in the generation of hot spots. The temperature of the hot spots would be as much as 300°C higher than the temperature measured by thermocouple. Because of this hot spot problem, data obtained by Choudhary et al. [5-7] are considered to be questionable [13]. In a pulse micro-reactor, the reactant gas is introduced in pulses, and because the amount of reactant introduced is small each time, hot spots are not generated and reliable data can be obtained. In this paper, we studied the activation of methane over NiO/Al$_2$O$_3$ catalysts using the pulse method. Some useful information about CH$_4$ activation was obtained. The mechanism of CH$_4$ interaction with NiO is discussed.

2. Experimental

Catalyst preparation. The NiO/Al$_2$O$_3$ catalyst (with 10 wt% of nickel) was prepared by impregnating Al$_2$O$_3$ powder with nickel nitrate (BDH, A.R. grade) solution. The paste generated was dried at 110°C and annealed at 400°C for decomposition. After being pressed and crushed, the material was sieved to a grain size of 20-40 mesh before being calcined at 800°C in air for 4 h.

Pulse reaction system. The reaction was carried out using a pulse microreactor. A schematic diagram of the system is shown in fig. 1. The reactor was made of stainless-steel tube with 4 mm i.d. For each study, 50 mg of NiO/Al$_2$O$_3$ catalyst

![Fig. 1. Schematic diagram of the pulse microreactor system: (1) helium, (2) methane, (3) oxygen, (4) hydrogen, (5) four-way valve, (6) gas mixing tube, (7) six-way valves, (8) sampling tubes, (9) thermocouple, (10) reactor, (11) temperature programmed oven, (12) 5A zeolite column, (13) Porapak Q, (14) thermal conductivity detector.](image-url)