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Pulse studies of CH_4 interaction with NiO/Al_2O_3 catalysts

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Pulse studies of the interaction of CH_4 and NiO/Al_2O_3 catalysts at 500°C indicate that CH_4 adsorption on reduced nickel sites is a key step for CH_4 oxidative conversion. On an oxygen-rich surface, CH_4 conversion is low and the selectivity of CO_2 is higher than that of CO. With the consumption of surface oxygen, CO selectivity increases while the CO_2 selectivity falls. The conversion of CH_4 is small at 500°C when a pulse of CH_4/O_2 ($CH_4 : O_2 = 2 : 1$) is introduced to the partially reduced catalyst, indicating that CH_4 and O_2 adsorption are competitive steps and the adsorption of O_2 is more favorable than CH_4 adsorption

Keywords: pulse reaction; NiO/Al_2O_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 CO and 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 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 CH_4/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_2O_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 microreactor, 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_2O_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_2O_3 catalyst (with 10 wt% of nickel) was prepared by impregnating Al_2O_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_2O_3 catalyst

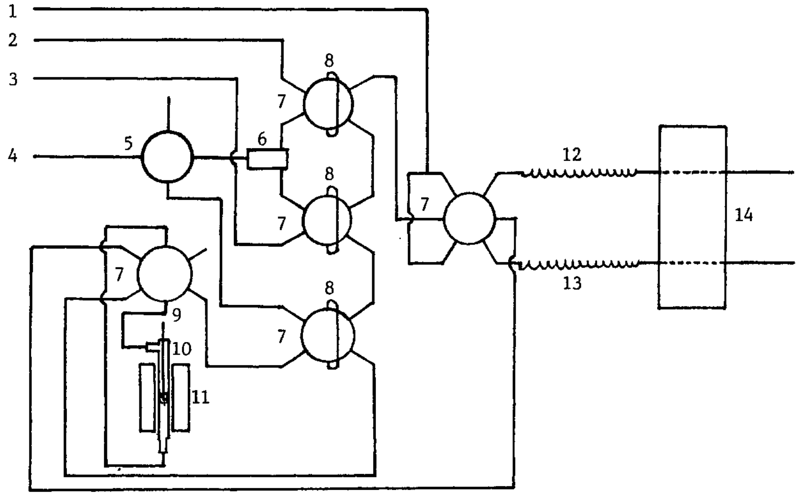

Fig. 1. Schematic diagram of the pulse microreactor system: (1) helium, (2) methane, (3) oxygen, (4) hydrogen, (5) four-way valve, (6) gas mixing tube, (7) six-way valves, (8) sampling tubes, (9) thermocouple, (10) reactor, (11) temperature programmed oven, (12) 5A zeolite column, (13) Porapak Q, (14)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

was used. The pulse volumes of CH_4, O_2, H_2 and CH_4/O_2 were 1.11, 0.44, 1.03 and 1.03 ml respectively. During the reaction, helium was used as carrier gas and its flow rate was 17 ml/min. At 500°C, in the absence of the catalyst NiO/Al_2O_3 or in the presence of the support material Al_2O_3, the blank runs showed no activity whatsoever under the reaction conditions mentioned in this paper.

3. Results and discussion

By introducing pulses of CH_4 to the catalyst bed at 500°C, we monitored the activity and selectivity of

(I) freshly prepared NiO/Al_2O_3 catalyst;

(II) NiO/Al_2O_3 catalyst partially reduced by one pulse of H_2 (1.03 ml) at 500°C;

(III) NiO/Al_2O_3 catalyst treated with CH_4/O_2 ($CH_4 : O_2 = 2 : 1$, pressure = 1 atm, flow rate = 54 ml/g s) for 10 min at 700°C.

In case I, the CH_4 conversion during the first pulse of CH_4 was extremely small, implying that the surface of the catalyst was not active (fig. 2a). However,

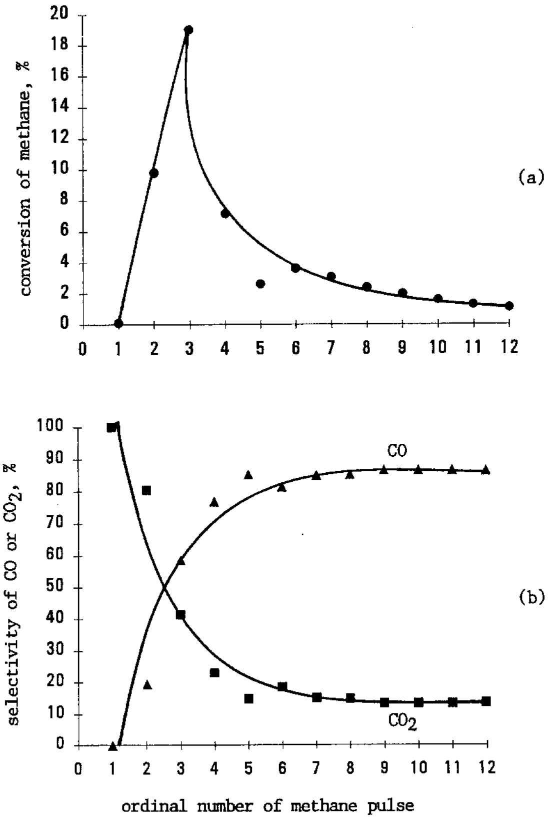

Fig. 2. The relationship between (a) CH_4 conversion and (b) selectivity of CO or CO_2 and ordinal number of CH_4 pulsing over freshly prepared NiO/Al_2O_3 catalyst at 500°C.

during the second pulse, CH_4 conversion was obviously higher with CO_2 as the main product (figs. 2a and 2b). CH_4 conversion was highest (ca. 19%) at the third pulse of CH_4. Further exposure of the catalyst to pulses of CH_4 resulted in the decline of CH_4 conversion and CO_2 selectivity, with the CO selectivity being observed to increase. After the sixth pulse, the conversion of CH_4 was 3.5% and it declined to 1% at the twelfth pulse. CO_2 selectivity was 100% initially and, after the fourth pulse, dropped to about 23% while the CO selectivity respectively increased from 0 to 77%.

In case II, the catalyst was partially reduced by one time of H_2 pulsing at 500°C. The conversion of CH_4 was highest (ca. 26%) at the first pulse of CH_4. Further exposure of the catalyst to pulses of CH_4 resulted in the decline of CH_4 conversion and CO_2 selectivity with the CO selectivity being observed to increase (fig. 3).

In case III, the catalyst was treated with CH_4/O_2. CH_4 conversion was ca. 25% at the first and second pulse and then declined gradually afterwards (fig. 4a). CO_2 selectivity was higher than CO initially and as the number of pulses increased, CO_2 selectivity dropped while CO selectivity rose (fig. 4b).

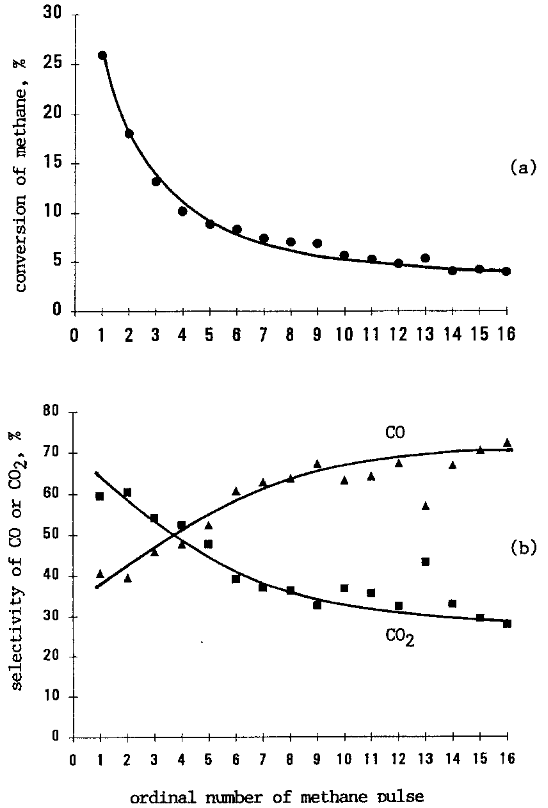

Fig. 3. The relationship between (a) CH_4 conversion and (b) selectivity of CO or CO_2 and ordinal number of CH_4 pulsing over NiO/Al_2O_3 catalyst reduced by one time of pulsing H_2 at 500°C.

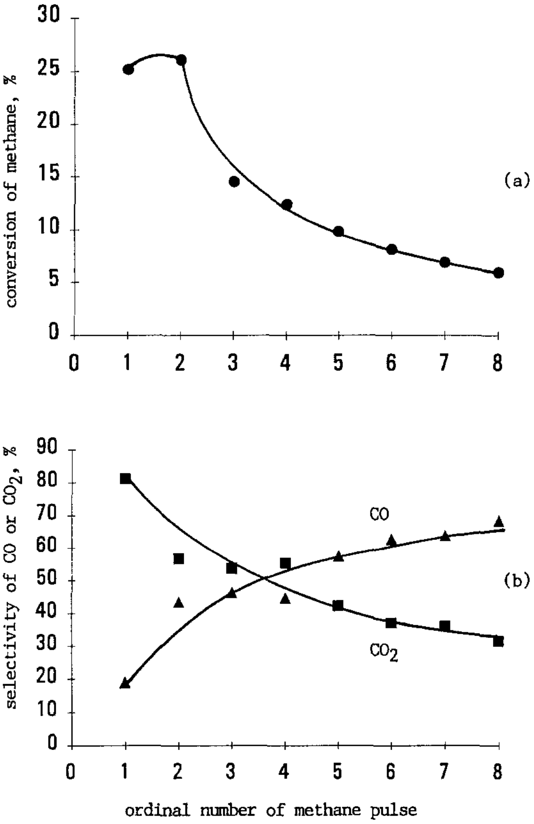

Fig. 4. The relationship between (a) CH_4 conversion and (b) selectivity of CO or CO_2 and ordinal number of CH_4 pulsing at 500°C over NiO/Al_2O_3 catalyst after pretreatment in $CH_4 + O_2$ ($CH_4 : O_2 = 2 : 1$) at 700°C.

Fig. 5 shows that, when a mixture of CH_4 and O_2 ($CH_4/O_2 = 2/1$) was pulsed to a NiO/Al_2O_3 catalyst which had been treated with CH_4/O_2 ($CH_4/O_2 = 2/1$, pressure = 1 atm, flow rate = 54 ml/g s) for 10 min at 700°C, the conversion of CH_4 at 500°C stayed at around 1% and the CO_2 selectivity was 100% at every pulse of CH_4/O_2.

A freshly prepared NiO/Al_2O_3 catalyst would have a surface composed of oxide. Initial CH_4 pulsing at 500°C showed little activation but CH_4 conversion definitely increased in the second and third pulsing (fig. 2). This may be because initial interaction between methane and the surface is that between $CH_4(g)$ and NiO(s). The process is possible but slow at 500°C. Since no CO and H_2 were detected at the first pulse of methane, initial Ni sites were mainly generated by total oxidation of methane. Once reduced sites are generated, CH_4 adsorption and dissociation become feasible, resulting in higher CH_4 conversion. This shows that reduced nickel sites have higher ability for CH_4 activation than nickel oxide sites. CH_4 conversion increased as the reduced nickel sites increased with the ordinal number of CH_4 pulses. However, as the surface is further reduced, it is deprived of

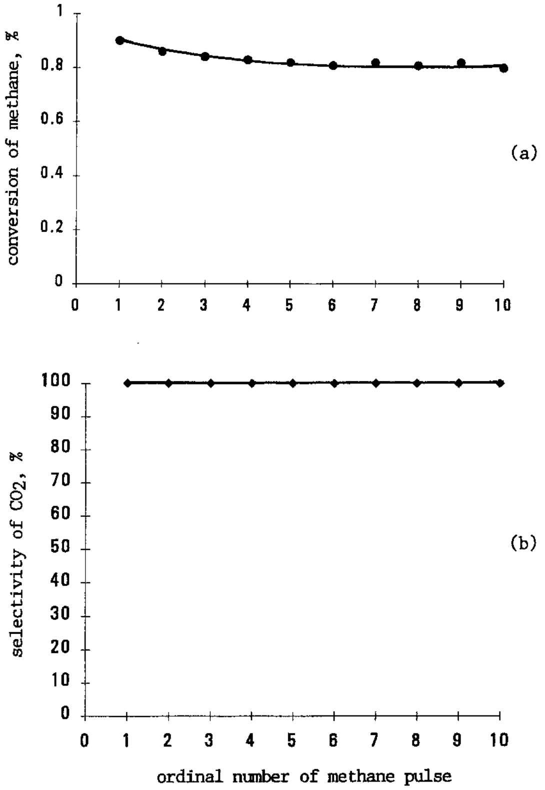

Fig. 5. The relationship between (a) CH_4 conversion and (b) selectivity of CO_2 and ordinal number of $CH_4/O_2(2/1)$ pulsing at 500°C over the NiO/Al_2O_3 catalyst after pretreatment in $CH_4 + O_2$ ($CH_4 : O_2 = 2 : 1$) at 700°C.

oxygen and CH_4 conversion reached a maximum and declined afterward. After the initial pulse of methane, CO and H_2 were generated, implying reduced Ni sites could be further generated by total as well as partial oxidation of methane. When NiO/Al_2O_3 was first partially reduced by one pulse of H_2, the conversion of CH_4 was at its highest during the first pulse of CH_4 (fig. 3). This is because enough amount of reduced nickel sites was already generated by the pulse of hydrogen before the first pulse of CH_4 was introduced. It has been shown that methane adsorbs dissociatively on Ni(100) [10,11], Ni(111) [9,10,12] and Ni(110) surfaces [10]. Campbell et al. showed that the reaction probability of methane on NiO films was significantly lower than that observed on the clean Ni(100) surface [11]. These results are consistent with our data over the NiO/Al_2O_3 catalyst.

After the NiO/Al_2O_3 catalyst was treated with CH_4/O_2 at 700°C, CH_4 conversion at 500°C reached 25% at the first pulse of CH_4 (fig. 4), indicating that some reduced nickel sites were generated in the CH_4/O_2 to syngas process at 700°C. This is consistent with the XPS and XRPD results obtained by Lunsford and coworkers [14].

At 500°C, CH_4/O_2 mixture reacted poorly with the reduced catalyst (fig. 5), indicating that the adsorptions of O_2 and CH_4 on the reduced sites were competitive processes. As O_2 chemisorption occurs more readily than CH_4 chemisorption, the surface is reoxidized, rendering the chemisorption of CH_4 unfavorable and resulting in poor CH_4 conversion.

In all cases, CO_2 formation was more favorable than CO initially and as the surface was deprived of oxygen, CO_2 selectivity decreased and CO selectivity increased. Based on the above observations, we propose the following mechanism for the interaction between CH_4 and NiO/Al_2O_3 at 500°C:

$$2NiO + \tfrac{1}{2}CH_4(g) \rightarrow 2Ni + \tfrac{1}{2}CO_2(g) + H_2O(g) \tag{1}$$

$$Ni + CH_4(g) \rightarrow CH_x(s) + (4-x)H(s) \tag{2}$$

$$CH_x(s) \rightarrow C(s) + xH(s) \tag{3}$$

$$H(s) + H(s) \rightarrow H_2(g) + 2Ni \tag{4}$$

$$C(s) + NiO \rightarrow Ni + CO(s) \tag{5}$$

$$CO(s) + NiO \rightarrow CO_2(s) + Ni \tag{6}$$

$$CO(s) \rightarrow Ni + CO(g) \tag{7}$$

$$CO_2(s) \rightarrow Ni + CO_2(g) \tag{8}$$

$$2H(s) + NiO \rightarrow H_2O(g) + Ni\,. \tag{9}$$

Comparing with step 2, step 1 is very difficult. After the initial generation of Ni sites in step 1, the activation of CH_4 occurs mainly according to step 2 and the generation of CO, CO_2 and H_2 follows the steps similar to those proposed by Hickman et al. [8] over Pt and Rh monoliths.

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