

# Broadened Pulse-Step Change—Isotopic Sharp Pulse Analysis of the Mechanism of Methane Partial Oxidation to Synthesis Gas

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The mechanism of the partial oxidation of CH<sub>4</sub> was studied by a transient response analysis of a broadened pulse combined with either a step change or a sharp isotopic pulse. Over the unreduced NiO/SiO<sub>2</sub> catalyst, the reaction between CH<sub>4</sub> and O<sub>2</sub> occurs via the Eley–Rideal mechanism, CH<sub>4</sub> in the gas phase (or weakly adsorbed) reacting with O<sub>2</sub> in the adsorbed state. In contrast, over the reduced NiO/SiO<sub>2</sub> catalyst, the reaction takes place by a Langmuir–Hinshelwood mechanism, CH<sub>4</sub> and O<sub>2</sub> reacting in the adsorbed states. In addition, isotopic pulses of <sup>18</sup>O<sub>2</sub> revealed that over the reduced catalyst lattice oxygen is formed and reduced by the carbon species; hence, on the reduced catalyst a dynamic redox process occurs.

## 1. Introduction

Two mechanisms have been suggested for the partial catalytic oxidation of methane to synthesis gas. In one, CO<sub>2</sub> and H<sub>2</sub>O are the primary products, and CO is a result of their reaction with CH<sub>4</sub>. In the other, CO is produced directly without the preformation of CO<sub>2</sub>. Prettre et al.,<sup>1</sup> who were the first to study the CH<sub>4</sub> partial oxidation over a nickel catalyst, concluded that the overall oxidation involves two stages: an initial exothermic oxidation of CH<sub>4</sub> to CO<sub>2</sub> and H<sub>2</sub>O followed by the endothermic reaction CH<sub>4</sub> + CO<sub>2</sub> → 2CO + 2H<sub>2</sub>. Some recent investigations brought support to this mechanism.<sup>2–6</sup> The other mechanism involves the pyrolysis CH<sub>4</sub> → C + 4H followed by the oxidation of C to CO.<sup>6–12</sup>

Regarding the active catalytic phase for the reaction, some of the researchers considered that the metal is the active phase.<sup>7–11,13,14</sup> However, Dissanayake et al.<sup>3</sup> identified three constituents in the used Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and suggested that CH<sub>4</sub> is oxidized to CO<sub>2</sub> and H<sub>2</sub>O over the regions containing NiAl<sub>2</sub>O<sub>4</sub> and/or NiO + Al<sub>2</sub>O<sub>3</sub> and that the steam and/or CO<sub>2</sub> reforming of CH<sub>4</sub> to CO and H<sub>2</sub> occur over the regions containing Ni/Al<sub>2</sub>O<sub>3</sub>. Van Looij and Geus<sup>15</sup> suggested that, in the parallel combustion of methane to CO<sub>2</sub> and reforming of methane, the combustion proceeds partly over NiO and more completely over partially oxidized nickel and that the reforming of methane to synthesis gas proceeds over metallic nickel sites.

Recently,<sup>16</sup> a new transient method, in which, instead of sharp pulses, both broadened pulses combined with step changes and broadened pulses combined with sharp isotopic pulses are employed, was developed. This combination of pulses provides richer dynamic information than the individual pulses. In the present paper it will be shown that this method allows us to obtain some information about the mechanism of partial oxidation of CH<sub>4</sub> over both the unreduced and reduced NiO/SiO<sub>2</sub> catalysts. Different mechanisms have been thus identified: (i) the CH<sub>4</sub> of the gas phase (or in a weakly adsorbed state) reacts with the O<sub>2</sub> adsorbed on the catalyst over the unreduced catalyst; (ii) a surface reaction between adsorbed CH<sub>4</sub> and O<sub>2</sub> species takes place over the reduced catalyst.

## 2. Experimental Section

**2.1. Catalyst Preparation.** NiO/SiO<sub>2</sub> (containing 13.6 wt % Ni) catalysts were prepared by impregnating SiO<sub>2</sub> (Aldrich) with an aqueous solution of nickel nitrate (Alfa). The paste thus obtained was dried at room temperature in air and then decomposed and calcined at 800 °C in air for 1.5 h. The BET surface area and average diameter of the pores were 362 m<sup>2</sup>/g and 52 Å, respectively.

**2.2. Transient Response Analysis of a Broadened Pulse Combined with a Step Change or with a Sharp Isotopic Pulse.** The transient analysis experiments were performed at 800 °C under atmospheric pressure. The catalyst powder (weight: 0.02 g) was held on quartz wool in a vertical quartz tube reactor of 2 mm inside diameter in an electronically controlled furnace of large heat capacity in order to keep the temperature constant. Helium (60 mL/min) was used as the carrier gas. The feed gas contained CH<sub>4</sub> and O<sub>2</sub> (CH<sub>4</sub>/O<sub>2</sub> = 2:1) and the isotopes <sup>13</sup>CH<sub>4</sub> (99%) and O<sup>18</sup><sub>2</sub> (99%) (Isotec Inc) were employed in the experiments.

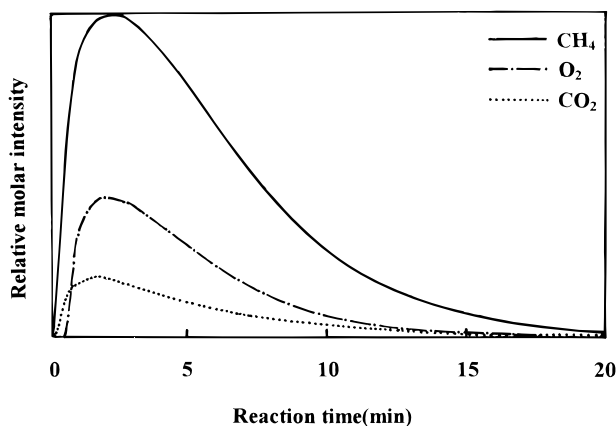
The method, which was proposed in our previous paper,<sup>16</sup> can be simply described as follows. A gas pulse of 2.5 mL is injected almost instantaneously into a carrier gas (He) and allowed to flow into a large tube (40 mm diameter and 164 mm length) in which the pulse is broadened to a width of about 20 min. From the broadening tube, the pulse flows more slowly to the reactor and finally to the MS equipment. During the broadened pulse, a step change from the feed gas to He, or a sharp isotopic pulse of 3 μL, is introduced at selected times in the broadened pulse. The reactants and products have been continuously detected with a MS equipment (HP Quadrupole, 5971 Series mass-selective detector) equipped with a fast response inlet capillary system.

## 3. Results

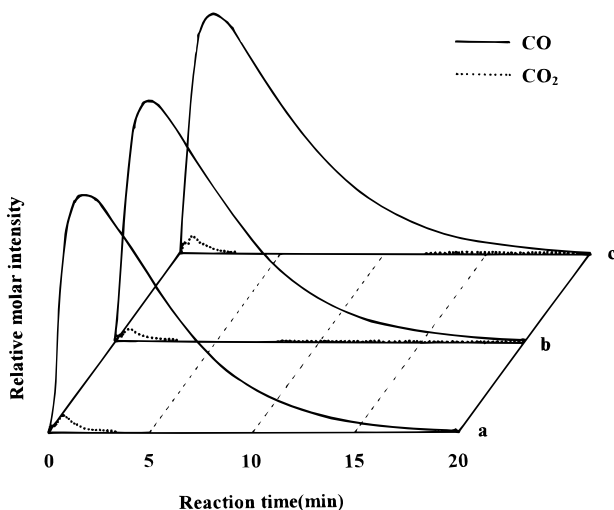
**3.1. Transient Response to a Broadened CH<sub>4</sub>/CO<sub>2</sub> Pulse over NiO/SiO<sub>2</sub>.** Over the unreduced catalyst, the response curves to a broadened pulse (Figure 1) show that no CO is present and only a relatively small amount of CO<sub>2</sub> is formed. Most of CH<sub>4</sub> and O<sub>2</sub> remain unreacted. After NiO/SiO<sub>2</sub> was reduced with six pulses of H<sub>2</sub> (2.5 mL), the response (Figure

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**Figure 1.** Responses to a broadened pulse of  $\text{CH}_4/\text{O}_2$  (2.5 mL) over an unreduced  $\text{NiO}/\text{SiO}_2$  catalyst at 800 °C.

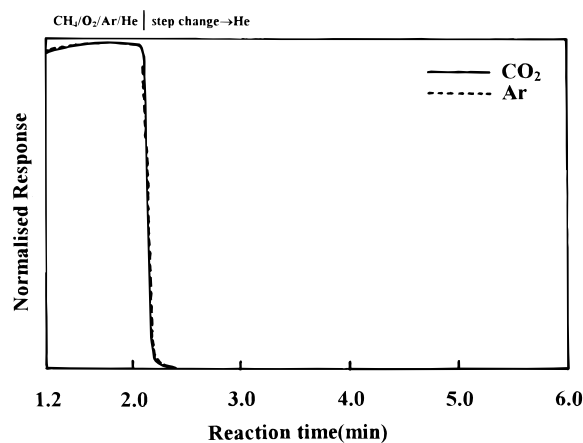


**Figure 2.** Responses to a broadened pulse of  $\text{CH}_4/\text{O}_2$  (2.5 mL) over a reduced  $\text{NiO}/\text{SiO}_2$  catalyst at 800 °C: (a) first pulse; (b) second pulse; (c) third pulse.

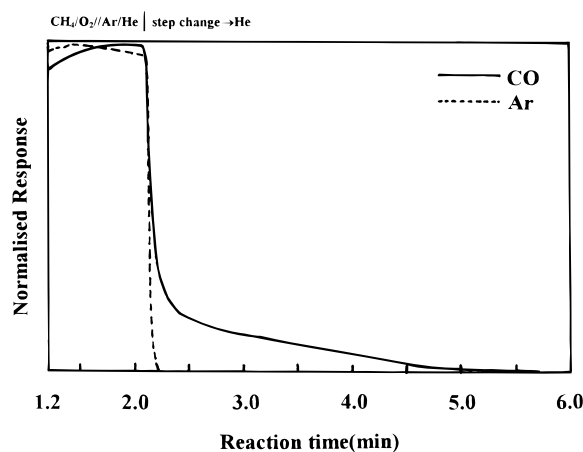
2) to the broadened pulse of  $\text{CH}_4/\text{O}_2$  shows the presence of CO and of a small amount of  $\text{CO}_2$  and is free of  $\text{CH}_4$ ,  $\text{O}_2$ , and water. Three successive pulses have been carried out. Since they are very similar, it is clear that the pulses do not change appreciably the surface of the catalyst.

**3.2. Transient Response to a Broadened Pulse Combined with a Step Change.** The response to a step change to He during the broadened  $\text{CH}_4/\text{O}_2/\text{Ar}/\text{He}$  (13.4% Ar as internal standard) pulse shows that, over the unreduced catalyst (Figure 3), the  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$  curves coincide with that of Ar; hence, the product  $\text{CO}_2$  does not exhibit a delay tail. In contrast, over the reduced catalyst (Figure 4), the tail of the CO response is 3.3 min longer than that of Ar.

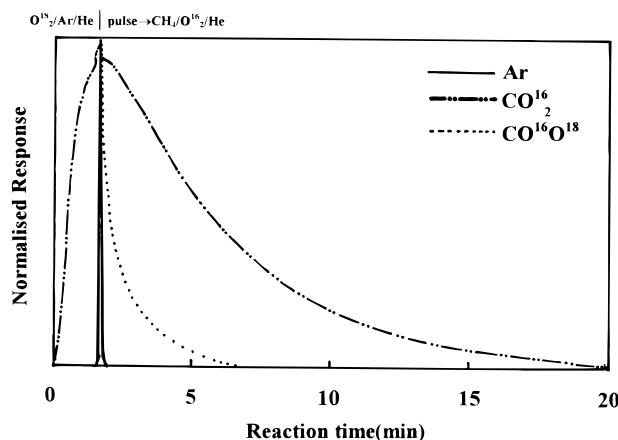
**3.3. Transient Response Analysis of a Broadened Pulse Combined with an Isotopic Sharp Pulse.** Sharp  $^{18}\text{O}_2/\text{Ar}$  (13.4% Ar) or  $^{13}\text{CH}_4$  (5% Ar) pulses were introduced during broadened  $^{12}\text{CH}_4/^{16}\text{O}_2$  pulses (Figures 5–7). Figure 5 shows that, over the unreduced catalyst, the response curve of  $\text{C}^{16}\text{O}^{18}\text{O}$  to a sharp pulse of  $^{18}\text{O}_2$  has a much longer tail, 5 min longer, than Ar, which has a width of only 0.1 min, and that no  $\text{C}^{18}\text{O}_2$  is present. Figure 6 shows that, over the reduced catalyst, the response curves of  $\text{C}^{18}\text{O}$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  to a sharp pulse of  $^{18}\text{O}_2/\text{Ar}$  have much longer tails than Ar, being 1.8 min longer. Figure 7 shows that the response of  $^{13}\text{CO}$  to a  $^{13}\text{CH}_4$  sharp pulse, over the reduced catalyst, has a somewhat longer tail than Ar. In addition, one can see that the tail of the  $\text{C}^{18}\text{O}$  response to an



**Figure 3.** Normalized responses to a broadened pulse of  $\text{CH}_4/\text{O}_2/\text{Ar}$  combined with a step change to pure carrier (He) over an unreduced  $\text{NiO}/\text{SiO}_2$  catalyst at 800 °C.



**Figure 4.** Responses to a broadened pulse of  $\text{CH}_4/\text{CO}/\text{Ar}$  combined with a step change to He over a reduced  $\text{NiO}/\text{SiO}_2$  catalyst at 800 °C (no  $\text{CO}_2$  was detected after the step change).

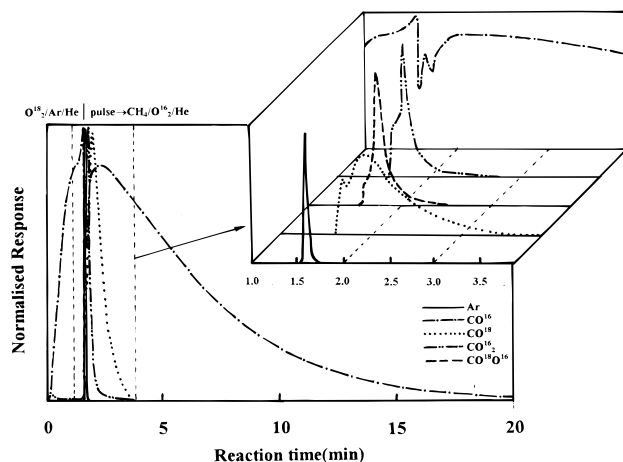


**Figure 5.** Normalized responses to a broadened pulse of  $\text{CH}_4/^{16}\text{O}_2$  combined with a sharp pulse of  $^{18}\text{O}_2/\text{Ar}$  over an unreduced  $\text{NiO}/\text{SiO}_2$  catalyst at 800 °C.

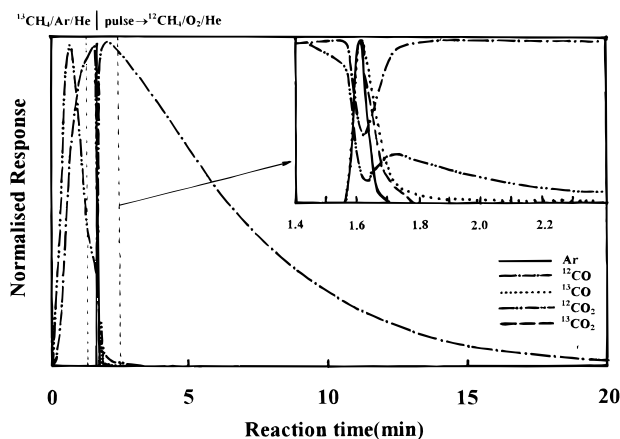
$^{18}\text{O}_2$  sharp pulse is much longer than the tail of the  $^{13}\text{CO}$  response to a  $^{13}\text{CH}_4$  sharp pulse (compare Figures 6 and 7).

#### 4. Discussion

Over the unreduced  $\text{NiO}/\text{SiO}_2$  catalyst, the response curves of  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$  to a step change from the feed gas to He coincide with that of Ar (Figure 3). Because in the absence of



**Figure 6.** Normalized responses to a broadened pulse of  $\text{CH}_4/\text{C}^{16}\text{O}_2/\text{Ar}$  combined with a sharp pulse of  $^{18}\text{O}_2/\text{Ar}$  over a reduced  $\text{NiO}/\text{SiO}_2$  catalyst at  $800^\circ\text{C}$ .



**Figure 7.** Normalized responses to a broadened pulse of  $^{12}\text{CH}_4/\text{O}_2$  combined with a sharp pulse of  $^{13}\text{CH}_4/\text{Ar}$  over a reduced  $\text{NiO}/\text{SiO}_2$  catalyst at  $800^\circ\text{C}$ .

the catalyst the conversion is extremely small, the above observations indicate that the formation of  $\text{CO}_2$  over the unreduced catalyst can occur (a) between weakly adsorbed species, (b) between one weakly adsorbed species and another species in the gas phase, or (c) between one strongly adsorbed and another weakly adsorbed or gas-phase species with rapid desorption of the product. However, the response of  $\text{C}^{18}\text{O}^{16}\text{O}$  over the unreduced catalyst to a sharp pulse of  $^{18}\text{O}_2/\text{Ar}$  during a broadened pulse of  $\text{CH}_4/^{16}\text{O}_2$  has a longer tail than Ar (Figure 5). This reveals that a strongly adsorbed oxygen or lattice oxygen species participates in the reaction. Therefore, over the unreduced catalyst, the reaction occurs between the gas-phase or weakly adsorbed  $\text{CH}_4$  and the strongly adsorbed or lattice oxygen (Eley–Rideal mechanism). Because during the sharp pulse of  $^{18}\text{O}_2/\text{Ar}$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$  (and not  $\text{C}^{18}\text{O}_2$ ) is formed, it is clear that  $^{18}\text{O}_2$  first dissociates to two  $^{18}\text{O}$  before reacting with  $\text{CH}_4$ . The fact that  $\text{C}^{16}\text{O}^{18}\text{O}$  has a long tail indicates that at least a part of  $^{18}\text{O}$  is stabilized by its exchange with the lattice O. The temperature programmed reaction experiments between  $\text{CH}_4$  and  $\text{NiO}$ <sup>17</sup> demonstrated that the lattice oxygen can be reduced by  $\text{CH}_4$ .

Over the reduced catalyst, the CO response to a step change to He, during the  $\text{CH}_4/\text{O}_2/\text{Ar}$ -broadened pulse, has a longer tail than that of Ar (Figure 4). The delay can be a result of (a) CO desorption and (b) CO formation by the surface reaction between the C and O species. Previously,<sup>16</sup> we have shown that the CO response to a step change from  $\text{CO}/\text{Ar}/\text{He}$  to He during a

broadened pulse of  $\text{CO}/\text{Ar}$  is near that of Ar. This indicates that the delay is not due to the desorption but to the surface reaction between the C and the O species. Consequently, the reaction over the reduced  $\text{NiO}/\text{SiO}_2$  catalyst takes place via the Langmuir–Hinshelwood mechanism, in which the adsorbed  $\text{CH}_4$  and  $\text{O}_2$  species are involved. This is further confirmed by the responses of  $^{13}\text{C}^{16}\text{O}$  or  $^{12}\text{C}^{18}\text{O}$  to sharp pulses of  $^{13}\text{CH}_4/\text{Ar}$  (Figure 7) or  $^{18}\text{O}_2/\text{Ar}$  (Figure 6) during  $^{12}\text{CH}_4/^{16}\text{O}_2$ -broadened pulses, which exhibit longer tails than that of Ar.

The long tail in the response of CO to a step change to He, during the broadened pulse of  $\text{CH}_4/\text{O}_2/\text{Ar}/\text{He}$  (Figure 4), indicates the presence of C species on the reduced catalyst. In contrast, there are no C species over the unreduced catalyst (Figure 3). Therefore, one can conclude that  $\text{Ni}^0$  is responsible for the activation of  $\text{CH}_4$ . This occurs because of the  $\sigma$ – $\pi$  coordination between the  $\sigma$  bonds of C–H in  $\text{CH}_4$  and the d orbitals of Ni. This reduces the C–H binding energy via the electron donation from the  $\sigma$  bond of C–H to a vacant d orbital of Ni and the back-donation from the filled d orbital of Ni to the vacant antibonding  $\sigma^*$  orbital of C–H. Indeed, the experiments of Ceyer<sup>18</sup> demonstrated that the CH bond is dissociated over Ni.

Over the reduced catalyst, the tail of the  $^{12}\text{C}^{18}\text{O}$  response to a sharp pulse of  $^{18}\text{O}_2/\text{Ar}$  (Figure 6) is much longer than that of the  $^{13}\text{C}^{16}\text{O}$  response to a sharp pulse of  $^{13}\text{CH}_4$  (Figure 7), both during the broadened pulse of  $^{12}\text{CH}_4/^{16}\text{O}_2$ . This indicates that the C species react more easily than the O species. Because the long tail of  $\text{C}^{18}\text{O}$  to the sharp pulse indicates that the  $^{18}\text{O}$  species are relatively stable (Figure 6), it is reasonable to consider that at least some of the  $^{18}\text{O}$  species are lattice oxygen atoms. Hence, a slow dynamic redox process consisting of lattice oxygen formation and its reduction by C species is at least partly responsible for the CO formation. This explains why after a pulse the catalyst does not remain oxidized (Figure 2). However, Figure 4 also reveals that initially, after the step change, the responses of Ar and CO coincide. This may be caused by another O species present on the surface of the catalyst, which reacts more rapidly with the C species.

## 5. Conclusion

The reaction mechanism between  $\text{CH}_4$  and  $\text{O}_2$  over the unreduced  $\text{NiO}/\text{SiO}_2$  catalyst differs from that over the reduced catalyst. The former takes place via the Eley–Rideal mechanism in which  $\text{O}_2$  in the adsorbed state reacts with the  $\text{CH}_4$  in the gas phase, while the latter takes place via the Langmuir–Hinshelwood mechanism in which adsorbed  $\text{CH}_4$  and  $\text{O}_2$  species react with each other.

## References and Notes

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