Transient Response Analysis via a Broadened Pulse Combined with a Step Change or an Isotopic Pulse. Application to CO_2 Reforming of Methane over NiO/SiO_2

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In this paper, a transient response analysis is developed by combining a broadened pulse with a step change or an isotopic pulse. The combined method provides information about the activation of the catalyst and the catalytic reaction mechanism. The method is applied to the CO_2 reforming of methane over NiO/SiO_2 at 800 °C. The response to the broadened CH_4/CO_2 (1:1) pulse over fresh NiO/SiO_2 exhibited an induction time during which no reaction between CH_4 and CO_2 occurred, indicating that NiO/SiO_2 had no activity. As the NiO was gradually reduced by CH_4, the reforming reaction took place, indicating that Ni^0 is the active site for this reaction. During the transient response to a step change to He in the broadened pulse of CH_4/CO_2 over a reduced NiO/SiO_2 catalyst at 800 °C, a long CO tail was observed; however, no such tail was noted in the response after a step change to He in the broadened pure CO pulse at 800 °C. This indicates that the CO desorption is rapid and that the surface reaction between C and O species constitutes the rate-determining step of the reforming reaction. The transient response to a sharp $^{18}O_2$ pulse introduced into the broadened $CH_4/C^{16}O_2$ pulse indicated that, over a reduced NiO/SiO_2 catalyst, $^{18}O_2$ replaced some $C^{16}O_2$ in the reaction with CH_4 to generate CO^{18} and that some Ni^0 was oxidized to $Ni^{18}O$. The long tail of CO^{18} indicates that carbon species reduce this NiO^{18} to Ni^0.

1. Introduction

One of the most important uses of methane is in the preparation of synthesis gas. As for now, steam reforming is the dominant commercial method for producing synthesis gas.[1,2] However, this process has a poor selectivity for CO and a too high H_2/CO product ratio, unsuitable for the methanol and the Fischer−Tropsch syntheses. Although the partial oxidation of methane can provide high activity and selectivity, and a suitable CO/H_2 ratio,[3−10] this process cannot be easily controlled due to the difficulty of removing the reaction heat from the reactor, particularly from large-scale equipment.[11,12] Therefore, in recent years, renewed interest in methane conversion to synthesis gas via the CO_2 reforming reaction has arisen.[13−22] This pathway provides a high CO selectivity and a more suitable H_2/CO ratio. Recently, Ni-based catalysts with high selectivity and activity and excellent stability have been reported.[18−22] However, there are few investigations regarding the activation process of NiO-based catalysts in the reactant atmosphere and the reaction mechanism.

Transient methods were often used in catalytic research to gain insight into the adsorption−desorption kinetics and the reaction mechanism.[23−28] They involve two kinds of techniques: the pulse technique, which provides unsteady-state information, and the step change, which provides information about the transient process from one steady state to another one. A steady-state tracing technique involving a step change in which one of the compounds is labeled with an isotope was also employed.[29] However, in the common pulse techniques,[26] the pulse width is $1-10^2$ s; it is about 1 ms in the temporal analysis of products (TAP) technique.[30] It is, therefore, difficult to make a step change in the reactant or to introduce an isotopic sharp pulse during a regular pulse to investigate the catalytic process.

In this paper, a transient response analysis is developed which combines a broadened pulse with a step change in reactants or

a sharp isotopic pulse which is injected any time in the broadened pulse. Using such a method, the CO_2 reforming of methane over NiO/SiO_2 catalyst is investigated.

2. Transient Response Analysis of the Broadened Pulse Combined with a Step Change or an Isotopic Pulse

Figure 1 shows how the broadening of the pulse was achieved. A gas pulse of 2.5 mL was injected almost instantaneously, using the six-way valve (5) and the sample tube (6), into a carrier gas (He) and allowed to flow via the four-way valve (7) into the broadening tube (8). In the latter tube, which has a diameter of 40 mm and a length of 164 mm, the pulse was broadened to about 20 min. From the broadening tube, the pulse flowed more slowly through the four-way valve (7) and then through the six-way valve (9) to the reactor and finally to the MS equipment. During the broadened pulse, a step change in the reactants, using the four-way valve (7), or a sharp isotopic pulse of 3 μL, using the six-way valve (9) and the sample tube (10), was introduced at selected times of the broadened pulse. The reactant and products have been continuously detected with MS equipment (HP quadrupole, 5971 Series mass selective detector).

3. Experimental Section

3.1. Catalyst Preparation. NiO/SiO_2 (containing 13.6 wt % Ni) catalysts were prepared by impregnating SiO_2 (Aldrich) with an aqueous solution of nickel nitrate (Alfa). The obtained paste was dried at room temperature in air and then decomposed and calcined at 800 °C in air for 1.5 h. The surface area and the pore size distribution of the catalyst were determined by nitrogen adsorption, using a Micromeritics ASAP 2000 instrument. The BET surface area and the average diameter of the pores were 362 m^2/g and 52 Å, respectively.

3.2. Transient Response Analysis. The transient experiments were performed at 800 °C under atmospheric pressure with the equipment presented in Figure 1. The catalyst powder (weight, 0.02 g) was held on quartz wool in a vertical quartz
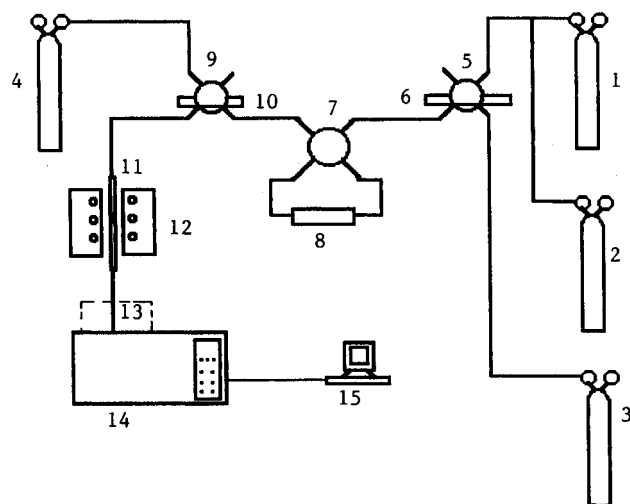

Figure 1. Transient response system: (1) CH_4/CO_2 (1:1) cylinder, (2) Ar cylinder, (3) He cylinder, (4) $^{18}O_2$ cylinder, (5) six-way valve, (6) sample tube, (7) four-way valve, (8) broadening tube, (9) six-way valve, (10) sample tube, (11) reactor, (12) electrical furnace, (13) inlet capillary system, (14) MS, (15) computer.
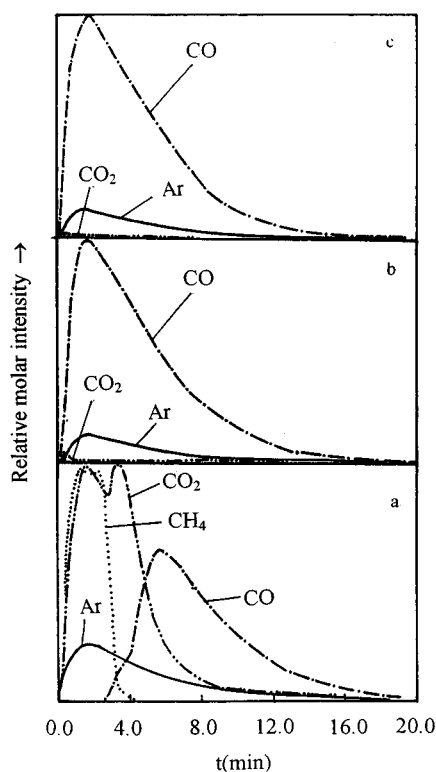

Figure 2. Responses of CH_4, CO_2, CO, and Ar as a function of time for broadened pulse of $CH_4/CO_2/Ar$ (2.5 mL) over a fresh NiO/SiO_2 catalyst at 800 °C: (a) first pulse, (b) second pulse, and (c) third pulse.

tube reactor (2 mm i.d.) in an electronically controlled furnace of large heat capacity to keep the temperature constant. Helium (60 mL/min) was used as the carrier gas. The feed gas contained CO_2, CH_4 (CO_2/CH_4 1:1), and 13.4% Ar as inner standard. The pulses were of 2.5 mL and 3 μL for the broadened reactant pulse and the short isotopic pulse, respectively.

4. Results and Discussion

4.1. Transient Response Analysis of the Broadened Pulse.
Figure 2 presents the response curves when only the broadened pulse is present; it contains the responses of three succesive pulses, each introduced after the previous one was exhausted. In the response curves of the first pulse, there are two peaks
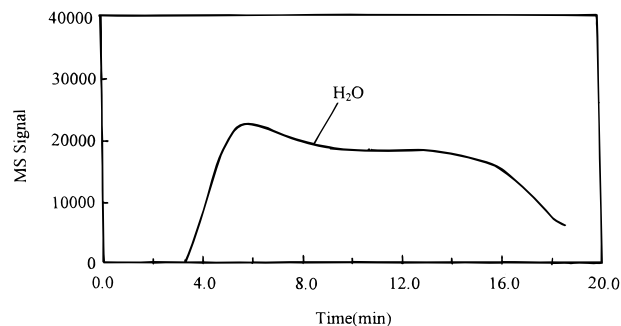

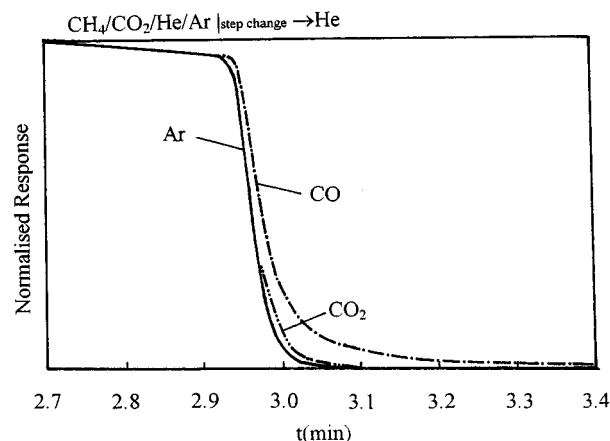**Figure 3.** Response curve of H_2O as a function of time for the first broadened pulse of $CH_4/CO_2/Ar$ (2.5 mL) in Figure 2.

Figure 4. MS signal response curves of CO_2, CO, and Ar as a function of time for a broadened pulse of $CH_4/CO/Ar$ combined with a step change to pure carrier (He) over NiO/SiO_2 subjected previously to 10 broadened succesive exhausted pulses.

for CO_2 at 1.8 and 3.5 min, a peak for CO at about 5.8min, and a peak for CH_4 at about 1.8 min. For the second pulse, there are very small peaks for CO_2 and CH_4 and a high one for CO. For the third pulse, the response is similar to the second one. This figure shows that the CO peak increases and the CO_2 peak decreases with increasing pulse number.

Figure 2 shows that, for the first pulse, the first CO_2 peak appears at the same position as the peaks of Ar and CH_4 and that no CO is present at that position. This indicates that the first CO_2 peak can be attributed to the CO_2 unreacted in the feed gas. The second CO_2 peak appears after that of Ar (with a time difference of 1.8 min), at a time at which CH_4 is no longer present. It can, therefore, be attributed to the CH_4 reaction with NiO, which results in the formation of Ni^0 and CO_2. It is worth noting that water was detected in the response curve after the first CO_2 peak but before the second CO_2 peak (Figure 3). This confirms that NiO is reduced by CH_4 to Ni^0. Calculations based on the second CO_2 peak of Figure 2a indicate that about 44% of the NiO of the catalyst was reduced to Ni^0. The CO peak appears after the second CO_2 peak, indicating that Ni^0 constitutes the active site for the production of CO. This also explains why the response curve of CO exhibits an induction time and why CO increases and CO_2 decreases with the pulse number (Figure 2).

4.2. Transient Response Analysis of the Broadened Pulse Combined with a Step Change.
The response to a step change in the broadened $CH_4/CO_2/Ar$ pulse was carried out over a catalyst previously subjected to 10 succesively exhausted CH_4/CO_2 (1:1) pulses. Figure 4 shows that, when $CH_4/CO_2/Ar/He$ is replaced via a step change with He, the CO_2 response curve almost coincides with that of Ar, whereas the CO response curve has a long tail. The long tail of CO may be due to (a) the CO desorption from the catalyst surface or (b) the CO formation
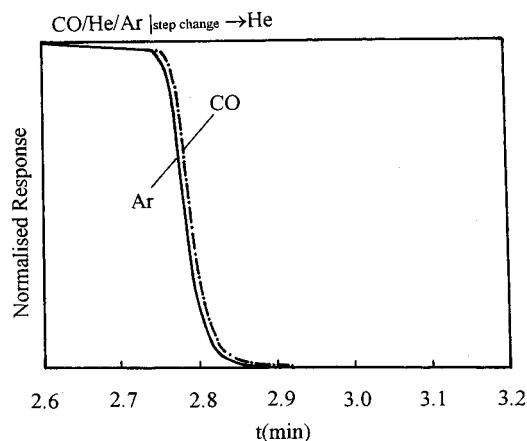
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Figure 5. MS signal response curves of CO and Ar as a function of time for a broadened pulse of CO/Ar combined with a step change to pure carrier over NiO/SiO₂ subjected previously to 10 broadened successively exhausted pulses.

by the surface reaction between the C and O species. To make a choice between the two, the response curve to a step change from CO/Ar/He to He in a broadened pulse of CO/Ar is presented in Figure 5, which shows that the CO response is near that of Ar. This eliminates the possibility (a) that the desorption of CO is responsible for the long tail; in other words, the long tail is due to the surface reaction between the C and O species, which constitutes the rate-determining step. In addition, the long CO tail also indicates that the C species cannot easily desorb. Consequently, the adsorbed species containing C cannot be CH₄, because of its small adsorption energy (about 6 kcal/mol). It is, therefore, reasonable to suggest that a dissociative adsorption of CH₄ takes place, i.e., $CH_{4(g)} + Ni \rightarrow \cdots \rightarrow CH_{x(s)} + (4 - x)H_{(s)}$.

4.3. Transient Response Analysis of the Broadened Pulse Combined with an Isotopic Sharp Pulse. The combination between the CO₂ reforming and the partial oxidation of CH₄ may become a useful process,[13] because the CO₂ reforming is endothermic, while the partial oxidation is exothermic. For this reason, a transient response of a sharp $^{18}O_2$/Ar pulse of 3 μL into a broadened $CH_4/C^{16}O_2$ pulse of 2.5 mL over a NiO/SiO₂ catalyst, previously subjected to 10 CH₄/CO₂ succesively exhausted pulses, was carried out. Figure 6 shows that the responses of CO^{18} and $C^{16}OO^{18}$ are much longer than that of Ar. The tail of CO^{18} is about 10 min long, whereas the Ar pulse has a width of only 0.1 min. This suggest that ^{18}O forms relatively stable species on the catalyst surface by oxidizing Ni^0 to $Ni^{18}O$. Figure 6 also shows that the response of $C^{16}O$ decreases and that of $C^{16}O_2$ increases rapidly when the $^{18}O_2$/Ar pulse is injected, and that, subsequently, they recover rapidly the original curves. However, no methane response was detected. The $C^{16}O$ decreases because $^{18}O_2$, being more reactive, replaces some of $C^{16}O_2$ in its reaction with CH₄ and generates $C^{18}O$. The $C^{16}O_2$ increases because it is replaced by $^{18}O_2$. No methane response is detected because it is completely consumed by its reaction with $C^{16}O_2$ and $^{18}O_2$.

5. Conclusion

This paper emphasizes that the transient response of a broadened pulse combined with a step change or a sharp isotopic pulse is a useful method in the study of heterogeneous processes. The following useful information was obtained regarding the CO₂ reforming of methane over NiO/SiO₂: (1)Ni^0 is the active site; (2) the reaction between C and O species on Ni^0 is the rate-determining step; and (3) the introduction of a small amount of $^{18}O_2$ in the broadened $CH_4/C^{16}O_2$ pulse replaces some $C^{16}O_2$ in the reaction with CH₄ and generates $C^{18}O$.
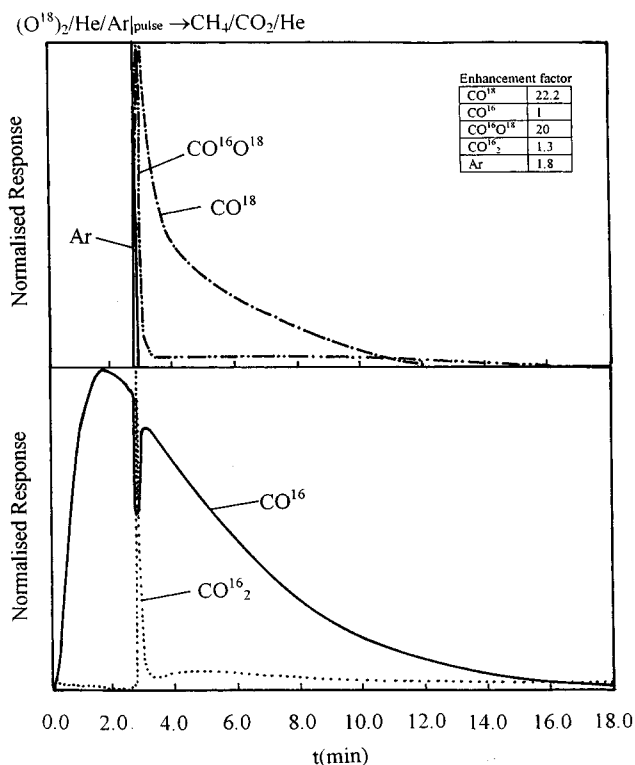
Figure 6. Normalized responses of $C^{16}O_2$, $C^{16}O$, $C^{18}O$, $C^{16}O^{18}O^{\cdot}$ and Ar as a function of time for the broadened pulse of $CH_4/C^{16}O_2$/Ar combined with a sharp pulse of $^{18}O_2$/Ar over NiO/SiO₂ subjected previously to 10 broadened succesively exhausted pulses.

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