Multiple Transient Response Methods To Identify Mechanisms of Heterogeneous Catalytic Reactions

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ABSTRACT

Identification of mechanisms of heterogeneous catalytic reactions is challenging because there are few effective in-situ techniques with which to determine reactive intermediates on surfaces. An effective multiple transient technique consisting of a combination of a broadened pulse with step changes and a sharp isotopic pulse was developed in our group. This technique provides much richer dynamic information than is obtainable from experiments with individual pulses or step changes in reactant concentration. In this Account, we illustrate the method by its application to high-temperature heterogeneous catalytic reactions.

1. Introduction

Understanding mechanistic details of surface-catalyzed reactions may pave the way to the design of new and improved catalysts. Determination of mechanistic details remains challenging because there are few effective in-situ techniques that allow characterization of reactive surface species, particularly for high-temperature reactions. The aim of this Account is to illustrate how a multiple transient response technique developed by our group provides useful mechanistic information for high-temperature catalytic reactions.

The conventional steady-state flow methods that are used widely to investigate kinetics of heterogeneous catalytic reactions are limited because under steady-state conditions, the elementary steps proceeding in series take place at the same rate, and the overall kinetics provides little insight into the mechanism. Transient response methods provide more information about mechanisms. Wagner and Hauffe[1] were the first to employ a perturbation method in surface catalysis, investigating the reaction of oxygen with hydrogen adsorbed on palladium by determining the electrical conductivity response to changes in the oxygen flow rate. However, their results were only qualitative. About half a century ago, a pulse method was suggested by Kokes, Tobin, and Emmett[2] as a microcatalytic technique, and it has been used extensively by many investigators (and the results were reviewed comprehensively in the literature[3,4]). This method has been found to provide much more information than what can be obtained from steady-state experiments, but it still falls short in the elucidation of the detailed mechanisms.

Isotopic labeling and isotope effects catalysis have provided a powerful tools to researchers.[5] Isotopic studies in catalysis started in the 1930s, just after the discovery of deuterium.[5] The early investigations were handicapped by the absence of a convenient method for isotopic analysis. The development and commercial production of mass spectrometers at the beginning of the 1950s stimulated a great expansion of isotopic investigations in catalysis. The combination of transient and isotope methods has provided much useful insight into catalytic reaction mechanisms.[6–14]

The transient flow reactor techniques that have been employed include introduction of reactant as pulses, which provides unsteady state information, and step changes in reactant concentration, which provide information about the transient process from one steady state to another. The pulse method is generally less informative than the step change method in identifying the rate-determining step of a catalytic reaction. The pulse transient starts and ends with the same stationary state, whereas the step transient ends at a new stationary state, thus providing additional information. However, in the conventional step-change transient mode, with a continuous reactant flow system, the step change of a reactant concentration (usually from a high value to zero) may result in a significant change in the catalyst temperature, most pronounced for highly exo- or endothermic reactions. Therefore, it may be difficult to hold the catalyst temperature constant during a step change. In contrast, in the pulse mode, the amount of reactant employed in each pulse may be so small that only a negligible change in the catalyst temperature occurs. Furthermore, in the common pulse techniques,[15] the pulse width is in the range of 1–100 s; it is about 1 ms in the temporal analysis of products (TAP) technique.[16] Because the pulses are so small, it is difficult to extract additional information by making during the regular pulse a step change in the reactant concentrations or introducing a pulse of an isotope. Our thought was to introduce a multiple transient

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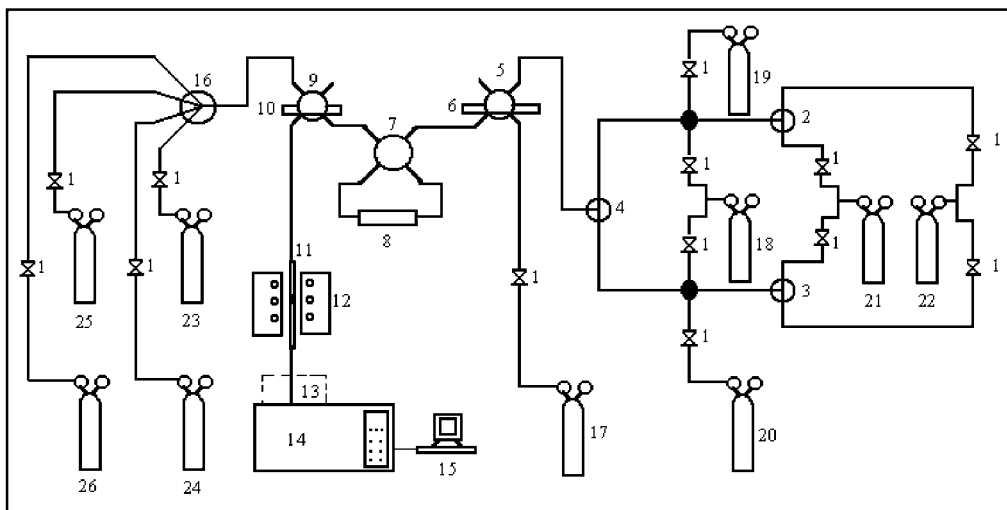
FIGURE 1. Pulse transient response system: (1) flow controller, (2−4) three-way valve, (5) six-way valve, (6) sample tube, (7) four-way valve, (8) broadening tube, (9) six-way valve, (10) sample tube, (11) reactor, (12) electrical furnace, (13) inlet capillary system, (14) mass spectrometer, (15) computer, (16) five-way valve, (17) He cylinder, (18) Ar cylinder, (19) CH_4 cylinder, (20) CD_4/CH_4 (1/1) mixture cylinder, (21) CO_2 cylinder, (22) O_2 cylinder, (23) $C^{18}O_2$ cylinder, (24) $^{13}CO_2$ cylinder, (25) $^{18}O_2$ cylinder, (26) $^{13}CH_4$ cylinder.

response technique[17−20] by using a broadened pulse combined with step changes and sharp isotopic pulses. This method combines the best features of the pulse, step change, and isotope techniques and can provide much richer dynamic information than the individual pulses and step changes. These techniques can be applied to various heterogeneous catalytic reactions, particularly to high-temperature catalytic reactions. In contrast, the usual techniques, such as the chemical trapping and the in-situ FT-IR techniques, are used with difficulty at high temperatures. This method offers the advantages of simplicity and economy. We illustrate its applicability to two high-temperature reactions, the partial oxidation of methane, and the CO_2 reforming of methane.

2. The Combined Transient Response Technique

Figure 1 is a schematic representation of the experimental apparatus. The procedure, simply described, is as follows: A reactant gas pulse is injected almost instantaneously with the six-way valve 5 and sample tube 6, into a carrier gas (He) and allowed to flow via the four-way valve 7 into a broadening tube 8 with a diameter of 40 mm and a length of 164 mm, where the pulse is broadened to about 20 min. From the broadening tube, the pulse flows more slowly through the four-way valve 7 and then through the six-way valve 9 to the reactor 11 and finally to the mass spectrometer (MS) 14. During the flow of the broadened pulse, a step change in the reactants is introduced with the four-way valve 7, or alternatively, a sharp isotopic pulse is introduced at selected times with the six-way valve 9 and sample tube 10. The reactants and products are continuously monitored with the mass spectrometer, resulting in the response curves of reactants and products. These response curves can provide information about the reaction mechanism and rate-determining step as follows:
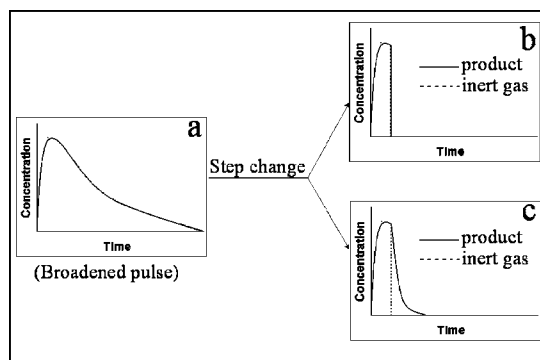

FIGURE 2. Transient response to a step change in a broadened pulse.

A step change in a broadened pulse during the reaction can lead to contrasting results (Figure 2) that depend on the reaction mechanism: (1) the concentration response of each of the products may coincide with that of an inert gas, which is introduced as internal standard with the reactants (Figure 2b), or (2) the concentration response of each of the products may exhibit a delay relative to the inert gas (Figure 2c). The presence of the former response curve (Figure 2b) indicates that the generation of the product had been instantaneously stopped when the concentration of the reactant became zero in the gas phase in contact with the catalyst. Such an observation indicates that at least one reactant is not adsorbed on the catalyst surface (for a surface reaction to occur, at least one of the reactants must be adsorbed). In other words, for a surface-catalyzed reaction with two reactants, this type of curve indicates that the reaction takes place between an adsorbed and another unadsorbed reactant (an Eley−Rideal mechanism[21]). The latter type of response curve (Figure 2c) shows that the formation of the product is not instantaneously stopped when all reactant concentrations become zero in the gas phase in contact with the catalyst. Such a continuation of the reaction occurs when
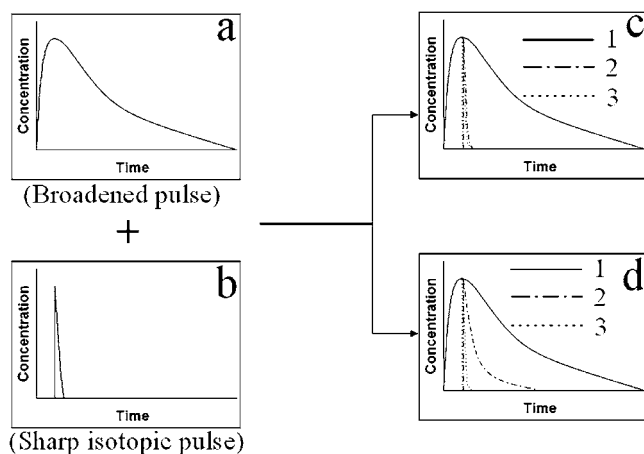
FIGURE 3. Transient response to a sharp pulse of isotopic tracer introduced into a broadened pulse of reactant (1, product without tracers; 2, isotopic product; 3, inert gas used as internal standard). In panel c, curves 2 and 3 coincide.

the adsorbed reactant species maintain the reaction for some time after the concentrations of all the reactants become zero in the adjacent gas phase. Therefore, this type of response curve indicates that all reactants are adsorbed on the catalyst surface before the reaction occurs, hence that the reaction takes place between adsorbed reactants (a Langmuir–Hinshelwood mechanism[21]). The combination of a broadened pulse and a sharp isotopic pulse can provide additional information. For an Eley–Rideal mechanism, the introduction of a sharp isotope reactant pulse into a broadened reactant pulse can determine which of the reactants is adsorbed and which is not. If the sharp isotopic pulse introduced into the broadened pulse leads to an isotopic product response curve that coincides with that of the inert gas introduced as internal standard in the sharp isotope pulse (Figure 3c), the isotopic reactant is not adsorbed. If the sharp isotope pulse into the broadened pulse leads to an isotopic product response curve that exhibits a delay compared to that of the inert gas (Figure 3d), then the isotopic reactant was adsorbed. For the Langmuir–Hinshelwood mechanism, any sharp reactant isotope pulse into the broadened pulse should lead to a delayed tail of the isotope product response curve (Figure 3d). The lengths of the response curve tails with different reactant isotope pulses are expected to be different. The stronger the adsorption of the reactant, the longer should be the tail of the isotopic product response curve. If the tail of the isotopic product curve is very long, the surface reaction is slow. In other words, the rate-determining step should be the surface reaction of the adsorbed species rather than the formation of adsorbed species.

Furthermore, the transient response test unit (Figure 1) can be used for pulse isotope-trace gas chromatography–mass spectrometry (GC-MS) experiments, just by addition of a gas chromatographic column upstream of the mass spectrometer.[20] For example, the procedure can be described simply as follows for the reaction of CH_4 and O_2 to give CO and H_2: A CH_4/CD_4 reactant gas pulse, injected through the six-way valve 5 and sample tube 6

into a carrier gas (He) and allowed to flow via the four-way valve 7 (bypassing the broadening tube 8), may be combined with a pulse of O_2 by using the six-way valve 9 and the sample tube 10. Then the carrier gas containing the mixture of CH_4 and CD_4 and O_2 is allowed to flow through a reactor, a gas chromatographic column and an on-line mass spectrometer, to determine the isotopic distribution of products. From the concentrations of CH_xD_y species, one can calculate the fractions of CH_4 and CD_4 involved in the H–D exchange reaction. From the concentrations of CO, CO_2, H_2, HD, and D_2, one can calculate the fractions of CH_4 and CD_4 converted via the partial oxidation of methane to give CO and (H_2 + HD + D_2). If the amount of methane involved in the H–D exchange reaction is much larger than that converted to the mixture of CO with (H_2 + HD + D_2), the dissociation of methane is inferred to be faster than the partial oxidation. In other words, the dissociation of methane is inferred not to be rate-determining. On the other hand, from the isotope distribution in the products, one can extract information about the intermediate species. For example, if CH_2D_2 is detected in the reaction of the mixture of CH_4, CD_4, and O_2, the CH_2 is inferred to be a surface intermediate.

In the following sections, the results obtained by us with the above techniques are illustrated and discussed for two reactions.

3. Methane Partial Oxidation

Over the past 20 years, extensive efforts have been made regarding both the direct and indirect conversion of methane to value-added products.[22-33] Direct conversion routes have been difficult to achieve because at the high temperatures necessary for high conversions, the formation of CO_2 is highly favored. Therefore, interest in the indirect conversion of CH_4, whereby methane is converted to methanol or other hydrocarbons via the synthesis gas (CO+H_2), has been renewed.[24-33] One of the major indirect processes is partial oxidation:

$$CH_4 + 1/2 O_2 \rightarrow CO + 2H_2, \quad \Delta H°_{298} = -36 \text{kJ/mol} \quad (1)$$
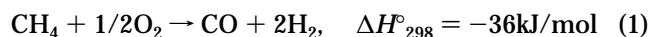
Over the past 10 years, the partial oxidation of methane has become one of the most active research topics in catalysis.[24-28] Mechanistic studies of this reaction remain a great challenge because this highly exothermic, fast reaction leads to an extremely high catalyst temperature. Consequently, most of the traditional techniques for elucidation of reaction mechanisms (such as chemical trapping and the in-situ infrared spectroscopy) are unsuitable. In contrast, the multiple transient response method is well suited for the reaction. In what follows, we show how the methods have helped to clarify some mechanistic issues for this reaction.

Multiple transient responses were used to select among the plausible mechanisms for the reaction in the presence of the unreduced and reduced catalysts.[18] The response to a step change of the feed to He during a broadened pulse of $CH_4/O_2/Ar$(13.4%Ar as internal standard) showed
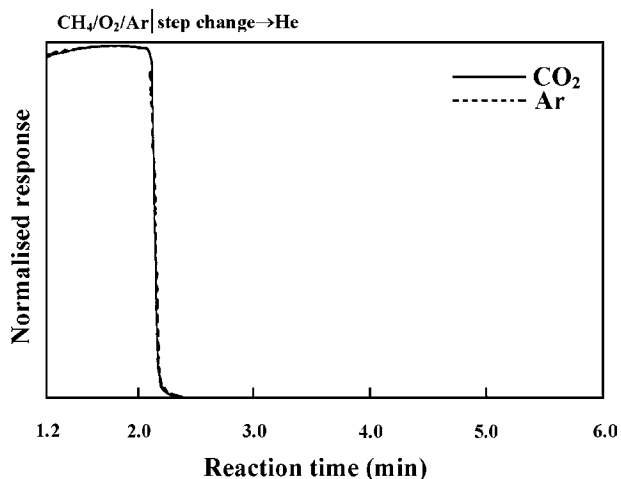
FIGURE 4. Normalized responses to a broadened pulse of $CH_4/O_2/Ar$ combined with a step change of the feed to pure carrier gas (He) for reaction in the presence of an unreduced NiO/SiO_2 catalyst at 800 °C.[18]
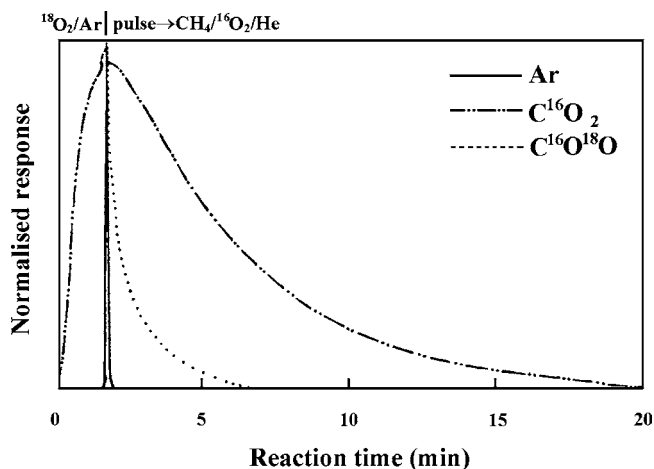

FIGURE 5. Normalized responses to a broadened pulse of $CH_4/^{16}O_2$ combined with a sharp pulse of $^{18}O_2/Ar$ for reaction in the presence of an unreduced NiO/SiO_2 catalyst at 800 °C.[18]

that, with the unreduced NiO/SiO_2 catalyst, the response curves of CO_2, O_2 and CH_4 to a step change from the feed gas to He coincide with that of the inert Ar (Figure 4). This result means that the formation of CO_2 on the unreduced catalyst occurred between one adsorbed and one gas-phase species. When a sharp $^{18}O_2/Ar(13.4\%)$ pulse was introduced into the reactor with unreduced catalyst during a broadened $^{12}CH_4/^{16}O_2$ pulse, the response curve of $C^{16}O^{18}O$ to the sharp $^{18}O_2$ pulse had a much longer tail, 5 min, than Ar, which had a width of only 0.1 min (Figure 5). This result indicates that a strongly adsorbed oxygen or lattice oxygen species participated to the reaction. Therefore, we infer that in the presence of the unreduced catalyst, the reaction occurred between gas-phase CH_4 and a strongly adsorbed (or lattice) oxygen, hence via an Eley−Rideal mechanism. Furthermore, the result of the $^{18}O_2/CH_4$ pulse to $Ni^{16}O/Si^{16}O_2$ catalyst showed that 12% and 18% of the CH_4 reacted with ^{18}O (from the gas phase) and ^{16}O (from the lattice oxygen of $Ni^{16}O$), respectively.[20] This result shows that the reaction of methane with the
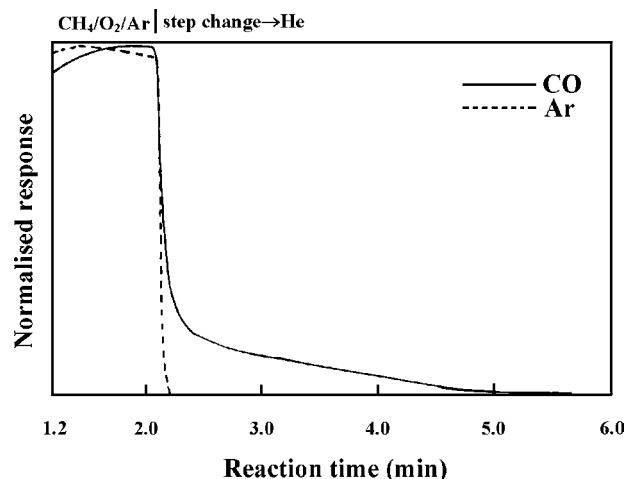

FIGURE 6. Normalized responses to a broadened pulse of $CH_4/O_2/Ar$ combined with a step change of the feed to pure carrier gas (He) for reaction in the presence of a reduced NiO/SiO_2 catalyst at 800 °C (no CO_2 was detected after the step change).[18]

lattice oxygen was facile. According to the above results, it is reasonable to suggest that CH_4 was oxidized mainly by the oxygen of the lattice, which was replenished by the oxygen of the gas atmosphere. This mechanism can be expressed as follows:

$$CH_{4(g)} + 4NiO \rightarrow CO_{2(g)} + 2H_2O + 4Ni \qquad (2)$$

$$2Ni + O_{2(g)} \rightarrow 2NiO \qquad (3)$$
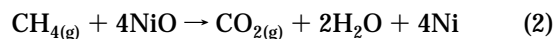
On the reduced NiO/SiO_2 catalyst, the CO response to a step change to He, during a $CH_4/O_2/Ar$ broadened pulse, had a longer tail than the inert Ar(Figure 6).[18] This delay can be a result of (a) CO desorption or (b) CO formation by a surface reaction between the C and O species. However, the CO response to a step change from CO/Ar to He during a broadened pulse of CO/Ar was found to coincides with that of Ar.[17] This observation indicates that the delay was not due to the desorption but rather to the surface reaction between the C and O species. Consequently, the reaction on the reduced NiO/SiO_2 catalyst is inferred to have taken place via a Langmuir−Hinshelwood mechanism, whereby the adsorbed CH_4 and O_2 species are both involved. Furthermore, the results of Figure 7 show that, when the reduced catalyst was used, the response curves of $C^{18}O$ and $C^{16}O^{18}O$ to a sharp pulse of $^{18}O_2/Ar$ during a broadened $^{12}CH_4/^{16}O_2$ pulse were characterized by much longer tails than Ar (1.8 and 1.2 min longer, respectively). Figure 8 indicates that, in the presence of the reduced catalyst, the response of ^{13}CO to a sharp $^{13}CH_4$ pulse during a broadened $^{12}CH_4/^{16}O_2$ pulse had a somewhat longer tail than Ar. These results further confirm the Langmuir−Hinshelwood mechanism on the reduced catalyst. Furthermore, in the reaction with the reduced catalyst, the tail of the $^{12}C^{18}O$ response to a sharp pulse of $^{18}O_2/Ar$(Figure 7) was much longer than that of the $^{13}C^{16}O$ response to a sharp pulse of $^{13}CH_4$(Figure 8), when both were observed during a broadened pulse of $^{12}CH_4/^{16}O_2$. This result indicates that the C species reacted more easily than the O species. The long tail of $C^{18}O$ to a

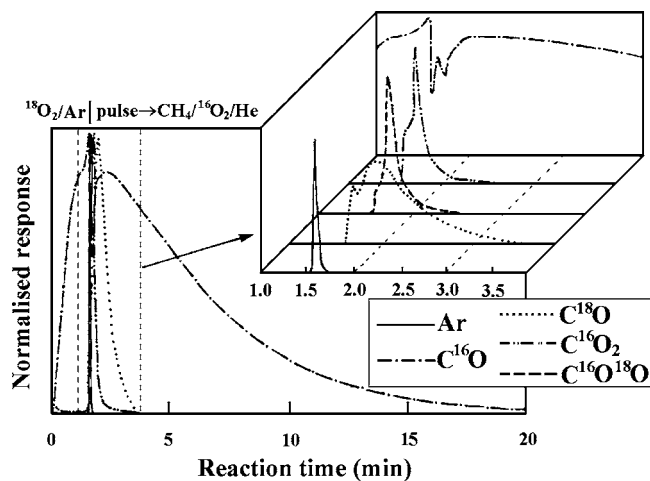**FIGURE 7.** Normalized responses to a broadened pulse of $CH_4/^{16}O_2$ combined with a sharp pulse of $^{18}O_2/Ar$ for reaction in the presence of a reduced NiO/SiO_2 catalyst at 800 °C.[18]

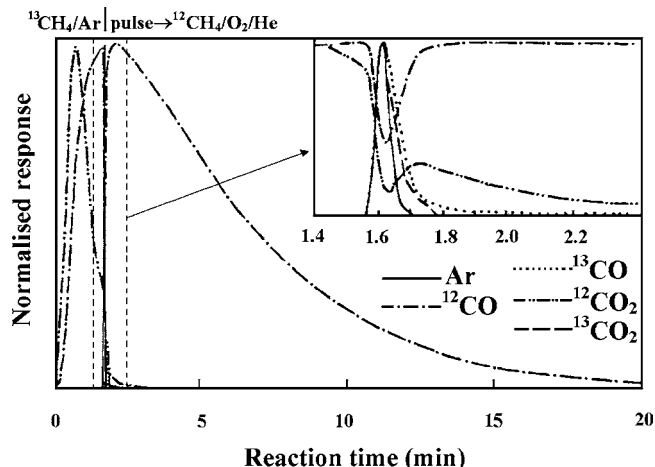**FIGURE 8.** Normalized responses to a broadened pulse of $^{12}CH_4/^{16}O_2$ combined with a sharp pulse of $^{13}CH_4/Ar$ for reaction in the presence of a reduced NiO/SiO_2 catalyst at 800 °C.[18]

sharp pulse indicates that the ^{18}O species are stable (Figure 7); it was therefore reasonable to consider that at least some of the O^{18} species were lattice oxygens. Hence, a slow dynamic redox process consisting of lattice oxygen formation and its reduction by C species is inferred to be at least partly responsible for the CO formation.

Furthermore, the gas chromatography—mass spectrometry isotope-tracer results obtained with a pulse of the $CH_4/CD_4(1/1)$ mixture with oxygen provide more detailed information regarding the C intermediate species.[20] It was found that when a pulse of $O_2/CH_4/CD_4$ (1/1/1) mixture was used, only CH_4 and CD_4, without CH_xD_y ($x + y = 4$, $x > 0$ and $y > 0$) were present in the product obtained with the unreduced NiO-containing catalyst, whereas, besides CH_4 and CD_4, CH_xD_y species were detected in the product obtained with the reduced catalyst (3%CH_4, 31%CH_3D, 38%CH_2D_2, 20%CHD_3 and 8%CD_4).[20] Whereas 28% of the methane (CH_4 and CD_4) in the feed gas was converted to CO and CO_2, 65% of the methane participated in the isotopic exchange reaction in the presence of the reduced catalyst. This comparison indicates that the H—D isotopic
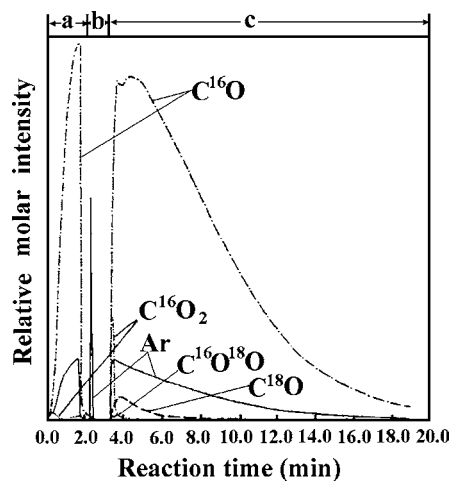

FIGURE 9. CO_2, CO, and Ar responses as a function of time resulting from a broadened pulse of $CH_4/C^{16}O_2/Ar$ interrupted with a step change in the feed to pure carrier gas, followed by an $^{18}O_2$ pulse and by a step change of the feed to the remaining interrupted $CH_4/C^{16}O_2/Ar$ pulse. The reaction was catalyzed by a reduced NiO/MgO solid solution.[19]

exchange reaction of methane was faster than the partial oxidation of methane to CO and H_2 in the presence of the reduced catalyst. In contrast, when the unreduced catalyst was used, no H—D isotopic exchange reaction of methane occurred. This result demonstrates that, on the reduced catalyst, the dissociation of methane to CH_x species was faster than the oxidation of the C species to CO and CO_2, and hence the rate-determining step was the reaction of the CH_x species with oxygen rather than the formation of the C species.

From the results of these experiments, the following mechanistic information can be extracted: (1) the reaction between CH_4 and O_2 occurs via an Eley—Rideal mechanism on the unreduced NiO/SiO_2 catalyst and via a Langmuir—Hinshelwood mechanism on the reduced NiO/SiO_2 catalyst; (2) a dynamic redox process occurs on the reduced catalyst; and (3) on the reduced NiO/SiO_2 catalyst, the cleavage of methane to CH_x ($x = 1-3$) species was faster than the oxidation of CH_x, and the latter constitutes the rate-determining step.

4. Oxygen Species in CO_2 Reforming of Methane

The CO_2 reforming of methane ($CH_4 + CO_2 = 2H_2 + 2CO$) is another important reaction because it may provide an effective way to utilize two greenhouse gases (CH_4 and CO_2). However, there are contrasting opinions about the mechanism of the CO_2 reforming of methane.[29–33] In what follows, we show that multiple transient response data clarify the role of the oxygen species in the CO_2 reforming of methane in the presence of a NiO/MgO solid solution catalyst at 800 °C.[19]

The data of Figure 9 show the response of a reduced NiO/MgO solid—solution catalyst to a broadened pulse of $CH_4/C^{16}O_2/Ar$, first interrupted with a step change to the carrier gas alone(region a), followed by a sharp isotopic $^{18}O_2/Ar$ pulse (region b) and a continuation after some

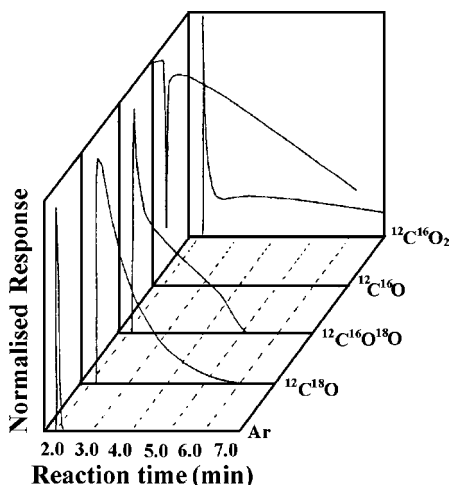**FIGURE 10.** $^{12}C^{16}O$, $^{12}C^{16}O_2$, $^{12}C^{18}O$, $^{12}C^{16}O^{18}O$, and Ar responses as a function of time to a broadend pulse of $^{12}CH_4/C^{16}O_2/Ar$ combined with a sharp pulse of $^{12}C^{18}O_2/Ar$. The reaction was catalyzed by a reduced NiO/MgO solid solution at 800 °C.[19]

FIGURE 11. $^{12}C^{16}O$, $^{12}C^{16}O_2$, $^{13}C^{16}O$, $^{13}C^{16}O_2$, and Ar responses as a function of time to a broadend pulse of $^{12}CH_4/C^{16}O_2/Ar$ combined with a sharp pulse of $^{13}CO^{16}_2/Ar$. The reaction was catalyzed by a reduced NiO/MgO solid solution at 800 °C.[19]

time with what remained from the interrupted pulse (region c).[19] After the catalyst had been partially reoxidized to Ni^{18}O by a sharp $^{18}O_2/Ar$ pulse (region b), a wide C^{18}O peak with a long tail was detected in the response to the step change from He to the remaining CH$_4$/C$^{16}O_2$/Ar pulse (region c). This result provides direct evidence that the lattice oxygen of NiO participated in the reaction of CH$_4$ and CO$_2$. The transient response to a sharp C$^{18}O_2$/Ar pulse of 3 μL into a broadened CH$_4$/C$^{16}O_2$ pulse of 2.5 mL free of Ar, when the catalyst was a reduced NiO/MgO solid solution, shows that the traces of C^{18}O and C$^{16}O^{18}$O are much longer than that of Ar (Figure 10). The C^{18}O tail was 4 min long, whereas that of Ar had a width of about 0.2 min. This result indicates that ^{18}O rapidly formed stable species on the catalyst surface. It is reasonable to consider that the stable species is Ni^{18}O, i.e., the lattice oxygen formed by the oxidation of Ni by C$^{18}O_2$. However, the transient response to a sharp $^{13}CO_2$/Ar pulse of 3 μL into a broadened $^{12}CH_4/^{12}CO_2$ pulse of 2.5 mL that was free of Ar showed that the trace of ^{13}CO was somewhat longer than that of Ar (Figure 11). This result indicates that the dissociation of CO$_2$ to O and CO was a rapid process. In the response to a sharp $^{13}CH_4$/Ar pulse of 3 μL into a broadened $^{12}CH_4/^{12}C^{16}O_2$ pulse that was free of Ar, the $^{13}C^{16}$O tail was much shorter than that of the $^{12}C^{18}$O response to a sharp pulse of $^{12}C^{18}O_2$/Ar into a broadened $^{12}CH_4/^{12}C^{16}O_2$ pulse. A possible interpretation of this difference is the existence of two kinds of oxygen species on the surface, one being adsorbed oxygen and the other lattice oxygen. The oxygen was formed rapidly on the surface via the dissociation of CO$_2$; it either oxidized zero valent nickel Ni° to NiO(lattice oxygen), with the NiO being slowly reduced by C species to Ni and CO, or it directly and more rapidly oxidized the carbon species. After the reduced NiO/MgO had been completely reoxidized, no CO was detected during the broadened pulse of CH$_4$/CO$_2$ at 800 °C, indicating that no reaction between CH$_4$ and CO$_2$ took place.[19] This observation implies that zero valent nickel (Ni°) must have been present for the
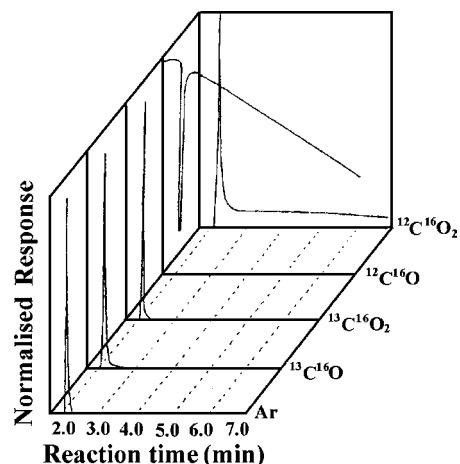
reaction to occur. In other words, during the continuous reaction only a fraction of Ni° was oxidized to NiO. Furthermore, that fraction of NiO was reduced again to Ni° by carbon species. Therefore, one can conclude that the lattice oxygen formation through the CO$_2$ dissociation and its reaction with carbon species constitutes a dynamic redox process.

In summary, the combined transient responses reveal that in the CO$_2$ reforming of methane on a NiO/MgO solid−solution catalyst, two kinds of oxygen form on the catalyst during the reaction: adsorbed oxygen, which react fast with carbon species, and lattice oxygen, which reacts slowly with carbon species. A redox cycle involving lattice oxygen formation through the oxidation of nickel and its reaction with carbon species takes place on the catalyst surface.

5. Conclusion

Results for a small number of examples show how the multiple transient response method, which combines the best features of pulse, step change, and isotope techniques, provides rich mechanistic information for surface-catalyzed reactions, including evidence of mechanism, surface reaction intermediate species, rate-determining steps, and dynamic changes of the catalyst state. The advantages of the method include high-efficiency, simple test unit and lack of restriction on the reaction conditions.

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