Role of lattice oxygen during CO_2 reforming of methane over NiO/MgO solid solutions

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The CO_2 reforming of methane over reduced NiO/MgO solid solution catalysts was studied at 800 °C by a novel transient method, which couples a broadened pulse of CH_4/CO_2 with a step change to the carrier gas and/or with a sharp isotopic pulse of either $^{18}O_2$, CO_2^{18} or $^{13}CO_2^{16}$. The response curves indicated that two kinds of oxygen were formed over the catalysts during reaction: adsorbed oxygen which reacts fast with C species and lattice oxygen which reacts more slowly with C species. One concludes that a redox cycle of lattice oxygen formation through the oxidation of Ni and its reaction with C species takes place on the catalyst surface.

Keywords: CH_4, CO_2, Ni, MgO, lattice oxygen, transient response

1. Introduction

Recently, we found that NiO/MgO has both excellent activity and selectivity as a CO_2 reforming catalyst, and rather high stability since it inhibits carbon deposition [1]. We brought evidence that NiO and MgO form a solid solution [2] and that Ni^0 constitutes the active site of the catalyst [1]. Even though there are different opinions about the mechanism of CO_2 reforming of methane [3–8], most researchers agree that the CO_2 dissociation to O and CO is a fast process. While it is reasonable to expect that the O species oxidize the active sites (Ni^0), the effect of the O species on the active site (Ni^0) has not yet been studied. In the present paper, a variant of a novel transient method [9,10], which combines a broadened pulse of CH_4/CO_2 with a step change to the carrier and/or an isotopic sharp pulse of either $^{18}O_2$, CO_2^{18} or $^{13}CO_2^{16}$, is employed to gather information about the formation and the role of lattice O during the CO_2 reforming of methane over NiO/MgO solid solution catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnating MgO powders (Aldrich, 325 mesh) with aqueous solutions of nickel nitrate (Alfa Chemicals), followed by drying at room temperature in air and finally by calcination at 800 °C in air for 1.5 h. X-ray powder diffraction demonstrated that NiO–MgO solid solutions were formed under the abovementioned conditions [2].

2.2. The transient response analysis

The transient response method which employs a broadened pulse was described in a previous paper [9]: A pulse of 2.5 ml was introduced almost instantaneously via a six-way valve into the carrier gas (He) and broadened to about 20 min in a tube of 40 mm diameter and 164 mm length. Two kinds of experiments have been carried out. In one of them, the broadened pulse was interrupted and replaced with the carrier alone (He). After a sharp isotopic pulse of O^{18}/Ar was injected (3 μl), the remaining broadened pulse plus the carrier were allowed to flow through the reactor. In the other one, a sharp isotopic pulse of $^{12}CO_2^{18}$/Ar or $^{13}CO_2^{16}$/Ar was injected into an Ar-free broadened pulse. The reactants and products have been continuously detected with an on-line mass spectrometer (HP Quadrupole, 5971 series mass selective detector) equipped with a fast response inlet capillary system. The calibration of the mass spectrometer was performed using mixtures of known composition.

The transient response experiments for the catalytic CO_2 reforming of methane were carried out at 800 °C and atmospheric pressure. The catalyst powder (weight: 0.02 g) was held on quartz wool in a vertical quartz tube reactor (2 mm inside diameter) located in an electronically controlled furnace of large heat capacity to keep the temperature constant. Helium (60 ml/min) was used as carrier and the pulses contained CO_2, CH_4 ($CO_2/CH_4 = 1:1$), and 13.4% Ar as inner standard. The sharp O_2^{18}, $^{12}CO_2^{18}$ or $^{13}CO_2^{16}$ pulses also contained Ar.

3. Results and discussion

The response over a reduced 9.7 mol% NiO/MgO solid solution catalyst to a broadened pulse of CH_4/CO_2^{16}/Ar, interrupted by a step change to the carrier alone (region a),

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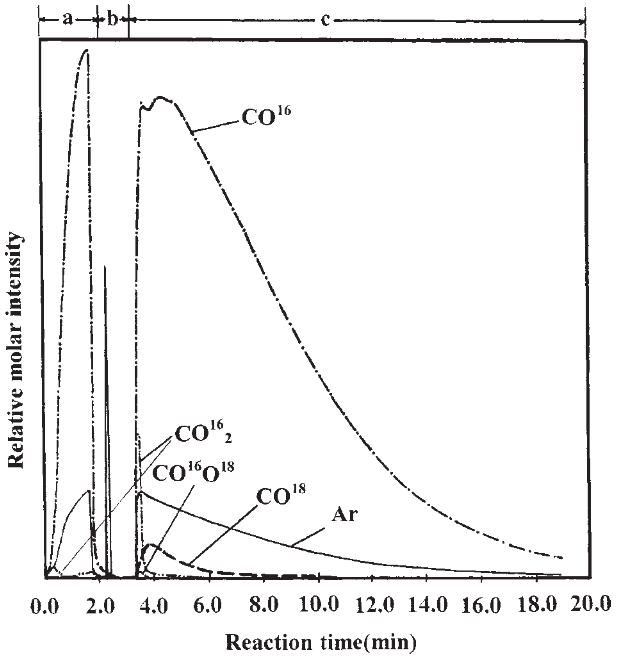

Figure 1. The CO_2, CO and Ar responses as a function of time to a broadened pulse of $CH_4/CO_2^{16}/Ar$ interrupted with a step change to pure carrier, followed by an O_2^{18} pulse and by a step change to the remaining interrupted $CH_4/CO_2^{16}/Ar$ pulse, over a reduced 9.7 mol% NiO/MgO catalyst.

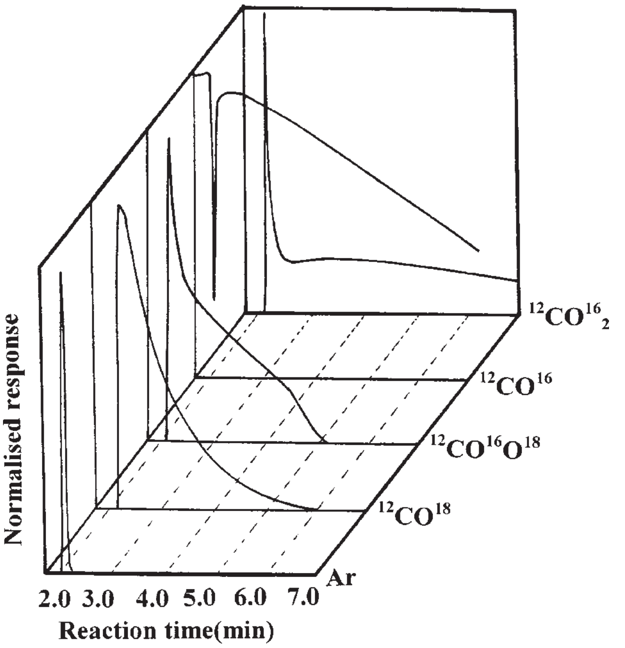

Figure 2. The $^{12}CO^{16}$, $^{12}CO_2^{16}$, $^{12}CO^{18}$, $^{12}CO^{16}O^{18}$ and Ar responses as a function of time to the broadened pulse of $^{12}CH_4/CO_2^{16}/Ar$ combined with a sharp pulse of $^{12}CO_2^{18}/Ar$ over the reduced 9.7 mol% NiO/MgO catalyst.

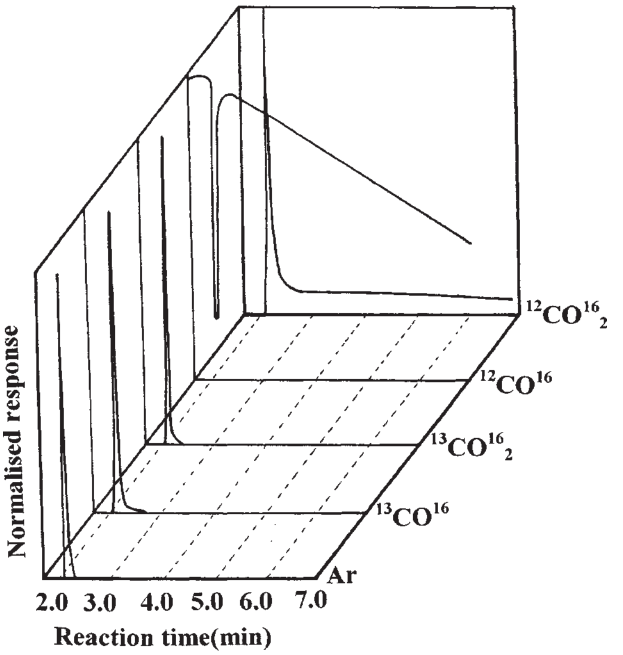

Figure 3. The $^{12}CO^{16}$, $^{12}CO_2^{16}$, $^{13}CO^{16}$, $^{13}CO_2^{16}$ and Ar responses as a function of time to the broadened pulse of $^{12}CH_4/^{12}CO_2^{16}/Ar$ combined with a sharp pulse of $^{13}CO_2^{16}/Ar$ over the reduced 9.7 mol% NiO/MgO catalyst.

followed by a sharp isotopic O_2^{18}/Ar pulse (region b) and continued after some time with the remaining interrupted pulse (region c) is presented in figure 1. After the catalyst is partially reoxidized to NiO^{18} by the sharp O_2^{18}/Ar pulse (region b in figure 1), a wide peak of CO^{18} with a long tail is detected in the response to the step change from He to the remaining $CH_4/CO_2^{16}/Ar/He$ interrupted pulse (region c in figure 1). This provides direct evidence that the lattice O of NiO participates in the reaction between CH_4 and CO_2.

The transient response to a sharp CO_2^{18}/Ar pulse of 3 μl introduced into the broadened CH_4/CO_2^{16} pulse of 2.5 ml free of Ar, over a reduced 9.7 mol% NiO/MgO solid solution catalyst, reveals that the CO^{18} and $CO^{16}O^{18}$ traces are much longer than that of Ar (figure 2). The tail of CO^{18} is 4 min long, whereas those of Ar and CO_2^{18} have a width of about 0.2 min. This indicates that O^{18} forms rapidly relatively stable species on the catalyst surface. The length of the tail being comparable to that in the previous experiment, which was performed under the same reaction conditions (compare figures 1 and 2), it is reasonable to conclude that the stable species is NiO^{18}, i.e., the lattice oxygen formed by the oxidation of Ni by CO_2. However, the transient response to a sharp $^{13}CO_2/Ar$ pulse of 3 μl introduced into the broadened $^{12}CH_4/^{12}CO_2$ pulse of 2.5 ml free of Ar shows that the ^{13}CO and $^{13}CO_2$ traces almost coincide with that of Ar (figure 3). This indicates that the dissociation of CO_2 to O and CO is a rapid process. Figure 4 shows that, in the response to a sharp $^{13}CH_4/Ar$ pulse of 3 μl introduced into a broadened $^{12}CH_4/^{12}CO_2$ pulse free of Ar, ^{13}CO has a somewhat longer tail than Ar. The tail of ^{13}CO is, however, much shorter than that of the response to the pulse of CO_2^{18}/Ar (figure 2). A possible interpretation of this difference is the existence of two kinds of oxygen on the surface, namely, adsorbed and lattice oxygen. One can conclude that oxygen is formed rapidly on the surface by

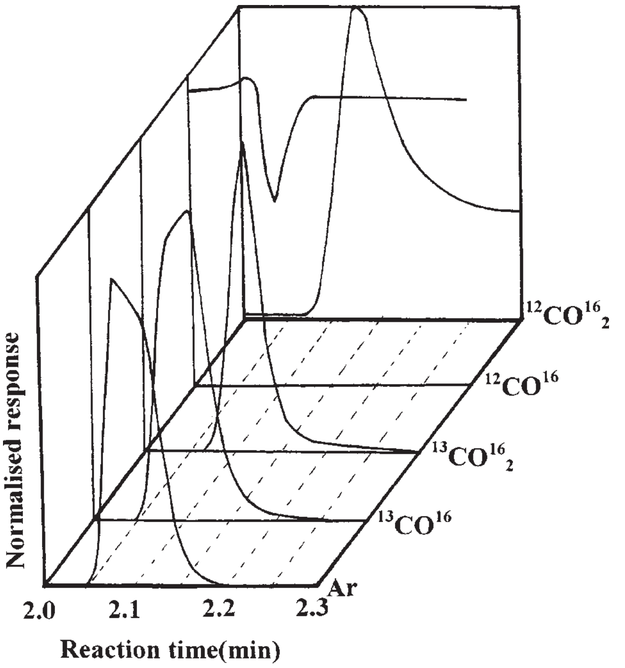

Figure 4. The $^{12}CO^{16}$, $^{12}CO_2^{16}$, $^{13}CO^{16}$, $^{13}CO_2^{16}$ and Ar responses as a function of time to the broadened pulse of $^{12}CH_4/^{12}CO_2^{16}/Ar$ combined with a sharp pulse of $^{13}CH_4/Ar$ over the reduced 9.7 mol% NiO/MgO catalyst.

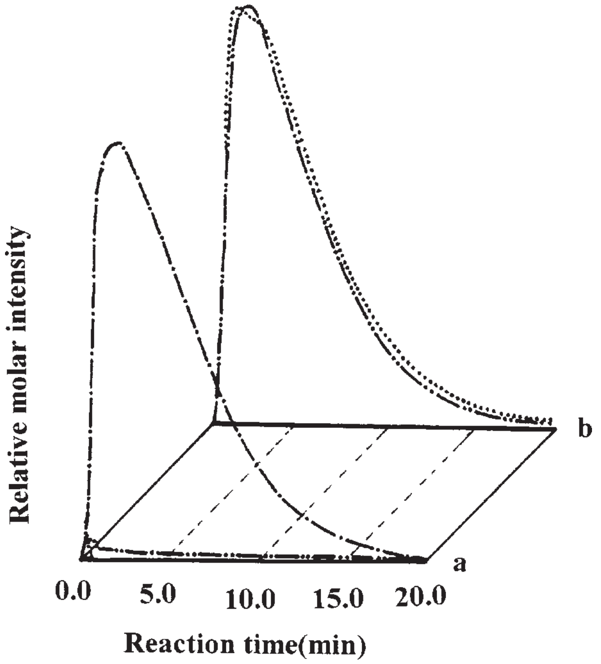

Figure 5. The CH_4, CO_2 and CO responses as a function of time to broadened pulses of $CH_4/CO_2/Ar$ (2.5 ml) over 9.7 mol% NiO/MgO catalyst at 800 °C: (a) pulse over the reduced catalyst; (b) pulse over the catalyst completely reoxidized with O_2; (····) CH_4; (—·—) CO; (—··—) CO_2.

the dissociation of CO_2; it either oxidizes Ni^0 to NiO (lattice oxygen), and the NiO is reduced slowly by C species to Ni and CO, or oxidizes directly, more rapidly, the carbon species.

Figure 5 shows that, after the reduced NiO/MgO was completely reoxidized with numerous oxygen pulses, no CO is detected during the broadened pulse of CH_4/CO_2 at 800 °C, indicating that no reaction between CH_4 and CO_2 takes place. This implies that Ni^0 must be present for the reaction to occur. In other words, during the continuous reaction only a fraction of Ni^0 is oxidized to NiO, fraction which is reduced again to Ni^0 by C species; therefore, the lattice O formation through CO_2 dissociation and its reaction with C species constitute a dynamic redox process.

References

[1] (a) E. Ruckenstein and Y.H. Hu, Appl. Catal. A 133 (1995) 149;
(b) Y.H. Hu and E. Ruckenstein, Catal. Lett. 36 (1996) 145;
(c) E. Ruckenstein and Y.H. Hu, Appl. Catal. A 154 (1997) 185.
[2] Y.H. Hu and E. Ruckenstein, Langmuir 13 (1997) 2055.
[3] V.C.H. Kroll, H.M. Swaan, S. Lacombe and C. Mirodatos, J. Catal. 164 (1996) 387.
[4] Z.L. Zhang and X.E. Verykios, Catal. Lett. 38 (1996) 175.
[5] S.B. Wang, G.Q.M. Lu and G.J. Milar, Energy & Fuels 10 (1996) 896.
[6] T. Osaki, T. Horiuchi, K. Suzuki and T. Mori, Catal. Lett. 44 (1997) 19.
[7] H.Y. Wang and C.T. Au, Catal. Lett. 38 (1996) 77.
[8] M.C.J. Bradford and M.A. Vannice, Appl. Catal. A 142 (1996) 97.
[9] Y.H. Hu and E. Ruckenstein, J. Phys. Chem. B 101 (1997) 7563.
[10] Y.H. Hu and E. Ruckenstein, J. Phys. Chem. B 102 (1998) 230.