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Pulse study of methane partial oxidation to syngas over SiO_2-supported nickel catalysts

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The reaction behaviors of CH_4/O_2 (2/1) with unreduced and reduced SiO_2-supported nickel (10 wt% metal) catalysts were investigated in a pulse micro-reactor at temperatures ranging from 600 to 800°C. In the interaction of CH_4/O_2 with unreduced NiO/SiO_2, the products are exclusively CO_2 and H_2O at or below 700°C. At 800°C, besides CO_2 and H_2O, CO and H_2 are formed. The reactivity at 800°C can be ascribed to the net generation of metallic nickel site at this temperature. In the reaction of CH_4/O_2 over reduced Ni/SiO_2, the main products are CO and H_2 with CO_2 and H_2O being the minor ones. The results indicate metallic nickel is the active site for methane partial oxidation to syngas. Normal deuterium isotope effects of similar magnitude were observed on the overall, as well as on the CO and CO_2 formation reactions with insignificant change in the product selectivities when CD_4 was used instead of CH_4, indicating that methane dissociation is a key step and that CO and CO_2 are formed via some common intermediates which are subject to kinetic deuterium isotope effect. The results of deuterium isotope effects can be reasonably explained based on the methane pyrolysis mechanism.

Keywords: methane oxidation; syngas; SiO_2-supported nickel (Ni/SiO_2); deuterium isotope effect

1. Introduction

The partial oxidation of methane to syngas has received much attention in the past years. The reaction is mildly exothermic and usually, a H_2/CO ratio of about 2, suitable for methanol and Fischer–Tropsch syntheses, is obtained. This catalytic process is considered to be more feasible than the methane oxidative coupling one for the utilization of methane and has advantages over the conventional steam reforming of methane to make syngas. Supported nickel is one of the typical catalysts for this process [1–7].

In 1946, Prettre et al. first reported that synthesis gas could be produced from methane and oxygen using a supported nickel catalyst in the 735 to 900°C temperature range and concluded that the overall oxidation reaction involved an initial strongly exothermic complete oxidation reaction of methane to CO_2 and H_2O, followed by the endothermic reforming reaction of the remaining methane by H_2O and/or CO_2. This viewpoint was accepted by many recent researchers [2,3,8–11]. However, Schmidt and coworkers [7,12–14] have shown that syngas can be produced with high H_2 and CO selectivities (> 90%) and high CH_4 conversion (> 80%) over Pt- or Rh-coated alumina monoliths in an autothermal flow reactor at ca. 1000°C and at residence times between 10^{-2} and 10^{-4} s, which was noticeably shorter than the time of ca. 1 s [15] usually adopted in a steam reforming reactor. With such short superficial contact time, they considered that the direct oxidation reaction should be independent of the reforming reactions and concluded that the primary surface reaction is methane pyrolysis followed by surface carbon oxidation and H_2 desorption. Choudhary and co-workers [4,5,16] reported that high selectivity to CO and H_2 could be achieved at temperature lower than 700°C on a variety of Ni- and Co-containing catalysts with high reactant gas space velocities (10^5–10^6 h^{-1}) and concluded that syngas was formed directly from methane oxidation. Matsumura et al. [10], however, pointed out that the amount of reactants fed in Schmidt's as well as Choudhary's cases was so large that the heat generated during the exothermic reaction would facilitate methane reforming via CO_2 and H_2O. Lunsford and co-workers [6] proved the existence of a large thermal gradient (as much as 300°C) within the catalyst bed during the methane oxidation reaction at high space velocities using an optical pyrometer and pointed out similar hot spots might be present on the catalysts studied by Choudhary et al. [4,5,16].

Concerning the active sites for methane partial oxidation to syngas, Lunsford and coworkers [3] proposed that the initial complete oxidation of methane to CO_2 and H_2O occurs on the unreduced NiO/Al_2O_3 catalyst and the reforming reactions of methane with the CO_2 and H_2O formed happen on the reduced Ni/Al_2O_3 catalyst. Buyevskaya et al. [17] suggested reduced and oxidized surface rhodium sites are the active sites for methane decomposition to surface carbon and methane complete oxidation to CO_2 respectively and CO is formed via a fast reaction of surface carbon species with CO_2 over Rh/Al_2O_3 catalyst.

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In order to eliminate the hot spots, pulse technique was used to study the mechanistic aspects of the conversion of CH_4/O_2 to syngas [18,19]. Previously, the reaction behaviors of CH_4 and CH_4/O_2 with SiO_2-supported copper and nickel catalysts at 600, 650 and 700°C were compared [19]. The results showed only in the reaction of CH_4/O_2 over reduced Ni/SiO_2, on which methane adsorbs dissociatively, would CO and H_2 be formed as main products, indicating that methane dissociation over metallic nickel sites is a key step for syngas formation and the reduced nickel sites are the active sites. However, it is not sure if the above conclusion is still correct at higher reaction temperature. In the present studies, pulse reaction of CH_4/O_2 with unreduced and reduced SiO_2-supported nickel catalysts was performed at a wide temperature range (from 600 to 800°C). In addition, in view of the fact that the C–H bonds in methane should be cleaved before CO formation in the process of methane partial oxidation to syngas, deuterium isotope effects were investigated by performing the $CH_4 + O_2$ and $CD_4 + O_2$ reactions alternately at 750°C to probe the mechanistic aspects of methane oxidation.

2. Experimental

2.1. Catalyst preparation

The SiO_2-supported nickel catalysts (with 10 wt% metal) were prepared by impregnating SiO_2 granule (Aldrich, 60–80 mesh) with the nickel nitrate (BDH, A.R. grade) solution followed by drying at 100°C for 12 h and annealing at 500°C for 2 h for decomposition. The catalysts so prepared are the unreduced ones and are signified as NiO/SiO_2. The catalysts treated in H_2 for 1 h at 500°C are the reduced ones and are expressed as Ni/SiO_2. (By means of H_2-adsorption, nickel dispersion was determined to be 3.6%.)

2.2. Pulse reaction

The reaction was carried out in a pulse micro-reactor [18]. The reactor was made of quartz tube with 4 mm i.d. A chromel–alumel thermocouple was introduced from the top of the reactor and inserted into the catalyst bed to measure the reaction temperature. During the pulse experiments, there was a constant flow (17 ml/min) of helium through the reactor and the reactant gas mixture was diluted and flushed in by the carrier gas. For each study, 50 mg of catalyst was used. The pulse volume of methane/oxygen (2/1) was 1.03 ml. The reactants and products were analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with TCD (MS5A and Porapak Q as columns, 50°C; helium as carrier gas). Selectivities (mol%) were calculated on the basis of carbon contents in the products. In the CH_4/O_2 experiments, the results of carbon balance are estimated to be within 5% accuracy. In the absence of the catalysts, the blank runs showed almost no activity below 700°C, and ca. 6.5% of methane conversion at 800°C.

2.3. Investigation of deuterium isotope effects

The experiment was carried out in such a manner that CH_4/O_2 was first pulsed over the pre-reduced catalyst to perform the $CH_4 + O_2$ reaction; after the eighth CH_4/O_2 pulse, $CD_4 + O_2$ reaction was carried out by pulsing in CD_4/O_2 instead. After the eighth pulse of CD_4/O_2 the $CH_4 + O_2$ reaction was carried out again. By performing the $CH_4 + O_2$ and $CD_4 + O_2$ reactions alternately in this way, deuterium isotope effects could be investigated. Average values of methane conversion and yields of CO and CO_2 in the $CH_4 + O_2$ and $CD_4 + O_2$ reactions were calculated with the exclusion of the first two points in each set of eight reaction points. The relative ratios (average value) of methane conversion, CO yield and CO_2 yield in the $CH_4 + O_2$ reaction to the corresponding ones in the $CD_4 + O_2$ reaction were used to express the magnitude of deuterium isotope effects.

Methane (99.9%), methane-d_4 (D, 99%), oxygen (99.7%), hydrogen (99.995%) and helium (99.995%) were used directly without further purification.

3. Results and discussion

3.1. CH_4/O_2 interactions with NiO/SiO_2

The products of CH_4/O_2 (2/1) interaction with NiO/SiO_2 at 600 and 700°C were exclusively CO_2 and H_2O. As shown in fig. 1a, methane conversion at these two temperatures remained roughly at 28% during the eight reaction points of CH_4/O_2 pulses. Since there were no CO and H_2 formed, it can be concluded that gas-phase steam and CO_2 reforming reactions had not taken place at 600 and 700°C.

However, besides CO_2 and H_2O, CO and H_2 were formed at 800°C. As shown in figs. 1a and 1b, during the first three reaction points, methane conversion was ca. 44% and the corresponding selectivity of CO increased slightly from 7.0 to 12.5%. From the third reaction point onward, methane conversion increased in a zig-zag manner, while CO selectivity increased greatly in a continuous way and reached a level of ca. 94% from the sixth point onward. At the eighth reaction point, both methane conversion and CO selectivity over NiO/SiO_2 were comparable with those over the reduced Ni/SiO_2 catalyst (fig. 2). At 800°C, during the first two reaction points, CO selectivity was less than 8%, indicating the contribution of gas-phase steam and CO_2 reforming reactions to the generation of syngas at 800°C were minor.

As reported previously [19], methane complete oxida-

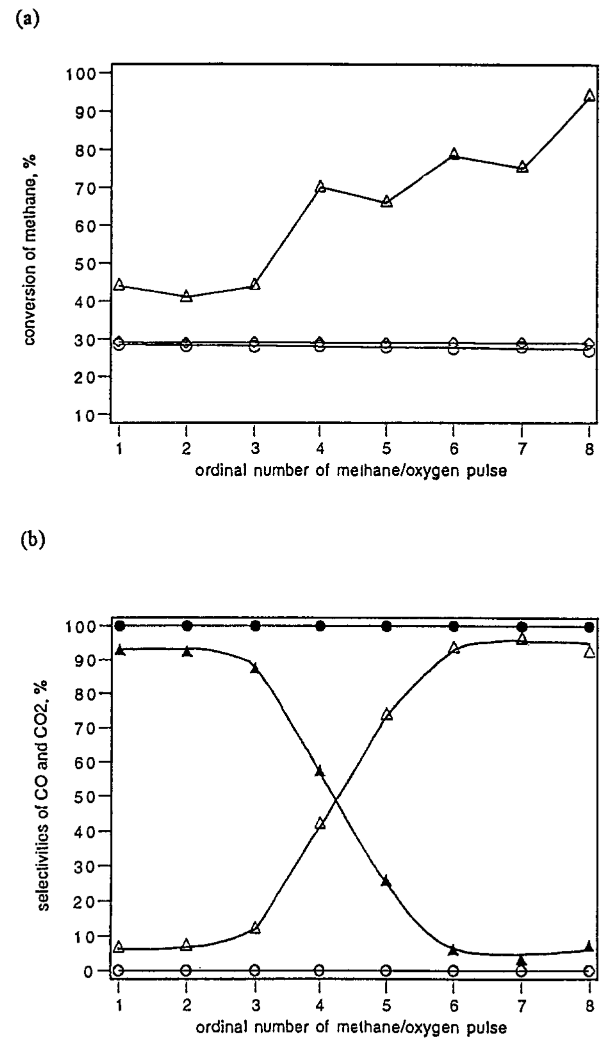

Fig. 1. The relationship of (a) CH_4 conversion and (b) CO (open symbols) and CO_2 (solid symbols) selectivities with the ordinal number of CH_4/O_2 pulsing over NiO/SiO_2 at 600 (○), 700 (◇) and 800 (△) °C. (Remark: the signs for 600 and 700°C are overlapping in (b).)

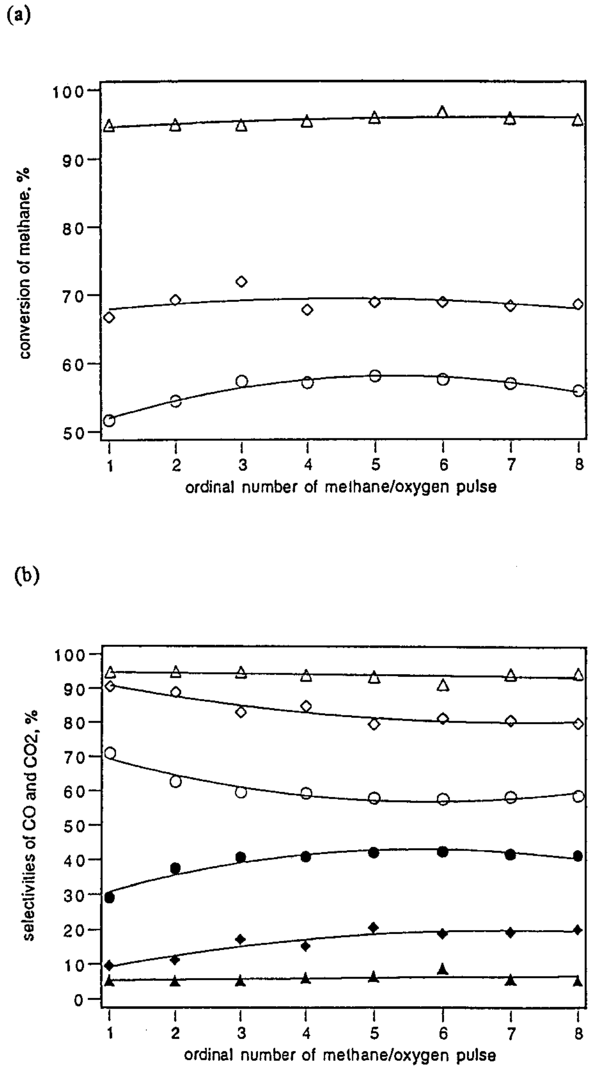

Fig. 2. The relationship of (a) CH_4 conversion and (b) CO (open symbols) and CO_2 (solid symbols) selectivities with the ordinal number of CH_4/O_2 pulsing over Ni/SiO_2 at 600 (○), 700 (◇) and 800 (△) °C.

tion occurs over NiO supported on SiO_2 granule, whereas methane decomposition occurs over metallic nickel in the reduced Ni/SiO_2 catalyst. Thus, the overall reaction for the first reaction point of CH_4/O_2 pulse over NiO/SiO_2 contained the following two reaction stages: First, complete oxidation reaction between methane and NiO took place to give CO_2 and H_2O and in the mean time Ni^{2+} was reduced to Ni^0; second, the resulting Ni^0 was either reoxidized to Ni^{2+} via reaction with gaseous oxygen, or acted as the active site for methane decomposition and oxygen dissociation to give surface carbon and oxygen respectively. Since at 600 and 700°C, the products of CH_4/O_2 interaction with NiO/SiO_2 were exclusively CO_2 and H_2O and methane conversion was constant with the number of CH_4/O_2 pulses, it can be inferred that Ni^0 formed in the first stage was reoxidized and the original state of the catalyst was restored after each reaction point of CH_4/O_2. However, at 800°C, from the third reaction point onward, both methane conversion and CO selectivity increased greatly, signifying the change in surface composition of the catalyst. It can be reasonably deduced that the metallic nickel formed in the first stage was sustained at 800°C and its amount increased with the number of CH_4/O_2 pulses until a stable state was reached. With the existence of reduced nickel sites, methane and oxygen dissociative adsorptions become feasible, resulting in the formation of syngas via surface carbon oxidation and surface hydrogen combination. With the gradual increase in the amount of metallic nickel, the catalytic activity and product distribution were gradually close to those observed in the reaction of CH_4/O_2 over Ni/SiO_2. The present results clearly indicate that metallic nickel is the active site for methane partial oxidation to syngas again.

3.2. CH_4/O_2 interaction with Ni/SiO_2

Over Ni/SiO_2 at 600, 700 and 800°C, the main products were CO, H_2 (selectivities > 60%) with CO_2 and H_2O being the minor ones (fig. 2). At all three temperatrures, oxygen conversion remained constantly at 100%. With the increase in reaction temperature, both methane conversion and CO selectivity increased noticeably. Based on the amount of methane converted and 100% of oxygen conversion at each reaction point, the molar ratio of surface carbon to oxygen was estimated to be ca. 1.1, 1.4 and 1.9 respectively at 600, 700 and 800°C. As reported previously [19], CO selectivity increased with increasing temperature in the oxidation reaction of surface carbon deposited on the Ni/SiO_2 catalyst if the molar ratio of surface carbon to oxygen was above one. The similar trend between CO selectivity and reaction temperature observed both in the reaction of CH_4/O_2 and in the oxidation reaction of surface carbon over Ni/SiO_2 implied that the primary surface reaction of CH_4/O_2 over Ni/SiO_2 was methane pyrolysis: $CH_4(s) \rightarrow C(s) + 4H(s)$, followed by oxidation of C(s) to CO and combination of H(s) to H_2.

Over Ni/SiO_2, oxygen and methane adsorbed competitively on metallic nickel. As discussed in section 3.1, nickel oxide suported on the SiO_2 granule can gradually be reduced to metallic nickel with the pulsing in of CH_4/O_2 (2/1) at the temperature of 800°C. So, even if a small amount of metallic nickel was oxidized to Ni^{2+} in the presence of oxygen, the oxidized nickel can be re-reduced via reaction with methane. Thus a certain amount of Ni^0 sites can be sustained to keep the formation of CO and H_2 going. Since methane adsorption on metallic nickel is an activation process, the adsorption rate is accelerated exponentially by temperature raising, whereas the surface coverage of O(s) adatoms decreases with rising temperature. Thus, one can expect the higher the temperature is, the higher the ratio of Ni^0/Ni^{2+} will be. The co-existence of Ni^0 and Ni^{2+} sites on nickel catalysts for syngas formation from CH_4/O_2 had been confirmed by XPS and XRPD studies by Lunsford and coworkers [3].

3.3. *Deuterium isotope effects*

Fig. 3 shows the variations of methane conversion, yields of CO and CO_2, and CO selectivity over the 10% Ni/SiO_2 catalyst at 750°C as related to the ordinal number of methane/oxygen pulses. As shown in fig. 3a, when the $CH_4 + O_2$ reaction was alternated to the $CD_4 + O_2$ one, methane conversion decreased noticeably; conversely, when $CD_4 + O_2$ was changed to $CH_4 + O_2$, methane conversion increased noticeably, indicating the overall reaction of methane oxidation showed a normal deuterium isotope effect. From figs. 3b and 3c, one can

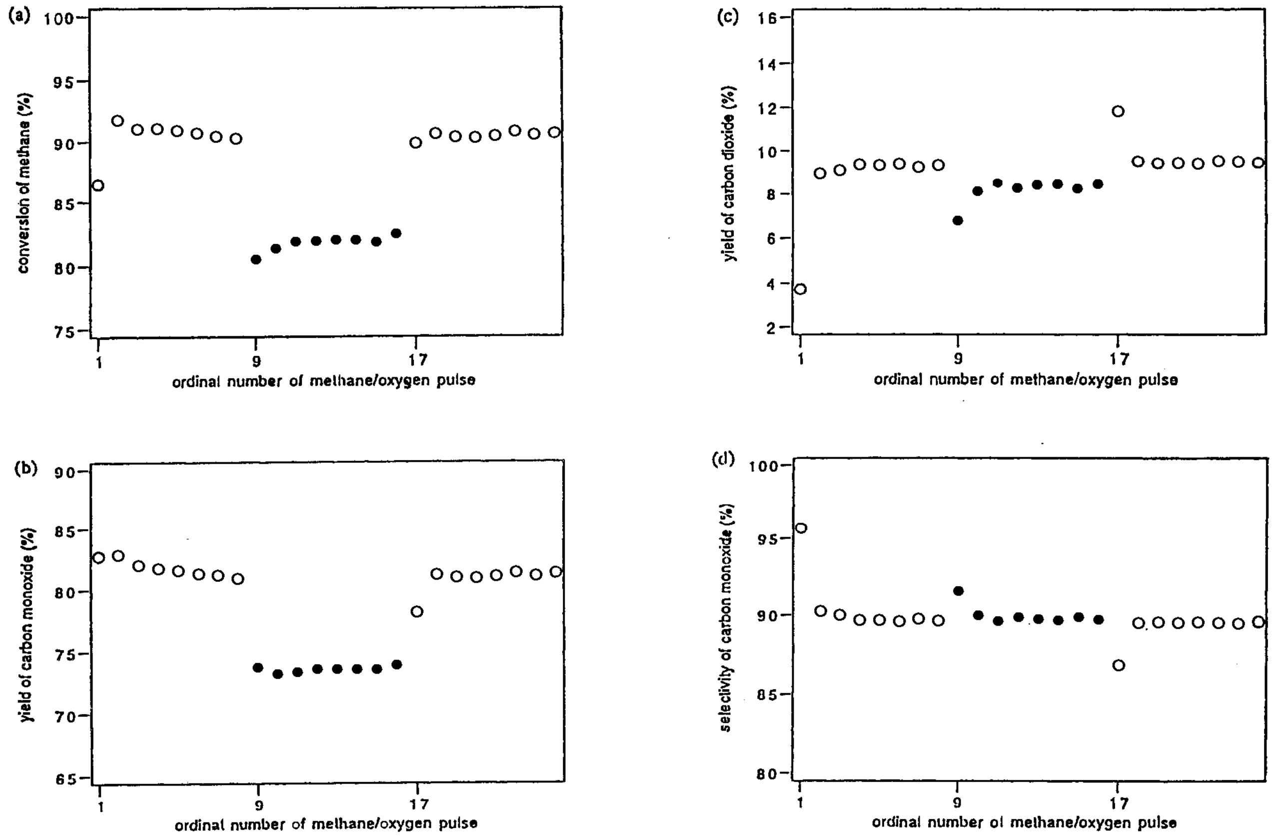

Fig. 3. The relationship of (a) CH_4 conversion, (b) CO yield, (c) CO_2 yield, and (d) CO selectivity with the ordinal number of methane/oxygen (open symbols for CH_4/O_2, solid symbols for CD_4/O_2) pulsing over Ni/SiO_2 at 750°C.

see that both the CO and CO_2 yields showed the same trend as methane conversion, signifying that the formation of both CO and CO_2 also showed normal deuterium isotope effects in methane partial oxidation reaction. Methane conversion, CO yield and CO_2 yield in the $CH_4 + O_2$ reaction were all about 1.11 times that in the $CD_4 + O_2$ reaction. In fig. 3d, selectivity of CO (CO_2 as well, though not shown) stayed at almost the same level within the alternations of $CH_4 + O_2$ and $CD_4 + O_2$, with the exception of the first point in each set of the eight reaction points, where stable state has not yet been reached, indicating the reaction for CO and CO_2 generation followed the same mechanism no matter CD_4 was used instead of CH_4. To summarize, when CD_4 was used instead of CH_4 to perform the methane oxidation reaction, the overall reaction, as well as the CO and CO_2 formation reactions all showed normal deuterium isotope effects of similar magnitude with almost no change in the product selectivities. From these results, it can be inferred that methane dissociation is a key step and that CO and CO_2 are formed via some common intermediates which are subject to kinetic deuterium isotope effect in the methane partial oxidation reaction. It is evident that these common intermediates are surface CH_x ($x = 0$–3) species originated from methane decomposition. The results of deuterium isotope effects observed in the present work can be reasonably explained based on the following methane pyrolysis mechanism:

$$\begin{tikzcd}
CH_{4,g} \arrow[r] & CH_{x,s} \arrow[r, "O_s"] & CO_s \arrow[r] \arrow[d, "O_s"] & CO_g \\
& & CO_{2,s} \arrow[r] & CO_{2,g}
\end{tikzcd}$$

According to the above mechanism, CO and CO_2 selectivities are mainly governed by the following two competitive reactions, namely, the desorption of CO_s to CO_g and the oxidation of CO_s to $CO_{2,s}$. When CD_4 was used instead of CH_4, the dissociation rate of methane and the formation rates of surface CH_x species decreased simultaneously due to normal deuterium isotope effects, leading to the decrease in the formation rates of both CO_s and $CO_{2,s}$; whereas the relative rate of CO_s desorption to CO_s oxidation is free from the deuterium isotope effect and remains almost unchanged, resulting in similar product selectivities.

4. Conclusion

(i) Under the experimental conditions adopted in the present work, reactions due to gas-phase steam and CO_2 reforming are minor. (ii) Metallic nickel is the active site for CO and H_2 formation. (iii) Methane dissociation is a key step in methane oxidation conversion. (iv) CO and CO_2 are formed via some common intermediates, namely, surface CH_x ($x = 0$–3) species. (v) The methane pyrolysis mechanism is advocated by the present work.

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