

[通 讯]

The Main Origin of CO₂ in Partial Oxidation of Methane to Syngas over a Ni/Al₂O₃ Catalyst*

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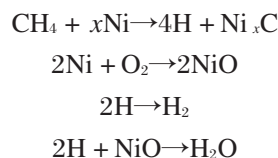
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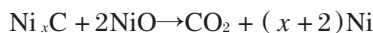
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Partial oxidation of CH₄ to syngas has been a hotspot of research with the advantages comparing to steam reforming process, such as low H₂/CO ratio (≈ 2), more energy-efficient, and high CH₄ conversion and selectivities to CO and H₂ with smaller reactor and short contact time ($\leq 10^{-2}$ s), etc. Although great progress in the studies of catalyst and production process has been made, the reaction mechanism over supported metal catalysts is still in argument. The typical viewpoints are represented by combustion-reforming mechanism^[1] and direct oxidation mechanism^[2]. Combustion-reforming mechanism means CH₄ firstly combines with O₂ to H₂O and CO₂, then the remaining CH₄ is reformed by H₂O and CO₂ to H₂ and CO. It's evident that CO₂ is a primary product and CO the secondary product. In the direct oxidation mechanism, methane firstly dissociates to H₂ and surface carbon species, then the latter react with surface oxygen species to CO. Hereby, CO is the primary product. Some authors think that CO₂ is also a primary product originating from the reaction between surface carbon species and surface oxygen species. Others regard CO₂ as a secondary product from further oxidation or disproportionation of CO.

In our previous work, the mechanism of partial oxidation of methane over a Ni/Al₂O₃ catalyst has been proposed^[3,4]:



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According to this mechanism, CO_2 , as a primary product, is mainly from the surface reaction between Ni_xC and NiO . Our work^[5] also showed that the conversion of CO by disproportionation limited by thermodynamic equilibrium is not more than 3.5% under the experimental conditions. Isotopic transient technique developed by the authors was used to study the origin of CO_2 , and further evidences of CO_2 mainly from the surface reaction between Ni_xC and NiO were given.

The apparatus and the preparation method of the 8 mol% $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst have been described earlier^[3]. 30 mg catalyst with the sizes 0.3–0.45 mm was placed in the middle of the quartz reactor with 5.5 mm inner diameter, and the rest space of the reactor was filled with 0.45–0.9 mm quartz sand to shorten the residence time of the reactants and products to accelerate the response speed of transient. The height of the catalyst bed is about 2 mm. An AI-FUZZY temperature controller combined with a K thermocouple controlled the reactor temperature. The products were detected by an on-line AMETEK quadrupole mass spectrometer with the minimum dwell time 3 ms and 8 channels. All experiments were carried out under atmospheric pressure and at 700 °C. The total flow-rate at the inlet of the reactor was 30 mL · min⁻¹. Both ^{13}CO (91.7 (mol)%) and $^{18}\text{O}_2$ (92.9 (mol)%) were produced by Merck Frosst Canada Company.

After $\text{CH}_4/\text{O}_2/\text{He}$ had reacted for 20 min over the catalyst pre-reduced at 700 °C in pure H_2 , transient switch to $\text{CH}_4/^{18}\text{O}_2/\text{H}_2/^{13}\text{CO}/\text{Ar}$ was conducted. The results were shown in Fig. 1. The purpose of adding a certain amounts of ^{13}CO to the reactants is to investigate the disproportionation of CO during partial oxidation of methane. The products after the switch include C^{18}O , $\text{C}^{16}\text{O}^{18}\text{O}$, CO , C^{18}O_2 , $^{13}\text{C}^{18}\text{O}$, $^{13}\text{CO}_2$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$. The selectivity to total carbon monoxide is 88%.

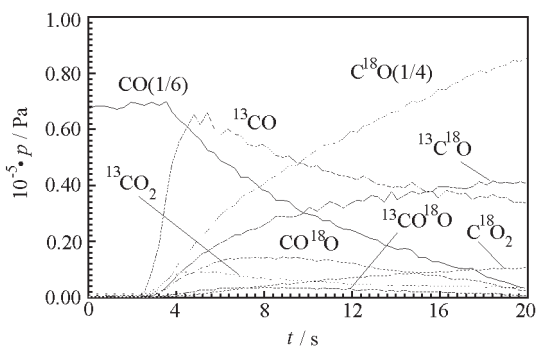


Fig. 1 Transient responses from 2/1/1 (mol) $\text{CH}_4/\text{O}_2/\text{He}$ to 2/1/2/1/1 (mol) $\text{CH}_4/^{18}\text{O}_2/\text{H}_2/^{13}\text{CO}/\text{Ar}$ at 700 °C

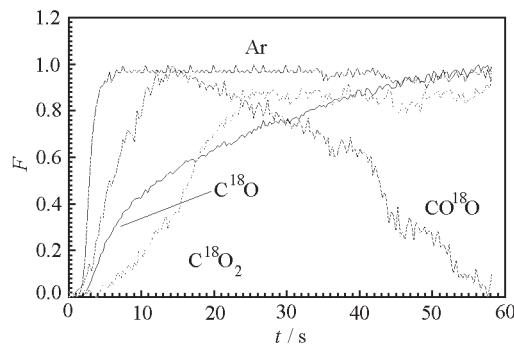
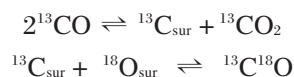


Fig. 2 Normalized transient responses of the switch from 2/1/1 (mol) $\text{CH}_4/\text{O}_2/\text{He}$ to $\text{CH}_4/^{18}\text{O}_2/\text{Ar}$ with the same ratio in steady state at 700 °C

If CO_2 is mainly from the disproportionation of CO during partial oxidation of methane, there should be more $^{13}\text{CO}_2$ after the switch. But in Fig. 1, the maximum content of $^{13}\text{CO}_2$ in total carbon

oxides is only about 1.5%. So CO₂ must mainly originate from other reactions. There is about 12% ¹³C¹⁸O in 20 s as in Fig. 1, this shows that disproportionation of ¹³CO occurs and is very rapid for ¹³C¹⁸O can only be formed from ¹³CO by



However, disproportionation of CO is limited by thermodynamic equilibrium and is not the main origin of CO₂. By the reaction, C in gas phase can exchange with surface C.

If CO₂ is mainly from further oxidation of CO, there should be more ¹³CO¹⁸O after the switch. In fact, the maximum content is only 1.2%. So further oxidation of CO is impossible to be the main origin of CO₂.

In Fig. 1, most of the carbon dioxide is CO¹⁸O at the beginning of the switch, and C¹⁸O₂ substitutes CO¹⁸O gradually with time on stream. After the switch, O can only be from the catalyst surface, and further oxidation of CO is not easy to occur under the experimental conditions. So CO¹⁸O is from the surface reaction among Ni_xC, NiO and Ni¹⁸O. With the decrease of NiO and the increase of Ni¹⁸O, the possibility to form CO¹⁸O decreases and the possibility to form C¹⁸O₂ increases gradually. So the intensity of C¹⁸O₂ increases gradually and the intensity of CO¹⁸O firstly increases and then decrease after the switch. CO¹⁸O and C¹⁸O₂ are the most abundant two carbon dioxides. Therefore, surface reaction between Ni_xC and NiO is the main origin of CO₂.

Steady-state isotopic transient experiment also supports the above conclusion. At 700 °C, after CH₄/O₂/He had reacted for 20 min over the reduced catalyst, steady-state transient switch was conducted from CH₄/O₂/He to CH₄/¹⁸O₂/Ar, where He and Ar were the tracers. The input responses of Ar, C¹⁸O, C¹⁸O₂, and CO¹⁸O were normalized with the formula

$$F = (y - y_0) / (y_\infty - y_0)$$

where F is the normalized intensity, and y_0 , y and y_∞ are the intensities at the beginning, at any time and at the end of response, respectively. The results are shown in Fig. 2. Ar, C¹⁸O and CO¹⁸O begin to respond nearly at the same time, but the response of C¹⁸O₂ has some delay compared to that of Ar, C¹⁸O and CO¹⁸O. At the beginning of the switch, on the catalyst surface there is more NiO and less Ni¹⁸O relatively, so the possibility to produce CO¹⁸O is higher than that to C¹⁸O₂. With the increase of surface ¹⁸O, the possibility to produce C¹⁸O₂ increases gradually, but the possibility to CO¹⁸O decreases. So the intensity of CO¹⁸O firstly increases then decreases after the switch, and the response of C¹⁸O₂ has some delay compared to inert tracer Ar.

The isotopic transient experiments showed that the main origin of CO₂ during partial oxidation of methane is the surface reaction between Ni_xC and NiO, but not the disproportionation of CO or the further oxidation of CO. The results support the direct oxidation mechanism of partial oxidation of methane proposed by the authors. Disproportionation of CO, restricted by thermodynamic equilibrium, is not the main origin of CO₂. The reaction is very rapid under experimental conditions, and during the reaction, the C in gas phase CO can exchange with surface C.

References

- 1 Ashcroft A T, Cheetham A K, Foord J S, *et al. Nature*, **1990**, **344**: 319
- 2 Hickman D A, Schmidt L D. *Science*, **1993**, **259**: 343
- 3 Shen S K, Li C Y, Yu C C. *Stud. Surf. Sci. Catal.*, **1998**, **119**: 765
- 4 Li Chunyi, Yu Changchun, Shen Shikong. *Acta Physico-Chimica Sinica*, accepted
[李春义, 余长春, 沈师孔. 物理化学学报 (*Wuli Huaxue Xuebao*), 已接收]
- 5 Li Chunyi, Yu Changchun, Shen Shikong. *Chinese Journal of Catalysis*, **1998**, **19**(5): 463
[李春义, 余长春, 沈师孔. 催化学报 (*Cuihua Xuebao*), **1998**, **19**(5): 463]

Ni/Al₂O₃ 催化剂上甲烷部分氧化制合成气反应 CO₂ 主要来源*

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摘要 负载型金属催化剂上甲烷催化部分氧化制合成气反应机理存在着燃烧 - 重整机理和直接氧化机理之争. 如果反应按燃烧 - 重整机理进行, 则 CO₂ 是反应的一次产物而 CO 是二次产物; 如果反应按直接氧化机理进行, 则 CO 是一次产物. 本文采用同位素瞬变技术, 对 Ni/Al₂O₃ 催化剂上甲烷部分氧化制合成气反应中 CO₂ 的来源进行了研究, 结果表明 CO₂ 同 CO 一样, 主要来源于催化剂表面 NiO 与甲烷分解生成的 Ni₃C 的反应, 这就有力地证明了反应按直接氧化机理进行. 研究结果还表明, CO 歧化或进一步氧化不是 CO₂ 的主要来源. 在实验条件下, CO 的歧化反应受到热力学平衡的限制, 转化率很低; 但反应进行得很快, 通过该可逆反应气相 CO 中的 C 可以与催化剂表面的 C 进行交换.

关键词: 部分氧化, 甲烷, 合成气, 主要来源, 二氧化碳

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