流化床中 $\text{CH}_4/\text{C}_3\text{H}_8$ 自热重整制合成气郭建忠¹, 侯昭胤², 郑小明²¹浙江农林大学化学系, 浙江临安 311300²浙江大学催化研究所, 浙江省应用化学重点实验室, 浙江杭州 310028

摘要: 在流化床反应器中, 考察了 Ni/SiO₂ 催化剂上 CH₄ 或 CH₄-C₃H₈ 临氧 CO₂ 重整 (自热重整) 制合成气反应性能。结果表明, 在 CH₄-C₃H₈ 混合气自热重整反应中, Ni 粒径较小催化剂的活性和抗积炭性能较高, CH₄ 和 CO₂ 转化率分别达 75.5% 和 72.6%。C₃H₈ 比 CH₄ 更易解离及被氧化, 部分 C₃H₈ 解离出来的中间产物 CH_x 物种可与吸附 H 结合为 CH₄, 因而降低了 CH₄ 的表观转化率; CH_x 也可与吸附的 CO₂ 物种反应生成 H₂ 与 CO, 从而促进了 CO₂ 的转化。

关键词: 甲烷; 丙烷; 自热重整; 合成气; 镍; 氧化硅; 负载型催化剂

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Autothermal Reforming of CH₄ and C₃H₈ to Syngas in a Fluidized-Bed ReactorGUO Jianzhong^{1,*}, HOU Zhaoyin², ZHENG Xiaoming²¹Department of Chemistry, Zhejiang A & F University, Lin'an 311300, Zhejiang, China²Key Laboratory of Applied Chemistry of Zhejiang Province, Institute of Catalysis, Zhejiang University, Hangzhou 310028, Zhejiang, China

Abstract: The catalytic properties of Ni/SiO₂ catalysts with different Ni particle size for the oxy-reforming of methane or methane-propane with CO₂ and O₂ (autothermal reforming) in a fluidized-bed reactor were investigated. The results show that Ni/SiO₂ catalysts with smaller Ni particle size exhibit higher catalytic activity and improved resistance to carbon deposition. The conversion of methane and carbon dioxide was 75.5% and 72.6%, respectively, for the methane-propane autothermal reforming reaction. The propane dissociates and is oxidized more easily than methane. The CH_x intermediate species from propane dissociation combines with the adsorbed hydrogen to produce methane, which results in a decrease in the apparent conversion of methane. Additionally, H₂ and CO are generated by the reaction with adsorbed CO₂, which promotes the conversion of the CO₂.

Key words: methane; propane; autothermal reforming; synthesis gas; nickel; silica; supported catalyst

天然气、煤层气和炼厂气中均含有大量的 CH₄ 和其它低碳烷烃。其中天然气是以 CH₄ (75%~90%) 为主的低碳烷烃混合物, C₂ 和 C₃ 含量约为 7%~15%, 储量非常大; 炼厂气是以 C₂~C₄ 为主的低碳烷烃、烯烃和 CH₄ 的混合物, 生成量占炼油总量的 3%~8%, 数量相当巨大, 目前主要通过火炬被烧掉, 既浪费了能源又排放了大量温室气体。因此在石油资源日益减少的情况下, 进行低碳烷烃的选择性转化制合成气和液体燃料的研究具有重要的现实

和理论意义。

目前, 相关研究主要集中在 CH₄ 的部分氧化及 CO₂ 重整制合成气^[1~10]。C₃H₈ 的 CO₂ 重整及部分氧化反应制合成气或 H₂ 也有报道^[11~14]。Corbo 等^[12] 研究了 Ni/Al₂O₃ 和 Pt/ZrO₂ 催化剂上 C₃H₈ 的部分氧化制合成气, 反应中除发生部分氧化外, 还存在燃烧、水气变换和生成 CH₄ 等副反应。

有关流化床反应器中低碳混合烷烃临氧 CO₂ 重整 (即自热重整) 制合成气报道较少^[15]。本课题组

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对 CH_4 自热重整制合成气做了大量、系统的研究^[5,16–18]. 因此, 本文以 C_3H_8 为低碳烷烃, 考察流化床反应器中 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整制合成气反应中, 不同 Ni 粒径的 Ni/SiO_2 催化剂的催化性能及抗积炭性能.

1 实验部分

1.1 催化剂的制备

按文献[5]方法, 分别配制一定浓度的 $\text{Ni}(\text{NO}_3)_2$ 和 $[\text{Ni}(\text{en})_3]^{2+}$ 溶液 (en 为乙二胺). 称取一定量的微球硅胶 (0.25~0.38 mm), 浸入定量的上述 Ni 溶液中, 充分搅拌, 超声振荡 30 min, 静置 24 h, 于 80°C 真空干燥 24 h, 再于 800°C 焙烧 4 h, 即得到 NiO/SiO_2 催化剂. 所有催化剂中 Ni 负载量均为 5%. 前期结果已表明, 以 $\text{Ni}(\text{NO}_3)_2$ 和 $[\text{Ni}(\text{en})_3]^{2+}$ 为前驱体制备的 NiO/SiO_2 催化剂经 H_2 还原后 Ni 的平均粒径分别为 45.0 和 4.5 nm^[5]; 下文中分别用 $\text{Ni}/\text{SiO}_2(\text{L})$ 和 $\text{Ni}/\text{SiO}_2(\text{S})$ 表示.

1.2 催化剂的评价

自热重整反应在常压流化床石英反应器中进行, 石英管内径 12 mm, 高 750 mm (流化段高度 500 mm). 催化剂置于 100 目不锈钢网上方. 原料气流量由 D07-12A/ZM 型质量流量计 (北京七星华创有限公司) 控制. 反应条件为: 原料气组成: $\text{CH}_4:\text{CO}_2:\text{O}_2 = 176:71:53$ 或 $\text{CH}_4:\text{C}_3\text{H}_8:\text{CO}_2:\text{O}_2 = 176:5:86:53$; 空速 $18\,000\text{ h}^{-1}$. 反应前催化剂在 H_2 (99.9%) 气流 (300 ml/min) 中以 20°C/min 升温至 700°C , 还原 1 h, 然后切换成反应气进行反应. 反应尾气经冷阱 (冰水) 冷凝并经无水高氯酸镁除水后, 用岛津 GC-8A 型气相色谱仪在线检测, TDX-01 柱 (当以 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气为原料时采用 Porapak Q 柱), TCD 检测器, Ar 为载气. 尾气流量由 LML 型湿式气体流量计 (长春市仪表总厂) 测量, 峰面积校正后采用归一法得到尾气组成. 催化剂的初始活性取反应 0.5 h 时数据. 整个反应过程中氧气全部被消耗.

反应物转化率 (X) 和产物选择性 (S) 的计算公式如下:

$$X(\text{CH}_4) = (F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}})/F_{\text{CH}_4,\text{in}}$$

$$X(\text{CO}_2) = (F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}})/F_{\text{CO}_2,\text{in}}$$

$$S(\text{H}_2) = F_{\text{H}_2,\text{out}}/(2(F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) + 4(F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}}))$$

$$S(\text{CO}) = F_{\text{CO},\text{out}}/((F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) + (F_{\text{CO}_2,\text{in}} -$$

$$F_{\text{CO}_2,\text{out}}) + 3(F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}}))$$

其中, F_{in} 和 F_{out} 分别为进料和尾气的流量.

1.3 催化剂的表征

催化剂的 X 射线衍射 (XRD) 测定在 Rigaku D/Max-IIIB 型 X 射线粉末衍射仪上进行, $\text{Cu K}\alpha$ 射线, 管流 40 mA, 管压 45 kV, 扫描速率 $0.02^\circ/\text{s}$. 反应后催化剂积炭量在 PE-TGA7 型热分析仪上测定. 样品先用高纯 N_2 于 300°C 预处理 30 min, 降温至 50°C 后切换成 O_2 , 以 10°C/min 升温至 800°C . 催化剂减轻的重量换算成每克催化剂的失重率即为催化剂的积炭量. Raman 表征在法国 Jobin Yvon 公司 LabRam-HR 800 型激光拉曼仪上进行, 使用 Ar 离子激光源, 波长为 514.5 nm, 激光的光强为 30 keV.

2 结果与讨论

2.1 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整反应

2.1.1 不同催化剂样品上 CH_4 ($\text{CH}_4\text{-C}_3\text{H}_8$) 自热重整反应活性

图 1 为 $\text{Ni}/\text{SiO}_2(\text{L})$ 催化剂上 CH_4 ($\text{CH}_4\text{-C}_3\text{H}_8$) 自热重整反应性能. 经多次检测原料气中的 O_2 和 C_3H_8 均完全消耗. 由图可见, 在催化剂上 CH_4 自热

图 1 $\text{Ni}/\text{SiO}_2(\text{L})$ 催化剂上 CH_4 ($\text{CH}_4\text{-C}_3\text{H}_8$) 自热重整反应性能

Fig. 1. Catalytic performance of the $\text{Ni}/\text{SiO}_2(\text{L})$ catalyst during the autothermal reforming of CH_4 and $\text{CH}_4\text{-C}_3\text{H}_8$. (a) CH_4 conversion; (b) CO_2 conversion. Reaction conditions: 700°C , GHSV = 18000 h^{-1} ; (1) $\text{CH}_4:\text{CO}_2:\text{O}_2 = 176:71:53$; (2) $\text{CH}_4:\text{C}_3\text{H}_8:\text{CO}_2:\text{O}_2 = 176:5:86:53$. L—large Ni particle size (45.0 nm) in the sample.

重整反应中 CH_4 和 CO_2 的转化率分别为 47.2% 和 27.5%。随着反应的进行, 催化剂迅速失活。当以 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气为原料时, CH_4 和 CO_2 转化率分别为 45.9% 和 39.7%。同样地, 随着反应的进行, 催化剂迅速失活。

图 2 为 $\text{Ni}/\text{SiO}_2(\text{S})$ 上 CH_4 ($\text{CH}_4\text{-C}_3\text{H}_8$) 自热重整反应性能。由图可见, 在 CH_4 自热重整反应中, CH_4 和 CO_2 的转化率分别为 77.0% 和 71.9%; 而在 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整反应中, CH_4 和 CO_2 的转化率分别为 75.5% 和 72.6%。反应 5 h 没有明显失活, 可见 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂表现出较高的活性与稳定性, 这主要归因于 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂上 CH_4 和 C_3H_8 解离活性高以及具有良好的抑制积炭作用^[5,19]。

图 2 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂上 CH_4 ($\text{CH}_4\text{-C}_3\text{H}_8$) 自热重整反应性能

Fig. 2. Catalytic performance of the $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst during the autothermal reforming of CH_4 and $\text{CH}_4\text{-C}_3\text{H}_8$. (a) CH_4 conversion; (b) CO_2 conversion. Reaction conditions: 700°C ; $\text{GHSV} = 18000 \text{ h}^{-1}$; (1) $\text{CH}_4:\text{CO}_2:\text{O}_2 = 176:71:53$; (2) $\text{CH}_4:\text{C}_3\text{H}_8:\text{CO}_2:\text{O}_2 = 176:5:86:53$.

综上所述, 在原料气中添加少量 C_3H_8 (约 2.5%) 后, 两个催化剂上 CH_4 的转化率均有所降低, 而 CO_2 转化率都有所升高。即添加少量的 C_3H_8 促进了 CO_2 的转化。在 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整反应过程中, C_3H_8 比 CH_4 更容易解离及氧化, 部分 C_3H_8 解离出来的中间产物 CH_x 物种可以与吸附 H 结合为 CH_4 , 降低了 CH_4 表观转化率; CH_x 也可与吸附的 CO_2 物种反应产生 H_2 与 CO , 促进了 CO_2 的转化。

2.1.2 温度及 $\text{CH}_4/\text{C}_3\text{H}_8$ 配比的影响

图 3 为温度和 C_3H_8 含量对 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整反应性能的影响。在 $\text{CH}_4\text{-CO}_2\text{-O}_2$ 原料中添加 C_3H_8 后, CH_4 转化率均降低, 特别在较低温度时更明显; CO_2 转化率升高, 且随着原料气中 C_3H_8 含量的增加而逐渐升高。由图可见, 600°C 时无 C_3H_8 时 CH_4 与 CO_2 的转化率分别为 47.9% 和 22.1%, 而添加 C_3H_8 后则分别为 40.0% 和 29.8%。在还原态金属表面上进行的烃类部分氧化或重整反应, 除了合成气, 还有 CH_4 生成; CH_4 的产生与其 CO_2 重整反应同时发生^[20], 因此 CH_4 表观转化率有所降低。另外, 由于 C_3H_8 比 CH_4 更易发生重整反应, 部分 C_3H_8 解离出来的中间产物 CH_x 物种可与吸附的 CO_2 物种反应产生 H_2 与 CO , 从而促进了 CO_2 的转化, 因而 CO_2 转化率有所升高。

图 3 温度和 C_3H_8 含量对 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂上 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整反应性能的影响

Fig. 3. Catalytic performance of the $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst during the autothermal reforming of $\text{CH}_4\text{-C}_3\text{H}_8$ as a function of reaction temperature and C_3H_8 content. (a) CH_4 conversion; (b) CO_2 conversion. Reaction conditions: 18000 h^{-1} ; (1) $\text{CH}_4:\text{CO}_2:\text{O}_2 = 176:71:53$; (2) $\text{CH}_4:\text{C}_3\text{H}_8:\text{CO}_2:\text{O}_2 = 176:5:86:53$; (3) $\text{CH}_4:\text{C}_3\text{H}_8:\text{CO}_2:\text{O}_2 = 176:10:100:53$.

2.2 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂的稳定性

图 4 是 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂上反应 50 h 的结果。由图可见, 随着反应的进行, CH_4 和 CO_2 转化率分别从 75.2% 和 72.6% 略降至 71.1% 和 67.6%。可见 $\text{Ni}/\text{SiO}_2(\text{S})$ 催化剂上 $\text{CH}_4\text{-C}_3\text{H}_8$ 混合气自热重整反

图 4 Ni/SiO₂(S) 催化剂上 CH₄-C₃H₈ 自热重整反应稳定性实验

Fig. 4. Time on stream for Ni/SiO₂(S) catalyst. Reaction conditions: 700 °C; CH₄:C₃H₈:CO₂:O₂ = 176:5:86:53; 18000 h⁻¹.

应的活性及稳定性较高。

2.3 催化剂失活分析

图 5 为新鲜的和反应后的 Ni/SiO₂(S) 催化剂的 XRD 谱。由图可见, 反应前后的催化剂上均未检测到 NiO 的衍射峰, 但反应后金属 Ni 的衍射峰 (44.5° 和 51.8°) 明显变尖, 说明 Ni 粒径增大。

图 5 Ni/SiO₂(S) 催化剂反应前后的 XRD 谱

Fig. 5. XRD patterns of Ni/SiO₂(S) catalysts. (1) Fresh sample; (2) Used for 50 h.

图 6 为反应后催化剂的 TG 曲线。可以看出, 该催化剂表面的积炭量为 2.3% 左右。因此, 催化剂的缓慢失活可能是由于在反应过程中, 部分活性中心发生烧结和积炭所致。

为进一步研究催化剂表面的积炭物种, 对反应后的催化剂进行了 Raman 表征, 结果示于图 7。样品分别于 1344 cm⁻¹ (D 带), 1575 cm⁻¹ (G 带), 2700 cm⁻¹ (G'带)^[21,22] 和 2926 cm⁻¹ 处出现谱峰。其中 D 带是无定形炭物种^[23], G'带是 D 带的谐波带, 而 2926 cm⁻¹ 处一般被认为是富含 H 的炭物种^[24]。

图 6 Ni/SiO₂(S) 催化剂在反应后的 TG 曲线

Fig. 6. TG curve of Ni/SiO₂(S) catalyst after reaction for 50 h.

图 7 Ni/SiO₂(S) 催化剂在反应后的 Raman 谱

Fig. 7. Raman spectrum of Ni/SiO₂(S) catalyst after reaction for 50 h.

这些炭物种在反应是可被消除。而 G 带一般认为是高度有序的石墨炭^[25]。它在反应中一般是惰性的, 很难被消除, 因而通常导致催化剂的失活。

3 结论

研究了流化床中 CH₄-C₃H₈ 混合气自热重整制合成气中不同 Ni 粒径的 Ni/SiO₂ 催化剂性能, 其中较小 Ni 粒径 (4.5 nm) 的催化剂具有较高的催化活性和稳定性。这可能是由于在 Ni/SiO₂(S) 催化剂上 CH₄ 和 C₃H₈ 解离活性高以及良好的抑制积炭性能。部分 C₃H₈ 解离出来的 CH_x 物种可与吸附的 CO₂ 物种反应生成 H₂ 与 CO, 可促进 CO₂ 的转化。随着反应时间的延长, 催化剂活性缓慢降低, 这主要是由于活性中心的部分烧结和类石墨炭的形成所致。

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英 译 文

English Text

A huge amount of CH_4 and other light alkanes exist in natural gas, coal-bed gas, and refinery gas. Natural gas,

which contains CH_4 (75%–90%) and $\text{C}_2\text{--C}_3$ (7%–15%), is a very rich energy reserve. The main components of refinery gas are $\text{C}_2\text{--C}_4$ alkanes, olefins, and methane and these make up 3%–8% of the total amount of oil refining. Currently, large amounts of natural resources are being burnt directly, which causes serious air pollution and emits a significant amount of greenhouse gases. Recently, the selective conversion of alkanes to synthesis gas and liquid fuel has received much attention because of their important roles in both practical and theoretical studies, and in industrial applications.

Current studies are focused on the production of syngas from partial oxidation and the CO_2 reforming of CH_4 [1–10]. CO_2 reforming and the partial oxidation of C_3H_8 to produce syngas or H_2 has also been reported [11–14]. Corbo et al. [12] reported the partial oxidation of C_3H_8 on $\text{Ni}/\text{Al}_2\text{O}_3$ and Pt/ZrO_2 for the production of syngas. These reactions suffer from side-reactions such as combustion, the water gas shift reaction, and the production of CH_4 .

Only a few studies have reported syngas production via the oxy-reforming of mixed alkanes with CO_2 and O_2 (autothermal reforming of mixed alkanes) [15]. Our group has systematically investigated the autothermal reforming of CH_4 to produce syngas [5, 16–18]. The objective of this work is to study the catalytic performance of Ni/SiO_2 catalysts with different Ni particle sizes for syngas production by the autothermal reforming of $\text{CH}_4\text{--C}_3\text{H}_8$ in a fluidized bed.

1 Experimental

1.1 Catalyst preparation

$\text{Ni}(\text{NO}_3)_2$ and $[\text{Ni}(\text{en})_3]^{2+}$ (en, ethylenediamine) were prepared as described previously [5]. The Ni catalysts were prepared via the direct impregnation of a certain concentration of $\text{Ni}(\text{NO}_3)_2$ and $[\text{Ni}(\text{en})_3]^{2+}$ solutions. The solution was treated ultrasonically for 30 min and underwent static handling for 24 h. After impregnation, the samples were dried for 24 h at 80 °C in vacuum and calcined at 800 °C in stagnant air for 4 h. The amount of Ni loading was controlled at 5% of the support mass. The previous results indicated that the mean Ni particle sizes of the catalysts prepared using $\text{Ni}(\text{NO}_3)_2$ and $[\text{Ni}(\text{en})_3]^{2+}$ were 45.0 and 4.5 nm [5], respectively. The two catalysts are designated $\text{Ni}/\text{SiO}_2(\text{L})$ and $\text{Ni}/\text{SiO}_2(\text{S})$.

1.2 Catalytic reactions

The autothermal reforming of CH_4 and $\text{CH}_4\text{--C}_3\text{H}_8$ was carried out in a quartz fluidized-bed reactor (i.d. 20 mm, height 750 mm, fluid height 500 mm) at atmospheric pressure. The feed gas flow rate was controlled by a mass flow

controller (D07-12A/ZM, Beijing Sevenstar Electronics Co. Ltd, Beijing, China). The reaction conditions were: $\text{CH}_4:\text{CO}_2:\text{O}_2 = 176:71:53$ (v/v) or $\text{CH}_4:\text{C}_3\text{H}_8:\text{CO}_2:\text{O}_2 = 176:5:86:53$ (v/v), gas hourly space velocity $18\,000\text{ h}^{-1}$. Before the reaction, the catalyst was reduced using a H_2 (99.9%, 300 ml/min) flow from 20 to 700 °C at a ramp speed of 20 °C/min and held at 700 °C for 1 h. The effluent gas was then cooled in an ice-water trap and analyzed with an online gas chromatograph (Shimadzu, GC-8A) equipped with a TDX-01 packed column (Porapak Q column in a $\text{CH}_4\text{-C}_3\text{H}_8$ autothermal reaction) and a thermal conductivity detector. Flow rates in the effluent were measured by a wet gas meter (LML, Changchun, China). A calibration area normalization was carried out to quantitatively determine the composition in the emission. No O_2 was detected in the effluent during the autothermal reforming reaction.

The conversion (X) and selectivity (S) were calculated as described below:

$$X(\text{CH}_4) = (F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}})/F_{\text{CH}_4,\text{in}}$$

$$S(\text{CO}_2) = (F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}})/F_{\text{CO}_2,\text{in}}$$

$$S(\text{H}_2) = F_{\text{H}_2,\text{out}}/(2(F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) + 4(F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}}))$$

$$S(\text{CO}) = F_{\text{CO},\text{out}}/((F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) + (F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}) + 3(F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}}))$$

where F_{in} and F_{out} are the feed gas and the effluent gas, respectively.

1.3 Catalyst characterization

X-ray diffraction (XRD) of the catalysts was performed using a Rigaku D/Max-III B X-ray diffractometer with nickel-filtered Cu K_α radiation and operated at 40 mA and 45 kV. Diffraction data were recorded using continuous scanning at a rate of $0.02^\circ/\text{s}$. The amount of deposited carbon was estimated using TG (Perkin-Elmer model PE TAC7/DX) from 50 to 800 °C at a ramp speed of 10 °C/min in 10% O_2 -90% N_2 . Before the analysis, the sample was pretreated in N_2 (99.999% pure) at 300 °C for 30 min. The amount of carbon deposition on the catalyst was calculated by converting the reduction of catalyst mass to mass loss per gram of catalyst. The properties of surface carbon was identified by Raman spectroscopy (LabRam-HR 800) using the 514.5 nm line of an argon laser operated at a laser power of 30 keV.

2 Results and discussion

2.1 Autothermal reforming of $\text{CH}_4\text{-C}_3\text{H}_8$

2.1.1 Catalytic performance of Ni/SiO_2 with different Ni particle sizes in CH_4 or $\text{CH}_4\text{-C}_3\text{H}_8$ autothermal reforming

Figure 1 shows the catalytic performance of the $\text{Ni/SiO}_2(\text{L})$ catalyst during the autothermal reforming

of CH_4 and $\text{CH}_4\text{-C}_3\text{H}_8$, respectively. No O_2 or C_3H_8 were detected in the effluent. The conversions of CH_4 and CO_2 were 47.2% and 27.5%, respectively, and this decreased quickly during methane autothermal reforming on the $\text{Ni/SiO}_2(\text{L})$ catalyst (Fig. 1(1)). Similarly, the conversions of CH_4 and CO_2 were 45.9% and 39.7% and decreased quickly during the autothermal reforming of $\text{CH}_4\text{-C}_3\text{H}_8$ (Fig. 1(2)).

Figure 2 shows the catalytic performance of the $\text{Ni/SiO}_2(\text{S})$ catalyst during the autothermal reforming of CH_4 and $\text{CH}_4\text{-C}_3\text{H}_8$. The conversions of CH_4 and CO_2 were 77.0% and 71.9% for methane autothermal reforming and 75.5% and 72.6% for $\text{CH}_4\text{-C}_3\text{H}_8$ autothermal reforming, respectively. No clear deactivation was detected within 5 h suggesting that the $\text{Ni/SiO}_2(\text{S})$ catalyst exhibited higher catalytic activity and improved stability and this may be attributed to the higher dissociation activity of CH_4 and C_3H_8 and the anti-carbon performance of the $\text{Ni/SiO}_2(\text{S})$ catalyst [5,19].

The aforementioned conversion of CH_4 decreased slightly while the conversion of CO_2 increased on the $\text{Ni/SiO}_2(\text{L})$ and $\text{Ni/SiO}_2(\text{S})$ catalysts when a small amount of C_3H_8 (about 2.5%) was added to the feed. These results indicate that the addition of C_3H_8 promotes the conversion of CO_2 . C_3H_8 dissociates and is oxidized more easily than CH_4 during $\text{CH}_4\text{-C}_3\text{H}_8$ autothermal reforming. The CH_x intermediate species from propane dissociation combines with adsorbed hydrogen to produce methane, which results in a decrease in the apparent conversion of methane but H_2 and CO is generated by reaction with adsorbed CO_2 to promote the conversion of carbon dioxide.

2.1.2 Effect of reaction temperature and ratio of $\text{CH}_4\text{-C}_3\text{H}_8$

Figure 3 shows the effect of temperature and $\text{CH}_4\text{-C}_3\text{H}_8$ ratio on the catalytic performance on $\text{Ni/SiO}_2(\text{S})$ during $\text{CH}_4\text{-C}_3\text{H}_8$ autothermal reforming. After increasing C_3H_8 in the $\text{CH}_4\text{-CO}_2\text{-O}_2$ feed, the conversion of CH_4 decreased particularly at lower temperatures. The conversion of CO_2 increased with a higher amount of C_3H_8 . The conversion of CH_4 and CO_2 were 47.9% and 22.1% without C_3H_8 at 600 °C, respectively, while the conversion decreased to 40.0% and 29.8% in the presence of C_3H_8 .

For the partial oxidation and reforming of hydrocarbons on the surface of a reduced metal the generation of CH_4 and the CO_2 reforming of CH_4 together with the production of syngas [20], which causes a decrease in the apparent conversion of CH_4 , was investigated. Furthermore, because C_3H_8 dry reforming might occur more easily than the CO_2 reforming of CH_4 , the CH_x intermediate species from propane dissociation can generate H_2 and CO via the reaction with adsorbed CO_2 to promote the conversion of carbon dioxide.

2.2 Stability of the $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst

A time on stream experiment only showed a slight decrease in the conversion of CH_4 and CO_2 from 75.2% and 72.6% to 71.1% and 67.6% on the $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst for 50 h (shown in Fig. 4), which indicates that the $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst has higher activity and better stability during $\text{CH}_4\text{-C}_3\text{H}_8$ autothermal reforming.

2.3 Analysis of catalyst deactivation

Figure 5 compares the XRD patterns of fresh and spent (50 h) $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst. No NiO diffraction peak was present for the fresh or the spent catalyst while the Ni diffraction peaks (at 44.5° and 51.8°) became obviously sharp. These results indicate that the Ni particles slowly increase in size as the time on stream increased.

Figure 6 shows the TG curve of the spent $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst (50 h). The amount of deposited carbon on the surface of the spent $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst (50 h) was 2.3%. Sintering of the catalyst's active site and the deposition of carbon can contribute to the slight deactivation.

A Raman spectrum of the deposited carbon on the spent $\text{Ni}/\text{SiO}_2(\text{S})$ catalyst (50 h) is shown in Fig. 7. Carbon species with Raman shifts at 1344 cm^{-1} (D band), 1575 cm^{-1} (G band), 2700 cm^{-1} (G' band) [21,22], and 2926 cm^{-1} were detected. The intensive peak at 1344 cm^{-1} (D band) is due to

amorphous carbon [23]. The G' band is a harmonic band of the D band. The band at 2926 cm^{-1} is assigned to a H-rich carbon species [24]. These carbon species can be eliminated during the autothermal reforming reaction. The band at 1575 cm^{-1} (G band) is commonly assigned to highly ordered graphite carbon [25], which is inert and not removed during the autothermal reforming reaction. These kinds of inactive carbon species will cause catalyst deactivation.

3 Conclusions

The autothermal reforming of $\text{CH}_4\text{-C}_3\text{H}_8$ to produce syn-gas was investigated over Ni/SiO_2 catalysts as a function of different Ni particle sizes in a fluidized bed reactor. The Ni-S catalyst exhibited higher catalytic activity and better stability, which might contribute to the higher dissociation activity of CH_4 and C_3H_8 , and the anti-carbon deposition behavior. The CH_x intermediate species from the dissociation of C_3H_8 can generate H_2 and CO by reaction with adsorbed CO_2 to promote the conversion of CO_2 . The reason for the slight decrease in catalytic activity might be the sintering of the active sites and the formation of graphite carbon on the surface of the catalyst.

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