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超低浓度甲烷在惰性颗粒中燃烧特性的实验研究

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摘　要: 通过实验的方法研究了固定床内, 惰性颗粒对超低浓度甲烷燃烧特性的影响特性, 同时考察了进气速度、进气浓度和床层温度对甲烷转化率的影响规律。实验表明, 在反应温度较低时, 几乎没有 CO_2 生成, CH_4 氧化生成了中间产物 CO; 随着反应温度的升高, CO 逐渐被氧化为 CO_2; 惰性颗粒的加入提高了 CH_4 的着火温度, 并在高温段抑制了甲烷的转换效率; 惰性颗粒的存在降低了 CO 最大峰值所对应的温度; 随着进气速度的降低, 床层温度的升高, 甲烷转化率增大; 而改变甲烷浓度对甲烷转化率基本没有影响。

关　键　词: 超低浓度甲烷; 惰性颗粒; 燃烧; 甲烷转化率
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引　言

矿井瓦斯气等超低浓度甲烷因常规技术较难利用而直接排向大气, 不仅造成了资源的浪费, 同时也加剧了温室效应和环境污染问题[1~3]。

由于超低浓度甲烷的含量极低($V_{vol} < 1\%$), 最多不超过 5%, 且甲烷浓度及通风流量波动较大的特点, 采用常规燃烧技术难以加以利用[4~6]。流化床燃烧技术具有燃烧效率高、气固接触面积大和燃料适应性广等特点为燃烧利用超低浓度煤层气提供了可能。Specchia S 和 Baron J 等学者采用催化剂颗粒作为床料研究了预混甲烷在流化床中的燃烧特性[7~9], 并取得了较好效果。然而为了降低使用催化剂的高昂成本, 常采用惰性颗粒替代催化剂。惰性颗粒的存在使得甲烷的燃烧过程发生了非均相的改变, 因此有必要对超低浓度煤层气在惰性颗粒流化床内的燃烧特性进行研究。

在流化速度较低时, 流化床反应器中的乳化相与固定床有相似之处, 因此采用惰性颗粒固定床反应器来研究预混超低浓度煤层气的燃烧特性, 以求增加对流化床反应器乳化相的了解。通过考察惰性颗粒种类、反应温度和进气速度等条件对燃烧特性的影响, 为进一步研究流化床中惰性颗粒对超低浓度甲烷燃烧的影响作用, 选择适合运行的床温范围等提供参考。

1　实验部分

本研究在以石英砂和三氧化二铝两种惰性颗粒为床料形成的固定床中进行, 实验系统如图 1 所示。反应器由两根大小不一的同轴陶瓷管(外管内径为 20 mm, 内管外径为 10 mm) 组成, 以减少铁/钢等金属壁面材料对实验结果的影响。管间形成的环形间隙为反应区, 反应区内惰性颗粒的填充长度为 250 mm, 床料两端采用耐高温的超细石英棉网固定, 以防止惰性颗粒吹散。

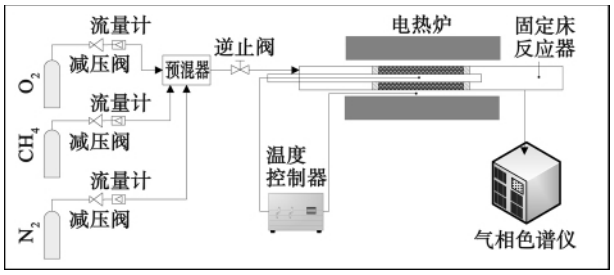

图 1　固定床反应器系统示意图
Fig. 1 Schematic diagram of a fixed bed reactor system

高压气瓶内的甲烷、氮气和氧气分别经减压阀减压, 流量计计量后进入预混器内, 充分混合形成超低浓度甲烷气体, 然后进入反应器。实验范围内, 甲烷体积浓度为 0.5% ~4%, 反应气总流量为 300 ~ 800 mL/min。反应器水平放置, 采用水平管式电阻炉加热, 加热的最大功率为 2 kW, 床温由温度控制器控制。在反应器出口对反应后的烟气进行采样, 采样的气体进入气相色谱仪(SC - 9700 型) 进行成分分析。甲烷转化率可用下式表示:

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$$X = \left(1 - \frac{C_{out}}{C_{in}}\right) \times 100\% \quad (1)$$

式中: C_{in}—入口处超低浓度甲烷中甲烷体积浓度,%; C_{out}—出口处烟气中甲烷体积浓度,%。

反应器内所采用的惰性床料为石英砂,氧化铝颗粒。在填充惰性颗粒之前,对空床反应器做相关实验以考察反应器壁面对燃烧反应的影响。然后再分别添加上述床料进行实验。惰性颗粒的粒径保持在 30 ~ 60 目之间。

2　结果与讨论

2.1　空床实验

图 2 给出了甲烷浓度为 0.75%,进气速度为 0.04 m/s 时,反应器出口烟气成份(CO,CO_2,CH_4) 随床温的变化趋势。从图中可以看出,在低于 800℃时,CO_2 的量极少,然后 CO_2 的量迅速增加; 在床温为 850℃时,CO 的生成量达到最大值,此时大约有 53% 的 CH_4 转化为 CO; 当 CH_4 浓度低于 0.05% 时,CO 快速氧化生成 CO_2,显然过多的 CH_4 存在会抑制 CO 氧化生成 CO_2,实验所得结果与 Artem A. Slepterev 和 Yikun Wang 等人所得结果吻合[10~11]。因此,可以看出,在温度较低时,CO 作为 CH_4 氧化燃烧的中间产物而大量存在,随着温度升高,CO 氧化形成的 CO_2。

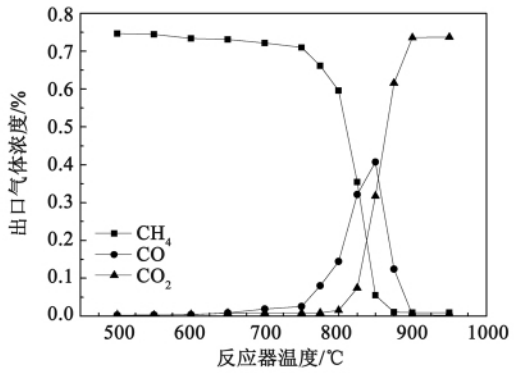

图 2　出口气体含量随温度变化曲线

Fig. 2 Gas content at the outlet vs. temperature

2.2　惰性颗粒对甲烷转换率的影响

图 3 给出了不同反应温度下(500 ~ 950℃) ,入口甲烷浓度为 1%,进气速度为 0.05 m/s 时,惰性颗粒固定床内甲烷转化率的变化曲线。由图中可以看出,随着反应温度的升高,惰性颗粒固定床内甲烷转化率也随之提高,而惰性颗粒的存在使得甲烷的着火温度从 650℃升高到 700℃,且甲烷转化率在 750 ~ 850℃间滞后于空床。这主要是惰性颗粒表面对活性自由基吸附造成的,使得甲烷的燃烧反应发生了非均相的转变。Valchos et al 研究指出[12~13],由于 H 原子及 CH_3 自由基被颗粒表面吸附,从而降低了气相反应中自由基的浓度,引起着火温度的升高,并对甲烷燃烧反应起到了一定的抑制作用。由图 3 可知,当温度大于 900℃时,甲烷均已基本转化完全,此时自由基的产生速率要远大于惰性颗粒对自由基的吸附速率,惰性颗粒对燃烧的抑制作用几乎可以忽略。

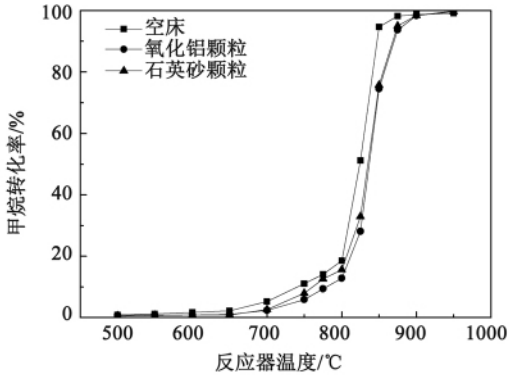

图 3　惰性颗粒对甲烷转化率的影响

Fig. 3 Effect of the inert particles on the methane conversion rate

2.3　初始浓度对甲烷转化率的影响

图 4 为初始浓度对甲烷转化率的影响曲线。图 4(a) 为床料是惰性颗粒氧化铝,进气速度为 0.05 m/s 时,不同反应浓度下甲烷转化率随温度的变化曲线。从图中可以看出,在不同的进气浓度下,甲烷的转化率随着反应器温度的升高而增加,在 800 ~ 900℃区间,其增加速率最快。图 4(b) 给出了温度为 825℃,进气速度为 0.05 m/s 时,甲烷转换率随甲烷初始浓度的变化曲线。对于空床,甲烷转换率保持在 50% 左右,高于石英砂和氧化铝颗粒固定床的 33% 和 28%,验证了惰性颗粒对甲烷转换率有抑制作用的特性。从图 4 可以看出,在相同温度下,随着初始甲烷浓度的增加,甲烷转换率基本保持不变,即在甲烷浓度较低时,甲烷转换率不会随着甲烷初始浓度的改变而改变[14]。

2.4　进气速度对甲烷转换率的影响

图 5 为进气速度对甲烷转化率的影响曲线。图 5(a) 床料是惰性颗粒石英砂,初始甲烷浓度为 1% 时,不同进气速度下甲烷转化率随温度的变化曲线。

从图中可以看出,在不同的进气速度下,甲烷的转化率随着反应器温度的升高而增加,在 800 ~ 900℃区间,其增加速率最快。图 5(b)给出了温度为 825℃,进气浓度为 1% 时,甲烷转换率随进气速度的变化曲线。随着进气速度的增加,空床内甲烷转化率下降速度要大于惰性颗粒固定床,但总的转化率仍高于惰性颗粒固定床。这是因为流速越低,反应停留时间越长,反应进行的越充分,相同温度下甲烷的转化率越高。相反则导致反应效率降低。而惰性颗粒对甲烷转换率有抑制作用,使得惰性颗粒床内的甲烷转化率低于空床。

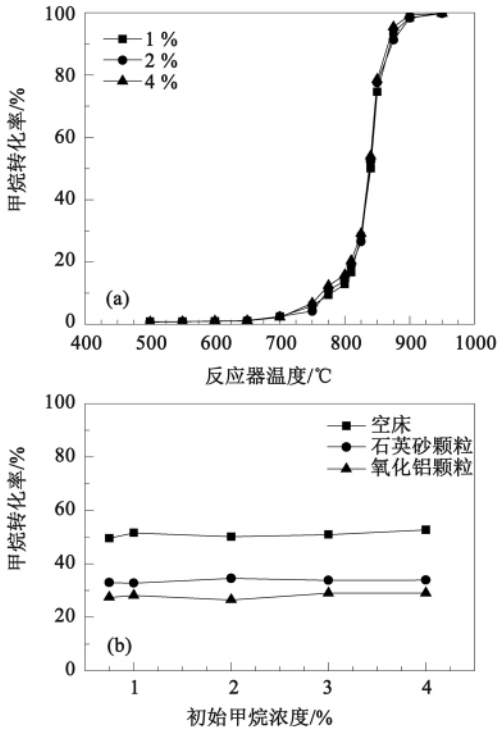

图 4 初始浓度对甲烷转化率的影响

Fig. 4 Effect of the initial concentration on the methane conversion rate

2.5 惰性颗粒对 CO 生成的影响

图 6 给出了惰性颗粒对 CO 生成特性的影响特性曲线。与空床反应相比,惰性颗粒的存在使得 CO 最大值时所对应的温度从 850℃降低到了 825℃;随着温度的增加,空床内 CO 的变化规律滞后于惰性颗粒固定床;750 ~ 825℃时惰性颗粒的存在显著增加了 CO 的排放浓度,随着温度的继续升高,影响逐渐减弱。这主要是由于该温度下,气相反应中的 OH 自由基被惰性颗粒表面吸附,OH 自由基是 CO 的主要氧化物,吸附导致 OH 自由基浓度下降,从而抑制了 CO 向 CO_2 的转变,必然导致 CO 浓度的增加[15]。随着温度的继续升高,自由基的产生速率远大于破坏速率,同时,相关研究表明,固体表面吸附的自由基层在一定高温下会发生解吸附反应,因此,CO 浓度存在一个最大值。实验测得固定床惰性颗粒存在时 CO 的浓度在 750 ~ 850℃下达到最大峰值。

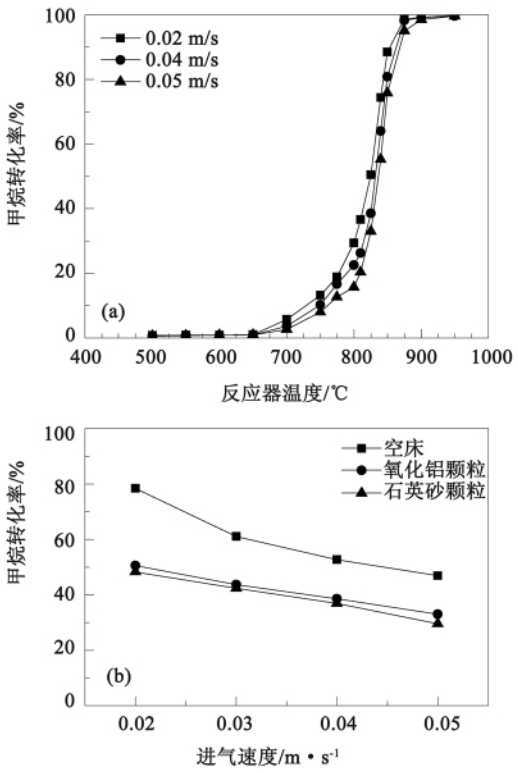

图 5 进气速度对甲烷转化率的影响

Fig. 5 Effect of the gas inlet velocity on the methane conversion rate

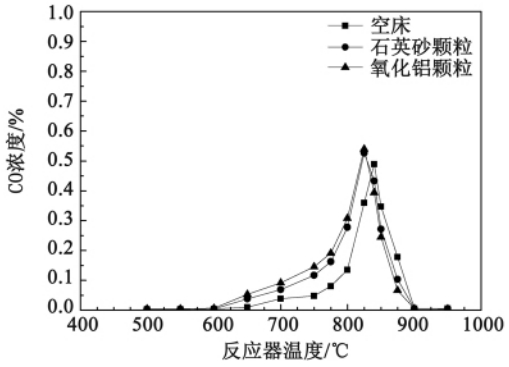

图 6 惰性颗粒对 CO 生成的影响

Fig. 6 Effect of the inert particles on the CO formation

3 结　论

通过对空床和惰性颗粒固定床内超低浓度甲烷的燃烧特性的对比实验研究,得到主要结论如下:

(1) 在反应温度较低时,几乎没有 CO_2 生成,CH_4 氧化生成了中间产物 CO,随着反应温度的升高,CO 逐渐被氧化为 CO_2;

(2) 惰性颗粒的加入提高了 CH_4 的着火温度,并在高温段抑制了甲烷的转换效率。床层温度在 750 ~850℃时,惰性颗粒通过破坏活性自由基抑制甲烷燃烧。床层温度高于 900℃时,惰性颗粒对燃烧的抑制作用几乎可以忽略;

(3) 随着进气速度的降低,床层温度的升高,甲烷转化率增大; 而改变甲烷初始浓度对甲烷转化率基本没有影响;

(4) 惰性颗粒对 CO 生成的影响明显,温度在 750 ~850℃时,CO 的排放浓度显著增加,并达到最大峰值。

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(陈　滨　编辑)

·书　讯·

《中国电气工程大典》出版

为反映我国电气领域最新的发展成就,传播电气领域最新的科学技术知识,由中国电力出版社联合中国电工技术学会、中国机械工程学会、中国电机工程学会、中国动力工程学会、中国水力发电工程学会五家学会历时五年多时间编撰出版了《中国电气工程大典》,共 15 卷,约 5000 万字,于 2010 年 4 月全部编辑出版完毕。

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石灰石分解特性及微观结构迁移规律研究 = Study of the Decomposition Characteristics of Limestone and the Law Governing the Migration of the Microscopic Structure [刊,汉] CHEN Hong-wei,CHEN Jiang-tao,WEI Ri-guang,SUO Xin-liang(College of Energy Power and Mechanical Engineering,North China University of Electric Power,Baoding,China,Post Code:071003) // Journal of Engineering for Thermal Energy & Power. - 2013,28(1). -73 ~77

By using a self-made thermogravimetric analyzer,a thermogravimetric test of the calcination and decomposition of limestone was conducted with the law governing the influence of temperature,calcination atmosphere and particle diameter on the decomposition process of limestone being obtained. Furthermore,by using a scanning electron microscope(SEM) and a specific surface area and porosity analyzer,the variation law governing the migration of the microscopic structure of the product obtained during the calcination and decomposition process was mainly investigated. The research results show that temperature is a key factor influencing the calcination of limestone,the higher the temperature,the quicker the reaction. The pressure component of carbon dioxide and an increase of the particle diameter can play a certain role in prohibiting the decomposition reaction of limestone. The specific surface area and pore volume of the product produced during the calcination of limestone will quickly increase with the continuation of the calcination. If going on calcinating after exceeding the time required for a total decomposition,the product of the calcination of limestone will begin to sinter,the specific surface area and pore volume will decrease. The original limestone has almost no pores. However,with the continuation of the calcination,micro-pore,middle-sized pores and big pores will emerge,assuming a dual-peak structure distribution. From the beginning to 2.5 min of the calcination,the middle-sized pores will increase in a relatively large quantity and during the time from 2.5 min to 6.5 min,the micro-pores and big pores will quickly come into being,however,the sintering will lead to a reduction of the number of the pores. **Key words:** limestone,decomposition characteristics,calcination reaction,microscopic structure

超低浓度甲烷在惰性颗粒中燃烧特性的实验研究 = Experimental Study of the Combustion Characteristics of Methane at an Ultra-low Concentration in Inert Particles [刊,汉] ZHANG Li,ZHENG Shi-wei,YANG Zhong-qing(Education Ministry Key Laboratory on Low-grade Energy Source Utilization Technology and System,Chongqing University,Chongqing,China,Post Code:400030) // Journal of Engineering for Thermal Energy & Power. -2013,28(1). -78 ~81

By adopting a test method,studied were the characteristics controlling the influence of inert particles on the combustion characteristics of methane at an ultra-low concentration and at the same time investigated was the law governing the influence of the inlet gas speed,inlet gas concentration and bed temperature on the conversion rate of methane. The test results show that when the reaction temperature is relatively low,there will be almost no carbon dioxide to be produced and the oxidation of CH_4 will produce an intermediate product CO. With a rise of the reaction temperature,the CO will be gradually oxidized to CO_2. An addition of inert particles will raise the ignition temperature of CH_4 and prohibit the conversion efficiency of methane in the high temperature section. A presence of inert particles will lower the temperature corresponding to the CO maximal peak value. With a decrease of the inlet gas speed and

an increase of the bed temperature, the conversion rate of methane will increase. However, to change the concentration of methane will basically have no influence on the conversion rate of methane. **Key words:** methane at an ultra-low concentration, inert particle, combustion, methane conversion rate

船用增压锅炉 NO_x 的生成机理及其排放量的近似计算方法 = NO_x Formation Mechanism of a Marine Supercharged Boiler and a Method for Approximately Calculating Its Emissions [刊,汉] QIN Xiao-yong, LI Jun (College of Power Engineering, Naval Engineering University, Wuhan, China, Post Code: 430033), ZHANG Xiao-dong (Scientific Research Department, Naval Engineering University, Wuhan, China, Post Code: 430033) // Journal of Engineering for Thermal Energy & Power. – 2013, 28(1). – 82 ~ 85

On the basis of analyzing the chemical reaction mechanism governing the NO_x formation in a marine supercharged boiler, presented was a method for approximately calculating the NO_x emissions of a marine supercharged boiler. The NO_x formation modes in a marine supercharged boiler mainly involve the thermal and fuel one. The NO_x formation amount in the thermal mode can be approximately calculated by using the effective temperature in the furnace, the equilibrium concentrations of N_2 and O_2 at the effective temperature of the furnace and the mean residence time of the combustion products in the furnace. The NO_x formation amount in the fuel mode can be approximately calculated by using the content of nitrogen in the fuel and the mean conversion rate of nitrogen. The furnace effective coefficient m″ is 0.9 and the mean conversion rate of the NO_x formation amount in the fuel mode is 0.36. The maximal error between the actually measured results and the calculated ones of the NO_x formation amount in the marine supercharged boiler is 5.6%, indicating that the method in question can meet the requirements for approximately estimating the NO_x emissions of a marine supercharged boiler. **Key words:** supercharged boiler, NO_x, emissions, approximate calculation method, effective temperature

不同配风方式下层燃炉煤层 NO_x 析出特性研究 = Study of the Precipitation Characteristics of NO_x in the Coal Bed of a Laminar Combustion Boiler Under Different Air Distribution Modes [刊,汉] DU Hai-liang, ZHANG Pin, LUO Yong-hao, LU Yi (Thermal Energy Engineering Research Institute, Shanghai Jiaotong University, Shanghai, China, Post Code: 200240) // Journal of Engineering for Thermal Energy & Power. – 2013, 28(1). – 86 ~ 92

The combustion characteristics of coal in large-sized particles in a laminar combustion boiler differ greatly from those of pulverized coal. To precisely master the law governing the precipitation of nitrogen element in a laminar combustion unit boiler, a contrast test of the precipitation characteristics of NO_x from the coal bed surface under different air distribution modes was performed. During the experiment, the NO_x concentrations and the O_2, CO_2, CO and H_2 concentrations on the coal bed surface of various coal ranks were tested and the data under different air distribution modes were compared and analyzed with the NO_x concentrations along the grate on the coal bed of a laminar combustion boiler featuring a dual peak distribution being obtained. Around 5 min after the boiler has been ignited from the coal bed, NO_x production formed its first peak value, the maximal peak value of the amount of NO_x formed from