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煤的模型化合物热解过程中HCN、NH_3的逸出规律

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摘　要：为了解煤燃烧过程中NO_x的生成机理，在600～1 400 ℃温度范围内，选取吡啶、吡咯为煤的含氮模型化合物，采取傅立叶红外光谱仪(Ft—Ir)和分光光度计连用方式，在等温连续式流动反应器中实验研究了模型化合物热解过程中HCN、NH_3的逸出规律。结果表明：HCN是模型化合物的热解产物中的主要含氮产物；吡啶、吡咯的HCN的转换率都随着温度的升高而增大；同温度下，吡咯的HCN生成率高于吡啶的HCN生成率，吡咯的NH_3生成率高于吡啶的NH_3生成率。

关　键　词：煤燃烧；氮；模型化合物；Ft-Ir

中图分类号：TQ534.9　　　文献标识码：A

1　前　言

煤是我国的主要能源，氮含量约0.5%～3%，在煤燃烧和气化时，氮元素转化为NO_x，严重污染人类生存环境[1～2]。为了更好控制NO_x的排放，煤燃烧过程中氮元素的迁徙规律受到了广泛的关注。由于燃烧过程中也是首先进行升温热解，至一定温度后才与O_2发生氧化反应。因此，研究煤燃烧初期——热解过程中氮元素的迁徙规律对整个NO_x的形成有着十分重要的意义。由于煤分子的复杂性以及其氮元素含量低，煤中的矿物质再热解时会起到催化作用，使得直接针对煤的机理研究变得困难，而采用模型化合物代替煤则能克服上述缺点，使其在机理研究中具有明显的优势[3]。

现有的XPS(X-ray Photoelectron Spectroscopy)和XPNES(X-ray Photoelectron Near Edge Spectroscopy)研究表明：煤中的氮元素主要以六元环吡啶氮、五元环吡咯氮、质子化吡啶和氮氧化物等形态存在。吡啶氮是较普遍的含氮形式，其含量随煤阶的增大而增加，一般为20%～40%，吡咯氮是煤中氮的主要存在形式，占氮总量的50%～80%[4]。也有研究表明：氮在镜质组中以吡咯和吡啶、在壳质中以氨基和吡啶、在惰质组中以氨基和吡咯形式存在[1]。所以，在NO_x形成的实验研究中，常用煤的模型化合物是一些简单的含氮杂环化合物，如：吡啶、吡咯、苯胺、喹啉、吲哚、咔唑等[5]。

模型化合物热解的前期研究中，研究结果是多样化的：Axworthy等人以吡啶、吡咯为模型化合物，得出HCN是主要产物，有NH_3生成；Sugiyama等人在吡啶热解实验中，NH_3是主要产物；Hämäläinen等人以咔唑为热解物质时，HCN、NH_3是主要产物[6]。

本实验选取吡啶、吡咯作为模型化合物，在600～1 400 ℃温度范围内，采用傅立叶红外光谱仪(Ft-Ir)和分光光度计连用，研究热解过程中HCN、NH_3的逸出规律。

2　实验装置和实验方法

2.1　实验系统

实验中，用恒定流量载气通过盛有模型化合物的容器，以此来实现微量进样。本实验选用纯度为99.999%的瓶装高纯氩气作为载气，流量500 mL/min，环境温度20 ℃，测得吡啶进样1.598 4 g/h，吡咯进样0.656 6 g/h；外径20 mm，总长900 mm的“U”形石英玻璃管作为反应器；加热炉选6 kW的SiC电炉，ZK—1可控硅温度控制器调节炉温。热解产物用Ft-Ir和分光光度计连用进行分析。实验中所用试剂均为分析纯，测量HCN使用的水为蒸馏水，测量NH_3中使用的所有水均为无氨水。实验时，从600～1 400 ℃，每50 ℃为一个测点，测量热解产物中HCN、NH_3的生成量。实验系统见图1。

2.2　Ft-Ir设备及测量原理

产物的检测在美国Perkin-Elmer公司生产的Spectrum One B型Ft-Ir上进行，分辨率4 cm^{-1}。使用10 cm玻璃气体吸收池，吸收池直径42 mm，取样时间5 min，选用CaF_2窗片，扫描范围900 cm^{-1}～4 000 cm^{-1}，扫描16次，扫描时间1 min。

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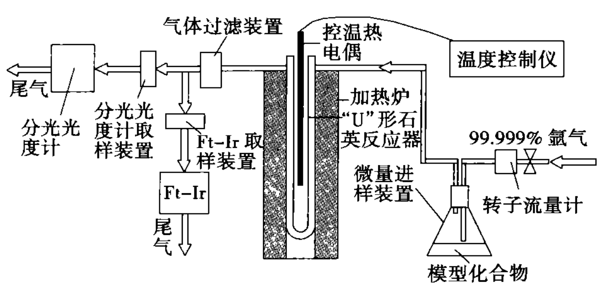

图1　实验系统示意图

2.3　分光光度计设备及测量原理

实验中用吡啶—巴比妥酸法比色法定量测量 HCN。选气泡式吸收管为吸收容器,10 mL 浓度为 1% NaOH 为吸收液,取样时间 2 min。吸收液稀释 10 倍后,依据 GB7487—87 滴定测量。测量时吸收波长 580 nm,采用 10 mm 比色皿。

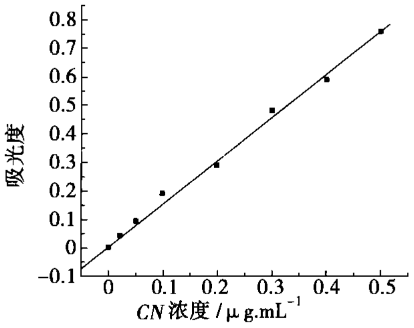

图2　CN 浓度与吸光度关系

次氯酸钠—水杨酸分光光度法定量测量 NH_3。测量 NH_3 中使用的所有水均为无氨水,气泡式吸收管为吸收容器,10 mL 浓度为 0.05 mol/L 硫酸为吸收液,取样时间 1 min。吸收液稀释至 50 mL,取 2 mL 到比色管,依据 GB/T14679—93 滴定测量。吸收波长 697 nm,采用 10 mm 比色皿。HCN 和 NH_3 的标准曲线如图 2(R=0.998 01)和图 3(R=0.998 31)所示。

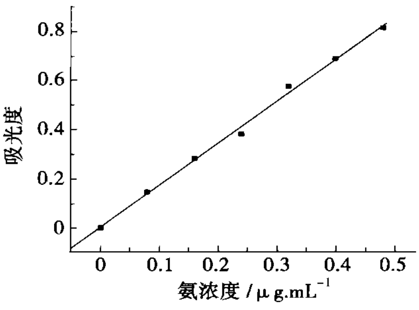

图3　氨浓度与吸光度关系

3　实验结果与分析

3.1　Ft-Ir 测量结果分析

图 4~图 5 分别给出了吡啶 1 100 ℃时的热解 Ft-Ir 图谱和吡咯 1 100 ℃时的热解 Ft-Ir 图谱,图中横坐标为波数(σ),纵坐标为透光率(T)。通过对图谱的解析以及与标准图谱的对比得出:图 4 和图 5 中 3 250 cm^{-1}~3 340 cm^{-1}处双峰,2 805 cm^{-1}处单峰,1 350 cm^{-1}~1 450 cm^{-1}间双峰同时存在,可以确定热解产物中含有 HCN;1 304 cm^{-1}、3 016 cm^{-1}处的单峰由热解产物 CH_4 产生;图 4 中 903 cm^{-1}与 966 cm^{-1}两个吸收峰可能由 NH_3 产生,但由于吸收峰太弱而且没有其它峰旁证,不能肯定产物中是否含有 NH_3,对产物中 NH_3 有无的进一步分析用分光光度法检测。

吡啶、吡咯热解产物的 Ft-Ir 分析表明,热解产物中主要含氮产物是 HCN。

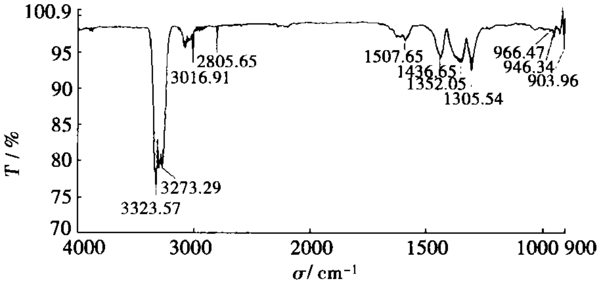

图4　吡啶 1 100 ℃时热解图谱

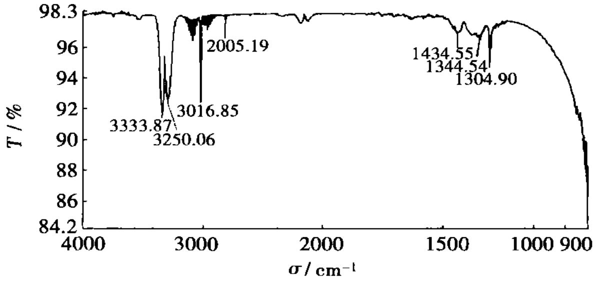

图5　吡咯 1 100 ℃时热解图谱

3.2　分光光度计测量结果分析

实验中,用次氯酸钠—水杨酸分光光度法进一步定性、定量测量产物中 NH_3,用吡啶—巴比妥酸法比色法定量测量 HCN 含量,取样时间 2 min。吡啶热解时取样时间内 HCN、NH_3 的生成量如图 6 所示,吡咯热解时取样时间内 HCN、NH_3 的生成量如图 7 所示。具体分析如下:

吡啶、吡咯热解产物中 HCN 含量随温度变化趋势相同,都随着温度升高而大幅增加,吡啶由 800 ℃时的 121.5 μg 增加到 1 380 ℃时的 1 890 μg。吡咯由

800 ℃时的 227.4 μg 增加到 1 380 ℃时的 1 283 μg。

模型化合物热解过程中确实释放出 NH_3，但是 NH_3 生成量远小于 HCN 生成量，同时二者随温度变化趋势也不同。吡啶热解产物中 NH_3 呈现随温度升高先下降，再升高；而吡啶热解产物中 NH_3 先随温度升高而下降，其后基本保持恒定值。吡啶 800 ℃时产物中 NH_3 含量 37.6 μg，900 ℃时达到最小值 22.2 μg，其后随着温度升高而增大，1 380 ℃时含量 30.6 μg。吡咯产物 800 ℃时 NH_3 含量 23.2 μg，随温度升高至 850 ℃时降至 13.1 μg，随后基本不变化。

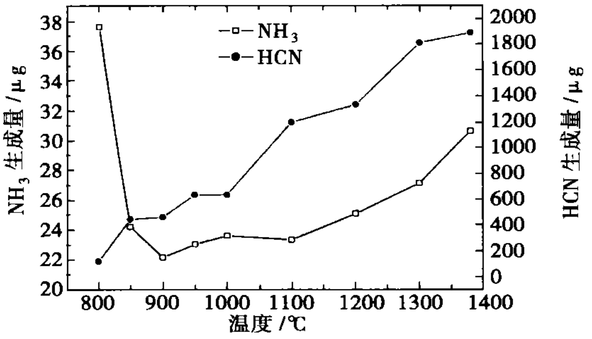

图 6 吡啶热解 HCN、NH_3 生成量

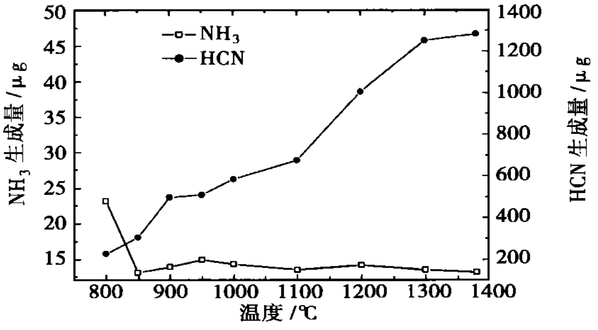

图 7 吡咯热解 HCN、NH_3 生成量

对热解产物进一步分析时引入生成率（P）。生成率的高低代表热解模型化合物时生成含氮产物（HCN、NH_3）的量的多少。生成率越高，热解相同质量模型化合物时产生含氮产物量越多。生成率的定义式：

$$P=\frac{\text{生成的 HCN 或}(NH_3)\text{中 N 的质量}}{\text{进入反应器的模型化合物中 N 的质量}}$$

吡啶、吡咯热解时的含氮产物生成率与温度关系如图 8 所示。吡啶热解时的 HCN 生成率远高于吡啶热解时的 NH_3 生成率，进一步说明模型化合物热解产物中的含氮产物主要是 HCN。相同温度下，吡咯热解时的 HCN 生成率高于吡啶热解时的 HCN 生成率，吡咯热解时的 NH_3 生成率高于吡啶的 NH_3 生成率。

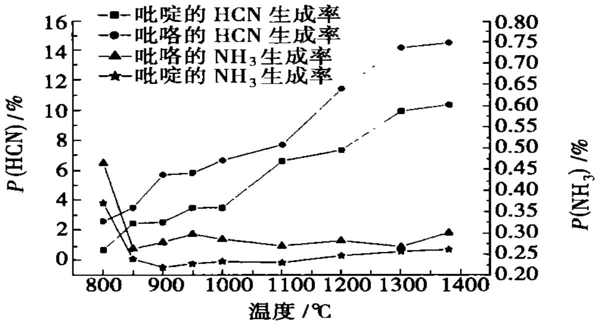

图 8 模型化合物的含氮产物生成率与温度关系

4 结 论

（1）吡啶、吡咯热解产物中能检测到的含氮化合物有两种：HCN 和 NH_3。

（2）HCN 的生成率远高于 NH_3 的生成率，HCN 是最主要含氮产物，是煤燃烧时生成的 NO_X 的主要中间产物。

（3）吡啶、吡咯的 HCN 生成率随温度升高而增大，吡啶从 800 ℃时的 0.668％增至 1 380 ℃时的 9.96％；吡咯从 800 ℃时的 2.58％增至 1 380 ℃时的 14.2％。

（4）相同温度下，吡咯的 HCN 生成率高于吡啶的 HCN 生成率，吡咯的 NH_3 生成率高于吡啶的 NH_3 生成率。

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By using gas in a steel cylinder to simulate flue gas during tests investigated was the impact on the dissolution rate of limestone exerted by the following factors: gas pH value and temperature of reaction in a micro-sized bubble bed and minute quantity of fluorine and chlorine ions in slurry. On the basis of mass action law and arrhenius equation a mathematical formula is proposed for calculating the limestone dissolution rate. With the physical meaning of various parameters being clarified it is possible to make a unified description of the limestone dissolution rate under various operating conditions. Meanwhile, various parameters of the dissolution rate of the limestone used during the tests were determined with a conclusion that the micro quantities of fluorine and chlorine ions are unfavorable to the dissolution of limestone. By making use of the model proposed by the authors it is feasible to compare the reactivity of different types of limestone and to design slurry tanks of appropriate size to suit various kinds of limestone. This is of great significance for the study of a wet flue-gas desulfurization process. **Key words**: limestone, dissolution rate, bubbling bed

闪蒸处理对石灰石脱硫性能的影响=**The Impact of Flash Evaporation Modification on the Desufurization Performance of Limestone Particles** [刊,汉] / CHEN Chuan-min, ZHAO Chang-sui, HAN Song, et al (Education Ministry Key Laboratory of Clean Coal Power Generation and Combustion Technology under the Southeastern University, Nanjing, China, Post Code: 210096) //Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). — 238~241

On a solid-particle pore diameter enlargement device constructed by the authors flash-evaporation modification tests on limestone particles were performed and an experimental investigation of calcination and desulfurization was carried out on samples in a gas-flow reactor. It is found that the flash-evaporation modification treatment may lead to an increase in limestone pore diameter. In addition, with the enlargement of limestone pore diameter the cross-linkage properties among the pores will be enhanced, resulting in a slight decrease in specific surface area. The pore diameter of calcination product CaO after the flash-evaporation modification of the limestone will shift in the direction of securing a larger pore size. In the meantime, due to the flash-evaporation modification the transport performance of the reaction gas has been significantly improved, thus decreasing the sintering effect in the calcination process. As a consequence, the specific surface area will be increased considerably. Under identical test conditions the desulfurization efficiency of samples after the flash-evaporation modification has been markedly enhanced. **Key words**: flash evaporation, modification, limestone, pore structure, desulfurization

不同煤种混煤燃烧时 NO_x 生成和燃尽特性的试验=**Experimental Research of the NO_x Generation and Burnout Characteristics During the Combustion of Blended Coals** [刊,汉] / WENG An-xin, ZHOU Hao, CEN Kefa (Research Institute of Thermal Energy Engineering under the Zhejiang University, Hangzhou, China, Post Code: 310027), ZHANG Li (Hunan Electric Power Prospecting and Design Institute, Changsha, China, Post Code: 410007) //Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). —242~245

The combustion characteristics of various coals (anthracite, lean coal and bituminous coal) and their blends were investigated in a one-dimensional sedimentation furnace. The impact on NO_x emissions of various factors was analyzed along with a discussion of the effect on burnout rate of different excess air factors, mixing/dilution ratios and the ratio of primary and secondary air. Test results indicate that when bituminous coal accounts for 25% of the blended coals the NO_x emissions are relatively low. In case of burning blended coals there emerged several NO_x emission peaks along the axis of the furnace, which are caused by the different characteristics of the coals taking part in the combustion. **Key words**: blended coal, NO_x emission, mixing/dilution ratio, burnout rate

煤的模型化合物热解过程中HCN、NH_3 的逸出规律=**The Law of HCN and NH_3 Escape during the Pyrolysis of Model Compounds of Coal** [刊,汉] / ZHAO Ke, TAN Hou-zhang, ZHOU Qu-lan, et al (Xi'an Jiaotong University, Xi'an, China, Post Code: 710049) //Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). —246~248

To understand the formation mechanism of NO_X during a combustion process, tests were conducted over the temperature range of 873-1 673 K by selecting pyridine and pyrrole as nitrogen-containing model compounds. With the combined use of a Fourier transform infrared spectrometer (Ft-Ir) and a spectrophotometer the law of HCN and NH_3 escape during the pyrolysis of model compounds was experimentally investigated in an isothermal continuous-flow reactor. The investigation results indicate that HCN is the main nitrogen-containing product in the pyrolysis products of model compounds. The conversion rate of pyridine and pyrrole will increase with a rise in temperature. Under a same temperature the HCN formation rate of pyrrole is higher than that of pyridine and the NH_3 formation rate of pyrrole is higher than that of pyridine. **Key words**: coal combustion, nitrogen, model compound, Fourier transform infrared radiation analyzer

氧化钙添加剂对烟气中汞分布的影响= **The Impact of CaO Additive on Mercury Distribution in Flue Gases** [刊, 汉] / WANG Quan-hai, QIU Jian-rong, YANG Jian-feng, et al (National Key Laboratory of Coal Combustion under the Huazhong University of Science & Technology, Wuhan, China, Post Code: 430074) //Journal of Engineering for Thermal Energy & Power. — 2004, 19(3). — 249~251.

Under the condition of one atmospheric pressure and within a temperature range of 273.15-1 273.15 K the impact of CaO and HCl formed during a combustion process on the morphology and distribution of trace element mercury was investigated through the use of an analytical method based on chemical thermodynamic-equilibrium. The results of the analysis indicate that elemental mercury is the main form of the mercury in the maximum temperature zone of coal combustion. With the reduction of temperature in flue gases the elemental mercury will undergo a chemical reaction, resulting in the formation of a bivalent mercury compound, which mainly assumes the form of $HgCl_2$(g). The results being forecast also show that an increase in chlorine elements can lead to an increased evaporation and emission of the mercury element. On the other hand, CaO(s) does not exercise a great influence on the behavior characteristics of mercury in the flue gases. There exists a relatively great difference between the results of chemical thermodynamic-equilibrium analysis and those of experiments. In spite of this, a comparison of the two sets of results still allows one to conclude that the CaO(s) has influenced the distribution characteristics of mercury element in the flue gases. This has been brought about mainly through a decrease in ash-particle surface area and/or a change in fly ash mineralogical and morphological features. **Key words**: coal, mercury, CaO, morphology

流化床部分煤气化实验研究= **Experimental Study of Coal Partial Gasification in a Fluidized Bed** [刊, 汉] / ZHOU Hong-cang, JIN Bao-sheng, ZHONG Zhao-ping, et al (Education Ministry Key Laboratory of Clean Coal Power Generation and Combustion Technology under the Southeastern University, Nanjing, China, Post Code: 210096) //Journal of Engineering for Thermal Energy & Power. — 2004, 19(3). — 252~255

On a small-sized coal partial-gasification test facility for a fluidized bed gasification tests of three kinds of coal were carried out under different operating conditions (namely, different coal feed rate, fluidized air flow rate and steam feed rate) with air and steam serving as gasifying agents. The results of the test show that the bed temperature decreases with an increase in coal feed rate and steam flow rate and also with a decrease in fluidized air flow rate. Within a certain range the CO content in gas will increase with an increase in coal feed rate, fluidized air flow rate and steam flow rate and also with a decrease in gasification degree. H_2 content in the gas will decrease with an increase in coal feed rate and gasification degree and also with a reduction in fluidized air flow rate and steam flow rate. CH_4 content will increase with an increase in coal feed rate, and will decrease with an increase in fluidized air flow rate, steam flow rate and gasification degree. Moreover, with a higher gasification degree the heating value of the generated gas will decrease. **Key words**: fluidized bed, coal partial gasification, experimental study

循环流化床中石油焦与煤混合燃烧温度场研究= **A Study of the Temperature Profile Resulting from the Mixed Combustion of Petroleum Coke and Coal in a Circulating Fluidized Bed** [刊, 汉] / WANG Wen-xuan, ZHANG Shou-yu, YUE Guang-xi (Department of Thermal Energy Engineering, Tsinghua University, Beijing, China, Post Code: 100084), ZHAO Chang-sui (Research Institute of Thermal Energy Engineering under the Southeastern University, Nan-