Conversion Mechanism of Toxic Hydrogen Cyanide by Magnesium Oxide at High Temperatures

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Hydrogen cyanide (HCN) is the most important precursor of NOx in coal combustion and is also a high toxic production in coal chemical industry. In the present study, investigations on HCN converting using magnesium oxides was carried out in a fixed bed at 300-1273 K and the original HCN was produced by the pyrolysis of pyridine. Effects of temperature, volume space velocity and initial HCN concentration on HCN conversion were considered. Results showed that temperature was the major factor affecting HCN conversion and it undergoes different conversion mechanism in different temperature scale. With the formation of CO at 723 K, HCN started to decrease and kept a constant value from 873 to 973 K. After 973 K, HCN decreased significantly and CH_4 from the pyrolysis of pyridine also decreased, but CO disappeared at 973 K. When temperature was higher than 1123 K, HCN was converted totally. In the isothermal experiments, N_2 was detected at 1123 K but not at temperatures lower than 923 K and the nitrogen element in N_2 was equal to that in the removal of HCN. It indicated that below 973 K MgO removed HCN by the pathway $MgO + 2HCN \rightarrow MgCN_2 + CO + H_2$. However, MgO acted as catalyst at above 973 K and HCN was converted to N_2 by the reaction $2C_xY_y + 2HCN \xrightarrow{\text{MgO}} N_2 + (y+1-z)H_2 + 2C_{x+1}H_z$.

Keywords: Pyridine, HCN, MgO, Temperature, Coal.

INTRODUCTION

Emission of nitrogen oxides from solid fuel combustion causes significant threat to the environment[1]. Considerable investigations have indicated that metal elements play important role in forming nitrogen oxides[2-6]. Some studies indicate that metal element causes a significant decrease of N_2O in fluidized bed combustion[7,8], while others argue that the influence is little[9]. The effect of metal elements on the emission of nitrogen oxides from coal combustion is still confusing.

Compared with abundant researches on the direct effect of metal elements on nitrogen oxides, less attention has been paid on the mechanisms related to the effect of metal element on the hydrogen cyanide, which is recognized as a predominant intermediate precursor of nitrogen oxides in converting of nitrogen in coal[10-12]. Coal nitrogen including volatile nitrogen and char nitrogen translates into HCN firstly in the process of combustion and then HCN reacts with O_2 to form nitrogen oxides, additionally, HCN can also reacted with nitrogen oxides and produced N_2 by reburning.

In the process of coal pyrolysis or gasification, the calcium oxide additive inhibits HCN formation but promotes the nitrogen in coal conversion to N_2 efficiently[13-21]. Therefore, the demonstration on the reaction mechanism between metal element and HCN is helpful to understand how metal element affects the emission of nitrogen oxides. Meanwhile, due to massive HCN from the coal chemical industry results in heavy toxicity, further study on the characterization of HCN reduction by metal element may also provide a new approach to solving the problem of HCN pollution[22].

On the basis of previous study on the characteristics of HCN removal using CaO[23], the present study mainly focuses on the mechanism of HCN converting by magnesium oxide, which is one of the low cost alkaline earth species. The effects of temperature, volume space velocity and initial HCN concentration are discussed. The original HCN was generated by the pyrolysis of pyridine and gaseous species (CO, HCN, H_2, CH_4 and N_2) were monitored quantitatively by using a Fourier transform infrared spectroscopy gas analyzer coupled with the gas chromatography.

EXPERIMENTAL

Concentrations of HCN, NO, N_2O, CO and CH_4 in flue gas were detected on-line by DX-4000 FT-IR gas analyzer (1.07 L gas analysis cell with a path of 5 m, resolution of 8 cm^{-1}, response time < 120 s, wave-number range of 4200-900 cm^{-1} and scan frequency of 10 spectra/s), made in Helsinki. The lowest detectable concentration was 1 ppm and the estimated
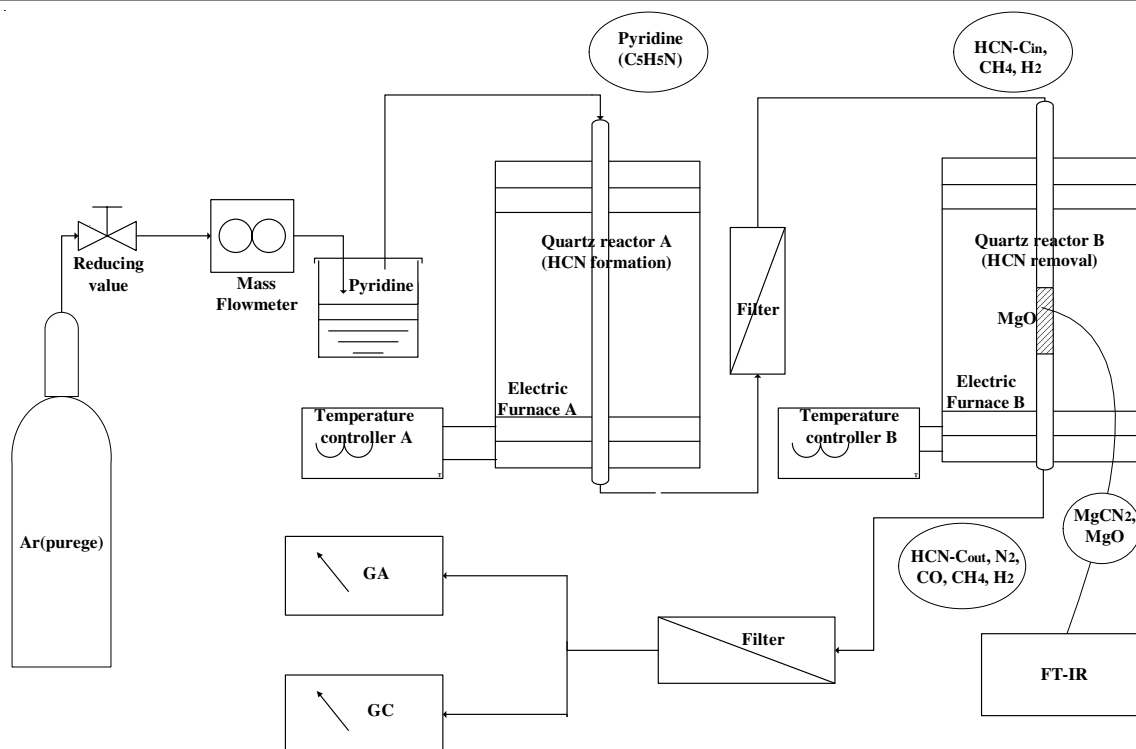
Fig. 1. Schematic diagram of experimental system for HCN formation and conversion

uncertainly limits of measurements were estimated to be within ± 2 %. Agilent-9800 GC (thermal conductivity detector, stationary phase of 5A molecule sieve, carrier gas of argon, column of 4 mm × 5 m, column temperature of 341 K) was used to quantify the concentration of H_2 and N_2.

HCN preparation (pyrolysis of pyridine): HCN is high toxic and is difficult to obtain its standard concentration gas, meanwhile, in the pyrolysis of the pyridine, HCN is generally believed to be the most important nitrogen-containing product[24]. Therefore, in the presented work, pyridine has been chosen as the source of HCN and pyrolysis of pyridine was performed in quartz reactor A at 1273 K. As shown in Fig. 1, volatile pyridine in vessel was carried out by high-purity argon (> 99.999 %). In order to guarantee the constant sample quantity, the flow rate of argon was controlled stable at 600 mL/min by mass flow meter. The long-time detection for HCN proved that the yield of gaseous species was stable and pyrolysis of pyridine can provide reliable HCN for the followed experiment of HCN removal. Before entering reactor B, the gaseous products from pyridine pyrolysis passed through a filter filled with $CaCl_2$ to remove water steam and residual pyridine from reactor A.

HCN converting by MgO: The experiment of HCN converting was carried out in quartz reactor B, which was 20 mm in inner diameter and 1000 mm in length. The electric furnace with a SiC tube as electrothermal element supplied heat to the reactor and could continuously work at temperature as high as 1473 K and the constant-temperature heating zone was longer than 600 mm. A Ni-Cr/Ni-Si thermocouple controlled by SHIMADEN FP93 PID regulator was used to measure the reaction zone temperature with a precision of ± 2 K. Analytically pure MgO powder that was squeezed in the mold at 5 MPa for

5 min and then crushed and sieved to 1.0-1.7 mm, was placed on an orifice in the middle of the reactor B.

RESULTS AND DISCUSSION

Conversion mechanisms of HCN under different temperature scales: Fig. 2 illustrates the effect of temperature on the outlet concentration of HCN (C_{out}), CO and CH_4 in the temperature programmed experiments under the condition that initial HCN concentration (C_{in}) was around 232 ppm and MgO stacking thickness was 12 mm.
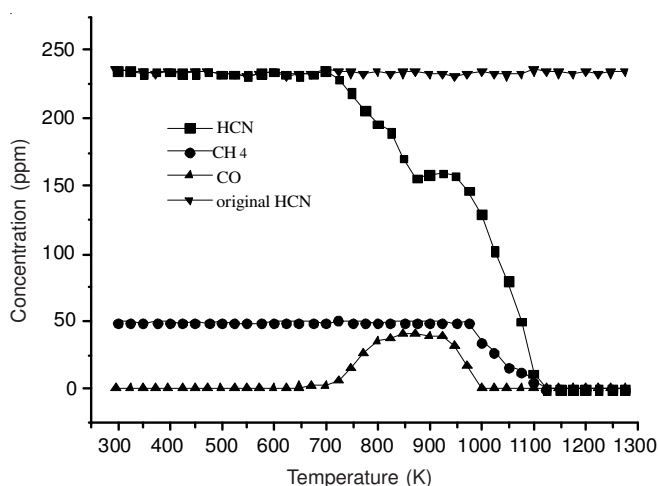

Fig. 2. Profile of gaseous species (HCN, CH_4, CO) at different temperatures

Fig. 2 showed the reduction of HCN started at 723 K. When the temperature increased to 873K, C_{out} decreased to 156 ppm and kept unchanged from 873 to 973 K. When the temperature further increased to 1123 K, C_{out} sharply fell to

0 ppm. In response to HCN reduction, the formation of CO also began at 723 K, but CO only existed in the region of 673-973 K. Lagging behind the change of HCN and CO, CH$_4$ did not decrease up to 973 K and fell to 0 ppm at 1123 K along with the further decrease in HCN.

Table-1 shows the profile of gaseous species at three typical temperatures (723, 923 and 1123 K) in isothermal experiments. Hydrogen mainly formed by pyridine pyrolysis in reactor A and accounted for the highest percentage. With the increase in temperature, the concentration of H$_2$ continued to rise. At the lower temperature of 723 and 923 K, N$_2$ was not present. When the temperature increased to even higher than 1123 K, the amount of nitrogen in form of N$_2$ was nearly equal to that in the initial HCN and there was no CH$_4$ and CO, which might mean that all the HCN had been converted to N$_2$. At 923 K, although HCN had decreased to 159 ppm, there was no formation of N$_2$. It was estimated that HCN may react with MgO to form MgCN$_2$ on the basis of previous study[23].

TABLE-1
PROFILES OF GASEOUS SPECIES AT THREE TYPICAL
TEMPERATURES DETECTED USING FTIR AND GC

| Temp. (K)	Inlet conc. of HCN (ppm)	Outlet conc. of several species (ppm)				
		HCN	CH$_4$	H$_2$	N$_2$	CO
723	232	229	50	525	0	7
923	232	159	53	573	0	41
1123	232	0	0	886	125	0

Results from Fig. 2 denote that MgO was highly efficient to remove HCN at high temperatures. Table-1 has also demonstrated that the components of gas species changed significantly at different temperatures, which indicates that the reaction mechanism between MgO and HCN may change with temperature.

CO existed only in the range of 673-973 K. Because experiments were performed in the inert atmosphere, there was no oxygen whether in pyridine or in its pyrolytic products from reactor A, so the oxygen in CO could only come from MgO.

At a lower temperature of 923 K, HCN concentration decreased, but there was no other nitrogen-containing species detected. Then the other nitrogen was suggested in the solid residues. Therefore, HCN and MgO might react by eqn. 1:

$$MgO + 2HCN \rightarrow MgCN_2 + CO + H_2 \qquad (1)$$

However, when the temperature increased to higher than 973 K, CO disappeared, CH$_4$ began to fall and HCN also started its second round decrease (Fig. 2). When the temperature was higher than 1123 K, HCN, CO and CH$_4$ disappeared totally and there were only H$_2$ and N$_2$ detected. It is concluded that at a temperature higher than 923 K, all the nitrogen in HCN had been transformed into N$_2$, there was no nitrogen left in solid residues. As seen from Table-1, at 1123 K the change of HCN concentration between inlet and outlet was 232 ppm and the outlet N$_2$ concentration was 125 ppm. Consequently, at higher temperature 1123 K the ratio of HCN/N$_2$ was probably equal to 2:1 and the reaction mechanism of HCN and MgO at a higher temperature was presumed to be like eqn. 2:

$$2C_xY_y + 2HCN \xrightarrow{MgO} N_2 + (y+1-z)H_2 + 2C_{x+1}H_z \quad (2)$$
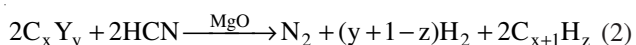
where C$_x$H$_y$ and C$_{x+1}$H$_z$ only refer to a general designation of hydrocarbon before and after passing through the MgO layer in reactor B, because the species of hydrocarbon from pyridine pyrolysis in reactor A were complex and there was only CH$_4$ detected and analyzed representatively in the process of experiments. This is similar to the conclusion that CaO catalyzes an efficient conversion reaction of char-nitrogen to N$_2$[9,25].

Effect of volume space velocity (SV) and initial HCN concentration (C$_{in}$) on the converting of HCN: To characterize the effective time of HCN passing through the MgO layer, volume space velocity (h^{-1}) was calculated by eqn. 3.

$$SV = \frac{Q}{V} \qquad (3)$$

where Q is the carrier gas flow rate (m^3/h), V is the stacking volume (m^3).

The converting rate of HCN was defined as η$_{HCN}$ according to the difference between C$_{in}$ and C$_{out}$ of reactor B by eqn. 4.

$$\eta_{HCN} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \qquad (4)$$

The effect of SV on η$_{HCN}$ were carried out with stable argon flow rate (600 mL/min) and C$_{in}$ (234 ppm) at 1123 K. It could be seen from Fig. 3 that with increased SV, η$_{HCN}$ decreased. HCN could be totally converted when the value of SV is lower than 10000 h^{-1}.
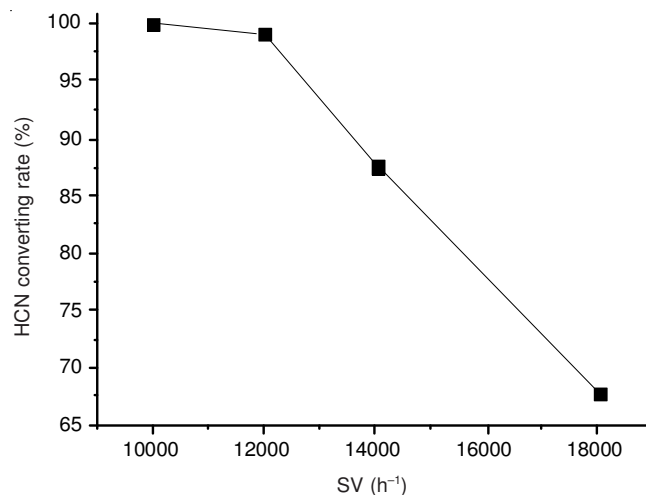

Fig. 3. Effect of volume space velocity on the coverting rate of HCN

Meanwhile, the effect of SV on the critical temperature, at which the η$_{HCN}$ was 100 %, was illustrated in Fig. 4. It could be seen that with the increasing in SV, the minimum temperature of HCN complete converting increased. In addition, the effect of C$_{in}$ on η$_{HCN}$ were carried out with stable SV (10000 h^{-1}) at 1123 K. Table-2 showed that the η$_{HCN}$ was over 99 % and even 100 %. The HCN could be converted totally with stable SV (10000 h^{-1}) at 1123 K.

TABLE-2
RELATION BETWEEN HCN CONVERSION
RATE AND INITIAL HCN CONCENTRATION

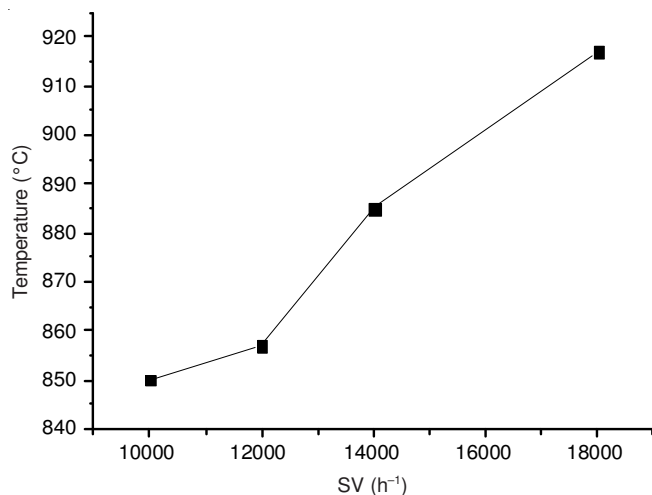| C$_{in}$ (ppm)	123.5	243	305	371.4	462.3	501
η$_{HCN}$ (%)	99.17	100	100	100	100	100

Fig. 4. Effect of volume space velocity on the minimum full converting temperature (η_{HCN} was 100 %)

Conclusion

The effects of temperature, volume space velocity (SV) and initial HCN concentration on the removal of HCN using MgO are investigated and the main conclusions are summarized as:

• The conversion of HCN starts at 723 K and keeps unchanged from 873 to 973 K. When the temperature further increases to 1123 K, HCN disappears. In response to HCN reduction, the formation of CO also begins at 723 K, but CO only exists in the region of 673-973 K. Methane does not decrease until 973 K and disappears at 1123 K. Nitrogen gas is detected until 1123 K and the nitrogen in N_2 was just equal to that in the removal of HCN.

• The mechanism of HCN removal varies at different temperature scales. At a lower temperature than 923 K, the mechanism of HCN removal is indicated as:

$$MgO + 2HCN \rightarrow MgCN_2 + CO + H_2$$
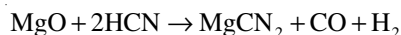
However, when the temperature is higher than 973 K, the reaction mechanism between HCN and MgO is

$$2C_xY_y + 2HCN \xrightarrow{\text{MgO}} N_2 + (y+1-z)H_2 + 2C_{x+1}H_z$$
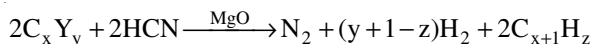
• With the increased volume space velocity the HCN removal efficiency decreases, while the minimum temperature at which HCN can be totally removed increases. Additionally, HCN removal efficiency can reach up to 100 %.

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