Simulation Study on Urea Thermal Decomposition for SCR Process of Thermal Power Plant

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Abstract. Urea was used for SCR reducer in many power plants, but its pyrolysis process was very complex, and this process was showed by the TGA-DSC experimental results. An effective method for urea-water solution thermal decomposition was investigated in this paper. The factors of temperature, O₂ concentration and catalyst had been mainly studied and analyzed. It can be concluded that in range of 200-650 ℃, with temperature increasing, the NH₃ conversion rate increased, HNCO could be hydrolyzed to produce NH₃ and CO₂ when temperature was higher than 400 ℃, and the NH₃ conversion rate was higher than 50%, and the maximal NH₃ conversion rate was 85.1% when temperature was 650 ℃; NH₃ conversion rate decreased with O₂ concentration in carrier gas increasing. More NH₃ was produced by hydrolysis of HNCO on SCR catalyst below 400 ℃, because the hydrolysis of HNCO took place at temperature lower than 400 ℃ mainly, however, the promotion of catalyst for hydrolysis of HNCO was not observed at higher temperature.

1. Introduction

Selective catalytic reduction (SCR) is presently the most effective technique for removing nitric oxides (NOx) in thermal power plants due to its high selectivity, good efficiency and economic characteristics [1, 2]. NH₃ is employed as reducing reagent mainly in SCR, reactions between the NOx and the introduced NH₃ take place and produce H₂O as well as N₂ according to the following reactions [3]:

\[
\begin{align*}
4NO + 4NH₃ + O₂ & \xrightarrow{\text{Catalyst}} 4N₂ + 6H₂O \\
2NO₂ + 4NH₃ + O₂ & \xrightarrow{\text{Catalyst}} 3N₂ + 6H₂O
\end{align*}
\]

However, because of difficulties in its storage, handling, and transportation, NH₃ might not be the most suitable reducing reagent for SCR, and it is often replaced by urea due to its nontoxicity in practice, without requirement of special safety precautions for handling and storage [4]. With the character of moisture absorbing, urea is generally transported in bagged manner in small amount. It is a challenge that plenty of urea need to be transported by vehicles for SCR process, but the urea transportation in bulk developed in China will be a good solution. At present, the urea pyrolysis process has been applying in many power plants to replace the original liquid ammonia evaporation process gradually in China.

The urea solution used in SCR process decomposes into NH₃ in the condition of high temperature, and the reaction processes are considered as follow: when urea solution is atomized into the high-temperature gas stream, the primary step for the decomposition is the evaporation of water from the droplets of urea solution.
Pure urea is then thermally decomposed into NH₃ and isocyanic acid (HNCO).

\[ H₂N – CO - NH₂(aq) \rightarrow H₂N – CO - NH₂(l or g) + xH₂O \]  

\[ H₂N – CO - NH₂(l or g) \rightarrow NH₃(g) + HNCO(g) \]  

HNCO is quite stable in the gas phase, but it is easily hydrolyzed on the surface of metal oxides, producing NH₃ and CO₂.

\[ HNCO(g) + H₂O(g) \rightarrow NH₃(g) + CO₂(g) \]

In theory, 1 mol of urea decomposes completely to produce 2 mol of NH₃ and 1 mol of CO₂.

However, the process of urea thermal decomposition is quite complicated. It includes many intermediate reactions and also produces many by-products, including biuret, cyanuric acid (CYA), ammelide, ammeline and melamine in the decomposing residue. Schaber et al. [5-7] investigated the thermal decomposition of urea in the range of 50-600 °C, and they confirmed that there were biuret, cyanuric acid (CYA), ammelide, ammeline and melamine in the decomposing residue. Koebel et al. [8] got similar results, and the character of high reaction activity of HNCO which could react with some intermediate products to form more complex compounds was confirmed. Chen et al. [9] analyzed the urea thermal decomposition by simultaneous TGA (thermogravimetric analysis) and MS (mass spectroscopy), concluded that the products included NH₃, HNCO, CO₂ besides the aforesaid compounds.

As an important and active by-product, HNCO is not beneficial to urea thermal decomposition, and the formation of NH₃ which is the target product of this reaction will also be affected. Yang et al. [10] studied the influence of H-ZSM₅ catalyst which was added into the thermally decomposing urea. The concentration of NH₃ in gas stream with catalyst was higher than that without catalyst, while the concentration of HNCO was lower. Sullivan et al. [11] found that the concentration of HNCO produced by thermal decomposition of urea-water solution with catalyst was rather low in low-temperature condition, and Sluder et al. [12] found that the HNCO in thermally decomposing gas stream of urea-water solution with SCR catalyst was undetected.

In the present study, thermally decomposing process of urea powder was studied by simultaneous TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). The experiments of urea-water solution thermal decomposition were taken by simulated experimental equipment in the conditions of varying temperature and O₂ concentration, and a massive SCR catalyst was used to investigate the catalysis in thermal decomposition of urea-water solution. These results could have some value for the application of urea-SCR in thermal power plants.

2. Experimental Approaches

2.1. Thermal Decomposition of Urea

Urea was obtained from Bei Jing Kang Pu Hui Wei Technology Co., Ltd (99% pure, ACS reagent grade). 12.673 mg urea powder was weighted and placed into an Al₂O₃ crucible, the thermally decomposing process was analyzed by a TGA-DSC analyzer (Netzsch STA-449F3, Germany). The sample was heated at 10 °C·min⁻¹ in range of 20-750 °C under N₂(g) purge.

2.2. Thermal Decomposition of Urea-Water Solution

The experimental set-up for urea-water solution thermal decomposition was showed in figure 1: 2.23 mol·L⁻¹ urea-water solution was continuously fed into the reactor system, and the feed rate of the solution was 0.75 mL·min⁻¹. The carrier gas was mixture gas of N₂ (99.99%) and O₂ (99.5%), and the velocity of carrier gas was 2500 mL·min⁻¹. The O₂ concentrations were 0, 1, 2, 5, 8 or 10 vol-%. The experiment with SCR catalyst was 100 vol-% N₂. The reaction temperature was varied from 200°C to 650 °C in steps of 50 °C. To analyze the NH₃ produced during the decomposition reaction, part of the reacted gas was passed through a series of absorption bottles each containing 100 mL of 0.02 mol·L⁻¹ HCl solution. Three absorbing bottles were employed, and the flow of reacted gas absorbed was 200
mL·min⁻¹, absorption time was 20 min. Then the concentration of ammonium ion (NH₄⁺) in absorption solution diluted was detected by ion chromatograph (Dionex ICS-3000, America), and the NH₃ concentration of reacted gas was calculated by NH₄⁺ concentration.

2.3. Catalyst Characterization
Three catalysts were characterized by X-ray diffraction (XRD, PANalytical B.V., Holland) and scanning electron microscope (SEM, Hitachi S-4800, Japan), a fresh catalyst, 1# catalyst used in 200-500 °C and 2# catalyst used in 500-650 °C. The sizes of 3 catalysts all were 5 cm×2 cm×2 cm (length, width and height, respectively). Measurements were carried out in the 2θ range from 10° to 80° using a step size of 0.026° with a time per step of 15 s, using Cu Kα radiation.

Figure 1. Experimental set-up for urea-water solution thermal decomposition. (1) Mass flow controllers; (2) carrier gases; (3) gas mixer; (4) solution storage tank; (5) peristaltic pump; (6) preheater; (7) reactor; (8) temperature control system; (9) condenser; (10) alkaline dryer; (11) NH₃ absorption bottles; (12) bottle for tail gas treatment.

3. Experimental Results

3.1. TGA-DSC Analysis
The TGA-DSC data of urea thermal decomposition was obtained by experiment and is showed in figure 2. Urea “critical temperatures”, defined as those temperatures corresponding to plateau regions, points of mass changing rapidly, or where phase changes were known to take place (melting points, etc.), were identified from the TGA-DSC plot. At 133 °C, solid urea melting occurred [13], and there was an obvious endothermic peak on the DCS curve. From room temperature to its melting point, little mass loss (0.50%) was observed. From 140 °C to 240 °C, urea mass decreased significantly, the mass loss was about 65%. In this region, DCS curve changed significantly as well, it indicated plenty of heat was absorbed. After 240 °C, the TGA curve got through a stationary region. From 300 °C to 350 °C, a second mass decreasing rapidly was observed, about 21% urea was vaporized. Meantime, much heat was absorbed. The rest urea decomposed slowly and completely after 350 °C.

3.2. Influence of Temperature on Urea-Water Solution Thermal Decomposition
The data of concentration and conversion rate of NH₃ in reacted gas was obtained and is showed in figure 3. With temperature increasing, the concentration of NH₃ in reacted gas increased, therefore, the NH₃ conversion rate increased. In range of 200-650 °C, the NH₃ conversion rate was affected by
temperature significantly, with the maximal 85.1% (650 °C), the minimal only 27.2% (200 °C). When temperature was 350 °C, the products of urea decomposition were NH₃ and HNCO mainly, and the NH₃ conversion rate was considerably high. HNCO could be hydrolyzed to produce NH₃ and CO₂ when temperature was higher than 400 °C [1], and the NH₃ conversion rate was higher than 50%.

![Figure 2. TGA-DSC curves of urea thermal decomposition.](image)

**Figure 2.** TGA-DSC curves of urea thermal decomposition.

**Figure 3.** Concentrations and conversion rates of NH₃ (100 vol-% N₂).

### 3.3. Influence of O₂ on Urea-Water Solution Thermal Decomposition

The NH₃ concentrations and conversion rates under various O₂ concentrations are showed in figures 4 and 5. Various O₂ concentrations took different influence, the increasing influence was taken by increasing O₂ concentration in 1-10 vol-%. The NH₃ concentration and conversion rate decreased substantially when O₂ concentration was higher than 5 vol-%. Even at 650 °C, the NH₃ conversion rate was only about 60% when O₂ concentration was higher than 8 vol-%.

![Figure 4. NH₃ concentrations under various O₂ concentrations.](image)

**Figure 4.** NH₃ concentrations under various O₂ concentrations.

![Figure 5. NH₃ conversion rates under various O₂ concentrations.](image)

**Figure 5.** NH₃ conversion rates under various O₂ concentrations.

### 3.4. Influence of Catalyst on Urea-Water Solution Thermal Decomposition

The NH₃ concentrations and conversion rates with and without SCR catalyst are showed in figures 6 and 7. It seemed that the influence of catalyst on urea-water solution thermal decomposition was existent but not very significant, when the temperature was lower than 400 °C, the NH₃ concentrations and conversion rates increased when SCR catalyst was used, while decreased a little in 400-650 °C. Some HNCO was hydrolyzed to produce NH₃ on catalyst in lower temperature while the promotion did not work in higher temperature, Fang et al. [6] confirmed that the catalytic hydrolysis of HNCO on catalyst took place in early stage of urea thermal decomposition, and the urea thermal decomposition could be promoted, but in later stage, this effect was not significant.

The results of 3 catalysts characterization are showed in figures 8 and 9. Figure 8 presents the X-ray diffraction patterns of fresh, 1# and 2# catalyst, it is observed that the 3 patterns are consistent with each other almost. And the SEM micrographs of 3 catalysts in figure 9 confirm that the property
of 1# and 2# catalyst did not change comparing with fresh one, since the aggregation of single particles on the surface of the used catalysts had not been caused by thermal treatment. So it can be concluded that the activity of catalyst was not affected in the process of urea-water solution thermal decomposition, and the decreasing of NH₃ concentration in reacted gas was not related to activity changing of catalyst.

Figure 6. NH₃ concentrations with and without SCR catalyst.

Figure 7. NH₃ conversion rates with and without SCR catalyst.

Figure 8. X-ray diffraction of fresh, 1# and 2# catalyst.

Figure 9. SEM micrographs of fresh, 1# and 2# catalyst.

4. Discussions

Three regions of mass loss were observed in TG curve significantly, the quality of urea decreased in the first region of 140-240 °C and the second region of 300-350 °C mainly, with about 65% and 21% mass loss in these two regions. In the first region, two endothermic peaks of DSC curve were quite significant and symmetric, it indicated that the reaction of urea thermal decomposition was rapid and uniform. After this region, slow reaction of urea thermal decomposition was observed. All the solid urea decomposed completely until temperature reaching 550 °C.

In the process of urea-water solution thermal decomposition, low NH₃ concentration in reacted gas was detected and low NH₃ conversion rate was obtained in the early stage. With temperature increasing, NH₃ concentration and conversion rate increased, the NH₃ conversion rate was higher than 50% when temperature reached 400 °C. The maximal NH₃ conversion rate was 85.1% when temperature was 650 °C. It was observed that most of urea decomposed when temperature was lower than 400 °C from the result of thermochemical experiment, but low NH₃ conversion rate was obtained in this temperature region, since many intermediates were produced and a spot of them were converted into NH₃. When temperature increased, more intermediates composed to produce more NH₃, causing higher NH₃ concentration and conversion rate in higher temperature. The NH₃ concentration and conversion rate were affected by O₂ in carrier gas in some extent. Some products could be oxidized to
form CO₂, NO, N₂O and other products in the process of urea-solution thermal decomposition, that leading to decreasing of NH₃ concentration and conversion rate.

Because of hydrolysis of HNCO on SCR catalyst (reaction 5), the NH₃ conversion rate increased comparing with the condition without SCR catalyst, and the hydrolysis of HNCO took place at temperature lower than 400 °C mainly. In 400-650 °C, most HNCO had been converted into NH₃, the matters keeping decomposing were those intermediates which were less than that produced in the condition without SCR catalyst. Therefore, the NH₃ conversion rate decreased in this region.

5. Conclusions
The decomposition efficiency of urea increased with temperature increasing, urea decomposition was fast and total when temperature was above 300 °C. In the range of 200-650 °C, NH₃ concentration in reacted gas and NH₃ conversion rate of urea-water solution thermal decomposition increased significantly with temperature increasing, and the maximal NH₃ conversion rate was 85.1%. O₂ in carrier gas was another factor affected the urea-water solution thermal decomposition, since some reaction products were oxidized by O₂. More NH₃ was produced by hydrolysis of HNCO on SCR catalyst below 400 °C, however, the promotion of catalyst for hydrolysis of HNCO was not observed at higher temperature.

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