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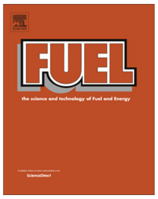

Full Length Article

Mass loss and evolved gas analysis in thermal decomposition of solid urea

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ABSTRACT

The effect of different oxygen concentration and heating rates on the mass loss and the formation of gaseous products (NH_3, N_2O and CO) during the thermolysis process of solid urea was studied and discussed by experiments, and the production mechanism of N_2O and CO was also explored and proposed. Experimental results show that there were four major stages of mass loss in each TGA curve and two sharp endothermic peaks in each DSC curve, and the peaks reflected urea melting and its decomposition. Little NH_3 was found in the exhaust gas at temperatures prior to 140 °C, confirming that little urea decomposed before the melting point, but above that the NH_3 production dramatically increased. The presence of O_2 lowered the highest NH_3 yield, possibly resulting from the oxidation of partial generated NH_3. At the same experimental condition, the N_2O production was approximately twice the CO production, but O_2 accelerated the formation of both of them, and more O_2 promoted more formation. The higher heating rate resulted in the less reaction time for urea thermolysis. Therefore, it not only led to the thermolysis process moving to the high temperature zone, but also brought about higher gaseous products concentration.

1. Introduction

The selective catalytic reduction (SCR) [1,2] and the selective non-catalytic reduction (SNCR) [3,4] are well-known promising processes for the control of nitrogen oxides (NO*x*) emitted from transportation engines, thermal power plants and cement industry by injecting nitrogen agents into the flue gases [5]. The SCR and SNCR processes transform NO*x* into harmless nitrogen and water vapor effectively. In the earlier days, aqueous or anhydrous ammonia remained as the most widely used reducing agent for quite a long time [6,7]. However, as a hazardous chemical, ammonia presents significant danger to human health, so its transportation, storage and handling trigger serious safety and environmental regulatory requirements [8]. Therefore, urea is nowadays proposed as the NH_3 source due to its non-toxicity and the ability to be carried on board much more easily and safety [9,10].

As published in open literature [11–13], after injected into the combustion exhausts, urea firstly decomposes into equimolar products of NH_3 and HNCO:

$$NH_2-CO-NH+2 \rightarrow NH_3+HNCO \tag{1}$$

If there is water vapor existing in the exhausts, HNCO may further react with H_2O to form additional NH_3 and CO_2 via hydrolysis according to the following reaction:

$$HNCO+H_2O \rightarrow NH_3+CO_2 \tag{2}$$

It has been reported that reaction (2) is rather slow at typical diesel exhaust temperatures, but an additional hydrolysis catalyst could significantly promote the reaction, and many different single and mixed metal oxides have been proved catalytic. Lundstrom et al. investigated the catalytic effect of titanium dioxide, Fe-Beta, and Alumina on urea decomposition and HNCO hydrolysis [14]. The experimental results showed that TiO_2 exhibited the best hydrolysis performance, while Fe-Beta produced huge amounts of ammonia and CO_2 due to selective adsorption of urea during the impregnation of the monolith in the urea solution. Kröecher and Elsener studied the urea decomposition with different catalytically active metal oxides in a fluidized bed reactor [15], and γ-Al_2O_3 was proved to be the best suited as a fluidized bed material among about 20 tested materials due to its high catalytic activity as well as relatively good stability. Hauck et al. explored the intrinsic kinetics and the surface chemistry of the HNCO hydrolysis with water on TiO_2 and the influence of other molecules present in the reactant stream such as NH_3, NO and NO_2 on this catalytic

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chemistry [16,17], and they derived a kinetic model for the overall rate of the HNCO hydrolysis on TiO_2 anatase.

It should be noted that during urea thermolysis different high molecular byproducts such as biuret, cyanuric acid (CYA), ammelide and ammeline may form as a result of HNCO participating in side reactions other than hydrolysis. Chen and Isa explored the thermal decomposition of urea by the simultaneous TG-DTA-MS [18], and the systematic reaction pathways were elucidated using the mass spectra of a series of urea derivatives. Schaber et al. analyzed the evolved gases and urea residues in the process of urea decomposition under open reaction vessel conditions [19]. The profiles of substances present versus temperature were given, and the detailed polymerization and depolymerization reactions of polymers in different "reaction" regions were studied and discussed. Bernhard et al. performed temperature programmed desorption and reaction experiments with urea, biuret, triuret, CYA and melamine on TiO_2-coated and inert cordierite monoliths [20], and a reaction network was developed for the uncatalyzed and catalytic decomposition of urea, showing the most important reactions of urea, HNCO, biuret, triuret, CYA, ammelide, ammeline and melamine under low-temperature operating conditions in SCR systems.

In the field of urea thermolysis research, previous studies mostly focused on accelerating the formation of gaseous NH_3 and restricting the generation of solid byproducts during urea thermolysis, since NH_3 performs as the important reducing agent in SCR and SNCR processes. However, little research has been carried out on the production of some gaseous byproducts such as N_2O and CO, which also do great harm to the atmospheric environment and human health. Actually, N_2O and CO could form in the thermal decomposition process of solid urea, and oxygen had significant influence on their production. Therefore, the effect of oxygen concentration on the formation of gaseous products (NH_3, N_2O and CO) during the thermolysis process of solid urea was discussed in this study, and the probable formation mechanism was explored and proposed. Moreover, in the thermolysis experiments, different heating rates were adopted to explore the effect of the heating rate on the mass loss properties of urea and the production properties of evolved gases NH_3, N_2O, and CO.

2. Experimental

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were performed on a TGA/DSC apparatus (Netzsch STA 409 PC Luxx) with 5.0 mg samples of solid urea ($\geq$99% purity, Sinopharm Chemical Reagent Co., Ltd) placed in a cylinder-like alumina crucible with a height of 4.0 mm, outer diameter of 6.8 mm and wall thickness of 0.5 mm. Two different heating rates were applied during the experiments, 5 °C/min and 10 °C/min, respectively with a temperature range of 20–450 °C. Dry N_2 was used as purge and protection gas, and the flow rate was set to 30 mL/min.

Since the amount of heated urea was quite small, signals of evolved gases could not be detected accurately by the gas analyzer (Gasmet Fourier Transform Infrared Dx4000). Therefore, a tubular quartz reactor with an inner diameter of 80 mm and a length of 900 mm was designed, as shown in Fig. 1. The reactor was heated through three independent sections, and its temperature was measured and adjusted by three thermocouples placed in the middle of each section and related automatic temperature controllers. The temperature variation range and the heating rates were the same as conditions in TGA/DSC experiments. Simulated gas from gas bottles was controlled and measured by flowmeters, and it flew into the reactor after merging in a mixer. The total gas flow rate was set to 2 L/min, and different O_2 volume concentration (0%, 5% and 10%) was adjusted with N_2 as the balance gas. In the experiments, the condition of 0% O_2 meant that all the 2 L/min gas was nitrogen, but the condition of 5% O_2 meant that the 2 L/min total gas was 1.9 L/min nitrogen with 0.1 L/min oxygen, while the condition of 10% O_2 meant that the 2 L/min total gas was 1.8 L/min nitrogen with 0.2 L/min oxygen. 100 mg samples of solid urea were placed in a cylinder-like alumina crucible with a height of 8.0 mm, outer

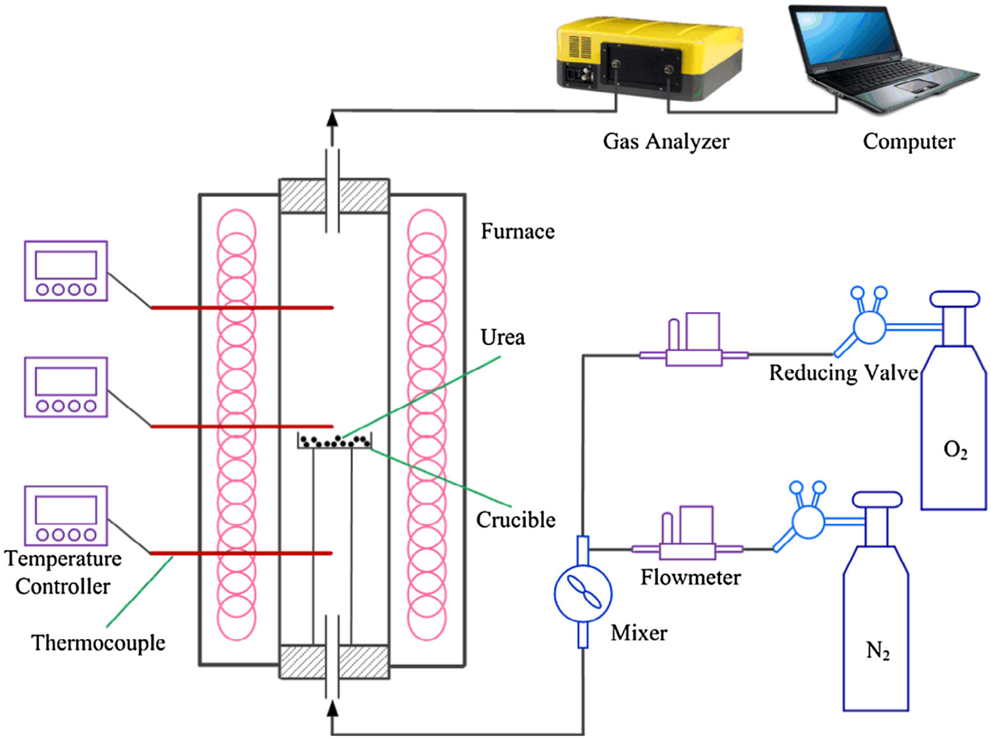

Fig. 1. Schematic of the experimental setup for urea thermolysis.