Experimental Study on Evaporation Characteristics of Ammonium Formate—Urea—Water Solution Droplet for Selective Catalytic Reduction Applications

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ABSTRACT: The evaporation behavior of ammonium formate—urea—water solution (AFUWS) droplet was studied for applications to selective catalytic reduction (SCR) systems. A number of experiments were performed with single AFUWS droplet suspended on the tip of a fine quartz fiber. To cover the temperature range of real diesel exhausts, droplet ambient temperature was regulated from 373 to 873 K using an electrical furnace. As a result of this investigation, AFUWS droplet revealed different evaporation characteristics depending on its ambient temperature. As ambient temperature increases, in addition to evaporation of water content, thermal decompositions of ammonium formate and urea were additionally observed. At high temperatures, it showed quite complicated behaviors such as bubble formation, distortion, and partial rupture after a linear $D^2$-law period. However, as temperature decreases, these phenomena became weak and finally disappeared. Also, droplet evaporation coefficients were retrieved from transient evaporation histories for various ambient temperatures, which yield a quantitative evaluation on evaporation characteristics of AFUWS droplet as well as provide valuable empirical data required for modeling or simulation works on SCR systems.

1. INTRODUCTION

Among various techniques of reducing diesel NO$_x$ to levels required by strict worldwide emission regulations, the most realistic solution is ammonia-selective catalytic reduction (SCR), which uses ammonia as a reducing agent. However, due to its inherent toxicity and handling problems with pure ammonia, aqueous urea is now practically utilized as an alternative to the direct use of ammonia for mobile SCR applications.

Once urea—water—solution (UWS) spray is injected into hot exhaust gas stream prior to reaching SCR catalyst, water content first evaporates from UWS. Next, ammonia is formed by both thermal decomposition of urea and hydrolysis of isocyanic acid as follows:

\[(\text{NH}_2)\text{CO} \rightarrow \text{NH}_3 + \text{HNCO} \quad (1)\]

\[\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \quad (2)\]

By collectively reviewing the literature, it is found that the state of aggregation urea is not clear during the evaporation of UWS; rather it can be varied among solid, molten, and gas phases depending on thermo-physical conditions.

However, in urea—SCR systems, several negative effects are possibly derived due to the use of UWS. First is the relatively high freezing point (−11°C for AdBlue, which contains 32.5% urea by weight), which makes it difficult to handle, transport, store, and use in cold temperature. This requires additional heating systems to prevent freezing of UWS. Furthermore, the amount of ammonia stored in AdBlue is rather small with approximately 0.2 kg NH$_3$/kg solution, which means that unnecessary weight is transported in the vehicle application.

Moreover, with using UWS, there is always a risk of deposits especially when the urea solution gets in contact with cold spots. Various urea decomposition products (i.e., biuret, cyanuric acid (CYA), ammelide, ammeline, melamine, etc.) and their polymeric complexes involving hydrogen bondings can be generated in urea—SCR systems. Fang and DaCosta reported that urea thermolysis involves two decomposition stages; one is the ammonia generation stage, which is desirable for reducing NO$_x$, whereas the other is the ammonia consumption stage, which promotes the formation of undesirable species. In particular, consecutive decompositions after ammonia consumption stage lead to the production of melamine complexes, (HNC$\equiv$NH)$_x$(HNCO)$_y$, which are considered as a major source in hindering the performance of catalyst by not only consuming a part of ammonia produced during urea thermolysis but also degrading the structural and thermal properties of the catalyst surface.

From a thermo-chemical calculation by Koebel and Strutz, it was reported that heat required to thermally decompose UWS is 144.8 kJ/mol for 76.93% urea solution, 263.1 kJ/mol for 50% urea solution, and 444.6 kJ/mol for 32.5% urea solution at 500 K. It is seen that with increasing water content the heat requirement for thermal decomposition of UWS increases. Thus, reducing agents with low water contents are favorable not only due to the avoidance of extra weight but also due to energetic consideration.

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The effort to find new SCR reducing agents as alternatives for UWS has been exercised in various experiments. Among others, Kröcher et al.\textsuperscript{9,11} proposed various ammonia precursor compounds as new SCR reducing agents such as ammonium formate, methanamide, and guanidinium formate. The main advantage of these alternative reducing agents resides in their much lower freezing point, which make a heating system unnecessary. Among these agents, ammonium formate turned out to be an additive for urea—water solution, which significantly lowers the freezing point of the solution. Denoxium-30, a solution of 26% ammonium formate and 20% urea in water, has a freezing point of $-30^\circ$C and improves in the DeNO$_x$ activity in the low temperature operation. Also, Denoxium solution showed a similar reduction capacity comparable to standard UWS.\textsuperscript{12}

In the first study of Koebel and Elsener,\textsuperscript{13} ammonium formate first dissociates in diesel exhaust gas to ammonia and formic acid, which further decomposes to water and CO at higher temperatures (above 573 K) as follows:\textsuperscript{11,13}

\begin{equation}
\text{HCOONH}_4 \rightarrow \text{NH}_3 + \text{HCOOH} \quad (3)
\end{equation}

\begin{equation}
\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad (4)
\end{equation}

After that, when using Denoxium-30 as a reducing agent, ammonia produced by the above reactions 1, 2, and 3 takes part in various deNO$_x$ reactions as a reductant. Main deNO$_x$ reactions under a typical diesel exhaust environment can be summarized as follows:\textsuperscript{5,14}

\begin{equation}
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (5)
\end{equation}

\begin{equation}
4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (6)
\end{equation}

\begin{equation}
4\text{NH}_3 + 3\text{NO}_2 \rightarrow 7/2\text{N}_2 + 6\text{H}_2\text{O} \quad (7)
\end{equation}

\begin{equation}
4\text{NH}_3 + 4\text{NO} + 3\text{O}_2 \rightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O} \quad (8)
\end{equation}

A sufficient understanding on the behavior of ammonium formate—urea—water solution (AFUWS) spray is a prerequisite for controlling the formation of various products derived by urea. However, there are lots of complexities involved in the evaporation process of AFUWS at a heated environment. Dissolved ammonium formate and urea influence the evaporation of water from AFUWS, and simultaneously ammonium formate and urea themselves undergo thermal decomposition as well as react to produce various species. Because of these difficulties, the evaporation behavior of AFUWS has not been clearly understood yet.

In our previous study by Wang et al.,\textsuperscript{15} the evaporation behavior of UWS droplet with AdBlue was investigated using suspended droplet experiment. Through a number of repeated measurements, the evaporation characteristics of UWS droplet were categorized into several groups according to ambient temperature, and microexplosion phenomenon was observed above 573 K. Also, after the complete depletion of liquid component constituting UWS droplet, solidified deposit was observed to remain at temperatures below 773 K, and its amount was reduced with increase in ambient temperature, while there was almost no deposit remaining at temperatures above 823 K.

In this study, the evaporation behavior of AFUWS droplet was experimentally observed over the temperature range of actual diesel exhaust. Measurements were conducted by changing the droplet ambient temperature by 50 K from 373 to 873 K. The main objectives of this study are to understand the evaporation characteristics of AFUWS droplet in various ambient temperatures and also to provide empirical evaporation coefficients, which can be utilized as reference data in modeling or simulation works on AFUWS spray. So far, to our knowledge, there have been few useful experimental data capable of quantifying the evaporation of AFUWS droplet over a wide range of temperatures.

The initial diameter of AFUWS droplets used in this experiment ranges from about 650 to 1150 $\mu$m. However, the initial Sauter mean diameter (SMD) of UWS spray applied in practical systems ranges between 20 and 150 $\mu$m.\textsuperscript{16} Therefore, in this study, for an extension of the results to much smaller-sized droplets, the effect of initial droplet size on its evaporation was investigated through a number of experiments under various initial diameters and ambient temperatures.

As typically appeared in the evaporation process of a multi-component fuel droplet, the phenomenon of violent droplet fragmentation, which is often referred to as microexplosion, is also observed during the evaporation of AFUWS droplets at elevated temperatures in this study. The basic mechanism responsible for microexplosion can be best explained through the diffusion limit model.\textsuperscript{17,18} More volatile components trapped inside the droplet due to diffusional resistance can be heated beyond the local boiling point and hence undergo internal superheating. This may eventually lead to the onset of homogeneous nucleation, while an extremely rapid rate of gasification causes intense internal pressure build-up, thereby leading to disruptive droplet fragmentation. Therefore, it was also discussed how microexplosion affects both the evaporation of AFUWS droplet and the formation of urea-derived deposits under various ambient temperatures.
2. EXPERIMENTS

2.1. Procedures and Facilities. In the current study, Denoxium-30 (contains 26.2% ammonium formate and 20.1% urea by weight) is used as a representative AFUWS. A schematic picture of the experimental apparatus is illustrated in Figure 1. In this section, experimental procedures and facilities are described, and further details can be found in Ghassemi et al. 19,20

First, an electrical furnace is lifted up away from a droplet suspension system, and its interior temperature is regulated to an intended value using a controller and thermocouple. At the same time, the inside of a cylindrical vessel (height = 0.8 m, inner diameter = 0.15 m) is refreshed by the outside air at room temperature.

Once the control of droplet ambient temperature is completed, then a single AFUWS droplet is suspended around a bead that is placed at the tip of a quartz fiber (diameter = 0.125 mm) using a droplet generator whose end part is equipped with a hollow stainless-steel needle (outer diameter = 0.21 mm). The movement of this droplet generator is adjusted by handling a lever, which causes liquid AFUWS to be transported to the bead whose diameter is approximately 0.25 mm, thereby generating a droplet. Here, for continuous monitoring of droplet ambient temperature, a K-type thermocouple was placed about 30 mm beside the suspended droplet.

The next step is to drop the electrical furnace to the position as shown by the dotted line in Figure 1. This then leads the suspended AFUWS droplet to be exposed to high temperature, which eventually initiates droplet evaporation. Glass window enables us to observe the evaporation process of droplet using a high-speed charge-coupled device (CCD) camera, and its transient variation of images is recorded on a computer.

It should be noted that there are several error sources in measuring the evaporation rate of AFUWS droplet under a constant temperature condition. Despite these errors, a certain degree of measurement accuracy may be conserved in this study.

For detailed information of experimental error sources, please refer to our previous study on the evaporation of UWS droplet. 15

2.2. Retrieval of Effective Droplet Diameter and Evaporation Coefficient. Figure 2 shows a sample image of AFUWS droplet that was captured during the evaporation process. Here, the needle beside the droplet-suspended fiber provides a reference scale of known diameter (0.21 mm). To extract droplet diameter from the photograph, a flexible image-processing program was developed using Visual Basic language. In this program, the number of pixels corresponding to the diameter of reference needle is first calculated. Next, an imaginary square of known area is drawn around droplet as shown in Figure 2. After that, the number of pixels that constitute droplet is calculated on the basis of intensity difference from surroundings. Finally, the circular area having the same number of pixels is calculated, which in turns gives an effective droplet diameter from the law of proportion with reference needle. This procedure is iteratively executed for each image file, which yields a temporal variation of droplet diameter during evaporation. Note that the shape of suspended droplet is not an exactly circular shape due to both gravitation and droplet—fiber interaction. This eccentricity becomes severe as initial droplet size decreases, which may lead to some measurement errors.

In general, the early lifetime of evaporating droplet shows a nonlinear behavior due to transient droplet heat-up by hot environment and subsequent thermal expansion. As the temperature of the droplet surface increases, evaporation starts before reaching boiling temperature. After that, a balance between thermal expansion and evaporation determines the size of droplet at that time. When the temperature inside the droplet reaches a quasi-steady state, only evaporation is effective on determination of droplet size. Starting from this stage, an evaporation process according to the $D^2$-law becomes valid. In droplet evaporation studies, the initial heat-up period does not have any importance.
because evaporation rate is generally evaluated by its subsequent period. Moreover, as initial droplet size becomes smaller, this initial heat-up period becomes negligible.\(^\text{19}\) Regarding the linear \(D^2\)-law part, droplet evaporation is quantitatively characterized by the following evaporation coefficient, \(K_e\).

\[
K_e = \frac{d(D^2)}{dt} \quad (9)
\]

This evaporation coefficient is extracted from the temporal variation of squared droplet diameter by measuring the slope of its linear regression part. In this study, the above procedure is also used to obtain the evaporation coefficient of AFUWS droplet.

### 3. RESULTS AND DISCUSSION

#### 3.1. Evaporation Characteristics of AFUWS Droplet with Various Ambient Temperatures.

Figure 3 displays normalized temporal histories of the diameter squared of AFUWS droplets evaporating at ambient temperatures ranging from 373 to 873 K. Note that, to minimize the initial droplet size effect on its evaporation, the droplets having similar initial diameters (from 0.868 to 0.941 mm) were selected from a number of experimental data. As is clearly shown in the figure, the evaporation behaviors of AFUWS droplets are evidently dependent on their ambient temperature. On the basis of this observation, the evaporation characteristics of AFUWS droplet can be classified into different cases in the following according to the variation of ambient temperature.

Also, Figure 3 reveals that droplet microexplosion begins to obviously appear at 623 K after approximately 15 s/mm\(^2\) with a fluctuating behavior, and it becomes more intense as the temperature increases. Figure 4 shows some sequential photographs of evaporating AFUWS droplet at 873 K, and microexplosion phenomenon is clearly observed here. As shown in the figure, the droplet seems to expand due to bubble formation inside it. Also, droplet distortion and fragmentation are seen. Note that these irregular behaviors are typically observed in the evaporation process of the multicomponent droplet.\(^\text{19}\)

Now it is worthwhile to compare current results to our previous results on microexplosion of the UWS droplet.\(^\text{15}\) Microexplosion of the AFUWS droplet begins at higher ambient temperature than that of the UWS droplet. In the case of the UWS droplet, microexplosion was observed at the temperature above 573 K. Also, the microexplosion intensity of AFUWS droplet is generally weaker than that of UWS droplet. These observations are because the amount of less volatile component (urea) inside the AFUWS droplet (containing 20.1% urea by weight) is smaller than that inside the UWS droplet (containing 32.5% urea by weight) so that diffusional resistance to more volatile component trapped inside AFUWS droplet becomes smaller than that of UWS droplet. Therefore, in the case of AFUWS droplet, the
bubble formation is weak, and microexplosion is incomplete as compared to the case of the UWS droplet. 19

3.2. For Ambient Temperatures of 373 and 423 K. Figure 5 presents the whole droplet lifetime history for each AFUWS droplet evaporating at 373 and 423 K, respectively. Here, each evaporation history of normalized droplet diameter squared is displayed up to 0.676 mm²/mm² for 373 K and up to 0.525 mm²/mm² for 423 K. This is because liquid component constituting AFUWS droplets is completely evaporated at these points, and thereafter almost no more reduction in droplet overall size is observed.

The melting points of ammonium formate and urea are known to be about 389 K and 406 K, respectively. Therefore, at ambient temperature of 373 K, only water content will evaporate from the AFUWS droplet. Accordingly, the AFUWS droplet evaporating at 373 K exhibits almost linear history as if it consists only of a single ingredient. On the other hand, at 423 K, ammonium formate and urea near droplet surface are expected to melt and thermally decompose into ammonia and formic acid according to reaction (3) and into ammonia and isocyanic acid according to reaction (1). Therefore, the evaporation history at 423 K seems to indicate three stages: vaporization of water, thermal decompositions of ammonium formate, and then urea. However, as shown in the figure, the evaporation history at this temperature can be divided into two distinguished branches with an obvious difference in their diminishing rates. During the first stage of the evaporation period, the water component first evaporates from AFUWS droplet. Musa et al. 23 compared the evaporation behavior of the urea solution droplet to that of distilled water, and therein almost no difference in their first-stage evaporation was observed. During the second stage of evaporation period, the gasification of ammonium formate may be a dominant mechanism responsible for diminishment in AFUWS droplet size. This view is consistent with the result produced by Solla et al. 12 who reported that ammonia gas evolution from ammonium formate starts at about 388 K. After the second stage of evaporation period, there is almost no more change in AFUWS droplet size. Hence, it is expected that urea gasification does not occur at 423 K in this study. This observation can be expected from studies of Solla et al. 12 and Schaber et al. 7 who reported that ammonia gas evolution from solid urea starts about 468 K and that a vigorous gas evolution from molten urea commences at 425 K, respectively. Also, in our previous study on evaporation of UWS droplet, gasification of urea was not observed at this temperature. 15

To estimate the evaporation coefficient of AFUWS droplet, the least-squares regression method was used with the data corresponding to the linear part of evaporation history except for both initial heat-up and final solidification periods. The estimated evaporation coefficients were given with actual measurement.

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Figure 6. Sequential photographs of evaporating AFUWS droplet at 373 K. Initial droplet diameter: 0.930 mm. Camera speed: 10 fps.

Figure 7. Normalized temporal variations of the diameter squared of evaporating AFUWS droplets with each least-squares fit to the linear water evaporation part (first stage), to the linear ammonium formate thermal decomposition part (second stage), and to the linear urea thermal decomposition part (third stage) at 473, 523, and 573 K. For 473 K, camera speed, 10 fps; ambient temperature range measured during evaporation, 470—475 K. For 523 K, camera speed, 10 fps; ambient temperature range measured during evaporation, 520—527 K. For 573 K, camera speed, 15 fps; ambient temperature range measured during evaporation, 571—757 K.
data in Figure 5. Note that, in the case of 423 K, two slope data are given for two stages of AFUWS droplet evaporation. It must be noted that solidified deposit remains after the complete depletion of liquid component evaporation from AFUWS droplets for both 373 and 423 K. Sequential photographs including evaporation and solidification processes of AFUWS droplet at 373 K are displayed in Figure 6. Close observations after 70 s indicate that solidified deposit undergoes no change until the end of camera capture. The deposit produced at 373 K may be composed of solidified ammonium formate and urea, because both species do not melt at this ambient temperature during the whole evaporation period. On the other hand, at 423 K, the deposit may consist of only solidified urea because the first urea-derived species, biuret, begins to be produced from the reaction of isocyanic acid with intact urea at \( \sim 433 \) K.\(^7\) When compared to the amount of solidified deposit of UWS droplet at 373 K\(^8\) after water content was completely evaporated, the remaining overall size of the AFUWS droplet (about 0.676 mm\(^2\)/mm\(^2\)) was larger than that of the UWS droplet (about 0.617 mm\(^2\)/mm\(^2\)). This observation may be because the amount of ammonium formate and urea forming the AFUWS droplet is more than that of the UWS droplet.

### 3.3. For Ambient Temperatures of 473, 523, and 573 K

Figure 7 plots normalized temporal variations of the diameter squared of evaporating AFUWS droplets for ambient gas temperature of 473, 523, and 573 K. As shown in the figure, evaporation histories in this temperature range can be divided into three distinguished stages due to the apparent difference in their diminishment rates. During the first and second stages of evaporation periods, water content evaporates completely, and the ammonium formate thermally decomposes subsequently as in the previous case of 423 K. The most distinguished feature at these ambient temperatures is that thermal decomposition of urea occurs during the third stage of evaporation period. Note that these multistage evaporation characteristics observed at these ambient temperatures support the plausible employment of the rapid mixing model for estimating evaporation rate of UWS droplet as in Birkhold et al.\(^16\)

Previously, at ambient temperature of 423 K, urea gasification seemed not to occur. However, at ambient temperature of 473—573 K, it was clearly observed after the complete depletion of water content and the thermal decomposition of ammonium formate component. This is because the decomposition of urea is rapidly enhanced at temperature above 425 K.\(^7\) Therefore, at temperatures of 473—573 K, the reduction rate of AFUWS droplet behavior should be respectively determined for each of three stages. Here, the least-squares method was also utilized to find the slope of each stage. A comparison of three evaporation histories presented in Figure 7 indicates that the differences among the slope of each stage become smaller as ambient temperature increases.
droplet diameter: 0.925 mm at 623 K, 0.868 mm at 673 K, 0.929 mm at 723 K, 0.936 mm at 773 K, 0.889 mm at 823 K, 0.941 mm at 873 K.

Referring to the pyrolysis experiment conducted by Schaber et al., the deposits generated at 473, 523, and 573 K probably consist of several urea-derived products such as biuret, CYA, ammelide, and ammiline with undecomposed urea itself.

3.4. For Ambient Temperatures of 623, 673, and 723 K.

Figure 9 shows normalized evaporation histories for ambient temperatures of 623, 673, and 723 K. The most prominent characteristic of evaporating AFUWS droplets at these ambient temperatures is the onset of microexplosion. In Figure 9, after the linear variation of droplet diameter squared during water evaporation period, the droplet re-expansion is observed with a fluctuating behavior. The reason for this fluctuation is that, as previously mentioned, the more volatile component trapped inside AFUWS droplet due to diffusional resistance is heated, which causes homogeneous nucleation, and thereby droplet internal pressure builds up. Here, the rates of both nucleation and diffusion compete against each other so that they influence droplet expansion characteristics. A comparison of three evaporation histories reveals that more intense fluctuation occurs at higher ambient temperature. A fast internal pressure build-up caused by rapid nucleation at higher temperature results in more aggressive evaporation behaviors such as bigger expansion, more severe bubble formation, and more disruptive fragmentation.

Another feature to be noted at these ambient temperatures is that two-stage type of evaporation characteristics is observed unlike the previous three-stage type for ambient temperature of 473–573 K. It is because microexplosion occurs after the first linear evaporation period. Therefore, as shown in Figure 9, evaporation histories at 623–723 K can be divided into two distinguished stages.

To obtain the evaporation coefficient for the first stage, the least-squares method was also applied to the linear part of experimental data. However, for the next evaporation stage, the use of the least-squares method is not justified due to droplet expansion and fluctuation so that its diminishment rate is simply estimated using the slope determined with two end points. Note that, in Figure 9, the difference in diminishment rates for both the first and the second stages becomes smaller as ambient temperature increases. Particularly, for ambient temperature of 723 K, the magnitude of the first stage evaporation rate is almost equal to that of the second stage as can be seen in Figure 9.

Photographs of solidified deposits remaining after the complete evaporation of AFUWS droplets for various ambient temperatures. Initial droplet diameter: 0.925 mm at 623 K, 0.868 mm at 673 K, 0.929 mm at 723 K, 0.936 mm at 773 K, 0.889 mm at 823 K, 0.941 mm at 873 K.

Figure 11 presents normalized evaporation histories of AFUWS droplets with each least-squares fit to the linear water evaporation part (first stage) and two-point estimation to the microexplosion part (second stage) at 773, 823, and 873 K. For 773 K, camera speed, 30 fps; ambient temperature range measured during evaporation, 767–779 K. For 823 K, camera speed, 30 fps; ambient temperature range measured during evaporation, 821–828 K. For 873 K, camera speed, 30 fps; ambient temperature range measured during evaporation, 880–868 K.

Photographs of solidified deposits remaining after the complete depletion of liquid component at temperatures from 623 to 873 K are displayed in Figure 10. As shown in the pictures, the amount of deposit remained was considerably reduced as ambient temperature rises from 623 to 673 K. This may be attributed to the fact that the decomposition of CYA is completed between 648 and 653 K and the sublimation and decomposition of ammelide significantly occurs at temperatures from 623 to 673 K.

3.5. For Ambient Temperatures of 773, 823, and 873 K.

Figure 11 presents normalized evaporation histories of AFUWS droplets for ambient temperature of 773, 823, and 873 K. In this temperature range, the second stage diminishment rate becomes faster than the first stage rate. This is primarily because droplet microexplosion occurs more aggressively as compared to the case for 623–723 K. Figure 11 reveals more intense second-stage evaporation behaviors than does Figure 9. Note that the difference in diminishment rates of both the first and the second stages becomes larger as ambient temperature rises from 773 to 873 K.
In this experiment, solidified deposits were still observed to remain up to 773 K, while almost no deposit was found for ambient temperatures of 823 and 873 K. It is known that ammelide is completely eliminated at about 873 K, while ammeline requires temperatures over 973 K. Therefore, it can be deduced that a tiny amount of ammeline is produced during the evaporation of AFUWS droplet. If ammeline was produced considerably, then a certain amount of deposit would be observed even at temperatures exceeding 823 K. Also, it is known that CYA is completely eliminated below 673 K. As a consequence, the deposits remaining at temperatures from 673 to 773 K are mainly composed of ammelide.

3.6. Initial Diameter Effect on the Evaporation of AFUWS Droplet. Figures 12–14, respectively, present each stage diminishment rate coefficient for various AFUWS droplet sizes evaporating at temperatures from 373 to 873 K in increments of 50 K. It should be noted that the range of ambient temperature measured during evaporation is somewhat different in each figure. Averaged lower and upper bounds for ambient temperature and their standard deviations are given in Table 1.

In general, as shown in Figures 12–14, it is evident that at lower ambient temperature, the effect of initial droplet diameter on evaporation coefficient is almost negligible. Yet at higher ambient temperature, the effect of initial droplet diameter is more pronounced, and evaporation coefficients increase with initial droplet diameter. In addition, the least-squares fits indicate that the increment of each coefficient with initial droplet diameter becomes larger as ambient temperature increases. This observation is consistent with the result studied by Xu et al.24
who reported that the evaporation coefficient increased in hot ambients with raising initial droplet diameter and that the evaporation coefficient increase with increasing the initial droplet diameter was larger at higher temperatures.

Also, Figure 15 shows a comparison of evaporation coefficients of urea thermal decomposition part for UWS droplets in our previous study and AFUWS droplets in current study at temperatures from 473 to 673 K. At ambient temperatures of 473–573 K, both rate coefficients for UWS and AFUWS droplets are very similar. However, as shown in the figure, there is some difference between diminishment rates for UWS and AFUWS droplets at temperatures above 623 K. The reason for this distinction is that, as previously mentioned, microexplosion intensity of AFUWS droplet is generally weaker than that of the UWS droplet. Therefore, in the case of AFUWS droplet, evaporation coefficients were smaller than that for the UWS droplet at temperatures above 623 K.

4. CONCLUSIONS

In this study, the evaporation behavior of AFUWS droplet for application to SCR is investigated using suspended droplet experiment. Through a number of repeated measurements, evaporation rates were extracted for various initial droplet diameters and ambient temperatures. As a consequence, the current study helps to understand the evaporation characteristic of AFUWS droplet quantitatively as well as qualitatively. Furthermore, this study provides some empirical data required in modeling or simulation works on SCR system using ammonium formate—urea—water solution as a reducing agent. A summary of the major results is as follows.

(1) On the basis of the current observations, the evaporation behavior of the AFUWS droplet can be categorized into different cases according to ambient temperature. At ambient temperature of 373 K, the AFUWS droplet exhibits almost linear history. At 423 K, the UWS droplet is divided into two distinct stages such as evaporation of water content and thermal decomposition of ammonium formate. At 473–573 K, thermal decomposition of urea starts to take place so that the three-stage type of evaporation characteristics is observed with obvious different evaporation rates. At 623–723 K, weak microexplosion appears, while the first-stage rate exceeds the second-stage rate. At 773–873 K, strong microexplosion happens, while the second-stage rate exceeds the first-stage rate.

(2) After the complete depletion of liquid component constituting the AFUWS droplet, solidified deposit is observed to remain at temperatures below 773 K. Its amount is reduced with increase in ambient temperature, while there is almost no deposit remaining at temperatures above 823 K.

(3) The diminishment rate of each evaporation stage increases as the initial size of AFUWS droplet increases. Also, the increment of each evaporation coefficient with initial droplet size becomes larger as ambient temperature increases.

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