Modeling of the Rates of Evaporation and Decomposition of Urea on SCR Catalyst

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This study was conducted as a part of the development of a simulation model for more efficient use of urea SCR in diesel vehicles by modeling each of the chemical reaction processes that comprise the process. In this study the evaporation behavior and the decomposition rate of urea on the SCR catalyst at relatively low temperatures (below 250°C), and their modeling were examined

SCR catalyst (3.2% Cu-CHA) and its hydrothermally deteriorated catalyst (800°C x 20h in 10% H_2O) were used. Also, non-porous silica was used to measure the urea decomposition rate on an inert material. The equilibrium gaseous concentration, decomposition rate, and temperature programmed reaction (TPR) of urea adsorbed on the SCR catalysts were measured using a laboratory-scale flow reaction system. The reaction system is characterized by using a tee joint (Swagelok SS-8M0-3) as the reaction tube, the sample (inert material or a mixture of inert material and catalyst) filled near the inner trifurcation, and its placement near the wall of a GC oven used for controlling the temperature of the reaction tube. Urea water was injected directly into the sample bed through the third connection. Gaseous urea, CO_2, HNCO, and NH_3 in the product gas were analyzed at 40-sec intervals using FTIR equipped with a multi-reflection gas cell.

The equilibrium concentration p_0 for solid urea evaporation was determined by measuring the concentration of gaseous urea produced in the reaction tube filled with quartz sand and fed with urea water at a predetermined temperature. The equation for p_0 for liquid urea above the melting point (133°C) was also obtained using the solid result and literature values for the heat of fusion.

solid urea (below 133ºC) $\log_{10} p_0 \text{ (\%)} = 10.7947 - 5028.2 / T$ (1)

liquid urea (above 133°C) $\log_{10} p_0 \text{ (\%)} = 8.9687 - 4287.1 / T$ (2)

The rate of urea decomposition was determined by feeding a fixed amount of urea water into the sample bed at a predetermined temperature under humidified air flow and measuring the change in CO_2 concentration produced after a short time. The catalytic and non-catalytic rate constants k_c and k_0 for the decomposition were formulated as follows.

$\log_{10} k_c \text{ (s}^{-1}) = 9.4060 - 4880.0 / T$ (3)

$\log_{10} k_0 \text{ (s}^{-1}) = 5.5601 - 3523.9 / T$ (4)

The process model for predicting the rate of urea evaporation and decomposition was constructed by using the BET adsorption equation,

$\theta = cx / \{(1 - x + cx)(1 - x)\}$ (5)

where x and c are relative concentration (p/p_0) of urea and the BET adsorption constant, respectively. The coverage of the first layer θ_1, and the total coverage over the second layer θ_{2+} are obtained as follows, respectively,

$\theta_1 = cx / (1 - x + cx)$ (6)

$\theta_{2+} = \theta_1 \cdot x / (1 - x)$ (7)

Furthermore, as the inverse function of Eq. (5)

$$x = \frac{(c - 2 - c/\theta) + \sqrt{(c - 2 - c/\theta)^2 + 4(c - 1)}}{2(c - 1)}$$ (8)
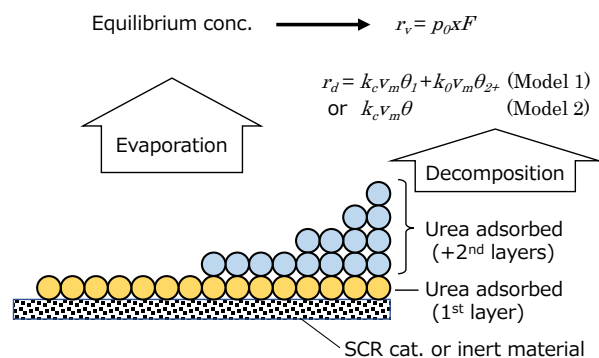

Fig. 1 Model of simultaneous evaporation and decomposition rates of urea based on BET adsorption.

is obtained, with which the equilibrium vapor pressure can be obtained from the adsorption amount θ.

Fig. 1 shows a schematic of the process model constructed using Eqs. (1)-(8), in which urea evaporation and decomposition proceed simultaneously. Two models were considered: a full BET model (Model 1) and a simplified BET model (Model 2).

In Model 1, the calculated decomposition rate (CO_2 concentration) was slightly smaller than the measured rate from 120°C to 180°C. In contrast, Model 2 showed good agreement in this area. From this model, it is expected to be possible to quantitatively predict the evaporation and decomposition behavior of urea adsorbed on the catalyst.