§4. Hydrogen and Methane Oxidation over Honeycomb Filter Platinum Catalysts Supported on SiC: Effect of Water Vapor

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Tritium removal system used for safety management in a fusion power plant would be required large processing volume, throughput and low pressure drop. To achieve these requirements, we have proposed the honeycomb type catalyst and absorbent instead of conventional pellet type materials. A filter catalyst based on SiC has been of use for the particulate filter of a diesel vehicle exhaust gas. The filter catalyst impregnated with noble metals can not only remove the fine particle materials but also burn them over the catalyst at elevated temperature. Also, it is characteristic of high heat resistance and corrosion resistance, high mechanical strength, heat conductivity and utilizing as heating unit. To investigate the effect of water vapor on the catalytic activity, the water vapor partial pressure in the feed gas stream was varied under the oxidation condition of hydrogen and methane in air.

The test sample of SiC catalyst is purchased from TYK Co. Specific dimensions of the honeycomb is 15 mm in diameter and 20 mm in length. The honeycomb cell density was 400 CPSI (cell per square inch). Platinum precious metal was impregnated by use of solution of it on the surface of honeycomb with Al_2O_3 wash coat. The density of precious metal on the honeycomb was 2 g/L. The gaseous of both hydrogen and methane is diluted with dry air. The gas components were adjusted approximately 0.1% of hydrogen and methane. The heater was controlled by a programmable temperature controller with a thermocouple on the heater. The temperature was kept at 428 K for hydrogen oxidation and 652 K for methane oxidation. The mixture gas flow rate was 252 sccm. Process gases were sampled at the inlet and outlet of the catalyst bed and their concentrations were analyzed by a gas chromatograph.

Figure 1 shows the effect of water vapor on reaction velocity. The degradation in the catalytic activity is observed for the increase of water vapor partial pressure. The water inhibition effect arises from the water adsorption on the catalysis surface. Water adsorption onto and desorption from the catalysis surface are in equilibrium. According to Kikuchi et al., the kinetic equations can be derived as follows[1]:

$$r_{H_2} = k_{r-H_2}[H_2]\theta_V, \quad r_{CH_4} = k_{r-CH_4}[CH_4]\theta_V \quad (1)$$

$$x_{H_2} = 1 - \frac{[H_2]}{[H_2]_0}, \quad x_{CH_4} = 1 - \frac{[CH_4]}{[CH_4]_0} \quad (2)$$

$$k_{r-H_2} = K_{H_2}\exp\left(\frac{-E_{a,H_2}}{RT}\right), k_{r-CH_4} = K_{CH_4}\exp\left(\frac{-E_{a,CH_4}}{RT}\right) (3)$$

where r_i represents the reaction rate of H_2 and CH_4, k_{r-i} is the surface reaction rate constant, θ_V is the fraction of vacancy sites on the catalyst surface, x_i is the conversion rate, $[H_2]$ and $[CH_4]$ are the gas concentration in the outlet of catalyst reactor, the subscript notation "0" represents the concentrations in the inlet of catalyst reactor, K_i is the pre-exponential factor, $E_{a,i}$ is the apparent activation energy, R the gas constant, T the temperature, the subscript notation "i" represents "H_2" and "CH_4", respectively. The fraction of vacancy sites, θ_V, is given by the Langmuir isotherm as

$$\theta_V = 1 - \theta_{H_2O} = 1 - \frac{K_{H_2O}[H_2O]}{1 + K_{H_2O}[H_2O]} = \frac{1}{1 + K_{H_2O}[H_2O]} \quad (4)$$

$$K_{H_2O} = K_{ads}\exp\left(\frac{-\Delta H_{ads}}{RT}\right), \quad (5)$$

where $[H_2O]$ is the water concentration, K_{H_2O} is the adsorption equilibrium constant, H_{ads} stands for the enthalpy of water adsorption, and K_{ads} is the pre-exponential factor. Consequently, under this experimental conditions, the kinetic expression results

$$r_{H_2} = \frac{k_{r-H_2}\left(1 - x_{H_2}\right)[H_2]_0}{1 + K_{H_2O}\left([H_2O]_0 + x_{H_2}[H_2]_0\right)}, \quad (6)$$

$$r_{CH_4} = \frac{k_{r-CH_4}\left(1 - x_{CH_4}\right)[CH_4]_0}{1 + K_{H_2O}\left([H_2O]_0 + x_{H_2}[H_2]_0 + 2x_{CH_4}[CH_4]_0\right)} \quad (7)$$

Kikuchi et al. reported the water adsorption enthalpy (ΔH_{ads}) on the surface of Pd catalyst supported on Al_2O_3, SnO_2 and Al_2O_3–NiO.[1] They found that the support material can considerably affect the H_{ads}. Especially, the catalyst supported by Al_2O_3 showed the most negative enthalpy of water adsorption among those catalysts. It indicates that coverage of the active sites on the surface by water is high. In this report, Al_2O_3 was utilized as a wash coat material for SiC. Thus, the water inhibition effect revealed themselves remarkably. Instead of Al_2O_3 as wash coat, we will prepare with the SiC honeycomb catalyst attached the wash coat of SnO_2, which exhibits the higher water inhibition effect.
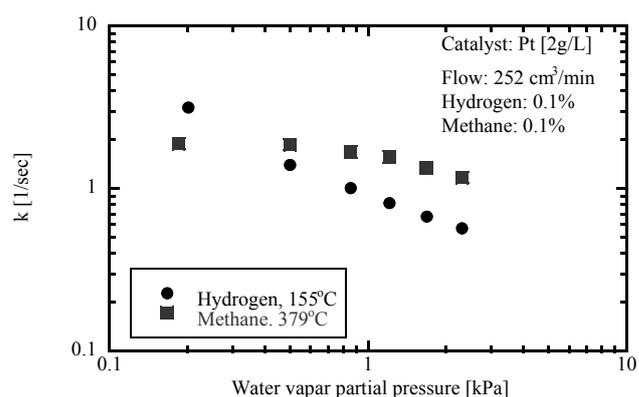

Fig. 1. The effect of water vapor partial pressure on the reaction velocity.

1). Kikuchi, R., et al., Applied Catalysis A, **232**, (2002) 23.