Thermal Non-equilibrium Activation of Carbon Dioxide on Cu catalysts

Methanol synthesis, $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$, over Cu-based catalysts has been considered as the most promising catalytic process for the conversion of $\text{CO}_2$, in which the formate ($\text{HCOO}$) formation, $2\text{CO}_2 + \text{H}_2 \rightarrow 2\text{HCOO}$, is essential step because the reaction rate is very small$^{1,2)}$. To clarify the dynamics and mechanism of formate synthesis from the $\text{CO}_2$ hydrogenation over Cu catalysts, here, we applied supersonic $\text{CO}_2$ molecular beam to directly collide with the pre-dosed atomic hydrogen on Cu surface. We found that formate is efficiently produced by irradiating $\text{CO}_2$ beam heated above $1050 \text{ K}$ to cold Cu(111) surfaces kept at $170 \text{ K}$ (Fig. 1). That is, both translational energy and vibrational energy of $\text{CO}_2$ are indispensable to overcome the reaction barrier of the formate formation. Furthermore, the reaction rate is independent of the surface temperature of Cu. This thermal non-equilibrium reaction between $\text{CO}_2$ and atomic hydrogen are well explained by the E-R type mechanism that energetically excited $\text{CO}_2$ directly attacks an adsorbed hydrogen atom without trapping of $\text{CO}_2$ on Cu surfaces, which is reproduced by density functional theory (DFT) calculations.

Fig. 1 TPD method traces the product after molecular beam irradiation of $\text{CO}_2$ at various nozzle temperatures on Cu(111). The simultaneous desorbing peaks of $\text{H}_2$ and $\text{CO}_2$ at the peak position of 410 K results from the products of formate decomposition. At the 298 K nozzle temperature, no formate is formed. The Cu(111) surface temperature is 170 K, and the exposure of $\text{CO}_2$ beam is $2.75 \times 10^{-4} \text{ L}$. In both nozzle temperature cases, the $\text{H}_2$ peak at around 310 K is due to the associative desorption of H atoms on Cu(111).

References