Vibration-driven reaction of CO_2 on Cu surface via Eley-Rideal type mechanism

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Abstract: The formate (HCOO) synthesis is known as the initial reaction step of methanol synthesis via Eley-Rideal type mechanism[1-2] ($CO_2 + H_a \rightarrow HCOO_a$, “a” denotes adsorbates). In experiment, we have irradiated hot CO_2 molecular beam (various translational and vibrational energy conditions) to Cu surface at 120−220 K with pre-adsorbed hydrogen to form formate adspecies. Experimental results indicate the vibrational energy of CO_2 is effective for the reaction, but not the translational energy; and the reaction rate is independent of the surface temperature. We conclude that vibrational energy occupies most of the activation energy of this reaction.

Keywords: Vibration-driven reaction, Eley-Rideal type mechanism, Hydrogenation of CO_2.

1. Introduction

Methanol synthesis ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) over Cu-based catalysts such as $Cu/ZnO/Al_2O_3$ is considered to be the most promising catalytic process for the conversion of CO_2. The hydrogenation of CO_2 into formate intermediates ($HCOO_a$) is especially an important reaction step for methanol synthesis insofar as it represents the initial activation process of CO_2 on Cu surfaces; this is because the reaction probability of the formation of formate is very low ($\sim 10^{-12}$) at 340 K. The formate is reported to be directly formed by the collision of CO_2 in gas phase with atomic hydrogen on Cu surface ($CO_2 + H_a \rightarrow HCOO_a$, “a” denotes adsorbates) via Eley-Rideal type mechanism[1-2]. The objective of this work is to clarify the effect of surface temperature, CO_2 translational energy (E_{trans}) and vibrational energy (E_{vib}) on formate synthesis.

2. Experimental

The experiment of formate formation under ultra-high vacuum condition was examined by reacting a hot CO_2 molecular beam (diluted with He) with pre-dosed cold atomic hydrogen (H_a) until saturated (coverage of 0.5 ML) on a Cu(111) and Cu(100) surface (H_a/Cu). The energy (translational energy and vibrational energy) of CO_2 is controlled by supersonic molecular beam technique. The atomic hydrogen was prepared by dissociation of H_2 on a hot W filament with desorption of H atoms. After the CO_2 beam irradiation, temperature-programmed-desorption (TPD) were successively carried out to detect the formation of formate.

3. Results and discussion

TPD results have showed the desorption of H_2 and CO_2 molecules due to the recombination of pre-adsorbed hydrogen atoms or the formate decomposition on Cu surface. These indicate that the formate originates from the reaction of CO_2 beam with H_a. By analyzing the TPD peak area of H_2 desorption, we can obtain the initial reaction probability (P_0) of formate synthesis.

To clarify this reaction dynamics, the effects of the surface temperature (T_{surf}), the translational energy and the mean vibrational energy ($\bar{E}_{\mathrm{vib}}$) of CO_2 on P_0 were examined on Cu(111) and Cu(100). As shown in Figure. 1A, P_0 is anomalously independent of the surface temperature in the range of 120–220 K under fixed E_{trans} = 1.97 eV and 1.46 eV, T_{vib} = 1000 K. This means a thermal non-equilibrium reaction, in which the rate of the formate formation is determined by the temperature or energy of CO_2 rather than the surface temperature.

Furthermore, the thermal non-equilibrium feature indicates the E-R type mechanism, in which the CO_2 molecule is not thermally equilibrated with the Cu surfaces but directly reacts with H_a.

Figure 1, B and C show the effects of E_{trans} and $\bar{E}_{vib}$ on P_0 on Cu(111) and Cu(100), respectively. P_0 increases upon increasing E_{trans} from 1.12 to 1.97 eV, where $\bar{E}_{vib}$ is constant at 142 meV. Although P_0 tends to be larger on Cu(111) compared to Cu(100), this increasing trend was observed for both surfaces. As for the $\bar{E}_{vib}$ dependence shown in Fig. 1C, P_0 also increases with $\bar{E}_{vib}$ between 87–142 meV (corresponding T_{nozzle} of 775–1000 K) for both surfaces with E_{trans} fixed at 1.30 eV and 1.56 eV. The slope for $\bar{E}_{vib}$ (Fig. 1C) is much greater than that for E_{trans} (Fig. 1B), indicating that the $\bar{E}_{vib}$ is much more efficient for overcoming the reaction barrier.

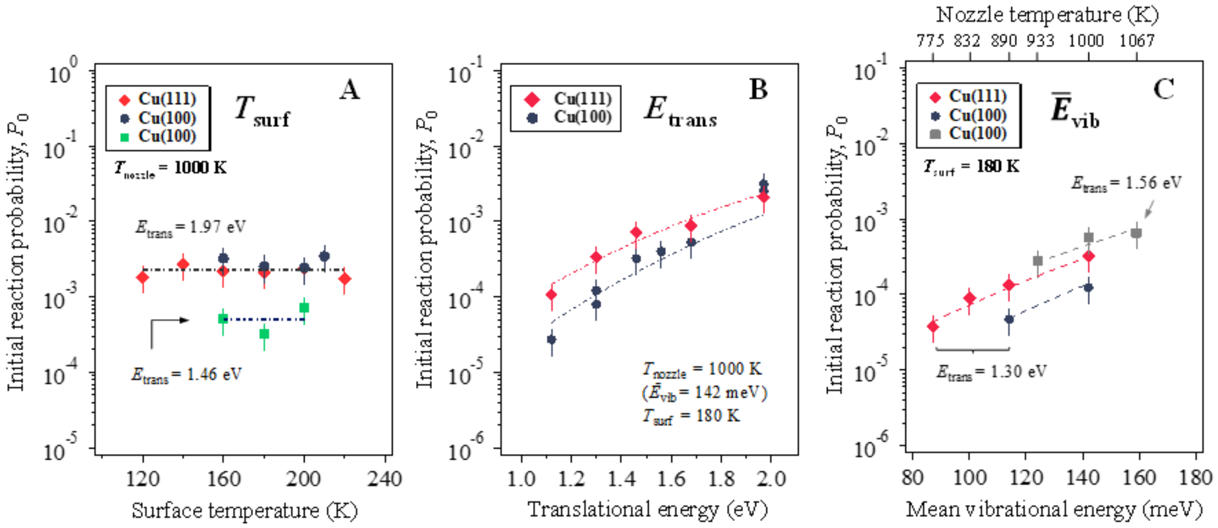

Figure 1. Effects of surface temperature (T_{surf}), CO_2 translational energy (E_{trans}), and CO_2 mean vibrational temperature ($\bar{E}_{vib}$) on the initial reaction probability (P_0) for formate formation on Cu(111) and Cu(100).

(A) T_{surf} dependence of P_0 at E_{trans} = 1.97 eV and E_{trans} = 1.46 eV. T_{nozzle} = 1000 K.

(B) E_{trans} dependence of P_0 at T_{nozzle} = 1000 K ($\bar{E}_{vib}$=142 meV) and T_{surf} = 180 K.

(C) mean vibrational energy $\bar{E}_{vib}$ (or T_{nozzle}) dependence of P_0 at E_{trans} = 1.30 and 1.56 eV and T_{surf} = 180 K

4. Conclusions

The surface temperature independence of P_0 and the energy of CO_2 dependence of P_0 indicate that formate synthesis proceeds via Eley-Rideal type mechanism. Vibrational energy of CO_2 occupies most of the activation energy of the reaction.

References

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