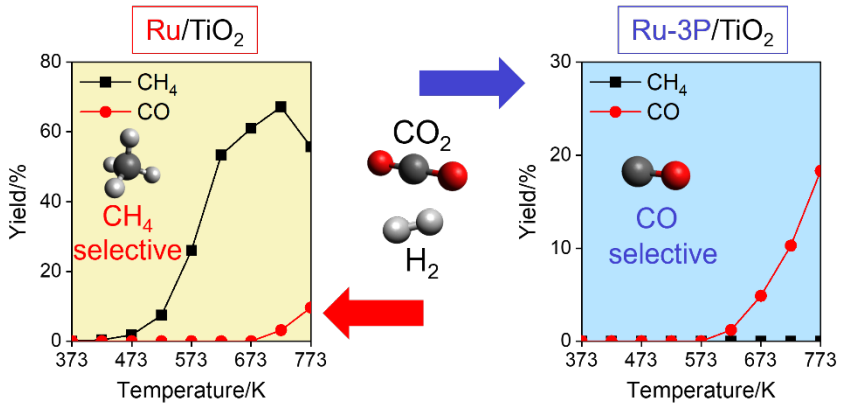
Phosphorus-Enhanced Supported Metal Catalysts: A Leap in Selective CO_2 to CO Conversion

Tetsuya Shishido*[a,b]

[a)]*Department of Applied Chemistry for Environment, Tokyo Metropolitan University, Tokyo, Japan*
[b)] *Research Center for Hydrogen Energy-Based Society, Tokyo Metropolitan University, Tokyo, Japan*

Extensive efforts are needed to develop CO_2 utilization technologies by using green hydrogen. Both the Sabatier reaction and the reverse water-gas shift (RWGS) reaction proceed competitively at ambient pressure. To achieve the selective formation of CH_4 or CO by CO_2 hydrogenation, it is necessary to reveal the dominant factor for changing the selectivity in CO_2 hydrogenation. We found that the RWGS reaction proceeds selectively by phosphorus-loaded metal (various 3d, 4d, and 5d metals) catalysts, while the Sabatier reaction proceeds mainly on TiO_2-supported metal catalysts. The cationic metal species on phosphorus-loaded metal catalysts were found to selectively produce CO by preventing the cleavage of the C-O bond of the CO molecule. No CO hydrogenation took place on phosphorus-loaded metal catalysts. Based on the kinetic analysis, the reaction orders of H_2 and CO_2 were estimated to be positive and 0th for phosphorus-loaded metal catalysts, and 0 and positive for TiO_2-supported metal catalysts, respectively. These results indicate that the rate-determining step (RDS) of CO_2 hydrogenation to CO over phosphorus-loaded metal catalysts would be the reaction process involving CO_2 (adsorption or activation). In the case of TiO_2-supported metal catalysts, the activation of H_2 or the bond formation (C-H or O-H) processes is the RDS to form CH_4.

Corresponding author shishido-tetsuya@tmu.ac.jp



CO_2 hydrogenation over Ru/TiO_2 and $Ru\text{-}3P/TiO_2$ catalysts
$CO_2/H_2/N_2/He$ = 10/40/5/45 mL min^{-1}, GHSV = 60000 mL $gcat^{-1}$ h^{-1}.