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Development of electroassisted catalysis based on surface protonics and alloying

(表面プロトニクスと合金化を駆使した電場触媒反応系の開拓)

For some endothermic reactions such as propane dehydrogenation (PDH), oxidative coupling of methane (OCM), and dry reforming (DR), a high reaction temperature is necessary to gain an appropriate yield due to the limitation of thermodynamics equilibrium limitation. However, side reactions and deactivation by metal sintering occur under such severe temperatures, hindering practical use. Using an external-force system is a promising and pioneering approach to overcome the thermodynamic limitation, resulting in low-temperature conversion. It is found that various catalytic reactions can occur with the assistance by electric field even at low-temperature, called surface protonics. By imposing an electric field to a catalyst, proton hopping via surface hydroxyl groups known as the Grotthuss mechanism can be facilitated, enabling strong proton collision with reactant molecules. Robust molecules, such as N_2 , CH_4 , and CO_2 , can be activated by surface protonics and transformed into value-added chemicals, even at low temperatures. Although electroassisted catalysis is a promising methodology, there is another problem; some of the product molecules are fragile and can be decomposed by strong proton collisions. Therefore, the delicate design of active sites is also necessary to obtain high yield. (1) First, the electroassisted PDH was investigated at low temperatures. By applying an electric field, the propane was activated by proton collision process even at low temperatures. Notably, alloying of Pt with In drastically modified the electronic state of Pt, which enhanced both the catalytic activity and selectivity. A propylene yield far beyond the equilibrium limitation was achieved by the combination of the surface protonics methodology and active site modification based on intermetallics. (2) Second, I discovered that doping Sm^{3+} into the surface of anatase TiO_2 successfully increased the concentration of surface hydroxyl groups of TiO_2 by charge compensation, which can determine the reaction rate of propylene formation from the previous study. Furthermore, the promotional effect of this surface engineering could be synergized with Pt-In alloying to achieve a drastic enhancement in the catalytic activity in electroassisted PDH reaction. (3) The electroassisted catalytic system was applied in various reactions, such as oxidative coupling of methen using carbon dioxide (CO_2 -OCM), and dry reforming of benzene (DRB). Over Pt-based binary alloys loaded on CeO_2 catalyst, the production of C2 and C3 hydrocarbons was greatly increased under an electric field, even at a low temperature. For DRB, the synergistic effect between surface protonics methodology and Ni-based ternary alloy drastically improved the activation of benzene. In summary, electroassisted catalysis based on surface protonics is an effective methodology to achieve low temperature conversion of robust molecules. With the delicate design of surface environment and modification of active sites by alloying, the catalytic activity and selectivity can be drastically enhanced.

Thus, the author is qualified to receive the PhD degree in engineering, Hokkaido University.