Space- and time-resolved *operando* spectroscopic studies of heterogeneous catalysts under unsteady-state operations

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Keywords: heterogeneous catalysis, *operando* spectroscopy, unsteady-state operation

There are several important catalytic technologies intentionally making use of dynamic changes in the reaction atmosphere (i.e. unsteady-state operation) to boost catalytic performance, especially product selectivity, by overcoming thermodynamic constraints. A notable example is NO_x storage-reduction (NSR) enabling challenging NO_x reduction in oxidizing atmosphere by creating oxidizing and reducing environments alternately. Another example is a process we have developed recently, so called CO_2 capture and reduction (CCR), based on an isothermal unsteady-state operation to combine CO_2 capture and reduction steps in one process.[1,2]

In this contribution, first our recent efforts to develop the process enabling the production of syngas ($CO+H_2$) and methane using CCR are presented.[1] For the synthesis of syngas, diluted CO_2 streams common in process flue gas (e.g. 5-13 vol%), even containing oxygen and water, can be fed to the reactor and relatively pure product stream can be produced. We investigated the catalytic reaction mechanisms by elucidating the nature of active sites and surface species using space- and time-resolved *operando* spectroscopy and diffraction (DRIFTS, XAFS and XRD).[3] Such *operando* characterization clarified that unique catalytically active phases are only formed under specific reaction conditions and the phases are responsible in achieving high CO_2 capture and reduction efficiencies.

Furthermore, a similar approach has been employed to elucidate the reaction mechanism of other reactions including NSR. Our recent work on space- and highly time-resolved *operando* studies of the surface chemical processes along the catalyst bed will be presented.

References

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