Università degli Studi di Padova

DiSC

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il **Prof. Tapio Salmi**

Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR)
FI-Turku-Åbo
Finland

terrà il seminario dal titolo:

Transient techniques in the investigation of catalytic processes

La presenza della S. V. sarà molto gradita

Prof. Tapio Salmi

Il Direttore del Dipartimento
Stefano Mammi

Transient techniques, such as step and impulse response experiments are well-established tools in the investigation of reaction mechanisms for catalytic gas-phase reactions. For gas-phase processes, very sophisticated techniques have been developed, e.g. isotope exchange methods, steady-state isotopic transient kinetic analysis (SSITKA) and temporary analysis of products (TAP). However, an essential part of industrially applied catalytic processes are carried out in three-phase systems, where heterogeneous catalysts co-exist and interact with gas and liquid phases. Typical examples are oxidation, epoxidation, hydrogenation and decarboxylation processes. For this kind of reaction systems, the detailed molecular mechanism is still in many cases unclear, even though the overall reaction scheme might be well-established. Experimentation and modeling of transient states of chemical reactors are of interest to describe reactor start-up and shut-down, to predict dangerous situations and to model reactors which are by purpose operated under dynamic conditions, such as reverse-flow fixed beds. Here we present recent experimental and modeling results of hydrogen peroxide direct synthesis, alkene epoxidation and sugar oxidation processes. Hypotheses are confirmed by dynamic modeling.

The catalysts used in hydrogen peroxide synthesis, alkene epoxidation and sugar oxidation were supported palladium (Pd), titanium silicalites (TS-1 and modifications), and supported gold (Au), respectively. Small catalyst particles were loaded together with inert material in tubular reactors, in order to guarantee isothermal operation. The flow patterns of gas and liquid phases were checked under non-reactive conditions by injecting inert tracers to the system. The gaseous reactants (alkenes, hydrogen and oxygen) were fed into the system together with aqueous hydrogen peroxide and a solvent, typically methanol, acetonitrale or water. The concentrations at the reactor outlet were measured by rapid GC.

The dynamic, time-dependent mathematical models consisted of partial parabolic differential equations (PDEs) which described the gas and liquid bulk phases and ordinary differential equations (ODEs) which described adsorbed species on the active sites of the catalysts. The flow pattern was assumed to follow the axial dispersion model, where the dispersion coefficient was obtained from the step change experiments with inert tracers. The PDEs were converted to ODEs by discretization of the axial coordinate with finite differences and the ODE system created was solved numerically with stiff ODE solvers implemented in gPROMS and Modest software. A combined simplex-Levenberg-Marquardt method was used in parameter estimation. For hydrogen peroxide synthesis, the step responses of the main products, H_2O_2 and H_2O showed very different dynamics: the response of H_2O_2 was much more rapid than H_2O, thus strongly indicating that H_2O_2 and H_2O are mainly formed through a consecutive route, i.e. the main origin of H_2O is hydrogenation of H_2O_2. For alkene epoxidation, the formation of secondary ring-opening products was confirmed by the step response technique. Furthermore, interesting catalyst activity phenomenon was observed in the epoxidation of 1-butene: the response of the epoxidation product showed an overshooting behavior, indicating the accumulation of reaction products inside the porous catalyst.

The lecturer, Dr Tapio Salmi is professor in chemical reaction engineering at Åbo Akademi, Finland. He has the highest research position in Finland, Academy Professor. He is the author and co-author of 660 scientific articles, four textbooks and he has supervised 70 doctoral theses in the field of chemical reaction engineering and catalysis.