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Rational Asymmetric Catalyst Design, Intensification and Modeling

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1. Introduction

The development of new catalysts for a variety of chemical processes, molecular-level fundamental understanding of how it works and knowledge of surface science, chemistry, materials science, process modeling, process systems engineering, etc. is needed. Catalyst design and kinetic modeling have long been based on chemical intuition, i.e., the combination of a large empirical database and qualitative concepts of chemical reaction engineering and surface science. Recently the first principle kinetic modeling has become an important tool to investigate catalytic reactions and catalyst structures for superior operational benefits by integrating first principle guided exploration and experimental data. Nanocatalysis design is the building blocks of the concept of micro-level controlled reaction engineering, and the size and shape dependant material properties are the key enabling factor of the emerging technology. The qualitative difference is infect the material properties those changes in 1-10nm scale. Drastic enhancement in capabilities in nanomaterial synthesis with increasing control in size and shape were observed in last two decades but the rational catalyst design criteria is still not mature. Consideration of reaction brings intrinsic complexity in nanomaterial topology development (for a catalyst design) and emphasize on systematic multiscale simulation method to design and forecast.

In the field of heterogeneous catalysis, desired topological improvements on the basis of experimental information is well known and tedious [1]. Advances in surface science enable data manipulation of individual atoms on the catalyst surface with experiments provides initial guess towards systematic design. Number of model based catalyst design strategies were reported in open literature like use of qualitative reasoning and knowledge-based systems [2, 3], computational models [4-6] and detailed microkinetic modeling for catalytic systems [7]. In order to get the job done, compositional analysis of physical, chemical, and/or biological properties and validation of appropriate molecular structure (robust forward model linked with material description and knowledge extraction from experiment). Reaction modeling systems, optimization, and artificial intelligence based tools

were extensively developed in automated environment to avoid reaction engineering expertise in building robust kinetic models. These tools allow rigorous analysis of multiple reaction mechanisms in the light of experimental data. Katare et al. [6] demonstrated kinetic model development for propane aromatization on H-ZSM-5 zeolite catalyst with a proof-of-concept in his studies.

Similarly, organometalic catalyst has interests in the broad areas of homogeneous catalysis, and catalyst modeling and mechanism elucidation. The main thrust of the field is in catalyst design and investigation of mechanistic aspects includes organic synthetic, organometallic and inorganic chemistry, molecular modeling and reaction monitoring. Fundamental research provide a theoretical basis and looks at the catalyst modeling using both experimental and theoretical techniques, providing information on active species and likely transition states. Ultimately helps in designing real experimental systems to be modeled with reliability and confidence. Mechanistic investigations using spectroscopic and kinetic methods help elucidate catalytic pathways and possible catalyst decomposition routes. Assessment and optimization of catalyst performance factors effecting catalyst behavior are important. The study of heterocyclic carbenes and synthesis of mixed carbene-donor ligands (transition metal complexes) were under extensive consideration. The structure, stoichiometric reaction behaviour and catalytic potential of the new complexes are the key goals to elaborate ways of manipulating the chemistry of the complexes in catalysis. The synthetic work is coupled with theoretical studies on orbital behavior and effects on the energetics of decomposition reactions. Synthesis of new polydentate ligands and their transition metal complexes offer prospects for the formation of new alkene polymerisation, copolymerisation and oligomerisation catalysts. Ligands with phosphorus, nitrogen and/or oxygen donors are the main classes of ligands and their selection depends on the metal being investigated. Therefore, methodology for catalyst discovery targets suitable strategy based on the conceptual tools of surface mechanism, molecular, bio and solid state chemistry.

2. Reaction modeling suite

The model building procedure needs rapid screening of reaction mechanistic hypothesis that could explain the experimental data. Number of user driven tools were available those facilitates knowledge archiving and retrieval to an automated reaction kinetic modeling. These modeling suites develop reaction mechanism and directly construct kinetic model. The architectural philosophy behind cumbersome mathematical modeling is shown in figure 1. Modelling can provide reaction energies (ΔH_r), energy barriers (ΔE_a), location of intermediates, etc. and it can explore catalyst composition, poisons, promoter's effect, efficiencies of catalysts using alternative routes, etc. In homogeneous catalyst design control of activity, ligand type, concentration of co-catalyst, molecular weight, tacticity (depends upon equilibrium), etc are also important.

The automated kinetic models development software tools of reaction networking, parameter optimization and overall kinetic modeling etc., are available in bulk like Reactor, Reaction Modeling Suite (RMS), KINAL A, Aspen Custom Modeler, gPROMS, Presto Kinetics, GREGPAK, Matlab, MLAB, ParaMetra, Scientist, Eurokin, polymath, Chemkin, Mitsubishi, MKM, IBM CKS, NetGen, XMG, Dynetica, Forcite, COMPASS, Sorption, CASTEP, DMol^3, Gepasi, Athena Visual Studio parameter estimation tool, E-cell, DBsolve,
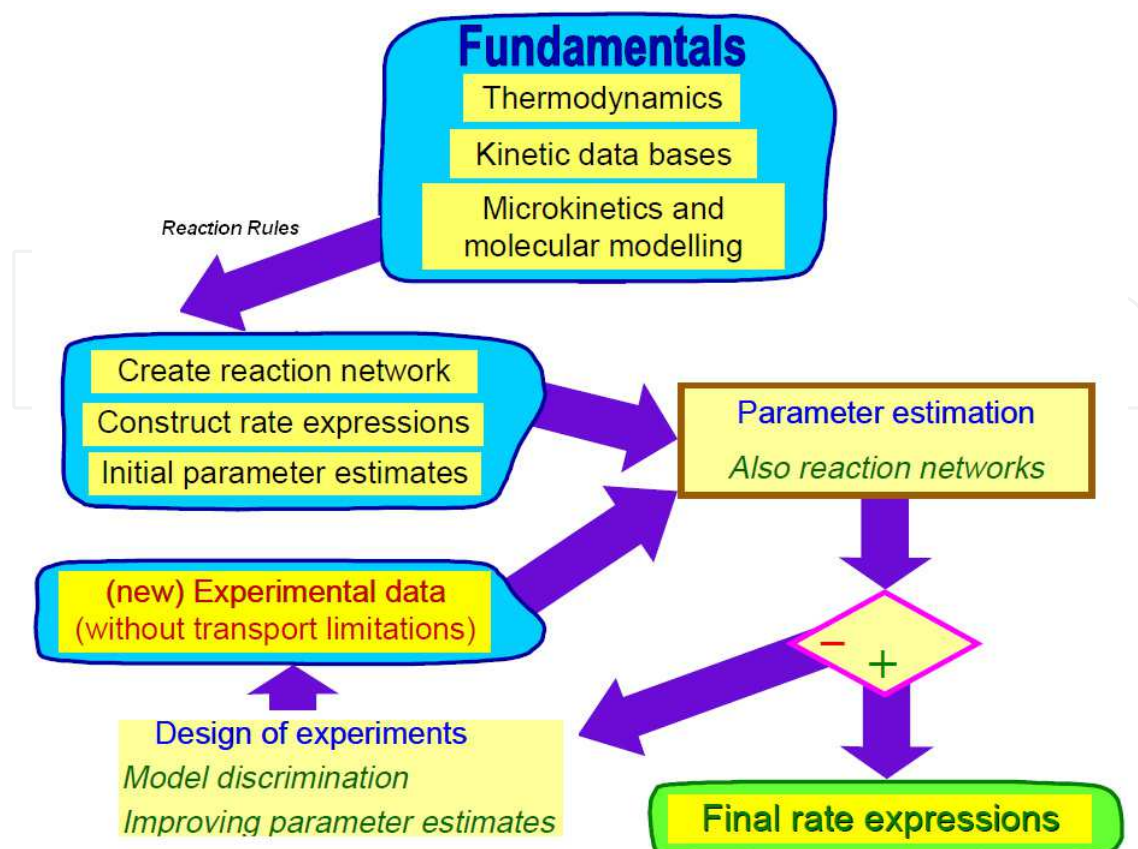
Fig. 1. Inventory of model building process

etc. For catalyst design Katare et al. developed a predictive model for surface reactions studies and claims to be rational and robust [6]. The key steps involved in this model building are generation of the simplest plausible reaction mechanism, translation of the reaction mechanism to a computationally tractable mathematical model, solving the model to estimate the parameters in light of high throughput and/or insufficient experimental data, refining the model to better fit the data by altering the mechanism, suggesting new experiments that could help in discriminate among multiple models. These software tools needed state of the art features for specific purposes [6]:

Reaction mechanism generation and networking

- Accurate representation of the large number of elementary reactions, overall reactions and species.
- Robust compiler that fallows the generic reaction rules to generate network generator.
- Pruning the reaction mechanism to get it in simpler and sophisticated.
- Reduce the number of thermodynamic and/or kinetic parameters to optimize based on thermokinetic and experimental data manipulation.

Kinetic parameter estimation

- Robust solvers that can handle large number of differential-algebraic equations and validate parameter estimation techniques.
- Evaluation of the multiple solutions for the parameters that explain the experimental data also.

Results and forecasting

- Discrepancies identification and optimization between the key features of model and experimental data that leads to design of experiment and questions on generated mechanism.
- Explain robustness of the model development with boundaries and shows statical analysis.

The most critical and important task in building a robust model is development of kinetic model and its also the most-time-consuming (excepting experimental or pilotplant campaigns). Without a satisfactory reaction mechanism and kinetics, a model may be applicable to narrow ranges of conditions and dangerous to use for predictions. The open literature information may not exactly match your conditions or catalyst formulation, therefore, formulation or selection of reaction-mechanism and rate expressions is best suggested. Establishing the reaction kinetics involves selection of rate expressions, and determination of rate parameters. Rate expressions involves four parameters; pre-exponential factor, activation energies, reaction order to each component and adsorption constants. The pre-exponential factors must be determined from the actual experimental data for catalyst or reaction conditions. This chapter give pathway to model information for catalyst design and intensification from state of the art reaction kinetics data generation, to the developing of computer-based knowledge organization for catalyst development, with brief review said techniques and models.

3. Thermodynamical consistency

In mechanism development and rate parameter optimization, thermodynamic consistency at both the enthalpic and entropic levels was often overlooked. An inconsistency in enthalpies gives incorrect solutions to the energy conservation equation, which lead towards ambiguous predictions of heat exchange, conversion, selectivity, etc.; while entropic inconsistency explains fundamental inconsistency (i.e. the pre-exponential factors). As there is no specific criterion for thermodynamic consistency evaluation and it distorts underlying equilibrium constant, only few published mechanisms are thermodynamically consistent [9-12]. In general, for any i-th reaction in a, the following equations form the basis of the enthalpic and entropic constraints [13]. For thermodynamically consistent mechanism the ratio of equilibrium constants (determined by gas phase thermochemistry) should be closer to 1 and for rigorous account of temperature variations data its necessary.

$$\Delta H_i = E_i^f - E_i^b = \sum_{j=1}^{L} c_{ij} \left(E_j^f - E_j^f \right), \qquad i = L + 1, I$$

$$A_i^f / A_i^b = e^{\Delta S_i / R}$$

$$\frac{\Delta S_i}{R} = \ln(A_i^f / A_i^b) = \ln \prod_{j=1}^{L} (A_j^f / A_j^b)^{c_{ij}} \, , \quad i = L + 1, I,$$

where f stands for the forward, b for backward reaction steps, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, ΔH is enthalpy change and

ΔS is entropy change of the reaction, respectively. For a linearly independent set of reactions network, if L is the size of reaction mechanism (unique in size) having I number of reactions, then $L \leq I$. The linear dependent reactions constraints can be expressed as c_{ij}, those are the coefficients of i-th linearly decomposed reaction onto the reaction basis.

4. Computer aided catalyst design

Computer aided catalyst design and intensification is an integrated approach in catalysis research and development, as chemical engineering is currently re-emerging under the label process intensification. The concept of process intensification is catalysis is new and not well established in the catalyst design industry. It is particularly well suited for the design and development of new catalyst. The incorporation of appropriately designed micro-structured catalytic having good control over the surface chemistry of the reaction is presented. Modelling of reactions at the active sites of catalysts also performed some times using density functional theory, and we will not discuss this here.

5. Reaction modeling suite

Reaction Modeling Suite (RMS) was developed by Purdue University, USA [6]. The quantitative kinetic description of a reaction mechanism involves specification of a differential and algebraic equation for each reaction component. RMS can develop reaction mechanism that typically involves more than 10 differential equations for a simple reaction and for complex mechanisms it can be 100 or more differential equations. Each set of differential equations includes a number of kinetic parameters that must be regressed from experimental data. It is a tedious, time-consuming task to develop code and solve the appropriate set of differential equation, where there is a real possibility of mistakes due to the complexity. The key steps involved in this process are reaction mechanism form chemistry rules, conversion of mechanism to a tractable mathematical model in computer language, integration of differential/algebraic set of equations with the suitable initial conditions, optimum model parameters estimation and finally analysis of reliability of the model parameters.

Each of the above steps requires considerable expertise, time and effort. Moreover, there are typically a number of potential kinetic models that need to be evaluated, and the model building/solving tasks must then be repeated for each new physical model. RMS presents the appropriate tools so that chemical experts can focus on chemistry without be overly burdened with the implementation of the required numerical methods. Purdue University, has successfully developed a set of systems tools, called the Reaction Modeling Suite (RMS) for rapid generation of complex kinetic models and evaluates these models with large, diverse sets of experimental data. These system tools are essential if model building and evaluation are to keep a pace commensurate with the rate of data production from high throughput experimentation [6]. In RMS, Chemistry Compiler takes a set of chemistry rules (i.e. any kinetic model is defined by a set of reaction rules), ensures that the rule set is chemically consistent, and finally generates the appropriate kinetic expressions. Next, an Equation Generator takes the kinetic expressions and develops the appropriate differential and algebraic equations in a form that can be solved numerically. Parameter Optimization is the next step, where the best set of parameters for a given model needed to describe the experimental data was determined i.e. non-trival for the large, nonlinear, coupled sets of

DAEs associated with complex kinetic mechanisms. Finally, a Statistical Analyzer has been developed to quantitatively assess the reliability of the model parameters with the ability to use nonlinear statistics. The RMS tools enable the nearly automatic analysis of multiple reaction mechanism and kinetics that assist catalyst design.

6. Catalyst intensification and optimization

The following is an overview of the catalyst modeling and optimization features necessary in developing attractive suite. Catalysts can be modeled in several different ways, with increasing levels of complexity by considering pellet balances, pellet factor effectiveness factor using is basic activity profiles, etc. With out pellet balances optimization is a very basic modelling level, it is not necessary to make any extra calculations due to the presence of a catalyst by expressing reaction kinetics in terms of composition of the catalyst. The catalyst composition can then be made an optimization variable. In the case of plug flow reactors, the composition can be varied along the length of the reactor, and viewed using the catalyst profile. Pellet factor calculation involves balances between component concentrations in the bulk, and within the catalyst pellet. The activity distribution inside the pellet is represented by a "Dirac-delta" function (infinite concentration at a single location). Although this cannot be achieved in practice, the Dirac-delta function can be closely approximated by a narrow step distribution of active material around the optimal location of the delta function without noticeable loss in performance.

Catalyst effectiveness factor calculations may involve Thiele modulus and effectiveness factor for the pellet. The effectiveness factor is a function of temperature, pressure and catalyst properties such as shape, size and diffusivity of components. When using this method the catalyst properties become optimizable parameters, and optimized profiles can be obtained. This method is sub-divided into basic activity profile as represented below:

• Uniform - The active material is uniformly distributed through the pellet.
• Egg-shell - The active material is concentrated at the pellet surface, and rarefied towards the centre.
• Egg-yolk - The active material is concentrated at the pellet centre, and rarefied towards the surface.
• Peaked - The active material is concentrated at a location partway between the centre and surface, and rarefied towards the centre and surface.
• Layered - The active material is distributed in a layer of thickness T, and location L from the pellet centre, where T and L are expressed in fractions of the pellet diameter.

The activity profiles are represented as infinitely variable profiles and by definition, when using the effectiveness factor method, the intrapellet mass balances are solved to determine the conentration profile throughout the catalyst pellet. There are also three further levels of complexity which can be selected to improve the model at the expense of computational time:

• Interphase mass balances causes the concentration profile between the pellet surface and the bulk material to be calculated.
• Interphase heat balances calculates the temperature profile between the pellet surface and the bulk material
• Intrapellet heat balances calculates the temperature profile within the catalyst pellet

Catalyst deactivation is defined as the steady degradation of the performance of the catalyst over time. Deactivation can be modeled by describing a deactivation correlation which relates the catalyst performance to its age. The deactivation factor varies from 1.0 (fresh catalyst) to 0.0 (fully depleted catalyst). If catalyst deactivation is significant it is important to consider its effect when optimising the catalyst properties. Properties which are optimal when the catalyst is fresh may become highly non-optimal by the time catalyst has degraded. By considering catalyst deactivation during optimization it is possible to design a catalyst that, while non-optimal initially, becomes optimal when its performance is averaged out over its lifespan. An additional factor which may be considered is the possibility of modifying the reactor temperature over time, to help minimize the impact of the catalyst deactivation.

Center of Process Integration, University of Manchester, United Kingdom provides a unique software suite have all above features named "REACTOR". Figure 2, 3 and 4 shows its user interface for optimizing catalyst properties. It also develops rate expressions and optimized the reactor at desired operating conditions. Heterogeneous catalyst's fluid-particle interface is modeled in mass and energy balance below
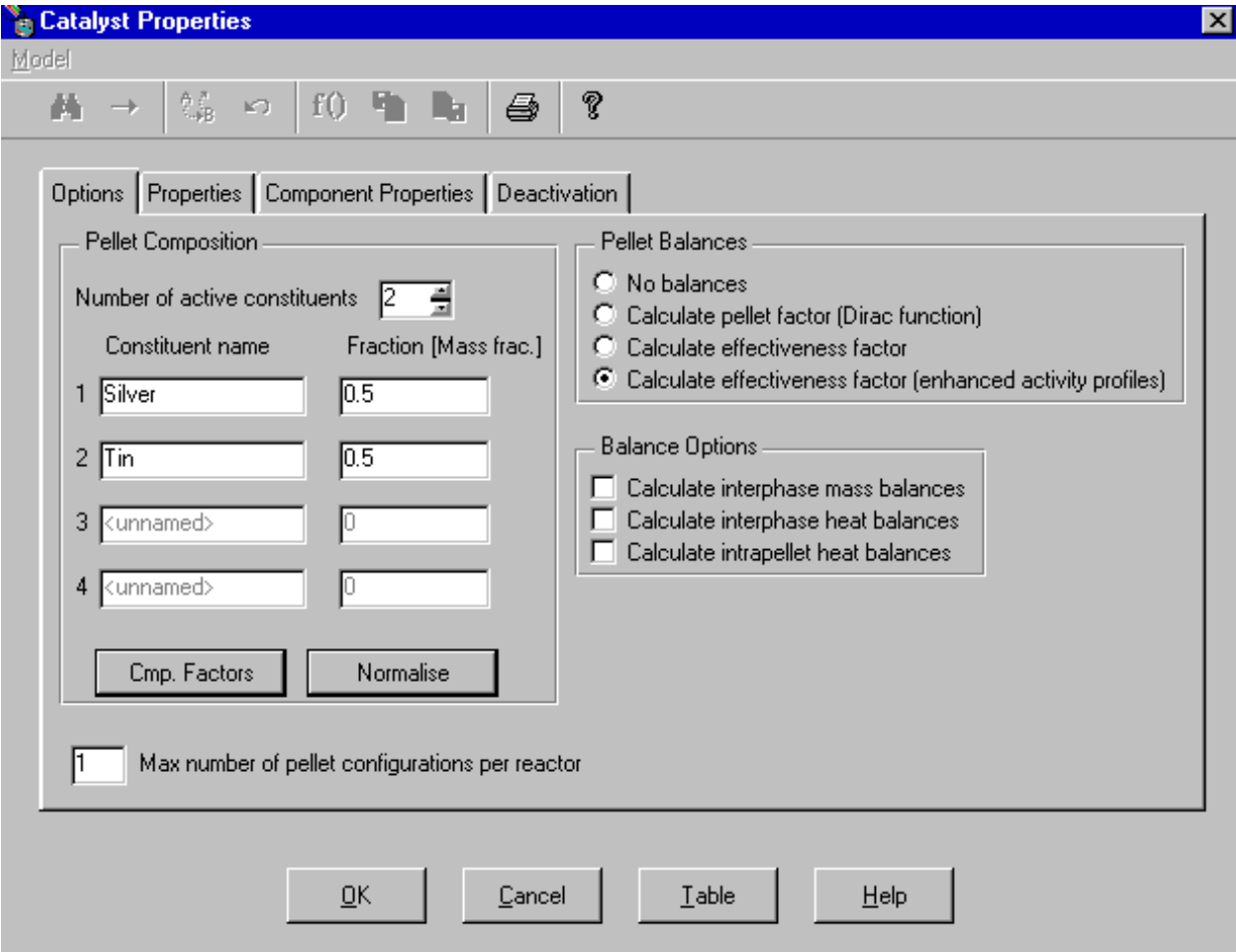

Fig. 2. Catalyst properties options in REACTOR

Mass balance:

$$k_{g,i}\left(C_{s,i} - C_{j,i}\right) = -D_{e,i}\frac{dC_i}{dz} = \eta \sum \left(V_{i,j} - R_{s,j}\right)\rho p S' \tag{1}$$

Energy balance:

$$h\left(T_s - T_g\right) = -\lambda \frac{dT}{dz} = \eta \sum \left(\Delta H_j - R_{s,j}\right)\rho p S' \tag{2}$$
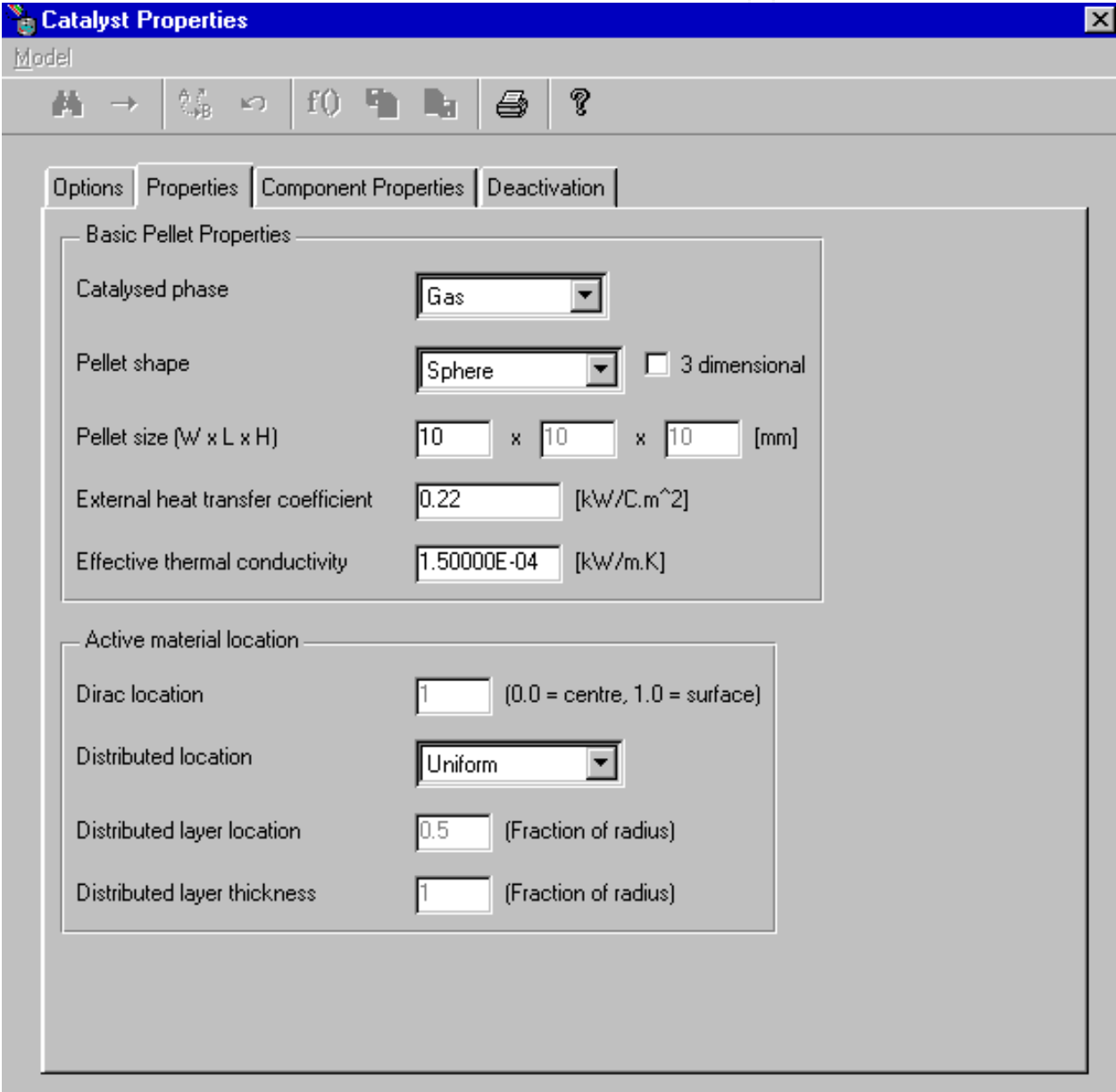

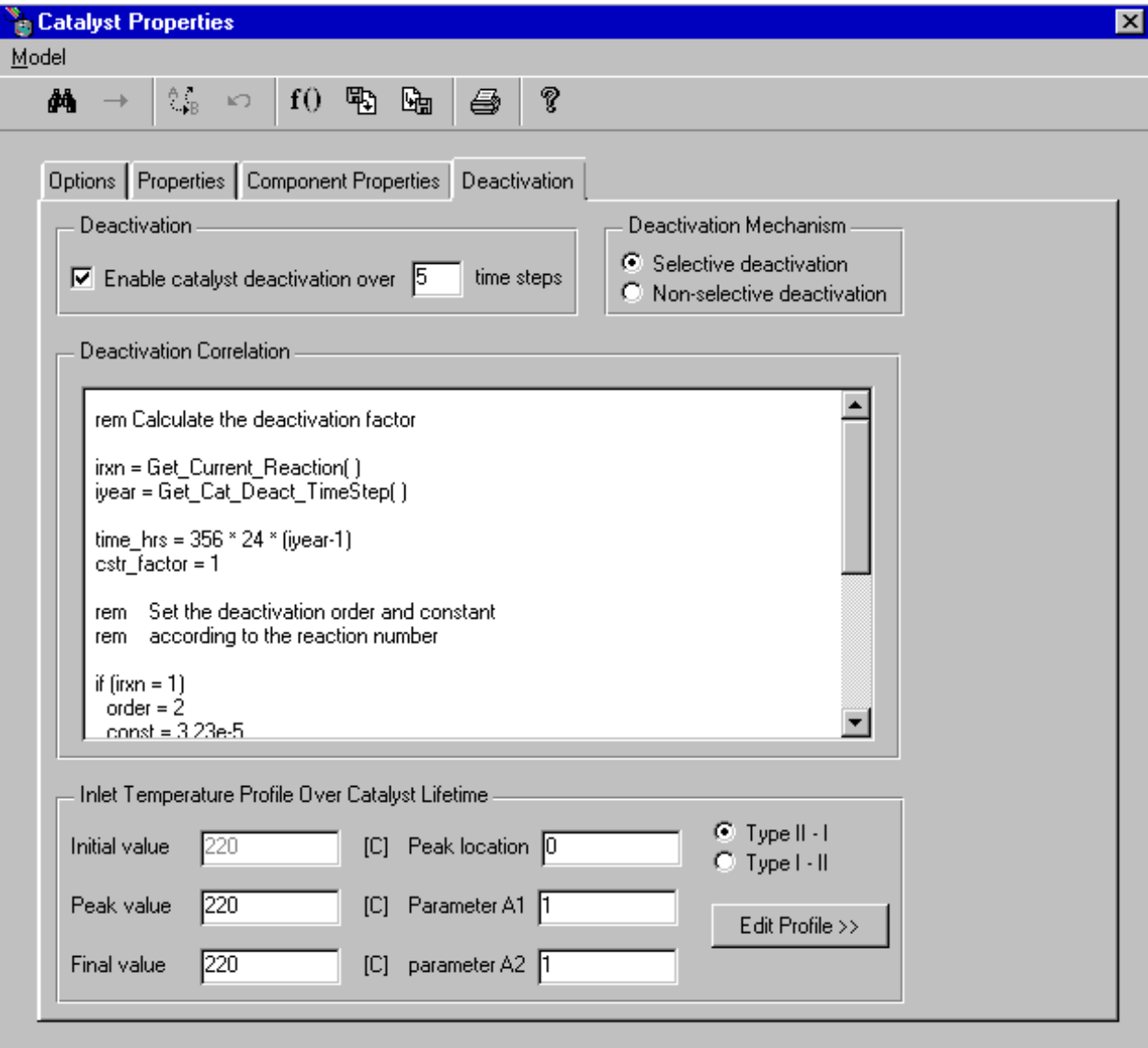
Fig. 3. Catalyst physical properties options in REACTOR

Fig. 4. Catalyst deactivation modeling window in REACTOR

7. Microchannel design and modeling

Microchannel has distinct identical channels and shape with characteristic dimensions in the order of micrometers and surface area-to-volume ratios ca. 50-100 times higher than those of their conventional counterparts. Due to the presence of high surface areas, sub-millimeter dimensions and metallic substrates usage, heat can be distributed quickly and uniformly distributed along the channel walls of the catalyst. High heat integration opertunities are available to drive endothermic and exothermic reactions independently and/or in parallel. The representative units can be modeled by incorporating two-dimensional continuity, momentum, energy conservation and species mass transport equations for the fluid and catalytic wall phase, and energy conservation equation for the metallic/catalytic wall phase. Simultaneous solution of these equations may carry out using finite elements methods. The model is then used to figure out the effects of various configurationally parameters such as wall thickness, type of wall material and the presence of micro-baffles on temperature distribution. The results forecast the parameters

affects the degree of heat flow between channels and provide useful insights for the design of microchannels/catalysts.

8. Thermoanalytical technique

Thermoanalytical techniques were considered as transient response techniques, those relate characteristic properties of solid catalysts to its temperature programmed heating. Exchanges of matter and/or energy between and/or on surfaces of the solid catalysts provide means to follow physical or chemical transformations. The response obtained against certain temperature (thermogram) reflects the nature of the system and suitable experimental conditions. This analysis is used as a tool for quantitative and qualitative analysis for evaluating the influence of different activity factors. The most common thermoanalytical techniques are listed in Table 1. Number of methods exists in the open literature for extraction of kinetics information from thermoanalytical data [14]. Particularly in the heterogeneous catalysis, these techniques are powerful tool for investigating the influence of composition, preparation method and pretreatment on the reactivity of the surface or bulk with gases.

Thermal analysis techniques	Characteristic factor monitored
TPx Temperature-programmed reaction Temperature-programmed desorption (TPD)	Gas composition at the reactor outlet Characterisation of adsorptive properties of materials, surface acidity, total adsorption and desorption capacity with temperature, temperatures of rate maxima, metal surface area and dispersion, surface energetic heterogeneity, binding states and energies of adsorbed molecules, mechanism and kinetics of adsorption and desorption
Temperature-programmed reduction (TPR)	Characterisation of redox properties of materials, consumption of reducing agent with temperature range, temperatures of rate maxima, valence states of metal atoms in zeolites and metal oxides, metal oxide and support interaction, indication of alloy formation in bimetallic catalysts
Temperature-programmed oxidation (TPO)	Characterisation of coke species in deactivated catalysts and redox properties of metal oxides, total coke content in deactivated catalysts, mechanism and kinetics of oxidation reactions, deactivation kinetic mechanism
Thermogravimetry (TG)	Weight of sample
Differential thermogravimetry (DTG)	Rate of weight changes
Thermomechanical analysis (TMA), Dilatometry	Specific volume of solid sample
Thermomagnetic analysis (TMA)	Magnetic susceptibility
DMC Differential microcalorimetry	Enthalpy difference between sample and reference

Table 1. Thermal analysis techniques and their uses

The suitable model can account for heterogeneity in terms of chemisorption by introducing a sufficient number of different adsorption states. The readsorption formulated and tested against experimental data by describing the intrinsic dynamics of an adsorption state as a quasiequilibrium adsorption/desorption between the gas phase and the surface. Conceptually it is potentially useful for the elucidation of fundamental reaction mechanistic information for design and intensification of catalyst. The transient response methods place similar requirements on experimentation as conventional methods of kinetic analysis. In slow transient input, all or part of the elementary reactions may proceed in quasiequilibrium and their individual rates then can not properly elucidated. In general this is based on nonlinear regression analysis, and omits assumptions of pseudo-steady state.

In our extensive studies of catalyst intensification we conduct series of kinetic analysis for TPx experiments in phenomenological way [15-17]. Modelling of TPD data is based on adsorption and desorption theories, while TPR and TPO call for gas-solid surface reaction mechanisms, which may include topochemical characteristics. Further the rate of surface reaction divided into intrinsic rate of reaction per area of reaction interface and change in the reaction interface in reaction [18]. In general kinetic analysis of thermoanalytical data where there is a linear temperature rise (β) represented in the rate equation, where, rate of reaction is proportional to Arrhenius temperature dependence, A is pre-exponential factor, E is activation energy, and these are function of degree of conversion, f(α).

$$\beta \frac{d\alpha}{dT} = A\,exp\left[\frac{-E}{RT}\right]f\left(\alpha\right) \qquad (3)$$

The transforming eq. 3 by taking natural logarithms on both sides gives

$$ln\left[\beta \frac{d\alpha}{dT}\right] = ln\left(Af(\alpha)\right) - \frac{E}{RT} \qquad (4)$$

The plot of ln($\beta d\alpha/dT$) versus 1/T results straight line at a selected conversion level, the slope of the line gives -E/R at certain conversion level. This also did not explain reaction mechanism but by varing activation energy E=E(α) results from the Friedman analysis explains that eq. 3 with a normal physico-chemical interpretation will not describes the reaction kinetics.

9. Design and intensification of Pt-Sn-based alkane dehydrogenation catalyst

The control of chemical reaction pathways at molecular level presents undoubtedly the most important scientific challenge on the way to fully sustainable, thermodynamically efficient chemical processes. Integrated molecular reaction control is one of the major breakthroughs in achieving sustainable and efficient chemical processes design. Numerous fundamental works on this topic have been reported in literature and it is now the key challenge to advance them in an interdisciplinary way towards the industrial catalysis. The molecular alignment and geometry of collisions as well as selectivity of desired product was tackled by catalyst topology. In this example we discusses Pt-Sn based catalyst design and intensification for light alkane dehydrogenation to light alkenes. Constraints of this reaction are very complex due to endothermic limitation and endothermicity.

Bringing more molecules at the energy levels exceeding the activation energy threshold by conductive heating but it offers only a macroscopic control over the reaction and is thermodynamically inefficient. There are two broader approaches to control stereochemistry of reaction. First consists of immobilizing the molecules during reaction in confined nano-spaces by imposing "hard walls"of structures or of other molecules, or to force reacting species to assume certain position inside the offered structure. The second approach consists in acting upon moving molecules with spatially oriented external fields. Methods for controlling molecular alignment and orientation via nano-structural confinement invite shape-selective and imprinted catalyst. Shape-selective zeolites (having distinct sized nano-cage) discriminate between reactants and products and between tran-sition states molecules within the pores [19, 20].

Pt-Sn-based catalysts supported on amorphous supports or zeolites, for propane dehydrogenation have been discussed in many studies [15-29]. The selection of Sn as a promoter has been explained in terms of geometric and/or electronic effects [30]. In the geometric effect, Sn decreases the size of platinum ensembles, which reduces hydrogenolysis and coking reactions. Sn also modifies the electronic density of Pt, either by positive charge transfer from the Snn+ species or the different electronic structures in Pt-Sn alloys [31]. The deactivation of Pt-based catalyst during propane dehydrogenation is fatal, and mainly due to the aggregation of Pt particles and carbon deposition [31, 32]. However, the mechanistic understanding is still controversial and the reaction results were not conclusive, especially on stability and selectivity. In early days much focus has been given to Pt-Sn-based catalysts supported on Al_2O_3 for propane dehydrogenation. But the lifetime of these catalysts is too short. Therefore, there is a growing interest in developing zeolite supported catalysts, e.g. Pt-Sn/ZSM-5 zeolite for propane dehydrogenation, because of longer activation times and higher conversions [15-17]. Many studies have improved the performance of Pt-Sn/ZSM-5 catalysts by adding a more metallic promoter (particularly from alkali or alkaline earth metals) like Na, Fe, Zn, etc. [33, 34] and by increasing the Si/Al ratio of the ZSM-5 support [16, 34]. However, ZSM-5 supported catalysts were detrimentally affected by frequent regeneration with steam [35] and have lower propylene selectivity [16]. ZSM-5 supported catalysts can further take part in cracking and their large pore size fails to create shape selectivity effect for propylene. Moreover comparing the effects of supports and additional promoters, it was observed that the performance of propane dehydrogenation reaction significantly dependent on support. In particular it was noted that the control of intermediates products to desired product over the bi-functional catalyst was significantly support dependent.

Detailed TPx experimentation and kinetic studies with continuous experimental validity took us towards the innovative design of Pt-Sn-based zeolite supported catalyst. In this case, competitive reactions present a picture of a nano-snooker game. Unfortunately, in practicing industrial reactors has very limited degree of control of molecular-level events, therefore the catalyst should be robust enough. Extensive analysis suggests SAPO-34 as support (almost inert to dehydrogenation), with good shape selective opportunities and hydrothermally stable. The silico-aluminophosphate zeolite SAPO-34 is a microporous sieve with a chabasite-like structure (structural code CHA), has an extremely good shape selective effect for propylene [36-38]. Their Bronsted acid sites are responsible for their activities and based on two distinct hydroxyls (OH-bridges to Al and Si) on the structural framework. The structure, acidity and catalytic properties of SAPO-34 depend on the number and

distribution of Si in the framework [39, 40]. Its Si based acid sites make it resistant to hydrothermal treatment and gives superiority over ZSM-5, where dealumination occur frequently [33, 34]. These observations suggest that the weak acidic support SAPO-34, which can sophisticatedly control the stereo-chemistry and gives shape selectivity effect for propylene in addition to being a bi-functional catalyst, Pt-Sn/SAPO-34.

The influences of the support on the reduction properties of Pt-Sn/SAPO-34 catalyst were analyzed by H_2-TPR and results are shown in Fig. 5. The reduction peaks at higher temperatures (above 450 ^{o}C) indicated that the Pt was well interacted with the support in the presence of Sn [5, 6, 14, 34]. The peak height and width increases with the increase in Sn loading, between 400 to 600 ^{o}C that may be due to joint reduction and valuable interaction between Pt and Sn on the SAPO-34 [24]. At higher temperatures towards Sn^o species forms. But the oxidation state of Sn (+2) in a bimetallic Pt–Sn catalyst was important, while the Pt-Sn alloy formation results in permanent deactivation [16, 24, 30]. The Pt attached to SnO is believed to be active for dehydrogenation reaction. The reduction peaks at the higher temperature indicated that the Pt had a strongly interaction with the SAPO-34 incomparative to other supports. The H_2 reduction results from Pt-Sn/SAPO-34 displayed sharp reduction peaks that confirmed the joint reduction and valuable interaction between Pt and Sn on the SAPO-34.
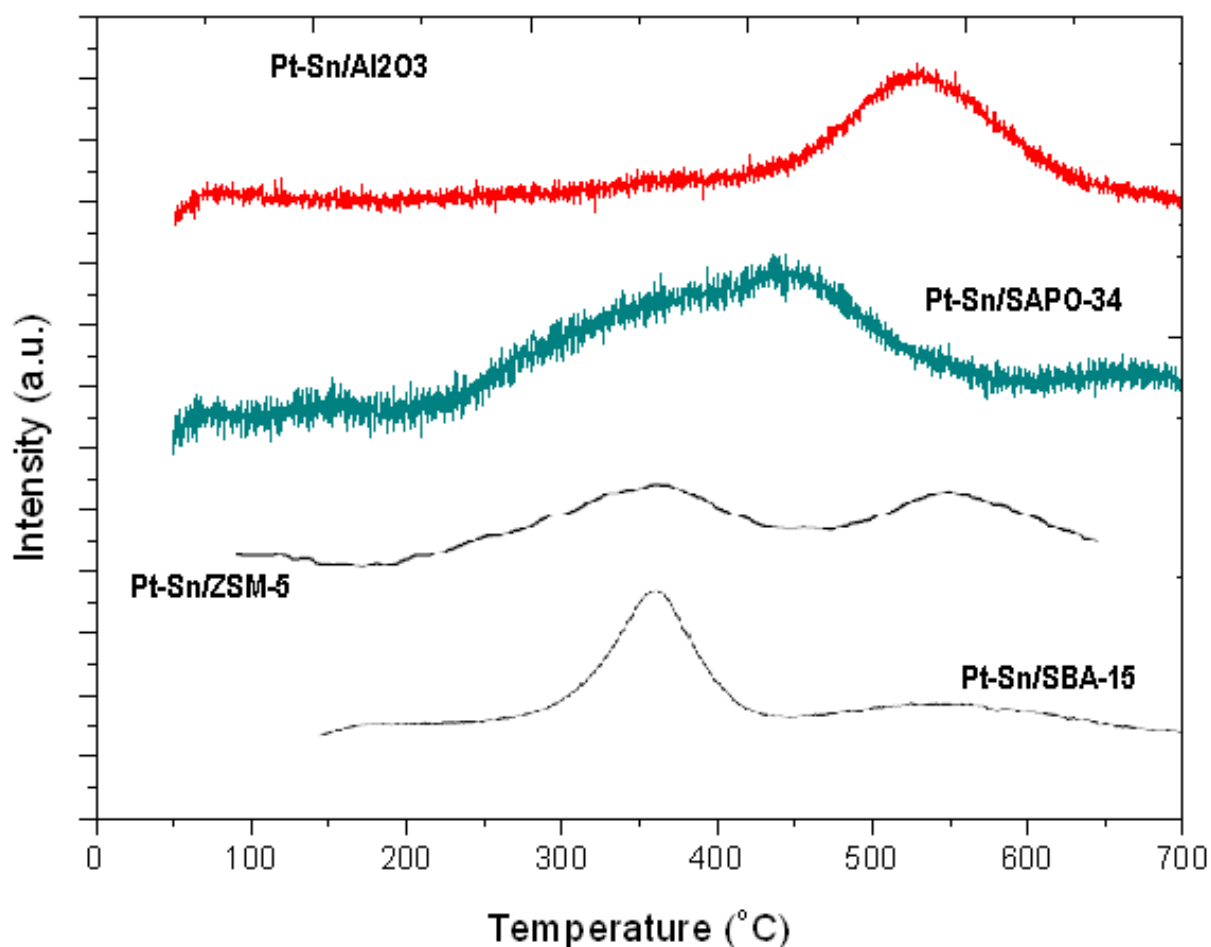

Fig. 5. H_2-TPR profiles of PtSn based different support catalysts of identical Pt and Sn composition.

Coke formation during propane dehydrogenation is the inherent factors that adversely affect catalyst performance. The amount of coke formed over different catalysts (after 8 hr reaction) was analyzed by TPO. The results are shown in Fig. 6. The typical TPO profile shows two successive peaks, indicating coke deposited on the metallic sites and support, while the peak height represents the intensity of deposition. The peaks between 300-400 ºC and 550 – 650 ºC corresponds to coke deposited on metallic site and support, respectively. It was noted that the strong electronic attachment over SAPO-34 facilitated the transfer of carbon deposits on metal sites to support. It's only possible when the metals are well interacted with the support. Moreover Sn modifies Pt ensembles by decreasing surface area and reduces carbon–metal bonds/interaction, and allows the intermediates to mobile easily to support [41].
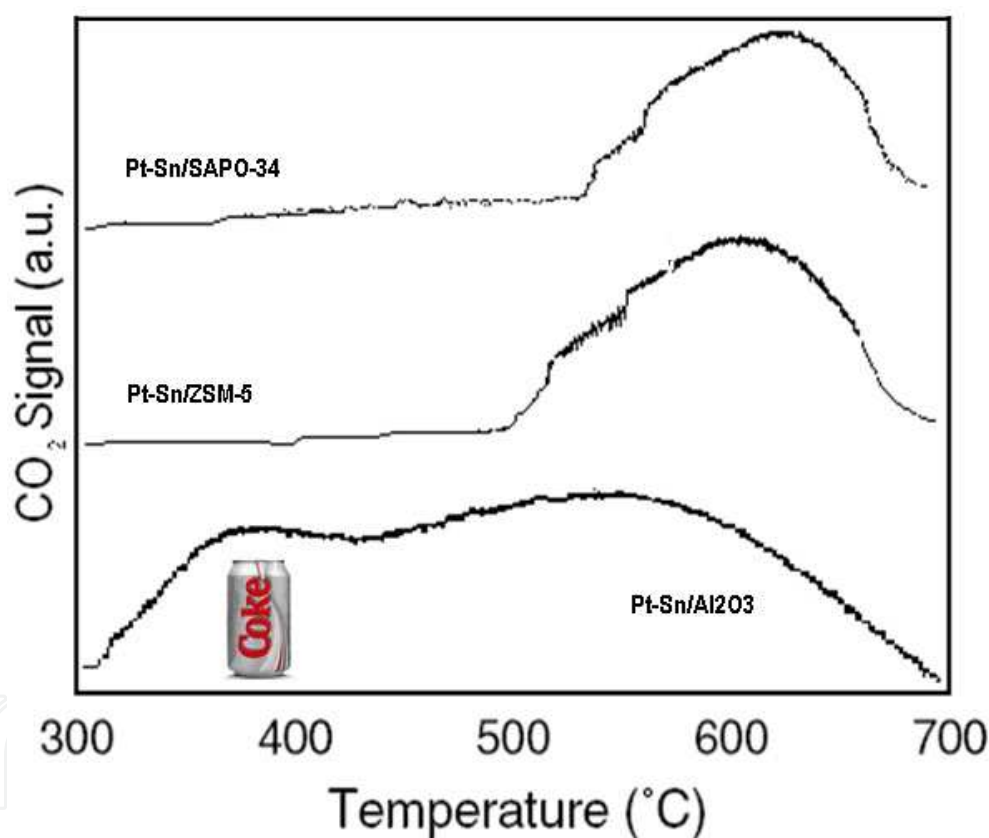
Fig. 6. TPO profiles of coke deposits on different supported PtSn-based catalysts after 8 hr propane dehydrogenation reaction under identical operating conditions.

The superiority of novel support SAPO-34 performance was experimentally verified (results are shown in Fig. 7 and 8), and it was observed that Pt-Sn/SAPO-34 catalyst controls the stereo-chemistry of propane dehydrogenation reaction much better than PtSn-based catalysts supported on ZSM-5 and Al_2O_3.
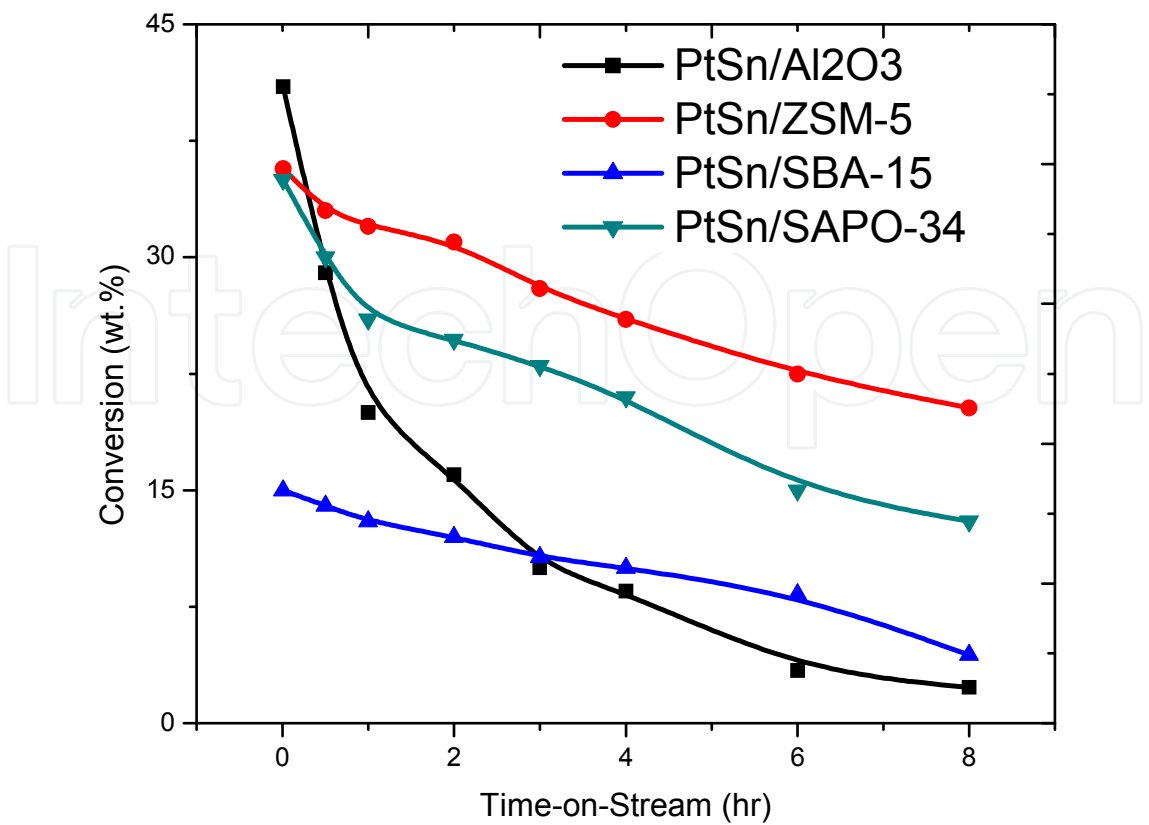
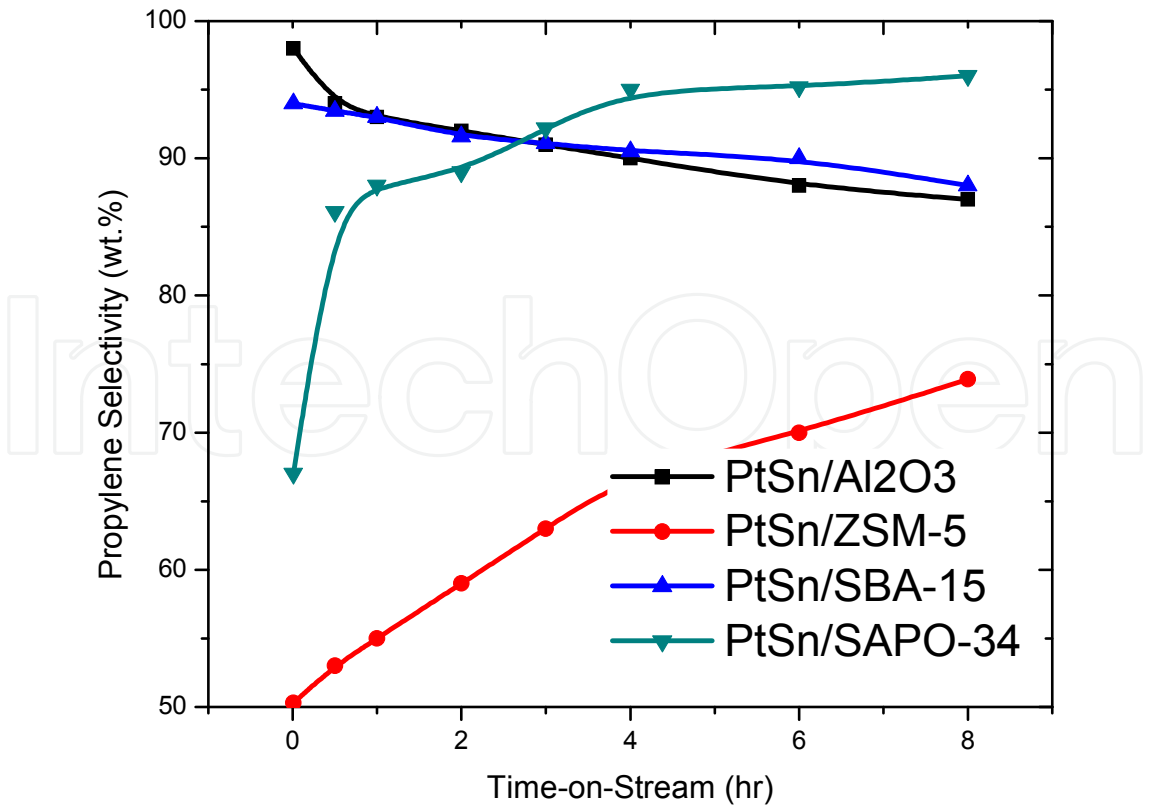Fig. 7. Catalysts activity at 586 °C for propane conversion

Fig. 8. Catalysts selectivity of propylene over different supported PtSn-based catalysts

10. Conclusion

Tight time and cost constraints force catalysis research to continuously reduce their experimental efforts during catalyst development and to facilitate the application of model-based strategy. Nevertheless, the effort of setting up a sophisticated model or criteria in coupling with novel TPx analysis for the design and intensification of catalysts is still higher. To overcome bottlenecks in catalyst modelling, considerable effort has to be spent with the systematization of kinetic models, formalization of reaction pathways, and development of knowledge-based software tools. This type of contribution claimed by number of software developers as discussed, while for the catalyst design we must need TPx analysis to achieve a robust design. It will be shown, how informal textual or metal-support information defining requirements on catalyst for a specified use. To find the optimal design under these uncertainties, a stochastic optimization method can be employed and verified by experimentation. In this work, the optimal properties of a catalyst for direct dehydrogenation of propane to propylene is presented, and uncertainties associated with the reactions and their parameters are modelled to design sustainable catalyst.

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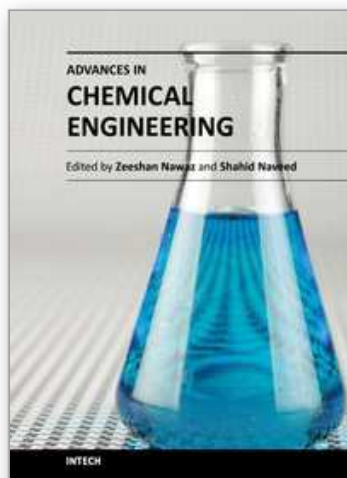
Advances in Chemical Engineering

Edited by Dr Zeeshan Nawaz

Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the sate of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic molding. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided in to two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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