

A General Exploratory Chemometrics Methodology For Catalytic System Identification

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Abstract

The system identification of unknown catalytic phenomena is often fraught with complications, and it is difficult to obtain quantitative kinetics and thermodynamic understanding of such chemical systems. Quantitative descriptions of catalytic phenomena constitute part of the inverse problem in chemistry and chemical engineering. In this paper, a novel chemometrics numerical methodology for general exploratory studies of complex catalytic systems is presented. Through the systematic implementation of various chemometrics techniques and logical rationalization, important chemical knowledge of little known or totally unknown catalytic systems can be elucidated. The chemical knowledge includes: (i) pure component spectra of observable species, (ii) chemical species identities and algebraic atom-free stoichiometries, (iii) postulated catalytic mechanism, (iv) algebraic reaction stoichiometries and corresponding extents of reaction matrices, (v) observable differential rate laws and activation kinetics, and (vi) observable activation and equilibrium thermodynamics parameters. This method was successfully applied to the complicated catalytic system of unmodified $\text{Rh}_4(\text{CO})_{12}$ catalyzed 1,3-cyclohexadiene hydroformylation, and is proven to be efficacious for obtaining coherent quantitative and qualitative answers for the aforesaid inverse problem.

1 Introduction

The pursuit for a coherent understanding of a catalytic system entails the following aspects of research, (i) experimentation, (ii) chemical analysis, (iii) data processing, and (iv) theorization of final chemical data. Each time a novel catalytic system arises, this entire research process has to be engendered and it usually takes years, if not decades to obtain a coherent understanding of the catalytic system. As such, it would be ideal to have a numerical methodology that expedites the extracting of pertinent information from analytical data acquired from well-designed experiments. In the present contribution, a general exploratory chemometrics methodology for such a purpose is explained. Schematic representations of this exploratory methodology are given in the following figures [1].

Figure 1 General Workflow for Exploratory Investigation of Unknown Catalytic Systems

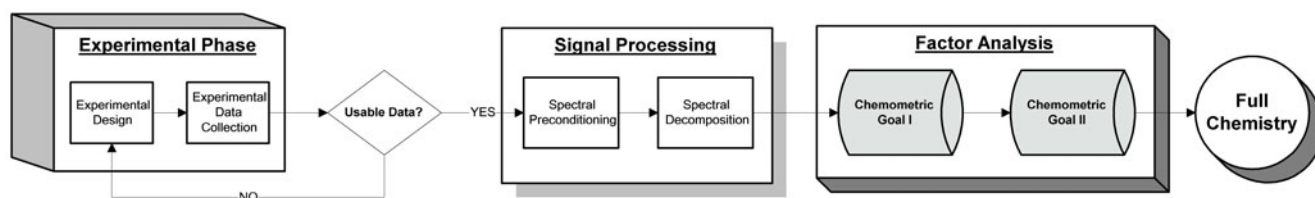


Figure 2 Schematic Representation of Exploratory Chemometrics Methodology for Catalytic System Investigations

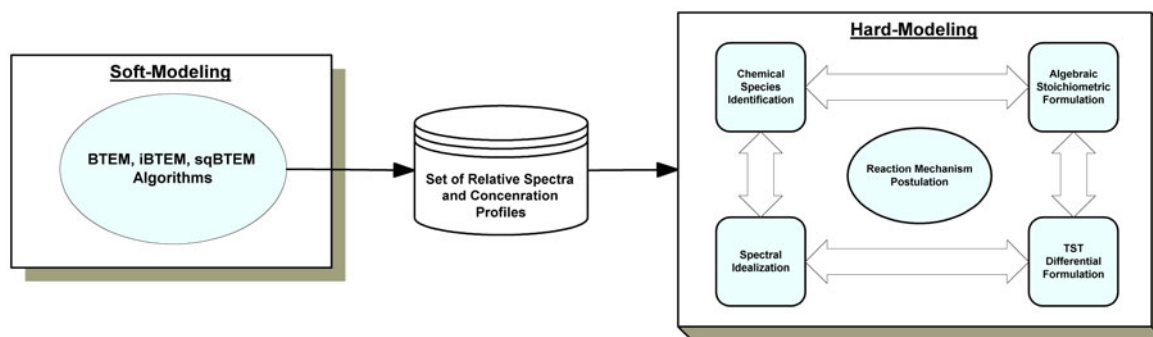


Figure 1 describes the entire workflow engendered for elucidating the full observable chemistry underlying a catalytic phenomenon via suitable *in situ* spectroscopic monitoring. The **experimental phase** includes design and collection of spectroscopic data. Once the acquired experimental data is ascertained to be useful for quantitative analysis, the collated data goes through a phase of **signal processing** that refines the signal-to-noise ratio of the spectroscopic data (preconditioning) and subsequently applies matrix decomposition to the preconditioned data. **Factor analysis** is then applied to the processed spectral data sets to elicit the full observable chemistry of the catalysis. There are two

stages within factor analysis, stage 1 encompasses the goal of finding the number of observable species and their individual pure component spectra (Chemometrics Goal I), via suitable *soft-modeling curve resolution techniques* (such as BTEM, iBTEM, sqBTEM algorithms). Stage 2 further analyzes the processed data sets using spectral information obtained in stage 1 of factor analysis to achieve Chemometrics Goal II, which includes the postulation and quantitative verification of *hard-models based on first principle chemistry*, e.g. spectral idealization, chemical species identification, reaction/catalytic mechanism postulation, algebraic stoichiometric formulations of chemical species atomic and atom-free, and reaction pathways stoichiometries, differential kinetic rate laws based on transition state theory (TST). Figure 2 captures the overall chemometrics methodology in the factor analysis phase.

The aforesaid general exploratory chemometrics methodology was successfully implemented to the real catalytic system of 1,3-cyclohexadiene hydroformylation, from which a coherent chemistry of the catalytic phenomenon and a lucid explanation for the poisoning effect of 1,3-cyclohexadiene on $\text{Rh}_4(\text{CO})_{12}$ hydroformylation catalytic precursor were consequently found.

2 Results and Discussion

Experimental design and experimentation for unmodified $\text{Rh}_4(\text{CO})_{12}$ catalyzed 1,3-cyclohexadiene hydroformylation is as follows. The analytical technique employed to obtain *in situ* data is FTIR spectroscopy via flow-through high-pressure infrared cell set-up [1]. The experimental design consists of a series of 17 experiments, performed at partial pressures of 1.5–3.0 MPa CO, 1.0–3.0 MPa H_2 and reaction temperatures of 25–40 °C. Variations in the reaction conditions were performed in order to (i) minimized possible spectral colinearity, and (ii) obtain reaction kinetic and thermodynamic information. The subsequent factor analysis was performed on 425 spectra with 4751 FTIR channels of data, for the wavenumber range [1550, 2500] cm^{-1} of 0.2 cm^{-1} interval.

The chemometrics analysis of the *in situ* FTIR data of 1,3-cyclohexadiene hydroformylation yields 6 organorhodium carbonyl spectra (of which 3 are new spectra) via soft-modeling curve resolution, with their chemical identities subsequently deduced. Their real absorptivities and moles are found via hard-modeling quantitative calculations. A plausible catalytic mechanism for the 1,3-cyclohexadiene hydroformylation was proposed and is subsequently verified by factor analysis of algebraic reaction stoichiometries and multi-linear regression of differential rate laws and thermodynamic parameters based on transition state theory. The observed slow oxoaldehyde formation was found to be due to the formation of three coordinatively saturated 18 valence electron carbonyl species, namely tricarbonyl π -allyl diene-rhodium, tetracarbonyl σ -allyl diene-rhodium and tricarbonyl (1,2- η^2 ,4- η^1 -cyclohexene) rhodium acyl, which are responsible for the poisoning of $\text{Rh}_4(\text{CO})_{12}$ catalytic precursor.

References

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- [1] Chew, W. Exploratory Chemometric Studies of Unmodified Rhodium Catalyzed Conjugated Diene Hydroformylations via In Situ FTIR Spectroscopy. *Ph.D. Thesis*. National University of Singapore. 2003.