

# Massively Parallel Entropy Based Pattern Recognition for System Identification in Catalytic Binuclear Elimination Reaction

Chuanzhao Li, Li Chen, Effendi Widjaja, Huajun Zhang, Liangfeng Guo, and Wee Chew

Department of Chemical and Biomolecular Engineering  
4 Engineering Drive 4  
National University of Singapore  
SINGAPORE 117576

Keywords: system identification, BTEM, catalytic binuclear elimination reaction, hydroformylation, in- situ FTIR, chemometrics

Prepared for Presentation at the 2004 Annual Meeting AIChE

Copyright © Chuanzhao Li, Li Chen, Effendi Widjaja, Huajun Zhang, Liangfeng Guo, and Wee Chew,  
National University of Singapore,

November 2004

Unpublished

AIChE Shall Not Be Responsible For Statements or Opinions Contained in Papers or Printed in its  
Publications

## Abstract

Recently, it was found that the simultaneous use of both  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{HRe}(\text{CO})_5$  in the homogeneous catalytic hydroformylation of cyclopentene to cyclopentane carboxaldehyde, leads to a dramatic increase in rate of reaction. Two experimental designs were planned and two sets of in-situ spectroscopic experiments performed using FTIR. The first experimental design without organic substrate added, and the second was performed in n-hexane solvent at 278-303K and 0.2-8.0 MPa total pressure using CO and  $\text{H}_2$ . A total of circa 4000 spectra were collected spectra on the interval 1550  $2500\text{cm}^{-1}$ .

Both of the data matrices were analyzed using SVD and our group-developed software tools including BTEM to solve the algebraic inverse problem and differential inverse problem. In particular, SVD was performed and circa  $s=10$  spectral patterns were recovered using exhaustive global searches using BTEM. The pure components were reconstructed, the mole numbers of each species were obtained and the reaction stoichiometry and reaction contents were determined.

From the first experimental design, one new previously unknown species  $\text{RhRe}(\text{CO})_9$  was identified. The second set data showed a very significant increase in aldehyde formation and TOF was observed in some experiments when both rhodium carbonyl and rhenium carbonyl complexes were used simultaneously. The kinetics of product formation shows a distinct linear-bilinear form in observables. Taken together, the results again support the existence of catalytic binuclear elimination. The new mechanism is described in detail.

## 1.0 Introduction

Stoichiometric binuclear elimination between mononuclear complexes leading to the elimination of a new organic product and the formation of a dinuclear complex has been well documented. This rather rare reaction is reviewed as well as the concept of catalytic binuclear elimination reaction (CBER). Catalytic binuclear elimination is exceptionally interesting from both a synthetic as well as kinetic viewpoint and it would constitute a well-defined reaction topological basis for synergism. Recently, our group reported two CBER examples with the use of Rh/Mn bimetallic catalytic hydroformylations. This present extends the investigations by using  $\text{Rh}_4(\text{CO})_{12}/\text{HRe}(\text{CO})_5$  with the newly developed BTEM/System Identification techniques. The experimental part requires (I) in-situ spectroscopy and the numerical part requires solution of (II) the spectral entropy-based pattern recognition problem (Goal A) and (III) algebraic structure problem and differential structure problem (Goal B).

## 2.0 Results and Discussion

Two experimental designs were planned and two sets of in-situ spectroscopic experiments performed using FTIR. The first experimental design without organic substrate added, and the second was performed in n-hexane solvent at 278-303K and 0.2-8.0 MPa total pressure using CO and H<sub>2</sub>. A total of circa 4000 spectra were collected spectra on the interval 1550-2500cm<sup>-1</sup>. The experimental data matrix  $A_{3651 \times 4751}$  or  $A^*_{856 \times 4751}$  is the sole input from the two experimental designs. Singular Value decomposition (SVD) for the first 25-50 right singular vectors is performed on A or A\*. The first 25-50 right singular vectors account for 99+% of the data. This is followed by the exhaustive application of the spectral pattern program Band-Target Entropy Minimization (BTEM) to the 60 selected channels using the 25-50 right singular vectors. The super-set of extracted spectral patterns were filtered to eliminate redundancies and those which are physically improbable. The resulting set contained an additional 6 spectral estimates, which are Rh<sub>4</sub>(CO)<sub>12</sub>, HRe(CO)<sub>5</sub>, RCORh(CO)<sub>4</sub>, cyclopentene, cyclopentene carboxaldehyde, and newly identified intermediate RhRe(CO)<sub>9</sub>. A large optimization problem is next solved to simultaneously determine the correctly scaled spectral patterns and the real moles of all the interesting solutes.

In the Rh<sub>4</sub>(CO)<sub>12</sub>/HRe(CO)<sub>5</sub> catalyzed hydroformylation of cyclopentene, a dramatic increase in both the catalytic rate and turn over frequency(TOF) was also observed in the experiments conducted when both metals were used simultaneously. Detailed in-situ FTIR measurements indicated the observable presence of a dinuclear complex RhRe(CO)<sub>9</sub>. The kinetics of product formation show a distinct linear-bilinear form in observables-  $k_1[\text{RCORh}(\text{CO})_4][\text{H}_2][\text{CO}]^{-1} + k_2[\text{RCORh}(\text{CO})_4][\text{HRe}(\text{CO})_5][\text{CO}]^{-2} - k_3[\text{RhRe}(\text{CO})_9][\text{RCHO}][\text{CO}]^{-2}$ . The first term represents the classic unicyclic rhodium catalysis while the other two terms indicate a reversible hydride attack on an acyl species.

### **3.0 Conclusions**

The present work systematically studied the homogenous bimetallic  $\text{Rh}_4(\text{CO})_{12}/\text{HRe}(\text{CO})_5$  catalyzed hydroformylation of cyclopentene. The in situ FTIR spectra were analyzed with the tool of total algebraic system identification. The results provided strong spectroscopic and kinetic experimental evidence for the existence of the bimetallic catalytic binuclear elimination reaction.

## **References**

- 1 Breslow, D. S.; Heck, R. F. *Chem. & Ind.* 1960, 467.
- 2 Li, C.; Widjaja, E.; Garland, M. *JACS.* 2003, 125, 5540-48.
- 3 Li, C.; Widjaja, E.; Garland, M. *Organometallics.* 2004, 23(17), 413-4138.
- 4 Chew, W.; Widjaja, E.; Garland, M. *Organometallics*, **2002**, 21, 1982-1990
5. Li, C.; Widjaja, E.; Chew, W.; Garland, M. *Angewandte Chemie I.E.*, **2002**, 20, 3785-3789.
- 6 Widjaja, E; Li, C.; Chew, W.; Garland, M. *Analytical Chemistry*, **2003**, 75, 4499-4507.
- 7 Widjaja, E; Li, C.; Garland, M. *J. Cat* , **2004**, 223(2), 278-289.
- 8 Chen, L. The Exploratory Chemometric Studies of the Homogeneous Rhodium Catalyzed Hydroformylation of Isoprene. Ph.D. Thesis, National University of Singapore. 2001.