AIDIC EFCE
ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Intensified production of renewable fuels and chemicals: design and optimization of heterogeneous aldol condensation catalysts.

Jeroen Lauwaert

Industrial Catalysis and Adsorption Technology (INCAT), Department of Materials, Textiles and Chemical Engineering (MaTCh), Ghent University, Valentin Vaerwyckweg 1, 9000 Ghent, Belgium

Corresponding author: Jeroen.Lauwaert@UGent.be

Highlights

- The cooperativity between amines and silanol groups or intermolecular acids is elucidated
- Amine structure and proton affinity effects are studied experimentally and computationally
- The reusability is optimized by adding water traces and tuning the support hydrophobicity

1. Introduction

Due to the continuously increasing world population and associated demand for energy and chemicals, fossil resources are depleting faster than ever before. Moreover, environmental concerns about the use of these resources urge the search for renewable alternatives. Lignocellulose is a type of non-edible biomass which may constitute a viable option for the sustainable production of fuels as well as chemicals. A highly promising route entails hemicellulose dehydration into furfural which is, subsequently, reacted with acetone in an aldol condensation to produce species with the desired carbon number. A techno-economic analysis of this process showed that, in its current state, the proposed technology can deliver fuels for a minimum selling price of $4.75 per gallon [1]. However, future improvements including increasing the yield and selectivity of several reaction steps and replacing homogeneous catalysts with heterogeneous alternatives, will reduce this to less than $3 per gallon.

This work focusses on the challenges with respect to replacing the traditional homogeneous aldol condensation catalysts with heterogeneous alternatives to enhance the overall process efficiency. A series of (organo)silica supported amines and cooperative acid-amine couples have been investigated. The properties affecting the amine site activity, *i.e.*, the amine surface density [2, 3], structure and proton affinity [3], the nature of the promoting acid site [4], the water content in the reaction mixture and the support hydrophobicity [5], have been systematically varied. The obtained insights allowed proposing an optimized heterogeneous amine catalyst.

2. Results and discussion

Silica supports were functionalized by replacing a fraction of the surface silanol groups with an amine. It was observed that the remaining silanol groups on the surface enhance the catalytic activity of the amines in the aldol condensation. This cooperative effect does not only depend on the concentrations of both types of sites but also on their spatial arrangement with respect to each other. Primary amine precursors have the tendency to exhibit hydrogen bond among themselves in the solvents which are traditionally used during the functionalization, resulting in a clustered arrangement of these amines on the catalyst surface [2]. In contrast, secondary amines have a lower tendency to form such hydrogen bonds and are more randomly distributed [3]. Both the clustered and the random arrangement deviate from the ideal checkerboard pattern, meaning that at a silanol-to-amine ratio of 1, not every amine is promoted by a neighboring silanol. Full promotion was in both cases obtained at a silanol-to-amine ratio of 1.7 [2, 3].

Although many primary, secondary, and tertiary amines have similar proton affinities, significant differences in catalytic activities for the aldol condensation have been observed [3]. This observation is attributed to the ability to form the key intermediate, *i.e.*, an enamine, and inhibiting species, *i.e.*, imines. While the crucial enamine cannot be formed on a tertiary amine, the inhibiting imine species can only be formed on primary amine. As a result, a secondary amine as active site that can form the reactive enamine without producing the

inhibiting imine exhibits the highest catalytic activity, provided that it is not subject to steric hindrance induced by a bulky substituent or conjugation of the nitrogen lone pair with an aromatic ring. A computational methodology has been developed to probe the steric and electronic effects induced by the amine substituents. After validation of the computational strategy against experimental data on homogeneous as well as heterogeneously supported amines, it is used to design new active sites for the amine catalyzed aldol condensation. From the calculations it is concluded that 3-propyl-pyrollidine and small acyclic secondary alkanolamines are promising candidates.

Besides the weakly acidic silanol groups, also other acids are observed to exhibit a promoting effect on the activity of amines in aldol condensations [4]. An intramolecular OH function provided by a primary alcohol incorporated on the β-carbon of the amine substituent exhibits a similar cooperativity as an intermolecular OH function provided by neighboring surface silanol groups. The highest activity was obtained when the alcohol-amine pair was surrounded by surface silanol groups, indicating the potential advantage of simultaneously activating both reactants by the formation of a hydrogen bond in contrast to the consecutive activation when there is only one promoting site in the vicinity of the amine. Changing the alcohol to stronger acids resulted in a decreasing cooperativity with increasing acid strength.

Co-feeding small amounts of water is found to inhibit the formation of stable site blocking species and, hence, improves the catalyst reusability. However, prolonged exposure to large water concentrations results in a loss of the cooperativity between the two types of sites, active site leaching and structural changes in the support material. This can be minimized by increasing the support hydrophobicity via incorporation of organic components in the framework of the silica [5].

Finally, by putting all of the obtained insights together, it is expected that an aliphatic organosilica functionalized with 3-propyl-pyrollidine promoted by surface silanols or a small acyclic secondary alkanolamine which possess an intramolecular cooperativity will exhibit excellent catalytic activities in the aldol condensation. Currently, we are attempting to synthesize these types of materials.

3. Conclusions

The aldol condensation catalyzed by supported amines has been investigated in detail. The cooperativity between the amine site and a weakly acidic surface silanol or an intermolecular acid site has been elucidated. The effects of the amine structure and proton affinity have been mapped and correlated with the aldol condensation reaction mechanism. Moreover, a computational methodology has been developed to probe the steric and electronic effects induced by the amine substituents. Subsequently, it has been shown that the support hydrophobicity can be tuned by incorporating organic components in the silica framework resulting in an increased stability in aqueous reaction mixtures. Additionally, the catalyst reusability is optimized by co-feeding of small amounts of water. Finally, some new optimized heterogeneous amine catalysts have been proposed.

References

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Keywords
Heterogeneous catalysis; Aldol reactions; Amines; Acid-base

Dr. Ir. Jeroen LAUWAERT — Curriculum Vitae

Personal

Name: **Jeroen Lauwaert**
Address: Kolveniersgang 49
9000 Gent, Belgium
Mobile Phone: (+32) 0485/57.88.15
E-mail: jeroen.lauwaert@gmail.com
jeroen.lauwaert@ugent.be

Date of birth: February 20th 1988
Place of birth: Dendermonde
Nationality: Belgian
Marital status: Married to Eline Slos
Drivers licence: B

Summary

I am a highly motivated young postdoctoral researcher with experience in heterogeneous catalysis and multi-phase reaction engineering. In 2011, I graduated as Master in Chemical Engineering at Ghent University. Afterwards, I started my doctoral research at the Laboratory for Chemical Technology in collaboration with the Center for Materials Ordered, Organometallics and Catalysis at the same university. My research focussed on the design of cooperative acid-base catalysts for aldol condensations. During my doctoral studies, I have developed several research skills including catalyst synthesis, characterization, performance testing and microkinetic modelling. In addition, I have applied the kinetic modelling techniques to thin film solar cells showing the methodology's versatility. In 2014, I have gained international experience in the group of prof. Chris W. Jones at Georgia Tech in Atlanta, USA. After obtaining my PhD in 2015, I moved to the research group Industrial Catalysis and Adsorption Technology and expanded my research field towards multi-phase reaction engineering. This research focusses on the effects of the thermodynamic non-ideality of liquid phases and differences between gas and liquid phase kinetics. Reactions that are being investigated in this context include acid-base catalyzed aldol condensations, esterifications catalyzed by heterogeneous acids, hydrodenitrogenations catalyzed by a sulphided NiMo catalyst, copper catalyzed hydrogenolysis of glycerol and palladium catalyzed Suzuki coupling reactions. In 2017, I obtained a postdoctoral fellowship allocated by the Research Foundation - Flanders (FWO) aiming at an intensified production of renewable fuels based on fundamental thermodynamics and elementary kinetics. This project mainly focusses on challenges with respect to aldol condensation and low temperature hydrogenation reactions. I also have experience in teaching and academic and social services. I have been involved in teaching activities regarding multiple programmes, *i.e.*, 'Bachelor and Master of Science in Chemical Engineering Technology', 'Bachelor of Science in Engineering: Chemical Engineering and Materials Science' and 'Master of Science in Chemical Engineering'. In addition to giving lectures and supervising exercise classes and practica, I have coached several master and doctoral students. I am also a member of several boards and committees including the faculty board.

Education

2011-2015 **PhD in Chemical Engineering at Ghent University, Belgium**
Subject: Design of Cooperative Acid-Base Catalysts for Aldol Condensations (Supervisors: Joris W. Thybaut and Guy B. Marin)

2009-2011 **Master in Engineering: Chemical Technology at Ghent University, Belgium**
Master Thesis: Development of a general microkinetic model for the hydroisomerization of n-alkanes on Pt/H-ZSM5 (Supervisor: Joris W. Thybaut)

2006-2009 **Bachelor in Engineering: Chemical Technology and Materials Science at Ghent University, Belgium**

2000-2006 **High School: Sint- Lodewijkscollege, Lokeren, Belgium**
Science – Mathematics

Work and Research Experience

October 2017 - Present **Postdoctoral fellow of the Research Foundation – Flanders (FWO) at the research group Industrial Catalysis and Adsorption Technology, Ghent University, Belgium**

October 2015 - Sept. 2017 **Postdoctoral research and teaching assistant at the research group Industrial Catalysis and Adsorption Technology, Ghent University, Belgium**

August 2015 - Sept. 2015 **Postdoctoral researcher at the Laboratory for Chemical Technology, Ghent University, Belgium**

August 2011 - August 2015 **PhD student at the Laboratory for Chemical Technology, Ghent University, Belgium**
Research stay abroad in prof. Jones' group at Georgia Institute of Technology, Atlanta, GA, USA (August – November 2014) funded with a travel grant for a long stay abroad (V428614N) allocated by FWO (Research Foundation – Flanders)

July 2010 **Internship as engineer at Yara Sluiskil B.V., Sluiskil-Terneuzen, The Netherlands**

July 2009 **Internship as engineer at Borealis Kallo N.V., Kallo-Kieldrecht, Belgium**

Publications, Book Chapters & Reports

Peer reviewed publications

1. *"Assignment of capacitance spectroscopy signals of CIGS solar cells to effects of non-ohmic contacts"*
   J. Lauwaert, L. Van Puyvelde, **J. Lauwaert**, J. W. Thybaut, S. Khelifi, M. Burgelman, F. Pianezzi, A. N. Tiwari, H. Vrielinck
   Solar Energy Materials And Solar Cells, 2013, 112, 78-83
   Ranking (2013): Q1, 28/251, subject category "Materials Science, Multidisciplinary", Impact factor = 5.030

2. *"Silanol-Assisted Aldol Condensation on Aminated Silica: Understanding the Arrangement of Functional Groups"*
   J. Lauwaert, E. De Canck, D. Esquivel, J. W. Thybaut, P. Van Der Voort, G. B. Marin
   ChemCatChem, 2014, 6, 255-264
   Ranking (2014): Q1, 31/139, subject category "Chemistry, Physical", Impact factor = 4.556

3. *"Modeling of capacitance transients of thin-film solar cells: A valuable tool to gain information on perturbing layers or interfaces"*
   J. Lauwaert, **J. Lauwaert**, L. Van Puyvelde, J. W. Thybaut, H. Vrielinck
   Applied Physics Letters, 2014, 104, 053502
   Ranking (2014): Q1, 21/144, subject category "Physics, Applied", Impact factor = 3.302

4. *"Effects of Amine Structure and Base Strength on Acid-Base Cooperative Aldol Condensation"*
   J. Lauwaert, E. De Canck, D. Esquivel, P. Van der Voort, J. W. Thybaut, G. B. Marin
   Catalysis Today, 2015, 246, 35-45
   Ranking (2015): D1, 4/71, subject category "Chemistry, Applied", Impact factor = 4.312

5. *"Spatial Arrangement and Acid Strength Effects on Acid-Base Cooperatively-Catalyzed Aldol Condensation on Aminosilica Materials"*
   J. Lauwaert, E. G. Moschetta, P. Van der Voort, J. W. Thybaut, C. W. Jones, G. B. Marin
   Journal of Catalysis, 2015, 325, 19-25
   Ranking (2015): D1, 4/135, subject category "Engineering, Chemical", Impact factor = 7.354

6. *"Facile synthesis of cooperative acid-base catalysts by clicking cysteine and cysteamine on an ethylene-bridged periodic mesoporous organosilica"*
   J. Ouwehand, **J. Lauwaert**, D. Esquivel, K. Hendrickx, V. Van Speybroeck, J. W. Thybaut, P. Van der Voort
   European Journal of Inorganic Chemistry, 2016, 13-14, 2144-2151
   Ranking (2016): Q2, 13/46, subject category "Chemistry, Inorganic and Nuclear", Impact factor = 2.444

7. *"Tuning Component Enrichment in Amino Acid Functionalized (Organo)silicas"*
   J. Lauwaert, J. Ouwehand, J. De Clercq, P. Cool, P. Van der Voort, J. W. Thybaut
   Catalysis Communications, 2017, 88, 85-89
   Ranking (2016): Q2, 47/145, subject category "Chemistry, Physical", Impact factor = 3.330

8. *"Effect of ion exchange resin functionality on catalytic activity and leaching of supported palladium nanoparticles in Suzuki cross-coupling"*
   B. Van Vaerenbergh, **J. Lauwaert**, W. Bert, J. W. Thybaut, J. De Clercq, P. Vermeir

ChemCatChem, 2017, 9, 451-457
Ranking (2016): Q1, 29/145, subject category "Chemistry, Physical", Impact factor = 4.803

9. *"Three-phase Robinson-Mahoney reactor as a tool for intrinsic kinetic measurements: Determination of gas-liquid hold up and volumetric mass transfer coefficients"*
J. Lauwaert, C. S. Raghuveer, J. W. Thybaut
Chemical Engineering Science, 2017, 170, 694-704
Ranking (2016): Q1, 32/135, subject category "Engineering, Chemical", Impact factor = 2.895

10. *"Synthesis of L-serine modified benzene bridged PMO and its catalytic performance towards aldol condensations"*
W. Huybrechts, **J. Lauwaert**, A. De Vylder, M. Mertens, G. Mali, J. W. Thybaut, P. Van Der Voort, P. Cool
Microporous & Mesoporous Materials, 2017, 251, 1-8
Ranking (2016): Q1, 10/72, subject category "Chemistry, Applied", Impact factor = 3.615

11. *"Recent advances on the utilization of layered double hydroxides (LDHs) and related heterogeneous catalysts in a lignocellulosic-feedstock biorefinery scheme"*
W. Y. Hernández, **J. Lauwaert**, P. Van Der Voort, A. A. Verberckmoes
Green Chemistry, 2017, 19, 5259-5516 (Front Cover)
Ranking (2016): D1, 1/31, subject category "Green & Sustainable Science & Technology", Impact factor = 9.125

12. *"The role of water in the reusability and stability of aminated mesoporous silica catalysts for aldol condensations"*
A. De Vylder, **J. Lauwaert**, D. Esquivel, J. De Clercq, P. Van Der Voort, J. W. Thybaut
ACS Catalysis (Submitted)
Ranking (2016): D1, 11/145, subject category "Chemistry, Physical", Impact factor = 10.614

Book chapters

1. *"Chapter 25: Reaction and Reactor Engineering"*
J. Lauwaert, J. W. Thybaut
Contemporary Catalysis: Science, Technology and Applications by Kamer, Vogt and Thybaut, Royal Society of Chemistry, 2017, 591-708

Reports

1. *"Bridging the Gap between Kinetics in Gas Phase and Non-Ideal Liquids Exhibiting Pronounced Polarity Effects"*
J. Lauwaert, J. W. Thybaut, G. B. Marin
Eurokin, 2015, 1-36

2. *"Polarity driven kinetics"*
J. Lauwaert, J. De Clercq, J. W. Thybaut
Eurokin, 2017 (in preparation)

Presentations

Oral presentations

1. *"Model Based Design of Acid Base Cooperative Catalysts for Aldol Condensation: Effects of Amine Structure and Base Strength"*
J. Lauwaert, E. De Canck, D. Esquivel, P. Van Der Voort, J. W. Thybaut, G. B. Marin
The 11th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts" (PREPA11), Louvain-la-Neuve, Belgium (2014)

2. *"Acid Strength Effects on Acid-Base Cooperative Aldol Condensation"*
J. Lauwaert, E. G. Moschetta, P. Van Der Voort, J. W. Thybaut, C. W. Jones, G. B. Marin
2014 AIChE Annual Meeting, Atlanta, USA (2014)

3. *"Bridging the Gap between Kinetics in Gas Phase and Non-Ideal Liquids Exhibiting Pronounced Polarity Effects"*
J. Lauwaert, J. W. Thybaut, G. B. Marin
42th Eurokin Workshop, Brussels, Belgium (2015)

4. *"PMOs as Cooperative Acid-Base Catalysts for Aldol Condensations"*
   J. Lauwaert, J. Ouwehand (duo presentation, co-first author), D. Esquivel, K. Hendrickx, V. Van Speybroeck, J. W. Thybaut, G. B. Marin, P. Van Der Voort
   N3C Symposium, Ghent, Belgium (2015)

5. *"Stabilization of metal nanoparticles by ion exchange resins and their applications"*
   B. Van Vaerenbergh, **J. Lauwaert**, P. Vermeir, J. De Clercq, J. W. Thybaut
   IEX 2016, Cambridge, United Kingdom (2016)

6. *"Evaluation of Cu based Catalysts for Glycerol Hydrogenolysis"*
   T. Rajkhowa, **J. Lauwaert**, J. W. Thybaut
   XMCR, Svetlogorsk, Russia (2016)

7. *"Polarity driven kinetics: Progress phase 1"*
   J. Lauwaert, J. De Clercq, G. B. Marin, J. W. Thybaut
   47th Eurokin Workshop, Paris, France (2017)

8. *"Synthesis of size-controlled nanoparticles by tuning the support properties and varying the reduction temperature"*
   B. Van Vaerenbergh, K. De Vlieger, **J. Lauwaert**, J. W. Thybaut, A. Verberckmoes, J. De Clercq, P. Vermeir
   Nanotech France 2017, Paris, France (2017)

9. *"A Three-phase Robinson-Mahoney reactor as a tool for intrinsic kinetic measurements: Determination of gas-liquid hold up and volumetric mass transfer coefficient"*
   J. Lauwaert, C.S. Raghuveer, J. W. Thybaut
   GLS-13, Brussels, Belgium (2017)

10. *"Improving Cu-alumina catalyst stability for glycerol hydrogenolysis by incorporation of lanthanum"*
    A. Bouriakova, **J. Lauwaert**, B. Katryniok, J. De Clercq, J. W. Thybaut
    Europacat, Florence, Italy (2017)

11. *"Polarity driven kinetics: Overview phase 1 and scope of phases 2 and 3"*
    J. Lauwaert, J. De Clercq, J. W. Thybaut
    49th Eurokin Workshop, Lyon, France (2017)

12. *"The Effect of Water on the Reusablility of Aminated Mesoporous Silica Catalysts for Aldol Condensations"*
    A. De Vylder, **J. Lauwaert**, J. De Clercq, P. Van Der Voort, J. W. Thybaut
    2017 AIChE Annual Meeting, Minneapolis, USA (2017)

13. *"Rational design of supported amine organocatalysts via computational probing of steric and electronic effects"*
    A. De Vylder, **J. Lauwaert**, M. Sabbe, M.-F. Reyniers, J. De Clercq, P. Van der Voort, J. W. Thybaut
    The 12th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts" (PREPA12), Louvain-la-Neuve, Belgium (2018) **(Submitted)**

Poster presentations

1. *"Amino Acid Functionalized Periodic Mesoporous Organosilicas as Asymmetric Bifunctional Catalysts"*
   J. Ouwehand, D. Esquivel, **J. Lauwaert**, J. W. Thybaut, P. Van der Voort
   NCCC, Noordwijkerhout, The Netherlands (2015)

2. *"Tuning the Physisorption Properties of Amino Acid Functionalized (Organo)silicas"*
   J. Lauwaert, D. Esquivel, P. Van Der Voort, J. W. Thybaut, G. B. Marin
   IAP P7/05 Annual meeting, Hasselt, Belgium (2015)

3. *"Continuous Flow Investigation of 'Green' Aldol Condensation"*
   H. Nalli, **J. Lauwaert**, A. De Vylder, P. Van Der Voort, J. W. Thybaut

NCCC, Noordwijkerhout, The Netherlands (2016)

4. *"Exploring the reusability of aminated silicas for aldol condensations"*
   A. De Vylder, **J. Lauwaert**, J. De Clercq, P. Van Der Voort, J. W. Thybaut
   CRF Symposium, Blankenberge, Belgium (2016)

5. *"Tuning the reusability of cooperative aminated silica catalysts for continuous-flow aldol condensations"*
   A. De Vylder, **J. Lauwaert**, J. De Clercq, P. Van Der Voort, J. W. Thybaut
   NCCC, Noordwijkerhout, The Netherlands (2017)

6. *"Tailoring component enrichment in (organo)silicas and resins to achieve enhanced catalyst performances"*
   J. Lauwaert, P. Van Der Voort, J. De Clercq, J. W. Thybaut
   Europacat, Florence, Italy (2017)

7. *"Chitosan as a sustainable heterogeneous catalyst for aqueous aldol condensation"*
   A. De Vylder, **J. Lauwaert**, E. Moens, S. Seghers, C. V. Stevens, P. Van Der Voort, J. De Clercq, J. W. Thybaut
   4th International Congress on Catalysis for Biorefineries (CatBior), Lyon, France (2017) **(Accepted)**

8. *"Acid site effects on Ni-Cu catalyzed hydrodeoxygenation of furfural condensation products to drop-in biofuels and -chemicals"*
   B. Haentjens, **J. Lauwaert**, P. S. F Mendes, J. M. Winne, J. De Clercq, J. W. Thybaut
   NCCC, Noordwijkerhout, The Netherlands (2018) **(Submitted)**

9. *"Improving the stability of aminated silica catalysts for continuous flow aldol condensations by tuning the hydrophobicity of the support material"*
   B. Biesemans, A. De Vylder, **J. Lauwaert**, J. De Clercq, P. Van Der Voort, J. W. Thybaut
   NCCC, Noordwijkerhout, The Netherlands (2018) **(Submitted)**

Grants & Awards

1. Travel grant for a long stay abroad (V428614N) allocated by FWO (Research Foundation – Flanders) amounting to €5148 (2014)
2. AIChE CRE Division Travel Award amounting to €312 (2014)
3. EFCATS Travel Grant for participation to Europacat amounting to €580 (2017)
4. Postdoctoral fellowship allocated by the Research Foundation - Flanders (FWO) (12Z2218N) (2017 – Present)