

60452 - Catalysis

Syllabus Information

Academic Year: 2022/23

Subject: 60452 - Catalysis

Faculty / School: 100 - Facultad de Ciencias

Degree: 543 - Master's in Molecular Chemistry and Homogeneous Catalysis

ECTS: 6.0

Year: 1

Semester: First semester

Subject Type: Compulsory

Module:

1. General information

1.1. Aims of the course

The global objective of the course is to provide the student with an advanced training in Catalysis including the principles, mechanisms and applications of the different types of catalysts that operate both in homogeneous phase, such as organometallic catalysts and organocatalysts, and in heterogeneous phase.

These approaches and objectives agree with the following Sustainable Development Goals (SDGs) of the United Nations Agenda 2030 (<https://www.un.org/sustainabledevelopment/es/>), in such a way that the acquisition of the learning results of this subject provides training and competence to contribute to a certain extent to its achievement. Goal 4: Quality education, Goal 7: Affordable and clean energy, Goal 9: Industry, innovation and infrastructures, Goal 12: Responsible consumption and production, and Goal 13: Climate Action.

1.2. Context and importance of this course in the degree

The course focuses on the study of the basic concepts of catalysis, the different types of catalysts, their mechanism of action and their applications. The course is divided into different blocks: i) basic concepts in catalysis, ii) fundamentals of organometallic catalysis, iii) applications and mechanisms of organometallic catalysts, iv) principles, classification and applications of heterogeneous catalysts, and v) design and mechanism of action of organocatalysts. Along the course, we present a selection of some of the cutting-edge research in catalysis and their potential to meet the new challenges for sustainable development.

The course is part of the compulsory module entitled *Molecular Chemistry and Catalysis*. It is a mandatory subject that is taught during the first semester of the course and it has a workload of 6 ECTS credits. The course provides an advanced training for understanding the basic principles in the design of catalysts for synthetic transformations following an efficient and selective manner. Since the development and optimization of catalysts is one of the main goals of many research groups at the ISQCH (Institute of Chemical Synthesis and Homogeneous Catalysis), this is a fundamental subject for the realization of the *Master's Dissertation* in this field of research.

1.3. Recommendations to take this course

A mastery of the basic concepts of chemical bonding, structure and reactivity of organic and inorganic compounds is recommended. Class attendance along with continued work facilitates to pass the course.

2. Learning goals

2.1. Competences

To be able to apply the acquired knowledge to address the study of new catalytic transformations.

To be able to apply concepts acquired in the field of inorganic, organic and organometallic chemistry to the design of catalysts.

To be able to apply the fundamentals of catalysis to the synthesis of chemicals following sustainable and environmentally friendly procedures.

To identify and use the most useful literature sources in the scientific research field of catalysis.

To appreciate the potential of the catalysis to face up the new challenges for a sustainable development

To be able to communicate conclusions of a scientific research work in the field of catalysis.

2.2. Learning goals

The student must identify the importance of catalysis in the development of sustainable chemical processes.

The student must know the different types of catalysts, their mode of action, advantages and disadvantages, as well as their principal applications.

The student should evaluate the activity, selectivity and environmental impact of the catalytic processes.

The student must identify key reactions in organometallic catalysis.

The student must know the main homogeneous reactions catalyzed by transition metal complexes and their reaction mechanisms.

The student should describe the different types of heterogeneous catalysts and the different strategies of immobilisation of molecular catalysts.

The student should describe the different types of organocatalyzed reactions and its applications.

The student must identify the current research lines in catalysis and its contribution to the scientific and technological development.

2.3. Importance of learning goals

Trained skills in this course should provide the student with an overall view of the main scientific research lines in catalysis and their importance in the development of new catalytic processes. The design of new catalysts and the optimization of catalytic processes are key steps in the development of sustainable chemical processes through the efficient use of scarce natural resources and energy.

3. Assessment (1st and 2nd call)

3.1. Assessment tasks (description of tasks, marking system and assessment criteria)

The evaluation of this course is based on the following activities, weighted as indicated:

- 1.- Control examination of theoretical, theoretic-practical questions and problems (**P1**) on **Topics 1-7**.
- 2.- Resolution of practical exercises, theoretic-practical questions and related practical activities (**T1**).
- 3.- Laboratory sessions (**T2**)
- 4.- Elaboration and oral presentation of a supervised individual or team-based practical work on a scientific paper (**T3**).
- 5.- Global Exam: Written theoretic and problem solving test (**P2**) on **Topics 8-14** to be performed within the global evaluation period. Students who had not been done the control **P1** or who had not get a mark of at least 4 out of 10 points must pass an additional exam (**P1'**) with questions and problems relatives to Topics 1-7.

In order to **average** the marks, it is essential to obtain a minimum mark of 4 points out of 10 in each of the two tests **P1 (P1')** and **P2**.

The final numerical mark will be the best of the following:

$$\text{Mark 1} = 0.30 \cdot (\mathbf{P1} \text{ ó } \mathbf{P1'}) + 0.45 \cdot \mathbf{P2} + 0.10 \cdot \mathbf{T1} + 0.05 \cdot \mathbf{T2} + 0.10 \cdot \mathbf{T3}$$

$$\text{Mark 2} = 0.38 \cdot (\mathbf{P1} \text{ ó } \mathbf{P1'}) + 0.57 \cdot \mathbf{P2} + 0.05 \cdot \mathbf{T2}$$

The rating of the students in the second annual examination session will consist in a single written exam that cover all themes of theory, problems or laboratory sessions defined as learning activities.

The number of official examination calls per registration and their use will be subjected to the statements of the *Regulation of Permanence in Master Studies* and the *Regulation of the Learning Assessment*:

<https://ciencias.unizar.es/normativas-asuntos-academicos>. The latest document will also regulate the general design and scoring criteria of the assessment activities, as well as the exam schedules and timetable for the post-examination review.

4. Methodology, learning tasks, syllabus and resources

4.1. Methodological overview

The methodology followed in this course is oriented towards achievement of the learning objectives. A wide range of teaching and learning tasks are implemented, such as:

1. Interactive lectures (4 ECTS)
2. Seminar and problem-solving sessions (1.5 ECTS)
3. Laboratory sessions (0.5 ECTS)

4.2. Learning tasks

The course includes the following learning tasks:

- Interactive lectures (4 ECTS: 40 hours). In one-hour sessions, students will acquire advanced knowledge of catalysis.
- Seminar and problem-solving sessions (1.5 ECTS: 15 hours). Students will work, individually or in small groups, with several case studies and scientific papers related with the course contents.
- Tutorials. Students will own 3 hours per week for individualized tutoring.
- Laboratory sessions (0.5 ECTS: 5 hours). Attendance is compulsory. The work done in these sessions will be shared with the other courses of the *Molecular Chemistry and Catalysis* module.

Teaching and assessment activities will be carried out in the classroom with all students onsite unless, due to the health situation, the provisions issued by the competent authorities and the University of Zaragoza arrange to carry them out by telematics means or in a reduced rotating capacity.

4.3. Syllabus

The course will address the following topics:

Basic concepts in catalysis

Topic 1. Introduction to catalysis: basic concepts.

Economic impact and challenges of catalysis. Catalysis and sustainable chemistry. Homogeneous catalysis, heterogeneous catalysis and biocatalysis. Activity and selectivity of the catalysts. Quantification of the environmental impact. Frontiers in catalysis: energy and environment.

Fundamentals of organometallic catalysis

Topic 2. Homogeneous catalysis with transition metals compounds.

Characteristics of transition metal based catalysts. Ligands and catalyst design. Indenyl effect, chelate effect. Bonding in coordination and organometallic compounds.

Topic 3. Reaction mechanisms: thermodynamic and kinetic aspects.

Reaction coordinate diagrams of catalytic reactions. Catalytic cycle: constituent species, steps and catalyst resting state. Kinetics models for two-step reactions. Selectivity determination.

Topic 4. Elementary steps.

Ligand-substitution processes. Oxidative Addition. Reductive elimination. σ -Bond metathesis. Migratory insertion. β -Hydride elimination. α -Hydride elimination and α -hydride abstraction. Nucleophilic attack on coordinated ligands. Electrophilic attack on coordinated ligands. Transmetalation.

Organometallic catalysis in homogenous phase: applications

Topic 5. Hydrogenation and hydrogen transfer reactions.

Introduction. Hydrogenation of alkenes: catalysts and mechanisms. Asymmetric hydrogenation. Asymmetric hydrogenation of ketones. Hydrogen transfer hydrogenation: mechanisms.

Topic 6. Hydrofunctionalization reactions.

Introduction. Hydrofunctionalization reactions: hydrocyanation, hydrosilylation, hydroboration and hydroamination.

Topic 7. Carbonylation reactions.

Introducción. Carbonylation of methanol. Olefin carbonylation: hydroformylation, hydroaminomethylation, hydrocarboxylation and hydroesterificación. Carbonylation of organic halides. Copolymerization of alkenes with carbon monoxide.

Topic 8. Carbon-carbon coupling reactions.

Fundamentals of cross coupling. Catalyst and ligand design. Heck reaction. Oxidative coupling of alkynes. Alkyne dimerization and polymerization.

Topic 9. C-H activation.

Fundamentals of C-H activation. Mechanisms. Directing groups. Fujiwara reaction. Murai reaction. Hydroacylation. $C(sp^3)$ -H activation reactions.

Topic 10. Olefin Metathesis.

Preparation of metal-alkylidenes. Catalysts design. Olefin metathesis reaction types. Selectivity. Alkyne metathesis.

Organocatalysis

Topic 11. Covalent activation.

Introduction to asymmetric organocatalysis. Activation pathways in organocatalysis. Organocatalysts acting through covalent activation. Mechanism of action and representative examples.

Topic 12. Activation through hydrogen bonds.

Organocatalysts acting through hydrogen bonding, weak interactions, phase-transfer catalysts. Mechanism of action and representative examples.

Supported Catalysts

Topic 13. Introduction to heterogeneous catalysis

Principles and concepts of heterogeneous catalysis. Classification of heterogeneous catalysts according to their composition.

Topic 14. Supported Catalysts.

Introduction. General methodologies for preparation and characterization of supported catalysts. Examples of industrial processes based on supported catalysts.

4.4. Course planning and calendar

Further information concerning the timetable, classroom, assessment dates and other details regarding this course, will be provided on the first day of class or please refer to the Faculty of Science <https://ciencias.unizar.es/calendario-y-horarios>, and the Master's <http://masterqmch.unizar.es> websites.

The submission of assignments will be done according to the schedule announced in advance.

The students will be provided with diverse teaching material either at reprography or through the University's virtual platform <https://moodle2.unizar.es/add>.

The subject of Catalysis will be taught during the first semester as well as the other compulsory subjects of this Master and the optional subjects Fundamental methodologies in synthesis and Bibliographic resources and databases. Throughout the course several control-exams and an individual or team-work will be performed. The dates of the control-exams and deadlines for the presentation of the works will be communicated well in advance.

The experimental practices of the course of *Catalysis* together with those corresponding to other subjects of the Module *Molecular Chemistry and Catalysis* constitute an integrated block. The laboratory sessions will be performed during the second half of the semester, the schedule and the laboratory will be announced well in advance.