Examination Catalysis
October 22 2012

Read attentively each question before you start writing down your solutions!

1. Use for each question a separate sheet of paper and write down on each sheet of paper your name and student number.
2. Suggestion: make a timeline to make sure that each question is properly answered.
3. Please show your ‘student ID’ (collegekaart) for the registration.

Success!

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1. Explain the following concepts (~ ½ sheet of paper for each concept)

1A. Biocatalysis (on separate page)

a. Transition state stabilization

b. Competitive inhibition

1B. Homogeneous Catalysis (on separate page)

a. Olefin polymerization

b. Oxidative addition

1C. Heterogeneous Catalysis (on separate page)

a. Ammonia synthesis catalysis and Gerhard Ertl

b. Pt-Rh/BaO/CeO_2/Al_2O_3 catalyst and its functioning

c. Fluid catalytic cracking, zeolite Y and protolytic cracking

2. Biocatalysis

A. Haloalkane dehalogenases are involved in the dehalogenation of organohalides that are found in industrial waste water. Depicted below are an example of a reaction catalyzed by the enzyme and the two catalytically active amino acids.

a. Insight into the mechanism of enzymes can be obtained by isotopic labeling studies. For haloalkane dehalogenases, it is found that running the reaction with isotopically labeled water ($H_2{}^{18}O$) for multiple turnovers (i.e. each enzyme converts many substrate molecules), leads to incorporation of one atom of ^{18}O in the product. However, if the reaction is run with a large excess of enzyme with respect to the substrate and *less than one equivalent* of labeled water, no ^{18}O is incorporated in the product:

Explain this observation by describing the mechanistic steps involved in the enzymatic process.

b. Haloalkane dehalogenases show enantioselectivity when a chiral haloalkane substrate is used:

The reaction shown is an example of a kinetic resolution. Explain what is meant with kinetic resolution (including what is meant with 'kinetic') and why enzymes are so ideally suited for this.

c. The enantioselectivity of the natural, wild-type enzyme is not sufficient, however (i.e. the enzyme is not enantioselective enough). If one would like to use the enzyme for an industrial process, the enantioselectivity needs to be improved.

   Describe how you would increase the enantioselectivity of the enzyme and comment on the individual steps involved in such a process.

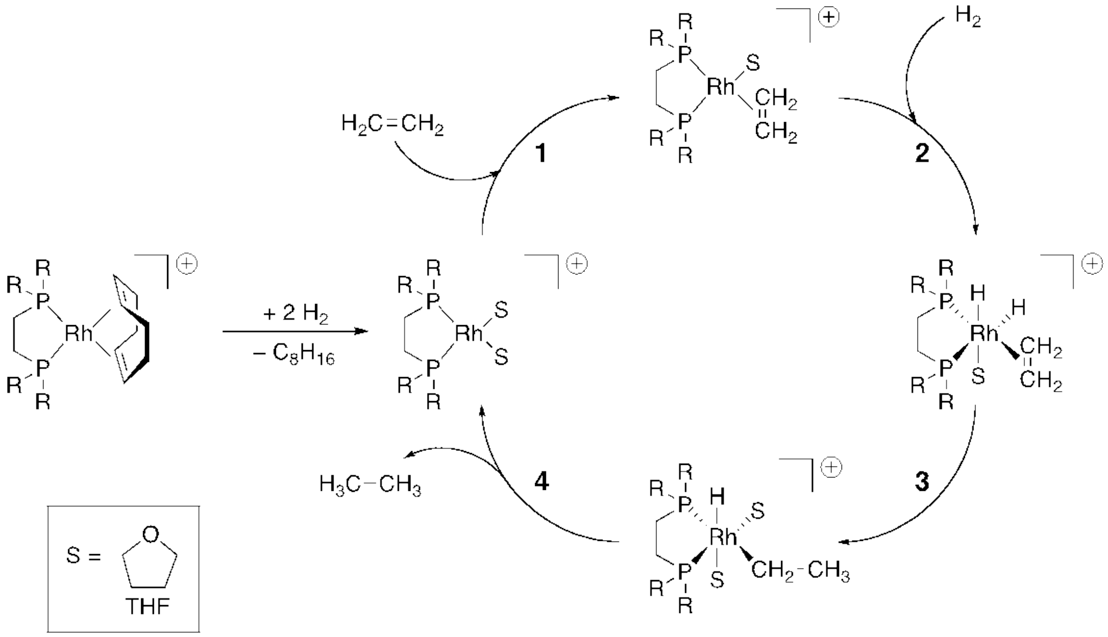
B. L-*tert*-leucine is a non-natural amino acid that is synthesized by a reductive amination reaction catalyzed the enzyme leucine dehydrogenase (LeuDH).

The enzymatic reaction is run in water and uses NADH as the oxidant for the reductive amination, generating NAD^+.

a. A second enzyme, formate dehydrogenase is also used in the process, as depicted below. Why is formate dehydrogenase needed in the process?
b. Ammonium formate ($[NH_4^+][HCOO^-]$) is used in excess in the reaction. Explain why.
c. The reductive amination reaction is preferably run in a continuous mode, using an enzyme membrane reactor. Give two major general advantages of using a membrane reactor over immobilization on a solid support.

3. Homogeneous Catalysis

The scheme below shows the mechanism of a homogenous catalytic reaction in which a cationic rhodium complex is used as the pre-catalyst. In this pre-catalyst, the rhodium ion is coordinated by a bidentate bis-phosphine ligand and a cyclo-octadiene (COD) ligand.



a. Give the overall reaction equation of the organic reaction that is catalyzed.

b. Why is the cationic rhodium-COD complex considered as a pre-catalyst and which reaction has to take place in order to change it into the actual catalyst?

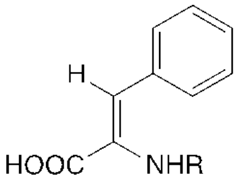
c. The actual rhodium catalyst contains the bisfosfine ligand and two solvent molecules (THF in this case) as the ligands. What is the number of valence electrons in this particular complex and in the complex formed in step 2?
(Rh(0): [Kr] $5s^1\ 4d^8$)

d. Describe how the alkene fragment is bound to rhodium in the complex that is formed in step 1. Which orbital interactions play an important role in the rhodium-alkene interaction?
(Use drawings to clarify your answer.)

e. Which elementary reaction steps take place in steps 1 through 4?

f. The overall reaction can be turned into an enantioselective reaction through the use of a chiral bis-phosphine ligand and, accordingly, a chiral rhodium complex. Propose a bis-phosphine ligand that can be used for this purpose and explain why this ligand is chiral.

g. Using the chiral complex you have proposed in the previous sub-question, which two products do you expect to form when the compound shown below is used as the substrate in the reaction? Explain in which step of the catalytic cycle it is determined which of the two products is formed.



4. Heterogeneous Catalysis

The alkylation of benzene (BE) with ethylene (ET) with zeolite ZSM-5 leads to the formation of ethylbenzene at 275ºC and 3 atm. The kinetic equation for this catalytic process is as follows:

$$r = k \times [K_{ET} \times p_{ET} \times K_{BE} \times p_{BE}]/[1 + K_{ET} \times p_{ET} + K_{BE} \times p_{BE}]^2$$

a. What is the reaction mechanism based on the above described kinetic equation? Propose a set of individual reaction steps and explain them in terms of the concept chemisorption.
b. What is the role of zeolite ZSM-5? Give some characteristics of this catalytic material and what could be the benefit of this zeolite material over zeoliet Y when catalyzing this process?
c. The maximum reaction rate is reached for a Si/Al ratio of 30. Explain the existence of such optimal Si/Al ratio for this process.
d. Calculate the time to reach a surface coverage of 25% for benzene when you know that for a Si/Al ratio of 30 the distance between two acid sites equals 16 nm and the sticking coefficient s of benzene is 0.2.
e. What is the time to reach the same surface coverage of 25% for ethylene when you know that the adsorption constant of ethylene is 10 times higher than that of benzene and the sticking coefficient s of ethylene is 0.8?
f. Discuss the (partial) pressure dependency of this catalytic reaction, based on the kinetic equation, when considering the adsorption constant differences between ethylene and benzene.
g. Calculate the activation energy of the non-catalyzed reaction when you know that the reaction rate at 275ºC is 7500 times smaller than the catalyzed reaction and the activation energy of the catalyzed reaction is 65 kJ.mol^{-1}. Assume that the pre-exponential factor A remains identical.

{$Z_w = p/[2\pi mkT]^{1/2} = (2.63 \times 10^{24}\ \text{m}^{-2}.\text{s}^{-1}) \times [\ p\ (\text{Pa})/\{(T\ (\text{K}) \times M\ (\text{g.mol}^{-1})\}^{1/2}$; 1 atm = 101325 Pa; $m_C = 12$; $m_H = 1$; and $R = 8.31\ \text{J.K}^{-1}.\text{mol}^{-1}$}

5. Intellectual property

You are the inventor and owner of a recently acquired European patent, which is officially registered in the Netherlands, France, Spain and Germany with the following conclusion/claim:

“1. Procedure for the manufacturing of ethanol from ethylene and water when contacted with a zeolite material with a SiO_2/Al_2O_3 ratio between 30 and 50.”

Which statement is correct? (only 1 answer is correct!)

A. Ethanol, manufactured in Polen based on a patented technology, is imported in Germany by beer brewery Am Prosit. Am Prosit makes a beverage containing 4% ethanol, which is solid in Germany. By doing so Am Prosit violates your patent.

B. Ethanol manufactured in Polen based on a patented technology is also used to make a beverage containing 4% ethanol. This beverage is imported and sold by beer brewery Am Prosit. By doing so Am Prosit violates your patent.

C. Company ZSM-5 has a granted European patent with a later priority date that is registered in Germany, Polen and Spain, with the conclusion/claim “Zeolite material with a SiO_2/Al_2O_3 ratio between 45 and 48 and containing 0.2-0.7 wt% palladium.” You make your own zeolite catalyst in the Netherlands. This zeolite material has a SiO_2/Al_2O_3 ratio of 46 and a Pd content of 0.4 wt% Pd. This catalyst is used in Spain in your commercial process to produce ethanol. By doing so you violate the patent rights of company ZSM-5.

D. Company Fralco makes use of your patented technology in the period before the priority date of your patent. Even more, Fralco has been applying the method in a confidential manner in France for some years. Because of all this, Fralco is now able to continue its manufacturing process and even may request to nullify your patent rights in France.