Tentamen Katalyse

27 oktober 2014

Lees alle vragen aandachtig door, voordat je met antwoorden begint!

1. Belangrijke opmerking – Er zijn 3 vragen (voor ieder cursusonderdeel 1 vraag). Maak iedere vraag op een *apart vel* en zorg ervoor dat op ieder vel je *naam en studentnummer* geschreven staat.
2. Suggestie – maak een planning om zeker te zijn dat er voor iedere vraag voldoende tijd is.
3. Collegekaart graag op tafel leggen voor registratie.

Succes!

Prof. B.M. Weckhuysen, Dr. M. Otte, Prof. R.J.M. Klein Gebbink and Dr. P.C.A. Bruijnincx

Oktober 2014

Vraag 1 – Heterogene Katalyse

Let’s hypothesize that you are working in a petrochemical complex and responsible for the operation of a fluid catalytic cracking (FCC) plant. Your job is to make sure that large amounts of vacuum gas oil (VGO) of different origins, very rich in metal ions most notably nickel, iron and vanadium, are converted into high quality gasoline. For this purpose, the FCC catalyst manufacturer brings you every day 15 ton of fresh FCC catalyst particles containing zeolite Y as the active phase.

1. What is the structure and composition of this FCC catalyst particle? What is the role of the different components constituting an FCC catalyst particle? What is the precise structure of the active phase? What is the active site within this active phase responsible for converting vacuum gas oil into gasoline?

2. Propose a set of individual reaction steps for making gasoline molecules when starting from a C30 hydrocarbon. What are the different types of reaction products you make from this hydrocarbon?

3. Calculate the activation energy of the non-catalyzed cracking reaction when you know that the reaction rate of the cracking reaction at 500ºC is 4000 times smaller than the rate of the catalyzed reaction. Experiments have indicated that the activation energy of the catalyzed reaction is 80 $kJ.mol^{-1}$. Assume that the pre-exponential factor A remains identical and that 1 atm = 101325 Pa and R = 8.31 $J.K^{-1}.mol^{-1}$.

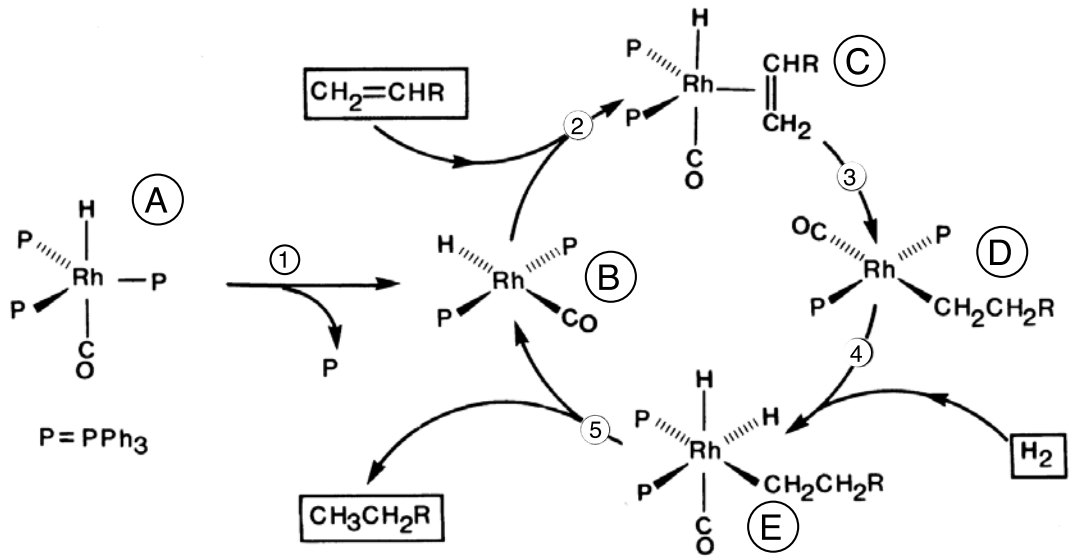
What is then the effect of the reaction temperature and pressure in the *riser reactor* on the overall gasoline yield?

4. Unfortunately the FCC catalyst manufacturer has not been able to provide you for 5 consecutive days with fresh FCC catalyst material. What is the effect of this event on the type of reaction products you make in the *riser reactor* assuming that you remain converting crude oil fractions very rich in nickel, iron and vanadium metal ions? Assume that the reaction environment in the riser reactor is *reducing* in nature. Explain then the reaction mechanism behind the change in type of reaction products. What would happen when you would switch your FCC feedstock from crude oil fractions to *used frying oil* for making French fries?

5. Assume again that the FCC catalyst manufacturer was not able to provide you for 5 consecutive days with fresh FCC catalyst material and that you remain converting crude oil fractions very rich in nickel, iron and vanadium metal ions. Surprisingly, you notice that there are traces of both acrolein and acrylonitrile in the headspace of the *regenerator unit* of the FCC plant. Explain this observation when taking into account that the reaction environment in the regenerator reactor is *oxidizing* in nature. Postulate the different reaction steps, including the reaction mechanisms, leading to the formation of both acrolein and acrylonitrile. What would have happened when the FCC catalyst particles contain zeolite ZSM-5 instead of zeolite Y?

Vraag 2 – Homogene Katalyse

The scheme below shows the mechanism of a homogeneous catalytic reaction.



a. Give the overall reaction equation of the organic reaction that is catalyzed. How is this reaction called?

b. Determine for the complexes C to E the formal oxidation state of the metal, the complex geometry and the number of valence electrons. Show how you get to the number of valence electrons! (Rh (0) = [Kr] $5s^1$ $4d^8$)

c. Which elementary reaction steps take place in the steps 1 to 5?

d. The scheme above shows the selective formation of a single reaction product. Mention at least two different products that may also form using this catalyst and reagents. Mention at which step or steps of the catalytic cycle the formation of these products are induced.

e. One of the ligands in complex A is CO. Explain the bonding of CO to a transition metal in detail.

- Show and name the two most important orbital interactions.

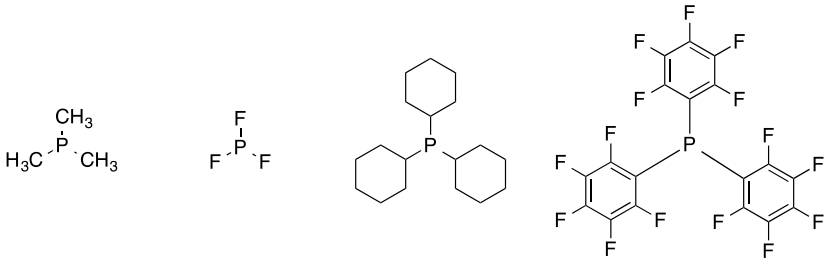
- Make use of pictures that show the orbitals that are involved.

f. Mention how each orbital interaction from question **d.** influences the IR stretching frequency of the CO ligand once bond to the metal in comparison to free CO.

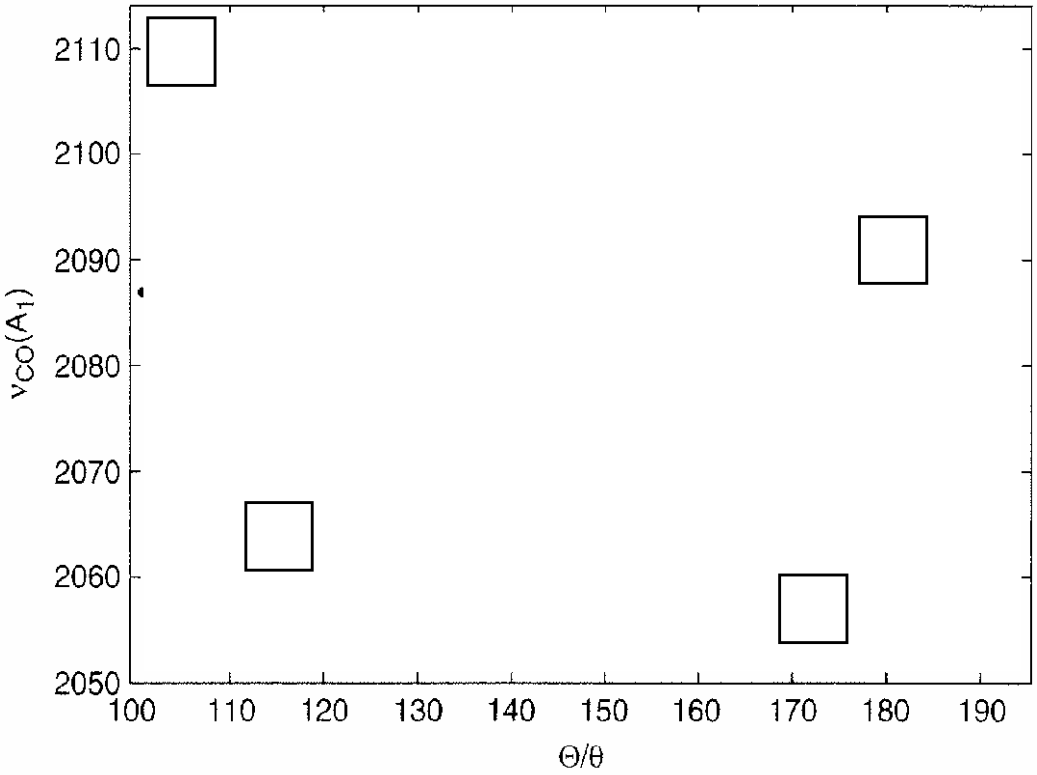
g. The diagram below shows a method how different phosphine ligands can be order regarding their Tolman electronic parameter and their Tolman cone angle.

a. Assign each of the following ligands to a box in the scheme:

A B C D

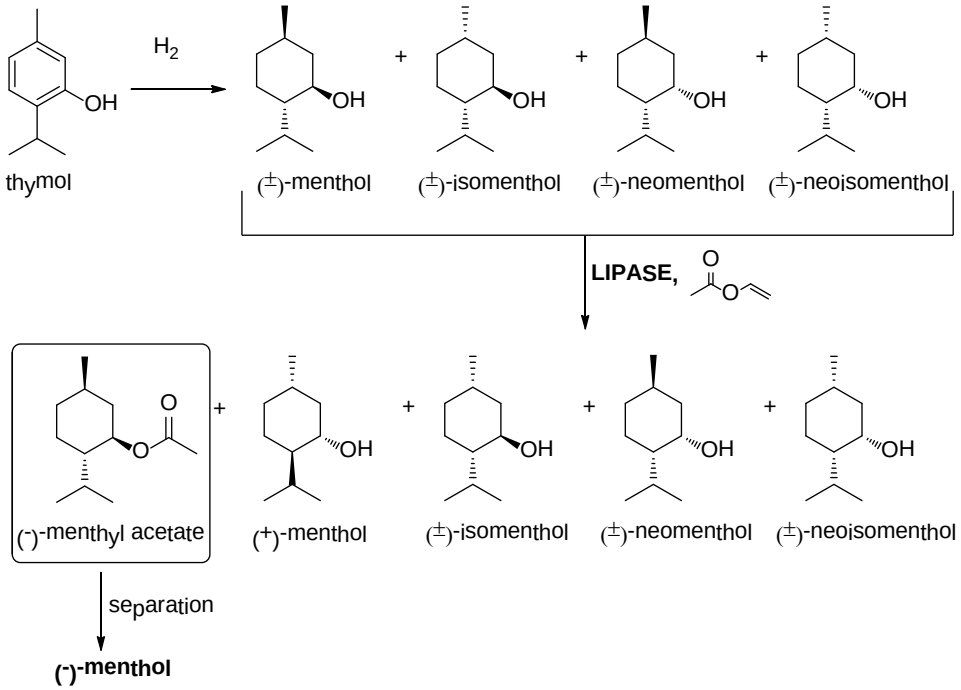


(Explain each of your assignment)



Vraag 3 – Biokatalyse

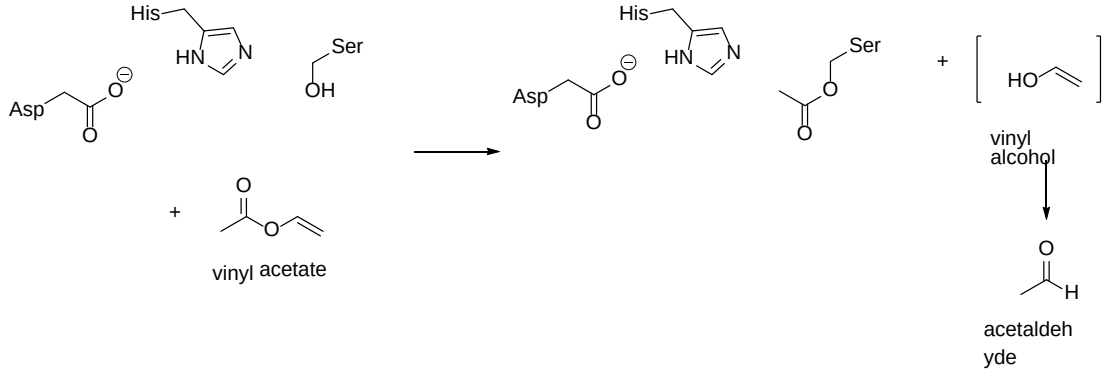
1. Shown is part of a catalytic process for the production of (-)-menthol, as patented by the company AECI. In the first step, thymol is hydrogenated to give a racemic mixture of four pairs of stereoisomers (see figure below; note that of each pair of enantiomers only one is drawn for sake of convenience). The second biocatalytic step consists of the lipase-catalyzed acetylation of this racemic mixture. The lipase stereoselectively converts one of the eight isomers, (-)-menthol, to (-)-menthyl acetate.



a. The lipase-catalyzed reaction is an example of a kinetic resolution. Explain what is meant with kinetic resolution and why enzymes are so ideally suited for this.

b. In the hydrogenation of thymol, about 60% of the thymol is converted to the (±)-menthol pair of enantiomers, with the other three pairs of diastereoisomers making up the remaining 40%. If the process is operated as shown above, the maximum yield of (-)-menthol would then be limited to about 30%. The company AECI nonetheless reports a yield of (-)-menthol that is nearly quantitative (meaning a 100% yield based on thymol). How would AECI have improved the system shown to get a higher yield of (-)-menthol?

The active site of lipases contains a catalytic triad. In the first step of the esterification reaction of (-)-menthol, a covalent intermediate is formed as shown below. Vinyl acetate is often used as the acetate-source in such lipase-catalyzed esterifications. The byproduct of this esterification reaction, vinyl alcohol, rapidly isomerizes in solution to acetaldehyde.

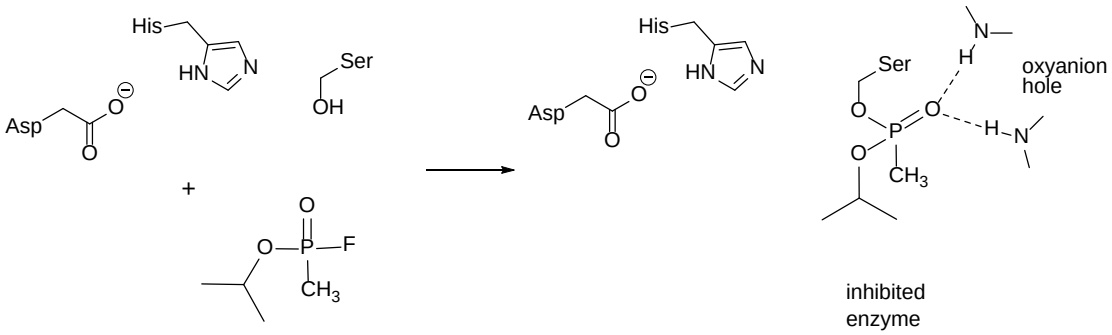


c. The use of a catalytic triad exemplifies the covalent catalysis strategy often seen in enzymes. Explain how the catalytic triad works and why covalent catalysis is such a good strategy for enzymatic catalysis.

d. The use of vinyl acetate as the acetate-source is a clever way of improving the yield of the process. Explain why.

e. The AECI process for (-)-menthol production is preferably done with immobilized lipase. Describe two methods of enzyme immobilization and discuss the general advantages and disadvantages of immobilizing an enzyme.

Lipases are very easily inactivated by organophosphorus compounds. An example of such an inhibitor is the nerve gas sarin. The structure of the active site after irreversible inhibition is shown:

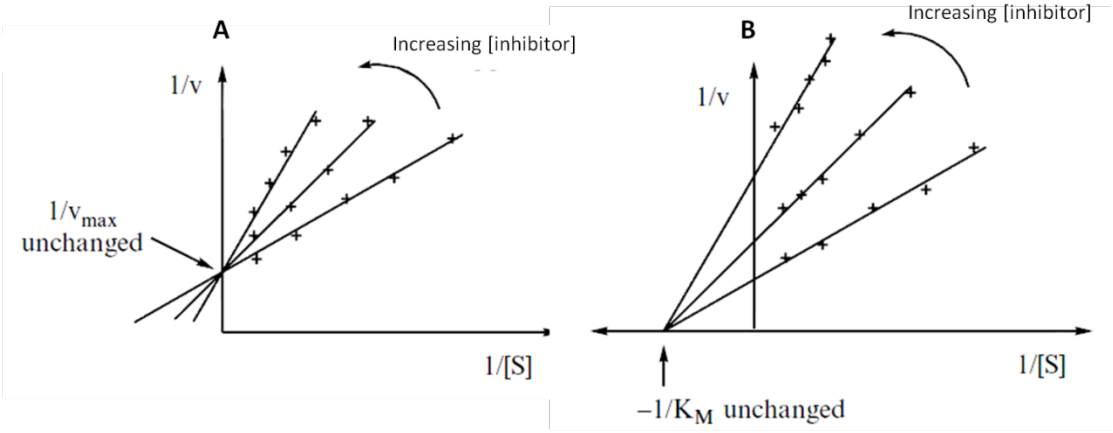


f. Explain why organophosphorus compounds such as sarin are such potent irreversible inhibitors of lipases.

g. In addition to the distinction between reversible vs. irreversible inhibition, one can also distinguish between competitive and non-competitive inhibitors. Non-competitive inhibiters lower the activity of the enzyme, but do this by binding to the enzyme at a site different from the active site. Kinetic studies can show to which class a certain inhibitor belongs. Shown are two Lineweaver-Burk plots of different concentrations of a competitive and non-competitive inhibitor. Which graph shows the effect of enzyme inhibition by a non-competitive inhibitor? Explain your answer.

Lineweaver–Burk Plot:

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_M}{v_{max}} \frac{1}{[S]}$$



Vraag 4 – Octrooicollege

You are a development researcher responsible for a big project at your company. You are in charge of building a new plant for producing a new catalyst, on which your company intends to spend about 25 million Euros. The plant will be located at Chemelot in Geleen, the Netherlands. The catalyst you have developed is an alumina-supported Fe-Co catalyst with the following characteristics:

Fe-Loading: 5.3 wt% as Fe_2O_3
Co-Loading: 6.7 wt% as CoO
Density: 0.867 gr/ml
BET surface area: 241 m^2/gr
Pore size distribution: Micropores (0-2 nm): 0.01 ml/gr
Mesopores (2-1000 nm): 0.4 ml/gr
Macropores: (>1000 nm): 0.2 ml/gr

You have found in your research that the catalyst needs be calcined at a specific temperature (450-475°C) in order to reach optimal activity. You have worked with a university research group to figure out why this is, and you have found that this treatment brings the cobalt in a tetrahedral coordination at the edge of metal-oxide clusters, which apparently makes them very active.
You receive a registered letter from the famous law firm Breckinger, Stahl and Reckhausen, with the following message:

“Dear sirs,
It has come to our attention that you intend to build a production facility for making a new catalyst. We would like to inform you that your intended operation infringed on a patent position of our client. Our client holds a patent application (US 2009/00135628, priority date 02-12-2009) with the following primary claim:

1. A heterogeneous catalyst comprising one or more transition metal oxides on a refractory support, preferably one of the transition metals oxides being Iron Oxide, more preferable the transition metal oxides being Iron Oxide and Cobalt Oxide, the alumina support has a pore volume of 0.3-0.8 ml / gr, more preferably 0.4-0.7 ml/gr, and a median pore diameter of 35 nm, in which the iron content is at least 5 wt% , and the cobalt content is at least 6 wt%.

In case you proceed with your production plans, our client intends to file for damages not less than 25 million dollars in court. You have two weeks to reply to this letter. If we do not receive a timely reply, we will file for the damages as stipulated above".

Of course, you are seriously worried, since Breckinger, Stahl and Reckhausen are known to fight vicious battles over these issues. You assume one of your main competitors is the client of the law firm.
Can you proceed with your intended production facility? If not, what should you do to make sure you can proceed? The patent mentioned in the letter does not seem to claim any specific coordination state for the cobalt. Could you patent your finding? If so, can you produce with your patent in hand?