**EXAM COVER PAGE**

**COURSE: Adsorption, Kinetics and Catalysis**
**COURSE CODE: SK-MAKC**
EXAM: Final Exam
TIME: 07-11-2017 from 13.30h to 16.30 h
LENGTH: 3h00m (plus 30m extra time = 3h30m)
PLACE: Beatrix Building – 7th floor

**IMPORTANT**
**- PLACE YOUR ID CARD (WITH PHOTO) ON THE TABLE**
**- WRITE YOUR NAME AND STUDENT NUMBER ON EVERY ANSWER SHEET**
**- USE A SEPARATE PAPER SHEET FOR PARTS A, B, C OF THE EXAM**
**- HAND IN YOUR EXAM (you may keep the question sheet)**

**EXAM SPECIFICS**
- This exam counts for 100% of the final grade.
- The minimum score of this exam needs to be at least 6.0 to prevent a re-exam. In order to be allowed to take a re-exam, the final grade for the course needs to be at least 4.0.
- Points per question are distributed as indicated at each question
- When answering the questions, please take the following into account: use the English language and write with a blue or black pen. Make sure that your writing is readable.

**PERMITTED EQUIPMENT**
Calculator (mobile phone and graphical calculator are not allowed)

**We wish you much success!**

Prof. K. P. de Jong
Prof. P. E. de Jongh
Prof. F. M. F. de Groot

**GENERAL EXAMINATION RULES**
- You are not allowed to leave the exam room in the first 30 minutes. Latecomers are allowed in up to 30 minutes after the start time.
- All electronic equipment needs to be switched off (including mobile phones), with the exception of electronic equipment allowed by the examiner.
- Your coat and closed bag are placed on the ground.
- Raise your hand when you need to go to the bathroom. 1 person at a time. Place your mobile phone visibly on your table just before you go.
- Raise your hand if you have a question about the exam, or need extra paper, etc.
- Not following the instructions of the examiner or surveillant can lead to exclusion from the exam.
- When fraud is suspected the exam will be confiscated immediately. The examiner will act according to the Education and Exam Regulations and will inform the Exam Committee and the Education Manager in writing within one work day.
- Upon receiving your result you can request the examiner for access to your graded exam. Possibly, a collective meeting will be organized.

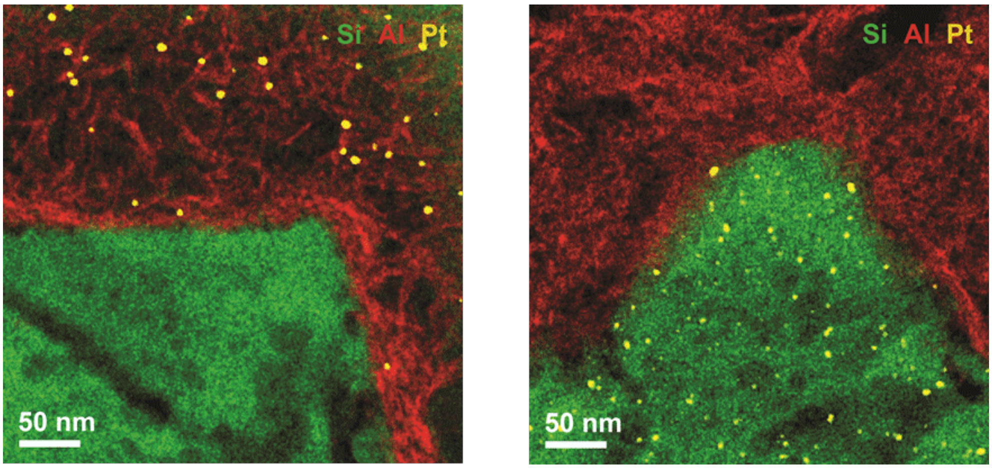
## Part A. Catalysis (37.5% of total grade)

**Question A-1 [40 points]**

In many oil refineries the production of high-octane gasoline involves the hydroisomerisation of normal-hexane. The $Pt/Al_2O_3$/zeolite catalyst used contains three components: platinum metal nanoparticles, a zeolite containing Brønsted acid sites and alumina as a binder. The alumina ($Al_2O_3$) binder can be considered as a kind of glue to keep the zeolite crystals together for formation of macroscopic bodies of an industrial catalyst. Please note that the zeolite crystals contain micropores whereas the alumina binder contains mesopores.

Please answer the following questions:

a. Describe the role of Pt in the catalyst to bring about the hydroisomerisation reaction. Provide equations of two reactions that are catalyzed by Pt. **[10 points]**
b. Describe the role of the acid sites ($H^+$) for the hydroisomerisation reaction. Provide reaction equations for three steps that take place on the acid sites. **[10 points]**
c. For $Pt/Al_2O_3$/zeolite materials we have been successful to deposit Pt nanoparticles either on the alumina binder (image below – left) or in the zeolite micropores (image below – right). Note: in the image below the zeolite crystals are green, the alumina red and the Pt nanoparticles yellow.




In our most recent research (with zeolite ZSM-5), the $Pt/Al_2O_3$/zeolite catalyst is more active when the Pt nanoparticles are present on the alumina binder than when the Pt nanoparticles are present in the zeolite. Provide a working hypothesis why this is. Also propose an experiment to (dis)prove your working hypothesis. **[20 points]**

**Question A-2 [40 points]**

Conversion of natural gas (mainly consisting of methane) to ultraclean diesel (consisting of normal-alkanes and iso-alkanes, nominally $C_{20}H_{42}$) is of growing importance. The overall scheme that consists of 3 key reaction steps is also referred to as Gas-To-Liquids (GTL). For the so-called Fischer Tropsch Synthesis – the central reaction in GTL – one makes use of supported cobalt catalysts.

Please answer the following questions:

a. Provide reaction equations of each of the 3 key reaction steps of GTL. **[10 points]**
b. Why is the diesel from the GTL process considered 'ultra clean'? Ultra clean compared to what? **[10 points]**
c. For the supported cobalt catalyst one wants to increase the activity normalized to catalyst weight. Provide two independent methods to increase the catalyst-weight based activity. **[20 points]**

**Question A-3 [40 points]**

The selective oxidation of ethylene (E) with oxygen to ethylene oxide (EO) is catalyzed by a supported silver catalyst. The catalyst support consists of spherical particles of 1.0 cm diameter. The effective diffusion coefficient through the porous support spheres of E and EO are estimated to be $1.0*10^{-6}$ $m^2.s^{-1}$. The reaction rate for E → EO is found to be first order in the concentration of E. The secondary reaction of EO with oxygen to $CO_2$ and $H_2O$ is first-order in the concentration of EO.

a. For specific reaction conditions it turns out that for E → EO the Thiele modulus $\phi = 1.0$. Calculate the rate constant for this reaction. In your calculations be explicit on the formulas and units used. **[10 points]**
b. For the observed value of $\phi = 1.0$ draw schematically the concentration profiles of E and of EO over the catalyst spheres. Discuss the consequences of the concentration profiles for both activity and selectivity. **[10 points]**
c. As an innovation in catalysts for ethylene epoxidation, hollow spherical support particles have been used. For a hollow spherical particle sketch concentration profiles for both E and EO and discuss the consequences for both activity and selectivity to EO in comparison to the non-hollow spheres considered in question A-3-b. **[20 points]**

## Part B. Kinetics, Chemisorption (37.5% of total grade)

**<u>Question B-1: [40 points]</u>**

In an overall reaction atom A reacts with two atoms B to a molecule $AB_2$, i.e. $A+2B \rightarrow AB_2$

There are two possible reaction mechanisms:

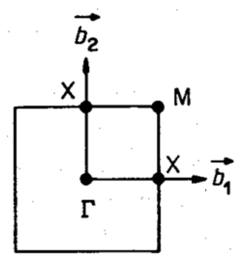
I: $A + B \leftrightarrow AB$, followed by $AB+B \rightarrow AB_2$.

II: $B + B \leftrightarrow B_2$, followed by $B_2+A \rightarrow AB_2$

( $\leftrightarrow$ indicates forward and backward reactions $k^+$ and $k^-$; $\rightarrow$ indicates only a forward reaction)

a. Give the equations for the reaction rate $d[AB_2]/dt$ for both mechanisms, assuming the steady state approximation for the intermediate species.
b. How can one experimentally determine what mechanism is correct?

**<u>Question B-2: [40 points]</u>**




Consider a two-dimensional square lattice of 2s-orbitals. The figure gives the reciprocal vectors $b_1$ and $b_2$. Γ indicates the point where both vectors are zero.

a) What point in the reciprocal lattice has the lowest energy? Explain.
b) What point in the reciprocal lattice has the highest energy? Explain.

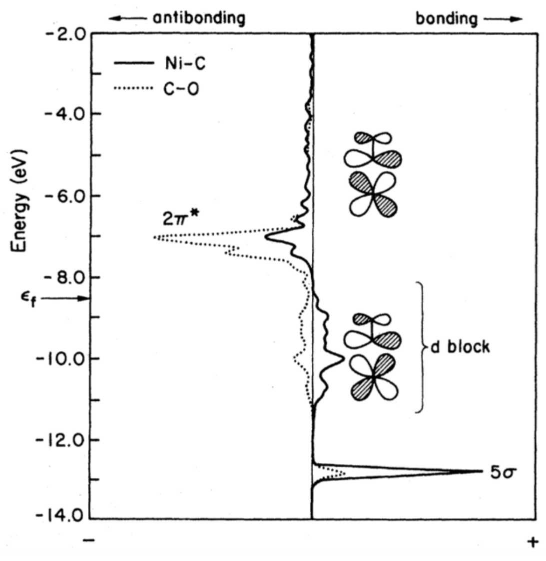
Consider now a two-dimensional square lattice of $2p_x$ orbitals.

c) What point in the reciprocal lattice has the lowest energy? Explain.

**<u>Question B-3: [20 points]</u>**

The figure shows the COOP diagram of a CO molecule adsorbing on a nickel surface. The states are occupied at energies lower than the Fermi level ($\epsilon_f$).

a) Use the COOP diagram to explain the effect of the adsorption of a CO molecule on a nickel surface for the bond length between carbon and oxygen.



## Part C. Physisorption (25% of total grade)

### Question C-1 (see also additional information on page 6)

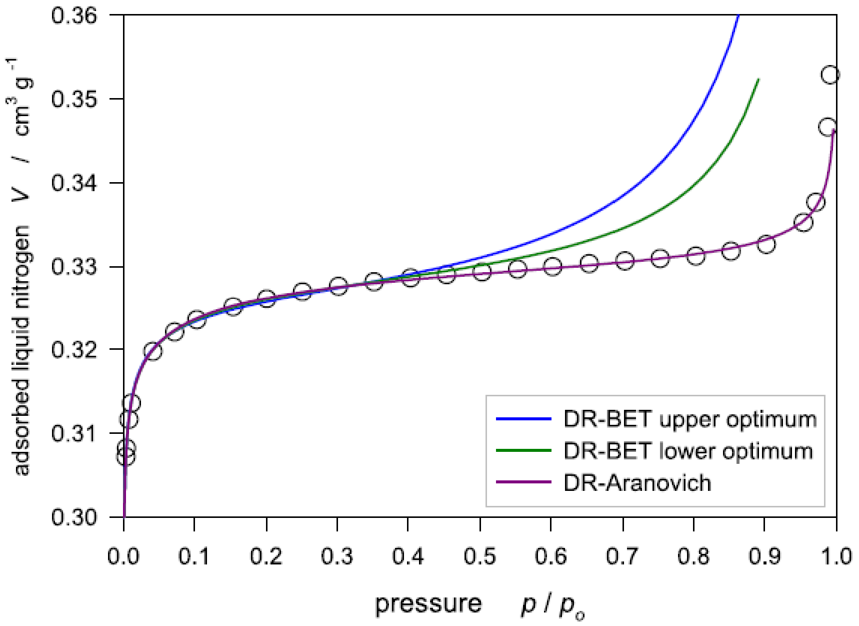
Capillary condensation occurs at a pressure $p$ and can be described using the Kelvin equation:

$$\ln\frac{p}{p_0} = -\frac{2v_l\gamma}{rRT}$$

a) What is the meaning of the symbol "$r$" in the Kelvin equation?

b) Give two reasons why the Kelvin equation loses its validity if $r$ becomes very small.

Below you find an experimental $N_2$ isotherm of an unknown porous sample measured at 77 K (taken from Buttersack et al, Micropor. Mesopor. Mater. 236 (2016) 63-70). The circles represent the data points for the experimental isotherm. The adsorption and desorption runs of the experiment give the same results. The blue line (the highest solid line) represents a fit with the BET equation.




c) Is the main pore volume in your opinion due to micropores, mesopores or macropores? Explain your answer.

d) The values that are given on the y-axis have a different unit than, as discussed during our lectures, is used in the vast majority of cases if physisorption data are reported in scientific literature. Mention which unit is most often used on the y-axis for experimental isotherms in scientific literature, and give an advantage and a disadvantage of the unit used here with respect to that mostly used in literature.

e) The fit using the BET equation yields a value of the BET constant $c$ of close to 10000. Explain why such a high $c$ value is obtained.

f) Give a possible reason why the BET fit gives higher values than the experimental measurement points in the pressure region of 0.6-0.9 relative pressure. Use in your answer one of the assumptions of the BET equation.

**Additional information:**

The volume of (ideal) gaseous $N_2$ at standard temperature (273 K) and pressure (1 atm) is 649 times that of liquid $N_2$ at 77 K.

For $N_2$ at 77K: $v_l = 30\ cm^3/mol$, $\gamma = 0.0085\ J/m^2$. R= 8.314 J $K^{-1}$ $mol^{-1}$

The BET model description of an isotherm is the following:

$$\frac{V_{ad}}{V_{ml}} = \frac{cp/p_0}{\left(1 - p/p_0 + cp/p_0\right)\left(1 - p/p_0\right)}$$

As a reference isotherm you can use the Harkins-Jura-de Boer (HJdB) isotherm:

with $p_r = p/p_0$.

$$t[\text{nm}] = \sqrt{\frac{0.1399}{0.034 - \log p_r}}$$