Name (Frist, Last):

ChE-403 Final Exam

Fall 2016

Date: January 17th 2017

Duration: 3 hours (8:15-11:15)

Total points: 100

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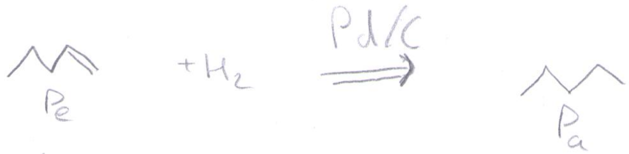
Problem 1

The hydrogenation of 1-pentene () to pentane () occurs in the gas phase in the presence of molecular hydrogen (H_2) over Pd/C.

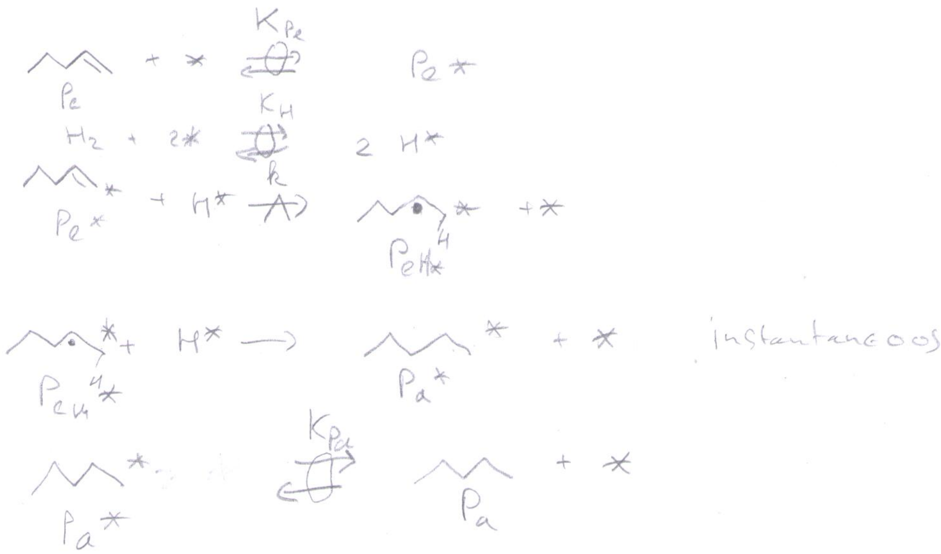
Propose a realistic sequence of elementary steps for this reaction and, by making various assumptions about these steps (state them!), demonstrate that the following kinetics can be derived:

$$r = \frac{cst1\sqrt{P_{H_2}}P_{pentene}}{\left(1 + cst2\sqrt{P_{H_2}} + cst3\,P_{pentene} + cst4\,P_{pentane}\right)^2}$$

25 points



Mech.



RDS:

$$r = \frac{k\,[Pe^*]\,[H^*]}{[*]^0}$$

$$[Pe^*] = K_{Pe}\,[Pe]\,[*]$$

$$[H^*] = \sqrt{K_H\,[H_2]}\;[*]$$

$$\rightarrow \quad r = \frac{k\,K_{Pe}\,[Pe]\sqrt{K_H[H_2]}\,[*]^2}{[*]^0}$$

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$$[*] = [*]_0 - ([H]^* + [P_a*] + [P_e*])$$

$$= [*]_0 - \left(\sqrt{K_H [H_2]} + K_{P_a} [P_a] + K_{P_e} [P_e]\right) [*]$$

$$\rightarrow [*] = \frac{[*]_0}{1 + \sqrt{K_H [H_2]} + K_{P_a} [P_a] + K_{P_e} [P_e]}$$

$$\rightarrow r = \frac{\overbrace{k_2 K_{P_e} \sqrt{K_H} [*]_0}^{cst\ 1} \sqrt{[H_2]}\ [P_e]}{\left(1 + \underbrace{\sqrt{K_H}}_{cst2} \sqrt{[H_2]} + \underbrace{K_{P_e}}_{cst3} [P_e] + \underbrace{K_{P_a}}_{cst4} [P_a]\right)^2}$$

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Problem 2

There is 2% NO in a smoke stream (assume 98% air) exiting a plant at 1173 K. The legislation imposes that we reduce the NO concentration to 0.04%. Using spherical catalyst pellets, NO is catalytically converted to N_2O.

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

In these conditions of heavy oxygen excess, the reaction can be treated as a first order reaction in NO.

The pipe where the smoke exits has an area of 20.3 cm^2 and can be filled with 1.4 10^6 $g_{cat}\ m^{-3}$ (overall bed density, ρ_B) of catalyst pellets leading to a superficial velocity (u) 4.9 10^{-4} m/s.

- Density of the catalyst pellet (ρ_p): 2.8 10^6 $g_{cat}\ m^{-3}$
- Catalyst pellet radius (R_p): 3 mm
- Effective diffusivity (D_{TA}^e): 1.8 10^{-8} $m^2\ s^{-1}$
- Gas diffusivity (D_{AB}): 2.0 10^{-8} $m^2\ s^{-1}$
- Fluid viscosity over its density ($\frac{\mu}{\rho}$) also known as *kinematic viscosity*: 1.5 10^{-8} $m^2\ s^{-1}$
- Rate constant: $k = 2.3\ 10^{-7}\ m^3\ s^{-1}\ g_{cat}^{-1}$

Note: the rate constant is normalized by catalyst concentration

We can assume that the particles are completely isothermal and that the flow through the reactor is plug flow (no dispersion). However, at these conditions, there are both external and internal mass transfer limitations.

How long should the reactor be to ensure that we follow the legislation?

30 points

PFR mass balance:

$$\frac{dC}{d\tau} = -r_{obs} = -k_{obs}\, C$$

$$\tau = L/U \qquad \eta_o = \frac{r_{obs}}{r_{max}} = \frac{k_{obs}\, C}{k'\, C} = \frac{k_{obs}}{k'}$$

$$\frac{dC}{dL} = -k'\eta_o\, C/U \rightarrow -\frac{dC}{C}\frac{U}{k'\eta_o} = dL$$

$$L = -\ln\left(\frac{C}{C_o}\right)\frac{U}{k'\eta_o} = \ln\left(\frac{C_o}{C}\right)\frac{U}{k'\eta_o}$$

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here $k' = k \rho_B$ (overall k in the bed)

We need $$\eta_o = \frac{\eta}{1 + \eta Da_{II}}$$

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh(\phi)} - \frac{1}{\phi}\right] \quad \text{or} \quad \eta = \frac{\tanh(\phi_o)}{\phi_o}$$

$$\phi = R_p\sqrt{\frac{k''}{D^e_{TA}}} \qquad \phi_o = \frac{R_p}{3}\sqrt{\frac{k''}{D^e_{TA}}}$$

here: $k'' = k \rho_p$ (overall k in the particles)

$$\phi_o = \frac{R_p}{3}\sqrt{\frac{k''}{D^e_{TA}}} = \frac{3 \cdot 10^{-3}}{3}\sqrt{\frac{2.8\,10^6 \cdot 2.3\,10^{-7}}{1.8\,10^{-8}}} = 5.98$$

$$\rightarrow \eta = \frac{\tanh(5.98)}{5.98} = 0.167$$ we need $Da_{II} = \frac{k_s}{\overline{k_c}}$

$\overline{k_c}$? for sherical catalyst pellets:

$$Sh = 2 + 0.6\, Re^{1/2}\, Sc^{1/3}$$

$$\rightarrow \overline{k_c} = \frac{D_{AB}}{2 R_p}\left(2 + 0.6\left(U \frac{\rho}{\mu} 2 R_p\right)^{1/2}\left(\frac{\mu}{\rho}\frac{1}{D_{AB}}\right)^{1/3}\right)$$

$$= \frac{2 \cdot 10^{-8}}{2.3\,10^{-3}}\left(2 + 0.6\left(\frac{4.9 \cdot 10^{-4}\; 2.3\,10^{-3}}{1.5\;10^{-8}}\right)^{1/2}\left(\frac{1.5\,10^{-8}}{2 \cdot 10^{-8}}\right)^{1/3}\right) = 3.2\;10^{-5}\;m/s$$

$$k_s = \frac{V_p}{S_p} k'' = \frac{R_p}{3} k \rho_p = \frac{3.3\,10^{-3} \cdot 2.3\,10^{-7} \cdot 2.8\,10^{6}}{3} = 7.08 \cdot 10^{-4}\;m/s$$

$\rightarrow Da_{II} = 22.1 \quad \rightarrow \quad \eta_o = \dfrac{0.167}{1 + 22.1 \cdot 0.167} = 0.036$ $\rightarrow$ both internal + external effects are significant!

$$L = \ln\left(\frac{C_0}{C}\right) \frac{U}{k' \eta_0} = \ln\left(\frac{2}{0.04}\right) \frac{4.9 \cdot 10^{-4}}{2.3\,10^{-7}\ 1.4 \cdot 10^{6}\ 0.036} = 0.17\,m$$

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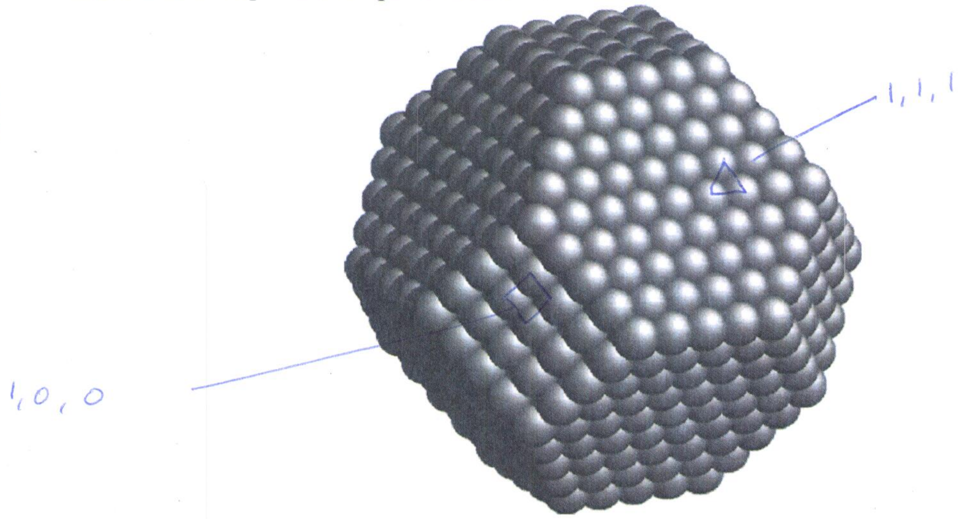
Problem 3

Metallic nanoparticles often adopts a geometrical shape called cuboctahedron or truncated octahedron (see figure). The polyhedron is made of all equivalent hexagon faces and all equivalent square faces.

1)



1) In the case of a silver nanoparticle (with a face centered cubic or FCC structure), attribute (and justify) the crystallographic planes corresponding to the two different faces of the particle.

2) In most conditions, which face type on this particle is most stable and why?

3) If we put this particle in a solution that included capping agents that stabilized the less stable plane (i.e. the one that you identified in 2) we could lead the particle to reorganize such that only this plane type remains (again the one that you identified in 2). What would be the final shape of this nanoparticle after this reorganization is finished and only this one plane type remains?

15 points

2) the 1,1,1 due to the higher density of atoms on the surface which increases the nb of nearest neighbors and hence decreases the surface energy.

3) a cube

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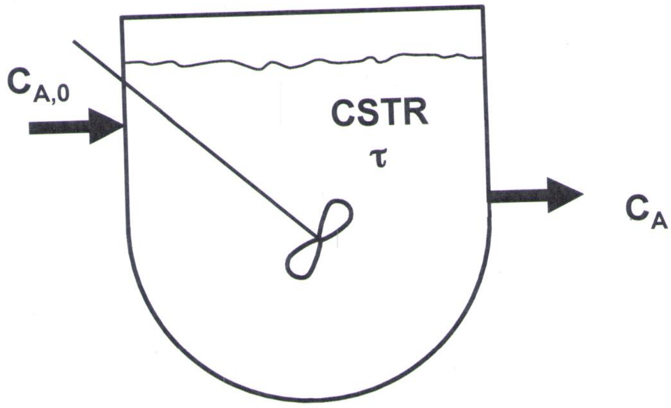
Problem 4

Consider a CSTR:



a) Use the function E(t) of a CSTR to calculate the outgoing concentration (C_A) for a reaction of order zero.

$$-r = \frac{dC_A}{dt} = -k$$

c) Is it the same expression as the one that you derive using a mass balance?

20 points

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a)

$$\frac{dC_A}{dt} = -k \qquad C_A = C_{A0} - kt$$

$$E(t) = \frac{\exp(-t/\tau)}{\tau}$$

$$\langle C_A \rangle = \int_0^\infty C_A \frac{\exp(-t/\tau)}{\tau}\, dt =$$

$$\int_0^\infty (C_{A_0} - kt) \frac{\exp(-t/\tau)}{\tau}\, dt =$$

using $\int_0^\infty x \exp(-x)\, dx = 1$

$$\frac{\tau}{\tau} \int_0^\infty \left(C_{A,0} - \tau k \left(\frac{t}{\tau}\right)\right) \exp(-t/\tau)\, d\,t/\tau =$$

$$\left[C_{A0} \exp\left(-\frac{t}{\tau}\right) \right]_{t/\tau = 0}^{t/\tau = \infty} - \tau k = C_{A,0} - \tau k$$

b) CSTR mass balance:

$$\frac{C_{A,0} - C_A}{\tau} = k$$

$$\rightarrow C_A = C_{A,0} - k\tau$$