



DEPARTMENT OF CHEMISTRY		
MODULE	CEM8X08	
	CATALYSIS	
CAMPUS	APK	
EXAM	SUPPLEMENTARY	JANUARY 2020

**DATE: JANUARY 2020**

**ASSESSOR (S)**

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**EXTERNAL MODERATOR**

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**DURATION**

**3 HOURS**

**MARKS 70**

**INSTRUCTIONS:**

1. This paper consists of 5 pages.
2. The examination is out of 70 marks and you have 3 hours to complete it.
3. Calculators are allowed but **no** cell phones may be used.
4. You can use a pen of any color **except** RED AND GREEN to write your answers.
5. Read the whole question paper carefully before you start answering. You are allowed to start with any question, just clearly number it in your answer sheet.

**QUESTION 1: General****(9 marks)**

- a) Using a diagram, explain the meaning of 'bite angle'. [2]
- b) Explain why homogeneous catalysts generally exhibit improved activity and selectivity compared to heterogeneous catalysts. [3]
- c) For olefins containing no functional groups, reactivity towards organometallic complexes varies depending on three main factors relating to olefin structure. Explain these factors. [3]

**QUESTION 2: Olefins oligo- and polymerisation****(18 marks)**

- a) Describe the differences between non-selective ethylene oligomerisation, selective ethylene trimerisation and selective ethylene tetramerisation by completing the table below:

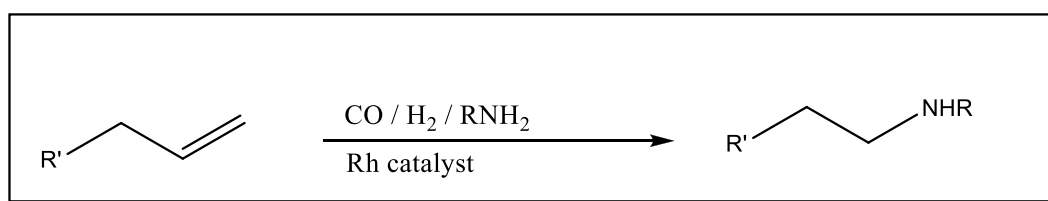
	<b>Non-selective ethylene oligomerisation</b>	<b>Trimerisation</b>	<b>Tetramerisation</b>
<i>Mechanism</i>			
<i>Product profile/Selectivity</i>			
<i>Catalyst</i>			
<i>Process design</i>			

[6]

- b) Draw the full catalytic cycle (reaction mechanism) for ethylene trimerisation and show formation of 1-hexene product (s). [5]
- c) 1,4-Butanediol is the solvent of choice in the ethylene growth reaction of SHOP process. Give reasons why 1,4-butanediol is the preferred or excellent solvent. [2]
- d) Explain, why are olefins good monomers for polymerisation reactions? [2]
- e) Teflon is the polymer that results from the polymerisation of fluorinated ethylene. Write a chemical formula for this reaction and give 2 remarkable properties of Teflon. [2]

### QUESTION 3: Carbonylation and Hydroformylation (24 marks)

- a) With the aid of a diagram, discuss the anionic catalytic cycle for the **Cativa process**, a carbonylation technology developed by BP for the production of acetic acid from methanol. Show the organic iodide, which supports the catalytic cycle, name the reaction steps and identify the rate determining step. [8]
- b) Why do bidentate ligands afford a more stable catalyst and better control of selectivity? Explain. [2]
- c) The partial pressure of CO plays an important role in hydroformylation reactions and the mechanistic cycle. Explain the effect of  $p_{\text{CO}}$  on reaction rate, selectivity and catalyst stability. [3]
- d) The transformation below is called hydroaminomethylation, first reported at BASF industry by Reppe over 60 years ago. There are four stages to this process, all of which occur in the same reaction vessel. Three of these are catalyzed by the same Rh catalyst,  $[\text{Rh}(\text{I})\text{L}_2]^+$  ( $\text{L}_2$  is a chelating bisphosphine). First, internal alkenes are isomerized to terminal alkenes. Next, the terminal alkene undergoes hydroformylation with a preference for formation of linear instead of branched aldehyde. Third, the aldehyde reacts with a primary amine (without catalysis) to give the imine, which undergoes Rh-catalyzed hydrogenation to the amine in the last step.



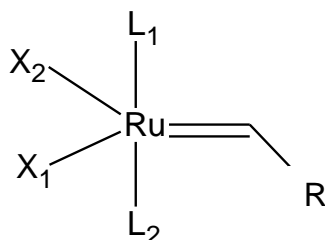
Provide the reaction mechanism of the hydroformylation of alkene using  $\text{L}_2\text{RhH}(\text{CO})_2$  as the catalyst:  $\text{L}$  = phosphine ligand. Name the reaction step and identify the rate determining step. [5]

- e) Biphasic hydroformylation is practiced commercially. What does it involve, and describe some advantages and limitations of such a process. [4]

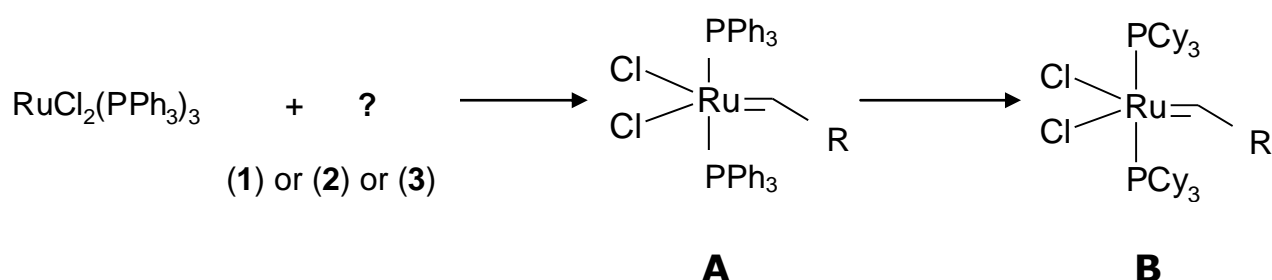
## QUESTION 5: Metathesis

(23 marks)

- a) Give all the primary metathesis products which can be produced from the metathesis of the following olefins: [4 x3]
- Cross metathesis of 1-octene
  - ADMET of 1,5-hexadiene
  - Self-metathesis of 1,3-butadiene
  - Cross metathesis of 2-pentene and 3-methyl-1-butene
- b) Grubbs catalysts can be heterogenised by attaching the complex to a solid support.
- What is the reason for doing this? [1]
  - What are the limitations of such an approach when anchored to: the neutral (L) and anionic (X) ligands. [2]
  - What are the limitations of such an approach when anchored to the alkylidene? [3]



c)



Consider the reaction scheme above and answer the following questions:

- (i) Metal alkylidenes such as **A** are reactive species and quite difficult to make. Describe 3 classes of reagents (**1**, **2** and **3**) which can be used to introduce the alkylidene moiety into a simple ruthenium precursor such as  $\text{RuCl}_2(\text{PPh}_3)_3$ . [3]

- (ii) Triphenylphosphine is not a good ligand for metathesis with homogeneous Grubbs-type catalysts.
- Why is tricyclohexylphosphine a preferred phosphine ligand?
  - How would one go about preparing complex **B** from **A**? [2]

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END

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