UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2009/2010 Academic Session

April/May 2010

KIE 358 – Current Topics In Industrial Chemistry
[Tajuk Semasa Kimia Industri]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of TWELVE printed pages before you begin the examination.

Instructions:

Answer any **FIVE** (5) questions.

You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

In the event of any discrepancies, the English version shall be used.

Answer **Five (5)** questions.

1. (a) What are meant by anodic and cathodic inhibitors? Briefly explain by using a potentiodynamic polarization curve the effects of anodic and cathodic inhibitors on the corrosion potential and the corrosion current density.

(10 marks)

(b) It is found that in polarization experiment of steel in sea water the value of Tafel constants, β_a and β_c, are 0.129 V decade^{-1} and 0.144 V decade^{-1}, respectively. The molar mass and the density of steel are 55.86 g mol^{-1} and 7.8 g cm^{-3}, respectively. If the measured polarization resistance (R_p) is 3.57 Ohm, calculate the corrosion current and the corrosion rate (in mil per year) of steel.

(10 marks)

2. Divalent metal experiences corrosion in an acid solution. The rate of both oxidation and reduction half – reactions are controlled by activation polarization. The following polarization data are known for both reactions:

Metal oxidation	Hydrogen ion reduction
E^o_{rev} = -0.90 V	E^o_{rev} = 0.00 V
i_a = 10^{-12} A cm^{-2}	i_c = 10^{-10} A cm^{-2}
β_a = 0.12 V decade^{-1}	β_c = -0.15 V decade^{-1}

(a) Determine the rate of corrosion of metal (in mol cm^{-2} s^{-1}) in acidic solution.

(b) Compute the value of the corrosion potential.

(20 marks)

3. (a) Corrosion of iron in acidic solution with and without the presence of inhibitor can be studied by means of electrochemical inpedance spectroscopy (EIS).

(i) Draw the equivalent circuits which reflect the corrosion process.

(ii) Using the Nyquist plot, show the effects of inhibitor concentrations which indicate the increase of inhibitor efficiency.

(iii) Depression on the capacitive semi-circle has always been encountered during the EIS study. Briefly explain why this phenomenon occurred.

(12 marks)

(b) What is the difference between anodic and cathodic corrosion protection? Briefly explain with the aid of schematic diagram, how protection by sacrificial anode can be achieved.

(8 marks)

4. (a) What is filiform corrosion and pitting corrosion? Describe briefly under which conditions these corrosion occurs.

(5 marks)

(b) Several types of metallic coatings are used to protect steel, including zinc, tin, nickel, and aluminium. In which of these cases will the coating provide protection even when the coating is locally disrupted? Explain.

(5 marks)

(c) Choose either RLi or RMgX. Discuss its preparation, properties and reactions to produce at least TWO organometallic compounds of the 1st row of transition metals.

(10 marks)

5. Catalytic hydrogenation using Wilkinson's catalyst, $(PPh_3)_3RhCl$, is a homogenous catalytic process. In a typical catalytic cycle, the catalyst transforms H_2 and an alkene to an alkane. This catalytic cycle involves several organometallic intermediates.

   (i) Draw a complete catalytic cycle for the catalytic hydrogenation using Wilkinson's catalyst.

   (ii) Describe the mechanism for the formation of alkane from H_2 and an alkene using Wilkinson's catalyst.

   (iii) Identify and name the 14, 16 and 18 electrons intermediate species involved in the catalytic cycle above.

   (20 marks)

6. (a) Draw the possible structure and describe the bonding in the following organometallic compounds:

   (i) $[Me(H)C=CHCH=CH(CHO)]Fe(CO)_3$

   (ii) $K[(RC\equiv CR)PtCl_3]$ where R = MeC(OH)Et

   (iii) $(ClAlMe_2)_2$

   (iv) $(C_5H_5)_2Fe$

   (12 marks)

   (b) Several organotransition metal compounds have been used to activate small molecules such as H_2, CO, CO_2, N_2, simple alkene and alkyne. By providing suitable examples, discuss briefly the activation of CO_2 with organotransition metal compounds.

   (8 marks)

7. (a) Suggest the reagent(s) and experimental condition(s) to convert the following starting material to the intended product:

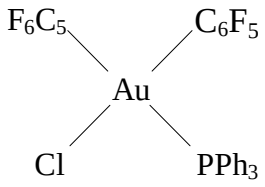
(i) $Mo(CO)_6 \rightarrow Ph_3PMo(CO)_5 \rightarrow Mo(CO)_4(PPh_3)_2$

(ii) $Al \rightarrow Al_2Ph_3$

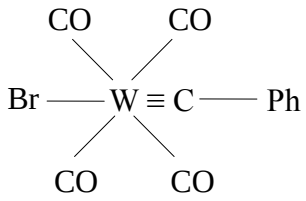
(iii) $(C_5H_5)_2Fe \rightarrow (C_5H_5)Fe(MeC_5H_4)$

(12 marks)

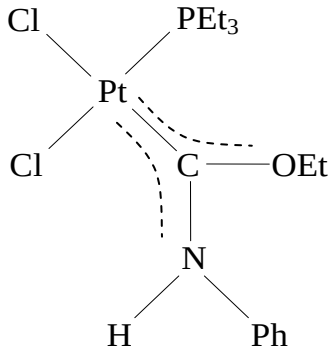
(b) Determine whether the following transition metal centre of the organometallic compounds obeys the 18-electron rule.



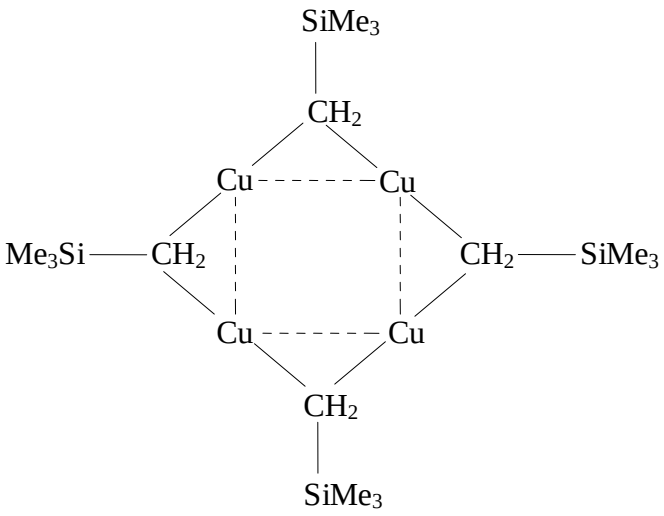
(i)



(ii)



(iii)



(iv)

(8 marks)

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

Jawab **Lima (5)** soalan

1. (a) Apakah yang dimaksudkan dengan perencat anodik dan katodik? Terangkan dengan ringkas menggunakan keluk pengutuban potensiodinamik kesan perencat anodik dan katodik kepada keupayaan kakisan dan ketumpatan arus kakisan.

(10 markah)

(b) Dalam eksperimen pengutuban keluli di dalam air laut didapati bahawa nilai pemalar Tafel, β_a dan β_c, ialah masing-masing 0.129 V decade^{-1} dan 0.144 V decade^{-1}. Jisim molar dan ketumpatan keluli ialah masing-masing 55.86 g mol^{-1} dan 7.8 g cm^{-3}. Jika kerintangan pengutuban (R_p) ialah 3.57 Ohm, hitunglah arus kakisan dan kadar kakisan (dalam mil per tahun) keluli tersebut.

(10 markah)

2. Logam dwivalen mengalami kakisan dalam larutan asid. Kadar tindakbalas setengah bagi pengoksidaan dan penurunan adalah dikawal oleh pengkutuban keaktifan. Data pengkutuban berikut diketahui bagi kedua-dua tindakbalas:

Pengoksidaan logam	Penurunan ion hidrogen
E^o_{rev} = -0.90 V	E^o_{rev} = 0.00 V
i_a = 10^{-12} A cm^{-2}	i_c = 10^{-10} A cm^{-2}
β_a = 0.12 V decade^{-1}	β_c = -0.15 V decade^{-1}

(a) Tentukan kadar kakisan logam tersebut (dalam mol cm^{-2} s^{-1}) di dalam larutan asid.

(b) Hitunglah nilai keupayaan kakisan.

(20 markah)

3. (a) Kakisan logam besi di dalam larutan berasid dengan kehadiran dan tanpa kehadiran perencat dapat dikaji dengan spektroskopi impedans elektrokimia (EIS).

(i) Lukiskan litar ekuivalen yang mengambarkan proses kakisan yang berlaku.

(ii) Dengan menggunakan plot Nyquist, tunjukkan kesan kepekatan perencat yang menunjukkan kenaikan keberkesanan perencatan.

(iii) Penurunan setengah-bulatan kapasitif selalu terjadi semasa kajian EIS. Jelaskan dengan ringkas kenapa fenomena ini berlaku.

(12 markah)

(b) Apakah perbezaan antara pencegahan kakisan secara anodik dan katodik? Terangkan dengan ringkas dengan bantuan lakaran rajah, bagaimana pencegahan dengan anod karbon dapat dilakukan.

(8 markah)

4. (a) Apakah kakisan filiform dan kakisan liang? Jelaskan dengan ringkas keadaan yang menyebabkan kakisan tersebut berlaku.

(5 markah)

(b) Beberapa jenis logam pelapis digunakan untuk mencegah keluli, termasuk zink, tin, nikel dan aluminium. Pelapisan logam manakah akan memberikan pencegahan walaupun lapisan itu mengalami kerosakan setempat. Jelaskan.

(5 markah)

(c) Pilih antara RLi atau RMgX. Bincangkan penyediaannya, sifatnya dan tindak balasnya bagi menghasilkan sekurang-kurang DUA sebatian organologam baris pertama logam peralihan.

(10 markah)

5. Penghidrogenan katalitik menggunakan mangkin Wilkinson, $(PPh_3)_3RhCl$, adalah suatu proses katalitik homogen. Dalam suatu kitar pemangkinan tipikal, mangkin menukarkan H_2 dan suatu alkena kepada suatu alkana. Kitar katalitik ini melibatkan beberapa perantaraan organologam.

(i) Lukiskan satu kitar pemangkinan lengkap bagi penghidrogenan katalitik menggunakan mangkin Wilkinson.

(ii) Terangkan mekanisme pembentukkan alkana daripada H_2 dan suatu alkena menggunakan mangkin Wilkinson.

(iii) Kenalpasti dan namakan spesies perantaraan 14, 16 dan 18 elektron yang terlibat dalam kitar pemangkinan di atas.

(20 markah)

6 (a) Lukis struktur yang mungkin dan terangkan pengikatan bagi sebatian organologam berikut:

(i) $[Me(H)C=CHCH=CH(CHO)]Fe(CO)_3$

(ii) $K[(RC{\equiv}CR)PtCl_3]$ di mana R = MeC(OH)Et

(iii) $(ClAlMe_2)_2$

(iv) $(C_5H_5)_2Fe$

(12 markah)

(b) Beberapa sebatian organologam peralihan telah digunakan bagi mengaktifkan molekul kecil seperti H_2, CO, CO_2, N_2, alkena and alkuna mudah. Dengan memberikan contoh yang sesuai, bincangkan secara ringkas pengaktifan CO_2 dengan sebatian organologam peralihan.

(8 markah)

7. (a) Cadangkan reagen dan ciri eksperimen bagi menukarkan bahan mula berikut kepada hasil yang diingini:

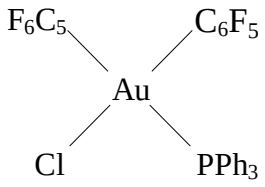
(i) $Mo(CO)_6 \rightarrow Ph_3PMo(CO)_5 \rightarrow Mo(CO)_4(PPh_3)_2$

(ii) $Al \rightarrow Al_2Ph_3$

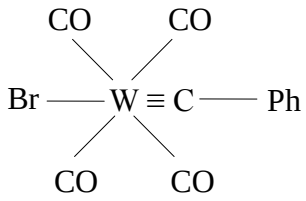
(iii) $(C_5H_5)_2Fe \rightarrow (C_5H_5)Fe(MeC_5H_4)$

(12 markah)

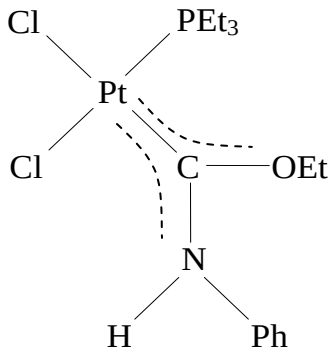
(b) Tentukan sama ada logam peralihan pusat bagi sebatian organologam berikut mematuhi peraturan 18-elektron.



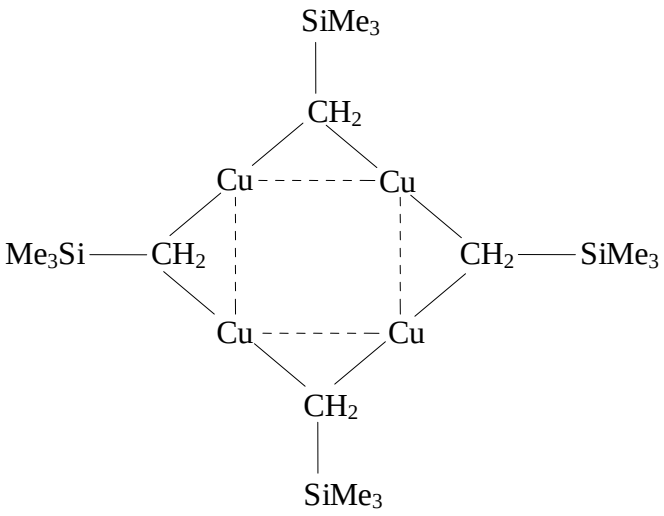
(i)



(ii)



(iii)



(iv)

(8 markah)

-oooOoooo-