Chem Factsheet

www.curriculum-press.co.uk Number 138

Industrial Uses of Transition Elements and their Compounds

Prior knowledge

You should be able to balance chemical equations, write chemical formulas, understand oxidation states and the Stock and IUPAC naming systems.

After working through this Factsheet you should be able to recall and understand the uses of certain transition metals and or their compounds

Introduction

Two commonly used definitions for transition elements are:

Transition elements have incomplete d sub-shell in either their atoms or their ions.

For Sc to Zn, Zn is excluded by this definition since its atom and ion (Zn^{2+}) both have d^{10} configurations.

Transition elements form at least one stable ion with partially filled d orbitals.

For Sc to Zn, both Sc and Zn are excluded by this definition since both form only one ion and the zinc ion (Zn^{2+}) has a complete d^{10} configuration while the scandium ion (Sc^{3+}) has a d^0 configuration

The uses of transition elements and their compounds usually depend on the fact that they have incompletely filled d orbitals. This statement will become clearer with many of the examples that follow.

1. Uses directly linked to the purity of the metal and hence the method of extraction

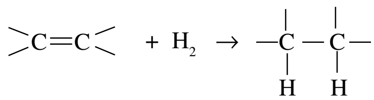
- **Titanium** alloys, which have very high strength:weight ratios, are principally used in the **aerospace industry for both engines and airframes**. Pure titanium is needed so it is not obtained via carbon reduction of titanium(IV) oxide (rutile) because the presence of titanium carbide as an impurity would make the titanium brittle. Instead, the TiO_2 is converted to $TiCl_4$ which is then reduced by either Na or Mg to produce pure titanium.

- Likewise, **tungsten** produced by carbon reduction of tungsten(VI) oxide would be brittle because of the presence of tungsten carbide. However, tungsten produced by reducing WO_3 with H_2 is pure and can be used for **filaments of electric lamps**.

- The presence of elemental carbon (rather than as a compound) as an impurity in other metals, **e.g. iron**, also makes them brittle. Thus cast iron contains carbon and is brittle and is not used where **flexibility** is needed. However it is used for structures such as bridges where it is **very strong under compression**. To produce iron with greater flexibility the blast furnace iron is converted into steel alloys.

2. Catalysts

- **Nickel** powder. This is a heterogeneous catalyst used for the partial hydrogenation of plant oils such as sunflower oil. Such plant oils contain esters of polyunsaturated carboxylic acids with most of the double bonds having the cis (Z) arrangement. Hydrogen gas is passed into the oil containing the powdered nickel catalyst at about 150^0C and 400 kPa for sufficient time for *only some* of the double bonds to be hydrogenated. This produces a "soft" solid; **spreadable margarine**.



> Note. Other transition metals, such as Pt and Pd, also catalyse hydrogenation reactions but Ni is used because it is cheaper.

- **Iridium based catalyst.** Ethanoic acid can be produced with a theoretical atom economy of 100% from methanol and carbon monoxide using $[Ir(CO)_2I_2]^-$ as catalyst. The company that developed this catalyst was given a Green Chemistry Award.

  $CH_3OH + CO \rightarrow CH_3COOH$

  The iridium based catalyst is an improvement on a similar **rhodium** based catalyst ($[Rh(CO)_2I_2]^-$) for several reasons including increased reaction rates, increased yields and less by-products.

  Ethanoic acid is also manufactured from butane using a **cobalt(II)** catalyst but the yield is only 35%.

  $C_4H_{10} + 3O_2 \rightarrow 2CH_3COOH + 2H_2O$

  The by-products are methanoic acid (20%), propanoic acid (15%) and propanone (30%).

- **Platinum, rhodium and/or palladium**. These expensive metals are used in **catalytic converters** to prevent harmful pollutants such as oxides of nitrogen, carbon monoxide and unburnt hydrocarbons entering the atmosphere. Since the pollutants are adsorbed by the surface atoms of these expensive catalysts only the thinnest layers of catalysts are needed and they can be spread on a ceramic support medium to give very large surface areas and hence minimise costs but maximising reaction rates. A honeycombed structure is most often used to maximise this effect. The Pt and Rh catalyse the decompositions of the oxides of nitrogen while both Pt and Pd catalyse the complete oxidation of carbon monoxide and unburnt hydrocarbons.

  e.g. $NO_2 \rightarrow ½N_2 + O_2$ and $CO + ½O_2 \rightarrow CO_2$
  so overall the equation is $NO_2 + 2CO \rightarrow 2CO_2 + ½N_2$

  The steps involved in these heterogeneous catalytic reactions are:
  i) adsorption of the harmful gases on to the catalytic surface
  ii) reaction on the solid catalytic surfaces and
  iii) desorption of the less harmful products, N_2 and CO_2.

The strength of the bond between adsorbed species and the surface atoms of the catalyst is of paramount importance; if too weak the impurities will not remain long enough on the surface for bonds to weaken and for reactions to occur. Conversely, if too strong, desorption will be very slow leading to a poor catalytic effect.

Vehicles with catalytic converters must use unleaded fuels otherwise lead will be irreversibly adsorbed and hence the catalysts will be poisoned. Thus their efficiency will be greatly reduced and the environment will be polluted by CO, NOx and unburnt hydrocarbons.

- **Vanadium(V) oxide**

This is a heterogeneous catalyst used in the **manufacture of concentrated sulphuric acid**. It catalyses the reaction between purified sulphur dioxide [sulphur(IV) oxide] and oxygen (from the air) at 450^{0}C and 2 atm to produce sulphur trioxide [sulphur(VI) oxide].

$SO_2(g) + ½O_2(g) \rightleftharpoons SO_3(g) \quad \Delta H^{\ominus} = -98.5\ kJmol^{-1}$.

The vanadium(V) oxide functions as a catalyst by providing an alternative route of lower activation energy than that of the direct reaction. This alternative route is possible because vanadium can change its oxidation state from +5 in V_2O_5 to +4 in V_2O_4 and back again.

Initially the V_2O_5 oxidises the SO_2 to SO_3 ;
$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ --- (1)

Then the O_2 oxidises the V_2O_4 back to V_2O_5 ;
$V_2O_4 + ½O_2 \rightarrow V_2O_5$ --- (2)

On adding (1) and (2), the two V_2O_4 species cancel out and the overall equation is obtained.

- **Iron**

Solid iron is used as the heterogeneous catalyst in the **manufacture of ammonia** by the Haber Process.Typical conditions for this reaction are 450^{0}C and 20000 kPa.

$½N_2(g) + 1½H_2(g) \rightleftharpoons NH_3(g) \quad \Delta H^{\ominus} = -46\ kJmol^{-1}$.

The iron catalyst is prone to being poisoned by sulphur impurities and so the gases must be purified prior to reaction; reduced efficiency of the catalyst would increase the cost of the Haber Process.

3. Other uses.

- **Iron in the manufacture of aminobenzene**

Nitrobenzene is converted to a salt of aminobenzene when heated with iron and dilute hydrochloric acid. This is a reduction. The very weakly basic aminobenzene is released from the salt by adding a stronger base. e.g. sodium carbonate solution.

$C_6H_5NO_2 + 3H_2 + HCl \rightarrow C_6H_5NH_3^+Cl^- + 2H_2O$

$2C_6H_5NH_3^+Cl^- + Na_2CO_3 \rightarrow 2C_6H_5NH_2 + 2NaCl + H_2O + CO_2$

In the laboratory, the more expensive metal tin (Group IV) and concentrated hydrochloric acid are used to carry out this reduction. Overall, the process can be simply represented as:

$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

- **cisPlatin** {cis-diamminedichloroplatinum(II)} $[Pt(NH_3)_2(H_2O)_2]$.

This is a **chemotherapy drug** used in the treatment of some cancers, including some carcinomas, lymphomas and sarcomas. After the drug is taken and it has passed through the cell wall, ligand substitution slowly occurs producing $[Pt(NH_3)_2(H_2O)Cl]^+$. However the aqua ligand is easily displaced allowing co-ordination with a basic site in DNA. This process is repeated for the second chloride ligand resulting in the DNA forming a second co-ordinate bond to the Pt. This cross-linking has the effect of preventing cell division and, when the cell cannot repair the damaged DNA, the cell dies.

- **Breathalyser**

Potassium dichromate(VI), $K_2Cr_2O_7$ is used to detect and measure alcohol content of a driver's breath. The suspect breathes into the breathalyzer and the sample bubbles through an orange solution of potassium dichromate(VI) in sulphuric acid. This is reduced to a solution of green chromium(III) sulphate in the presence of ethanol, which is oxidised to ethanoic acid. The reaction is catalysed by silver nitrate, a homogeneous catalyst. The amount of colour change is directly related to the blood alcohol concentration (BAC / mg of ethanol per 100 ml of blood). In the U.K. the legal limit is 80 mg / 100 ml or 0.08%. (In most countries it is less than 0.08% and may be zero for the first five years after passing your test!)

The half-equations are:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ---- (1)

$C_2H_5OH + 3H_2O \rightarrow 2CH_3COOH + 4H^+ + 4e^-$ ---- (2)

Since the numbers of electrons are different, multiply (1) by 2 and (2) by 3 to make the number of electrons equal so that they cancel out when the half-equations are added. (There must be equal numbers of electrons so that the amounts of reduction and oxidation are equal.) This gives:

$2Cr_2O_7^{2-} + 16H^+ + 3C_2H_5OH \rightarrow 4Cr^{3+} + 5H_2O + 6CH_3COOH$

Note: these chemical breathalysers are mostly superseded by IR-based devices.

- **Photochromic sunglasses**

Photochromism, with reference to sunglasses, is a reversible reaction caused by the absorption of visible / UV radiation when a reactant and a product have different absorption spectra. **When the radiation is absorbed a change in colour or a change in darkening of the material occurs**.

The most commercially used inorganic photochromic systems involve very small silver halide (excluding AgF) crystals dispersed though a glass matrix. For example silver chloride undergoes the following reversible reaction which is catalysed by copper(II) ions; as silver is produced a darkening occurs.

$AgCl \rightleftharpoons Ag + ½Cl_2$

Summary

To make / do	Margarine from plant oils.	Ethanoic acid from CH_3OH & CO	Remove exhaust pollutants	Sulphuric acid	Ammonia.
Transition metal / compound and its role	Ni catalyst	$[Ir(CO)_2I_2]^-$catalyst	Pt, Pd, Rh catalysts	V_2O_5 catalyst	Fe catalyst

To make / do	Aminobenzene.	Treat some cancers	Analyse breath for ethanol	Photochromic sunglasses.
Transition metal / compound and its role	Iron (tin lab.) with HCl(aq) makes H_2	cisPlatin prevents cell division	Oxidant: $K_2Cr_2O_7$ in H_2SO_4	AgCl / Ag photochromic system

Practice questions

1. Write the equations for the reduction of a) titanium(IV) chloride by magnesium and b) tungsten(VI) oxide by hydrogen. (Tungsten symbol is W)

2. Alpha-linolenic acid has the molecular formula $C_{18}H_{30}O_2$ and a molar mass of 278 g mol^{-1}. (H=1, C=12, O=16). It has three cis(Z)-double (>C=C<) bonds and it is called an omega-3 fatty acid since one of these double bonds is three carbon atoms from the last carbon atom (the omega carbon). It is found in many vegetable oils including rapeseed.
   (a) If when a sample of rapeseed oil is hydrogenated two of the double bonds become saturated what is:
   (i) the molecular formula and the molar mass of the acid formed
   (ii) the percentage increase in molar mass.
   (b) Identify a catalyst for the process
   (c) Why is the process done?

3. (a) Identify one metal *always* used in catalytic converters.
   (b) Using catalytic converters explain what is meant by *adsorption*?
   (c) Name the three stages that have to take place if the pollutants nitrogen(II) oxide and carbon monoxide are to be removed from the exhaust gases of a vehicle and write one equation for their removal.

4. Define the term heterogeneous catalyst and give one example of a *compound* that is a heterogeneous catalyst.

5. Explain why the quote, “The National Highways Traffic Safety Administration has found that dieters and diabetics may have propanone levels much higher than others. Propanone is one of the substances that can be falsely identified as ethanol by some breathalysers”. Using your knowledge of ketones, should this be true?

Answers

1. (a) $TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti.$
   (b) $WO_3 + 3H_2 \rightarrow W + 3H_2O$
2. (a) (i) $C_{18}H_{34}O_2$,
   (ii) $(4/278)\times 100 = 1.4(4)\%$.
   (b) Ni.
   (c) To make margarine.
3. (a) Pt.
   (b) Adsorption: the reactant (e.g. carbon monoxide) molecule bonds to the surface atoms of the Pt catalyst
   (c) Stages: adsorption (of pollutants), reaction(s) and desorption (of the products). $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$.
4. The reactant and catalyst are in different phases. On example is V_2O_5.
5. No. Ketones are not oxidized by acidified potassium dichromate(VI).

Acknowledgements: This Factsheet was researched and written by Bob Adam. ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***