Review Article

Metal-Organic Frameworks (MOFs)

Dr. Vajira P. Bulugahapitiya
Department of Chemistry, University of Ruhuna

Metal-organic frameworks (MOFs) are a new class of hybrid inorganic-microporous crystalline materials. MOFs possess the properties of both organic porous material (eg: Charcoal) and inorganic porous material (eg: Zeolites) and unique properties associated with hybrid material. MOFs are formed using metal or metal clusters linked by organic ligands (linkers) using coordinative bonds. Metal Organic Frameworks are also named as Metal – Organic microspores materials, porous coordination networks or porous coordination polymers. These materials can be one-dimensional (1-D) chains, 2-D layers, or 3-D networks MOFs have attracted a great deal of attention since last two decades due to their enormous structural and chemical diversity, unique porous properties (nano-scale pore size between 0.4–6 nm) and superior surface area. Therefore, large number of MOFs have been synthesized so far and different applications has been explored such as gas storage, gas capture, gas separation, enantiomeric separation, enantio-selective catalysis, molecular recognitions, luminescent and fluorescent materials, sensors, energy conversions, ion exchange, drug storage and drug delivery etc.[1,2].

Metals used in MOFs

A large number of MOFs have been prepared using different metals. The most common metals employed in MOFs are Cu or Zn. Other transition metals such as Ni, Mn, Crand Cd are also used in some preparation. In recent development of MOFs, the metals, Pt, Pd and Rh have been successfully used. Use of lighter metals such as Be, Al in MOFs has also been explored recently [2].

Organic linkers used in MOFs

The organic molecules used in coordination networks are typically, mono-, di-, tri-, or tetravalent ligands [6, 21]. Those compounds are mainly carboxylic acids (Figure 1). Organic linkers can be achiral or chiral molecules [16]. Chiral molecules are important in preparing MOF with chiral recognition ability. In addition to carboxylic acids, some pillar ligands are being used in preparing microporous materials. These pillar ligands are usually aliphatic or aromatic amines as shown in figure 2 [7]. As new development of MOFs, some complex ligands prepared from metals and organic acids have been utilized in MOFs [3,4].

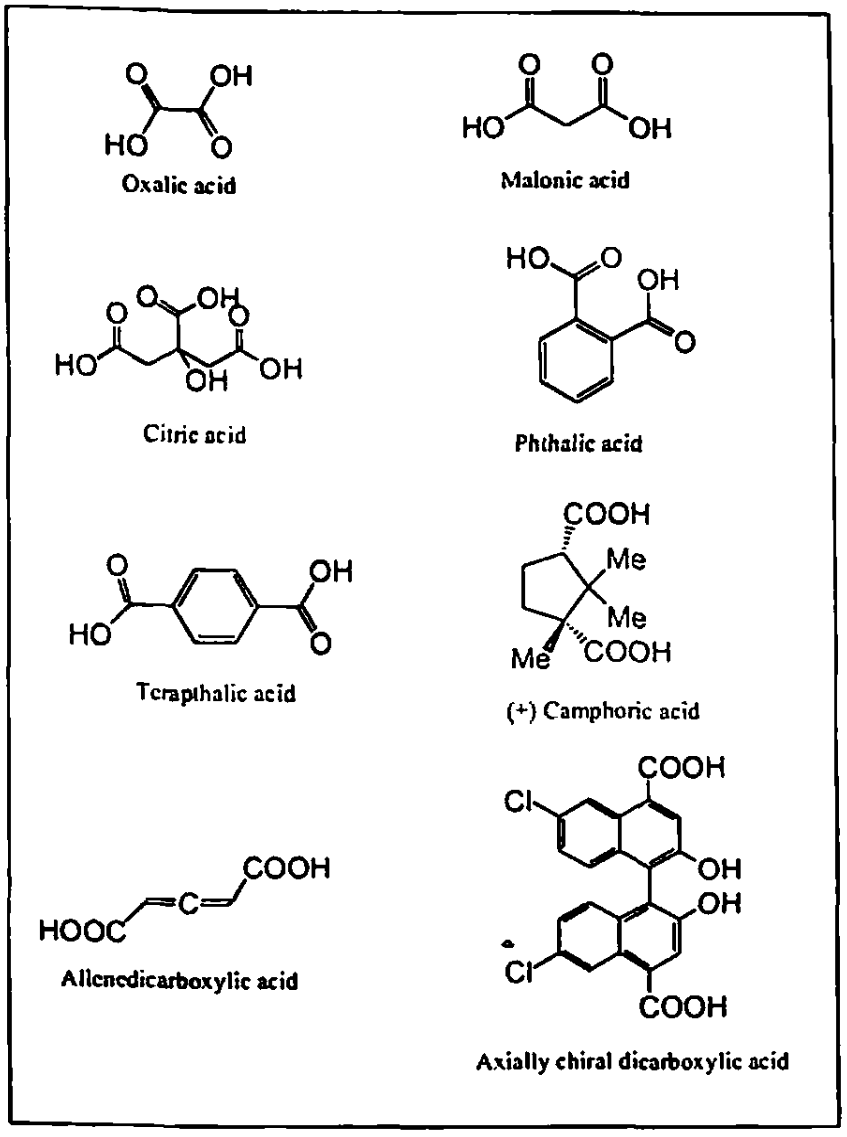


Figure 1 : Possible organic linkers in MOF

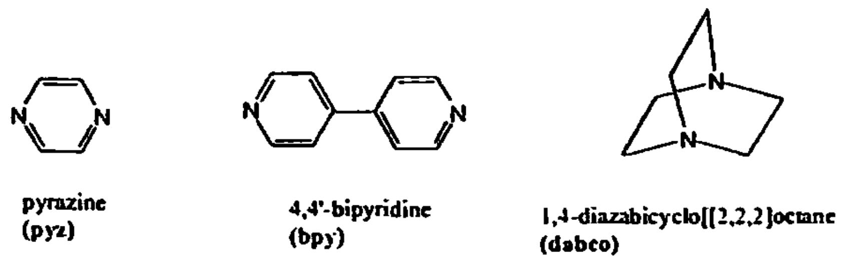


Figure 2 : Possible pillar ligands in MOF

Synthesis of Metal Organic Frameworks

Following synthesis methods are being used in preparing of MOFs

(a). Conventional Synthesis (solvothermal and nonsolvothermal synthesis)

The term conventional synthesis is usually applied to reactions carried out by conventional electric heating [2,17, 21]. The reaction temperature is one of the main parameters to be considered in the synthesis of MOFs. The two temperature ranges are normally used.

i. solvothermal
ii. nonsolvothermal

Solvothermal procedure involves loading ligands, metal salts, and solvents in a closed vessel,and heating the mixture above the boiling points of the solvents. Solvothermal reactions have proven to be an effective synthetic approach for the formation of 3D networks with high crystallinity [4]. Therefore, this method is frequently used in the synthesis of MOFs. Sometimes template molecules are added to facilitate the formation of networks [1].

In nonsolvothermal procedure, reactions take place below or at the boiling point under ambient pressure.

The solvents used in above two process are H_2O, DMF, DMSO, DMA etc. Acetonitrile and methanol are used in low temperature synthesis. Some potential MOFs have even been obtained at room temperature by just mixing the starting materials [2].

b. Mechanochemical Synthesis

In mechanochemical synthesis, the mechanical breakage of intramolecular bonds followed by a chemical transformation takes place [2]. Its use for the synthesis of porous MOFs was first reported in 2006.

Mechanically activated MOFsynthesis has many advantages:

i. It is a green synthetic process. The reactions can be carried out at room temperature under solvent free conditions. Therefore organic solvents can be avoided.

ii. Short reaction times, normally synthesis completes within 10 - 60 min, can lead to quantitative yields.

iii. Some cases, metal salts can be replaced by metal oxides which results in the formation of water as the only side product.

iv. The use of minute amounts of solvents, the so-called liquid-assisted grinding (LAG), is possible in mechanochemical synthesis.

c. Sonochemical Synthesis

Sonochemical synthesis takes place upon application of high-energy ultrasound to the reaction mixture.156-157. Ultrasound is cyclic mechanical vibration with a frequency between 20 kHz - 10 MHZ [2].

As the wavelength is much larger than the molecular dimensions, no direct interaction between ultrasound and molecules, but when high-energy ultrasound interacts with liquids, cyclic alternating areas of high and low pressure are generated and it accelerated the reactions.

In addition to above methods, some other specific methods such as microwave assisted synthesis electrochemical synthesis etc. are used for the preparation of MOFs [1,2].

Some examples for the potential MOFs, their synthesis, structure and properties

HKUST-1 : $Cu_3(C_9H_3O_6)_{4/3}$

HKUST-1 is porous coordination network which consists of copper as the metal and benzene-1,3,5-tricarboxylic acid as the organic linker. This was first reported in 1999 by Williams and co-workers (5). HKUST-1 forms as a blue colour crystals and it has been synthesized by heating Copper nitrate hemipentahydrate with benzene-1,3,5 tricarboxylic acid in solvent mixture of equal parts of DMF, ethanol and deionized water. The structure of $Cu_3(C_9H_3O_6)_{4/3}$ is shown in Figure -1. HKUST-1 is a commercially available product named as BasoliteTM C300.

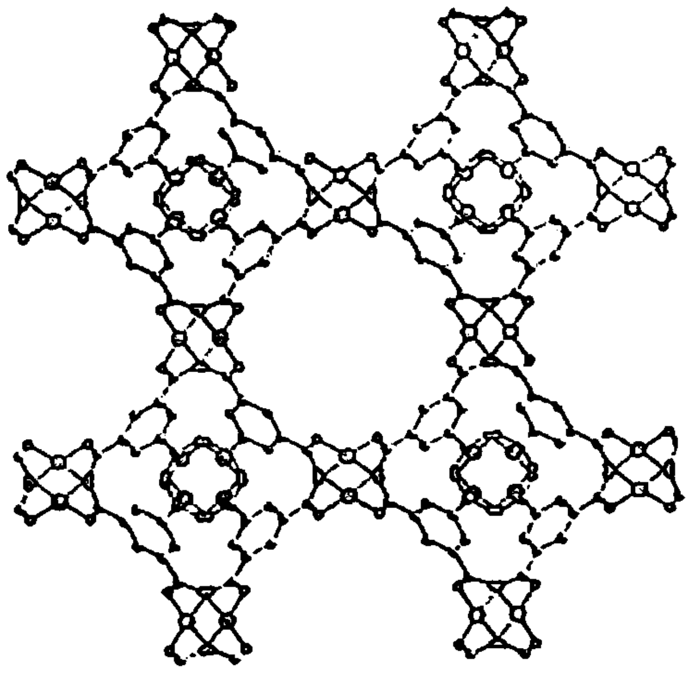


Figure. 1 : Ball and stick representation of HKUST-1.

HKUST-1 is a 3D system of large square-shaped pores (9 Å). HKUST-1 membranes have also been prepared from a pre-oxidised copper net as the porous support under solvothermal synthesis conditions. Many investigation of HKUST-1 for different applications such as H_2 storages, gas separations, catalysis etc. have been reported (8].

$Zn_4O(BDC)_3$

The MOF prepared using Zn^{2+} and benzenedicarboxylic acid is named as $Zn_4O(BDC)_3$ (BDC = 1,4-benzenedicarboxylate) (Figure 2) [9, 10]. One of the first metal–organic frameworks investigated for hydrogen storage was $Zn_4O(BDC)_3$ which is cubic carboxylate-based framework. This compound has been widely studied for its hydrogen storage ability. At 77 K, $Zn_4O(BDC)_3$ has showed an excess gravimetric uptake of hydrogen ; 1.3 wt% at 1 bar and 5.1 wt% at 50 bar. The gas storage properties obtained for $Zn_4O(BDC)_3$ depends on the methods utilized in its preparation and activation.

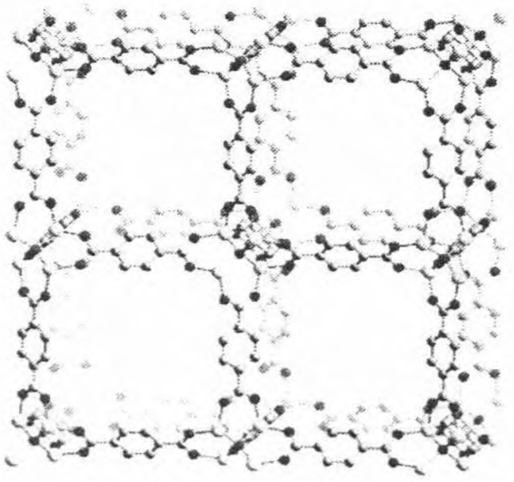


Figure 2: A portion of the crystal structure of $Zn_4O(BDC)_3$.

$Zn_4O(BTB)_2$

MOFs with a very high surface area exhibit an increased micropore volume. Low bulk density for the MOF is obtained when the micropore volume is high [9]. For example, the MOF: $Zn_4O(BTB)_2$ where BTB is 1,3,5-benzenetribenzoate, in this MOF, tetrahedral 6, $[Zn_4O]$ units are linked via a large, triangular tricarboxylate ligand (Figure. 3). At 77 K, this compound has shown a maximal excess H_2 uptake of 76 mg H_2 per 1076 mg compound.

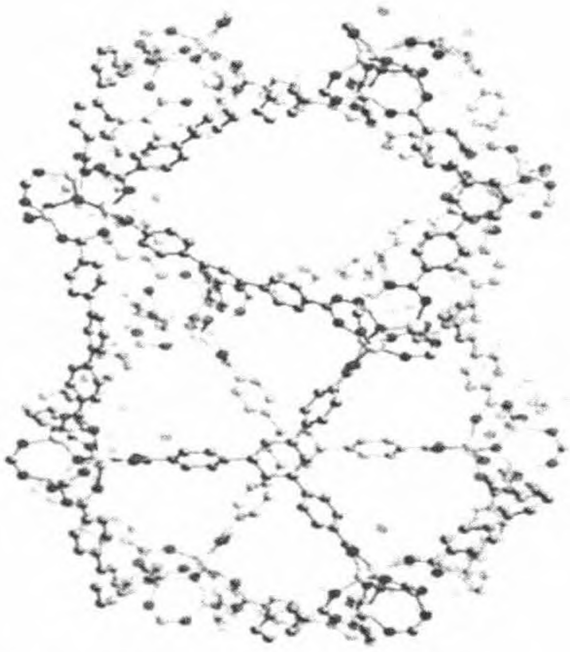


Figure 3: crystal structure of $Zn_4O(BTB)_3$.

MOFs with hetero bimetallic networks

In the recent development of MOFs, coordination networks consisted of two metal units (hetero bimetallic network) have been prepared with improved properties [3].

Examples : $Cd\{Pt(nic)_4\}n\ 5nH_2O$
$[Zn\{Pt(nic)_4\}(H_2O)_4]n\ nH_2O$

In these MOFs, two metals such as Cd/Pt and Zn/Pt are included as metal ends. Nicotinic acid is used as the organic linker. At first, complex ligand, $[Pt(nic)_4]$ is synthesized by a solvothermal method in water solution containing of $[PtCl_4]$ and nicH (nicotinic acid) . Then, MOFs, Cd–Pt and Zn–Pt have been synthesized by one-pot slow evaporation method [3].

The above heterobimetallic MOFs act as useful heterogeneous photoreduction catalyst for water as well as selective H_2 gas adsorption materials versus N_2 gas. A novel three-dimensional interpenetrated coordination polymer containing Zn and Pd metals with isonicatinic acids has been synthesized by Mory and co workers [11]. This MOF is [Zn{Pd(INA)4}]n (INA = isonicotinate) and it has been utilized as a hydrogen production catalyst for photochemical reduction of water.

The use of Pt(II) or Pd(II) complex ligand will be an effective approach because Pt(II) and Pd(II) complexes have been widely used as homogeneous catalysts in catalytic reactions such as hydrogenation reactions, water photoreduction reactions and activation of C-H bonds in hydrocarbons etc.

MOFs with accessible metal sites

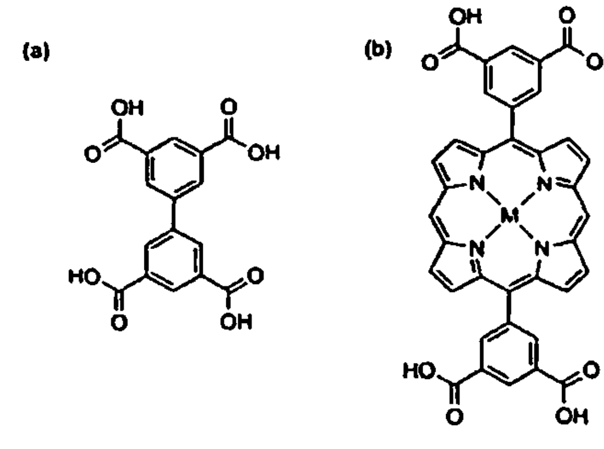
Some metal-organic frameworks have been synthesized with incorporation of accessible metal sites (AMSs) or functional building blocks into porous MOFs [12]. Examples for the AMS containing building blocks : metallosalens, N-heterocyclic carbene (NHC) complexes, and metalloporphyrins. Metalloporphyrins can be found in nature and have unique catalytic, electronic, and optical properties. Therefore MOFs with accessible metal sites are expected to have higher gas-adsorption capacity and as well as to act as specific catalysts.

Many porphyrin-based MOFs have been synthesized.

Example -1: rhodium carboxylate microporous MOFs incorporating various metallo-TCPPs: $[Rh_2(MTCPP)]$ ($M = Cu^{2+}, Ni^{2+}, Pd^{2+}$). This has been used as catalysts for the hydrogenation of olefins with high turnover frequencies [13,14].

Example-2 : $[Cu_2(MDDCPP)]$ [$M = Zn^{2+}, Ni^{2+}, Pd^{2+}, Mn^{3+}(NO_3), Ru^{2+}(CO)$], which have been synthesized using MDDCPP [$M = Zn^{2+}, Ni^{2+}, Pd^{2+}, Mn^{3+}Cl, Ru^{2+}(CO)$] building blocks. These complexes have exhibited permanent porosity and good N_2 and H_2 adsorption properties.

The structure of DDCPP is shown below with the analogue structure of H_4BPTC (Figure 4)



H_4BPTC DDCPP

Figure 4: Structure of DDCPP

There are advantages for incorporating porphyrine moieties in MOFs. The physical and chemical properties of metalloporphyrins can be controlled by proper functionalization of the porphyrin core through some chemical reactions in order to enhanced the properties of corresponding MOFs.

Characterization of MOFs

Metal-Organic Frameworks are supramolecules having complex structures and higher molecular weights. Those are oligomers and polymers with definite crystalline structures. After synthesis, characterization of MOFs is a difficult task due to their complex structure. The following techniques are commonly used in characterization [17, 18, 19].

a. Elemental analyses.
b. X-ray crystallographic analysis
c. NMR spectroscopy
d. UV-visible spectroscopy
e. FT-IR spectroscopy

Application of MOFs

MOFs have shown wide range of applications in their first twenty years of existence. As there is fast growing interests in this field and the possibility of preparing infinite number of MOFs with diverse structures and unusual properties, many more potential applications will be explored in future as well.

Some applications of MOFs are described below;

Gas storage

MOFs have received much attraction as potential gas storage material ie: hydrogen and methane [1,9,10,20]. Hydrogen is important as a vehicular fuel source. Microporous materials have pores less than 20A is important in strong interactions between gas molecules and the pore walls making them good candidates for gas storage and gas separation applications. It has been reported that highest hydrogen storage capacity is possible when the pore size is about 7 A^0. In addition to pore sizes, higher surface areas, low densities, and thermal stability of MOFs are good properties for gas storages.

Usually gases are stored in tanks under higher pressure. In contrast, tank charged with a porous adsorbent (MOFs) enables a gas to be stored at a much lower pressure. Thus, high pressure tanks and multi-stage compressors can be avoided providing a safer and more economical gas storage method using MOFs. This gas storage application of MOFs gives alternative solution for global fuel crisis anticipated due to gradual reduction of fossil fuel.

Selective gas adsorption and separation

MOFs are very promising candidates for selective gas adsorption, which can lead to gas separation [1, 21]. Gas separations is an essential element in petrochemical and other industries. Conventional separation methods used are distillation and condensations process which are high energy consumptions process. Polymer based membrane separation techniques and adsorption-based techniques using zeolites, molecular sieves, carbon nanotubes, aluminosilicates, and silica gel are also used.

As a low energy and environmentally friendly gas separation process, application of MOFs is promising. MOFs can act as material for gas separations layers based on two principles, which are adsorbate–surface interactions and size-exclusion effect(molecular sieving effect). The two effects are capable of working independently as well as cooperatively.

Eg: Selective gas adsorption of O_2 over N_2 based on size-exclusion of MOFs and separation of alkane isomers from natural gas based on adsorbate-surface interactions.

Recently, MOFs thin film have been prepared for gas separation purpose using many MOFs under solvothermal conditions [22].

MOFs as heterogeneous catalysts

At present, MOFs are explored to be used as heterogeneous catalysts [1, 11]. Active sites are generated in MOFs due to their high metal content and highly crystalline nature.

The catalytic systems based on three-dimensional interpenetrated MOF, [Zn{Pd(INA)4}]n (INA = isonicotinate), has been developed for the catalysis of decomposition of water into hydrogen and oxygen using sunlight (11). This will be a promising solution for the global fuel crisis and environmental problems associated with that. The MOF, $[Ni_8L_{12}]^{20-}$ (H_3L = 4,5-imidazoledicarboxylic acid) has shown stable catalytic activity for the oxidation of CO to CO_2.

The MOF, $[In(OH)L]\cdot xPy$ (L =4,4_(hexafluoroisopropylidene)bis(benzoic acid)) has proven to be an efficient heterogeneous catalyst for acetalization of aldehydes (1]. The catalysis activity of MOF which is doped with other metal catalysts has been demonstrated for oxidation of hydrocarbon etc. The 3D MOF, $([Cd(4btapa)_2(NO_3)_2]\cdot 6H_2O\cdot 2DMF)n$, has been synthesized and successfully accommodated Knoevenagel condensation reactions of benzaldehyde with active methylene compounds.

MOF as molecular switches

The porosity of MOFs provides interesting phenomena in regards to magnetic properties.

Due to the magnetic properties of functionalized MOF, MOFs with electronic switching centers have been developed [1].

MOFs as luminescence material and sensors

Some MOFs exhibit photophysical properties. The photophysical properties arises due to the metal ions, or specific organic ligands. Lanthanide metal ions have been widely used in MOF syntheses due to their coordination diversity and luminescent properties. Example for the MOF with luminescence properties $[Ba_2(H_2O)4[LnL_3(H_2O)_2](H_2O)n\mathrm{Cl}]$, (L = 4,4-disulfo-2,2-bipyridine-N,N-dioxide, Ln = Sm, Eu, Gd, Tb, Dy)[1]. Stilbene-based MOFs have shown luminescence properties. In addition, some guest molecules are incorporated into MOFs without disturbing the structure in order to achieve luminescence. The MOFs that possess luminescent properties together with size- or shape-selective sorption properties are being used as sensing devices.

MOFs in Analytical Chemistry

Unusual properties of MOFs such as high surface area, good thermal stability, uniform structured nanoscale cavities, and the availability of in-pore functionality and outer-surface modification are attractive for diverse analytical applications [23]. Therefore, different MOFs have been explored for various analytical applications from sampling to chromatographic separation etc.

Examples for the analytical application encountered with MOFs are,

(1) bulk microsized MOFs as sorbents for in-field sampling and solid-phase extraction
(2) nanosized MOFs and engineered thin films of MOFs as coatings for solid-phase microextraction
(3) MOFs as stationary phases for high-resolution gas chromatography
(4) MOFbased tandem molecular sieve platform for selective extraction and high-resolution GC
(5) microsized solvent resistant MOFs as stationary phases for high-performance liquid chromatography etc.

MOFs in drug storage and drug delivery

After administration, delivering of drugs into blood stream at controlled rate is a very important task in human body. Some delivery systems have been developed which include polymeric-based systems, liposome based systems, microporous zeolites, mesoporous silicon, and other mesoporous materials etc. As MOFs possess tunable structures and high porosities make them excellent drug delivery vehicles. Many investigations are being carried out in order to apply MOFs in drug delivery and storage purpose (1, 16).

As mentioned above, the field of hybrid inorganic–organic framework materials, MOFs, represents one of the fastest growing areas in materials chemistry because their enormous structural and chemical diversity make large opportunities for creating many technologically important properties. There is a huge scope for creating unusual properties or unique combinations of properties with MOFs that are not possible in purely inorganic or organic systems alone. The mechanical properties such as elasticity, hardness, plasticity, yield strength, and fracture toughness characteristics are very important properties associated with the application of MOFs []

References

1. Ryan J. Kuppler, Daren J. Timmons, Qian-Rong Fang, Jian-Rong Li , Trevor A. Makal, Mark D. Young, Daqiang Yuan, Dan Zhao,Wenjuan Zhuang, Hong-Cai Zhou(2009), Potential applications of metal-organic frameworks, Coord. Chem. Rev, 253, 3042–3066.
2. Norbert Stock, Shyam Biswas (2012), Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, Chem. Rev., 112, 933–969
3. Yuhei Miyazaki, Yusuke Kataoka, Wasuke Mori, Tatsuya Kawamoto (2012), Synthesis, crystal structures and properties of novel heterobimetallic

Cd–Pt and Zn–Pt coordination polymers using nicotinic acid, Inorganic Chemistry Communications 25, 14–17.

4. Dan Zhao,Daren J. Timmons,Daqing Yuan, Hong-Cai Zhou (2011), Tuning the Topology and Functionality of Metal-Organic Frameworks by Ligand Design, Acc. Chem. Res.44, 2, 123–133.
5. Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.,Williams, I. D (1999). Science, 283, 1148.
6. Peili Teo, T.S. Andy Hor (2011), Spacer directed metallo-supramolecular assemblies of pyridine carboxylates, Coord. Chem. Rev, 255, 273–289.
7. Kihara Nobuhiro, Vajira P. Bulugahapitiya, (2007), Construction of nanoporus materials functionalized by axial chirality: 3rd International symposium on Chemistry on Coordination Space, December 9-12, Awaji, Hyogo, Japan
8. Darren Bradshaw, Ashesh Garai and Jia Huo (2012), Metal–organic framework growth at functional interfaces: thin films and composites for diverse applications, Chem. Soc. Rev., **41**, 2344–2381.
9. Leslie J. Murray, Mircea Dinca˘ and Jeffrey R. (2009), Long Hydrogen storage in metal–organic framework, Chem. Soc. Rev., 38, 1294–1314
10. H.; Zhu, G.; Hewitt, I. J.; Qiu, S. "Twin Copper Source" Growth of Metal-organic FrameworkMembrane: Cu3(BTC)2 with High Permeability and Selectivity for Recycling H2 (2009). J. Am. Chem. Soc., 131 (5), 1646–1647.
11. Yuhei Miyazaki,1 Yusuke Kataoka,2 Yasutaka Kitagawa,2 Mitutaka Okumura,2 and Wasuke Mori (2010), Hydrogen Production from Water Using Novel Three-dimensional Interpenetrated ZnPd Coordination Polymer, Chem. Lett. 39, 878-880.
12. Satoshi Matsunaga, Nanako Endo, Wasuke Mori(2012), Microporous Porphyrin-Based Metal Carboxylate Frameworks with Various Accessible Metal Sites: [Cu2(MDDCPP)] [M = Zn2+, Ni2+, Pd2+, Mn3+(NO3),Ru2+(CO)], *Eur. J. Inorg. Chem.* 4885–4897.
13. Satoshi Matsunaga,* Ken-ichi Hasada, Kenji Sugiura, Naoki Kitamura, Yuri Kudo, Nanako Endo, and Wasuke Mori (2012), Hetero Bi-Paddle-Wheel Coordination Networks: A New Synthetic Route to Rh-Containing MetalOrganic FrameworksBull. Chem. Soc. Jpn. 85, 4, 433-438.

14 Satoshi Matsunaga, Nanako Endo, and Wasuke Mori (2011), A New Metal Carboxylate Framework Based on Porphyrin with Extended π-Conjugation, *Eur. J. Inorg. Chem.*, 4550–4557.

15, Satoshi Matsunaga, Nanako Endo, and Wasuke Mori (2012), Microporous Porphyrin- Based Metal Carboxylate Frameworks with Various Accessible Metal Sites: [Cu2(MDDCPP)] [M = Zn^{2+}, Ni^{2+}, Pd^{2+}, $Mn^{3+}(NO_3)$, $Ru^{2+}(CO)$], *Eur. J. Inorg. Chem.* 2012, 4885–4897.

16. Kristine K. Tanabe and Seth M. Cohen (2011), Postsynthetic modification of metal– organic frameworks—a progress report, *Chem. Soc. Rev.*, 40, 498-519.
17. Satoshi Matsunaga,* Ken-ichi Hasada, Kenji Sugiura, Naoki Kitamura, Yuri Kudo, Nanako Endo, and Wasuke Mori (2012), Hetero Bi-Paddle-Wheel Coordination Networks: A New Synthetic Route to Rh-Containing Metal Organic Frameworks Bull. Chem. Soc. Jpn. Vol. 85, No. 4, 433-438.
18. Satoshi Matsunaga, Nanako Endo, Wasuke Mori (2011), New Metal Carboxylate Framework Based on Porphyrin with Extended π- Conjugation *Eur. J. Inorg. Chem.*, 4550–4557.
19. Manabu Kyuzou, Akihiro Maeda, Moritaka Wada, Syunya Watanabe, Tohru Takei, Tetsushi Ohmura, Yoshikazu Kowaguchi, Wasuke Mori, and Jiro Tanaka (2011),Thermochromism and Magnetic Susceptibility of Copper(II) Anthracene-9-carboxylateBull. Chem. Soc. Jpn. 84,. 5, 491-495.
20. Hui Wu, Jason M. Simmons, Yun Liu, Craig M. Brown, Xi-Sen Wang, Shengqian Ma,Vanessa K. Peterson,Peter D. Southon,Cameron J. Kepert, Hong-Cai Zhou, Taner Yildirim,Wei Zhou (2010), Metal–Organic Frameworks with Exceptionally High Methane Uptake: Where and How' is Methane Stored?Chem. Eur. J. 16, 5205 – 5214.
21. Miral Shah, Michael C. McCarthy, Sonny Sachdeva,Alexander K. Lee, and Hae-Kwon Jeong (2012), Current Status of Metal_Organic Framework Membranes for Gas Separations: Promises and Challenges Ind. Eng. Chem. Res, 51, 2179–2199.
22. O. Shekhah,a J. Liu,a R. A. Fischerb and Ch. Wo (2011), MOF thin films: existing and future applications Chem. Soc. Rev., 40, 1081–1106.
23. Zhi-Yuan Gu, Chen-Xiong Yang, Na Chang, Xiu-Ping Yan (2012), Metal-Organic Frameworks for Analytical Chemistry: From Sample Collection to Chromatographic Separation ACC. Chem, Res, 45, 5,734–745.

24. Jin Chong Tan and Anthony K. Cheetham (2011), Mechanical properties of hybrid inorganic–organic framework materials: establishing fundamental structure–property relationships Chem. Soc. Rev., 40, 1059–1080.

Organometallic Chemistry – Part 1

Dr Buddhie S. Lankage

Introduction

Organometallic chemistry is a branch of coordination chemistry and it is a study of chemical compounds containing M-C bonds. Transition and non-transition metal complexes are widely used as organometallic reagents (e.g. MeMgI and *n*-BuLi) and catalysts (e.g. $[RhCl(PPh_3)_3]$ and $[Pd\{P(C_6H_5)_3\}_4]$) to prepare organic compounds.

The types of metals bonded to carbon are,

1. The *main group elements* such as the alkali and alkaline earth metals, and the more metallic elements in *p* block (ns^2 np^x - *p* orbitals contain valence electron(s)) the vertical groups of 3, 4, 5 and 6, i.e.

$$^{5}B = 1s^2 / 2s^2\, 2p^1$$
$$^{15}P = 1s^2 / 2s^2\, 2p^6 / 3s^2\, 3p^3$$

   Generally, most electropositive elements form M^+R^- ionic type compounds, e.g. $Na^+(\eta^5\text{-}C_5H_5)^-$. Less electropositive metals such as Li and Mg form covalent M-C bonds, e.g. PhMgCl.

2. *Transition metals* (*d* block elements), i.e.

$$^{23}V = 1s^2 / 2s^2\, 2p^6 / 3s^2\, 3p^6\, \underline{3d^3 / 4s^2} = [Ar]\, \underline{d^5}$$
$$^{28}Ni = 1s^2 / 2s^2\, 2p^6 / 3s^2\, 3p^6\, \underline{3d^8 / 4s^2} = [Ar]\, \underline{d^{10}}$$

The types of **ligands** are alkyl (R = $-CH_3$), carbonyl (C≡ O), olefin {acetone $-(CH_3)_2C{=}O$)}, acetylene (HC≡ CH), arenes (conjugated cyclic compounds, i.e. phenyl=benzene and aryls=functional groups attached to benzene) and allyl ($C_3H_5^-$ /$=CH_2{=}CH{-}CH_2^-$) groups.

Organometallic compounds are distinguished by the prefix "organo-" e.g.

- Organopalladium compounds – $[PdCl(\eta^3\text{-allyl})]_2$
- Organomagnesium compounds – Grignard reagents, e.g. iodomethylmagnesium (MeMgI) and diethylmagnesium (Et_2Mg)
- Organolithium compounds – *n*-butyl lithium (*n*-BuLi)
- Organozinc compounds – diethylzinc (Et_2Zn)
- Organocopper compounds – lithium dimethylcuprate ($Li^+[Me_2Cu]^-$).

The term "metalorganics" usually refers to metal-containing compounds lacking direct metal-carbon bonds but which contain organic ligands. Metal β-diketonates, alkoxides and dialkylamides are representative members of this class.

$[Ni(\eta^3\text{-allyl})_2]$ and ferrocene $[Fe(\eta^5\text{-}C_5H_5)_2]$ are examples of organometallic compounds containing organic ligands.

In addition to transition metals, lanthanides, actinides and semimetals, elements such as boron, silicon, arsenic and selenium do form similar compounds, e.g. organoborane compounds – triethylborane (BEt_3).

Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

Organic chemistry:

- more or less covalent C-A bonds (i.e. A = OH, OR and CH_3)
- rigid element environments
- fixed oxidation states

Inorganic chemistry:

- primarily ionic M-B bonds (i.e. B = O and Cl), coordinate/dative-covalent M-L bonds (i.e. L = bpy-bipyridine)
- variable and often fluxional environments
- variable oxidation states

Organometallic chemistry:

Knowledge of inorganic and coordination chemistry is useful to understand geometries, electron counts and oxidation states of organometallic compounds. Similarly organic chemistry knowledge is useful in understanding and the tuning reactivity. This starts with analyzing reaction mechanisms and identifying the use of specific organic reagents such as solvents.

Organic *vs* organometallic reactivity

Organic chemistry:

- C-C/C-H: nearly covalent
- $C^{\delta+}\text{-}X^{\delta-}$: polar (partly ionic)

- reactivity dominated by nucleophilic attack at C S_{N2} and S_{N1} like reactions.

Organometallic chemistry:

- C is the negative end of the M-C bond ("umpolung")
- reactivity dominated by electrophilic attack at C or nucleophilic attack at M, associative and dissociative substitution at M

Factors governing the reactivity of organometallic compounds

- M-C, M-X bond strengths
- Electronegativity of M (polarity of M-C bonds)
- Number of *d* electrons
- Coordination number
- Steric hindrance

Basic chemistry that needs to know for organometallic chemistry

It is important to know the basic chemistry of elements in the periodic table and their physical and chemical properties.

1. Electronegative/Electropositive concepts

The tendency of an atom to attract an electron to itself is called its electronegativity. The electronegativity/electropositivity of an element can be regarded as being related to ionization energy and electron affinity, and can be evaluated in various ways.

Where do the partial positive and negative charges in a molecule reside? e.g. $H^{\delta+}$-$F^{\delta-}$. This is important for determining how much electron density will be donated from a ligand to a metal and where a nucleophile or electrophile will attack for chemical reactions.

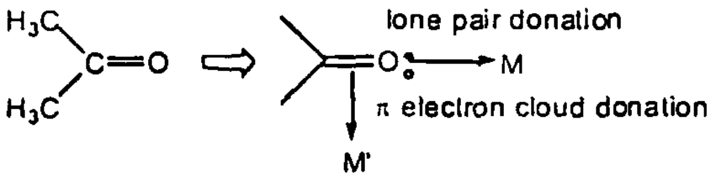
2. Lewis dot structures and valence electron counts

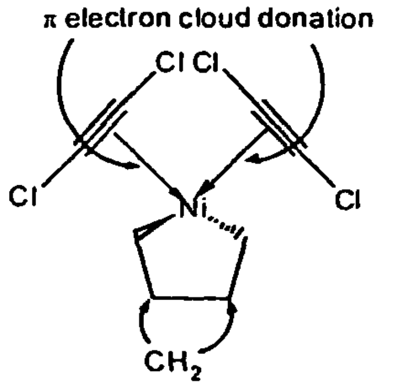
Important for determining the number of electrons on a ligand and what is the charge of the ligand. Generally, deal with ligands with even number's of electrons. If a ligand has an odd number of electrons add additional electrons to get to an even number, usually to form a closed shell electron configuration with a formal negative charge(s). Common Exceptions are B and Al.

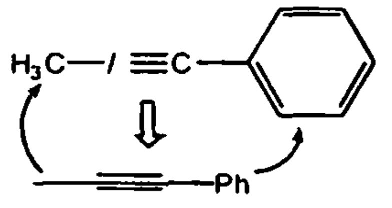
3. Oxidation States (OS)

Oxidation state of a metal in a coordination compound can be defined as the charge left on the metal when all the ligands are removed from the metal. For example, $[MX_2L_3]$ when L is a neutral ligand and X is a mono-anionic ligand, the OS of M is +2. This number relates to the total charge of the negative ions.

4. Organic line notation for drawing structures







5. Electron Density

The presence of energetically accessible valence electrons around an atom. Electrons are represented by a probability distribution spread out over a region of space defined by the nature of the orbital: s, p, d, f, and/or hybrid orbitals such as sp^3, sp^2, sp, etc. Atoms with large number of valence electrons or completely filled valence orbitals such as Pt(0) d^{10} and/or contracted orbitals (due to the attractive forces between the nucleus and the electrons) have a high electron density. Atoms with fewer valence electrons (e.g. ^{37}Rb(0) = [Kr] $\underline{5s}^1$) and/or diffuse orbitals (electrons spread out over a larger region of space) can be considered to have low electron densities. Do not confuse electron density with electronegativity.

6. Electron-rich

Atoms that are willing to donate electron pairs readily to other atoms are considered electron rich. Ease of ionization is another property associated with electron-rich atoms. The willingness to share or donate electron pairs is related to lower electronegativity, larger numbers of valence electrons, good donor groups on the atom in question, negative charges, or some combination of these factors. Using organic terminology can consider an electron-rich atom to be a good nucleophile (electron pair donor).

7. Electron-deficient (poor)

Atoms that are NOT willing to donate or share electron pairs to other atoms are called electron deficient. These atoms typically have lower lying empty orbitals that can accept electron pairs from other atoms. The un-willingness to donate or share electron pairs could be caused by high electronegativity, cationic charge(s), lack of electron pairs, or some combination of these. In General, many (but not all) electron-deficient atoms/molecules can considered to be good electrophiles (electron-pair acceptor) and certainly poor donors.

Examples:

Fluoride anion, F^-: This anion has high electron density due to the negative charge, filled octet of electrons, and small size. But cannot consider it to be electron-rich, meaning a good electron donor. The extremely high electronegativity of a fluorine atom means that it desperately wants to pick up an extra electron to form the fluoride anion, which is extremely stable. The filled valence orbitals are fairly low in energy for F^- and generally poor donors. It is certainly not electron-deficient as it doesn't have any low-lying empty orbitals and does not want to accept any more electrons. It is not electron-rich either since it is a very poor nucleophile and generally a poor ligand for most metals (except those in high oxidation states). It is almost impossible to chemically oxidize F^-.

Methyl anion, CH_3^-: This anion is very electron-rich and a powerful nucleophile. The electron-richness comes from the lower electronegativity of carbon and the high energy of the anionic sp^3-hybridized lone pair that makes it a strong donor group. It is also very easily oxidized, pointing to the presence of a high-energy lone pair orbital.

8. Ionisation Energy (IE/kJ mol^{-1})

IE is the energy required to remove an electron in the gas phase, $M(g) \rightarrow M^+(g) + e^-$.

The distinction between IE and electrode potential (EP) should be clearly understood. The EP applies to the loss of an electron not in the gas phase, $M(s) \rightarrow M^+(aq) + e^-$.

The electrochemical series is a list of metals in order of electrode potential. The order of IEs is not necessarily the same.

9. Electron Affinity (EA/kJ mol^{-1})

EA is the energy change when one mole of isolated gaseous atoms gains one mole of electrons to form a mole of negatively charged ions, $X(g) + e^- \rightarrow X^-(g)$.

10. General trends in periodic table

Main group elements

The 1st IE decreases down the group as the outer electrons become progressively further from the nucleus and also there is more shielding because of the extra filled orbitals.

In any group there is a decrease in electronegativity down the group. Across a period there is an increase in electronegativity from left to right.

In any period there is a decrease in atomic radius from left to right. There is a net increase in atomic radius down the group.

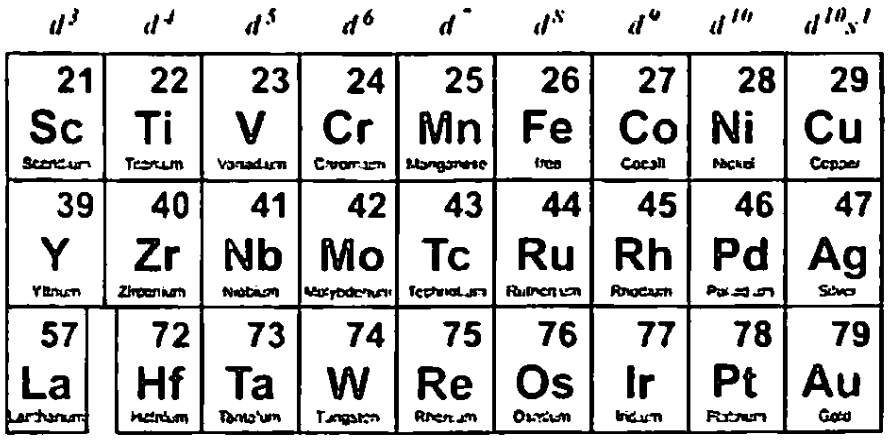
Also down the group, the metallic character increases because of shielding of outer most electrons from the nucleus due to large number of electrons in between. Therefore, these electrons are easier to be lost. In case of non-metals, they have high electron negativity, so it becomes extremely difficult for them to loose an electron, hence in their case, oxidation number decreases.

For example, group 4 elements (C, Si, Ge, Sn and Pb), Pb^{2+} is more stable than Pb^{4+} (e.g. $PbCl_4 \rightarrow PbCl_2 + Cl_2$) and Sn^{4+} is more stable than Sn^{2+}. This is due to the *inert-pair effect* and *relativistic contraction* (heavier the element greater the effect).

Transition metals

The relatively small increase in successive IEs causes most of the transition metals to exhibit multiple oxidation states separated by a single electron. E.g. Mn, forms compounds in every oxidation state between −3 and +7. Because of the slow but steady increase in IEs across a row, high oxidation states become progressively less stable for the elements on the right side of the *d* block.

The occurrence of multiple oxidation states separated by a single electron causes many, if not most, compounds of the transition metals to be paramagnetic, with one to five unpaired electrons. This behaviour is in sharp contrast to that of the *p*-block elements, where the occurrence of two oxidation states separated by two electrons is common, which makes virtually all compounds of the *p*-block elements diamagnetic.



d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au

Early Transition Metals
low electronegativities
higher oxidation states
"harder" metal centers

Late Transition Metals
higher electronegativities
lower oxidation states
"softer" metal centers

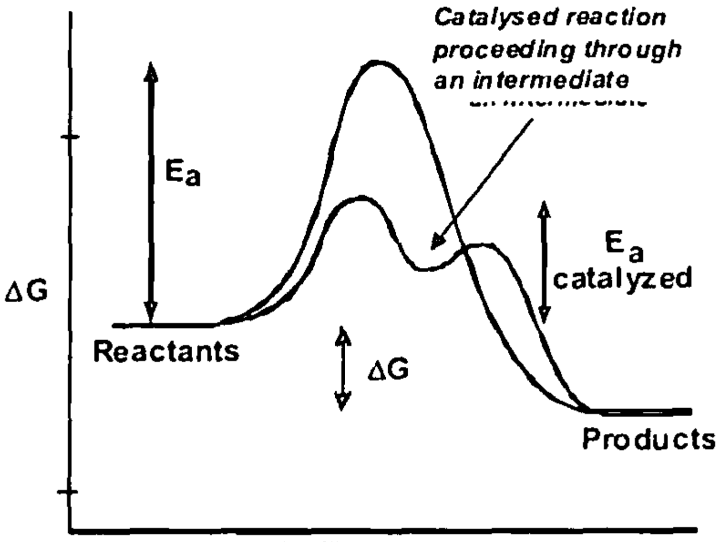
11. Metal catalysis

$$A + B \xrightarrow{[catalyst]} C$$

A catalyst is a substance that increases the rate of the reaction without itself being consumed (but it is involved) in the reaction. After the reaction has finished the unchanged catalyst should be able to recover from the reaction mixture.

A catalyst speeds up the rate at which a chemical reaction reaches equilibrium. The overall thermodynamics of the reaction is NOT changed by the catalyst. Therefore, very endothermic (non-spontaneous) reactions are usually NOT suitable for catalytic applications.

A catalyst provides a lower energy pathway for the production of products from reactants, thus allowing the reaction to proceed faster. It lowers the activation energy for a reaction (kinetics) – it does NOT change the thermodynamics of a reaction.



A catalyst provides an alternate mechanism (or pathway) for the reactants to be transformed into products. The catalysed mechanism has an activation energy that is lower than the original uncatalysed reaction. An excellent catalyst will lower the activation energy the most.

To be continued in the next issue.

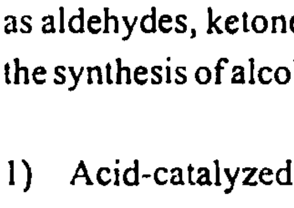
*

Synthesis of Alcohols from Alkenes

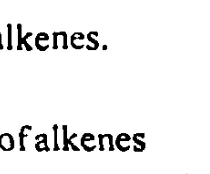
Dr. Ireshika De Silva

Alcohols are organic compounds which contain a hydroxyl (-OH) group/s on a saturated carbon atom of the molecule. These compounds are very common in the laboratory and are useful in nature, our homes and industries. These can be categorized as primary, secondary and tertiary.

CH_3OH	CH_3CH_2OH
Methyl alcohol	Ethyl alcohol (1°)



2-Propanol (2°)

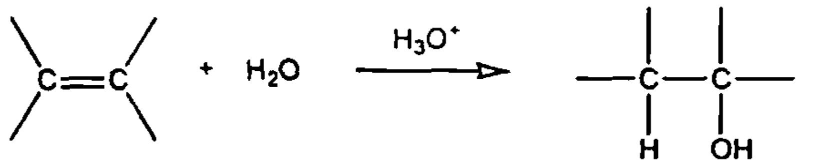


2-Methyl-2-propanol (3°)

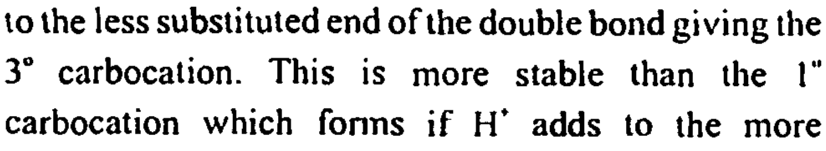
Alcohols can be directly synthesized from alkenes, alkyl halides, and carbonyl compounds such as aldehydes, ketones and esters. This article describes the synthesis of alcohols from alkenes.

1) Acid-catalyzed hydration of alkenes

In an acidic medium, alkenes react with water to produce alcohols. This is known as hydration. This is an addition reaction. In general, a hydrogen atom from water adds to one carbon of the double bond and a hydroxyl group adds to the other carbon.

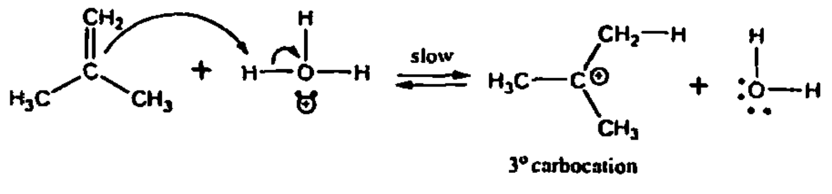


This reaction follows **Markovnikov's rule**. That means, the electrophile (ie H^+) adds to the less substituted end of the double bond to give more stable carbocation. The order of the carbocation stability is 3°>2°>1°> CH_3. Consider the acid-catalyzed hydration of 2-methylpropene. 2-Methyl-2-propanol is the only product of this reaction.

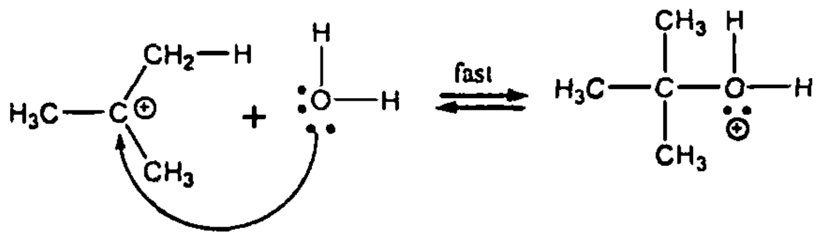


Only product Does not form

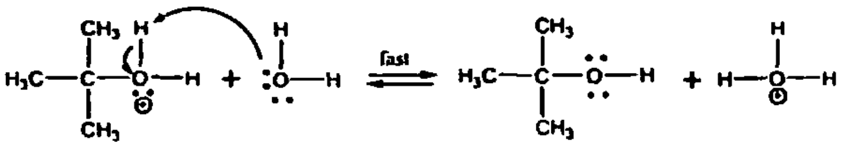
Let us consider the mechanism of this reaction to understand why it is so. The first step of this reaction is the protonation of the double bond. A proton (H^+) adds to the less substituted end of the double bond giving the 3° carbocation. This is more stable than the 1° carbocation which forms if H^+ adds to the more substituted end.



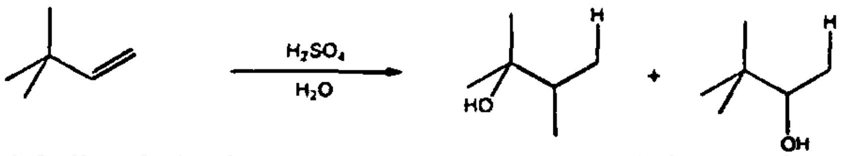
Now, water attacks (Nucleophilic attack) the positively charged carbon to form a protonated alcohol.



Finally, deprotonation of the protonated alcohol by water gives the alcohol.

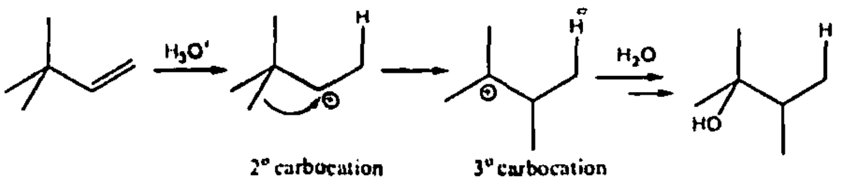


One of the major limitations of the acid-catalyzed hydration method is rearranging of the initial carbocation to a more stable one, if it is possible. This can lead to a mixture of constitutional isomeric alcohol products. The acid-catalyzed rearrangement of 3,3-dimethyl-1-butene produces 2,3-dimethyl-2-butanol as the major product.



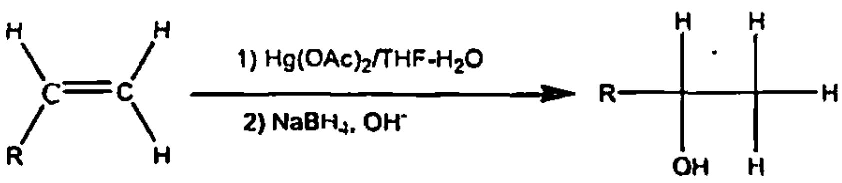
3,3-dimethyl-1-butene Major product Minor product

A methyl group shifts to the 2° carbocation to form the 3° carbocation which is more stable. Finally, reaction with water gives the 2,3-dimethyl-2-butanol as the major product and 3,3-dimethyl-2-butanol as the minor product.



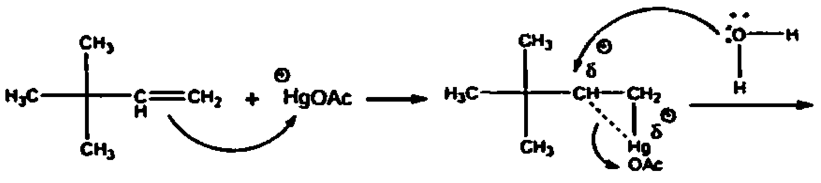
2) Oxymercuration-demercuration of alkenes

This is a one-pot, two step reaction.

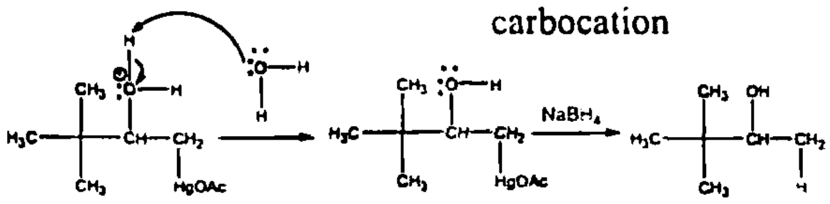


Mercuric-acetate, $Hg(OCOCH_3)_2$ [$Hg(OAc)_2$] is involved in the first step. It dissociates to form positively charged mercury species $Hg(OAc)^+$, which acts as the electrophile in this reaction. In oxymercuration, $Hg(OAc)^+$ attacks the double bond and form mercury-bridged carbocation. Then water attacks the more substituted carbon (Why?) leaving -HgOAc on the less substituted carbon. Note the anti orientation of the -OH and the -HgOAc. $NaBH_4$ (a reducing reagent) is used in demercuration step. It replaces $Hg(OAc)^+$ with a hydrogen atom. The reaction that replaces the -HgOAc with hydrogen is not stereo controlled. Therefore, though, the -OH and the –HgOAc are in anti orientation, the final product is a mixture of both syn and anti addition of –OH and –H.

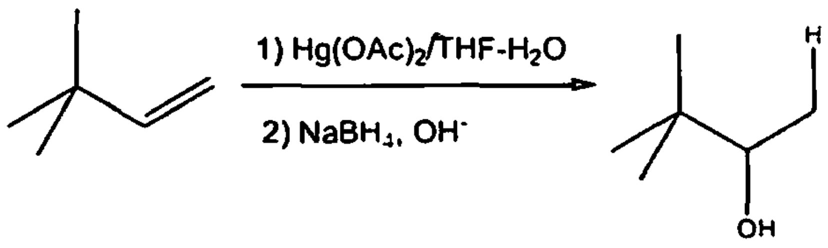
$$Hg(OAc)_2 \rightleftharpoons {}^{\oplus}HgOAc + OAc^{\ominus}$$



Mercury-bridged carbocation

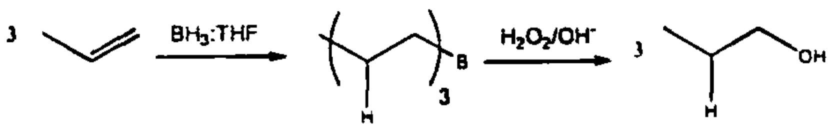


In the final product, H is on the less substituted carbon and –OH on the more substituted carbon. That means the oxymercuration-demercuration of alkenes also follows the **Markovnikov's rule**. Rearrangements of intermediates do not occur in this reaction. Oxymercuration-demercuration of 3,3-dimethyl-1-butene forms only 3,3-dimethyl-2-butanol in contrast to its acid-catalyzed hydration we discussed earlier.

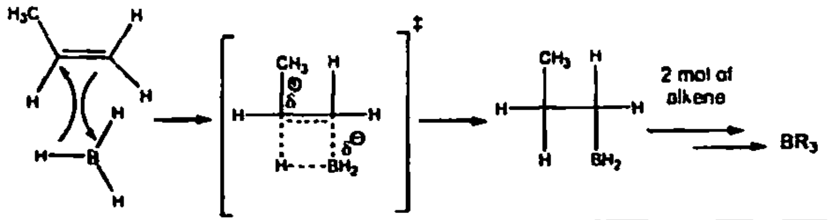


3) Hydroboration of alkenes

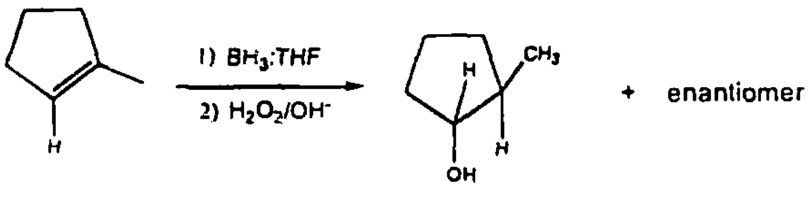
This is also a one-pot, two-step reaction. Hydroboration of alkenes is carried out with a solution of borane in tetrahydrofuran (BH_3:THF). When alkenes are treated with BH_3:THF, boron hydride adds successively to the double bonds of three alkene molecules.



The boron atom always adds to the less substituted carbon due to the steric hindrance at the more substituted end, and the hydrogen atom adds to the more substituted carbon atom. The addition of borane to alkene is a one-step reaction and it proceeds via a cyclic transition state. This trialkylborane is oxidized and hydrolyzed by adding hydrogen peroxide in an aqueous base to give the alcohol.



In the final product, the hydrogen is attached to the more substituted end and the –OH to the less substituted end. Therefore, not like above two methods, this method gives the anti-Markovnikov's addition product. The addition of H and boron takes place from the same face (*syn* addition) of the double bond. The oxidation with H_2O_2 does not change the stereochemistry. Hence the final product has the syn stereochemistry.

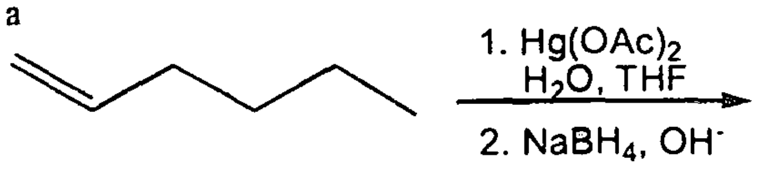


The three methods which have been discussed in here are useful for the synthesis of alcohols from alkenes with different regiochemistry and stereochemistry. Acid-catalyzed hydration and oxymercuration –demercuration of alkenes follows the Markovnikov's rule. Rearrangement of the initial carbocation in acid-catalyzed rearrangement leads to mixture of products. However, rearrangements do not takes place in oxymercuration-demercuration and hydroboration-oxidation of alkenes. Further, acid-catalyzed hydration and oxymercuration-demercuration give both syn and anti addition products. Hydroboration-oxidation of alkenes gives only the syn addition product.

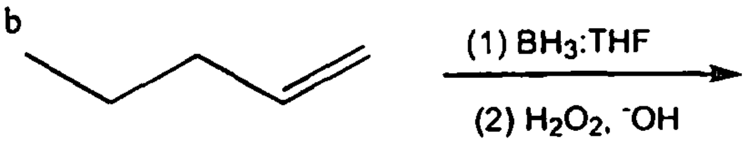
Exercise

1. Predicts the major products of the following reactions.

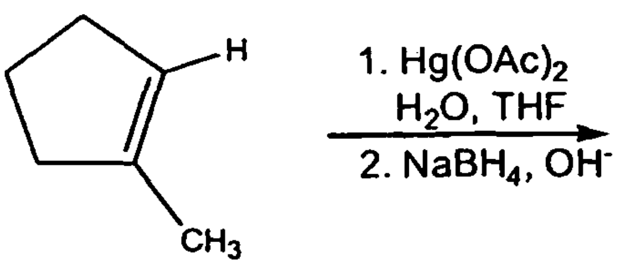
a



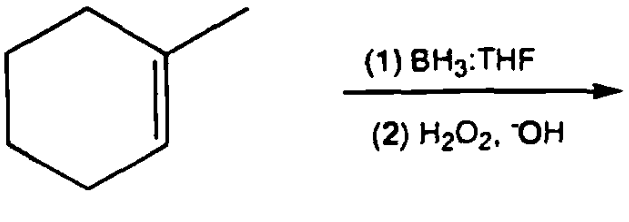
b



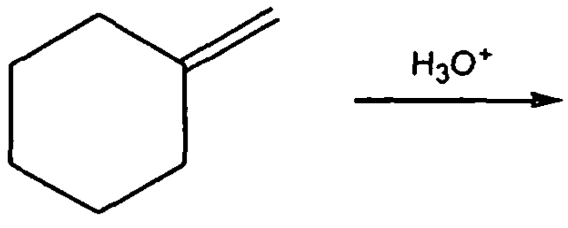
c



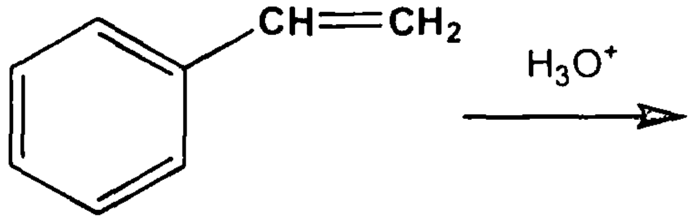
d



e



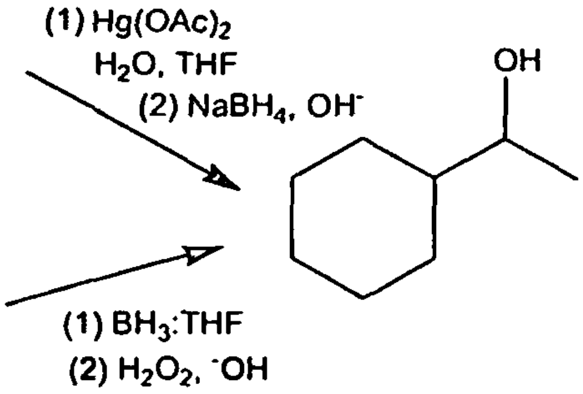
f



2) What alkenes might the following alcohol have been prepared from?

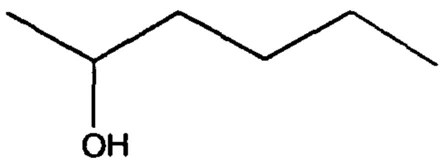
a)

b)

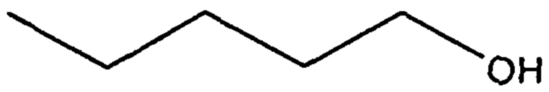


Answer Key

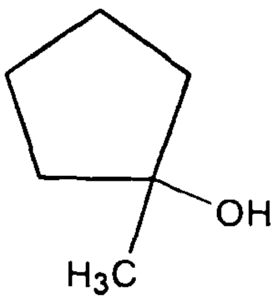
1. a



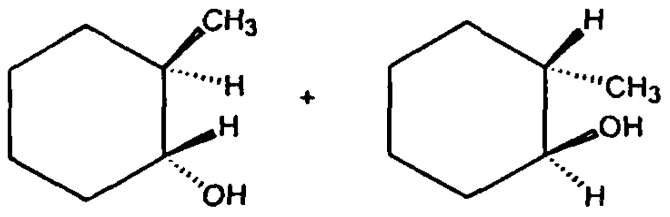
b



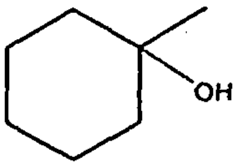
c



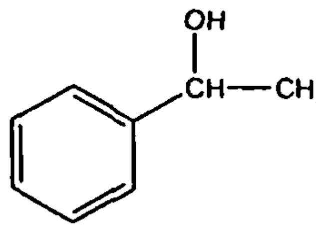
d



e

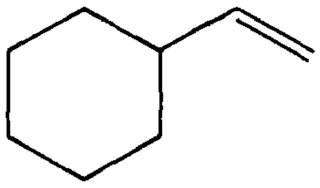


f

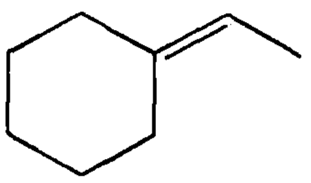


2.

a



b



IUPAC - sponsored events in 2014

1] 12 – 17 January 2014, Bangalore, India
27th International Carbohydrate Symposium (ICS 2014)
Contact person: Prof. N. Jayaraman ics27@orgchem.iisc.ernet.in

2] 27 – 28 February 2014, Blankenberge, Belgium
Chemistry Conference for Young Scientists
Contact person: Prof. Thomas Vranken Thomas.vranken@chemcys.be

3] 5 – 7 March 2014, Suva, Fiji
International Conference on Applied Chemistry 2014
Contact person: Prof. S. Sotheeswaran, sotheeswaran@hotmail.com

4] 3 – 4 April 2014, Colombo, Sri Lanka
Professional Chemistry Education and Research for Industrial Development and Sustainable Economic Growth
Contact person: Prof. Ramanee D. Wijesekera ramanee@chem.cmb.ac.lk

5] 2 – 6 June 2014, St. Petersburg, Russia
8th International Symposium on Molecular Mobility and Order in Polymer Systems
Contact person: Prof. Tatiana Birshtein birshtein@imc.macro.ru

6] 26 – 30 June 2014, Kharkiv, Ukraine
Modern Physical Chemistry – 2014 (MPC '14)
Contact person: Dr Olexander Lebed beketov2014@karazin.ua

7] 13 – 18 July 2014
23rd International Conference on Chemistry Education (ICCE-23)
Contact person: Prof. Judith C. Poë Judith.poe@utoronto.ca

8] 13– 18 July 2014, Bordeaux, France
XXVth IUPAC Symposium on Photochemistry
Contact person: Dr Dario M Bassanid. bassani@ism.u-bordeaux1.fr

9] 10 – 14 August 2014, San Francisco, California, USA
13th International Congress on Pesticide Chemistry
Dr Kenneth D. Rackekracke@dow.com

IUPAC &ChemRAWN Sponsored event

8 – 11 November 2014, Dakha, Bangladesh
ChemRAWNConference on Herbal Medicine – 2014
Chairperson, Task Group: Prof. Mohammed Mosihuzzaman mmosihuzzaman@yahoo.com

Note: See also www.iupac.org/home/conferences.html for further details

BIG Event in 2015

The 48th General Assembly (Aug 6 – 13, 2015) and the 45th World Chemistry Congress (Aug. 9 – 14, 2015), Busan, Korea. **Smart Chemistry Better Life**

Call for Nominations for Institute of Chemistry Gold Medal 2014 by 31st March *(Under Revised Rules)*

This Gold Medal was the very first of such awards to be donated to the Institute and was made possible through a generous donation made by **Mascons Ltd** in memory of their founder **Mr A Subramanium** in 1978/79. It recognised contributions made to National Development through research and development involving Chemical Sciences. The Gold Medal Fund was supplemented recently through a further contribution from Mascons Ltd. This criteria governing the award were changed in 2011 since there were no applicants since 2007 in order to enable the award to be made to a mid-career Chemist in recognition of honorary services to the Institute.

Nominations are now being invited for the 2014 Award from amongst **Corporate Members** of the Institute who have fulfilled the following minimum criteria:

- Nominees should be not more than 55 years of age and should have been Corporate members of the Institute for at least 10 years on 1st of June 2014
- Nominees should have made significant contributions towards the activities of the Institute through yeoman services in an honorary capacity during the period of membership. These activities could include holding office, membership in committees, coordination of events such as workshops, social events etc.

Nominations could be made by any **corporate member** of the Institute and should include the consent of the nominee and details of the contributions made by the nominee in accordance with the above guidelines. The Award will be presented at the 43rd Annual Sessions. **Nominations should be forwarded to reach the Hony. Secretary, IChemC not later than 31st March 2014.**

CALL FOR NOMINATIONS – IUPAC AWARDS/ PRIZES

1] **Thieme - IUPAC Prize 2014**

The prize is awarded to a scientist under 40 years of age as of 1 January 2014, whose research has had a major impact in synthetic organic chemistry.
Deadline for nominations: 13 December 2013
For more details visit: www.thieme-chemistry.com/en/our-service/conferences/thieme-iupac-prize/call-for-nominations.html

2] **Polymer International-IUPAC Award**

The 4th Polymer International-IUPAC Award for Creativity in Applied Polymer Science or Polymer Technology is now open. Nominees must be under the age of 40 on 31 December 2014
Deadline for nominations: 31st October 2013
For more details visit:
http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)10970126/homepage/polymer_internations_iupac_award.html

ChemRawn/IUPAC Conference on
"WASTE MANAGEMENT"
Rome, May 2015

Nominations are requested from the members for the International Advisory Board of distinguished scientists who can do the lectures on the following.

Topics

Urban waste management
Energy recovery from waste
Waste management in the medical industry
Organic waste management
Waste recycling
Waste management in developing countries

Chemical Education

3- 4 April , 2014
International Conference
Colombo - Sri Lanka

Ruby Anniversary International Conference

organized by the

College of Chemical Sciences (CCS)

of the

Institute of Chemistry Ceylon (IChemC)

Theme:

Chemical Education & Research for Industrial Development & Sustainable Growth in a Knowledge Based Economy

The International Conference on **Chemical Education** that is being held on **3rd – 4th April 2014** to commemorate the completion of four decades of formal professional chemical education provided by our institute is expected to be attended a large number of distinguished chemists from many countries throughout the world. We are expecting support and international funding from IUPAC, TWAS, Chemical Weapons Convention and RSC to enable a wider participation. The **Inauguration** on 3rd April at **Waters Edge, Capital City** will incorporate the **10th CCS Convocation** with distinguished Chemist **Professor Atta-ur-Rahaman,** former Federal Minister of Higher Education in Pakistan, as Chief Guest, delivering the Convocation Address. An Ex-Co meeting of the Federation of Asian Chemical Societies (FACS) will also be held in Colombo in conjunction with the conference on **2nd April 2014**.

Deadline for abstracts is 15th November 2013 and further details are available on the website www.ichemc.edu.lk/icce2014/ and preliminary flyer. The Second announcement will be released in September 2013.

The Conference Secretariat is located at the Headquarters of the Institute of Chemistry Ceylon at Adamantane House, 341/22, Kotte Road, Rajagiriya, Sri Lanka

Category of Participants	Overseas Participants	IChemC Members Residing in Sri Lanka	Local Participants
Early Bird Registration Until 31st January 2014	US $ 150	LKR 3000.00	LKR 5000.00
Regular Registration Until 28th February 2014	US $ 175	LKR 4000.00	LKR 6000.00
Late Registration After 28th February	US $ 200	LKR 5000.00	LKR 7000.00

Contact us

Chairman: Prof. J N O Fernando (oleap@ichemc.edu.lk)
Co-Chairs: Prof. H D Gunawardhena (hdg@chem.cmb.ac.lk)
Prof. S Sotheeswaran (sotheeswaran@ichemc.edu.lk)
Joint Honorary Secretaries:
Ms. Kumudhini Goonatilleke (kumudinigoonetilleke@yahoo.com)
Ms. Dulanjalee Attanayake (dula@ichemc.edu.lk)

Telephone: +94 11 2861653, +94 11 2861231, +94 11 4015230
Email: ichemc@sltnet.lk