Recent Studies on the Catalytic Action of Transition Metal Oxides and Complexes

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Abstract: In this review we present some important recent work on the catalytic action of some transition metals. Different types of synthesized transition metal catalysts including oxides and complexes are discussed, and an overview of their physicochemical characterization techniques is reported. The review is devoted to the catalytic activity of these catalysts towards the transformations of many organic reactions e.g. oxidation, hydroxylation, epoxidation, hydrogenation, hydrolysis……etc.

Key word: Transition metal catalysts; oxides; complexes; organic reactions.

INTRODUCTION

Heterogeneous catalytic processes are of great importance in industry. They are quite important in the refining of petroleum. About 70 % of all crude oil pass through such process. On the other hand, Adsorption and desorption phenomena occur frequently in all fields of our every days life as well as in many industrial and technical applications. This starts with simple glues and ends with the filters for pollutant gases in large power plants.

Transition metals can act as catalysts for two reasons. First, because they can have several oxidation states. They can take part in electron transfer reactions. Second, transition metals and their ions can provide sites at which reactions can take place. They can bond to a wide range of atoms and molecules e.g. those with lone pair or p electrons forming complexes with different numbers of bonds. Not only they can form four and six numbers of bonds but also sometimes two, three and five. This feature gives them a high probability to form the suitable intermediates required for preceding the catalytic reactions. They can show catalytic behavior when dissolved in solutions or as solids i.e., homogeneous or heterogeneous catalysts.

Adsorption and desorption processes are also important elementary steps in the complicated chain of reactions that make up a typical mechanism in heterogeneous catalysis. Before the reaction can start at all, the reactant atoms or molecules must adsorb at the solid surface. Then they will diffuse along the surface, react with each other or with the surface to generate reaction intermediates, and eventually, in most cases after several reaction steps, the final products have to desorb from the surface.

Transition Metal Oxide Catalysts: Transition metal oxides are commonly employed as active catalysts for oxidation – reduction reactions due to the presence of incomplete d- orbital in their atoms. CuO, Fe2O3 and CuO–Fe2O3 samples supported on low cost cordierite (2MgO–2Al2O3–5SiO2, commercial grade) were prepared by wet impregnation method using finely powdered support material, copper and/or iron nitrates. The extent of loading was varied between 5 and 20 wt.% CuO, Fe2O3, or CuO–Fe2O3. The physicochemical, surface and catalytic properties of the various solids calcined at 350–700 °C were investigated using X-ray diffraction (XRD), energy despersive X-ray (EDX), and nitrogen adsorption at 77 K. Loading of 20 wt.% CuO–Fe2O3 on the cordierite surface followed by calcination at 350 °C resulted in a solid–solid interaction between some of CuO and Fe2O3, yielding iron cuprate Fe3CuO4, according to

\[ \text{CuO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{CuO}_4 \]
which decomposed at 500 °C yielding copper and iron oxides. The S_BET of cordierite increased several times by treating with small amounts (5-20 wt.%) of Fe_2O_3 or CuO. The increase was more pronounced by treating with Fe_2O_3. The catalytic activity of the cordierite increased progressively by increasing the amount of oxide(s) added. The observed considerable increase in the S_BET of the cordierite sample due to treatment with Fe_2O_3 could not be attributed to the possible growth of a finely divided and porous Fe_2O_3 phase on top surface layers of the treated solids. This assumption seems logical simply because the amount of Fe_2O_3 added is small (5 wt.%) and the increase in its amount up to 20 wt.% exerted a limited increase in the S_BET of the treated samples. So, one may expect an effective dissolution of a portion of Fe_2O_3 in the lattice of the cordierite that might be followed by creation of new pores. The oxidation of CO by O_2 over CuO/cordierite, Fe_2O_3/cordierite and CuO–Fe_2O_3/cordierite solid catalysts calcined at 350, 500 and 700 °C was measured at 220, 250 and 280 °C. The results showed that the catalysis of CO-oxidation by O_2 follows first-order kinetics over various investigated solid catalysts. The mixed oxides system supported on cordierite and calcined at 350–700 °C showed catalytic activities much bigger than those measured for the individual supported systems. The synergistic effect manifested in case of solids calcined at 350 °C was attributed to the formation of surface iron cuprate. The significant increase in surface concentration of copper species on top surface layers of the solids treated with mixtures of copper and ferric oxides could be responsible for the synergistic effect for the mixed oxide catalysts calcined at 500 or 700 °C.

The catalytic oxidation of 1,2-dichlorobenzene has been systematically investigated over a series of transition metal oxides (i.e., Cr_2O_3, V_2O_5, MoO_3, Fe_2O_3, and Co_3O_4) supported on TiO_2 and Al_2O_3.[2] The activity of the different catalysts for this reaction depends on the nature of the transition metal oxide used, with Cr_2O_3- and V_2O_5-based catalysts being the most active ones. With the exception of the cobalt oxide catalysts, the TiO_2-supported systems were more active than the corresponding Al_2O_3-supported ones, indicating that the metal oxide–support interactions are significant in this reaction. Experiments conducted in the presence of water indicate an inhibiting effect for the V_2O_5- and Cr_2O_3-based catalysts and a promoting effect for Co_3O_4/TiO_2. The Fe_2O_3- and MoO_3-based catalysts were unaffected by the presence of water. Competitive adsorption between the surface species and water is suspected to be the reason for the inhibition, while the promoting effect can be attributed to the reaction of water with surface Cl. In situ FTIR studies indicate the presence of carboxylates (i.e., acetates and formates), maleates, and phenolates on the surfaces of all catalysts studied under reaction conditions. These surface species were reactive in the presence of gas-phase oxygen and are potential intermediates for the oxidation of 1,2-dichlorobenzene.

Until recently, nitrous oxide (N_2O) had received little attention as an atmospheric pollutant. Its harmful impact on the environment is now well recognized. N_2O plays a significant role in the destruction of the ozone layer. It is broken down in the stratosphere by photolysis, which initiates a chain of cyclic reactions leading to stratospheric ozone destruction. N_2O is also a major greenhouse gas. The main industrial applications in which levels of produced N_2O are of great concern include chemical processes associated with the production and use of nitric acid and N_2O emissions from automobile engines are also significant, particularly under lean burn conditions and when aged catalytic converters are used. A large number of catalysts have been tested for the decomposition of N_2O, such as noble metals (Pt, Au, Ru and Rh), pure oxides (NiO, CoO, CoO, CuO and MgO), mixed oxides (solid solutions, perovskites and spinels) and zeolites exchanged or impregnated with transition metal ions (ZSM-5, ZSM-11, Beta, Mordenite, USY, Ferrierite, A, X exchanged / impregnated with Fe, Ni, Co, Rh, Ce, Mn, Ru or Pd). The most active catalysts consist of metal-exchanged ZSM-5 (Cu, Co, Rh, Ru, Fe). The decomposition of nitrous oxide to nitrogen and oxygen using a series of monolithic (ceria-alumina washcoated cordierite) supported transition metal (Cu, Fe, Co, Ni, Mn) and noble metal (Ir, Rh) oxide catalysts has been studied using gas chromatography[1]. The effect of combining a transition metal with a noble metal has also been investigated. A synergetic effect was observed between transition metal and noble metal oxides in the presence of a small amount of water for some of the catalysts. The synergy between Fe-Ir and Ni-Ir was also verified under dry conditions. X-ray photoelectron spectroscopic measurements on these catalysts indicate that Fe, Rh and Ir are present predominantly as Fe_2O_3, RhO_2 and IrO_2, while significant amounts of Co and Ni ions may migrate inside the support to form cobalt and nickel aluminate. Only the Fe-Ir catalyst showed a significant interaction between the noble metal and the transition metal. The effect of water, oxygen and carbon monoxide on the catalytic behaviour of the five most active catalysts (Ni-Ir, Ni-Rh, Fe-Ir, Co-Ir, Ir) has also been investigated. Oxygen and water were found to inhibit the catalytic activity, although the extent of oxygen inhibition is limited, presumably due to the presence of ceria in the monolith washcoat support. Conversely, carbon monoxide greatly enhances catalytic activity.
M-Mg-Al hydrotalcites (where M = Cu$^{2+}$, Co$^{2+}$ and Cu$^{2+}$ + Co$^{2+}$) with M ranging from 5 to 20 % (as atomic ratio) were prepared by co- precipitation method. Obtained samples were characterized by XRD and TGA techniques. The influence of transition metal content on thermal decomposition of hydrotalcites was observed. Calcination of the hydrotalcites at 600 °C resulted in the formation of mixed oxides with surface areas in the range 71–154 m$^{2}$/g. Calcined hydrotalcites were tested as catalysts in the selective catalytic reduction of NO with ammonia (NO-SCR)$^{[4]}$. The catalytic activity depends on the kind of transition metal, as well as its content. For the NO-SCR, the following reactivity order was found: Cu-Mg-Al > Cu-Co-Mg-Al > Co-Mg-Al. Temperature-programmed methods (TPD, TPSR, stop flow-TPD), as well as FT-IR spectroscopy have been applied to determine interaction of NO and NH$_3$ molecules with the catalyst surface.

Steam reforming of methanol (CH$_3$OH + H$_2$O $\rightarrow$ 3H$_2$ + CO$_2$) has been investigated with various ZnO-supported a group 8–10 metal catalysts in the presence of oxygen$^{[5]}$. The catalysts may be classified into two groups according to their catalytic actions and properties. One group includes Pd/ZnO and Pt/ZnO catalysts, which are active for the steam reforming in the absence of oxygen. In the presence of oxygen, however, partial oxidation of methanol (CH$_3$OH + (1/2)O$_2$ $\rightarrow$ 2H$_2$ + CO$_2$) rapidly proceeds and the conversion of methanol into hydrogen is drastically enhanced. These catalysts are composed of PdZn and PtZn alloys, which catalyze the steam reforming and the partial oxidation of methanol in the absence and presence of a oxygen, respectively. In addition, for Pd/ZnO catalysts, high Pd loading favors the partial oxidation, whereas lower Pd loading is beneficial to the oxidation of methanol similar to the second group of catalysts. The second group includes other group 8–10 metal catalysts such as Fe, Co, Ni, Ru and Ir, which have no alloy components, in contrast to the first group. The decomposition of methanol (CH$_3$OH $\rightarrow$ 2H$_2$ + CO) occurs with these catalysts in the absence of oxygen in preference to the steam reforming. In the presence of oxygen, the oxidation of methanol (CH$_3$OH + (3/2)O$_2$ $\rightarrow$ 2H$_2$O + CO$_2$) occurs predominantly and the production of hydrogen is not so improved, although the total conversion of methanol is increased.

The water gas shift reaction (WGSR): H$_2$O(g) + CO(g) $\rightarrow$ H$_2$(g) + CO$_2$(g) is an important component of several industrial processes. It is primarily used to produce high-purity hydrogen, for example, for ammonia synthesis. Because the reaction is moderately exothermic, low temperature favors a high equilibrium conversion of CO. In industrial applications the reaction is run at pressures around 25 - 35 bar. To achieve the highest feasible conversion, two adiabatic stages with cooling in between are needed: a high temperature shift at 310–450 °C with a catalyst based on iron oxide structurally promoted with chromium oxide, followed by a low temperature shift in the temperature range of 210–240 °C, where the typical industrial catalyst is copper with zinc oxide and aluminum oxide as supported materials. The copper catalyst undergoes deactivation at temperatures higher than 300 °C, as the copper particles sinter because of surface migration$^{[6]}$. In recent years there has been renewed interest in the WGS reaction in connection with fuel cell-powered vehicles, where hydrogen is obtained via partial oxidation and steam reforming of hydrocarbons. The reformed fuel contains 1– 10 % CO, which, apart from being a pollutant, also poisons the Pt anode in the fuel cell, because of its strong adsorption to the electrode surface$^{[7]}$. The lowering of the CO content is limited by equilibrium at the operating temperature of the conventional Cu/ZnO/Al$_2$O$_3$ WGS catalyst in the reformer system. The development of a more active catalyst would allow one to lower the temperature and reduce the volume of the reformer system.

**Transition Metal Complex Catalysts:** New Schiff-base square planar complexes of nickel (II) with $N,N'$/-bis (2-hydroxyphenyl)ethylendimidine (BHE) and $N,N'$/-(2-hydroxyphenyl)acetamide (HA) have been prepared in good yield by direct interaction of 2-amino phenol, glyoxal / methylacetatotate and NiCl$_2$ and characterised by physico-chemical analysis. The structures of the two ligands are shown in Fig. 1. Catalytic ability of NiL complexes were examined$^{[8]}$ and found that both the complexes can effectively catalyze the epoxidation of olefins viz. cyclohexene, 1-hexene, cis- and trans-stilbenes, indene in the presence of NaOCl as oxidant. The following working mechanism was proposed for the epoxidation of alkenes.

\[
[Ni^{II}L] + OC\cdot - \rightarrow [Ni^{III}L(O)]
\]

\[
[Ni^{III}L(O)] + S - \rightarrow [Ni^{II}L] + SO \ (L = BHE \ or \ HA)
\]

In the proposed mechanism, nickel(IV)–oxo intermediate formed in the reaction of Ni$^{III}$L with OC$\cdot$ transfer its oxo-atom to the reacting olefin S to produce corresponding epoxide (SO).

Condensations of aromatic aldehydes with 2,2' /-diamino-1,1'-binaphthyl or 2-amino-2-hydroxy-1,1'-binaphthyl afford various chiral binaphthyl Schiff-base ligands, the most common of which are potentially tetradentate with a N$_2$O$_2$ donor set. The chiral binaphthyl Schiff-base ligands have been shown to
form stable complexes with metal ions of Al(III), Ti(IV), Cr(III), Mn(II)/Mn(III), Fe(II)/Fe(III), Co(II)/Co(III), Ni(II), Cu(II), Zn(II), Y(III), Zr(IV), Ru(II), and Pd(II); some of such complexes have been characterized by X-ray crystallography. Catalytic studies reveal that these types of chiral metal complexes are active catalysts\(^9\) for stereoselective organic transformations including hydroxylation of styrene, aldol reactions, alkene epoxidation, trimethylsilylcyanation of aldehydes, desymmetrization of meso-N-sulfonylaziridine, Baeyer-Villiger oxidation of aryl cyclobutanone, Diels-Alder reactions of 1,2-dihydroydipyrine, and ring-opening polymerization of lactide.

A series of bidentate and tridentate (S)-2-amino-2'-hydroxy-1,1'-binaphthyl (S)-NOBIN) derivatives was synthesized and tested as chiral ligands in the Ru-catalysed enantioselective transfer hydrogenation of acetophenone with 2-propanol as in Scheme 1\(^{[10]}\). The (S)-NOBIN was prepared as in Fig. 2. The imine derivatives (S)-6,5 (S)-8,6 (S)-10 from (S)-NOBIN and (S)-7, (S)-9 from (S)-NOMBIN were prepared by reaction with salicyaldehyde, 2-pyridinecarbaldehyde and 2-formylphenyl(diphenyl)phosphine. The ligand (S)-11 was obtained from (S)-8 by NaBH\(_4\) reduction. The starting materials (S)-2-(S)-5, the Schiff base ligands (S)-6-(S)-10 and the amine (S)-11 was used together with the procatalyst Ru(PPh\(_3\))\(_2\)Cl\(_2\) in the enantioselective transfer hydrogenation of acetophenone with 2-propanol. The structure of ligands used [(S)-NOBIN derivatives] are represented in Fig. 3. Despite the similarities in chemical structures, only the imine derived from (S)-NOBIN and 2-pyridinecarbaldehyde and the corresponding amine (obtained by NaBH\(_4\) reduction of the imine) afforded (S)-1-phenylethanol in nearly quantitative yields and outstanding enantioselectivities of up to 97% e.e.

With the aim of elucidating the mechanism of oxidative processes initiated by copper(II)–carbohydrate interactions, new isatin–Schiff base copper(II) complexes (Scheme 2), [Cu(isaen)H\(_2\)O]ClO\(_4\)\(_2\)2H\(_2\)O (12), and [Cu(isaepy)\(_2\)](ClO\(_4\))\(_2\)2H\(_2\)O (13), where isaen = \(N\)-[(3-indolin-2-one)-1,3- ethylenediamine and isaepy = \(N\)-[(3-indolin-2-one)-2-aminoethyl pyridine were isolated, and characterized by elemental analyses, UV–Vis, FTIR, EPR, and molar conductivity measurements. These imine ligands are capable of modifying selectively of the copper(II) ion in a pH controlled process, through keto–enolic equilibria similar to those occurring with carbohydrates. Therefore, the obtained complexes had their catalytic activity in the oxidation of common carbohydrates (glucose, fructose and galactose) by molecular oxygen, compared to that of an analogous complex [Cu(isapn)](ClO\(_4\))\(_2\) (14), previously reported\(^{[11]}\). The determined rate law, from kinetic curves of oxygen consumption, showed a pseudo-first-order dependence both on the catalyst and substrate concentrations, followed by a saturation effect, for all the compounds studied. Further, the pH profile indicated that reaction occurs significantly only in very alkaline medium (pH \(\geq 10\)), and some influence of ionic strength (controlled by carbonate buffer) was also verified. The participation of very reactive intermediates in the oxidative degradation of the substrates was monitored by EPR spin trapping, while final products were identified by capillary electrophoresis. The experimental rate law indicated that enolization of the substrate and the coordinated ligand is essential for the process occur. The steps of the mechanism for carbohydrate oxidation are proposed bellow. Assuming that step2 refers to a rapidly achieved keto-enol equilibrium involving the catalyst, with the prevailing enol-form at very high pH as verified by spectroscopic techniques, and that step (1) and (3) are rate-determining steps.
Fructose + OH⁻ → Fru-enediol + H₂O K₁=k₁/k₋₁     (1)
Cu²⁺L + OH⁻ → Cu²⁺L_enol⁻ + H₂O K₂                   (2)
Fru-enediol + Cu²⁺L_enol⁻ → [(Fru-enedio) Cu²⁺L_enol] K₃ (3)
[(Fru-enedio) Cu²⁺L_enol] → Cu²⁺L_enol + Fru-enediol⁻ fast (4)
Catalyst Regeneration:
Cu²⁺L_enol + O₂ → O₂⁻ + Cu²⁺L_enol                 (5)
H₂O₂ + Cu²⁺L_enol → Cu²⁺L_enol + OH⁻ + OH⁻          (6)
O₂⁻ + Cu²⁺L_enol + H₂O → Cu²⁺L_enol + HO₂⁻ + OH⁻ (7)
Reaction termination:
Fru-enediol⁻ + O₂ → products + H₂O₂                 (11)
Reactions propagation:
OH⁻ + Fru-enediol → Fru-enediol⁻ + H₂O             (8)
OH⁻ + HCOO⁻ → CO₂⁻ + H₂O                         (9)
Cu²⁺L_enol + H₂O₂ → Cu²⁺L_enol + HO₂⁻             (10)
"Cu²⁺L_enol is the enol form of the complex (stable in alkaline medium)."
Scheme 2:

where I is the intermediary species involving interaction between the substrate and the catalyst, \([\text{Fru-enediol} \text{CuIILenol}]\), which is rapidly decomposed into the corresponding reduced CuIL species and Fru-enediol' radical, by internal electron transfer.

Optically active epoxides are key intermediates in organic chemistry because they can undergo stereospecific ring-opening reactions, giving rise to a wide variety of biologically and pharmaceutically important compounds. A series of chiral macrocyclic Mn(III)Salen complexes has been prepared with two salicylidene moieties linked in their 3 and 3' positions by aliphatic polyether bridges of variable lengths or by a more rigid aromatic junction arm. X-ray structures of ligand precursors and of complex 17 have been performed. All complexes have been used in the asymmetric epoxidation of 1,2-dihydronaphthalene with NaOCl as oxygen atom donor and exhibited modest enantiomeric excesses\(^{[12]}\). The synthetic pathway for Mn\(^{III}\)-Salen complexes 15–18 including the diethylene glycol junction arm is illustrated in Scheme 3. The Reimer–Tiemann method (NaOH/CHCl\(_3\))\(^{[13]}\), involving a dichlorocarbene as active species, allowed to obtain 2,3-dihydroxy-5-tert-butylbenzaldehyde with a yield of 8\%. Despite a poor yield, this reaction is easy to carry out, requires inexpensive reagents and 2,3-dihydroxy-5-tert-butylbenzaldehyde can be easily obtained on gram scale. 2,3-Dihydroxy-5-tert-butylbenzaldehyde has been isolated as colorless crystals by recrystallization in hexane. The \(^1\)H NMR spectrum gives a deshielded chemical shift for one phenolic proton, which is in good agreement with the observation of an intramolecular hydrogen bond between the aldehyde oxygen and the neighbouring hydroxy group in the structure. The dialdehyde compound was prepared according the one-step procedure by reaction of 2,3-dihydroxy-5-tert-butylbenzaldehyde with two equivalents of NaH in DMSO to give the dianion, which was treated with 0.5 equivalent of diethylene glycol ditosylate. The template synthesis of complexes
15–18 was realized by mixing the dialdehyde, the desired chiral diamine and manganese(II) acetate in stoichiometric proportions, in ethanol under a nitrogen atmosphere (Scheme 3). After air oxidation and exchange of the axial anionic ligand, compounds 15-18 were isolated in good yields (74-89%). Complexes 19 and 20 were prepared in a similar manner, starting from triethylene glycol ditosylate or 1,3-benzenedimethanol-di-p-tosylate as junction bridge and (1S,2S)-(+)-1,2-diaminocyclohexane (Scheme 4). The asymmetric epoxidation of 1,2-dihydronaphthalene using the six complexes 15–20 described above has been evaluated (Scheme 5). Reactions were carried out using NaOCl as oxidant at room temperature. The epoxidations were typically performed with a substrate, oxidant and catalyst ratio of 1:2:0.05. The results obtained showed epoxide yield with ee values of 20% and 23% for complexes 20 and 19, respectively.

Complex 19 was selected to be tested with two cis-disubstituted olefins and several oxidants, namely NaOCl, PhIO and n-Bu₄NHSO₅. 2,2'-Dimethylchromene oxide was obtained from 2,2'-dimethylchromene with ee values of 56% and 74% when using 19 and NaOCl and PhIO, respectively.

A variety of oxovanadium(V) complexes have been shown to catalyze the oxidation of sulfides by using peroxides as oxygen atom donors. Schiff-base ligated oxovanadium complexes have provided excellent results (e.g., 98% yield, 91% ee, 60% yield, 95% ee) in the oxidation of disulfides. Peroxo complexes made of tridentate and tetradeptate Schiff-base oxovanadium(IV) complexes were found to yield quick progress of reaction and conversion of methyl phenyl sulfide to the corresponding sulfoxide in 80–95% yield in CDCl₃ and in 30–80% yield (by tridentate Schiff-base complexes) in CD₃OD in 30 min. However, some...
of the tridentate Schiff-base complexes probably with low stabilities were found to be decomposed by tertbutylhydroperoxide[15]. Pentadentate Schiff-base complexes of oxovanadium(IV), the ligands of which were derived from salicylaldehyde derivatives with a variety of substituents and two kinds of amines (2,2'-bis(aminooethyl)amine and 3,3'-bis(aminopropyl)amine), were prepared, and their coordination geometries in the solid state were determined by X-ray diffraction and IR measurements and those in CH2Cl2 by EPR measurements. They were found to retain distorted octahedral coordination in the solid state. They showed the structural change depending on the type of the substituent. The complexes which reacted with tert-butylhydroperoxide converted methyl phenyl sulfide to the corresponding sulfoxide at lower rates of reaction than tridentate N-salicylidene-2-aminoethanolato oxovanadium(IV) ([VO(salae)]) and tetradentate (N,N'-bis(salicylidene)ethylenediaminato)oxovanadium(IV) ([VO(salen)])[16].

α-Amino acid Schiff-base complexes of oxovanadium(IV), whose ligands have amino acid side chains with coordinating functional groups, retained coordination geometries in which the amino acid side chains were probably coordinated in the axial position with a phenolate oxygen, a carboxylate oxygen, an imine nitrogen, and a solvent being bound in the equatorial plane. As for amino acid ester Schiff-base complexes, the amino acid side chains were coordinated in the equatorial plane in the place of the carboxyl group in the case of the amino acid Schiff-base complexes. The amino acid Schiff-base complexes of oxovanadium(V) were present as dimers in dichloromethane. Peroxo complexes prepared from the Schiff-base complexes of oxovanadium(V) converted methyl phenyl sulfide to the corresponding sulfoxide in 80–90% yield in CDCl3 and in 30–70% yield in CD3OD in 30 min[17]. They converted the sulfide in a stereoselective manner yielding the sulfoxide in small enantiomeric excess (5–20%).

The hydrolysis of carboxylic acid esters is of paramount importance in biological and industrial processes. Therefore, groups have developed the biomimetic models for metalloenzyme which catalyzes the hydrolysis of carboxylic acid esters in biological body. These biomimetic models provide insight into the mechanism by which metalloenzyme may operate and consequently provide a theoretical base for designing highly effective artificial metalloenzyme. The macrocyclic Schiff base complexes of Macrocyclic Schiff base ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclodeca-4,11-dienedihydrogen perchlorate, C16H32N4·2HClO4 (HTDP, Fig 4) with Cu(II) and Zn(II) in Brij35(C12H25(OCH2CH2)23OH) micellar solution are investigated kinetically for the catalytic hydrolysis of p-nitrophenyl acetate (PNPA) and p-nitrophenyl picolinate (PNPP) at 30 °C[18]. The results indicate that different mechanisms are operative for the two complexes in the hydrolysis of PNPA and PNPP. The Cu(II) complex can only catalyze the hydrolysis of PNPP by the mechanism which involves the nucleophilic attack of external hydroxide ion on the carbonyl, while the Zn(II) complex can accelerate the hydrolysis of both PNPP and PNPA, by way of the intramolecular nucleophilic attack of zinc-bound hydroxide ion on carbonyl, while the Zn(II) complex can accelerate the hydrolysis of both PNPP and PNPA, by way of the intramolecular nucleophilic attack of zinc-bound hydroxide ion on carbonyl for PNPP and the less effective intermolecular nucleophilic attack of zinc-bound hydroxide ion on carbonyl for PNPA, respectively (Fig. 5). The catalytic activity of Zn(II) complex is close to or even higher than that of Cu(II) complex.
Fig. 5: (a) The possible mechanism for hydrolysis of PNPP catalyzed by CuL in Brij35 micellar solution, (b) the possible mechanism for ZnL-H2O promoted hydrolysis of PNPP in Brij35 micellar solution and (c) the possible mechanism for ZnL-H2O promoted hydrolysis of PNPA in Brij35 micellar solution.

Chiral salen-metal complexes 21-32 (Fig. 6) have been tested as phase transfer catalysts for the asymmetric C-alkylation of Schiff's bases of alanine and glycine esters with benzyl bromides under phase-transfer catalysis (PTC) conditions (solid sodium hydroxide, toluene, ambient temperature, 1±10 mol% of the catalyst), Scheme 6a. Analysis of the results indicated that in the absence of a transition metal, the salen ligands did not produce any asymmetric induction in the product. In other words, the disodium salt of the ligand, which would form under the PTC condition, was not an efficient asymmetric catalytic of the alkylation reaction under the reaction conditions. The best catalyst (24 or 26), derived from a Cu(II) complex of (1R, 2R or 1S,2S)-[N,N'-bis(2'-hydroxybenzylidene)-1,2-diaminocyclohexane], was used with different alkylating agents (Scheme 6a,b) and gave α-amino and α-methyl-α-amino acids with enantiomeric excesses of 70-96%.[19] Previously, it was reported that the coupling products are preferred when CH2Cl2 is used; and (2) the quinone yield increases when THF is utilized. In CH2Cl2 with 2,4-dtbp, the yield of the coupling product based on the complex amount, is in the order 34, 33, and 35 with yields of 6300, 4700 and 200%, respectively. Low temperature UV–Vis results of the reaction of 33 with H2O2 showed the growth of peaks at 390 and 580 nm indicative of a m-η1:η1-hydroperoxo intermediate. At -50 °C, this spectrum does not change. But when warmed to 0 °C, a spectrum similar to the original spectrum was obtained. This probably indicates hydrogen radical abstractions of the peroxy intermediate from solvents, and if excess H2O2 is present, the peroxy intermediate may again be formed. This reusability of the complex explains the high yield using 33 and 34.

OsVIII-catalysed oxidation of m-hydroxybenzaldehyde by alkaline Fe(CN)63 has been studied in the 0.01–0.05 M [OH-] range. Higher [OH-] concentrations were not possible as the substrate turned yellow at [OH-] > 0.05 M. The very low solubility of the substrate in H2O restricted the kinetic study to [OH-] < 0.01 M. A mechanism, consistent with the results was proposed and reported[21].
Fig. 6: Chemical structure of Chiral salen-metal complexes.
Three different palladium(II) complexes Pd(NN)Cl₂ and two different palladium(0) complexes Pd(NN)(dmfu) (dmfu = dimethylfumarate) containing NN pyridyl-imine ligands, have been prepared and used as pre-catalysts for the coupling between iodobenzene and methyl acrylate (Meac) (Heck reaction)\(^{22}\). All the reactions have been conducted in DMF at 80 °C, using Et₃N as base and a Pd:Phl:Meac:Et₃N= 1:1000:1100:1000 molar ratio. In all cases the complete conversion of iodobenzene into trans-methylcynnamate has been observed within 2.5 h of reaction. At the end of the catalytic reactions the dimeric species [Pd₂I₆][Et₃NH]₂ has been recovered, pointing out a partial palladium loss from the starting complex species. A poisoning Hg(0) test has shown a heterogeneous nature of the catalytic reactions and this indicates that the Pd(NN) complexes act as metallic palladium reservoirs. The dimer [Pd₂I₆][Et₃NH]₂ probably forms from soluble palladium(0) particles arising from the complex decomposition once the substrates have been totally consumed. Interestingly, the dimer [Pd₂I₆][DMFH]₂ has been obtained by reacting PdCl₂ with Phl and Meac in DMF at 80 °C.

Organometallic NCN-pincer complexes are air-stable and versatile compounds that are finding extensive application in catalysis and material science. As part of a programme investigating group 10 metal containing pincer complexes, it has been reported the facile three step synthesis of platinum species 36 starting from isophthaldehyde (Scheme 7)\(^{23}\). These cationic complexes act as Lewis acid catalysts for the Michael reaction between ethyl α-cyanoacetate and methyl vinyl ketone, and the Diels–Alder reaction between acrylonitrile and cyclopentadiene. Also, It has been reported the synthesis of related platinum 37 and palladium 38 bisoxazoline containing NCN-pincer complexes, and these are also active as catalysts for the Michael reaction of activated nitriles\(^{24}\). Complexes 37 and 38 (Fig. 7) also catalyze the aldol reaction between isonitriles and aldehydes, and in all of this chemistry evidence points to the pincer complexes activating the nitrile or isonitrile substrate through coordination to the group 10 metal. The addition of trimethylsilyl cyanide (TMSCN) to benzaldehyde catalysed by complexes 36-38 to give the corresponding cyanohydrin\(^{25}\) was studied as follows (Scheme 8). In the absence of a catalyst, combining benzaldehyde with 1.25 equivalents of TMSCN did not result in the formation of cyanohydrin. Under the same conditions in CH₂Cl₂, addition of 1 mol% of 36a (R=CH₃, X=OTf) resulted in the clean formation of cyanohydrin following addition of 3N HCl to hydrolyze the TMS ether initially formed in the reaction. Reducing the catalyst loading to 0.1 mol% gave an essentially identical result, although a further ten-fold reduction in loading resulted in a significantly reduced conversion. Toluene proved inferior as a solvent and the tetrafluoroborate complex 36b (R=Ph, X=BF₄⁻) is a less effective catalyst. Platinum bisoxazoline complexes 37a (R=R'=Me, R=H, X=OTf) and 37b (R=R'=Me, R=NO₂, X= OTf), and palladium bisoxazoline 38a (R=R'=Me, X= OTf), also resulted in good conversion to cyanohydrin under the standard conditions used.

Two multidentate ligands: N,N-di-(propionic acid-2-yl)-2,9-diaminomethyl-1,10-phenanthroline (DPDP) and N,N-di-(3'-methylbutyric acid-2-yl)-2,9-diaminomethyl-1,10-phenanthroline (DMDP) were prepared by the route shown in Scheme 9 \(^{26}\). The hydrolytic kinetics of p-nitrophenyl phosphate (NPP) catalyzed by complexes of DPDP and DMDP with La(III), Gd(III) have been studied\(^{27}\). Both LnL and LnLH₀ (L = DPDP or DMDP) have been examined as catalysis for the hydrolysis of NPP in aqueous solution at 298 K, I = 0.10 mol dm⁻³ KNO₃ at the pH range 7.4–9.1, respectively. Kinetic studies showed that both LnL and LnLH₀ have catalytic activity, but LnLH₀ is more active than LnL in the hydrolysis of NPP. The second-order rate constants for the hydrolysis of NPP are \(k_{\text{cat, LnLH₀}}=0.01399 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}, k_{\text{cat, LnL}}=0.0000110 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\) for complexes GdLH₁ and GdL₁, respectively. A new mechanism was proposed for the hydrolysis of NPP catalyzed by LnL and LnLH₀ \(^{26}\).

Reactions of Organic Azides Catalyzed by Transition Metal Complexes: Organic azides are reactive molecules, which can be represented by the resonance formulas (X) and (Y) (Fig. 8). For the aromatic derivatives another resonance formula (Z) can be considered (Fig. 8).

Reactions of Organic Azides with Unsaturated Hydrocarbons: The iron(II) and manganese(III) porphyrin complexes reported as in Fig. 9 are the derivatives usually employed as catalysts in several reactions. It was ruthenium(II) and, for the first time, cobalt(II) complexes as catalysts in the amination reactions of unsaturated and saturated hydrocarbons. By using Ru(TPP)(CO) 39, Fig. 10, \(\text{TTP} = \text{dianion of 5,10,15,20-tetraphenylporphyrin}\) as catalyst and \(p\)-NO₂C₆H₄N₃ as the organic azide, allylic amines or aziridines have been obtained, depending on the olefin employed as substrate (Schemes 10 and 11)\(^{27,28}\). Cyclohexene (Scheme 10, \(R¹ = R² = R³ = H \) \(n = 1\)) reacts without a catalyst very slowly with \(p\)-NO₂C₆H₄N₃ to give the corresponding aziridine. One could speculate that the mechanism of reactions shown in Schemes 10 and 11 is similar, the only difference being the transition state, which in one case leads to the allyl amine and in the other to the aziridine. Recently, bis-oxo ruthenium derivative, Ru(TPP)(O)₉, has been used as catalyst in the amination of olefins.
This complex, for which the synthesis has been optimized and the reactivity towards CO and alkenes has been investigated\[28\], proved to be a better catalyst than Ru(TPP)(CO) 39.

**Reactions of Organic Azides with Benzylic Derivatives:** The reactions of hydrocarbons that contain a benzylic group with aromatic azides catalyzed by Co(II)(porphyrin) derivatives leads to the formation of the corresponding amine\[29\]

\[
\text{Co}^{II}(\text{porphyrin}) \quad \text{ArR'CHAr} + \text{ArN}_3 \rightarrow \text{ArR'C-NHAr'} - \text{N}_2
\]

When at least one of the R substituents is hydrogen, the catalytic reaction proceeds further, at least in part, to give the corresponding imine

\[
\text{ArR'HC-NHAr'} + \text{ArN}_3 \rightarrow \text{ArR'C=NAr'}
\]

**Reactions of Organic Azides with Sulfer-containing Compounds:** Asymmetric C-N bond formation was achieved in a highly enantioselective manner by using Ru(Schiff base) (CO) 40, Fig. 11, catalyzed sulfimidation and the subsequent sigmatropic rearrangement\[30\]. Treatment of allyl aryl sulfides with toluene p-sulphonyl azide (TsN\(_3\)) in the presence of the ruthenium catalyst, followed by hydrolysis of the resulting N-allyl-N-aryltio toluene sulfonamides provided N-allyl toluenesulfonamides in high enantiomeric excesses (Scheme 12). Enantioselective imidation of alkyl aryl sulfides with N-alkoxycarbonyl azides as nitrene precursors was affected with the same catalyst\[31\].
Fig. 7: Chemical structure of organometallic complexes 37 and 38.

Fig. 8: Resonance formulas for aliphatic (X,Y) and aromatic RN₃ (Z).

Fig. 9: Metal–porphyrin complexes: (A) aryl substituent in the meso position of the porphyrin ring and (B) alkyl substituent in the beta position of the porphyrin ring.

Fig. 10: Chemical structure of Ru(TPP)(CO), (39).
Fig. 11: Chemical structure of Ru(Schiff base)(CO), (40).

Scheme 9:

Scheme 10:

Scheme 11:

Scheme 12:
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