Recent Developments in Use of Heteropolyacids, Their Salts and Polyoxometalates in Organic Synthesis

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Recent Developments in Use of Heteropolyacids, Their Salts and Polyoxometalates in Organic Synthesis

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Heteropolyacids, their salts and polyoxometalates have been used as catalysts in wide range of organic reactions such as multi components, oxidation, reductions, electrochemical and photochemical reactions. There have been tremendous and continued efforts to modify the catalytic performance of heteropoly acids such as supporting them on MCM, silica gel, *etc*. In this review, we have attempted to bring some of new applications of heteropolyacids in organic reactions and recent approaches on modifying them, into focus.

INTRODUCTION

The application of heterogeneous acid catalysts in place of homogeneous acid catalysts in organic synthesis is an attractive area of research in the laboratory as well as in the industrial context. The advantages of the heterogeneous catalysts over the homogeneous catalysts include stability (toward air and moisture), lack of corrosion, ease of handling, recovery and regeneration [1].

Heteropolyanions are polymeric oxoanions formed by the condensation of more than two different mononuclear oxoanions [2]. These compounds show very high catalytic activity for some acid-catalyzed reactions. HPAs are usually solids that are insoluble in non-polar solvents but highly soluble in polar ones. The use of HPAs in non-polar solvents improves product selectivity and also provides easy separation of HPAs from the reaction mixture [3].

Heteropolyacids are found to act as outstanding catalysts in electrophilic transformations [3]. They are known to possess a strong purely Bronsted acidity, the acidity which being more profound than many mineral acids or conventional solid acids such as amorphous SiO_2 Al_2O_3, H_3PO_4/SiO_2, HX and HY zeolites [4]. They are water tolerant and can work as both homogenous and heterogenous catalysts [5]. Although, they possess Bronsted acidity, they are found to be very efficient in catalyzing reactions that conventionally use Lewis acids. They have been found to exhibit excellent catalytic properties in the dehydration of diols [6], rearrangements [7], tetrahydropyranylation of alcohols [8] and Friedel-Crafts alkylation [9] and Prins reaction.

The use of heteropolyacids, HPAs, as catalyst for fine organic synthesis processes is developing and synthesis of antioxidants, medicinal preparations, vitamins and biologically active substances has been reported by using them [10]. In addition, these catalysts are very important for industries related with fine chemicals as flavors, pharmaceutical and food industries [11]. Heteropoly acids, their salts and polyoxometalates as heterogenous, efficient and eco-Friendly catalysts in organic reactions have extensively been reviwed by Firouzabadi *et al*. recently [12].

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In the following sections, we wish to up date some recent advances in application of heteropolyacids (HPAs), their salts, and also polyoxometalates in organic synthesis.

SYNTHESIS OF HETEROCYCLIC COMPOUNDS

Coumarin Synthesis

Coumarin is the parent organic compound of a family of naturally occurring phytochemicals found in many plant species, including lavender, sweet clover, strawberry, apricot, cherry and cinnamon. The oxygen of this heterocycle is best known for its fragrance, described as a vanilla-like odour or the aroma of freshly mowed hay. It is also used to prepare other chemicals, in particular antioxidants [13].
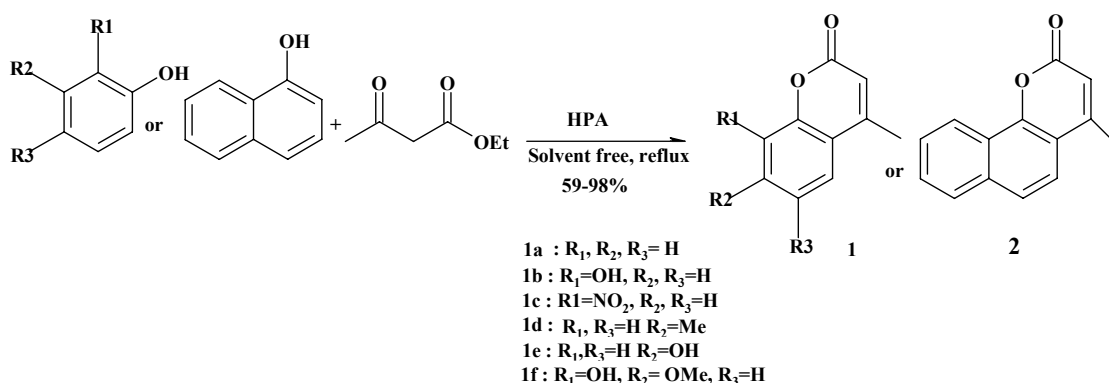
Different heteropolycompounds were used as catalysts in the synthesis of coumarins from phenols and ethyl acetoacetate. The $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ Keggin heteropolyacids were supported on different types of silica. On the other hand, the aluminium salts of these heteropolyacids and that of the $H_4SiW_{12}O_{40}$ acid were prepared. The catalytic activity using several phenols such as resorcinol, 3,5-dimethoxyphenol, α-naphtol and β-naphtol were determined. High yield of product was obtained in the case of 4-methyl-7-hydroxycoumarin (80-95%), 4-methyl-5,7-dimethoxy-coumarin (60-92%) and 4-methyl-7,8-benzocoumarin (90%). However, the 4-methyl-5,6-benzocoumarin yield was low. The use of microwave radiation as power source increases the reaction yield and mainly decreases the reaction time [14].

Recently the formation of 4-methylnaphtho-(1,2-b)-pyran-2-one (coumarin) from the condensation of α-naphthol and ethylacetoacetate in a solvent free system and under heating conditions, using a variety of heteropolyanions including: Keggin, Dawson, Preyssler, mixed addenda and sandwich types, was performed. The obtained data vividly indicated that sodium 30-tungstopentaphosphate, $[NaP_5W_{30}O_{110}]^{14-}$, so-called Preyssler's anion, with high hydrolytic (pH 0-12) and thermal stability is the catalyst of choice. This catalyst catalyzed the synthesis of other coumarin derivatives **1a-1f** and **2** in high yields and good selectivity (Scheme 1) [15].

In another attempt to synthesis the coumarine derivatives, using heteropolyacids, coumarin-3-carboxylic acids and 3-acetylecoumarins **3a-3f** were obtained in high yields with excellent purity from *ortho*-hydroxybenzaldehydes and 1-ethylacetoacetate or malonic acid after a 2 h reflux in ethanol in the presence of a catalytic amount of different heteropolyacids (HPAs) [16] (Scheme 2). The less reactive 1-(2-hydroxy-phenyl)-ethaone was first reacted with alcoholic ammonia to form ketimines, which were then condensed with 1-ethylacetoacetate or malonic acid to generate 4-methyl coumarin-3-carboxylic acids and 4-methyl-3-acetylecoumarinsin moderate yields.
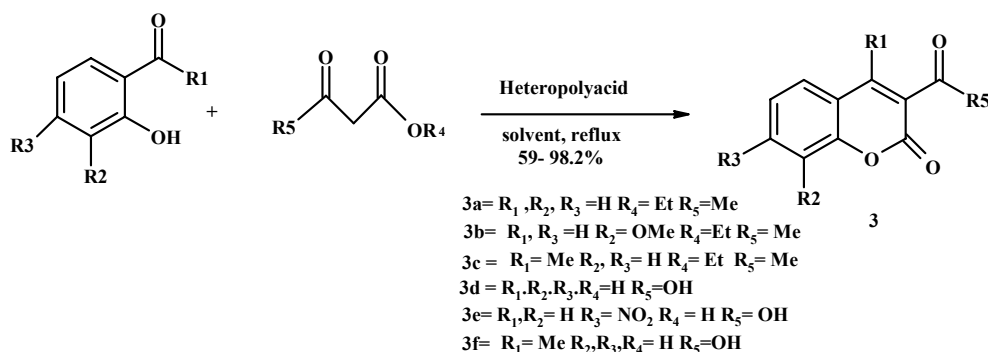
2-Amino-4H-Chromenes

2-Amino-chromenes represent an important class of compounds being the main components of many naturally occurring products. They can also widely be utilized as cosmetics, pigments [17] and potential biodegradable
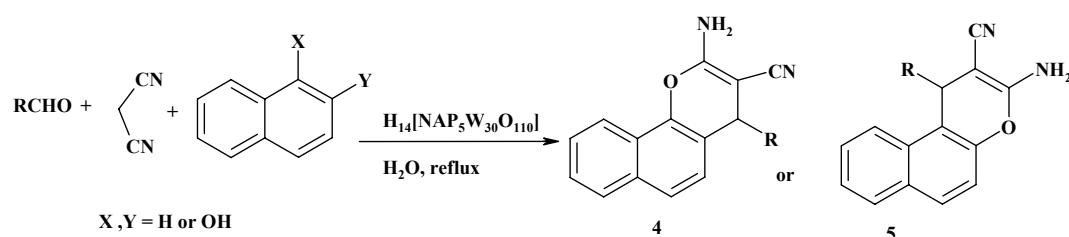

1a : R₁, R₂, R₃=H
1b : R₁=OH, R₂, R₃=H
1c : R1=NO₂, R₂, R₃=H
1d : R₁, R₃=H R₂=Me
1e : R₁,R₃=H R₂=OH
1f : R₁=OH, R₂= OMe, R₃=H

Scheme 1

3a= R_1, R_2, R_3 =H R_4= Et R_5=Me
3b= R_1, R_3 =H R_2= OMe R_4=Et R_5= Me
3c = R_1= Me R_2, R_3= H R_4= Et R_5= Me
3d = R_1.R_2.R_3.R_4=H R_5=OH
3e= R_1,R_2= H R_3= NO$_2$ R_4 = H R_5= OH
3f= R_1= Me R_2,R_3,R_4= H R_5=OH

Scheme 2

X ,Y = H or OH

Scheme 3

Table 1. Synthesis of Substituted 2-Amino-Chromenes Catalyzed by $H_{14}[NaP_5W_{30}O_{110}]$

Entry	R	Phenol	Time (h)	Yield (%)[a]
1	C_6H_5	α-Naphthol	3	91
2	C_6H_5	β-Naphthol	2.75	93
3	$4\text{-}NO_2C_6H_4$	α-Naphthol	4.5	90
4	$4\text{-}NO_2C_6H_4$	β-Naphthol	4.25	93
5	$4\text{-}MeOC_6H_4$	α-Naphthol	3.25	91
6	$4\text{-}MeOC_6H_4$	β-Naphthol	3	92
7	$4\text{-}ClC_6H_4$	α-Naphthol	4	90
8	$4\text{-}ClC_6H_4$	β-Naphthol	4	91
9	$3\text{-}NO_2C_6H$	α-Naphthol	4.5	92

[a]Yields refer to isolated products.

agrochemicals [18]. These compounds have been of interest to the medicinal chemist for many years.

$H_{14}[NaP_5W_{30}O_{110}]$ was used successfully as an efficient catalyst in reaction of aldehydes , malonitrile alfa and beta-naphtoles for the synthesis of **4** and **5** (Scheme 3). This procedure offered several advantages including mild reaction conditions, cleaner reactions, high yields of products as well as a simple experimental and work-up procedure which made it a useful and attractive process for the synthesis of these compounds. Most importantly, water was chosen as a green solvent for these reactions (Table 1) [19].

Synthesis of 14-Aryl-14H-Dibenzo[a,j]xanthene

In recent years, much attention has been directed towards

the synthesis of 14-substituted-14-H-dibenzo[*a,j*] xanthene derivatives due to the fact that these compounds possess a variety of biological and therapeutic properties, such as antibacterial [20] antiflammatory [21] antiviral activities [22] as well as in photodynamic therapy [23] and as antagonism for paralyzing action of zoxozolamine [24]. Furthermore, these heterocycles show useful spectroscopic properties and are used as dyes [25] in laser technologies [26] and in fluorescent materials for visualization of biomolecules [27].

An efficient and facile synthesis of biologically active 14-substituted-14-H-dibenzo[*a,j*] xanthene derivatives **6** were reported via three-component condensation reaction of α-naphthol and aldehydes in the presence of a catalytic amount of Preyssler type heteropolyacid, under solvent-free conditions (Scheme 4). This method was very easy, rapid and high yielding reaction for the synthesis of dibenzo xanthene derivatives (Table 2) [28].

Another Iranian research group developed synthesis of 14-substituted-14-H-dibenzo[*a,j*] xanthene derivatives *via* three-component condensation reaction of α-naphthol and aldehydes, using $H_6P_2W_{18}O_{62}.24H_2O$ (WD acid), $H_3PW_{12}O_{40}.6H_2O$ (PW acid), silica gel supported WD acid and silica gel supported PW acid under solvent-free conditions at 100 ºC (Table 3) [29].

Benzimidazole Synthesis

The benzimidazole ring is a crucial pharmacophore in drug discovery. Benzimidazole derivatives are unique and broad-spectrum class of antirhino/enteroviral agents. They exhibit significant activity against several viruses [30].

A number of synthetic methods have been developed in recent years to uncover a variety of new reagents for the synthesis of benzimidazole derivatives [31]. However, the reported yields in these methods are moderate to poor. In
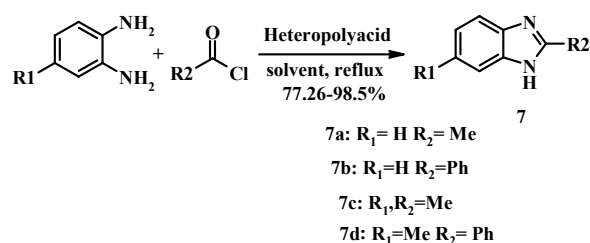

Scheme 4
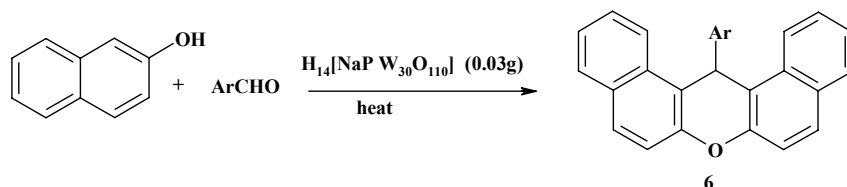
Table 2. Solvent-Free Synthesis of 14-Substituted-14-H-Dibenzo[*a,j*] Xanthene Derivatives Catalyzed by $H_{14}[NaP_5W_{30}O_{110}]$

| Entry	Aldehyde	Time (min)	Yield (%)[a]
1	Benzaldehyde	30	98
2	4-Chloro-benzaldehyde	45	99
3	4-Nitro-benzaldehyde	60	99
4	3-Nitro-benzaldehyde	60	98
5	4-Methyl-benzaldehyde	60	98
6	4-Methoxy-benzaldehyde	120	50
7	4-Hydroxy-benzaldehyde	120	50
8	2-Methoxy-benzaldehyde	80	96
9	β-naphthol	105	98
10	Propionaldehyde	90	97

[a]Yields refer to isolated products.

Table 3. Preparation of Dibenzoxanthene Using WD Acid (I), SiO$_2$-WD Acid (II), PW Acid (III) and SiO$_2$-PW Acid (IV)

Entry	Aldehyde	Time (h)/Yield%			
		I	II	IV	III
1	Benzaldehyde	1/89	0.5/89	0.5/89	0.5/89
2	2-Chloro-benzaldehyde	1/81	1/87	1/91	0.5/87
3	4-Chloro-benzaldehyde	1.5/89	1/90 (91,90,89)[b]	1.5/88	0.5/94 (92,84,80)[b]
4	4-Bromo-benzaldehyde	1/91	1/96	1/91	1/91
5	4-Fluoro-benzaldehyde	1/90	0.5/96	1/85	0.5/95
6	3-Nitro-benzaldehyde	1/80	1.5/89	1.5/84	0.5/89
7	4-Nitro-benzaldehyde	1/94	1/84	1/80	1/84
8	4-Methyl-benzaldehyde	1.5/86	1/91	1.5/91	1/91

7a: R$_1$= H R$_2$= Me

7b: R$_1$=H R$_2$=Ph

7c: R$_1$,R$_2$=Me

7d: R$_1$=Me R$_2$= Ph
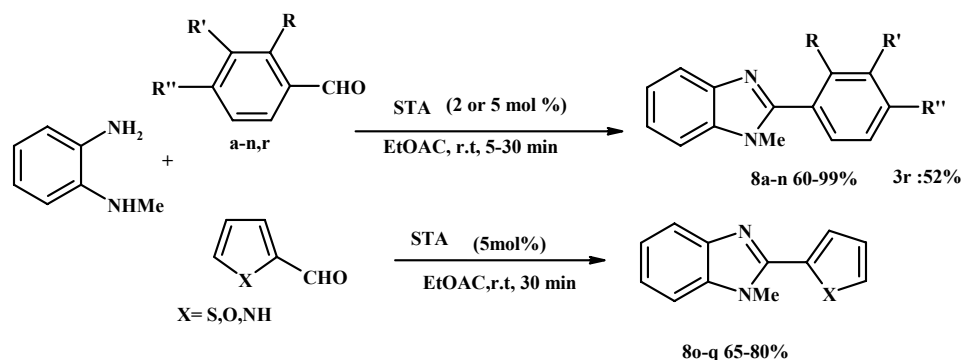
Scheme 5

Scheme 6

addition more than one step is involved in the synthesis of these compounds.
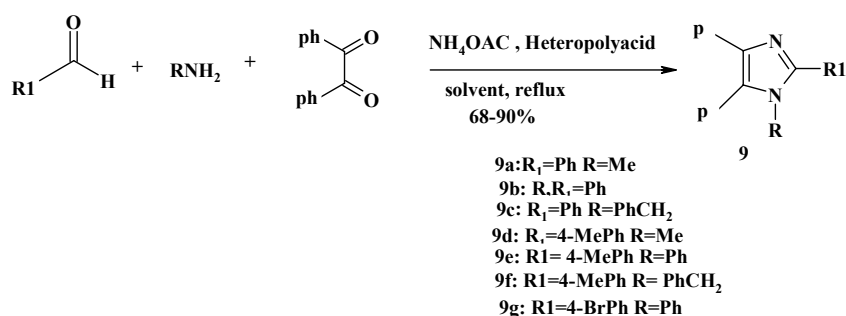
Synthesis of benzimidazole derivatives **7a-7d** by cyclization of *ortho*-phenylenediamine (*o*-PDA) and acyl chlorides in the presence of a catalytic amount of various type of HPAs including, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$], H$_4$[PMo$_{11}$VO$_{40}$], H$_5$[PMo$_{10}$V$_2$O$_{40}$] and H$_6$[P$_2$W$_{18}$O$_{62}$] has been reported

(Scheme 5) [32].

The Keggin heteropolyacid, silicotungstic acid (STA), H$_4$SiW$_{12}$O$_{40}$, has been demonstrated to be highly efficient for an expeditious, one-pot synthesis of 1-methyl-2 (hetero)arylbenzimidazoles (**8a-8r**) from N-methyl-1,2-phenylenediamine and (hetero)aryl aldehydes in ethyl acetate at room temperature (Scheme 6). The catalyst worked equally

Table 4. Synthesis of 1-Methyl-2-(Hetero)arylbenzimidazoles from 1a Using STA as Catalyst

Entry	2R/R'/R''/X	%mol of STA	Product	Time (min)	Yield (%)
1	a: R=R' =R'' =H	5	a	30	73
2	b: R=NO$_2$; R' =R'' =H	2	b	5	99
3	c: R=R'' =H; R' =NO$_2$	2	c	5	92
4	d: R=R'=H; R'' =NO$_2$	2	d	5	95
5	e: R=R'=H; R'' =CN	2	e	15	90
6	f: R=R' =H; R'' =Me	2	f	30	95
7	g: R=R' =H; R'' =Cl	2	g	20	99
8	h: R=R' =H; R'' = Br	2	h	30	99
9	i: R = OH; R' =R =H	5	i	30	62
10	j: R=R' =H; R'' =OH	5	j[a]	30	78
11	k: R=R' =H; R'' =OMe	5	k	60	80
12	l: R=H; R',R'' =OCH$_2$O	5	l[a]	30	74
13	m: R=H; R'=R'' =OMe	5	m[a]	30	61
14	n: R=H; R' =OMe; R''=OH	5	n[a]	30	60
15	o: X = S	5	o	30	80
16	p: X=NH	5	p	30	79
17	q: X=O	5	q	30	65
18	r: R=R' =H; R'' =NMe$_2$	5	r[a]	30	52

[a]New compounds.

9a: R$_1$=Ph R=Me
9b: R,R$_1$=Ph
9c: R$_1$=Ph R=PhCH$_2$
9d: R,=4-MePh R=Me
9e: R1= 4-MePh R=Ph
9f: R1=4-MePh R= PhCH$_2$
9g: R1=4-BrPh R=Ph

Scheme 7

well for *N*-phenyl-1,2-phenylenediamine (Table 4) [33].

The four-component condensation of benzil, benzaldehyde derivatives, primary amines and ammonium acetate catalyzed by Keggin heteropolyacids such as H$_3$[PW$_{12}$O$_{40}$], H$_4$[SiW$_{12}$O$_{40}$], H$_3$[PMo$_{12}$O$_{40}$], H$_4$[PMo$_{11}$VO$_{40}$], HNa$_2$[PMo$_{12}$O$_{40}$] as an efficient and facile one-pot synthesis of tetrasubstituted imidazoles (**9a-9g**) has been successfully

performed (Scheme 7) [34].

It was shown that Keggin-type heteropolyacid H$_4$[PMo$_{11}$VO$_{40}$] is a highly efficient solid acid catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles. The catalyst could be reused after a simple work-up, with a gradual decline of its activity being observed. The reaction appeared to be heterogeneously catalyzed. High yields, relatively short
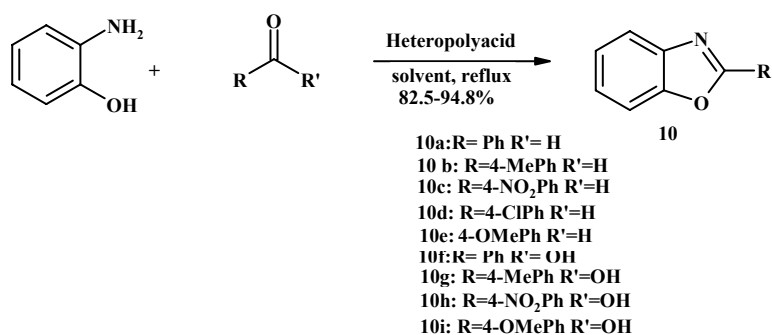
Scheme 8

reaction times, simplicity of operation and easy work-up were some advantages of this protocol.

Synthesis of 2-Arylbenzoxazoles

The use of three Keggin type of HPAs including, $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$ and $H_3[PMo_{12}O_{40}]$ in the synthesis benzoxazole derivatives (**10a-10i**) from reaction of 2-aminophenol with benzaldehydes and benzoic acids and the effects of reaction parameters such as the type, amount of HPA and solvent on the yield of reaction has been recently reported (Scheme 8) [35].

Comparison of these two methods for the synthesis of benzoxazole derivatives showed that condensation of 2-aminophenol with benzoic acids using heteropolyacids under refluxing condition led to better yields than benzaldehydes. In addition, higher amount of heteropolyacid and more reaction time was required for the latter.

Synthesis of Isoxazole Derivatives

Heteropolyanions with different structures, including keggin, dawson, preyssler, mixed addenda, and sandwich types, catalysed the formation of 1,3-diphenyl-isoxazole (**11**) from the condensation of 1,3-diphenyl-propane-1,3-dione and hydroxylamine hydrochloride in different solvents and under heating conditions. The data indicated that $H_3PW_{11}CuO_{40}$ was the catalyst of choice and could catalyze the synthesis of other isoxazole derivatives in high yields and good selectivities (Scheme 9) [36].

Quinoline Derivatives

Dihydroquinoline moiety is found in a wide variety of
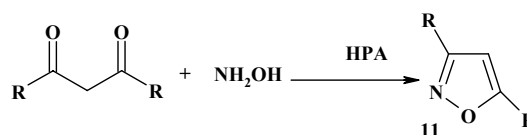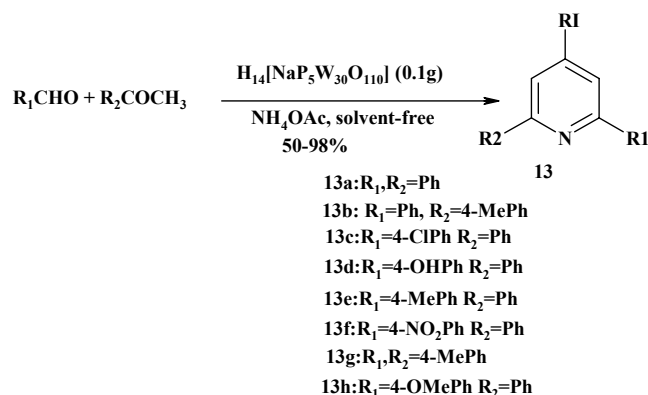

Scheme 9
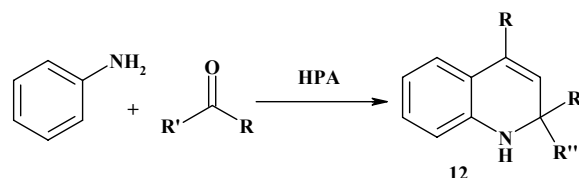
Scheme 10

natural products and they have attracted a lot of attention from synthetic organic chemists [37]. They form the parent bicyclic system for an extensive array of medicinally interesting compounds. Substituted dihydroquinolines have been used to produce potent drugs with bactericidal, anti-malarial and anti-inflammatory properties [38].

Substituted 2,2,4-dihydroquinolines (**12**) have been synthesized in good yields from anilines and acetone and methyl ethyl ketone using silicotungstic acid as the catalyst. It was observed that acetonitrile was the best solvent in promoting the reaction (Scheme 10). The optimum catalyst amount for achieving very good yields was found to be five percent. The reactions were clean and the products isolated with minimal work-up. The reaction yields were found to be higher for anilines with electron withdrawing groups (Table 5) [39].

Table 5. Synthesis of 2,2,4-Substituted Dihydroquinolines

Entry	Substrate	Ketone	Time (h)	Yield (%)
1	aniline	Acetone	6	84
2	3-Chloro-aniline	Acetone	4	94
3	4-Nitro-aniline	Acetone	6	89
4	4-Methoxy-aniline	Acetone	8	80
5	Aniline	Butan-2-one	7	83
6	3-Chloro-aniline	Butan-2-one	5	90
7	4-Nitro-aniline	Butan-2-one	7	87
8	4-Methoxy-aniline	Butan-2-one	10	77

$$R_1CHO + R_2COCH_3 \xrightarrow[\substack{NH_4OAc, \text{ solvent-free} \\ 50\text{-}98\%}]{H_{14}[NaP_5W_{30}O_{110}] \ (0.1g)} \mathbf{13}$$

13a: R_1,R_2=Ph
13b: R_1=Ph, R_2=4-MePh
13c: R_1=4-ClPh R_2=Ph
13d: R_1=4-OHPh R_2=Ph
13e: R_1=4-MePh R_2=Ph
13f: R_1=4-NO$_2$Ph R_2=Ph
13g: R_1,R_2=4-MePh
13h: R_1=4-OMePh R_2=Ph

Scheme 11

2,4,6-Triarylpyridines

The pyridine ring system is present in various natural products, and many pyridine derivatives exhibit a broad range of biological activities [40]. Due to their p-stocking ability, some pyridines are used in supramolecular chemistry [41]. These compounds have also been evoked considerable attention in recent years as these endowed with wide range of pharmaceutical activities such as antimalarial, vasodilator, anesthetic, anticovulsant, and antiepileptic and agrochemicals such as fungicidal, pesticidial and herbicidal [42].

Preyssler type heteropolyacid was found to be an efficient catalyst for the synthesis of biological significant, 2,4,6-triarylpyridines(**13a-13h**) in good yields (Scheme 11) [43]. The used method had several advantages including mild conditions, excellent yields, use of inexpensive, recyclable and reusable catalyst, utilizing cheap and available ammonium source, simple operation and work-up. Additionally, the protocol did not require volatile and hazardous organic solvents. The elimination of the solvents had obvious environmental benefits in regard to the depletion of solvent waste; the simplicity and efficiency of the overall process.

1,4-Dihydropyridyl Derivatives

In recent years, an increasing interest has been focused on the synthesis of 1,4-dihydropyridyl compounds owing to their significant biological activities [44]. In particular, dihydropyridine drugs such as nifedipine, nicardipine and amlodipine are effective cardiovascular agents for the treatment of hypertension [45].

In view of the importance of polyhydroquinoline derivatives, many classical methods for the synthesis of polyhydroquinoline derivatives were reported [46].
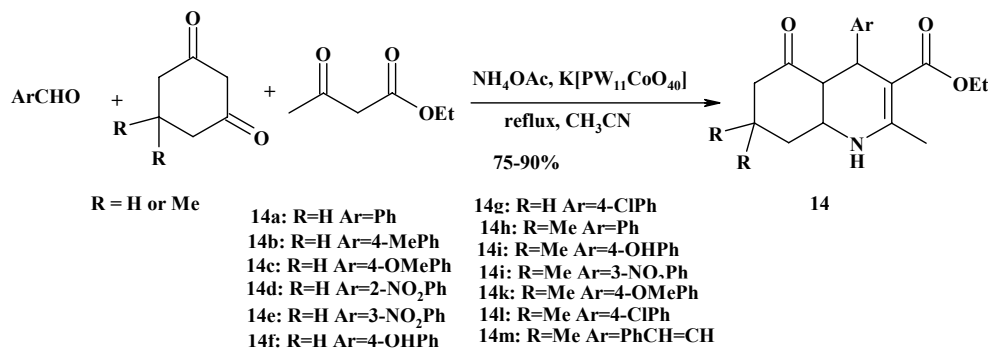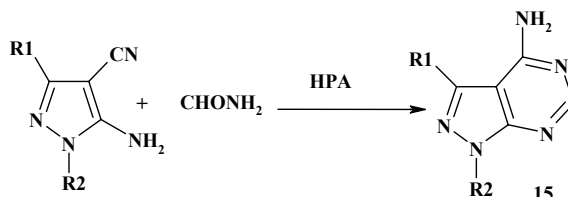
Scheme 12

Scheme 13

An easy and efficient method to prepare a variety of 1,4-dihydroquinoline derivatives (**14a-14m**) from the reaction of different aryl aldehydes, 1,3-cyclohexanediones, ethyl acetoacetate and ammonium acetate in the presence of catalytic amount of $K_7[PW_{11}CoO_{40}]$ under reflux condition as a clean, general and inexpensive reaction has been successfully developed. Relatively short reaction times, very simple performance and work-up procedure, and high yields were some of advantages of this procedure. The catalyst was recyclable and could be reused without significant loss of activity. $K_7[PW_{11}CoO_{40}]$ was also non-corrosive and environmentally benign and presents fewer disposal problems. The use of this solid acid catalyst allowed replacement of the usual soluble inorganic acids, contributing in this way to the reduction wastes (Scheme 12) [47].

4-Amino-Pyrazolo[3,4-d]pyrimidine

The adenine analogues, 4-amino-pyrazolo[3,4-d]pyrimidines have proved to affect nucleotide synthesis in two different ways. It can either bind to adenine phosphoribosyl transfers, an enzyme responsible for the transfer of phosphoribosyl group from pp-ribose-p to exogenous purine [48], or it can inhibit purine synthesis de novo (from nonpurine components) [49]. Inhibition of purine

synthesis de nove has been considered as the cause of the cytotoxic activity of 4-APP.

Various heteropolyacids such as $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}/SiO_2$ have been used for the synthesis of 4-amino-pyrazolo[3,4-d]pyrimidine derivatives (**15**) from the reaction of 1-substituted-5-amino-4-cyano-pyrazoles and formamid under classical heating and microwave irradiation (Scheme 13) [50]. The microwave-solid acid combination, led to a nice and convenient catalytic synthesis of 4-aminopyrazolo[3,4-d]pyrimidines with much reduced reaction times compared to traditional conditions. Among the above catalysts, heteropolyacid, $H_3PW_{12}O_{40}$ showed the best catalytic activity in term of yields and reaction times (Tables 6 and 7).

Synthesis of Biginelli-Type 3,4-Dihydropyrimidine-2(1H)-ones

The Biginelli's reaction consists in the condensation of an aldehyde, a beta-ketoester and urea in the presence of an acid catalyst [51]. However, this reaction suffers from the requirements of harsh conditions, long reaction times and frequently low yields. 3,4-Dihydropyrimidin-2(1H)-ones are interesting compounds and play an important role in synthetic, therapeutic and bioorganic chemistry [52].
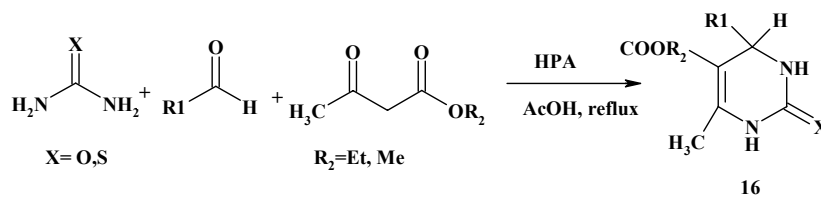
A catalytic method for the synthesis of Biginelli-type 3,4-

Table 6. Catalytic Synthesis of 4-Amino[3,4-d]pyrimidines under Microwave Irradiation (1000 W)

Entry	R1	R2	Time (min)	Percentage yield of product		
				$H_3PW_{12}O_{40}$	$H_3PMo_{12}O_{40}$	$H_3PW_{12}O_{40}/SiO_2$
1	H	Me	12	71	66	59
2	H	Me	10	88	68	61
3	H	2,4-Dinitrophenyl	10	72	61	62
4	Me	Me	12	88	72	58
5	Me	Ph	8	81	77	63

Table 7. Catalytic Synthesis of 4-Amino[3,4-d]pyrimidines in Acetic Acid under Thermal Conditions

Entry	R1	R2	Time (h)	Percentage yield of product		
				$H_3PW_{12}O_{40}$	$H_3PMo_{12}O_{40}$	$H_3PW_{12}O_{40}/SiO_2$
1	H	Me	6	63	35	46
2	H	Me	5	82	58	53
3	H	2,4-Dinitrophenyl	8	44	26	29
4	Me	Me	7	59	40	45
5	Me	Ph	6	75	45	63

Scheme 14

dihydropyrimidin-2(H)-ones (**16**) using $H_3PMo_{12}O_{40}$ as an efficient, reusable and eco friendly heterogeneous inorganic catalyst has been reported (Scheme 14). It is noteworthy to mention that the catalyst was reusable. Even after 3-5 runs for the Biginelli reaction, the catalytic activity of $H_3PMo_{12}O_{40}$ was almost the same as that of the freshly used catalyst. $H_3PMo_{12}O_{40}$ is non-corrosive and environmentally benign and presents fewer disposal problems (Ttable 8) [53].

12-Tungstophosphoric acid as a recyclable catalyst was also used for synthesis of 3,4-dihydropyrimidin-2(1H)-one by a one-pot three-component cyclocondensation. It was estableshed that this catalyst was efficient and cost effective for this reaction [54].
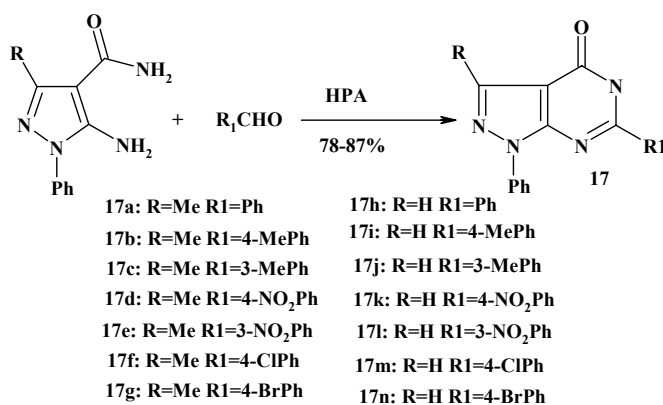
Synthesis of 6-Aryl-1H-Pyrazolo[3,4-d]pyrimidin-4[5H]-ones

Pyrazolo[3,4-d]pyrimidines are of considerable chemical and pharmacological importance as purine analogues [55]. Various compounds with related structures also posses antitumor and anti-leukemia activities [56]. Therefore,

Table 8. Biginelli Reaction Using $H_3PMo_{12}O_{40}$

Entry	R1	R2	X	Time (min)	Yield (%)[a]
1	ph	Et	O	5	80
2	4-Meph	Et	O	4	75
3	4-OMeph	Et	O	4	70
4	4-Clph	Et	O	6	80
5	4-Brph	Et	O	6	65
6	4-Meph	Et	O	4.5	67
7	2-NO$_2$ph	Et	O	6	72
8	3-NO$_2$ph	Et	O	7	70
9	4-NO$_2$ph	Et	O	5	60
10	2-furyl-	Et	S	4	57
11	ph	Et	S	4	50
12	4-OMeph	Me	O	5	65
13	4-Clph	Me	O	5.5	70
14	3-NO$_2$ph	Me	O	5	60

[a]Yields refer to the isolated pure products.

17a: R=Me R1=Ph
17b: R=Me R1=4-MePh
17c: R=Me R1=3-MePh
17d: R=Me R1=4-NO$_2$Ph
17e: R=Me R1=3-NO$_2$Ph
17f: R=Me R1=4-ClPh
17g: R=Me R1=4-BrPh

17h: R=H R1=Ph
17i: R=H R1=4-MePh
17j: R=H R1=3-MePh
17k: R=H R1=4-NO$_2$Ph
17l: R=H R1=3-NO$_2$Ph
17m: R=H R1=4-ClPh
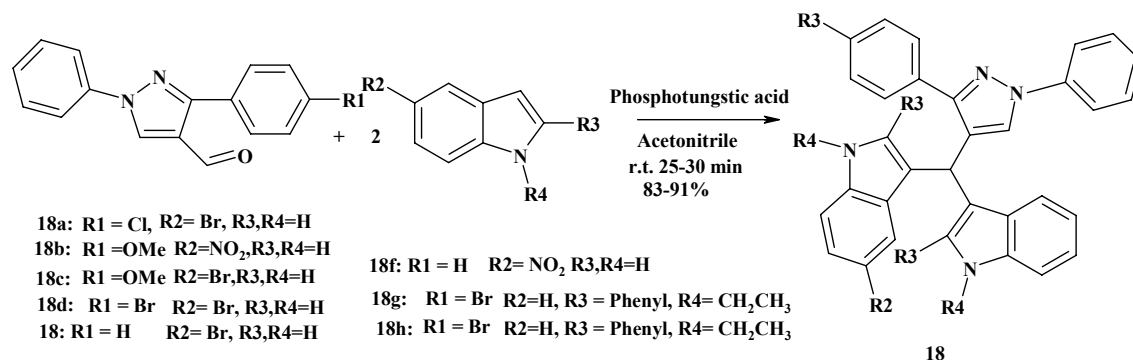17n: R=H R1=4-BrPh

Scheme 15

investigation about new methods and synthesis of new derivatives of these compounds attracted considerable amount of interest.
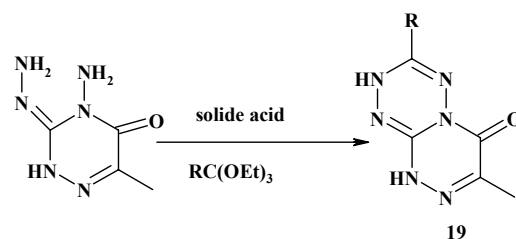
Reaction of 5-amino-1-phenyl-1H-pyrazolo-4-carboxamide with aromatic aldehyde in the presence of heteropolyacids, $H_3PW_{12}O_{40}$ and $H_{14}[NaP_5W_{30}MoO_{110}]$ gave derivatives of 6-aryl-1H-pyrazolo[3,4-d]pyrimidin-4[5H]-ones (**17a-17n**) (Scheme 15). It was confirmed that heteropolyacid with Preyssler structure shows higher activity and yields due to the higher number of acidic protons [57].

Synthesis and Anti-Microbial Activity of Pyrazolylbisindoles

A series of pyrazolylbisindole derivatives (**18a-18h**) have been synthesized by reacting substituted pyrazole aldehydes with substituted indoles using phosphotungstic acid, a Keggin type heteropoly acid as catalyst. The synthesized pyrazolylbisindoles were evaluated for anti-microbial activities. The effect of pyrazolylbisindoles on the mycelial growth of plant pathogenic fungi was revealed (Scheme 16) [58].

Scheme 16

18a: R1 = Cl, R2= Br, R3,R4=H
18b: R1 =OMe R2=NO₂,R3,R4=H
18c: R1 =OMe R2=Br,R3,R4=H
18d: R1 = Br R2= Br, R3,R4=H
18: R1 = H R2= Br, R3,R4=H

18f: R1 = H R2= NO₂ R3,R4=H
18g: R1 = Br R2=H, R3 = Phenyl, R4= CH₂CH₃
18h: R1 = Br R2=H, R3 = Phenyl, R4= CH₂CH₃

Scheme 17

Synthesis of [1,2,4]triazino[4,3-b][1,2,4,5]tetrazines

Triazino-terazines are a class of heterocyclic systems, which have not received much attention. Literature survey showed only few methods for the synthesis of [1,2,4]triazino[1,2,4,5]terazine system [59,60].

Catalytic performance of Preyssler, $H_{14}[NaP_5W_{30}O_{110}]$, and Keggin, $H_3[PW_{12}O_{40}]$, heteropolyacids as pure and supported on silica, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, $H_3[PW_{12}O_{40}]/SiO_2$, have been studied in cyclocondensation of 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5(2H)-one (4-AHMT) with orthoesters for synthesis of **19**. The catalytic activity of various forms of these catalysts in different solvents was compared with other classical catalysts, such as H_2SO_4 and HY-zeolite. In all cases the best yields were obtained, using $H_{14}[NaP_5W_{30}O_{110}]$ (Scheme 17) [61].

Synthesis of Quinoxaline

Well-Dawson heteropoly acid was used as an effective catalyst for the synthesis of biologically active quinoxaline derivatives (**20a-20k**) from the condensation of 1,2-dicarbonyl compounds with *o*-phenylenediamine at room temperature in excellent yields (Scheme 18) [62].

The optimum yield of the products was obtained when 1 mol% of catalyst was used. Among the solvents tested for this

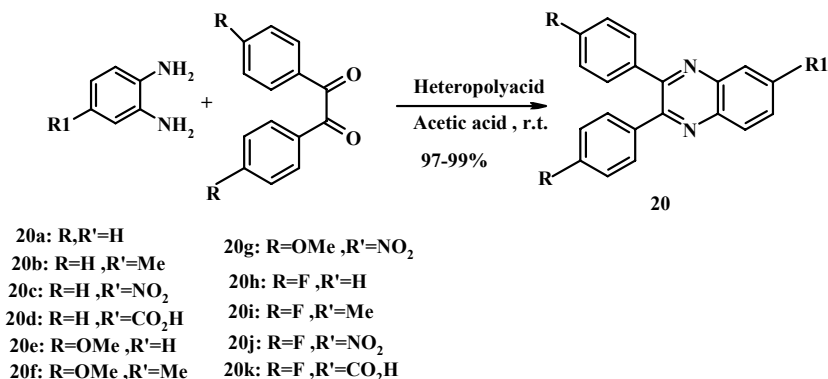reaction including CHCl₃, CH₃CN, H₂O and AcOH, the latter was found to be most efficient.

Synthesis of 1,5-Benzodiazepine Derivatives

Benzodiazepines and their polycyclic derivatives are a very important class of bio-active compounds. They are finding numerous new applications and are widely used as anticonvulsant, anti-inflammatory, analgesic, hypnotic, sedative and anti-depressive agents [63]. Benzodiazepines are also valuable intermediates for synthesis of fused ring compounds such as triazolo, oxadiazolo-, oxazino-, and furano-benzodiazepines [64].
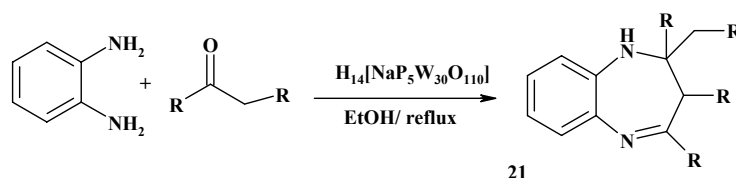
Recently a convenient and efficient protocol for the synthesis of 2,3-dihydro-1,5-benzodiazepines (**21**) via condensation of *o*-phenylenediamine derivatives with a variety of ketones using, $H_{14}[NaP_5W_{30}O_{110}]$ as a green recyclable and heterogeneous catalyst has been developed (Scheme19) [65]. The simple experiment procedure combined with ease of recovery and reuses of this catalyst made this procedure quite simple, more convenient and environmentally benign (Table 9).

A simple method for the condensation of *o*-phenylenediamines (*o*-PDA) with 1,3-diketones using catalytic amount of different type of HPAs including,

20a: R,R'=H
20b: R=H ,R'=Me
20c: R=H ,R'=NO$_2$
20d: R=H ,R'=CO$_2$H
20e: R=OMe ,R'=H
20f: R=OMe ,R'=Me

20g: R=OMe ,R'=NO$_2$
20h: R=F ,R'=H
20i: R=F ,R'=Me
20j: R=F ,R'=NO$_2$
20k: R=F ,R'=CO$_2$H

Scheme 18

Scheme 19

Table 9. H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] Catalyzed Synthesis of 1,5-Benzodiazepines in Ethanol at 78 ºC

Entry	Diamine	Ketone	Time (min)	Yield (%)[a]
1	*o*-phenylenediamine	Acetone[b]	75	92
2	*o*-phenylenediamine	2-Butanone	60	94
3	*o*-phenylenediamine	Cyclohexanone	120	95
4	*o*-phenylenediamine	Acetophenone	75	92
5	*o*-phenylenediamine	4'-Methyl acetophenone	60	89
6	*o*-phenylenediamine	4'-Hydroxy acetophenone	105	85
7	*o*-phenylenediamine	4'-Nitro acetophenone	100	84
8	4-Methyl-*o*-phenylenediamine	Acetone[b]	60	95
9	4-Nitro-*o*-phenylenediamine	Acetone[b]	90	94
10	4-Nitro-*o*-phenylenediamine	Cyclohexanone	3	80

[a]Yields are analyzed by GC. [b]The reactions are carried out in refluxing acetone as solvent.
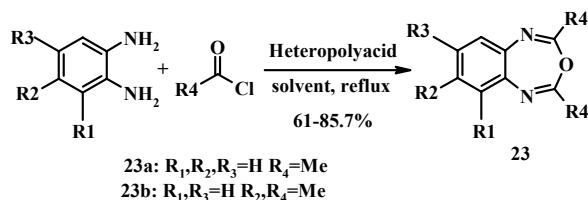
H$_{14}$[NaP$_5$W$_{30}$O$_{110}$], H$_5$[PMo$_{10}$V$_2$O$_{40}$], and H$_6$[P$_2$W$_{18}$O$_{62}$] as the catalyst to synthesize 3H-1,5-benzodiazepines (**22a-22e**) has been reported [66]. The results indicated that the nature of the catalyst played an important role on their catalytic activities. The highest yield of products has been achieved in the presence of H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] as catalyst, and H$_5$[PMo$_{10}$V$_2$O$_{40}$] gave lowest yields (Scheme 20).

Synthesis of 3,1, 5-Benzoxadiazepines

Recently the result of a study on the use of three type of heteropolyacids including Preyssler, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$], Keggin, H$_4$[PMo$_{11}$VO$_{40}$] and Wells-Dawson, H$_6$[P$_2$W$_{18}$O$_{62}$] in the synthesis of 3,1,5-benzoxadiazepines (**23a-23b**) from the condensation of phenylenediamine(*o*-PDA) and acyl chlorides has been reported. The effects of reaction parameters such as
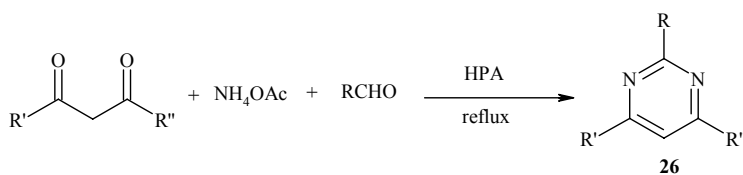
22a: R'=H R=Me
22b: R'=Me R=Me
22c: R'=NO, R=Me
22d: R'=H R=Ph
22e: R'=Me R=Ph

Scheme 20

23a: R$_1$,R$_2$,R$_3$=H R$_4$=Me
23b: R$_1$,R$_3$=H R$_2$,R$_4$=Me
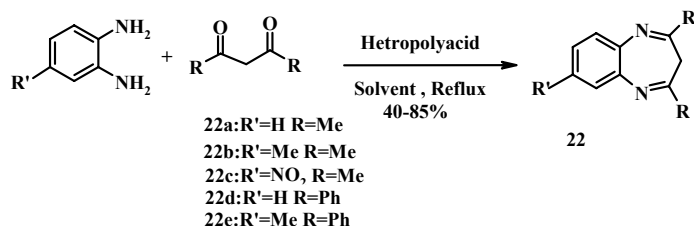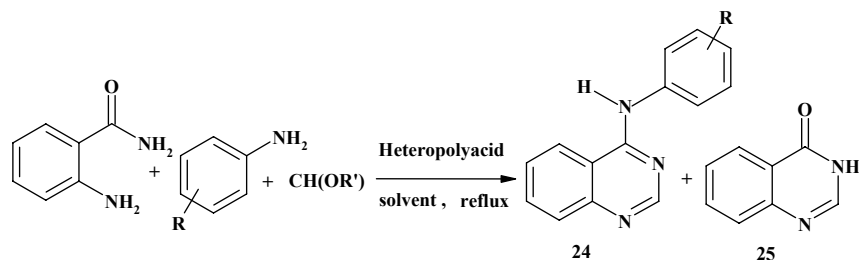
Scheme 21

Scheme 22

Scheme 23

the type of HPA, temperature and reaction times on the yield of reactions have also been studied (Scheme 21) [67].

Synthesis of 4-Arylaminoquinazolines

Recently Keggin type heteropolyacids including H$_6$[PMo$_9$V$_3$O$_{40}$], H$_5$[PMo$_{10}$V$_2$O$_{40}$], H$_4$[PMo$_{11}$VO$_{40}$] and H$_3$[PMo$_{12}$O$_{40}$] have been used for multi-component synthesis of 4-arylaminoquinazolines **24** from the reaction of 2-aminobenzamide, orthoesters and substituted anilines. In all reactions **25** was obtained as by product in low yield. The effects of reaction conditions and different heteropolyacids have been studied. It has been proved that Keggin type

heteropolyacids are efficient, reusable and eco-friendly heterogeneous inorganic catalysts. The advantages of this method are the easy work-up procedure and high yields of products (Scheme 22) [68].

Synthesis of Pyrimidines

Pyrimidines **26** are synthesized via a one-pot, three-component, reaction between a 1,3-diketone, benzaldehydes and ammonium acetate in the presence of catalytic amounts of Keggin-type heteropolyacids, including H$_6$[PMo$_9$V$_3$O$_{40}$], H$_5$[PMo$_{10}$V$_2$O$_{40}$], H$_4$[PMo$_{11}$VO$_{40}$] and H$_3$[PMo$_{12}$O$_{40}$] under refluxing condition in good yields (Scheme 23) [69].

R= H, Br, CN
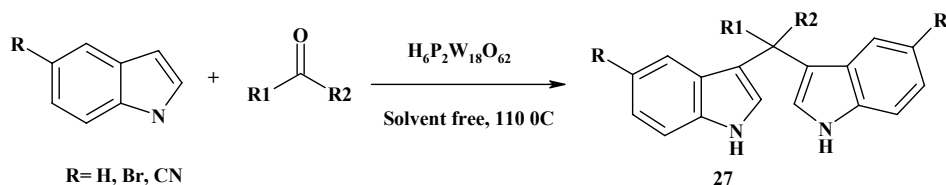
Scheme 24

Table 10. Solvent-Free Synthesis of Bis(indolyl)methane Derivatives Catalyzed by Diphosphooctadecatungstic Acid

Entry	Aldehyde	R	Time (min)	Yield (%)[a]
1	C_6H_5CHO	H	40	96
2	$4\text{-}ClC_6H_4CHO$	H	25	98
3	$4\text{-}NO_2C_6H_4\ CHO$	H	15	98
4	$3\text{-}NO_2C_6H_4\ CHO$	H	25	98
5	$4\text{-}MeOC_6H_4CHO$	H	20	95
6	$2\text{-}MeOC_6H_4CHO$	H	30	94
7	$4\text{-}MeC_6H_4\ CHO$	H	40	97
8	$4\text{-}OHC_6H_4\ CHO$	H	25	95
9	$C_6H_5CH{=}CHCO$	H	150	45
10	Cyclohexanone	H	70	60
11	C_6H_5CHO	CN	50	90
12	$4\text{-}NO_2C_6H_4\ CHO$	CN	60	90
13	$4\text{-}MeOC_6H_4CHO$	CN	65	80
14	Cyclohexanone	CN	90	70
15	C_6H_5CHO	Br	25	95
16	$4\text{-}NO_2C_6H_4\ CHO$	Br	95	94
17	$3\text{-}NO_2C_6H_4\ CHO$	Br	50	90

[a]Yields refer to isolated products

CONDENSATION REACTIONS

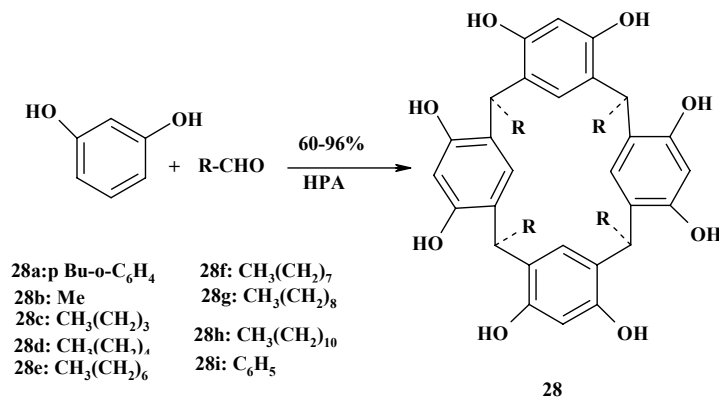### Synthesis of Bis(indolyl)methanes

A simple, efficient and convenient procedure for the synthesis of bis(indolyl)methane derivatives (**27**) under solvent-free conditions in the presence of a catalytic amount of Wells-Dawson type heteropolyacid has been developed (Scheme 24). Some advantages of this procedure are: the experimental simplicity and the easy work-up procedure use of a green, easy to handle and reusable catalyst, high yields, and absence of volatile and hazardous solvents. Moreover, there is no need for dry solvents or protecting gas atmospheres (Table 10) [70].

Synthesis of Calix[4]resorcinarenes

Interest in the chemistry of calixarenes has increased in recent years. Of particular significance has been the preparation of a range of calix[4]resorcinarene derivatives in high yields [71]. Self-assembled monolayers of resorcinarene derivatives on gold surfaces provide an important starting point for fabricating and operating nanoscale devices for advanced information technologies. Resorcinarene derivatives have also been used as stationary phase in achiral capillary gas chromatography for the separation of positional isomers of

28a:p Bu-o-C$_6$H$_4$ 28f: CH$_3$(CH$_2$)$_7$
28b: Me   28g: CH$_3$(CH$_2$)$_8$
28c: CH$_3$(CH$_2$)$_3$
28d: CH$_3$(CH$_2$)$_4$ 28h: CH$_3$(CH$_2$)$_{10}$
28e: CH$_3$(CH$_2$)$_6$ 28i: C$_6$H$_5$

Scheme 25

29a:R=H R'=Ph
29b:R=H R'=p-OMe
29c:R=H R'=o-OMe
29d:R=Me R'=Ph
29e:R=Me R'=p-OMe
29f:R=Me R'=o-OMe
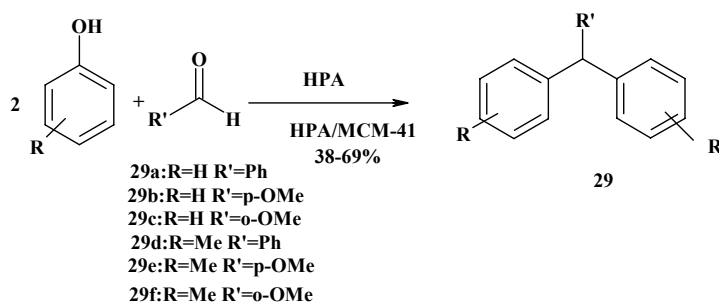
Scheme 26

substituted benzenes [72].

Microwave-assisted synthesis of calix[4]resorcinarenes by cyclocondensation of various aldehydes (**28a-28i**) and resorcinol catalysed by 12-tungstophosphoric acid type Keggin (H$_3$PW$_{12}$O$_{40}$.13H$_2$O) or concentrated HCl has been performed. Excellent isolated yields (up to 90%) were attained within short reaction times (typically, 3-5 min) when the reaction was performed under microwaves irradiation (Scheme 25) [73].

Bisphenol Synthesis

Bisphenol is an important chemical intermediate for the preparation of industrially important epoxy resins and polycarbonates that are used in molding, casting, sealing, coating, encapsulating, adhesives and laminating, in the preparation of reinforced plastics and other chemical materials [74].

Bisphenol synthesis is probably the second most important industrial process based on resin catalysts, the first being the synthesis of methyl tert-butyl ether (MTBE). Sumoto et al. reported that most of the compounds showed significant antiviral activity [75].
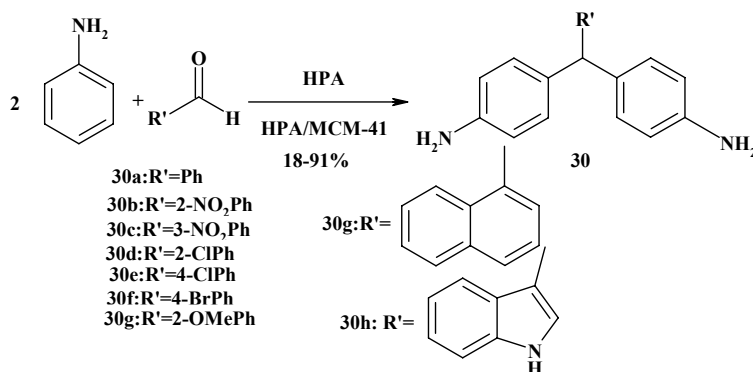
The most common method of bisphenol synthesis is the condensation of a ketone or aldehyde with phenol in the presence of an acidic condensing agent.

As the MCM-41 is known to be a type of mesoporous silica with a very high surface area and hence, is expected to be a suitable supporting material, particularly for the transformation and/or preparation of larger molecules. The HPA was impregnated into Si-MCM-41 material to prepare supported Keggin heteropolyacid (HPA or H$_3$PW$_{12}$O$_{40}$) catalysts [76].

Liquid-phase bisphenol derivatives (**29a-29f**) synthesis from phenolic compounds using aldehydes condensation reaction has been investigated over heteropolyacid (HPA) and supported HPA catalysts, with various percentage of impregnation (Scheme 26).

HPA showed better activity than the supported HPA

30a:R'=Ph
30b:R'=2-NO$_2$Ph
30c:R'=3-NO$_2$Ph
30d:R'=2-ClPh
30e:R'=4-ClPh
30f:R'=4-BrPh
30g:R'=2-OMePh

30g:R'=

30h: R'=

Scheme 27

catalyst. The acidity of the catalyst increased with increase in HPA loading; the pore size and pore diameter decreased with increase in HPA loading on the sample. Reusability of the catalyst also showed that HPA and supported catalyst were better catalysts for the commercial processes. The steric hinderance played an important role in the yield of bisphenol. The donating group present in the aldehyde influenced the yield. This work illustrated some specific properties of the HPA and the inorganic matricies containing HPA [76].

Condensation of Aromatic Aldehydes with Aniline: Synthesis of DATPM Derivatives

Triphenyl methane and its amino substituted derivatives are widely employed as dyes and as antifungal agents in commercial fish hatcheries. These compounds have also been employed as precursors in high performance polymer synthesis, in host-guest chemistry and in material science. Several DATPMs have been evaluated as copper corrosion inhibitors. DATPMs present a number of interesting structural properties in solid and solution that have been much studied. One of the most competitive industrial processes for the production of DATPMs is through acid-catalyzed condensation of aniline with aromatic aldehydes [77].

The mesoporous Si-MCM-41 was synthesized by hydrothermal method and various wt.% (20 and 30 wt.%) of HPW were loaded on Si-MCM-41 by wet impregnation method. The catalytic activity of the catalyst was tested over the condensation reaction of aniline with various aromatic aldehydes at refluxing temperature under liquid-phase condition, which yields highly commercial product namely diamino triphenyl methanes (DATPMs) **30a-30h** (Scheme 27).

The effects of various parameters like catalyst, mole ratio, solvent and substituent effect on the formation of DATPMs were optimized.

The catalytic activity of the catalysts has shown the following order: $H_3PW_{12}O_{40} \cdot nH_2O$ > $H_3PMo_{12}O_{40} \cdot nH_2O$ > $H_4SiW_{12}O_{40} \cdot nH_2O$ > 20 wt.% HPW/MCM-41 > 30 wt.% HPW/MCM-41 > HM > Hβ > HY > HZSM-5 > Al-MCM-41. The results showed that mole ratio of 4:1 (aniline:aldehyde) gave higher yield than the other mole ratios. Acetonitrile and ethyl acetate showed better activity especially in the case of supported materials than toluene when they were used as a solvent [77].
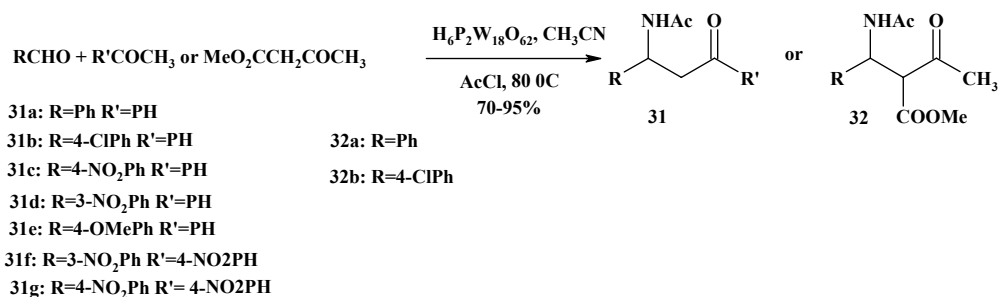
Synthesis of β-Acetamido Ketones and Esters

The β-acetamido carbonyl skeletons exist in a number of biologically or pharmalogically important compounds [78]. The best known route for the synthesis of these compounds is the Dakin-West reaction [79], which involves the condensation of an α-amino acid with acetic anhydride in the presence of a base *via* an azalactone intermediate [80].

An alternative and simple procedure for the synthesis of β-acetamido ketones/esters **31a-g**, **32a-32b** using Wells-Dawson heteropolyacid as an eco-friendly, reusable, inexpensive and efficient catalyst has been reported in literatures [81] (Scheme 28).

High yields, relatively short reaction times, simplicity of operation and easy work-up procedure were some advantages of this protocol.

In another related work the synthesis of β-acetamido ketones using trimethylsilyl chloride instead of acetyl chloride in the presence of a wide range of heteropolyacids, including:

17

RCHO + R'COCH$_3$ or MeO$_2$CCH$_2$COCH$_3$ $\xrightarrow[\substack{\text{AcCl, 80 0C} \\ \text{70-95\%}}]{\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}, \text{CH}_3\text{CN}}$

31a: R=Ph R'=PH
31b: R=4-ClPh R'=PH
31c: R=4-NO$_2$Ph R'=PH
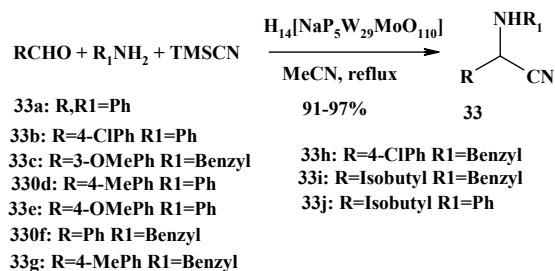**31d:** R=3-NO$_2$Ph R'=PH
31e: R=4-OMePh R'=PH
31f: R=3-NO$_2$Ph R'=4-NO2PH
31g: R=4-NO$_2$Ph R'= 4-NO2PH

32a: R=Ph
32b: R=4-ClPh

Scheme 28

Scheme 29

RCHO + R$_1$NH$_2$ + TMSCN $\xrightarrow[\substack{\text{MeCN, reflux} \\ \text{91-97\%}}]{\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]}$

33a: R,R1=Ph
33b: R=4-ClPh R1=Ph
33c: R=3-OMePh R1=Benzyl
330d: R=4-MePh R1=Ph
33e: R=4-OMePh R1=Ph
330f: R=Ph R1=Benzyl
33g: R=4-MePh R1=Benzyl

33h: R=4-ClPh R1=Benzyl
33i: R=Isobutyl R1=Benzyl
33j: R=Isobutyl R1=Ph

Scheme 30

Keggin, Wells-Dawson and Preyssler type has been succssesfully performed [82]. The proposed mechanism is shown in Scheme 29.

Synthesis of α-amino Nitriles

Synthesis of some α-amino nitriles **33a-33j** by nucleophilic addition reaction of aldehydes and amines with TMSCN in presence of a catalytic amount of H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] in excellent yields has been reported [83] (Scheme 30).
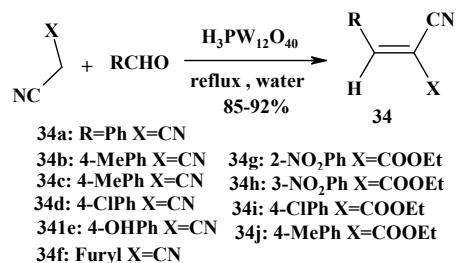
Recyclability of catalyst with no loss in its activity, simple experimental procedure and product isolation, use of nontoxic, noncrrosive and inexpensive catalyst were the feature of that new protocol to prepare α- amino nitriles.
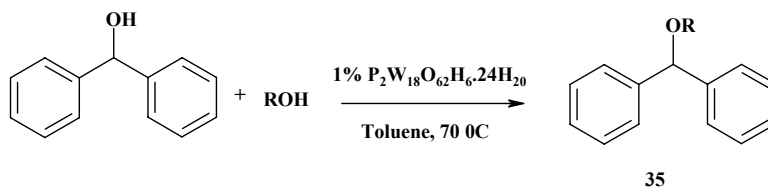
Knoevenagel Condensation

12-Tungstphosphoric acid was found to be an efficient,

environmentally attractive and reusable catalyst for knoevenagel condensation of malononitrile and ethylcyanoacetate with various aldehydes in refluxing condition for synthesis of **34a-34j** derivatives (Scheme 31) [84].

The effect of different solvents on this reaction was

$\xrightarrow[\substack{\text{reflux , water} \\ \text{85-92\%}}]{\text{H}_3\text{PW}_{12}\text{O}_{40}}$

34a: R=Ph X=CN
34b: 4-MePh X=CN
34c: 4-MePh X=CN
34d: 4-ClPh X=CN
341e: 4-OHPh X=CN
34f: Furyl X=CN

34g: 2-NO$_2$Ph X=COOEt
34h: 3-NO$_2$Ph X=COOEt
34i: 4-ClPh X=COOEt
34j: 4-MePh X=COOEt

Scheme 31

Scheme 32

Table 11. Preparation of DPM-Ethers from Alcohols and Phenols Using both Bulk and Silicasupported $P_2W_{18}O_{62}.24H_2O$

Entry	R	Time (h)	Yield (%) WD	Time (h)	Yield (%) WD40/SiO$_2$
1	Methanol	1[a]	93	1[a]	94(94,93)[d]
	Methanol	4[b]	78		
	Methanol	10[c]	-		
2	Isopropanol	1[a]	91	1[a]	85
3	n-Butanol	1	83	1	85
4	*Tert*-Butanol	1.5	87	1.5	86
5	Allylic Alcohol	1	89	1.5	89
6	Benzyl alcohol	0.5	84	0.5	83
7	2-Phenethylalcohol	1	81	1	81
8	Benzhydrol	1	95	0.5	96
9	Phenol	1	84	1	84(85,85)d
10	4-Methyl-phenol	1	85	1	85
11	3-Methyl-phenol	1	83	1	84
12	4-Nitro-phenol	1	81	1	80

[a]60 ºC; [b]40 ºC; [c]20 ºC; [d]In parentheses, yields obtained in the first and second reuse of the catalyst.

studied. The results estsblished that water was the best solvent for this reaction. The catalyst was reusable and could be used for at least three times.

PROTECTION REACTIONS

Preparation Diphenylmethyl (DPM) Ethers

An efficient and facile preparation of diphenylmethylethers (benzydryl ethers, DPM-ethers)(**35**) from benzhydrol and alcohols or phenols has been reported (Scheme 32). Wells-Dawson heteropolyacid (H$_6$P$_2$W$_{18}$O$_{62}$.24H$_2$O), bulk or supported on silica showed catalytic activity for DPM-ethers preparation in toluene, at 60-80 ºC, in 0.5-1.5 h. In these conditions twelve diphenylmethylethers of alcohols and phenol were obtained which excellent yields (78-96%). The heterogeneous reaction conditions provided a very simple, environmentally friendly, clean, economical and selective protocol, for the preparation of unsymmetrical ethers. The catalyst was easily recycled and reused without loss of the catalytic activity (Table 11) [85].

Acylation of Alcohols

The protection of alcoholic and phenolic hydroxyl group is an important transformation in organic synthesis [86]. Among the various protecting groups used for this purpose, acyl is one of the most common groups in view of its easy introduction, being stable to the acidic reaction conditions, and also easily removable by mild alkaline hydrolysis [87].

A rapid, efficient and environmentally benign catalytic method for the acylation of alcohols by Ac_2O in the presence of $H_5PV_2Mo_{10}O_{40}$ as a recyclable heterogeneous catalyst has been recently performed (Scheme 33). When the reaction was carried out without added solvent, benzylic and non-benzylic hydroxy groups could be efficiently converted into corresponding acetates (**36a-36r**). It is noteworthy to mention that the catalyst could be used for subsequent cycles of acylation without any loss of its catalytic activity. In contrast to many other acids, storage of this non-hygroscopic and non-corrosive solid HPA did not need special precautions, *e.g.*, it could be stored on a bench top for months without losing its catalytic activity [88].

Another catalytic method for acetylation of alcohols and phenols using $H_{14}[NaP_5W_{30}O_{110}]$ as an efficient, reusable and eco-friendly heterogeneous inorganic catalyst has been reported. The salient features of these reactions were, use of 1-1.5 equivalent of substrate to acetic anhydride and catalytic amounts of $H_{14}[NaP_5W_{30}O_{110}]$ which is concomitatant to solventless and catalytic nature of the reaction. High yields, working at room temperature and short reaction time with an easy workup procedure were other features of this reaction. The catalyst was also reusable after filtration and could be used at least five times without lose of appreciable catalytic activities (Scheme 34) [89].

Selective acetylation of alcohols and benzyl amines with ethyl acetate in presence of $H_6[PMo_9V_3O_{40}]$ (1 mol%) under refluxing condition has been performed. Phenols and anilines were not affected under the reaction conditions. Selective transformation of alcohols could be achieved in presence of phenole and aniline derivatives using this method (Scheme 35) [90].

The direct acetylation of alcohols, phenols to corresponding acetylated compounds and salicylic acid to acetylsalicylic acid has been performed. The major goal described in this method was the design and development of application for the heteropolyacids in industry. In order to extend the scope of this acetylation reaction, it was carried out on a variety of substrates using a typical procedure where (0.14-0.56 mol%) of heteropoly acids and 1-1.5 equivalent of substrate to acetic anhydride were added at room temperature. The general efficiency of this reaction was evident from the variety of hydroxyl compounds including primary, secondary,
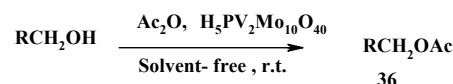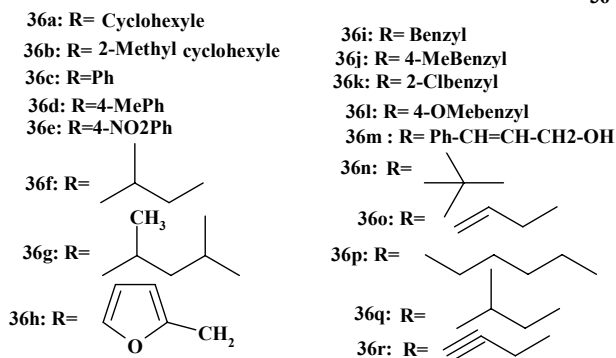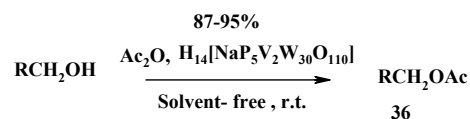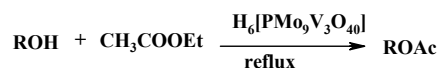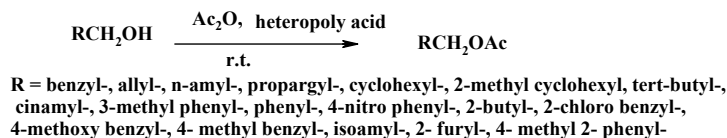
tertiary, benzylic alcohols and phenols, which reacted in excellent yields and relative short reaction times. Primary alcohols acetylated within less time than secondary and tertiary alcohols. In order to evaluate the merit and worthy of this procedure, 1,2-pentanediol was used as a starting material in the presence of Wells-Dowsen heteropolyacid ($H_6[P_2W_{18}O_{62}]$) and acetic anhydride under the same reaction condition. After 120 min, 2-hydroxypentyl acetate was only obtained. It is very interesting to note that tertiary and secondary alcohols such as t-butanol and 4-methyl-2-pentyl alcohol could also be acetylated with satisfactory yields and there was no elimination product in the mixture (Scheme 36) [91].

Acylation of Carbonyl Compounds

Acylal formation is one of the most widely used processes for protection of carbonyl compounds. Due to the remarkable

$$RCH_2OH \xrightarrow[\text{Solvent- free , r.t.}]{Ac_2O, \ H_5PV_2Mo_{10}O_{40}} RCH_2OAc$$

36

Scheme 33

87-95%

$$RCH_2OH \xrightarrow[\text{Solvent- free , r.t.}]{Ac_2O, \ H_{14}[NaP_5V_2W_{30}O_{110}]} RCH_2OAc$$

36

36a: R= Cyclohexyle
36b: R= 2-Methyl cyclohexyle
36c: R=Ph
36d: R=4-MePh
36e: R=4-NO2Ph
36f: R=
36g: R=
36h: R=

36i: R= Benzyl
36j: R= 4-MeBenzyl
36k: R= 2-Clbenzyl
36l: R= 4-OMebenzyl
36 m : R= Ph-CH=CH-CH2-OH
36n: R=
36o: R=
36p: R=
36q: R=
36r: R=

Scheme 34

$$ROH \ + \ CH_3COOEt \xrightarrow[\text{reflux}]{H_6[PMo_9V_3O_{40}]} ROAc$$

Scheme 35

$$RCH_2OH \xrightarrow[\text{r.t.}]{Ac_2O, \text{ heteropoly acid}} RCH_2OAc$$

R = benzyl-, allyl-, n-amyl-, propargyl-, cyclohexyl-, 2-methyl cyclohexyl, tert-butyl-, cinamyl-, 3-methyl phenyl-, phenyl-, 4-nitro phenyl-, 2-butyl-, 2-chloro benzyl-, 4-methoxy benzyl-, 4- methyl benzyl-, isoamyl-, 2- furyl-, 4- methyl 2- phenyl-
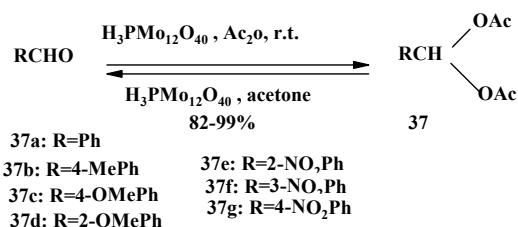
Scheme 36

stability of 1,1-diacetates, (acylals), toward a variety of reaction conditions, such as aqueous acids, neutral and basic media [92], synthesis of them is one of the method of choice to protect a carbonyl compound in multi-step organic synthesis. In addition, they can be used as building blocks for the synthesis of dienes for Diels-Alder cycloaddition reaction [93].

The use of $H_3PMo_{12}O_{40}$ as an inexpensive, reusable, easy to handle, non-corrosive and environmentally benign catalyst for the synthesis of 1,1-diacetates **37a-37g** from aromatics aldehydes and their deprotections has been developed (Scheme 37) [94]. The advantages of this procedure were simplicity of operation, the high yields of products, high selectivity and the recyclability of the catalyst. In this reaction, the catalyst could be recovered by filtration and washing with n-hexane, and subjected to a second or even another reaction. The recycled catalyst was used for five successive reactions without appreciable loss of activity.

In another related work, acylals were prepared from aliphatic and aromatic aldehydes using heteropolyacid (SiPW-8) encapsulated into the framework of mesoporous silica as catalysts in a solvent-free procedure. The catalyst was very effective and reusable for the production of 1,1-diacetates from aldehydes under a mild reaction condition (Table 12) [95].

Esterification

Esterification of acetic acid with butanol has been studied in a heterogeneous reaction system, using a variety of solid acid catalysts. Comparative esterification experiments have been carried out using the homogeneous catalysts sulphuric acid, polyoxometalates toluenesulphuric acid and a heteropolyacid. The catalysts have been characterised using gas adsorption analysis (BET), X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature-programmed decomposition (TPD) techniques. The weight-based activity of the heterogeneous catalysts decreased in the

$$RCHO \underset{\substack{H_3PMo_{12}O_{40}, \text{ acetone} \\ 82\text{-}99\%}}{\overset{H_3PMo_{12}O_{40}, Ac_2O, \text{ r.t.}}{\rightleftarrows}} RCH\genfrac{}{}{0pt}{}{OAc}{OAc}$$

37

37a: R=Ph
37b: R=4-MePh
37c: R=4-OMePh
37d: R=2-OMePh
37e: R=2-NO,Ph
37f: R=3-NO,Ph
37g: R=4-NO$_2$Ph

Scheme 37

Table 12. Deprotection of Acylals Using $H_3PMo_{12}O_{40}$

Entry	R	Time (min)	Yield (%)
1	C_6H_5-	40	98
2	4-Me-C_6H_4-	15	96
3	2-MeOC_6H_4-	22	94
4	4-MeOC_6H_4-	12	95
5	4-ClC_6H_4-	20	92
6	2-NO$_2C_6H_4$-	45[a]	96
7	3-NO$_2C_6H_4$-	25[a]	98
8	4-NO$_2C_6H_4$-	45[a]	94

[a]The reaction was carried out in refluxing acetone.

following order: Smopex-101 > Amberlyst 15 > sulphated ZrO_2 > H-USY-20 > H-BETA-12.5 > H-MOR-45 > Nb_2O_5 > H-ZSM-5-12.5. The low activity of ZSM-5 was a result of internal diffusion limitations in the medium sized pores of this zeolite type material. For H-MOR the low activity could be explained by pore blocking in the one dimensional H-MOR channels. For the H-USY-type zeolites, the influence of the Si/Al ratio on catalytic activity has been examined. Although the amount of acid sites decreases with an increase in the Si/Al ratio, an optimum Si/Al ratio of 20 has been found. The activity of sulphated zirconia showed an optimum calcination temperature, even though both the amount and acidity of the acid sites increased monotonically with calcination temperature. Most likely, at higher calcinations temperatures
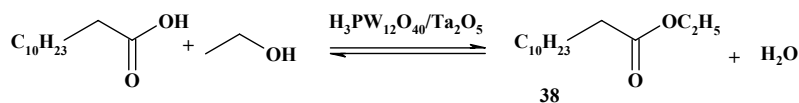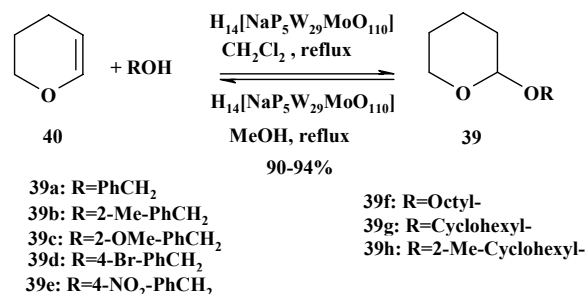
Scheme 38

Lewis acid sites were formed and Bronsted acid sites were removed. As Bronsted acid sites were essential for catalysis of esterification reactions this explaind the decrease in activity [96].

Mesoporous polyoxometalate-tantalum pentoxide composite catalyst, $H_3PW_{12}O_{40}/Ta_2O_5$, was prepared by a one-step sol-gel-hydrothermal method in the presence of triblock copolymer surfactant. Structure, morphology and surface textural property of the composite were characterized. As-prepared $H_3PW_{12}O_{40}/Ta_2O_5$ was applied as a solid acid catalyst for esterification reaction of lauric acid with ethanol, to give **38**. An important pretreatment step in the production of biodiesel from renewable feedstocks. Superiority of the $H_3PW_{12}O_{40}/Ta_2O_5$ was highly active and selective to the esterification reaction, in addition, it was environmentally friendly and catalytically stable with resistance to leaching of the Keggin unit into reaction media (Scheme 38) [97].

Direct esterification of butanol to butylbutanoate in the absence of butanoic acid has been investigated by a series of green solid acid catalysts, including $H_{14}[NaP_5W_{30}O_{110}]$, **$H_{14}$-$P_5$**, $H_{14}[NaP_5W_{29}MoO_{110}]$, **$H_{14}$-$P_5Mo$** and silica supported $H_{14}[NaP_5W_{30}O_{110}]$, **$H_{14}$-$P_5$/SiO$_2$**, with H_2O_2 as oxidizing agent at reflux and at room temperatures. The performance of these eco-friendly catalysts were compared with H_2SO_4. Maximum butylbutanoate yield and product selectivity (100%) was observed by using **H_{14}-P_5Mo** as the catalyst. The effects of various parameters such as catalyst type, reaction times, reaction temperatures, and molar ratio of *n*-butanol to hydrogen peroxide have been studied. The green catalysts could be easily recovered and recycled with retention of their initial structure and activity [98].

A series of eco-friendly solid acid catalysts, including $H_{14}[NaP_5W_{30}O_{110}]$, H_{14}-P_5, $H_{14}[NaP_5W_{29}MoO_{110}]$, H_{14}-P_5Mo, and silica supported $H_{14}[NaP_5W_{30}O_{110}]$, H_{14}-P_5/SiO$_2$ have been used as catalysts for esterification of salicylic acid with aliphatic alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, t-butanol, 1-pentanol, and 2-pentanol) and benzylic

Scheme 39

alcohols (benzyl, 2-methylbenzyl, 2-chlorobenzyl, 4-bromobenzyl, 3-nitrobenzyl, and 4-methoxy benzyl) alcohol. The performance of different forms of Preyssler's anion in the presence of dichloroethan as the solvent of choice was compared with H_2SO_4. In all cases, maximum of ester yields and product selectivity (100%) was observed by using H_{14}-P_5 as catalyst. The esterification reactions were extended with other aliphatic and aromatic acids [99].

Tetrahydropyranylation of Alcohols

Tetrahydropyranylation of alcohols and phenols and regeneration of THP ethers **39a-39h**, **40a-40h** using catalytic amount of $H_{14}[NaP_5W_{30}O_{110}]$ has been performed successfully (Scheme 39) [100]. For protection of alcohols, 3,4-dihydro-2H-pyran (DHP) and catalytic amount of catalyst has been reflux in CH_2Cl_2 to yield the corresponding THP ethers. THP ethers in metanole in presence of catalyst has been refluxed to afford corresponding alcohols and phenols

CARBON-CARBON BAND FORMATION AND CYCLOADDITION REACTIONS

[3+2] Cycloaddition of Azomethine Ylides

1,3-Dipolar cycloaddition reactions are efficient methods for the construction of heterocyclic units in a highly regio- and stereoselective manner [101]. In particular, the chemistry of

Table 13. $H_4[Si(W_3O_{10})_3]$ Catalyzed Cycloaddition Reactions

Entry	R	Method A		Method B		Method C		Method D	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	H	8.1	45	3.2	79	2.9	83	3.0	87
2	p-Cl	8.4	46	3.3	75	3.1	83	3.0	86
3	p-Me	9.5	43	3.6	78	3.4	81	3.2	87
4	p-OMe	9.5	42	3.6	79	3.4	84	3.2	87
5	p-NO$_2$	9.3	48	3.0	85	2.7	88	2.8	92
6	p-NMe$_2$	9.9	37	3.8	78	3.5	82	3.3	86
7	H	8.8	47	3.1	77	2.9	84	2.9	88
8	p-Cl	8.9	45	3.2	76	2.8	81	3.0	85
9	p-Me	9.0	43	3.3	75	3.0	84	2.3	86
10	p-OMe	9.6	46	3.6	78	3.1	82	3.2	88
11	H	8.7	42	3.0	75	2.7	81	2.8	86
12	p-Cl	8.9	46	3.2	80	2.8	83	2.8	88
13	p-Me	9.6	43	3.6	77	3.1	80	3.2	85
14	p-OMe	9.6	35	3.7	80	3.3	85	3.2	87
15	p-NMe$_2$	9.8	30	4.0	76	3.4	80	3.7	85
16	H	8.8	47	3.3	79	3.0	83	2.8	86
17	p-Cl	9.0	46	3.6	77	3.1	85	3.0	87
18	p-Me	8.9	40	3.8	74	3.2	80	3.3	85
19	p-OMe	9.6	42	3.9	78	3.3	86	3.1	86
20	p-Br	8.9	47	3.3	82	3.0	81	2.9	88

T (h) = time in hours; Y (%) = yield percent. Method A: toluene/reflux. Method B: $H_4[Si(W_3O_{10})_3]$/methanol/reflux. Method C: $H_4[Si(W_3O_{10})_3]$/acetonitrile/reflux. Method D: $H_4[Si(W_3O_{10})_3]$-silica/acetonitrile/reflux.

azomethine ylides has gained significance in recent years as it serves as an expedient route for the construction of nitrogen-containing five-membered heterocycles which constitute the central skeleton of numerous natural products [102]. Among various aza heterocycles, functionalised pyrrolizidines are a class of alkaloids with significant biological activity [103].
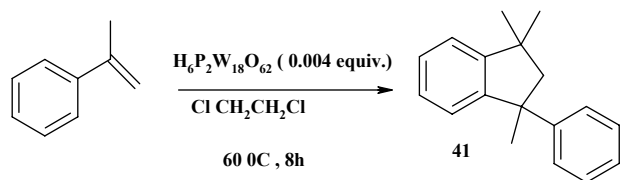
$H_4[Si(W_3O_{10})_3]$ was used as an efficient catalyst in the 1,3-dipolar cycloaddition reaction of azomethine ylides for the efficient four-component, one-pot synthesis of a series of novel dispiroindenoquinoxaline pyrrolizidines.

This catalyst offered several advantages including mild reaction conditions, cleaner reaction profiles, shorter reaction times and better yields with high degrees of regio- and stereoselectivities (Table 13) [104].
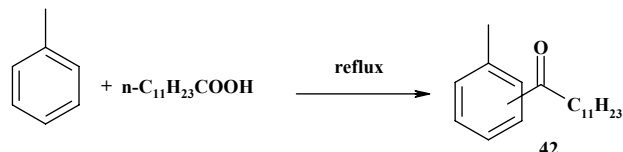
Selective Dimerization of α-Methylstyrene to 1,1,3-Trimethyl-3-Phenylindan

It has been reported that heating of a 1,2-dichloroethane solution of isopropenyl-benzene containing a catalytic amount of $H_6P_2W_{18}O_{62}$ led to 1,1,3-trimethyl-3-phenylindan **41** while no reaction was observed at room temperature. A very low amount of the catalyst, 0.004 equiv., was sufficient to induce, at 60 ºC. The full conversion of the substrate occurs in 8 h (Scheme 40) [105]. The selectivity of the process dependeds on the concentration of the substrate. Indeed, product was produced in more than 90% yield from a 0.2 M solution while the increase of the substrate concentration led to side-products. The reaction was not sensible to the nature of the atmosphere since the exchange of argon for air led to product without
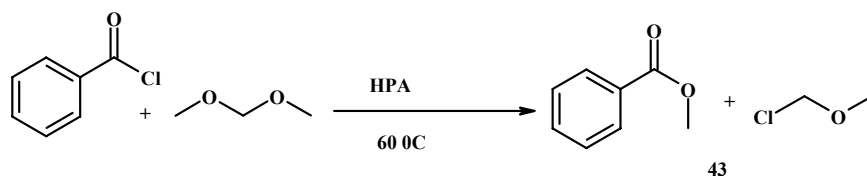
Scheme 40

Scheme 41

Scheme 42

groups is an essential task for the synthesis of multifunctional molecules. Methoxymethyl ethers are commonly employed for the protection of alcohols in the synthesis of natural products [107]. These are stable compared to a variety of commonly used reagents, such as strong alkali, Grignard reagents, butyllithium, lithium aluminium hydride, *etc*. and are readily removed by mild acid treatment. The commonly employed methods for the preparation of methoxymethyl ethers is based on the reaction of the corresponding alkoxide anions with chloromethyl methyl ether (MOM-Cl) [108].

An efficient synthetic procedure for chloromethyl methyl

erosion of the yield. Lower amount of the catalyst and the reaction temperature were considered as the advantages of this method.

Friedel-Crafts Acylation of Arenes with Carboxylic Acids

Polyvalent-metal (Ti^{4+}, Fe^{3+}, Sn^{4+}, Bi^{3+} and Ru^{3+}) salts of dodecatungstophosphate acted as effective heterogeneous catalysts for Friedel-Crafts acylation of aromatics with carboxylic acids to yield **42**. The Fe^{3+} salt showed high yields and the highest turnover number (2500) reported to date and could be reused without loss of activity, providing one of the greenest routes to aromatic ketones (Scheme 41) [106].

This novel catalytic system provided the greenest route to aromatic ketones reported to date, because water is the only side product, catalyst/product separation was easy, and the catalysts, having higher yield and TON than previously reported catalysts, were recyclable and water-tolerant.

MISCELLANEOUS REACTION

Synthesis of Chloromethyl Methyl Ether

Protection of one functional group in the presence of other

ether (MOM-Cl) was described using heteropolyacids as catalyst.

A modified procedure for the synthesizing of chloromethyl methyl ether (**43**) has been performed in which benzoyl chloride and dimethoxymethane were used as starting materials employing HPAs and their salts as catalysts (Scheme 42) [109]. The results of this study showed that $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $Cs_{2.5}H_{0.5}$ $PW_{12}O_{40}$ were efficient catalysts for the synthesis of MOM-Cl under solvent-free conditions (Table 14).

Nitration of Phenol

Nitration of aromatic compounds is widely used in organic syntheses and in industrial applications [110]. The most important nitro aromatic compounds in environmental chemistry are nitro-PAHs and nitrophenols [111]. The nitration of phenol is a fundamental process, because nitrophenols are important intermediates for the manufacture of drugs and pharmaceuticals. Among these compounds *ortho*-nitrophenol (*o*-nitrophenol) is an important starting material used in multiple step synthesis of valuable compounds [112].

Recently recyclable, eco-friendly, easily prepared and inexpensive vanadium(V)-substituted polyoxomolybdates

Table14. Effect of Various Heteropolyacids in the Synthesis of MOM-Cl a

Entry	Catalyst	Yield b (%)	TOFc (h^{-1})
1	$H_3PW_{12}O_{40}$	79	26
2	$H_4SiW_{12}O_{40}$	66	16
3	$H_3PMo_{12}O_{40}$	59	12
4	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	58	21

a) Reaction conditions: benzoyl chloride/dimethoxymethane (1:1). All the reactions were carried out for 4 h in the presence of 1.5 g of HPA catalyst. b) Isolated yield. c) TOF: moles of MOM-Cl produced per mol of catalyst per hour.

Table 15. Catalytic Nitration of Phenol in the Presence of Different Solvents

Entry	solvent	catalyst	Time (h)	Yield (%)^a
1	CCl_4	$H_4[PMo_{11}VO_{40}]$	5.0	93
2	CH_2Cl_2	$H_4[PMo_{11}VO_{40}]$	5.5	82
3	$CHCl_3$	$H_4[PMo_{11}VO_{40}]$	6.0	50
4	CCl_4	$H_5[PMo_{10}V_2O_{40}]$	2.5	96
5	CH_2Cl_2	$H_5[PMo_{10}V_2O_{40}]$	3.0	58
6	$CHCl_3$	$H_5[PMo_{10}V_2O_{40}]$	4.0	41
7	CCl_4	$H_6[PMo_9V_3O_{40}]$	1.5	100
8	CH_2Cl_2	$H_6[PMo_9V_3O_{40}]$	1.5	87
9	$CHCl_3$	$H_6[PMo_9V_3O_{40}]$	2.0	85

^{a}Yields analyzed by GC.

have been used as catalyst for regioselective nitration of phenol using nitric acid (Table 15). The effect of various solvents and heteropolyacids have been studied in this work. Important features of this protocol are high regioselectivity, simplicity and versatility of process engineering, decreasing reactor and plant corrosion problems and environmentally safe disposal. The catalyst can be easily recovered, regenerated and reused without loss of structure and appreciable activity, thus providing economic and environmentally friendly method for the nitration reaction [113].

Nitration of aromatic compounds has been carried out in the presence of divanadium-substituted molybdophosphoric acid, $H_5[PMo_{10}V_2O_{40}]$, as catalyst and a mixture of nitric acid and acetic anhydride as nitration agent. In the presence of this heteropolyacid, *ortho-* and *para*-nitro compounds were

obtained in good to excellent yields (Table 16) [114].

A simple method for mononitration of phenols and synthesis of nitrophenoles (**44**) using iron(III) nitrate or bismuth(III) nitrate pentahydrate as the nitrating agent in conjunction with a catalytic amount of tungstophosphoric acid cesium salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ or $H_3PW_{12}O_{40}$, has been reported. The reaction occurs in dichloromethane at room temperature. Iron(III) nitrate catalyzed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has been demonstrated as a suitable nitrating system for the mononitration of phenols with high selectivity and efficiency (Scheme 43) [115].
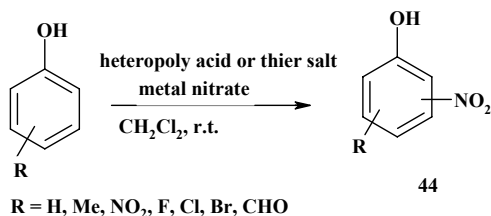
Alkylation of Phenols

Long-chain (>C8) alkyl phenols are used in the industry in the manufacture of surfactants, as antioxidants and as

25

Table 16. Heteropolyacid-Catalyzed Nitration of Aromatic Compound

Entry	R	Product	Time (h)	Yield (%)[a]
1	*Ph*OMe	4-No$_2$-*Ph*OMe	3.0	30
		2-No$_2$-*Ph*OMe		70
2	*Ph*OH	2-No$_2$-*Ph*OMe	3.0	22
3		4-No$_2$-*Ph*OMe		44
4	4-Br*Ph*OH	4-Br-2,6-No$_2$-PhOH	5.0	100
5	*Ph*NHOAc	2-No$_2$-*Ph*NHOAc	9.0	60.3
6		4-No$_2$-*Ph*NHOAc		1.3
7	*Ph*NMe$_2$	2-No$_2$-*Ph*NMe$_2$	0.7	17
8	Naphth	2-No$_2$- Naphth	3.0	84
9	2-OH-Naphth	1,4-NO$_2$-2-OH-Naphth	1.5	63
10	*Ph*Br	2-No$_2$-*Ph*Br	1.0	62
11	*Ph*I	2-No$_2$-*Ph*I	7.0	22
12	3,5-Me*Ph*	2,6-Me*Ph* No$_2$	0.25	79
13	*Ph*COMe	3-No$_2$*Ph*COMe	9.0	41

[a]Yields analyzed by GC.

Scheme 43

additives in lubricants and plastics. These are typically manufactured by the alkylation of phenol with the corresponding long-chain olefins or alcohols over acid catalysts such as BF$_3$ and ion exchange resins [116].

Several catalysts have been reported for t-butylation of phenol which includes Lewis acids such as AlCl$_3$ and BF$_3$, Bronsted acids such as H$_3$PO$_4$, H$_2$SO$_4$, HF and HClO$_4$, cation exchange resins, porous materials, supercritical and near supercritical water and ionic liquids [117].

Under mild conditions a liquid phase alkylation of phenol with 1-octene has been studied in the presence of Preyssler catalyst, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]. The proposed mechanism is shown in Scheme 44. This polyanion with high hydrolytic stability (PH = 0-12), high thermal stability, and high acidic

strength showed good activity. The effects of various parameters on the yield of product, including catalyst type, reactant molar ratio, solvent type and reaction time were studied. Comparison between Keggin type heteropolyacids, H$_5$[PMo$_{10}$V$_2$O$_{40}$], H$_6$[PMo$_9$V$_3$O$_{40}$]and Wells-Dawson, H$_6$[P$_2$W$_{18}$O$_{62}$] with Preyssler's anion showed that this polyanion reacted better than the other studied heteropolyacids without any degradation of the structure (Table 17) [117].

Butylation of *p*-cresol with *tert*-butanol was investigated on titanium modified with 12-tungstophosphoric acid (TPA/TiO$_2$) catalyst under vapor phase conditions. Catalysts with different TPA loadings (10-25 %wt.) and calcination temperatures (650-750 ºC) were prepared by suspending titanium hydroxide in methanol solution of TPA followed by drying and calcination. These catalysts were characterized by surface area, XRD, ^{31}P MAS NMR, XPS, NH$_3$-TPD, and FTIR pyridine adsorption. XRD results indicated that the presence of TPA retarded the crystallization of titanium and stabilized TiO$_2$ in anatase phase. ^{31}P MAS NMR indicated the presence of TPA in various forms (dispersed, highly fragmented and Keggin intact). These catalysts showed both Bronsted and Lewis acidity, and 20% TPA on TiO$_2$ calcined at
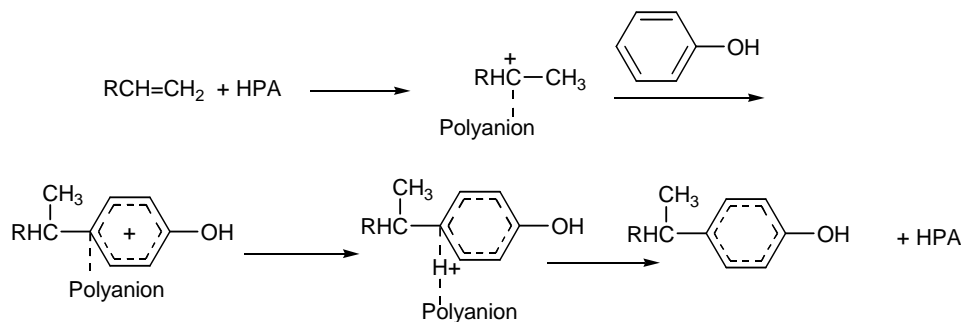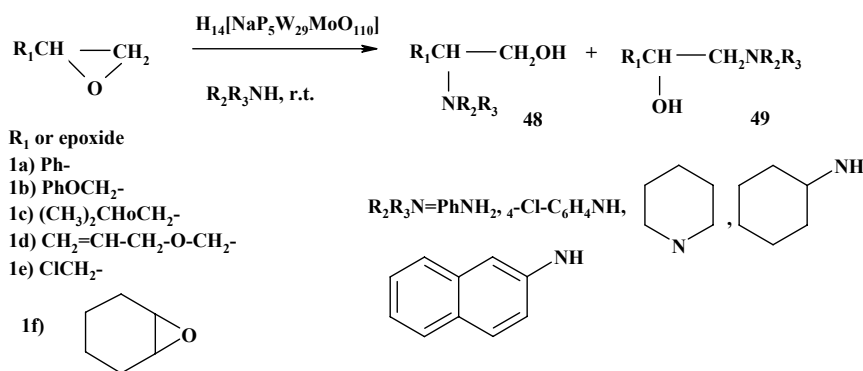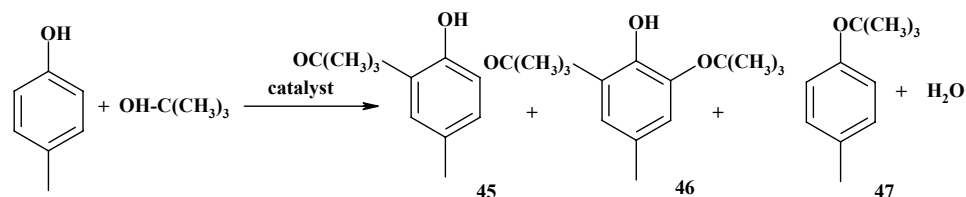
Scheme 44

Table 17. Effect of Temperature and Catalyst Type on Phenol Conversion and Product Distribution

Catalyst	Temperature (ºC)	Phenol conversion (%)	Product distribution (%)[a]		Selectivity to monooctyl phenol
			p-Isomer	Others	
$H_{14}[NaP_5W_{30}O_{110}]$	190	87.8	86.5	1.3	100
	200	76.2	71.7	4.5	100
	225	63.4	57.1	6.3	100
	250	43.2	36.5	6.7	100
	275	31.8	24.7	7.1	100
$H_6P_2W_{18}O_{62}$	190	78.4	76.8	1.6	100
	200	68.5	65.1	3.4	100
	225	59.3	53.5	5.8	100
	250	37.2	30.7	6.5	100
	175	24.6	17.6	7.0	100
$H_5PMo_{10}V_2O_{40}$	190	75.1	72.8	2.3	100
	200	65.7	60.8	4.9	100
	225	53.4	47.2	6.2	100
	250	29.3	22.8	6.5	100
	275	21.8	14.1	7.7	100
$H_6PMo_9V_3O_{40}$	190	72.1	69.4	2.7	100
	200	53.4	48.6	4.8	100
	225	43.7	38.1	5.6	100
	250	24.7	18.6	6.1	100
	275	19.9	12.6	7.3	100

$H_{14}[NaP_5W_{30}O_{110}]$ (0.01 mmol); phenol: 1-octene (feed ratio) = 1:4; reaction time = 6 h. a) Yields analyzed by GC.

700 ºC (from here after words 20% TT-700) had the highest Bronsted as well as total acidity. Further, the catalytic activities were examined in *tert*-butylation of *p*-cresol with *tert*-butanol. The catalytic activity depended on TPA coverage, and the highest activity corresponded to the monolayer of TPA on titanium. The most active catalyst 20% TT-700 gave 82% conversion of *p*-cresol and 89.5% selectivity towards 2-*tert*-butyl cresol (**45**), 2,6-di-*tert*-butyl cresol (**46**) 7.5% and cresol-*tert*-butyl ether (**47**) 3% under optimized conditions. The activity was always higher than that of WO_3/ZrO_2, sulfated

Scheme 45

Scheme 46

zirconia (SZ), USY, H- zeolites and montmorillonite K-10 (K-10mont) under similar conditions (Scheme 45) [118].

Preparation of Dichloropropanol (DCP) from Glycerol

Direct preparation of dichloropropanol (DCP) from glycerol was carried out in a batch reactor using $H_3PMo_{12-x}WXO_{40}$ (X = 0-12), $H_4SiMo_{12-x}WXO_{40}$ (X = 0-12), $H_{3+x}PW_{12-x}VXO_{40}$ (X = 0-3), and $H3+XPMo_{12-x}VXO_{40}$ (X = 0-3) heteropolyacid (HPA) catalysts. Acid properties of the HPA catalysts were then determined by NH_3-TPD measurements in order to correlate the catalytic activity with the acid property of the catalysts. The acid strength of the HPA catalyst played a key role in determining the catalytic performance in the reaction. The selectivity for DCP increased with increasing acid strength of the catalyst. Among the catalysts tested, $H_3PW_{12}O_{40}$ with the highest acid strength showed the best catalytic performance. [119]

Aminolysis of Epoxides with Amines

A simple and efficient method has been developed for the synthesis of alfa- amino alcohols **48**, **49** by ring opening of epoxides in presence of catalytic amount of $H_{14}[NaP_5W_{30}O_{110}]$

at room temperature under solvent free condition. The reaction worked well for both aromatic and aliphatic amines (Scheme 46) [120].

OXIDATION REACTIONS

Selective Oxidation of Sulfides to Sulfoxides

The selective oxidation of sulfides to sulfoxides is of interest because of the importance of sulfoxides as synthetic intermediates in organic synthesis. Sulfoxides are important in organic synthesis as an activating group, they have been utilized extensively in carbon bond-forming reactions [121], as building blocks, especially as chiral auxiliaries [122], and they play key roles in the activation of enzymes [123].

By partial proton substitution of $H_3PMo_{12}O_{40}$ (PM$_{12}$) on different amines, new class of Keggin-type structure catalysts were synthesized For example quinoline, cinchonidine and cinchonine form the following catalysts respectively. QuiH$_3$PMo$_{12}$O$_{40}$, (PM12Qui), CidH$_3$PMo$_{12}$O$_{40,}$ (PM$_{12}$Cid), and CinH$_3$PMo$_{12}$O$_{40}$ (PM$_{12}$Cin). These catalysts were used for selective oxidation of sulfides to sulfoxides **50a-50h** (Scheme 47) [124].

Although the catalytic activity of PM$_{12}$Cin was lower than

Scheme 47

50a: R=Ph R'=Me
50b: R=4-MePh R'=Me
50c: R=Ph R'=Et
50d: R=Ph R'=Benzyl

50e: R. R'=Benzyl
50f: R' R=Ph
50g: R, R'=Butyl
50h: R=Ph R'=CH$_2$OH
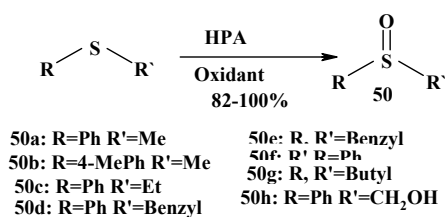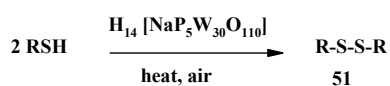
Scheme 48

other amine salts of Keggin-type heteropolyacids, but this catalyst has the advantage on being insoluble in the mixture reaction. The replacement of acetonitrile (solvent) by a green solvent such as ethanol increases the catalytic activity of PM$_{12}$Cin.

Oxidation of Thiols to the Corresponding Disulfide

Conversion of thiols to disulfides is important from both biological and synthetic points of view. In biological systems, thiols are oxidized by flavins, cytochromes and dehydroascorbic acid to control the cellular redox potential and prevent oxidative damage On the other hand, disulfides are important reagents in organic synthesis and can be used to

prepare sulfinyl and sulfenyl compounds [125] (Scheme 48). [NaP$_5$W$_{30}$O$_{110}$]$^{14-}$ successfully was used for oxidation of thiols to disulfides **51** (Table 18) [126]. The greatest advantages of this procedure arise from its employment of greenness and reusable catalyst, high yields, in most case reaction was solvent free and side reaction products of acid catalyzed were not found in this procedure.

N-Oxidation of Pyridine Carboxylic Acids

Pyridine N-oxides in nanotechnology, industry and medicine, are important. Pyridine N-oxides are also versatile synthetic intermediates and the chemistry and applications of N-oxides have recently received much attention due to their usefulness as synthetic intermediates and their biological importances [127]. Heterocyclic N-oxides are also useful as protecting groups, auxiliary agents, oxidants, ligands in metal complexes and catalysts [128].

Recently Preyssler's anion has been used as an effective catalyst for the selective oxidation of pyridine carboxylic acids such as: pyridine-2-carboxylic acid (picolinic acid), pyridine-3-carboxylic acid (nicotinic acid), pyridine-2,3-dicarboxylic acid (quiniolinic acid) and other pyridines such as: 3-methyl pyridine (3-picoline) and 2-aminopyridine (Table 19) [129].

In another related work, in the presence of hydrogen peroxide as an oxidizing agent, the heteropoly anions H$_6$P$_2$W$_{18}$O$_{62}$, H$_6$P$_2$Mo$_{18}$O$_{62}$, α-K$_3$PW$_9$Mo$_3$O$_{40}$, α-K$_7$PW$_9$Mo$_2$O$_{39}$, H$_4$PMo$_{11}$VO$_{40}$, H$_5$PMo$_{10}$V$_2$O$_{40}$ and H$_6$PMo$_9$V$_3$O$_{40}$ were studied as catalysts for the N-oxidation of

Table 18. Oxidation of Thiols to the Corresponding Disulfides Using H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]

Entry	Thiols	Disulfide	Yield (%)
1	*p*-Tolylthiol	Di-*p*-ditolyldisulfide	98
2	Thiophenol	Diphenyldisulfide	97
3	Naphtylthiol	Di-naphtyldisulfide	91
4	Cyclohexylthiol	Dicyclohexyldisulfide	95
5	*p*-Chlorophenylthiol	Bis[*p*-chlorophenyl]disulfide	97
6	Ethanethiol	Diethyldisulfide	92
7	propylthiol	Dipropyldisulfide	95
8	Octylthiol	Dioctyldisulfide	98
9	Phenyl-methanethiol	Dibenzyldisulfide	94
10	*sec*-Butylthiol	Di-*sec*-butyldisulfide	97

Table 19. N-Oxidation of Pyridine Carboxylic Acids Using H_2O_2 and Preyssler Catalyst

Entry	Substrate	Catalyst	Yield (%)[a]
1	3-Methyl-pyridine	H_{14}-P_5Mo	95
	3-Methyl-pyridine	H_{14}-P_5	82
2	2-Amino-pyridine	H_{14}-P_5Mo	74.4
	2-Amino-pyridine	H_{14}-P_5	62.5
3	2-Bromo-pyridine	H_{14}-P_5Mo	Trace
	2-Bromo-pyridine	H_{14}-P_5	Trace
4	Pyridine-2-carboxylic acid	H_{14}-P_5Mo	92.8
	Pyridine-2-carboxylic acid	H_{14}-P_5	79.5
5	Pyridine-3-carboxylic acid	H_{14}-P_5Mo	67.3
	Pyridine-3-carboxylic acid	H_{14}-P_5	56.5
6	Pyridine-2,3-dicarboxylic acid	H_{14}-P_5Mo	61.7
7	Pyridine-2,3-dicarboxylic acid	H_{14}-P_5	48.5

a) Reaction conditions: pyridine (5×10^{-3} mmol), hydrogen peroxide (7.5 ml), catalyst (3×10^{-5} mol), toluene as solvent (10 ml), reflux, 6 h.

picolinic acid, in various solvents such as toluene, benzene and carbon tetrachloride. These highly selective oxidations, gave good to excellent yields of the related N-oxide along with decarboxylation at 2-position of the ring. Among the catalysts tested, α-$K_3PW_9Mo_3O_{40}$ catalyzed the selective N-oxidation into related N-oxide product most efficiently. The effect of some operative variables, such as the mole numbers of hydrogen peroxide, amount of the catalyst, and the reaction time were studied. The reaction conditions were optimized [130].

Alcohol Oxidation

The oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important functional group transformations in organic synthesis [131]. Recently, the use of molecular oxygen as terminal oxidant has received great attention for both economic and environmental benefits.

Highly efficient catalytic system was made up of a novel polyoxometalate ($Na_{6.3}$- $Fe_{0.9}[AlMo_{11}O_{39}]$.$2H_2O$) as catalyst has been reported [132]. A solid catalyst was indiscerptible in both water and organic solvents which has high selectivity and are active for the aerobic oxidation of a variety of alcohols to corresponding aldehydes or ketones **52a-52m** (Scheme 49). Catalytic results, indicate that the polyoxometalate catalyst is a
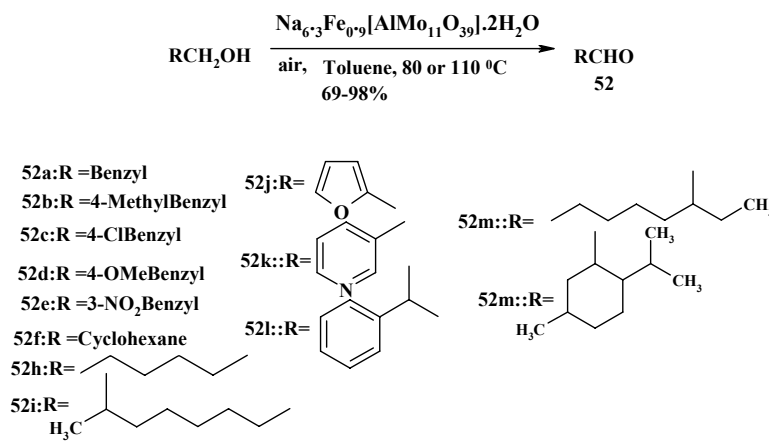
green, selective, and efficient aerobic catalyst for alcohol oxidation. It selectively oxidized alcohols to their corresponding carbonyls under mild aerobic conditions without using sacrificial reducing agents and pure O_2. This reaction system displayed an important merit, that is, more facile in catalyst/product separation and catalyst reuse.

Oxidation of various alcohols in refluxing condition in acetic acid, using preyssler type of heteropolyacid supported onto silica gel, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, (0.03 g) in a heterogeneous system has been performed successfully (Table 20) [133].

This catalyst offered advantages including simplicity of operation due to the heterogeneous nature of reaction, easy work-up, high yields of products, high selectivity, reusability and the recyclability of the catalyst.

Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$, has been used in oxidation of benzyl alcohols. Under mild conditions, monosubstituted benzyl alcohols were oxidized to benzaldehydes and benzoic acids in presence of hydrogen peroxide as an oxidant. This catalyst with high hydrolytic and thermal stability and high acidic strength has shown good activities. The effects of various parameters on the yields of products, including the catalyst type, a nature of the substitutents and temperature were studied. Comparison

$$\text{RCH}_2\text{OH} \xrightarrow[\substack{\text{air,} \quad \text{Toluene, 80 or 110 }^0\text{C} \\ 69\text{-}98\%}]{\text{Na}_{6\cdot3}\text{Fe}_{0\cdot9}[\text{AlMo}_{11}\text{O}_{39}].2\text{H}_2\text{O}} \text{RCHO} \atop 52$$

52a:R =Benzyl

52b:R =4-MethylBenzyl

52c:R =4-ClBenzyl

52d:R =4-OMeBenzyl

52e:R =3-NO$_2$Benzyl

52f:R =Cyclohexane

52h:R=

52i:R=

52j:R=

52k::R=

52l::R=

52m::R=

52m::R=

Scheme 49

Table 20. Oxidation of Alcohols Using H14-P5 Supported onto Silica Gel

Entry	Substrate	Time (min)	Yield(%)
1	Benzylalcohol	13	99
2	2-hydroxy-Benzylalcohol	10	98
3	2-Methyl-Benzylalcohol	12	99
4	4-Bromo-Benzylalcohol	14	99
5	4-Nitro-Benzylalcohol	15	98
6	Furanyl-methanol	30	97
7	Propenol	18	96
8	Butanol	18	96
9	Octan-2-ol	20	98
10	Decan-2-ol	21	97
11	cyclohexanole	20	99
12	2-Phenyl-ethenol	20	98

between Keggin's heteropolyacids, $H_3[P_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$ and $H_4[SiMo_{12}O_{40}]$, and Preyssler's anion showed that this polyanion react similar to Keggin's acids without any degradation of the structure [134].

A Korean research group modified surface of mesostructured cellular foam (MCF) silica by grafting 3 aminopropyl-triethoxysilane (APTES) to have the positive charge, and thus, to provide sites for the immobilization of $H_3PMo_{12}O_{40}$ [135]. By taking advantage of the overall negative charge of $[PMo_{12}O_{40}]^{3-}$, $H_3PMo_{12}O_{40}$ catalyst was chemically immobilized on the aminopropyl group of surface modified MCF (SM-MCF) silica as a charge matching component. It was revealed that $H_3PMo_{12}O_{40}$ species were finely and molecularly dispersed on the SM-MCF silica *via* chemical immobilization.

In the vapor-phase ethanol conversion reaction, the $H_3PMo_{12}O_{40}$/SM-MCF silica catalyst showed a higher ethanol conversion than the bulk $H_3PMo_{12}O_{40}$ catalyst. Furthermore, the $H_3PMo_{12}O_{40}$/SM-MCF silica catalyst exhibited an enhanced oxidation catalytic activity (formation of acetaldehyde) and a suppressed acid catalytic activity (formation of ethylene and diethylether) compared to the mother catalyst. The enhanced ethanol conversion and oxidation catalytic activity of $H_3PMo_{12}O_{40}$/SM-MCF silica catalystwas attributed to fine dispersion of $H_3PMo_{12}O_{40}$ species on the SM-MCF silica via chemical immobilization Fig. 1.

Recently this Korean research group synthesized nitrogen-containing mesostructured cellular foam carbon (N-MCF-C). The N-MCF-C was then modified to have a positive charge for the immobilization of $[PMo_{10}V_2O_{40}]^{5-}$. By taking advantage of the overall negative charge of $[PMo_{10}V_2O_{40}]^{5-}$, $H_5PMo_{10}V_2O_{40}$ (PMo$_{10}$V$_2$) catalyst was chemically immobilized on the N-MCF-C support as a charge matching component. The PMo$_{10}$V$_2$/N-MCF-C catalyst was applied to the vapor-phase oxidation of benzyl alcohol [136].
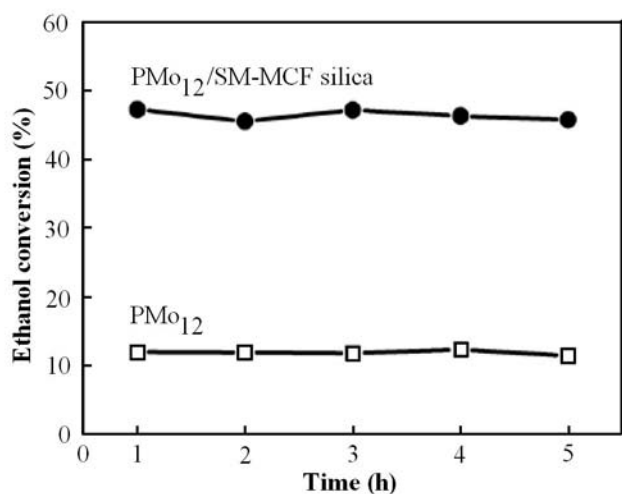
Figure 2 shows the catalytic performance of unsupported

Fig. 1. Ethanol conversions over bulk PMo_{12} and PMo_{12}/SM-MCF silica catalysts at 230 ℃.
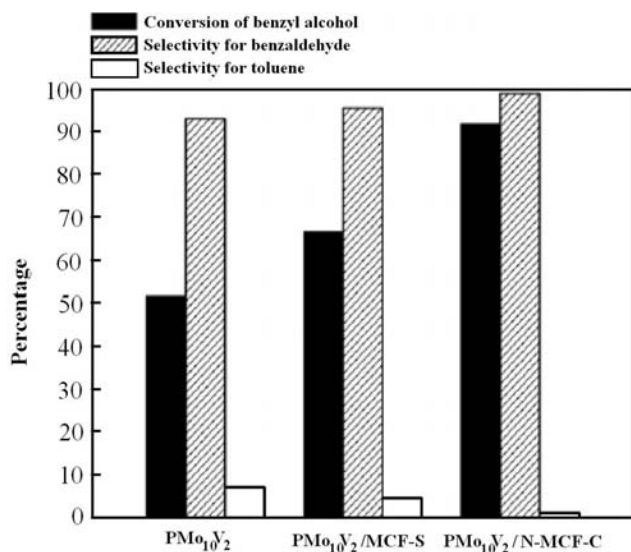

Fig. 2. Catalytic performance of unsupported $PMo_{10}V_2$, $PMo_{10}V_2$/MCF-S, and $PMo_{10}V_2$/N-MCF-C in the vapor-phase oxidation of benzyl alcohol at 260 ℃ after a 5 h reaction.

$PMo_{10}V_2$, $PMo_{10}V_2$/MCF-S, and $PMo_{10}V_2$/N-MCF-C in the vapor-phase oxidation of benzyl alcohol at 260 ℃ after a 5 h reaction. The conversion of benzyl alcohol increased in the order of $PMo_{10}V_2$ < $PMo_{10}V_2$/MCF-S < $PMo_{10}V_2$/N-MCFC.

Mono-substituted Keggin-polyoxymetalate complex $Na_6[SiW_{11}ZnH_2O_{40}].12H_2O$ was demonstrated to be an effective catalyst for the selective oxidation of alcohols in the presence of hydrogen peroxide as oxidant. The reaction was carried out in an aqueous/oil biphasic system, which allowed easy recovery of catalyst, under relative mild conditions. The catalyst could be reused five times without appreciable loss of activity [137].

In another work related to oxidation of alcohol, alfa-Butyrolactone, alfa-caprolactone and 2-cumaranone were synthesized from related diols, using Preyssler heteropolyacids, $H_{14}[NaP_5W_{30}O_{110}]$ and $H_{14}[NaP_5W_{29}MoO_{110}]$ as catalyst, and hydrogen peroxide as oxidizing agent. The performance of eco-friendly Preyssler catalysts was compared with H_2SO_4 and the catalytic activity of H_2SO_4 is found to be lower than Preyssler catalysts. The effects of various parameters such as amount of diol, temperature, solvent and time were studied. In all cases, the Preyssler catalyst was easily recovered and recycled with retention of their initial structure and activity (Table 21) [138].

$Na_9[SbW_9O_{33}]$ in conjunction with a phase transfer catalyst, methyltricapryl ammonium chloride, demonstrated to be highly efficient for selective oxidation of variety of alcohols with aq. H_2O_2 to yield corresponding carbonyls. Most simportantly the reactions were carried out in the absence of any organic solvents especially halogenated solvents. In case of allylic alcohols, the catalyst was highly selective for the alcohol oxidation reaction and least selective for epoxidation reaction in the presence of aq. H_2O_2. IR Studies supported the formation of peroxo intermediate species and also supported the stability of the catalyst in the presence of phase transfer compound under the present experimental condition. The catalyst could be reused after careful decomposition of peroxide of the final reaction mixture [139].

A catalytic system consisting of both $Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}].12H_2O$ (SiW_9Al_3) and water as solvents (a small quantity of organic solvents were used as co-solvent for a few substrates) was used for selective oxidation of alcohols to ketones (aldehydes) using 30% H_2O_2 without any phase-transfer catalyst under mild reaction conditions. The catalyst system allowed easy product/catalyst separation. Under the given conditions, the secondary hydroxyl group was highly chemoselectively oxidized to the corresponding ketones

Table 21. Lactonization of Diols by Preyssler Catalyst in Various Solvents at Reflux Temperature for 4 h

Entry	Solvent	Substrate	%Product yield	
			H_{14}-P_5	H_{14}-P_5Mo
1	Chloroform	Butane-1,4-diol	88.50	96.00
2	1,2-Dichloroethan	Butane-1,4-diol	86.80	93.50
3	Tetrachloride carbon	Butane-1,4-diol	82.90	90.70
4	Chloroform	Hexane-1,6-diol	90.00	98.50
5	1,2-Dichloroethan	Hexane-1,6-diol	83.80	97.50
6	Tetrachloride carbon	Hexane-1,6-diol	79.80	95.50
7	Chloroform	(2-Hydroxymethyl-phenyl)-methanol	82.90	96.70
8	1,2-Dichloroethan	(2-Hydroxymethyl-phenyl)-methanol	78.30	94.40
9	Tetrachloride carbon	(2-Hydroxymethyl-phenyl)-methanol	71.30	94.40

in good yields in the presence of primary hydroxyl group within the same molecule, and hydroxides were selectively oxidized even in the presence of alkene. Benzylic alcohols were selectively oxidized to the corresponding benzaldehydes in good yields without over oxidation products in solvent-free conditions. Nitrogen, oxygen, sulfur-based moieties, at least for the cases where these atoms are not susceptible to oxidation do not interfere with the catalytic alcohol oxidation [140].

Recently heteropolyacid ($H_3PW_{12}O_{40}$)/SiO_2 nanoparticles has been synthesized by a microemulsion technique to prevent the dissolution of HPA in polar solvents including water. The particle size was controlled within the range from 100 to 500 nm. The surface properties including the BET surface area, acidity and catalytic activity depended on the particle size of HPA/SiO_2. The reduction of particle size of HPA/SiO_2 improved the surface area and the acidity of the nanoparticles. The interaction of HPA with silica surfaces was observed by solid state NMR. Selective ethanol oxidation was tested as probe reaction on HPA/SiO_2. The catalytic activity of ethanol oxidation was enhanced with the reduction of the particle size of HPA/SiO_2.

The catalytic properties of HPA in the silica nano phase might be different from those in the bulk base due to the physico-chemical differences of nano phase [141].

Deamination of Some *N*-Amino Nitrogen Heterocycles

Deamination reaction from N-aminotriazines and N-

aminotriazoles using Preyssler's anion, in refluxing condition in acetic acid, yielding **53a-53c** and **54a-54d**, has been reported (Scheme 50) [142].

In the presence of Preyssler's anion, the amines were oxidized to the corresponding N-nitrosamines and then N-NO bond cleavage occurred (Scheme 51). N-Nitrosamines can produce NO through a homolytic cleavage of the N-NO bond, and also could form NO^+ through a heterolytic cleavage of the relevant bond [143].

Oxidation of Aldehydes

The ecological and economic advantages inherent in the direct use of molecular oxygen as oxidant for catalytic oxidative transformations are eminently clear and polyoxometalates have over the last 15-20 years played an important part in the search to find new approaches in the utilization of molecular oxygen as an oxidizing reagent.

Polyoxometalates of the alfa-Keggin structure [$Mo_{12}VO_{39}$ (μ_2-OH)$_{10}$ H_2{$X^{II}(H_2O)_3$}$_4$] (X = Ni, Co, Mn and Cu), have been synthesized and were used as heterogeneous catalysts for the aerobic oxidation of aldehydes to carboxylic acids [144]. The selectivity of the reaction was highly dependent on the identity of the aldehyde. Aliphatic linear aldehydes, *e.g.* octanal, and benzaldehyde react quantitatively and selectively to the respective carboxylic acids. Also aα-keto aldehyde (phenylglyoxal) was oxidized selectively to phenylpyruvic acid.

Other substrates suffered from lower selectivity manifested by formation of formate esters by Dakin type reactions, or

Scheme 50

53a: X=O Y=S
53b: X, Y=S
53c: X=S Y=SMe

54a: Z=Me
54b: Z=Ph
54c: Z=Et
54d: Z=H
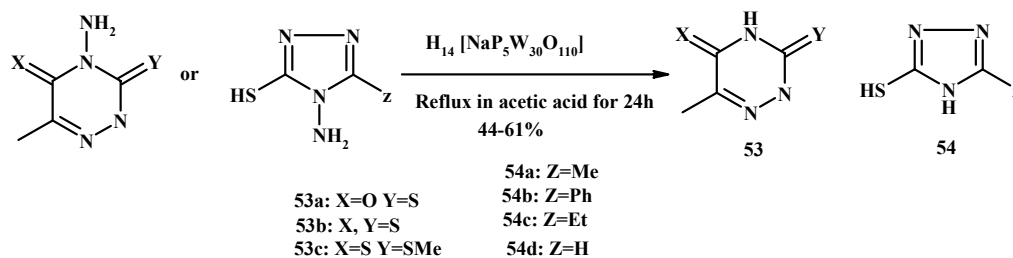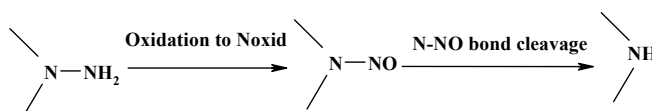
Scheme 51

Table 22. Yields of the Oxidation Reactions of Benzaldehydes Catalyzed by $H_{14}[NaP_5W_{30}O_{110}]$

Entry	Aldehyde	Percentage yield selectivity of benzoic acids (%)	Selectivity (%)
1	4-ClC_6H_4CHO	100	100
2	4-BrC_6H_4CHO	91	100
3	$4\text{-NO}_2C_6H_4\ CHO$	84.5	100
4	4-MeC_6H_4CHO	73.5	96
5	3-MeC_6H_4CHO	70	98
6	2-MeC_6H_4CHO	13.5	95
7	2-OHC_6H_4CHO	Trace	90
8	3-OHC_6H_4CHO	Trace	90
9	4-OHC_6H_4CHO	Trace	91

Reaction conditions: catalyst, 10-5 mol; substrate, 10-3 mol; solvent: acetonitrile (2 ml), H_2O (3 ml), hydrogen peroxide (0.03 mol); reflux for 8 h.

allylic oxidation that can lead to decarboxylation and formation of ketones or allylic alcohols depending on the specific substrate.

Preyssler's anion, with formula $[NaP_5W_{30}O_{110}]^{14-}$, catalyzes the oxidation of aromatic aldehydes to related carboxylic acids by hydrogen peroxide as oxidizing agent, under microwave irradiation, or at 70 ºC. Both homogeneous and heterogeneous Preyssler's catalysts (as $H_{14}[NaP_5W_{30}O_{110}]$) were used and had their activity compared with those of some Keggin structures. The data indicated that Sodium30-tungsto pentaphosphate, the so-called Preyssler's anion, with high hydrolytic (pH = 0-12) and thermal stability was the best

catalyst with high yield and good selectivity. Under microwave irradiation, this polyanion supported on SiO_2 was found to be an excellent catalyst for aldehydes with low loss factor in 1-2 min (the loss factor is a measure of the ability of the material to dissipate energy). The effects of various parameters, including catalyst type, nature of the substituent in the aldehyde and temperature, on the yield of the carboxylic acids were studied (Table 22) [145].

Oxidation of Primary Aromatic Amines

The oxidation of amines is a fundamental reaction for the synthesis of *o*-containing amine derivatives and both industry

$$RC_6H_4NH_2 \xrightarrow{\text{Preyssler catalyst/H}_2O_2} (RC_6H_4)_2N_2O + (RC_6H_4)_2N_2$$

R = 3-Cl, 4-Cl, 4-Br, 4-Methyl, 3-NO$_2$ **55**
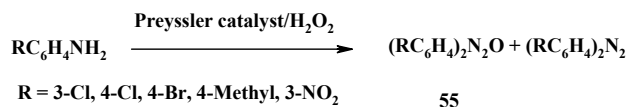
Scheme 52

Scheme 53

and academia have paid considerable attention to them. Therefore, a variety of oxidation and catalytic methods have been investigated [146].

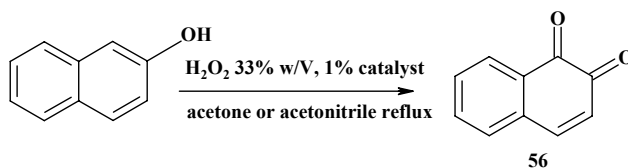Many substituted anilines were converted into the corresponding azoxy benzenes **55** as major products, with hydrogen peroxide, using Preyssler catalyst [147].

The ability of various Preyssler catalysts as pure, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$], mixed addenda, H$_{14}$[NaP$_5$W$_{29}$MoO$_{110}$], and cetylpyridinium acidic salt, was investigated. In all cases, the highest yield of azoxy compounds was observed, using H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] as catalyst. The oxidations of anilines with 30% H$_2$O$_2$ catalyzed by Preyssler catalysts in various solvents with different molar ratio of amine to oxidant, have been investigated and the results showed that the reaction yields were affected by changing the solvent as well as molar ratio of amine:oxidant (Scheme 52).

Arene and Phenol Oxidation

Quinones are useful compounds as synthetic intermediates as well as biologically active compounds. Many kinds of quinone derivatives play important roles in biosystems. Some quinones show bioactivities and are used as medicine intermediates. Quinones are usually prepared by direct oxidations of monohydroxy and dihydroxy aromatic compounds or arenes. There is a large number of stoichiometric oxidizingagents for quinone preparations from aromatic compounds.

The fused polycyclic systems were catalytically oxidized with H$_2$O$_2$ using a lacunary phosphotungstic acid derivative whose formula is Na$_8$H[ΔPW$_9$O$_{34}$].19H$_2$O (Δ-PW$_9$).22. The reaction was carried out under homogeneous conditions of catalysis at 55 ℃, using acetone as solvent. Under such

conditions, the naphthols were selectively oxidized in the presence of phenols. It was observed that the conversion to quinones from naphthols was higher than that from polycyclic fused systems [148].

Considering the performance of the above mentioned reactions, the 2-naphthol oxidation was selected to test the complex heteropolytungstate catalysts.

These catalysts were derived from the coupling of two fragments [PW$_9$O$_{34}$] (lacunar, Keggin-like, Δ-PW$_9$) of general formula K$_{10}$[(PW$_9$O$_{34}$)2M$_4$(H$_2$O)$_2$].20H$_2$O in which M stands for Co, Zn and Mn divalent ions. The reaction was evaluated by using acetone and/or acetonitrile solvents at their reflux temperatures. Under such conditions, the b-naphthol was selectively oxidized to 1,2-naphthoquinone **56** (Scheme 53). The catalytic selectivity and the influence of the heteropolytungstate metallic clusters on the primary lacunar phase were also comparatively analyzed (Table 23).

Cyclohexene Oxidation

The effect of the number of protons in the Ti(IV)-monosubstituted Keggin polyoxometalate Na$_5$-nHnPTiW$_{11}$O$_{40}$ (n = 1-5; Ti-POM) on its catalytic behaviour in cyclohexene (CyH) oxidation with aqueous H$_2$O$_2$ in MeCN has been performed. It has been found that Ti-POMs with n = 2-5 catalyse efficiently CyH oxidation to yield *trans* cyclohexane-1,2-diol as the main reaction product, while Ti-POM containing only one proton showed lower activity in CyH oxidation and produced allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, along with comparable amounts of the corresponding epoxide and diol.

The obtained results strongly supported homolytic oxidation mechanism for CyH oxidation in the presence of the

Table 23. Oxidation of 2-Naphtol with Hydrogen Peroxide Catalysed by D-PW$_9$ and M-Mhase (M: Co, Zn and Mn Divalent Ions) in Different Reactionconditions

Entry	Solvent	Catalysts	Time (min)	Conversion	1,2-Naphtoquinone selectivity (%)
1	Acetone	D-PW9	60	100	83
2	Acetone	Co-phase	60	100	94
3	Acetone	Zn-phase	60	100	69
4	Acetone	Mn-phase	60	100	77
5	Acetonitrile	D-PW9	10	80	90
5'	Acetonitrile		13	100	87
6	Acetonitrile	Co-phase	10	72	96
6'	Acetonitrile		20	100	89
6''	Acetonitrile		60	100	88
7	Acetonitrile	Zn-phase	10	76	88
7'	Acetonitrile		15	100	80
8	Acetonitrile	Mn-phase	10	77	89
8'	Acetonitrile		15	100	84

[a]Acetonitrile 56 ºC.

monoprotonated Ti-POM and heterolytic oxygen-transfer mechanism in the presence of Ti-POMs having two and more protons (Table 24) [149].

Oxidative Aromatization of Hantzsch 1,4-Dihydropyridines

1,4-Dihydropyridines (1,4-DHPs) are a class of model compounds of NADH coenzyme, and calcium channel antagonists (CCAs) [150]. These compounds have been established as one of the first line drugs for treatment of hypertension because of their promising depressor effect and relatively good tolerability [151].

A variety of Hantzsch 1,4-dihydropyridines were oxidized to the corresponding pyridines **57a-57j** in high yields in the presence of H$_6$PMo$_9$V$_3$O$_{40}$, a Keggin type heteropolyacid, in refluxing acetic acid. The heteropolyacid was found to be reusable. The effects of various solvents and heteropolyacids were studied (Scheme 54) [152].

Oxidative Cleavage of C = N bond

Oximes, hydrazones and semicarbazones are useful protecting groups [153] and are widely used for purification and characterization of carbonyl compounds, as they are highly crystalline and stable compounds. Their synthesis from non-carbonyl compounds [154] provides an alternativeway to aldehydes and ketones. There has been great interest in the development of mild techniques for the conversion of oximes into their corresponding carbonyl compounds [155], but only a little attention has been paid for the regeneration of carbonyl compounds from hydrazones and semicarbazones [156].

An efficient and improved procedure for oxidative cleavage of C-N bond has been developed in the presence of H$_6$[PMo$_9$V$_3$O$_{40}$] as a green and reusable catalyst in refluxing acetic acid [157]. It was demonstrated that H$_6$[PMo$_9$V$_3$O$_{40}$], a Keggin-type heteropolyacid, is a highly efficient solid acid catalyst for oxidative cleavage of C= N bond. The method had advantages in terms of yield, heterogeneous nature, expenses, availability of reagents and reusability of the green catalyst, short reaction times and easywork-up procedure (Scheme 55).

Oxidation of Dimethyl Ether to Dimethoxymethane

The catalytic oxidation of dimethyl ether (DME) to dimethoxymethane (DMM) was carried out over MnCl$_2$ modified different heteropolyacid catalysts. Kinds of supports and the catalyst packing structure were investigated. Besides, the possible reaction pathway of DME direct-oxidation to

Scheme 54

57a: R1=H R2=Et
57b: R1=Me R2=Et
57c: R1=Et R2=Et
57d: R1=Ph R2=Et
57e: R1=Isopropyl R2=Et

57f: R1=4-MePh R2=Et
57g: R1=4-OMePh R2=Et
57h: R1=4-ClPh R2=Et
57i: R1=2-NO2Ph R2=Et
57j: R1=3-NO2Ph R2=Et

X= - NH-Ph, NHCSNH2, -OH
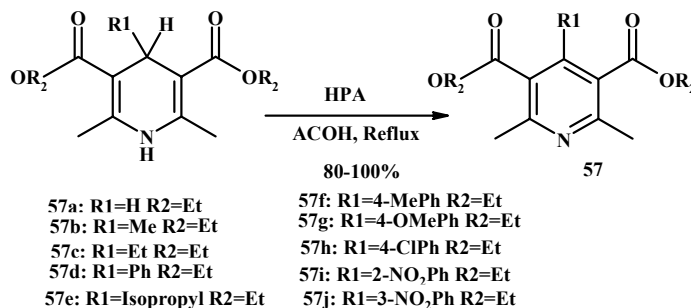
Scheme 55

DMM was also discussed. The results showed $H_4SiW_{12}O_{40}/SiO_2$ modified with $MnCl_2$ exhibited a better catalytic performance than other heteropolyacids. SiO_2 was the better supporting materials than the materials used as support. The synergistic effects of the acid sites offered by $H_4SiW_{12}O_{40}$ and the redox sites mainly offered by MnO_2 significantly improve the catalytic activity of the catalyst [158].

Dehydrogenation of Isobutyric Acid

UV-Visible spectroscopy studies of heteropolyacid (HPA) catalysts in solid were carried out with an aim of utilizing absorption edge energies as a probe of catalytic oxidation performance of the HPA catalysts. The absorption edge energies were correlated with the catalytic performance of HPA catalysts in the oxidative dehydrogenation of isobutyric acid. The correlation between catalytic oxidation performance and absorption edge energies of HPA catalysts demonstrated that the absorption edge energies could be utilized as a correlation parameter for the reduction potentials (oxidizing powers) of the HPA catalysts, and furthermore, as a probe of catalytic oxidation performance of the HPA catalysts [159].

Hydroformylation of Alkyl Alkenes

Heteropolyacids impregnated with rhodium(I) or (III) complexes were prepared and used as supported catalysts in the hydroformylation of alkyl alkenes. Two general types of

catalysts were prepared and tested: rhodium(I) or (III) in the presence and in the absence of the heteropolyacid $H_3PW_{12}O_{40}$, $25H_2O$ (adopted as HPW12) supported on MCM-41 (30 A°). 1-Octene was chosen as a model substrate. Different types of supported catalysts were tested in the hydroformylation of 1-octene and other alkyl alkenes. The effects of the temperature and the type of solvent on the reaction were studied. The results showed that the supported catalysts containing the heteropolyacid $H_3PW_{12}O_{40}$, $25H_2O$ (HPW12) along with rhodium(I) or (III) gave higher catalytic activity. In addition, the recycling of the supported catalysts was studied and the results showed again the important effect of the presence of HPW12 on the recycling of the rhodium catalysts [160].

Epoxidation of Alkenes with H_2O_2

The Keggin-type di-vanadium-substituted silicotungstate $[\gamma 1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ (**I**) with the {VO-(μ-OH)$_2$-VO} core catalyzed the epoxidation of various alkenes using only 1 equiv. H_2O_2 with the high epoxide yield and high efficiency of H_2O_2 utilization under very mild reaction conditions. Notably, this system showed unique stereospecificity, diastereoselectivity, and regioselectivity, which are quite different from those reported for the epoxidation systems including $[\gamma SiW_{10}O_{34}(H_2O)_2]^{4-}$ (Scheme 56) [161].

REDUCTIONS

Vapor-Phase Oxidative Dehydrogenation of Isobutyric Acid

One of the great advantages of HPA catalysts is that their catalytic properties can be controlled in a systematic way by replacing protons or by substituting frame work transition-

37
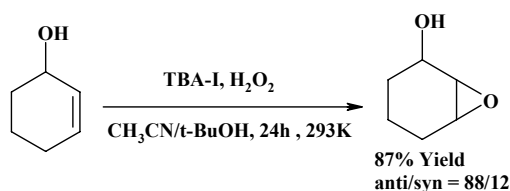
Scheme 56

Scheme 57

metal atoms with different metals [162]. It is well known that vanadium-containing HPAs have a strong reduction potential (oxidizing power) [163].

Recently Vanadium-containing $H_{6+x}P_2Mo_{18-x}V_xO_{62}$ (x = 0, 1, 2 and 3) Wells-Dawson heteropolyacid (HPA) catalysts were used in the oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA). Vanadium-containing $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 0, 1, 2 and 3) Keggin HPA catalysts were also investigated for t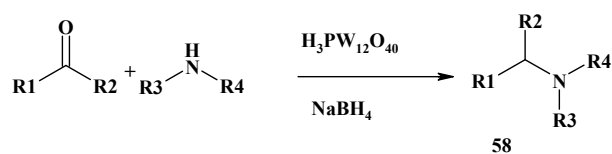he purpose of comparison. The reduction potentials of $H_{3+x}PMo_{12-x}V_xO_{40}$ and $H_{6+x}P_2Mo_{18-x}V_xO_{62}$ catalysts were determined by temperature-programmed reduction (TPR) measurements. The reduction potentials of $H_{3+x}PMo_{12\_x}V_xO_{40}$ and $H_{6+x}P_2Mo_{18-x}V_xO_{62}$ catalysts showed volcano-shaped curves and exhibited the same trend with respect to vanadium substitution. The conversions of IBA over $H_{3+x}PMo_{12-x}V_xO_{40}$ and $H_{6+x}P_2Mo_{18-x}V_xO_{62}$ catalysts also showed volcanoshaped curves and exhibited the same trend with respect to vanadium substitution. However, the $H_{6+x}P_2Mo_{18-x}V_xO_{62}$ catalysts showed a higher reduction potential and a higher conversion of IBA than the $H_{3+x}PMo_{12-x}V_xO_{40}$ catalysts at the same level of vanadium substitution.

A correlation between reduction potential and catalytic activity of the HPA catalysts clearly demonstrated that the conversion of IBA increased monotonically with increasing reduction potential of the HPA catalysts, across both families of vanadium-containing HPA catalysts examined in this work [164].

Direct Reductive Amination and Selective 1,2-Reduction of a,b-Unsaturated Aldehydes and Ketones

Direct reductive amination (of carbonyl compounds) or one-pot reductive alkylation (of amines) is attractive methods for the preparation of amine derivatives in organic synthesis [165].

A simple and convenient procedure for direct reductive amination of aldehydes and ketones with sodium borohydride for synthesis of **58** has been studied (Sheme 57). The reaction has been carried out in methanol in the presence of a catalytic amount of $H_3PW_{12}O_{40}$ (0.5 %mol) (Table 25).

a,b-Unsaturated aldehydes and ketones could be easily converted into the corresponding allyl alcohols **59** by reaction with $H_3PW_{12}O_{40}$ (0.5 mol%)/NaBH$_4$ (Scheme 58) [166].

Hydrogenation of Propanoic Acid

Bulk Keggin heteropoly acids (HPAs) $H_{3+n}[PMo_{12}-nV_nO_{40}]$ (n = 0-2) and their Cs^+ salts catalysed the vapour-phase hydrogenation of propanoic acid at 350 ºC and 1 bar H$_2$ pressure, yielding propanal together with 3-pentanone and propane as the main products. Catalyst acidity (controlled by Cs substitution) had crucial effect on the reaction selectivity. As the Cs content increased, the selectivity to propanal passed a maximum (74-76%). At the same time, the selectivity to propane sharply decreased, whereas 3-pentanone selectivity increased monotonously. This indicated that 3-pentanone is likely to form *via* Cs propanoate intermediate. Partial substitution of Mo(VI) by V(V) in the $PMo_{12}O_{40}^{3-}$ anion had a small effect on the catalyst performance. Initially crystalline, the catalysts became amorphous after reaction, with their surface area significantly reduced. As evidenced by FTIR, $H_4[PMo_{11}VO_{40}]$ and its Cs salts, possessing a higher thermal stability, retain the Keggin structure in their bulk after reaction, whereas less stable $H_3[PMo_{12}O_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ derivatives undergo decomposition. This showed that the as-made crystalline heteropoly compounds were catalyst precursors rather than the true catalysts. The reaction over $Cs_{2.4}H_{1.6}[PMo_{11}VO_{40}]$ was zero order in propanoic acid with an activation energy of 85 kJ mol^{-1}. The formation of propanal was suggested to occur *via* a Mars–Van Krevelen mechanism [167].

Table 25. Direct Reductive Amination of Aldehydes and Ketones

Entry	R1	R2	R3	R4	Yield (%)
1	*tert*-Butyl	H	Phenyl	H	100
2	Phenyl	H	Phenyl	H	93
3	4-Cl-C_6H_4	H	Phenyl	H	89
4	4-NC-C_6H_4	H	Phenyl	H	91
5	2-NO_2-C_6H_4	H	Phenyl	H	95
6	4-Pyridyl	H	Phenyl	H	100
7	2-Furyl	H	Phenyl	H	86
8	*trans*-Cinnamyl	H	Phenyl	H	100
9	Citryl	H	Phenyl	H	98
10	Benzyl	Me	Phenyl	H	96
11	Phenyl	Me	Phenyl	H	90
12	*iso*-Propyl	H	Ethyl	Ethyl	84
13	2-Furyl	H	Ethyl	Ethyl	81
14	4-Pyridyl	H	Ethyl	Ethyl	87
15	4-Me-C_6H_4	H	Ethyl	Ethyl	89
16	4-Cl-C_6H_4	H	Ethyl	Ethyl	89
17	*trans*-Cinnamyl	H	Ethyl	Ethyl	90
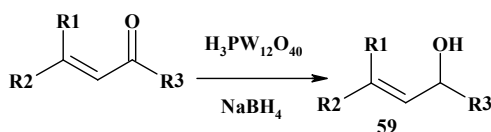
Scheme 58

ELECTROCHEMICAL REACTIONS

Electrochemistry and AElectrocatalysis of Polyoxometalate-Ordered Mesoporous Carbon Modified Electrode

In recent year electrochemical properties of POMs have been intensively studied [168] An important reason is the ability of POMs anions to accept various numbers of electrons giving rise to mixed-valency species, which has made these compounds very attractive in electrode modification and electrocatalytic research [169]. Immobilization of POMs on electrodes not only simplifies their electrochemical study but also facilitates their applications [170].

A convenient and efficient method for the functionalization of ordered mesoporous carbon (OMC) usingvpolyoxometalate $H_6P_2Mo_{18}O_{62}\cdot xH_2O$ (P2Mo18) has been developed [168]. By the method, glassy carbon (GC) electrode modified with P_2Mo_{18} which was immobilized on the channel surface of OMC was prepared and characterized for the first time. The large specific surface area and porous structure of the modified OMC particles resulted in high heteropolyacid loading, and the P_2Mo_{18} entrapped in this order matrix was stable. The electrochemical behavior of the modified electrode was studied in detail, including pH-dependence, stability and so on. The cyclic voltammetry (CV) and amperometry studies demonstrated that P_2Mo_{18}/OMC/GC electrode has high stability, fast response and good electrocatalytic activity for the reduction of nitrite, bromate, idonate, and hydrogen peroxide. The mechanism of catalysis on P_2Mo_{18}/OMC/GC electrode was discussed. Moreover, the development of our approach for OMC functionalization suggested the potential applications in catalysis, molecular electronics and sensors.

Heteropolyacid in Glass Electrolytes for the Development of H_2/O_2 Fuel Cells

Today, the challenge of the fuel cell technology is to render fuel cells economically competitive, but there are also many practical problems to overcome. Many variables must be simultaneously juggled, including the temperature throughout

the cell (which changes and can sometimes destroy a cell through thermal loading), as well as reactant and product levels in various cells. The construction materials must be chosen in order to comply with a variety of tasks and at the present time very few many ceramic materials fill all the requirements completely. The durability and lifetime of the cells can be serious issues in some cases, low power densities in others. Solving all of these issues has as of yet not been decisively accomplished and thus remains the challenge.

In a research on electrochemical activity of H_2/O_2 fuel cells based on the influence of a heteropolyacid glass membrane with a Pt/C electrode at low temperature [171]. A maximum power density of 23.9 mW cm^{-2} was achieved at an operating temperature of 30 ºC when using a P_2O_5-SiO_2-PMA (4-92-4 mol%) glass membrane and a 0.1 mg cm^{-2} Pt/C electrode. This result indicated that the membrane thickness influenced the cell performance of the fuel cell. The H_2/O_2 fuel cells were evaluated by measuring the cell potential and plotting this against the current density and it was observed that a thin electrode/electrolyte showed the best performance in the fuel cell. The power density values increased with increasing humidity as a function of operating time, and correspondingly the current density value also increased at equivalent operating conditions. These results indicated that the membrane and the MEA preparation conditions were key factors for the performance performance of a fuel cell. By summarizing the results of the present study, it could be concluded that heteropolyacid-containing glasses were promising candidates for use as proton-conductors in H_2/O_2 fuel cells. Among the various kinds of fuel cells, the H_2/O_2 fuel cell was the choice of most portable power devices, and this was basically due to its convenient low operating temperature. The possibility of using glasses as electrolytes will became the challenge for the glass membrane community in future days as a result of the heteropolyacid-containing glass material having shown high proton conductivity. Thus the development of new low-cast proton conducting glass membranes is a necessity.

Polyoxometalate-Deposited Pt/CNT Electrocatalyst *via* Chemical Synthesis for Methanol Electrooxidation

Recently Polyoxometalate anion $PMo_{12}O_{40}^{3-}$ (POM) is chemically impregnated into a Pt supported carbon nanotubes

(Pt/CNTs) catalyst that has been prepared *via* a colloidal method [172]. The POM-impregnated Pt/CNTs catalyst system (Pt/CNTs-POM) showed at least 50% higher catalytic mass activity with improved stability for the electrooxidation of methanol than Pt/CNTs or POM-impregnated Pt/C (Pt/C-POM) catalyst systems. The enhancement in electrochemical performance of the Pt/CNTs-POM catalyst system could be attributed to the combined beneficial effects of improved electrical conductivity due to the CNTs support, highly dispersed Pt nanoparticles on the CNTs, and increased oxidation power of the polyoxometalate that could assist oxidative removal of reaction intermediates adsorbed on the Pt catalyst surface.

12-Tungstophosphoric Heteropolyacid Anions Encapsulated in Chemically Modified Mesoporous Silica FSM-16 and Its Electrocatalytic Reduction for Nitrite

As is known, nitrite ions are widely involved in food preserving and are a possible carcinogenic substance. The electrochemical reduction of nitrite ions to the corresponding reduced from in aqueous solution has received considerable attention due to its interference in our environment and high toxicity to human bodies. Direct reduction of nitrite at a bare glass carbon electrode needs a large negative potential. It is thus difficult to directly detect nitrite using this property [173].

12-Tungstophosphoric heteropolyacid anions (PW_{12}) were assembled successfully on the chemically modified mesoporous silica FSM-16. The framework of FSM-16 is maintained upon inserting the guest compound. The composite PW/FSM-16$_{(m)}$-based electrodes had the capability of catalyzing the reduction of nitrite and could be expected as amperometric sensors for nitrite [174].

Electrochemical Behavior and Luminescent Properties of a Multilayer Film Containing Mixed-Addenda Polyoxometalates $K_{10}H_3[Eu(SiMo_9W_2O_{39})_2]$ and Tris(2,2'-Bipyridine)ruthenium(II)

Inorganic-organic composite films containing the mixed-addenda heteropolytungsto-molybdate $K_{10}H_3[Eu(SiMo_9W_2O_{39})_2] \cdot xH_2O$ (abbreviated as EuSiMo$_9$W$_2$) and tris(2,2'-bipyridine)ruthenium(II) Ru(bpy)$_3^{2+}$ (abbreviated as Ru(bpy)$_3$) were fabricated by the layer-by-layer self-assembly method.

UV-Vis spectroscopy showed that the absorbance values at characteristic peaks increased linearly with the number of $EuSiMo_9W_2/Ru(bpy)_3$ bilayers, suggesting that the deposition process was linear and highly reproducible from layer to layer. The composition of the multilayer film was measured by X-ray photoelectron spectra. Atomic force microscopy presented a correspondingly uniform surface morphology and ahomogeneity of the multilayer films. The film exhibited photoluminescence arising from the d-π* metal-to-ligand transition of Ru^{2+}, and $^5D_0$ metastable state to terminate levels in the 7FJ (J = 0-4) ground-state multiplet transitions of Eu^{3+}. The film also exhibited catalytic activities toward the reduction of IO_3^-, H_2O_2, BrO_3^-, NO_2^- and the oxidation of $C_2O_4^{4-}$. It may provide a novel material as bifunctional electrocatalysts and fluorescence probes in biochemistry, luminescence sensors, electroluminescent optical devices, and so on [175].

A Novel Composite Polymer Electrolyte Containing Room-Temperature Ionic Liquids and Heteropolyacids for Dye-Sensitized Solar Cells

A novel composite polymeric gel comprising room-temperature ionic liquids (1-butyl-3-methyl-imidazolium-hexafluorophosphate, $BMImPF_6$) and heteropolyacids (phosphotungstic acid, PWA) in poly(2-hydroxyethyl methacrylate) matrix was successfully prepared and employed as a quasi-solid state electrolyte in dye-sensitized solar cells (DSSCs). These composite polymer electrolytes offered specific benefits over the ionic liquids and heteropolyacids, which effectively enhanced the ionic conductivity of the composite polymer electrolyte. Unsealed devices employing the composite polymer electrolyte with the 3% content of PWA achieved the solar to electrical energy conversion efficiency of 1.68% under irradiation of 50 mW cm^{2-} light intensity, increasing by a factor of more than three compared to a DSSC with the blank $BMImPF_6$-based polymer electrolyte without PWA. These composite polymer electrolytes could be attractive alternative to previously reported whole transporting materials for the fabrication of the long-term stable quasi-solid state or solid state DSSCs [176].

PHOTOCATALYTIC REACTIONS

Photocatalytic Degradation of Textile Dye X-3B

The increasing organic compounds in wastewater has raised serious environmental problem [177]. Various methods have been used to degrade or remove these contaminates by physical, chemical, photochemical and microbiological process [178]. Semiconductors (TiO_2, ZnO, Fe_2O_3, SnO_2, WO_3, *etc.*) act as photocatalysts in photochemical process have received a great deal of attention for their potential to utilize the solar photons [179]. There are a number of similarities between polyoxometalates (POMs) and semiconductor mental oxides [180]. The photochemistry of POMs can be regarded as a model for the photochemical processes on semiconductor mental oxides surfaces.

Titanium dioxide functionalized with Keggin type polyoxometalate (POMs) $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (XW_{12}; X^{n+} = P^{5+}, Si^{4+} and Ge^{4+}) were prepared by sol-gel method. The Keggin structure and dispersion state of POMs were monitored by FT-IR and XRD. The composites showed higher photocatalytic activity than pure TiO_2, pure POMs or mechanical mixture of TiO_2 and POMs for X-3B degradation. Among the three POMs-TiO_2 hybrid materials, the reactivity was: PW_{12} > SiW_{12} > GeW_{12}. With different loading weights for the same POMs, the reactivity followed the order: 30 wt.% > 15 wt.% > 45 wt.% [181].

POM-Based Magnetic Photocatalyst

The photocatalytic performance of a novel polyoxometalate (POM)-based magnetic photocatalyst was studied by photocatalytic degradation of a model compound (formic acid) in an annular fluidized bed photoreactor. Degradation rate, apparent quantum efficiency, and energy efficiency were evaluated and compared with suspended TiO_2 fine particles (Degussa P25) and quartz sand supported TiO_2 photocatalysts. All degradation experiments were conducted under fully irradiated photoreaction (FIP) conditions. Results showed that this novel POM-based magnetic photocatalyst exhibited 2.7-4.2 times higher initial degradation rate and 2.7-3.8 times higher apparent quantum efficiency than the quartz sand supported TiO_2 photocatalyst, depending on the pH of the solution. Though it had lower degradation efficiency and apparent quantum efficiency than suspended P_25, it was proved that this POM-based magnetic photocatalyst could be efficiently separated from treated water by high-gradient

magnetic separation (HGMS), while the separation for P25 fine particles was quite difficult. The magnetic field/gradient in a lab-constructed HGMS was modeled and simulated by finite element analysis (FEA) to examine the particle capture feasibility. Experimental results proved that separation efficiency higher than 90.1% could be achieved under investigated conditions, *i.e.*, flow velocity lower than 1.375 mm s^{-1} under the studied magnetic photocatalyst [182].

Structure, Photochromic, and Electrochemical Properties of Dioctadecylamine/H$_3$PMo$_{12}$O$_{40}$ Langmuir-Blodgett Film

The Langmuir-Blodgett (LB) technique was used to construct a well-defined and structure-controllable photochromic material-a highly ordered multilayer film composed of dioctadecylamine and 12-molybdophosphoric acid (PMo$_{12}$). Well-ordered lamellar structures was identified using Xray diffraction, polarized IR, and Raman spectra, and a packing model of the two components in the LB film was determined. It was found that the Keggin structure and fundamental features of the PMo$_{12}$ ion maintained in the hybrid film. This hybrid LB film displayed photochromic properties upon UV light irradiation and the following process from first-order kinetics was observed. The photochromism exhibited the ability to switch between colorless and blue. A fading process occurred when the film was exposed to ambient air or O$_2$ in the dark. During the color change, the packing structure of the film was well maintained. The electrochemical behavior of the hybrid LB film by cyclic voltammetry in detail was examined and different kinetic mechanisms for the film before and after irradiation were proposed [183].

Preparation of Mesoporous Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$/TiO$_2$ Nanocomposites with Enhanced Photocatalytic Activity

Nanocomposite photocatalysts, cesium hydrogen salts of 12-tungstophosphoric acid coupled with anatase TiO$_2$ (Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$/TiO$_2$, x = 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, respectively), were prepared *via* one-step sol-gel method followed by hydrothermal treatment at 200 ºC with a heating ramp of 2 ºC min^{-1}. Several characterization techniques, UV-Vis diffuse reflectance spectroscopy (UV-Vis/DRS), inductively coupled plasma atomic emission spectroscopy

(ICP-AES), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) patterns, Raman scattering spectroscopy, field emission scanning electron microscopy (FESEM), and N$_2$ adsorption/desorption analysis, were combined to confirm the structure integrity of the Keggin units in the composites and investigate the phase structure and optical absorption properties, morphology, and surface textural properties of the composites. The photocatalytic activities of Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$/TiO$_2$ were evaluated by the degradation of three model organic molecules including 4-nitrophenol (4-NP), methyl orange (MO), and rhodamine B (RB) under UV-light irradiation. For comparison, the photocatalytic activities of the parent Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ and Degussa P25 were studied under the same conditions. The results showed that as-prepared nanocomposite photocatalysts were substantially more effective than the starting Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ and Degussa P25. The high photoactivities of as-prepared nanocomposites could be attributed to the higher surface acidity, mesoporosity, and the synergistic effect existed between the Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ and the TiO$_2$ matrix [184].

Photocatalytic Decomposition of a Perfluoroether Carboxylic Acid by Tungstic Heteropolyacids in Water

The photochemical decomposition of perfluoroether carboxylic acid C$_2$F$_5$OC$_2$F$_4$OCF$_2$COOH (EEA), which is being introduced in industry as a surfactant alternative to environmentally persistent and bioaccumulative perfluorocarboxylic acids, was investigated by use of water-soluble tungstic heteropolyacids H$_3$PW$_{12}$O$_{40}$ and H$_4$SiW$_{12}$O$_{40}$ and the results were compared with those of conventional techniques, UV-Vis light irradiation in the presence of H$_2$O$_2$, treatment with Fenton's reagent, and heterogeneous TiO$_2$ photocatalyst. H$_4$SiW$_{12}$O$_{40}$ induced little photochemical decomposition of EEA. Irradiation with UV-Vis light in the presence of H$_2$O$_2$ and treatment with Fenton's reagent also led to little decomposition of EEA. Alternatively, irradiation of EEA at wavelengths of >290 nm in the presence of H$_3$PW$_{12}$O$_{40}$ under an oxygen atmosphere efficiently decomposed EEA to F$^-$ and CO$_2$. The reaction followed pseudo-first-order kinetics, and the decomposition rate was almost identical with that of the corresponding perfluorocarboxylic acid, that is, C$_5$F$_{11}$COOH. The proposed

reaction mechanism involves redox reactions between EEA, the heteropolyacid catalyst, and oxygen, followed by C-C bond cleavage between $C_2F_5OC_2F_4OCF_2$ and COOH (induced by the photo-Kolbe mechanism), and subsequent formation of $C_2F_5OCF_2COOH$ and trifluoroacetic acid. EEAwas also photocatalytically decomposed by TiO_2 with a rate constant comparable with that by $H_3PW_{12}O_{40}$. Although the reactivity of TiO_2 toward perfluorocarboxylic acids was reported to be very low, EEA, which has ether linkages in the perfluoroalkyl chain, was clearly decomposed to F^- and CO_2. This fact suggests that oxidative active species other than OH radicals significantly participate in the reaction [185].

Preparation, Characterization and Photocatalytic Applications of Amine-Functionalized Mesoporous Silica Impregnated with Transition-Metal-Monosubstituted Polyoxometalates

Amine-functionalized mesoporous silica materials impregnated with transition-metal-monosubstituted polyoxometalates, $K_5[M(H_2O)PW_{11}O_{39}](EtO)_3SiCH_2CH_2CH_2$ NH_2-MCM-48 (M = Co/Ni), were prepared by coordination of nickel/cobalt centers in the clusters with the amine surface groups in amine-functionalized mesoporous silica supports. The materials obtained were characterized by powder X-ray diffraction (XRD), UV-Vis diffuse reflectance spectra (UV-Vis-DR), infrared (IR) spectra, magic-angle spinning ^{31}P MAS NMR, transmission electron microscopy (TEM) and nitrogen adsorption measurements, indicating that the primary Keggin structures remained intact in as-prepared composites, and the composites possessed mesoporous structures. The composites exhibited UV-photocatalytic activity to degrade dye rhodamine B (RB), and the pesticides including hexachlorobenzene (HCB) and methylparathion (MPT). Leakage of $K_5[M(H_2O)PW_{11}O_{39}]$ from the support was hardly observed during the photocatalytic tests, attributed to strong coordination interactions between the Keggin units and the amine-functionalized silica surface [186].

Preparation and Heterogeneous Photocatalytic Activity of Mesoporous $H_3PW_{12}O_{40}$/ZrO_2 Composites

A series of mesoporous zirconia supported Keggin units with different $H_3PW_{12}O_{40}$ loading levels (5-20 wt.%) and phase structures (amorphous, tetragonal, and the mixed phases

of tetragonal and monoclinic) were prepared by a modified wet impregnation method. The phase structures, chemical structures, optical absorption properties, surface physicochemical properties, and morphologies of the composites were well-characterized *via* X-ray diffraction (XRD) patterns, FT-IR spectroscopy, Raman scattering spectroscopy, UV-Vis diffuse reflectance spectroscopy (UV-Vis/DRS), nitrogen adsorption/desorption determination, and field emission scanning electron microscopy (FESEM), indicating that the primary Keggin structure remained intact after formation of the composites, and impregnation of the Keggin unit into the surface of ZrO_2 framework has an influence on the electronic properties of the ZrO_2. The heterogeneous photocatalytic activity of as-prepared composites was studied *via* the model reactions of degradation of an aqueous 4-nitrophenol (4-NP) and dye methylene blue (MB) under aerobic condition, indicating that the photocatalytic activity of the composites was influenced by the factors such as phase structures, optical absorption properties, and surface physicochemical properties of the composites [187].

OTHER DEVELOPMENTS

Synthesis and Physicochemical Properties of Zr-MCM-41 Mesoporous Molecular Sieves and Pt/$H_3PW_{12}O_{40}$/Zr-MCM-41 Catalysts

For the first time, modifications of the surface and framework of Si-MCM-41 by depositing a heteropolyacid on the surface and by introducing foreign Zr^{4+} ions into the framework was investigated. The Zr-modified Si-MCM-41 mesoporous materials (hereafter referred as WSZn, n ¼Si/Zr ¼25, 15, 8, 4) were synthesized through a surfactant-templated preparation approach, using low-cost fumed silica as the Si precursor. After impregnation with 25wt% of $H_3PW_{12}O_{40}$, the surface Bronsted acidity of the Pt/$H_3PW_{12}O_{40}$/WSZn catalysts was greatly enhanced by 2-10 times relative to the bare WSZn support. Two kinds of supported heteropolyacids were formed: (i) bulk-like heteropolyacid crystals with unchanged Keggin structures, and (ii) highly dispersed heteropolyacid with distorted Keggin units. The formation of various kinds of heteropolyacid structures is closely related to the interaction between the heteropolyanions and the hydroxyl groups in the

host support [188].

Immobilization of a Heteropolyacid Catalyst on the Aminopropyl-Functionalized Mesostructured Cellular foam (MCF) Silica

Mesostructured cellular foam (MCF) silica with high surface area (>600 m^2 g^{-1}) and large pore volume (>1.16 cm^3 g^{-1}) was synthesized *via* a surfactant templating method. The MCF silica was then modified by grafting 3-aminopropyl-triethoxysilane (APTES) to create a positive charge on the surface, and thus, to provide sites for the immobilization of H$_3$PMo$_{12}$O$_{40}$. By taking advantage of the overall negative charge of [PMo$_{12}$O$_{40}$]$^{3-}$, the H$_3$PMo$_{12}$O$_{40}$ catalyst was chemically immobilized on the aminopropyl group of the surface modified MCF silica as a charge matching component. The mesopore structure of MCF silica was maintained even after the surface modification step and the subsequent immobilization step of H3PMo$_{12}$O$_{40}$. The H$_3$PMo$_{12}$O$_{40}$ species were finely and molecularly dispersed on the surface modified MCF silica *via* chemical immobilization [189].

Direct Incorporation of Heteropolyacids into Organized Mesoporous Silica

The direct incorporation of Keggin-type heteropolyacid H$_3$PW$_{12}$O$_{40}$ (PW) in a mesoporous organized silica molecular sieve during the synthesis was studied. The synthesis of silica-organized materials containing heteropolyacid was carried out in acidic media either by associating a nonionic/cationic surfactants or just a non-ionic surfactant. The decomposition temperature of solids containing PW and prepared with TX100/CTMA, Tergitol 15-S-12 and Tween 60 starts at 130, 115 and 135 ºC, respectively. The BET surface area of these solids is measured to be 892, 735 and 787 m^2 g^{-1}, respectively. Their pore diameters are equal to 31, 24 and 34 A°, respectively [190].

Highly Active Deep HDS Catalysts Prepared Using Mo and W Heteropolyacids Supported on SBA-15

A series of Mo (W) catalysts promoted by Ni and supported on pure siliceous SBA-15 was prepared using Keggin-type heteropolyacids (H$_3$PMo$_{12}$O$_{40}$ or H$_3$PW$_{12}$O$_{40}$) as active phase precursors. These catalysts were compared with corresponding NiMo(W)/SBA-15 catalysts prepared from the

traditional precursors (ammonium heptamolybdate, ammonium metatungstate). Prepared catalysts were characterized by N$_2$ physisorption, small- and wide-angle XRD, UV-Vis DRS, FT-IR, TPR, ^{31}P MAS NMR, HRTEM and evaluated in hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT). It was found that both Mo and W catalysts prepared from heteropolyacids showed better performance in deep HDS of 4,6-DMDBT than the counterparts prepared from traditionally used Mo (W) ammonium salts. The possible reasons of this phenomenon are discussed [191].

Environmentally Friendly Synthesis of Wells-Dawson Heteropolyacids Active Acid Sites Investigation Through TPSR of Isopropanol

Fosfo-tungstic and fosfo-molybdic Wells-Dawson heteropolyacids, H$_6$P$_2$W$_{18}$O$_{62}$.xH$_2$O and H$_6$P$_2$Mo$_{18}$O$_{62}$.xH$_2$O, respectively, were synthesized through ion-exchange. This novel method possesses a higher yield (~90%) than the conventional organic route (~70%). Wells-Dawson heteropolyacids are obtained when the corresponding ammonium salt [(NH$_4$)$_6$P$_2$W$_{18}$O$_{62}$.13H$_2$O or (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$.12H$_2$O] is kept in contact with an acid resin [about (1:0.8) salt:resin weight ratio] up to 3 days. The use of an organic media instead of an aqueous media greatly favors the completeness of the exchange. Temperature programmed surface reaction of chemisorbed isopropoxy species towards propylene allows determined the number of active acid surface/bulk sites and the activation energy of the surface reaction. This parameter provided evidences of the influence of the central phosphorous atom and oxide supports on the acid strength of the active sites [192].

Isomerization of Linear Butane to Isobutene

Water minimized a decrease in conversion for the isomerization of linear butene to isobutene on silica-supported heteropolyacid (H$_4$SiW$_{12}$O$_{40}$) catalysts while maintaining high selectivity toward isobutene. The role of water was related to surface acidic properties (number of surface acid sites and acid strength) and characteristics of hydrocarbon deposits (extent of deposits and hydrogen/carbon ratio), as determined by benzonitrile and ammonia temperature-programmed desorption as well as temperature-programmed oxidation of

fresh and spent catalysts. It appears that highly unsaturated hydrocarbon deposits consisting of 8-12 carbon units covered surface acid sites, especially strong acid sites, limiting the isomerization reaction. Water in the feed was helpful in preserving the acid sites and decreasing the number of carbon units in the hydrocarbon deposits. Thus, conversion occurred more readily in the presence of water than in the absence of water [193].

Support Effects on Ru-HPA Bifunctional Catalysts: Surface Characterization and Catalytic Performance

The behaviour of three metal-acid bifunctional catalysts, where the metal was Ru and the acid function was a heteropolyacid (HPA), was compared in the hydroconversion of n-hexane. Both the activity and the selectivity pattern depended on the used support: silica, high surface area graphite (HSAG) or zeolite KL. While Ru-HPA-SiO$_2$ gave selectivity to isomerization products of 97%, the Ru-HPA-KL sample gave a selectivity of 96% to hydrogenolysis products. And, the performance of Ru-HPA-HSAG lied between that for Ru-HPA-SiO$_2$ and Ru-HPA-KL, giving both isomerization and hydrogenolysis products, with selectivities of 45 and 54%, respectively. The series of techniques applied to characterize the catalysts have assisted in understanding the catalytic performance. The HPA phase has been detected over all the HPA-modified supports, but different acid sites strength distributions have been determined by calorimetry of NH$_3$ adsorption, following the order HPA-SiO$_2$ > HPA-HSAG > HPA-KL. Also, different Ru species have been observed on the catalysts surface due to the interaction between the Ru precursor and the HPA support. Finally, the analysis of the results has suggested that the support determines the role played by both metal and acid functions, which separately would lead to hydrogenolysis and isomerization reactions, respectively [194].

Ethylene and Diethyl-Ether Production by Dehydration Reaction of Ethanol over Different Heteropolyacid Catalysts

Dehydration reaction of ethanol was investigated in a temperature range of 140-250 ºC with three different heteropolyacid catalysts, namely tungstophosphoricacid (TPA), silicotungsticacid (STA) and molybdophosphoricacid

(MPA). Very high ethylene yields over 0.75 obtained at 250 ºC with TPA was highly promising. At temperatures lower than 180 ºC the main product was diethyl-ether. Presence of water vapor was shown to cause some decrease of catalyst activity. Results showing that product selectivities did not change much with the space time in the reactor indicated two parallel routes for the production of ethylene and DEE. Among the three HPA catalysts, the activity trend was obtained as STA > TPA > MPA [195].

Determination of Pesticides Using Heteropolyacid Montmorillonite Clay-Modified Electrode with Surfactant

Redox behavior of three pesticides, namely isoproturon, carbendazim and methyl parathion was investigated electrochemically using hetropolyacid montmorillonite clay-modified glassy carbon electrode in the presence and absence of a surfactant, cetyl trimethyl ammonium bromide. A solution of 0.1 M H$_2$SO$_4$ in 50% aqueous alcohol (pH 1.0) was found to be suitable medium for electroanalysis. Isoproturon exhibited one well-defined oxidation peak around 1.2 V along with one more oxidation and reduction peaks. Carbendazim showed only one well-defined anodic peak around 1.4 V. Methyl parathion exhibited one well-defined reduction peak around -0.26 V and the oxidation peak appeared around 0.510 V. In the second cycle, a new cathodic peak was found around 0.420 V. The presence of surfactant enhanced the peak current and hence stripping voltammetric determination procedures for all the three pesticides were developed. Square wave stripping mode was employed and the maximum current experimental conditions were arrived at. Calibration plot was made for all the three pesticides. The determination limit and standard deviations were arrived at. The applicability of the method was also verified in a soil sample and water analyte [196].

Solvothermal Synthesis of ZnO Microspheres

With the assistance of Keggin-type polyoxometalate (POM) H$_3$PW$_{12}$O$_{40}$.nH$_2$O (PW$_{12}$), ZnO microspheres have successfully been synthesized by a direct route, using zinc acetate dihydrate solid and dilute PW$_{12}$ absolute ethanol solution at 120 ºC for 24 h. The effects of PW$_{12}$ concentration and reaction time were investigated. The results showed that

PW_{12} played a vital role for the formation of the ZnO microspheres during the solvothermal treatment and the original framework of PW_{12} was not destroyed after the solvothermal treatment. Finally, the room temperature photoluminescence (PL) spectrum of the ZnO microspheres exhibited a sharp and strong ultraviolet (UV) emission at 390 nm and a quite weak visible emission at around 520 nm, respectively [197].

Dehydration of Xylose into Furfural

Cesium salts of 12-tungstophosphoric acid, $Cs_xH_{3-x}PW_{12}O_{40}$ (Cs$_x$PW), in the bulk form or supported on medium-pore MCM-41 (3.7 nm) or large-pore (9.6 nm) micelle-templated silicas was reported to be active solid acid catalysts for the cyclodehydration of xylose into furfural, in a toluene/water solvent system (T/W) or in dimethyl sulfoxide (DMSO). The catalytic results were comparable to those obtained using sulfuric acid, under similar reaction conditions. The initial activities increased in the order $H_3PW_{12}O_{40}$ < $Cs_{2.0}$PW < $Cs_{2.5}$PW < silica-supported CsPW catalysts (15, 34 wt% PW). Higher HPA loadings, larger pore diameter of the parent silica support, and higher reaction temperatures lead to higher furfural yields. The stability and reusability of the MCM-41-supported CsPW is higher in DMSO than in T/W [198].

Network Films of Conducting Polymer-Linked Polyoxometalate-Modified Gold Nanoparticles: Preparation and Electrochemical Characterization

The ability of Keggin-type phosphododecamolybdate ($PMo_{12}O_{40}^{3-}$, PMo_{12}) to undergo chemisorption on solid surfaces (including gold) was explored to convert (by ligand place-exchange and phase transfer to aqueous solution) the alkanothiolate-modified Au nanoparticles of controlled size (prepared in toluene) into a stable colloidal solution of PMo_{12}-protected gold nanoparticles, PMo_{12}-AuNPs, the sizes of which were *ca.*, 4-5 nm as determined by transmission electron microscopy. By dip-coating, PMo_{12}-AuNPs were assembled on carbon electrode substrates. The step-by-step assembly, by which alternate exposures to the solutions of PMo_{12}-AuNPs and either anilinium cations or pyrrole monomers, was utilized to grow in controlled manner hybrid network films in which the negatively charged PMo_{12}-AuNP deposits were linked, or electrostatically attracted, by ultra-thin, positively charged conducting polymer (polyaniline or polypyrrole) structures. The three-dimensionally distributed PMo_{12}-AuNPs immobilized within the polypyrrole-based composite film exhibited some electrocatalytic reactivity towards reduction of hydrogen peroxide [199].

A Novel Sandwich Polyoxotungstogermanate: Synthesis, Crystal Structure and Magnetic Property of $[Pr(GeW_{11}O_{39})_2]^{13-}$

A novel sandwich-type polyoxometalate built on the lancunary Keggin-type polyanion $[GeW_{11}O_{39}]^{8-}$ and trivalent rare earth ion, $K_{11.5}H_{1.5}[Pr(GeW_{11}O_{39})_2].29H_2O$ has been synthesized and characterized by IR spectroscopy, UV electronic spectroscopy, luminescencespectroscopy, cyclic voltammetry and single crystal X-ray diffraction. In compound $K_{11.5}H_{1.5}[Pr(GeW_{11}O_{39})_2].29H_2O$, PrIII cation sandwiched between two $[GeW_{11}O_{39}]^{8-}$ anions was of eight coordination and occupies square anti-prismatic geometry. The magnetic investigation of compound $K_{11.5}H_{1.5}[Pr(GeW_{11}O_{39})_2].29H_2O$ demonstrated the presence of an antiferromagnetic interaction in that compound [200].

Polyoxometalate Salts of Cationic Nitronyl Nitroxide Free Radicals

Purely organic crystalline materials showing ferromagnetism have attracted the interest of synthetic chemists for a long time [201]. These materials consist in a crystalline arrangement of open-shell molecules that propagate magnetic interactions in such a way that bulk ferromagnetism becomes possible at very low temperatures. Among the readily available paramagnetic molecules, the family of nitronyl nitroxide (NN) free radicals has been thoroughly studied due to its persistence and ease of functionalization [202]. Also, single crystals can be grown by simple techniques and the molecules can be organized in the solid state using the concepts of crystal engineering [203]. For instance, hydrogen bonding and other types of non-covalent interactions have been used to create specific crystal packings by design [204]. The challenge is now to control the sign and strength of magnetic interactions between neighboring molecules, a problem that is also being addressed from a theoretical point of view. For many years, the main guideline for the design of

magnetic interactions in organic ferromagnets came from McConnell first proposal, establishing that ferromagnetic coupling arises from intermolecular interactions between atoms carrying spin densities of opposite signs [205].

The cationic nitronyl nitroxide free radical of the N-methylpyridinium type p-MepyNN has been combined with $[Mo_8O_{26}]^{4-}$ and Keggin $[SiW_{12}O_{40}]^{4-}$ polyanions to afford salts (p-MepyNN)$_4$[Mo$_8$O$_{26}$].DMSO (DMSO = dimethylsulfoxide) and (p-MepyNN)$_4$[SiW$_{12}$O$_{40}$].6DMF (DMF = dimethyl-formamide). Their structural and magnetic properties were studied [206].

Self-Assembly of [b-As(V)W$_8$O$_{31}$]$^{9-}$ Subunit in Hydrothermal Nsystem with Moderate Acidity: Synthesis, Crystal Structure and Characterizations of Dimeric Arsenotungstate H$_2$[{Cu(phen)}$_8$(b-AsW$_8$O$_{31}$)$_2$].2.5H$_2$O

A novel dimeric arsenotungstate based on tetravacant subunit, H$_2$[{Cu(phen)}$_8$(b-AsW$_8$O$_{31}$)$_2$].2.5H$_2$O (phen = 1,10-phenanthroline), has been prepared by hydrothermal methods with moderate acidity and characterized by elemental analyses, IR (25-650 ºC), EPR, XPS, TG-DTA, and single-crystal X-ray diffraction. This compound represented the first arsenotungstate example based on tetravacant Keggin polyanions. Furthermore, the comparison of b-Asw$_8$O^{9-}$_{31}$ with few known tetravacant blocks exhibits the variety of XW8On$^-$$_{31}$ family in synthesis methods and existent forms [207].

Heteropoly Acid Supported on Titania as Solid Acid Catalyst in Alkylation of p-Cresol with $tert$-Butanol

Butylation of p-cresol with $tert$-butanol was investigated on titania modified with 12-tungstophosphoric acid (TPA/TiO$_2$) catalyst under vapor phase conditions. Catalysts with different TPA loadings (10-25 wt.%) and calcination temperatures (650-750 ºC) were prepared by suspending titanium hydroxide in methanol solution of TPA followed by drying and calcination. These catalysts were characterized by surface area, XRD, ^{31}P MAS NMR, XPS, NH3-TPD, and FTIR pyridine adsorption. XRD results indicated that the presence of TPA retarded the crystallization of titania and stabilized TiO$_2$ in anatase phase. ^{31}P MAS NMR indicated the presence of TPA in various forms (dispersed, highly fragmented and Keggin intact). These catalysts showed both Bronsted and Lewis acidity, and 20% TPA on TiO$_2$ calcined at 700 ºC (from here after words 20% TT-700) had the highest Bronsted as well as total acidity. Further, the catalytic activities were examined in $tert$-butylation of p-cresol with $tert$-butanol. The catalytic activity depended on TPA coverage, and the highest activity corresponded to the monolayer of TPA on titania. The most active catalyst 20% TT-700 gave 82% conversion of p-cresol and 89.5% selectivity towards 2-$tert$-butyl cresol (TBC), 2,6-di-$tert$-butyl cresol (DTBC) 7.5% and cresol-$tert$-butyl ether (CTBE) 3% under optimized conditions. The activity was always higher than that of WO$_3$/ZrO$_2$, sulfated zirconia (SZ), USY, H-β zeolites and montmorillonite K-10 (K-10 mont) under similar conditions [208].

Silylated Pillared Clay (SPILC): A Novel Bentonite-Based Inorgano-Organo Composite Sorbent Synthesized by Integration of Pillaring and Silylation

The feasibility of synthesizing inorgano-organo composites based on bentonite-silylated pillared interlayered clays (SPILCs) has been examined by pre-pillaring of bentonite with the Keggin ion (hydroxyaluminum polycation) and then silylating with alkylchlorosilanes. The results of organic carbon content analysis, FTIR, XRD, and DTA/TG indicated that the silyl group could be successfully grafted to the inner surface of pillared interlayered clays (PILCs) through reaction with the -OH groups of the pillars and the d-spacing of synthesized PILCs and SPILCs were almost the same. SPILCs had both the higher organic carbon content relative to original bentonite and PILCs and the better surface and pore properties relative to surfactants-modified organobentonites. A comparison of the modifier demand of SPILCs and CTMAB-bentonites indicated that the silylation of PILCs was a modifier-economized process for organically modification of bentonite. The heat-resistant temperature of SPILCs, 508 ºC for OTS-Al-PILC and 214 ºC for TMCS-Al-PILC, are more excellent organobentonites. Unlike the partition-predominated sorption mechanisms of organobentonites, both adsorption and partition are important components of sorption mechanism of SPILCs. The VOC sorption capacity of SPILCs was approximately same with that of organobentonites and the hydrophobicity of SPILCs is superior to that of PILCs [209].

Synthesis and Characterization of New Tungstosilicate Aggregates Assembled with a Mixture of Mono- and Trivacant Keggin Fragments

It was shown that the reaction mixture of two lacunary Keggin-type polytungstosilicates $K_8[\alpha\text{-}SiW_{11}O_{39}]$ and $Na_9[A\text{-}\beta\text{-}SiW_9O_{34}H]$ in aqueous solution with different pH values led to the isolation of two new aggregates $K_4Na_{11}Li_5[Si_3W_{26}O_{94}]$.~$21H_2O$ and $K_5Na_{11}[Si_2W_{19}O_{69}(H_2O)]$. ~$22H_2O$. Single crystal X-ray diffraction analyses reveal that the polyoxoanion of $K_4Na_{11}Li_5[Si_3W_{26}O_94]$.~$21H_2O$ consists of two $\{B\text{-}a\text{-}SiW_9O_{34}\}$ trivacant Keggin units and one B-type hexavacant $\{B\text{-}SiW_6O_{26}\}$ fragment which were connected by two disordered $\{WO_6\}$ octahedra to form a C-shaped aggregate. Compound $K_5Na_{11}[Si_2W_{19}O_{69}(H_2O)]$.~$22H_2O$ was composed of two $\{A\text{-}a\text{-}SiW_9O_{34}\}$ building blocks linked by a $\{WO(H_2O)\}$ segment. These two structural topologies were firstly observed in polytungstosilicate family and their possible assembly routes were speculated [210].

Hydrothermal Syntheses, Crystal Structures and Thermal Decompositions of two Novel Heteropolytungstates with Anion-Chain Structure Formed by Monosubstituted Keggin Units

Two novel heteropolytungstates, $[Cu(en)_2][Hen]_2$ $[HPW_{11}CuO_{39}].2H_2O,H_2en]_4[SiNaW_{11}O_{39}]Cl.2H_2O$ have been prepared under mild hydrothermal conditions and structurally characterized by elemental analysis, TG, IR, and single-crystal X-ray diffraction. Compounds $[Cu(en)_2][Hen]_2[HPW_{11}CuO_{39}]$.$2H_2O$, $H_2en]_4[SiNaW_{11}O_{39}]Cl.2H_2O$ exhibited a straight chain structure in which monosubstituted Keggin anions were connected through their terminal oxygen atoms. Compound $[H_2en]_4[SiNaW_{11}O_{39}]Cl.2H_2O$ was a rare example of a disorder-free monovacant Keggin. The deformation of the Keggin structure caused by the replacement of one tungsten atom was indicated. A large number of hydrogen bonds exist between ethylenediamine molecules, water molecules and anion-chains, which built a three-dimensional architecture. Their thermal decomposition mechanism was inferred and includes a carbonization-oxidation reaction of organic contents [211].

UV-Vis Absorption Edge Energy of Heteropolyacids (HPAs) as a Probe of Catalytic Performance of HPAs in the Oxidative Dehydrogenation of Isobutyric Acid

UV-Visible spectroscopy studies of heteropolyacid (HPA) catalysts in solid were carried out with an aim of utilizing absorption edge energies as a probe of catalytic oxidation performance of the HPA catalysts. The absorption edge energies were correlated with the catalytic performance of HPA catalysts in the oxidative dehydrogenation of isobutyric acid. The correlation between catalytic oxidation performance and absorption edge energies of HPA catalysts demonstrated that the absorption edge energies could be utilized as a correlation parameter for the reduction potentials (oxidizing powers) of the HPA catalysts, and furthermore, as a probe of catalytic oxidation performance of the HPA catalysts [212].

Spectroscopic Studies of Eu(III) Keggin's and Dawson's Polyoxotungstates Substituted by Acetato and Oxalato Ligands

Eu(III) Keggin's and Dawson's type of polyoxometalates (POM) complexes were synthesized and spectroscopically characterized. This work presents results obtained for chosen hybrids of acetato $K_{12}[\{Eu(SiMo_xW_{11-x}O_{39})(H_2O)\}2(CH_3COO)_2] \cdot nH_2O$, $K_{16}[\{Eu(CH_3COO)(H_2O)_2 (P_2W_{17}O_{61})\}_2] \cdot nH_2O$ and oxalate $(NH_4)_{29}K_5[\{Eu(P_2W_{17}O_{61})\}4(C_2O_4)3(H_2O)_4] \cdot nH_2O$, where $x = 0, 1$. The solid state compositions of the hybrids were characterized by using elemental and ICP-AES analysis, derivatography and FTIR spectroscopy. Luminescence characteristics (intensity, quantum yields, luminescence lifetimes and excitation spectra in the range of the $5D0 \leftarrow 7F0$ transition) of the synthesized Eu(III) acetato and oxalato complexes were determined in the solid phase and in solution, and they were compared to their parent Eu(III):POM complexes of 1:1 stoichiometry (ML) [213].

Keggin Polyoxometalates-Supported Assembly of 2D Supramolecular Isomers: Synthesis, Crystal Structures and Characteristics of Two Novel Hybrid Host-Guest Complexes

Two novel hybrid host-guest architectures based on metal-organic fragments and Keggin polyoxometalates, namely $[\alpha\text{-}Cu_{12}(trz)_8]^-$ $[PMo_{12}O_{40}].H_2O$ and $[\beta\text{-}Cu_{12}(trz)_8][PMo_{12}O_{40}].2H_2O$ (trz = 1,2,4-triazole), have been prepared under hydrothermal conditions and characterized by single-crystal X-ray diffraction (XRD), elemental analysis, powder XRD, ESR, FT-IR, UV-Vis and thermogravimetric analysis (TGA). The $[Cu_{12}(trz)_8]^{4+}$ hosts in compounds $[\alpha\text{-}Cu_{12}(trz)_8]^-$

$[PMo_{12}O_{40}].H_2O$ and $[\beta\text{-}Cu_{12}(trz)_8][PMo_{12}O_{40}].2H_2O$ were two-dimensional (2D) supramolecular isomers, which present 44 topology based on $Cu_4(trz)_4$ cyclic units and 63 topology based on $Cu_3(trz)_3$ cyclic units, respectively. The metalmacrocyclic $Cu_8(trz)_8$ and $Cu_9(trz)_9$ rings represent the largest examples in the coordination chemistry of 1,2,4-triazole. 2D metal-organic fragments and Keggin anions both are connected *via* hydrogen bonds and Cu….O short contacts to form interesting 3D host-guest architectures of $[\alpha\text{-}Cu_{12}(trz)_8]^{-}$ $[PMo_{12}O_{40}].H_2O$ and $[\beta\text{-}Cu_{12}(trz)_8][PMo_{12}O_{40}].2H_2O$ [214].

CONCLUSIONS

In this review some of applicatios of heteropolyacides and their salts have been discussed. Heteropolyacids can be used as an acidic catalyst in various organic reactions such as oxidatrion, reduction and multi- component reactions. From the reported results it can be concluded that heteropolyacids are efficient, reusable, green and inexpensive catalyst and their use has been growing rapidly. Many efforts have been devoted to improve the characteristics and nature of heteropolyacids by using various supports such as mesoporous compounds and silica. Beside catalytic activities in the organic reactions, heteropolyacids show interesting applications in photochemistry and electrohemistry.

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