

Aerobic oxidation of aldehydes catalyzed by ϵ -Keggin type polyoxometalates $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ ($\text{X} = \text{Ni}, \text{Co}, \text{Mn}$ and Cu) as heterogeneous catalysts

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Abstract

Polyoxometalates of the ϵ -Keggin structure $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ ($\text{X} = \text{Ni}, \text{Co}, \text{Mn}$ and Cu), have been synthesized. While the nickel substituted compound was known, the cobalt, manganese and copper analogs are new. These ϵ -Keggin polyoxometalates are insoluble and, except for the nickel analog, could not be obtained in crystalline form. The IR spectra indicate that for cobalt and manganese substitution the compounds are isostructural to the nickel derivative. The ϵ -Keggin polyoxometalates were used as heterogeneous catalysts for the aerobic oxidation of aldehydes to carboxylic acids. 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. 2-Methyl-undecanal reacted quite selectively yielding as minor product 2-undecanone by decarboxylation. 2-Phenylpropanal showed more significant β -methyl cleavage. Substrates with a variety of functional moieties such as myrtenal and 5-norbornene-2-carboxaldehyde yielded considerable amounts of formates via a Dakin type reaction and allylic oxidation products.

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1. Introduction

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. However, the ground state properties of molecular oxygen place in our path considerable difficulties, which need to be surmounted. The limiting properties are the radical nature of molecular oxygen, the strong oxygen–oxygen bond and the fact that one electron reduction of oxygen is generally not thermodynamically favored. The ground state properties of molecular oxygen lead to the situation that often under typical liquid phase metal-catalyzed reaction conditions, reactions proceed by the well-known auto-oxidation pathway.

Despite the limitations, polyoxometalates have been investigated as catalysts and successfully used for aerobic oxidation

reactions that are based on various mechanistic motifs. The oldest and possibly most developed of all the mechanistic motifs is one whereby, the polyoxometalate activates the reaction substrate, either organic or inorganic, rather than the oxygen that serves as the ultimate oxidant. In such catalytic reactions the polyoxometalate, often phosphovanadomolybdates of the Keggin structure, undergoes a redox type interaction involving electron transfer with the reaction substrate leading to its oxidation and concomitant reduction of the polyoxometalate. Molecular oxygen is used to reoxidize the reduced polyoxometalate [1].

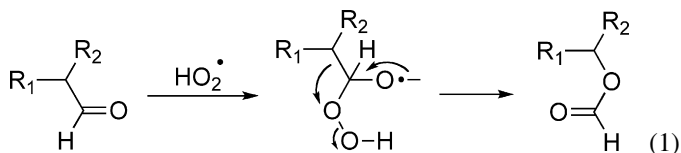
Polyoxometalates with the required redox properties can also be used in a straightforward manner as autooxidation catalysts. In this way the trisubstituted Keggin compound $[\text{M}_3(\text{H}_2\text{O})_3\text{PW}_9\text{O}_{37}]^{6-}$ ($\text{M} = \text{Fe}^{\text{III}}$ and Cr^{III}) and $[\text{Fe}_2\text{M}(\text{H}_2\text{O})_3\text{PW}_9\text{O}_{37}]^{7-}$ ($\text{M} = \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}$ and Zn^{II}) were used in the autooxidation of alkanes such as propane and isobutane to acetone and *t*-butyl alcohol [2]. $[\text{Fe}_2\text{Ni}(\text{OAc})_3\text{PW}_9\text{O}_{37}]^{10-}$ was used to oxidize alkanes such as adamantane, cyclohexane, ethylbenzene and *n*-decane [3]. An interesting recent application of such an autooxidation is the oxidation of 3,5-di-*tert*-catechol by iron and/or vanadium substituted polyoxometalates [4]. Also $[\text{Co}^{\text{II}}\text{PMo}_{11}\text{O}_{39}]^{5-}$, was used

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as a bifunctional catalyst for the autooxidation of cumene to the hydroperoxo/peroxo intermediate followed by oxygen transfer to an alkene such as 1-octene to yield epoxide [5].

One way to utilize molecular oxygen in autooxidation reactions is to oxidize a sacrificial reagent to yield peroxo and oxo radical species as intermediates. In possibly the most synthetically interesting case, a polyoxometalate may initiate a radical chain reaction between oxygen and an aldehyde as sacrificial reagent. Aldehydes are practical sacrificial reagents because the relatively low carbon–hydrogen homolytic bond energy allows easy formation of the initial intermediates. Also some aldehydes such as isobutyraldehyde are readily available and inexpensive. As for all peroxygen species, these active intermediates may then be used for the epoxidation of alkenes, the oxidation of alkanes to ketones and alcohols, and for the Baeyer–Villiger oxidation of ketones to esters. This has been demonstrated using both vanadium ($\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$) and cobalt ($[\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{5-}$) containing Keggin type polyoxometalates as catalysts with isobutyraldehyde as the preferred acylperoxo/peracid precursor [6]. Interestingly the aerobic oxidation of aldehydes to carboxylic acids by polyoxometalates has seldom been investigated as a synthetically useful transformation although Hill and coworkers have studied such reactions in the context of air decontamination [7].

Normally, simple linear aliphatic aldehydes and aromatic benzaldehyde derivatives can be selectively oxidized with molecular oxygen to the corresponding carboxylic acids. One prominent group of aldehydes that are difficult to oxidize selectively are those that are susceptible to the Dakin reaction, Eq. (1), that probably proceed through a Baeyer–Villiger type mechanism. Aldehydes substituted at the β -position and also α,β -unsaturated aldehydes commonly react in this way to yield formate esters as shown below.



For example, the oxidation of 2-ethylhexanal has been researched both in the presence and absence of metal carboxylates. The highest selectivity to carboxylic acid in the absence of catalyst was 71.4%, whereas a maximum selectivity of 80.8%, was reached in the presence of Mn(II) ethylhexanoate [8]. Another “problematic” set of aldehydes is unsaturated aldehydes, where allylic oxidation to an alkene moiety may compete with the aldehyde oxidation. This competition is mostly a function of the C–H bond strengths (homolytic bond dissociation energies) at the susceptible carbon–hydrogen bond. Similarly, a tertiary carbon atom adjacent to the aldehyde may lead to decarboxylation and formation of a ketone, for example formation of acetone from isobutyraldehyde.

Thus, we were interested to test whether transition metal substituted polyoxometalates would be effective for selective aldehyde oxidation to carboxylic acids. Two types of compounds were surveyed, the known transition metal substituted Keggin compounds [9], $\text{Q}_4\text{HX}(\text{H}_2\text{O})\text{PM}_{11}\text{O}_{39}$ ($\text{Q} = \text{B}_4\text{N}$,

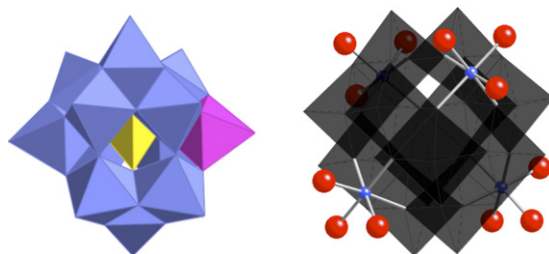


Fig. 1. Transition metal substituted polyoxometalates used in the aldehyde oxidation experiments. $\text{Q}_4\text{HX}(\text{H}_2\text{O})\text{PM}_{11}\text{O}_{39}$ (left) and $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ (right).

$\text{X} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{M} = \text{Mo}, \text{W}$) and the now newly disclosed insoluble ϵ -Keggin type polyoxometalates [10] $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ where $\text{X} = \text{Zn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}$ and Cu^{II} , Fig. 1.

2. Experimental

2.1. Catalyst synthesis

The ϵ -Keggin polyoxometalates $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4] \cdot x\text{H}_2\text{O}$ where $x = \text{Zn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}$ and Cu^{II} were synthesized by treating a 50/50 $\text{H}_2\text{O}/\text{acetic acid}$ solution of $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ and $\text{M}(\text{OOCCH}_3)_2 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Zn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}$, and Cu^{II}) with an excess of hydrazine sulfate as a reducing reagent. The resulting solution is stored for 3 days at 65°C . During this period the ϵ -Keggin polyoxometalate product precipitates; these polyoxometalates are insoluble. For $\text{X} = \text{Ni}$, the precipitate is crystalline and its structure was as presented in Fig. 1 [10a]. The characterization of $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ for $\text{X} = \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}$ and Cu^{II} was by FTIR spectroscopy (see Fig. 2) through comparison with previously reported $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4] \cdot 14\text{H}_2\text{O}$ and elemental analysis. $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4] \cdot 14\text{H}_2\text{O}$ Calcd (found): Ni 9.36 (9.3); Mo 45.94 (44.57). $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Co}^{\text{II}}(\text{H}_2\text{O})_3\}_4] \cdot 12\text{H}_2\text{O}$ Calcd (found): Co 9.54 (9.5); Mo 46.54 (46.98). $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Mn}^{\text{II}}(\text{H}_2\text{O})_3\}_4] \cdot 14\text{H}_2\text{O}$ Calcd (found): Mn 8.82 (8.7); Mo 46.21 (45.23).

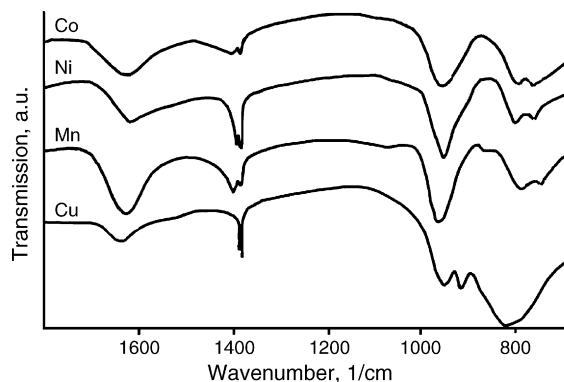


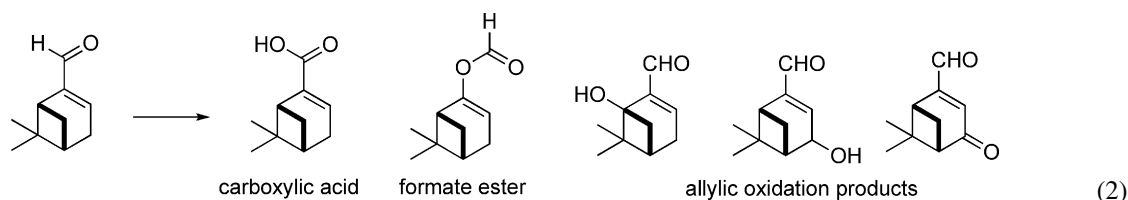
Fig. 2. IR spectra of $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$, $\text{X} = \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}$ and Cu^{II} .

$[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Cu}^{\text{II}}(\text{H}_2\text{O})_3\}_4]\cdot 14\text{H}_2\text{O}$ Calcd (found): Cu 10.06 (10.2); Mo 45.58 (45.02).

α -Keggin type polyoxometalates, $\text{Q}_4\text{HX}(\text{H}_2\text{O})\text{PM}_{11}\text{O}_{39}$ (Q = tetrabutyl ammonium, X = Co^{II} , Mn^{II} and M = Mo, W) were prepared according to the reported literature method [11], wherein first one prepares the lacunary polyoxometalate with the quaternary ammonium cation, $\text{Q}_4\text{H}_3\text{PM}_{11}\text{O}_{39}$, which after purification is metalated.

2.2. Catalytic oxidation

The catalytic reactions were carried out in 15 mL glass pressure tubes in thermostated oil baths with magnetic stirring. Typically, 0.9 mmol substrate (all highest purity commercial products) were dissolved in 1 mL toluene. The polyoxometalate (0.9 μmol) was added to the mixture. Oxygen (2 bar) was



introduced to the pressure tube. After the appropriate reaction time, the reactions were quenched by cooling (if necessary) and the oxygen pressure was released. Analysis was performed by GC (quantification by area) and GC–MS for product identification (in the absence of reference standards) using a 30 m 5% phenylmethylsilicone column with a 0.35 mm internal diameter and a 0.25 μm coating of the support phase.

3. Results and discussion

ϵ -Keggin polyoxometalates $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ where X = Zn^{II} , Ni^{II} , Co^{II} , Mn^{II} and Cu^{II} , were synthesized according to the known literature method for $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ [10a]. These polyoxometalates were *insoluble in all solvents*. The elemental analysis was consistent with the ϵ -Keggin structure as presented in Fig. 1

(right). Further confirmation of the structural homology of the series of compounds was obtained by IR spectroscopy, Fig. 2. From the figure, one may observe that in the range relevant for molybdenum–oxygen bonds, 1000–700 cm^{-1} , the spectra for the ϵ -Keggin polyoxometalates for X = Ni^{II} , Co^{II} and Mn^{II} are similar, lending support to the idea that for these transition metals the compounds are isostructural, whereas for X = Cu^{II} , the formulation of the compound as having a ϵ -Keggin structure is rather questionable. Despite the uncertainty of the structure of the copper analog it was used in the further catalytic studies. The peaks at 1380–1400 cm^{-1} are attributable to the water of hydration.

The catalytic activity of various metal substituted ϵ -Keggin polyoxometalates and transition metal substituted polyoxometalates for the aerobic oxidation of aldehydes then was tested using myrtenal, Eq. (2), as a model substrate, Table 1. Reactions were carried out in toluene as a preferable reaction medium.

The catalytic activity of the various ϵ -Keggin compounds (insoluble, thus the reaction was heterogeneous) was similar except when $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ or $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Zn}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ were used. These compounds were inactive. In the case of Cu^{II} and Co^{II} the reaction temperature also had little effect; ambient and elevated temperatures gave similar conversions and selectivity to carboxylic acid. In the case of the α -Keggin transition metal substituted polyoxometalates (soluble, thus the reaction was homogeneous) the results showed that substitution by Co^{II} was preferable to Mn^{II} whereas the identity of the addenda atoms (Mo or W) had little effect. Interestingly, with the same transition metal substitution, both the heterogeneous and homogeneous catalyst system showed similar activity and product selectivity. Therefore, the catalytic activity of the ϵ -Keggin compound, $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Co}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$, as one of the better catalysts in the myrtenal oxidation was then

Table 1

The aerobic oxidation of myrtenal catalyzed by $[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ and $((\text{C}_4\text{H}_9)_4\text{N})_4\text{HPX}(\text{H}_2\text{O})\text{M}_{11}\text{O}_{39}$

Catalyst	Conversion	Selectivity (mol%)		
		Carboxylic acid	Formate ester	Allylic oxidation
$[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Zn}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$	0	–	–	–
$[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$	0	–	–	–
$[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Co}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$	67 (68)	70 (54)	16 (15)	14 (31)
$[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Mn}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$	62 (14)	52 (50)	16 (10)	32 (40)
$[\text{Mo}_{12}^{\text{V}}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Cu}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$	73 (60)	53 (52)	9 (15)	38 (33)
$((\text{C}_4\text{H}_9)_4\text{N})_4\text{HPCo}^{\text{II}}(\text{H}_2\text{O})\text{Mo}_{11}\text{O}_{39}$	83 (84)	52 (60)	20 (24)	28 (16)
$((\text{C}_4\text{H}_9)_4\text{N})_4\text{HPCo}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$	83 (58)	52 (60)	20 (25)	28 (15)
$((\text{C}_4\text{H}_9)_4\text{N})_4\text{HPMn}^{\text{II}}(\text{H}_2\text{O})\text{Mo}_{11}\text{O}_{39}$	85 (56)	35 (40)	20 (20)	45 (40)
$((\text{C}_4\text{H}_9)_4\text{N})_4\text{HPMn}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$	78 (4)	45 (100)	24 (0)	31 (0)

Reaction conditions: 0.9 mmol myrtenal; 9 μmol catalyst; 2 bar O_2 ; 1 mL toluene, 75 $^\circ\text{C}$, 16 h. The values in parentheses are for reactions at room temperature.

Table 2

The aerobic oxidation of additional aldehyde substrates catalyzed by $[\text{Mo}_{12}\text{V}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Co}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$

Substrate	Conversion (mol%)	Selectivity, carboxylic acid	Selectivity, other
Octanal	>99	>99	–
5-Norbornene-2-carboxaldehyde ^a	85	30	Formate ester (39), other (31) ^b
Phenylglyoxal	>99	>99	–
Benzaldehyde	>99	>99	–
Pyridine-3-carboxaldehyde	25	>99	–
2-Methylundecanal	98	88	2-Undecanone (12)
2-Phenylpropanal	92	40	Acetophenone (60)
Citronellal	30	100	–
2-Methylcinnamaldehyde	No reaction		

Reaction conditions: 0.9 mmol substrate; 9 μmol catalyst; 2 atm O_2 ; 1 mL toluene, 75 °C, 16 h.^a Room temperature.^b According to the mass spectrometer these are possibly doubly oxidized species.

surveyed in the aerobic oxidation of additional aldehydes, Table 2.

The results show that the selectivity may vary significantly and is very much substrate dependent. As predicted, for a linear aliphatic aldehyde (octanal) the reaction was quantitative and selective to the carboxylic acid. A model keto-aldehyde, phenylglyoxal, was quantitatively oxidized to the corresponding phenylketo acid, indicating that this catalyst appears selective for such aerobic transformations. Similarly, in the oxidation of pyridine-3-carboxaldehyde, the pyridine moiety did not affect the selectivity although the reaction was sluggish compared to benzaldehyde, which reacted quantitatively and selectively. The oxidation of citronellal (3,7-dimethyl-6-octenal) was also rather selective to the corresponding citronellic acid with no oxidation allylic to the alkene moiety although again the oxidation was slow. 2-Methylcinnamaldehyde was surprisingly non-reactive. 5-Norbornene-2-carboxaldehyde showed a profile similar to myrtenal with an even lower selectivity to the carboxylic acid. 2-Methylundecanal was reactive and quite selective with a good yield of 2-methylundecanoic acid; some oxidation at the carbon adjacent the aldehyde moiety, presumably forming the hydroxy-aldehyde functionality, led to carbon–carbon cleavage (decarboxylation) and formation of 2-undecanone. Not surprisingly, this effect was more pronounced in the oxidation of 2-phenylpropanal and led to formation of acetophenone. Counter to expectation, in both cases no formate ester products were observed by a Dakin type reaction. It should be noted that the IR spectrum of the compounds appears unchanged after heating for 5 h at 75 °C in toluene using 4-methylbenzaldehyde as substrate, indicating that the ϵ -Keggin polyoxometalates are stable and unchanged during the catalytic reaction.

4. Conclusions

New polyoxometalates of the ϵ -Keggin structure $[\text{Mo}_{12}\text{V}\text{O}_{39}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{X}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$ (X = Ni, Co, Mn and Cu), have been synthesized and used as heterogeneous catalysts for the aerobic oxidation of aldehydes to the corresponding carboxylic acids. For linear aliphatic and benzylic aldehydes the reactions are selective; also a α -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 allylic oxidation that can lead to decarboxylation and formation of ketones or allylic alcohols depending on the specific substrate.

Acknowledgements

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