Catalysis
Science &
Technology

PAPER

View Article Online
View Journal | View Issue

Cite this: *Catal. Sci. Technol.*, 2014, 4, 648

Keggin type transition metal substituted phosphomolybdates: heterogeneous catalysts for selective aerobic oxidation of alcohols and alkenes under solvent free condition†

Soyeb Pathan and Anjali Patel*

Received 21st September 2013,
Accepted 23rd October 2013

DOI: 10.1039/c3cy00717k

www.rsc.org/catalysis

Environmentally benign oxidation of alcohols and alkenes over transition metal substituted phosphomolybdates with molecular oxygen as an oxidant and TBHP as an initiator was carried out. The influence of different parameters on the conversion as well as the selectivity was investigated. All the catalysts showed good catalytic activity with excellent selectivity for the desired products as well as a higher TON. The system not only catalyzes the reaction but also avoids the use of organic solvents as it was carried out under solvent free conditions. Moreover, the catalysts could be recovered and reused four times without a significant loss in their activity and selectivity. A probable reaction mechanism was also proposed for the oxidation of alcohols and alkenes.

1. Introduction

The catalytic oxidation of organic compounds is still a challenge in modern chemistry and the industrial world[1–3] as oxygenated derivatives, especially carbonyl compounds, have extensive applications in perfumery, dyestuff and agro chemical industries.[4–6] Because of the unreactivity of present catalysts with molecular oxygen, traditional procedures for oxidation have employed more reactive forms of oxygen *i.e.* toxic and hazardous oxidants based on chromates, hypochlorites, and permanganates in stoichiometric amounts or a large excess.[7] However, these procedures have some drawbacks, such as the use of relatively expensive oxidizing agents, lack of selectivity, metal waste generation and the use of non-green halogenated solvents, which are economically and environmentally undesirable. Although reports are available on transition metal complex catalyzed oxidation reactions,[8] these catalytic systems suffer from poor recycling of the complexes due to difficult separation and rapid loss of activity. Hence, from the view point of green chemistry, the search for efficient and heterogeneous catalytic systems exploiting clean oxidants such as molecular oxygen is highly desirable.[9,10]

In this context, polyoxometalates (POMs) are excellent candidates because of their redox properties.[11–16] Recently, a subclass of polyoxometalates (POMs), transition metal substituted POMs (TMSPOMs), have gained importance due to their distinctive electrochemical, magnetic, medicinal and catalytic properties.[17–20] They can also be rationally modified on the molecular level, including shape, size, charge density, redox states and stability.[20,21] It has been reported that the addition of transition metals is expected to influence the redox properties considerably, particularly when they are incorporated in the primary structure of the Keggin ion.[22,23] A literature survey shows that many reports on aerobic oxidation catalyzed by transition metal silicotungstates and phosphotungstates, *i.e.* $[XW_{11}M(L)O_{39}]^{5-}$ (X = P, Si, M = transition metal, L = ligand) are available.[24–29]

It is well known that phosphomolybdates are better catalysts for oxidation reactions than their tungstate counterparts.[30] Among phosphomolybdates, mono vanadium substituted phosphomolybdates, $PVMo_{11}O_{40}^{4-}$, have been widely investigated in the selective aerobic oxidation of alkanes,[31–33] alkenes,[34,35] alcohols,[14,36], isobutyric acid,[37–41] and phenol.[42] At the same time, reports on aerobic oxidation catalyzed by Ru-substituted phosphomolybdates[43,44] and Fe-substituted phosphomolybdates[45,46] are also available. However, in most applied protocols, catalytic oxidation requires harsh temperature conditions, the use of relatively expensive transition metals (V, Ru) as well as the use of organic solvents.

So, looking at the importance of oxidation reactions as well as considering the economic and ecological aspects, it was thought to be of interest to develop a sustainable catalytic

---

*Polyoxometalates and Catalysis Laboratory, Department of Chemistry, Faculty of Science, The M. S. University of Baroda, Vadodara 390 002, India.
E-mail: aupatel_chem@yahoo.com*

† Electronic supplementary information (ESI) available: A detailed study on aerobic oxidation of styrene over $PMo_{11}M$ (M = Co, Mn, Ni), Scheme S1. See DOI: 10.1039/c3cy00717k

system for the aerobic oxidation of alkenes and alcohols based on (relatively inexpensive) transition metal substituted phosphomolybdates under solvent free conditions. Recently, we have reported the synthesis and characterization[47] of the cesium salt of Keggin type mono transition metal(II)-substituted phosphomolybdates ($PMo_{11}M$; M = Co, Mn, Ni) and its use as an efficient catalyst for the oxidation reaction with H_2O_2 as an oxidant.[48,49] So, in order to extend the viability of these catalysts, we here explore their use as sustainable catalysts for solvent free oxidation of alcohols and alkenes with molecular oxygen. The catalytic activity of the recycled catalysts was evaluated under optimized conditions and a probable reaction mechanism was also proposed.

2. Experimental

2.1. Materials

All the chemicals used were of A.R. grade. 12-Molybdophosphoric acid, $H_3PMo_{12}O_{40}$, NaOH, $Na_2MoO_4{\cdot}2H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, styrene, α-methyl styrene, benzyl alcohol, cyclopentanol, 1-hexanol, 1-octanol and dichloromethane were obtained from Merck and used as received.

2.2. Synthesis of the transition metal substituted phosphomolybdates[47]

$H_3PMo_{12}O_{40}$ (PMo_{12}, 1.825 g, 1 mmol) was dissolved in water (10 mL) and the pH of the solution was adjusted to 4.3 using an NaOH solution. $Co(CH_3COO)_2{\cdot}4H_2O$ (0.249 g, 1 mmol) dissolved in a minimum amount of water was mixed with the above hot solution. The pH of the solution was adjusted to 4.5 (pH 4.3 for nickel substituted phosphomolybdate). The solution was heated at 80 °C with stirring for 1 h and filtered hot. A saturated solution of CsCl was added drop wise to the hot filtrate and allowed to stand. The as-obtained crystals were very poorly soluble in any solvent and no recrystallisation was carried out. The obtained dark reddish brown crystals were filtered, air dried and designated as $PMo_{11}Co$. Other transition metal (M = Mn and Ni) substituted phosphomolybdates were also synthesized according to a similar method by taking the corresponding metal-acetate salt. The obtained materials were designated as $PMo_{11}Mn$ and $PMo_{11}Ni$ respectively.

2.3. Characterization

A detailed study on the characterization of the synthesized materials can be found in our earlier publications.[47–50] The main characterization of the catalysts, such as elemental analysis, TG-DTA, DRS and ESR, is given for the readers' convenience. Elemental analysis was carried out using a JSM 5610 LV combined with INCA instrument for EDX-SEM. The total weight loss was calculated by the TGA method on the Mettler Toledo Star SW 7.01 up to 600 °C. FTIR spectra of the samples were recorded as KBr pellets on a Perkin Elmer instrument. The DR-UV-Visible spectrum was recorded at room temperature on a Perkin Elmer LAMBDA instrument. ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer (room temperature and scanned from 2000 to 3200 gauss).

2.4. Oxidation reactions

The catalytic activity was evaluated for the oxidation of alcohols using molecular oxygen as an oxidant and TBHP as an initiator. The oxidation reactions were carried out in a batch type reactor operated under atmospheric pressure. In a typical reaction, a measured amount of the catalyst was added to a three necked flask containing alcohol at 90 °C. The reaction was started by bubbling O_2 into the liquid. A similar procedure was followed for the alkene oxidations with a reaction temperature of 80 °C. The reactions were carried out by varying different parameters, such as the amount of the catalyst, reaction time and reaction temperature. After the completion of the reaction, the catalyst was removed and the product was extracted with dichloromethane. The product was dried with magnesium sulphate and analyzed on a gas chromatograph using a BP-1 capillary column. The product was identified by a comparison with the authentic samples and finally by gas chromatography–mass spectroscopy (GC–MS).

3. Results and discussion

3.1. Analytical techniques

Based on the single crystal as well as the elemental analysis,[47,48] the chemical formula for the isolated complexes is $Cs_5[PM(H_2O)Mo_{11}O_{39}]{\cdot}6H_2O$ (M = Co, Mn, Ni).

TGA of all of the catalysts show a weight loss of 4.2–4.83% at 150 °C, corresponding to 7 H_2O molecules. Similarly, DTA of all the catalysts showed an endothermic peak at around 130 °C due to water of crystallization. An exothermic peak in the region of 415–430 °C indicates crystallization of the MoO_3 phase after decomposition of the Keggin unit.

Table 1 shows the DRS spectra values for PMo_{11}, $PMo_{11}Co$, $PMo_{11}Mn$, and $PMo_{11}Ni$. Absorption bands at ~200 and 285 nm are observed for PMo_{11}, due to O → Mo charge transfer. The DRS spectra of $PMo_{11}Co$, $PMo_{11}Mn$, and $PMo_{11}Ni$ show two peaks. The peaks in the region of 210–235 and 260–300 nm correspond to O → Mo charge transfer, indicating the formation of the $PMo_{11}O_{39}$ lacuna in the synthesized compounds. The observed shift compared to that of PMo_{11} may be due to the substitution of the transition metal. A broad band in the 560–580, 390–430 and 550–600 nm regions, corresponding to the presence of Co^{II}, Mn^{II}, and Ni^{II}, was observed in $PMo_{11}Co$, $PMo_{11}Mn$, and $PMo_{11}Ni$ respectively.

Table 1 DRS data of PMo_{11}, $PMo_{11}Co$, $PMo_{11}Mn$, and $PMo_{11}Ni$

Material	O → Mo charge transfer	d–d transition
PMo_{11}	200, 285	—
$PMo_{11}Co$	235, 300	560–580
$PMo_{11}Mn$	210, 260	390–430
$PMo_{11}Ni$	270, 300	550–600

Furthermore, the presence of Co(II), and Mn(II) in the synthesized complex was confirmed by ESR (Fig. 1). The ESR spectra of $PMo_{11}Co$ show eight hyperfine signals (Co^{2+}; $I = 7/2$) with a g value of ~2.66, confirming the presence of paramagnetic Co(II) in an octahedral or distorted octahedral environment. Similarly, the ESR spectra of $PMo_{11}Mn$ show six signals (Mn^{2+}; $s = 5/2$), and the g value of ~2 indicates the presence of Mn(II) with octahedral or distorted octahedral symmetry and thus confirms the presence of paramagnetic Mn(II).

3.2. Catalytic activity

All of the reactions were carried out without catalysts in order to confirm that the catalytic activity is due to $PMo_{11}M$. It was found that no oxidation takes place without catalysts. A detailed study was carried out on the oxidation of benzyl alcohol and styrene using $PMo_{11}M$ (M = Co, Mn, Ni) as catalysts, and a study on other alcohols and alkenes was carried out under optimized conditions.

3.2.1. Oxidation of alcohols. A detailed study was carried out on the oxidation of benzyl alcohol over $PMo_{11}M$ (M = Co, Mn, Ni) by varying different parameters, such as the reaction temperature, the amount of the catalyst and the reaction time, to optimize the conditions for maximum conversion and selectivity. Generally, oxidation of benzyl alcohol gives benzaldehyde and benzoic acid. However, benzaldehyde was characterized as the major oxidation product in the present case.

3.2.1.1. Effect of temperature. In order to determine the optimum temperature, the reaction was investigated at three different temperatures, 70, 90 and 110 °C, keeping the other parameters fixed (20 mg of catalyst, reaction time of 24 h). The results are presented in Fig. 2. The results show that conversion increased with increasing temperature from 70 to 110 °C for all the catalysts. At the same time, on increasing the temperature from 90 to 110 °C, a drastic decrease in the selectivity of benzaldehyde was observed. This is due to over oxidation of benzaldehyde to benzoic acid at elevated temperatures. So a temperature of 90 °C was used for further studies.

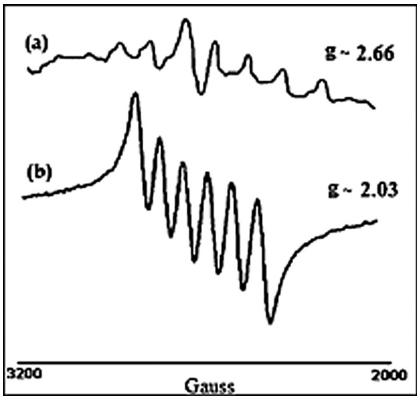


Fig. 1 ESR spectra of (a) $PMo_{11}Co$ and (b) $PMo_{11}Mn$.

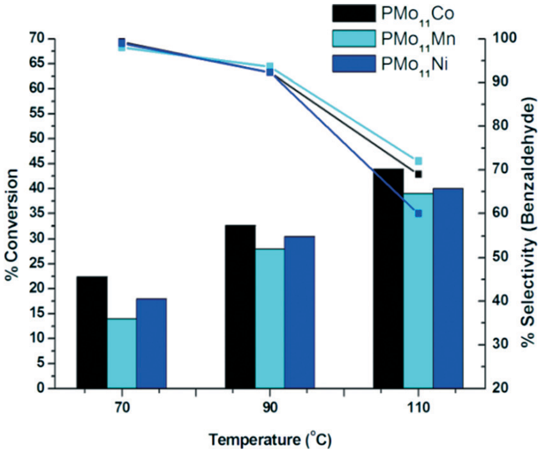


Fig. 2 Effect of temperature, % conversion is based on benzyl alcohol; benzyl alcohol = 100 mmol, TBHP = 0.2%, time = 24 h, amount of catalyst = 20 mg.

3.2.1.2. Effect of catalyst amount. The effect of the amount of the catalyst on the conversion was studied and the obtained results are shown in Fig. 3. With an increase in the amount of the catalysts *i.e.* concentration of metal contains, the % conversion also increases. This suggests that the transition metal functions as an active site for oxidation. It is very interesting to observe the difference in the selectivity of the products with an increase in the concentration of the catalyst.

It is observed from Fig. 3 that with a lower amount of the catalysts, >96% selectivity of benzaldehyde is obtained. On increasing the amount of the catalysts (more than 15 mg), the selectivity for benzaldehyde decreases. This may be due to the fact that with an increase in the amount of the active species the reaction becomes fast, which favours the conversion of the formed benzaldehyde to benzoic acid. Thus, the

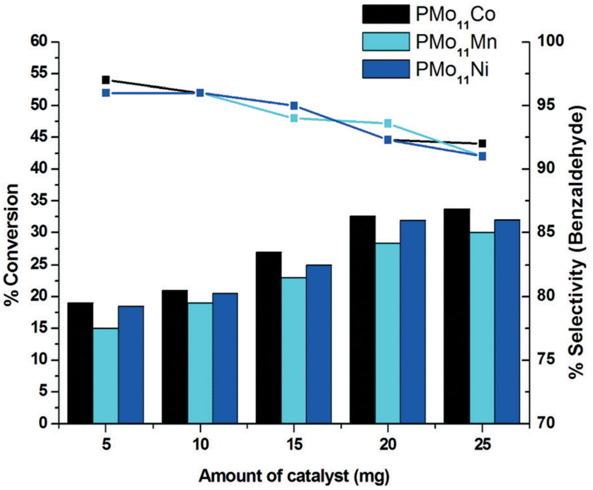


Fig. 3 Effect of catalyst amount, % conversion is based on benzyl alcohol; benzyl alcohol = 100 mmol, TBHP = 0.2%, temp. = 90 °C, time = 24 h.

amount of the catalysts was optimized to 20 mg for optimum conversion and selectivity.

Effect of reaction time. The percentage of conversion was monitored at different reaction times and the result is presented in Fig. 4. It can be seen from Fig. 4, that with an increase in the reaction time, the % conversion also increases. The initial conversion of benzyl alcohol increased with the reaction time. This is due to the fact that more time is required for the formation of the reactive intermediate (substrate + catalyst) which is finally converted into the products. For, $PMo_{11}Co$, a 32.6% conversion of benzyl alcohol with 92.3% selectivity for benzaldehyde was observed at 24 h. When the reaction was allowed to continue after 24 h, no significant change in the conversion was observed, but the selectivity for benzaldehyde was decreased. This is because of over oxidation of benzaldehyde to benzoic acid. A similar trend in activity was observed for $PMo_{11}M$ (M = Mn, Ni). So, the reaction time was optimized as 24 h.

It is known that in a kinetically consecutive reaction, conversion is a function of both time and the catalyst amount, and the selectivity is itself a function of conversion. Therefore, the optimal catalyst amount depends on the reaction time chosen, and *vice versa*. Hence, to study the above, the oxidation of benzyl alcohol was carried out by varying the time with two different amounts (15 mg and 20 mg) of $PMo_{11}Co$ as the catalyst and the results are presented in Fig. 5. From Fig. 5 it is clear that for each time interval, the observed % conversion is less with 15 mg compared to that of 20 mg. However, at the same time, no significant difference (<1.5%) in the selectivity for benzaldehyde was observed. Thus, 20 mg of the catalyst and a 24 h reaction time was selected for the optimum conversion and selectivity.

The optimum conditions for the optimum conversion of alcohol and selectivity for benzaldehyde over $PMo_{11}M$ (M = Co, Mn, Ni) are: 20 mg of the catalyst, a 24 h reaction time and a reaction temperature of 90 °C.

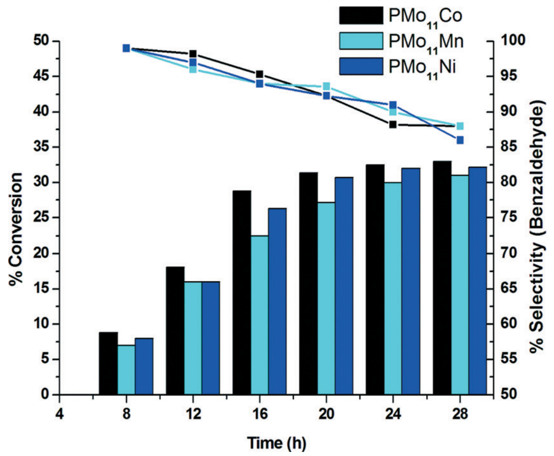


Fig. 4 Effect of reaction time, % conversion is based on benzyl alcohol; benzyl alcohol = 100 mmol, oxidant = O_2, TBHP = 0.2%, temp. = 90 °C, amount of catalyst = 20 mg.

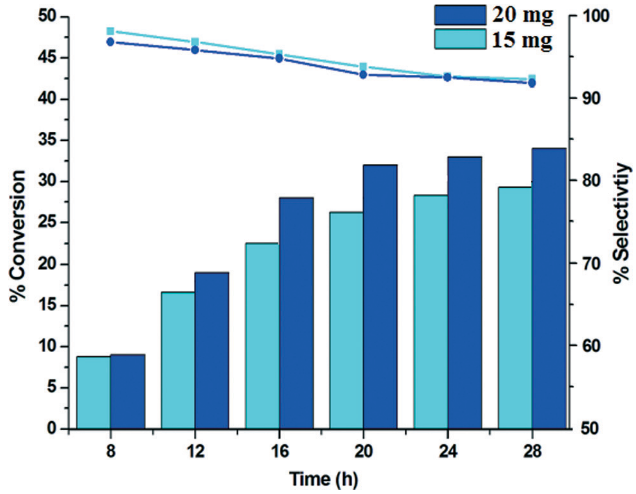


Fig. 5 % Conversion is based on benzyl alcohol; benzyl alcohol = 100 mmol, oxidant = O_2, TBHP = 0.2%, temp. = 90 °C, catalyst = $PMo_{11}Co$.

So, in order to explore the scope and limitations of the present catalytic system, oxidation of different alcohols was also carried out using $PMo_{11}M$ (M = Co, Mn, Ni) under the optimized conditions and the results are presented in Table 2.

It can be seen from Table 2 that $PMo_{11}Co$ and $PMo_{11}Ni$ show almost the same conversion of benzyl alcohol whereas a lower conversion of benzyl alcohol was observed for $PMo_{11}Mn$. From the results, it is clear that the activity of the catalyst is governed by the reduction potential of the metals used for the substitution, which is in good agreement with reported results (Fig. S4, ESI†).[48] It can be seen from Table 2 that, as with benzyl alcohol oxidation, a similar trend in the activity of $PMo_{11}M$ (M = Co, Ni, Mn) was observed for the oxidation of other alcohols, such as cyclopentanol, 1-hexanol and 1-octanol, *i.e.* $PMo_{11}Co$ shows better activity compared to $PMo_{11}Mn$ and $PMo_{11}Ni$. The order of the activity of the

Table 2 Oxidation of alcohols with O_2 using $PMo_{11}M$ (M = Co, Mn, Ni)[a]

Catalyst	Alcohols	% Conv.	Products (% selectivity)	TON
$PMo_{11}Co$	Benzyl alcohol	32.6	Benzaldehyde (92.3)	4281
	Cyclopentanol	29.8	Cyclopentanone (100)	3913
	Cyclohexanol	29.2	Cyclohexanone (100)	3834
	1-Hexanol	20.6	1-Hexanal (100)	2705
	1-Octanol	NC	—	—
$PMo_{11}Mn$	Benzyl alcohol	28.3	Benzaldehyde (93.6)	3628
	Cyclopentanol	24.3	Cyclopentanone (100)	3115
	Cyclohexanol	23.7	Cyclohexanone (100)	3038
	1-Hexanol	15.9	1-Hexanal (100)	2038
	1-Octanol	NC	—	—
$PMo_{11}Ni$	Benzyl alcohol	31.9	Benzaldehyde (92.3)	4075
	Cyclopentanol	27.6	Cyclopentanone (100)	3526
	Cyclohexanol	24.1	Cyclohexanone (100)	3078
	1-Hexanol	17.7	1-Hexanal (100)	2261
	1-Octanol	NC	—	—

[a] Conversion is based on the alcohols; alcohol, 100 mmol; oxidant, O_2: 0.2% TBHP; amount of catalyst = 20 mg; temp. = 90 °C, time = 24 h, NC = no conversion.

catalysts for oxidation is $PMo_{11}Co > PMo_{11}Ni > PMo_{11}Mn$. It can be observed from Table 2 that oxidation of a secondary alcohol is easier compared to primary aliphatic alcohols. This observed trend is in good agreement with other reports.[51] It is also observed that, in all cases, very good selectivity for the desired product with a high TON is obtained. It is known that oxidation of long chain alcohols (C_8 and onwards) is still a challenging task because of lower reactivity[52] and thus, the present catalytic system is also not applicable to less reactive long chain primary alcohols, such as 1-octanol.

3.2.2. **Oxidation of alkenes.** A detailed study, similar to the benzyl alcohol oxidation, was carried out on the oxidation of styrene using $PMo_{11}M$ (M = Co, Mn, Ni) by varying different parameters, such as the reaction temperature, catalyst amount and reaction time, in order to optimize the conditions using the environmentally benign oxidant O_2 (Fig. S1–S3, ESI†). Generally, oxidation of styrene gives styrene oxide, benzaldehyde, acetophenone, diol, phenyl acetaldehyde, and benzoic acid. However, benzaldehyde was characterized as the major (>87%) oxidation product along with styrene oxide, and benzoic acid as the minor product (13%) in the present case.

The optimum conditions for the maximum % conversion of styrene (>36%) with >87% selectivity for benzaldehyde with $PMo_{11}M$ are: 20 mg of the catalyst, an 8 h reaction time and a reaction temperature of 80 °C.

In order to see the scope of the present catalytic system, oxidation of alkenes was also carried out over $PMo_{11}M$ under optimized conditions and the results are presented in Table 3.

From the results it is clear that, similar to alcohol oxidation, styrene and substituted styrene was efficiently oxidised to the desired product by $PMo_{11}M$ (M = Co, Mn, Ni) and the order of activity for oxidation is $PMo_{11}Co > PMo_{11}Ni > PMo_{11}Mn$. Generally, the oxidation of styrene gives styrene oxide, benzaldehyde, diol, benzoic acid and acetophenone. However, in the present case, a C=C cleaved carbonyl compound was characterized as a major product. It is well known that the stable product benzaldehyde was observed as the major product *via* i) direct oxidative cleavage of C=C of styrene and ii) fast conversion of styrene oxide to benzaldehyde. It has been reported by Vancheesan *et al.*[53] that the use of TBHP with transition metal based catalysts activates the metal centre. The interconversion of the two oxidation states for the metal complexes, corresponding to an oxidative addition and reductive elimination, are responsible for effective catalysis. Hence, the activated catalysts attack the C=C site in the case of styrene and preferentially follow an oxidative cleavage route rather than epoxide formation.[54] Thus, the obtained results are in good agreement with the reported explanation. In all cases, excellent selectivity (88–93%) for the desired product with a very high TON is obtained. As the present catalytic system followed oxidative cleavage rather than epoxide formation, cyclic olefins do not undergo epoxidation. Also, C=C bond cleavage in cyclic olefins is a difficult task and therefore no ring opening product was obtained. Thus, the present catalytic system is not applicable for the oxidation of cyclic olefins.

Table 3 Oxidation of alkenes with O_2 using $PMo_{11}M$ (M = Co, Mn, Ni)^a

Catalyst	Alkenes	% Conv.	Products (% selectivity)	TON
$PMo_{11}Co$	Styrene	41.1	Benzaldehyde (92.2)	5253
	α-Methyl styrene	36.2	Acetophenone (93.1)	4627
	^{a}Cyclohexene	NC	—	—
$PMo_{11}Mn$	Styrene	35.9	Benzaldehyde (90.7)	4602
	α-Methyl styrene	30.3	Acetophenone (91.1)	3885
	^{a}Cyclohexene	NC	—	—
$PMo_{11}Ni$	Styrene	39.9	Benzaldehyde (87.2)	5074
	α-Methyl styrene	34.3	Acetophenone (87.1)	4362
	^{a}Cyclohexene	NC	—	—

^{a} Conversion is based on the alkenes; alkene, 100 mmol; oxidant, O_2: 0.2% TBHP; amount of catalyst, 20 mg; 80 °C, ^{a}60 °C time, 8 h.

3.3. Control experiment

A controlled experiment for the oxidation of benzyl alcohol with $CsPMo_{11}$, $CsPMo_{12}$, and $PMo_{11}M$ (M = Co, Mn, Ni) was carried out under optimized conditions and the results are presented in Table 5. It can be seen from Table 5 that in the $CsPMo_{11}$ and $CsPMo_{12}$ catalyzed oxidation reactions, very low conversion of the substrates with 80–90% selectivity for benzaldehyde was obtained. However, $PMo_{11}M$, showed good conversion, *i.e.* >18 % more conversion, and excellent selectivity for benzaldehyde was observed. The controlled experiment shows that $PMo_{11}M$ (M = Co, Mn, Ni) are better catalysts

Table 4 Controlled experiment for the oxidation of benzyl alcohol and styrene with $CsPMo_{11}$, $CsPMo_{12}$, $PMo_{11}M$ (M = Co, Mn, Ni) under optimized conditions^a

			% Selectivity	
Entry	Catalyst	% Conversion	Benzaldehyde	Other
1	$CsPMo_{11}$	13.4^a/16.5^b	91.2^a/90.1^b	8.8^a/9.9^b
2	$CsPMo_{12}$	6.2^a/11.3^b	87.2^a/82.2^b	12.8^a/17.8^b
3	$PMo_{11}M$	28–33^a/39–41^b	92–93^a/87–92^b	7–8^a/8–13^b

^{a} % Conversion is based on the substrate (^{a}benzyl alcohol, ^{b}styrene); substrate = 100 mmol, O_2, TBHP = 0.2%, temp. = ^{a}90, ^{b}80 °C, time = ^{1}24 h, ^{2}8 h, amount of catalyst = 25 mg ($PMo_{11}M$), 18 mg ($CsPMo_{12}$), 27 mg PMo_{11}.

Table 5 Oxidation of benzyl alcohol and styrene with fresh and regenerated catalysts^a

			Selectivity (%)
Substrate	Cycle	Conversion (%)	Benzaldehyde
^{1}Benzyl alcohol	Fresh	32.6^a/28.3^b/31.9^c	92.3^a/93.6^b/92.3^c
	1	32.6^a/28.3^b/31.9^c	92.0^a/93.4^b/92.2^c
	2	32.6^a/28.1^b/31.8^c	92.2^a/93.4^b/92.0^c
	3	32.4^a/28.1^b/31.8^c	92.2^a/93.4^b/92.1^c
	4	32.3^a/28.0^b/31.7^c	92.1^a/93.3^b/92.1^c
^{2}Styrene	Fresh	41.1^a/35.9^b/39.9^c	92.2^a/90.7^b/87.2^c
	1	41.1^a/35.7^b/39.9^c	92.2^a/90.5^b/87.1^c
	2	41.0^a/35.6^b/39.7^c	92.1^a/90.4^b/87.4^c
	3	41.0^a/35.6^b/39.7^c	92.0^a/90.4^b/87.0^c
	4	41.0^a/35.6^b/39.5^c	92.0^a/90.5^b/86.9^c

^{a} % Conversion is based on the substrate; substrate = 100 mmol, TBHP = 0.2%, temp. = ^{1}90, ^{2}80 °C, time = ^{1}24 h, ^{2}8 h amount of catalyst = 20 mg, catalysts = $PMo_{11}M$ (M = ^{a}Co, ^{b}Mn, ^{c}Ni).

compared to their parent ($CsPMo_{12}$) and lacunary counterpart ($CsPMo_{11}$). From this experiment it can also be concluded that although the transition metal can act as an active centre for oxidation, the possibility of the involvement of the Mo species cannot be ruled out.

3.4. Heterogeneity test and recyclability

The decomposition or leaching of the metal content from $PMo_{11}M$ was confirmed by carrying out an analysis of the used catalyst (EDX) as well as the product mixtures (AAS). For all the catalysts, the analysis of the used catalyst did not show an appreciable loss in the metal content compared to the fresh catalyst. Analysis of the product mixtures shows that if any metal was present, it was below the detection limit, which corresponded to less than 1 ppm.

Furthermore, a heterogeneity test was carried out for the oxidation of benzyl alcohol (Fig. 6a) and styrene (Fig. 6b) over $PMo_{11}Co$ as examples. For rigorous proof of heterogeneity, the test[54] was carried out by filtering the catalyst from the reaction mixture at 90 °C after 12 h (for styrene; 80 °C after 4 h) and the filtrate was allowed to react for up to 28 h (for styrene; 8 h). The reaction mixture after 12 h and the filtrate were analyzed by gas chromatography. A similar test was carried for $PMo_{11}M$ (M = Mn, Ni). No change in the % conversion as well as % selectivity was found, indicating the present catalysts fall into category C,[54] *i.e.*, the active species does not leach and the observed catalysis is truly heterogeneous in nature.

The catalysts are heterogeneous in nature and hence, can be easily separated by simple filtration followed by washing. The catalyst was washed with dichloromethane and dried at 100 °C. Oxidation of benzyl alcohol and styrene was carried out with the recycled catalysts under the optimized conditions. The obtained results are presented in Table 4. As can be seen from the table, there was no appreciable change observed in the conversion as well as the selectivity, which shows that the catalysts are stable and can be regenerated for repeated use (up to four cycles).

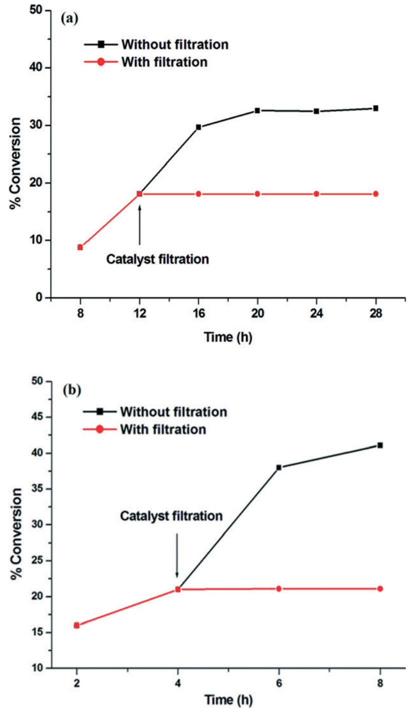


Fig. 6 % Conversion is based on the substrate ([a]benzyl alcohol/[b]styrene); amount of $PMo_{11}Co$ = 20 mg; molar ratio of the substrate (100 mmol), O_2, TBHP = 0.2%, temperature [a]90 °C, [b]80 °C.

3.5. Comparison with reported catalysts

Comparative data for the aerobic oxidation of benzyl alcohol and styrene over the present catalysts and reported catalysts is given in Tables 5 and 6 respectively.

Mizuno *et al.* reported the aerobic oxidation of alcohol catalyzed by $[(n\text{-}C_4H_9)_4N]_4H[SiW_{11}Ru^{III}(H_2O)O_{39}]\cdot 2H_2O$.[55] 36% conversion of benzyl alcohol was obtained with 65% selectivity for benzaldehyde using O_2 as the sole oxidant. However, this reaction required a very long time (120 h), relatively high temperature (110 °C) and isobutyl acetate solvent. Similarly, Ueda *et al.* carried out the aerobic oxidation of benzyl alcohol catalyzed by Mo–V–O oxide as a heterogeneous catalyst using toluene as a solvent and 22% conversion was observed with excellent selectivity (>99) for benzaldehyde.[56] However, the reaction was carried out in toluene as a solvent. On other hand, $PMo_{11}M$ (M = Co, Mn, Ni) gives 28–33% conversion and excellent selectivity (92–93%) towards benzaldehyde (TON 3628–4281) in 24 h under solvent free mild conditions.

Xu *et al.* reported the use of Mo-exchanged zeolite (Mo–Y) as a catalyst for the oxidation of styrene with air + TBHP using DMF as a solvent.[57] 15.7% conversion of styrene with 34.8% and 65.2% selectivity for benzaldehyde and the epoxide was found in 5 h for Mo–Y. In comparison with the present catalysts $PMo_{11}M$ (M = Co, Mn, Ni), it was found that Mo–Y is better in terms of selectivity for the epoxide (Table 7).

However, at the same time, an excellent selectivity for benzaldehyde was observed for $PMo_{11}M$ (M = Co, Mn, Ni). Moreover, the reported reactions were carried out with a lower concentration of styrene (3 mmol) and a higher amount of the catalyst (300 mg) at a higher temperature (90 °C) in DMF as a solvent, while the present catalytic system offered solvent free oxidation reactions with a relatively higher concentration of styrene (100 mmol) and a lower amount of the catalyst (20 mg) at a lower temperature (80 °C).

3.6. Probable reaction mechanism

In order to study the reaction mechanism, the same set of reactions were carried under two different conditions: (i) styrene + oxidant + TBHP and (ii) styrene + oxidant + $PMo_{11}M$. In both cases, the reaction did not progress significantly. These observations indicate that the liberation of O_2 from TBHP was not sufficient for the reaction to proceed nor activate M^{2+} to M^{3+}, necessary for provoking the reaction under the optimized conditions. Hence, it may be concluded that in the present study, TBHP acts as a radical initiator only.

Table 6 Comparison of the catalytic activity for the aerobic oxidation of benzyl alcohol with reported catalysts

Catalyst	Reaction conditions[a]	% Conv.	% Selectivity Benzaldehyde	TON	Ref.
[a]TBA–SiW$_{11}$Ru	1 : 2 : 120 : 110 : 3	36	65	540	[55]
[b]Mo–V–O oxide	0.7 : 30 : 24 : 80 : 1.6	22	>99	—	[56]
[c]PMo$_{11}$M (M = Co, Mn, Ni)	100 : 25 : 24 : 90 : 0	28–33	92–93	3628–4281	Present work

% Conversion is based on benzyl alcohol; solvent = [a]isobutyl acetate/[b]toluene; [c]TBHP was used as an initiator.[a] Benzyl alcohol: amount of catalysts (mg): time (h): temperature (°C): solvent (g).

Table 7 Comparison of the catalytic activity for the aerobic oxidation of styrene with reported catalysts

Catalyst	Reaction conditions[a]	% Conv	% Selectivity Benzaldehyde	Epoxide other	Ref.
[a]Mo-exchanged zeolite	3 : 300 : 5 : 90 : 10	15.7	34.8	65.2	[57]
[b]PMo$_{11}$M (M = Co, Mn, Ni)	100 : 25 : 8 : 80 : 0	39–41	87–92	3–6	Present work

% Conversion is based on styrene; [a]solvent = DMF; [a]air as the oxidant, [b]O_2 as the oxidant and TBHP was used as an initiator.[a] Styrene: amount of catalysts (mg): time (h): temperature (°C): solvent (g).

In order to confirm the radical mechanism, an experiment was carried out using an excess of *i*-PrOH as a radical terminator and the result is presented in Fig. 7. When the free-radical terminator was added to the oxidation of styrene (at 4 h), the reaction stopped and no significant increase in the conversion of styrene was observed.

Based on the above observations, a tentative reaction mechanism for the aerobic oxidation of styrene with TBHP as an initiator is proposed in Scheme 1. It has been reported that, in the case of transition metal substituted polyoxotungstates, transition metals behave as active centres for catalysis.[58,59] It has also been reported that for TMSPOMs catalysts containing metal cations in low valency states and involving O_2 as an oxidant always follow the radical chain mechanism induced by an M–O_2 intermediate.[60,61] In the present catalytic system, the mechanism is expected to follow the same path. It is expected that the reaction of M^{2+} with TBHP causes the oxidization of M^{2+} to M^{3+} *in situ*. The activation of this species takes place with a radical (*tert*-BuO˙) generated during the decomposition of TBHP and the attack of O_2 simultaneously, which results in the formation of the activated species $OOM^{3+}PMo_{11}$.

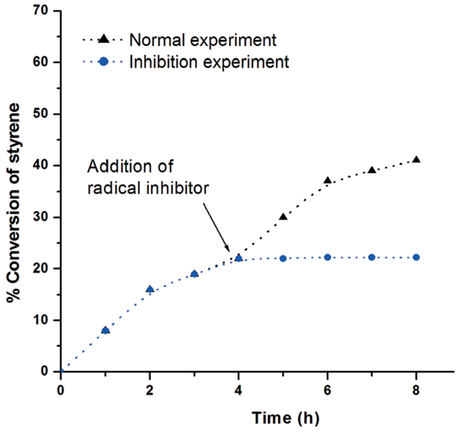
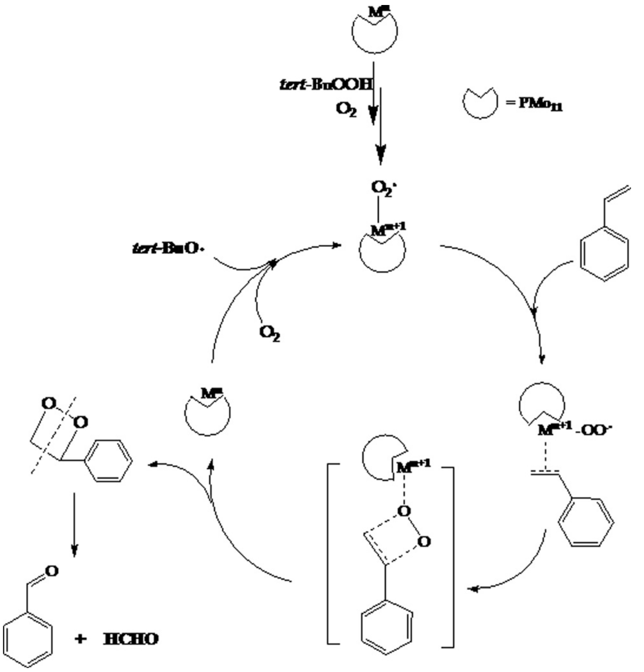


Fig. 7 Inhibition experiment with *i*-PrOH as a radical terminator (blue), without *i*-PrOH under optimized conditions (black), catalyst = $PMo_{11}Co$.



Scheme 1 Proposed reaction mechanism for the oxidation of styrene using O_2.

$$PMo_{11}M^{n} + tert\text{-}BuOOH \rightarrow PMo_{11}M^{n+1} + tert\text{-}BuO^{\bullet} + OH^{-}$$

This activated species ($^{\bullet}OOM^{3+}PMo_{11}$) then attacks the substrate. The metal-superoxo intermediate reversibly binds styrene, attacking the reaction site which results in the oxidation of the substrate to form the products. Thus, it is believed that the $^{\bullet}OOM^{3+}PMo_{11}$ intermediate may be responsible for the oxidation of styrene. However, activation of the catalyst may also be possible with different radicals (*tert*-BuOO$^{\bullet}$, *tert*-BuOOO$^{\bullet}$, OH$^{\bullet}$), generated during the decomposition of TBHP. Although attempts to isolate the activated catalyst have been made, it was not possible to isolate and characterize the active catalyst as it is highly reactive in nature. Similarly, a mechanism for alcohol oxidation was also proposed in which the active species $^{\bullet}OOM^{3+}PMo_{11}$ is responsible for the oxidation of alcohols to the corresponding carbonyl compounds (Scheme S1, ESI†). However, at the same time, as described in the controlled experiment, addenda atoms (Mo species) may also be involved in the catalytic cycle.

4. Conclusion

In conclusion, we have come up with a sustainable catalytic system for the oxidation of alcohols and alkenes catalyzed by transition metal-substituted phosphomolybdates under mild reaction conditions. The superiority of the catalysts lies in obtaining a higher selectivity for the desired product with an excellent TON. The present catalytic system is applicable to a variety of alcohols and substituted styrenes. Moreover, the removal of the catalysts consists of a single filtration and the catalysts can be re-used for up to four cycles without any significant loss in conversion as well as selectivity. The advantages of reusable catalysts for aerobic oxidation under solvent free conditions make this methodology interesting from an economic and an ecological point of view.

Acknowledgements

Mr. Soyeb Pathan is thankful to the University Grants Commission (UGC-MANF), New Delhi for providing financial assistance.

Notes and references

1 Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu and K.-X. Su, *Chem. Rev.*, 2005, **105**, 1603–1662.

2 G. Franz and R. A. Sheldon, in *Ullmann's Encyclopedia of Industrial Chemistry*, ed. B. Elvers, S. Hawkins and G. Shulz, VCH, Weinheim, 5th edn, 1991, vol. A(18), pp. 261–311.

3 J. T. Lutz, in *Technology*, ed. M. Kirk-Othmer, D. Grayson, G. J. Eckroth and C. I. Bushey, Wiley, New York, 3rd edn, 1980, vol. 9, p. 251.

4 D. H. Pybus and C. S. Sell, *The Chemistry of Fragrances*, RSC Paperbacks, Cambridge, 1999.

5 R. P. Singh, H. N. Subbarao and S. Dev, *Tetrahedron*, 1979, **35**, 1789–1793.

6 T. Fey, H. Fischer, S. Bachmann, K. Albert and C. Bolm, *J. Org. Chem.*, 2001, **66**, 8154–8159.

7 R. A. Sheldon, *Stud. Surf. Sci. Catal.*, 1991, **59**, 33–54.

8 S. L. Regen and C. Koteel, *J. Am. Chem. Soc.*, 1977, **99**, 3837–3838.

9 R. A. Sheldon and I. W. C. E. Arends, in *Advances in Catalytic Activation of Dioxygen by Metal Complexes*, ed. L. I. Simandi, Kluwer Academic Pub, Dordrecht, 2003, pp. 123–155.

10 J. Piera and J.-E. Bäckvall, *Angew. Chem., Int. Ed.*, 2008, **47**, 3506–3523.

11 Y. Ding, B. Ma, Q. Gao, G. Li, L. Yan and J. Suo, *J. Mol. Catal. A: Chem.*, 2005, **230**, 121–128.

12 G. Peng, Y. Wang, C. Hu, E. Wang, S. Feng, Y. Zhou, H. Ding and Y. Liu, *Appl. Catal., A*, 2001, **218**, 91–99.

13 M. Li, J. Shen, X. Ge and X. Chen, *Appl. Catal., A*, 2001, **206**, 161–169.

14 J. Yang, D. W. Lee, J. H. Lee, J. C. Hyun and K. Y. Lee, *Appl. Catal., A*, 2000, **195**, 123–127.

15 W. Li, K. Oshihara and W. Ueda, *Appl. Catal., A*, 1999, **182**, 357–363.

16 N. Mizuno, M. Tateishi and M. Iwamoto, *J. Catal.*, 1996, **163**, 87–94.

17 D. L. Long, R. Tsunashima and L. Cronin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1736–1758.

18 M. T. Pope and A. Muller, *Polyoxometalate chemistry: from topology via self assembly applications*, Kluwer, Dordrecht, 2001.

19 M. T. Pope and A. Muller, *Polyoxometalates: from platonic solids to antirectroviral activity*, Kluwer, Dordrecht, 1994.

20 C. L. Hill, *Chem. Rev.*, 1998, **98**, 1–2.

21 L. Bi, F. Hussain, U. Kortz, M. Sadakane and M. Dickman, *Chem. Commun.*, 2004, 1420–1421.

22 R. Neumann and A. M. Khenkin, *Chem. Commun.*, 2006, 2529–2538.

23 S. Yamaguchi, S. Sumimoto, Y. Ichihashi, S. Nishiyama and S. Tsuruya, *Ind. Eng. Chem. Res.*, 2005, **44**, 1–7.

24 M. K. Harrup and C. L. Hill, *Inorg. Chem.*, 1994, **33**, 5448–5455.

25 J. E. Lyons, P. E. Ellis Jr. and V. A. Durante, *Stud. Surf. Sci. Catal.*, ed. R. A. Grasselli and A. W. Sleight, Elsevier Scientific, Amsterdam, 1991, p. 99.

26 J. E. Lyons, P. E. Ellis Jr., H. K. Myers Jr., G. Suld and W. A. Langdale. *U. S. Pat.*, 4803187 1989.

27 N. Mizuno, T. Hirose, M. Tateishi and M. Iwamoto, *Chem. Lett.*, 1993, **22**, 1839–1842.

28 O. Kholdeeva, V. A. Grigoriev, G. M. Maksimov, M. A. Fedotov, A. V. Golovin and K. I. Zamaraev, *J. Mol. Catal. A: Chem.*, 1996, **114**, 123–130.

29 K. Yamaguchi and N. Mizuno, *New J. Chem.*, 2002, **26**, 972–974.

30 M T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.

31 F. Jing, B. Katryniok, E. Bordes-Richard and S. Paul, *Catal. Today*, 2013, **203**, 32–39.

32 S. Shinachi, M. Matsushita, K. Yamaguchi and N. Mizuno, *J. Catal.*, 2005, **233**, 81–89.

33 G. Centi, J. L. Nieto, C. Iapalucci, K. Bruckman and E. M. Serwicka, *Appl. Catal.*, 1989, **46**, 197–212.

34 E. G. Zhizhina, M. V. Simonova, V. F. Odyakov and K. I. Matveev, *Appl. Catal., A*, 2007, **319**, 91–97.

35 S. Benadji, P. Eloy, A. Leonard, B.-L. Su, C. Rabia and E. M. Gaigneaux, *Microporous Mesoporous Mater.*, 2012, **154**, 153–163.

36 N. Lingaiah, K. M. Reddy, N. S. Babu, K. N. Rao, I. Suryanarayana and P. S. SaiPrasad, *Catal. Commun.*, 2006, **7**, 245–250.

37 C. Marchal-Roch, N. Laronze, N. Guillou, A. Tézé and G. Hervé, *Appl. Catal., A*, 2000, **199**, 33–44.

38 W. Tonghao, L. Yuchun, Y. Hongmao, W. Guojia, Z. Hengbin, H. Shiying, J. Yuzi and Z. Kaiji, *J. Mol. Catal.*, 1989, **57**, 193–200.

39 M. Akimoto, H. Ikeda, A. Okabe and E. Echigoya, *J. Catal.*, 1984, **89**, 196–208.

40 K. Y. Lee, S. Oishi, H. Igarashi and M. Misono, *Catal. Today*, 1997, **33**, 183–189.

41 N. Laronze, C. Marchal-Roch, N. Guillou, F. X. Liu and G. Hervé, *J. Catal.*, 2003, **220**, 172–181.

42 A. Kholdeeva, A. V. Golovin, R. I. Maksimovskaya and I. V. Kozhevnikov, *J. Mol. Catal.*, 1992, **75**, 235–244.

43 R. Neumann and M. Dahan, *J. Chem. Soc., Chem. Commun.*, 1995, 171–172.

44 R. Neumann and M. Dahan, *Polyhedron*, 1998, **17**, 3557–3564.

45 C. Knapp, T. Ui, K. Nagai and N. Mizuno, *Catal. Today*, 2001, **71**, 111–119.

46 N. Mizuno, J.-S. Min and A. Taguchi, *Chem. Mater.*, 2004, **16**, 2819–2825.

47 A. Patel and S. Pathan, *J. Coord. Chem.*, 2012, **65**, 3122–3132.

48 S. Pathan and A. Patel, *Appl. Catal., A*, 2013, **459**, 59–64.

49 S. Pathan and A. Patel, *Ind. Eng. Chem. Res.*, 2013, **52**, 11913–11919.

50 S. Pathan and A. Patel, *Dalton Trans.*, 2013, **42**, 11600–11606.

51 E. Balogh-Hergovicha and G. Speier, *J. Mol. Catal. A: Chem.*, 2005, **230**, 79–83.

52 A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *ACS Catal.*, 2011, **1**, 48–53.

53 A. S. Kanmani and S. Vancheesan, *J. Mol. Catal. A: Chem.*, 1999, **150**, 95–104.

54 A. Sheldon, M. Walau, I. W. C. E. Arends and U. Schuchurdt, *Acc. Chem. Res.*, 1998, **31**, 485–493.

55 K. Yamaguchi and N. Mizuno, *New J. Chem.*, 2002, **26**, 972–974.

56 F. Wang and W. Ueda, *Catal. Today*, 2009, **144**, 358–361.

57 G. Xu, Q.-H. Xia, X.-H. Lu, Q. Zhang and H.-J. Zhan, *J. Mol. Catal. A: Chem.*, 2007, **266**, 180–187.

58 C. L. Hill and R. B. Brown Jr., *J. Am. Chem. Soc.*, 1986, **108**, 536–538.

59 J. Wang, L. Yan, G. Li, X. Wang, Y. Dinga and J. Suoa, *Tetrahedron Lett.*, 2005, **46**, 7023–7027.

60 L. Xinrong, X. Jinyu, L. Huizhang, Y. Bin, J. Songlin and X. Gaoyang, *J. Mol. Catal. A: Chem.*, 2000, **161**, 163–169.

61 X. Zhang, Q. Chen, D. C. Duncan, R. J. Lachicotte and C. L. Hill, *Inorg. Chem.*, 1997, **36**, 4381–4386.