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Sn(IV) phosphonates as catalysts in solvent-free Baeyer–Villiger oxidations using H_2O_2†

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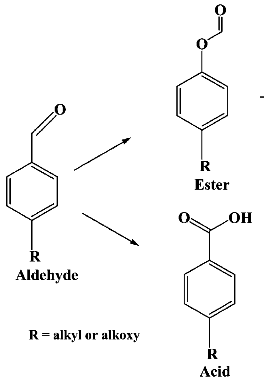
We have designed a new family of layered Sn(IV)phosphonate (SnPP) materials which are very efficient catalysts in the BV oxidation of aromatic aldehydes without any solvent and using aqueous H_2O_2 (30%) as the oxidant.

The Baeyer–Villiger (BV) oxidation is the oxidative cleavage of a carbon–carbon bond adjacent to a carbonyl, which converts ketones to esters and aldehydes to phenols. The conventional BV oxidation involves the use of an organic peracid. This is one of the main drawbacks of this procedure as the organic peracid is expensive, hazardous and ecologically unattractive as it produces carboxylic acid salts as the byproduct.[1] The use of alternative pathways such as the *in situ* generation of the organic peracids by the action of oxygen with sacrificial aldehydes, or the use of H_2O_2 with a catalyst, has been widely researched. The use of hydrogen peroxide is a "green" process as water is the byproduct of this oxidation. The main challenges to this procedure are the compatibility of the solvent with aqueous H_2O_2 and finding the right catalyst which would activate the peroxide in the presence of water. There are a number of reports on the oxidation of cyclic ketones[2–5] using hydrogen peroxide but only a few on aromatic aldehydes mainly because of the poor reactivity of the aromatic aldehydes. Homogenous catalysts such as SeO_2 and arylseleninic acids have been found to be efficient in the oxidation of aromatic aldehydes using aqueous hydrogen peroxide.[6] Corma *et al.*[7–10] have designed Sn-beta zeolite and Sn-MCM-41 heterogeneous catalysts for the reaction of aromatic aldehydes with hydrogen peroxide in non halogenated solvents such as dimethylformamide and dioxane. They suggest that the catalyst activates the carbonyl compound and not the hydrogen peroxide and this makes these catalysts more selective. We have developed a family of porous Sn(IV)phenylphosphonates that are layered materials, possess high surface area and with pore diameters in the 10–20 Å range.[11,12] We have used these materials as catalysts in the BV reaction and found them to be extremely active for the oxidation of aromatic aldehydes using 30% aqueous H_2O_2 solution. The most fascinating part of these catalysts is that the reaction proceeds more efficiently in the absence of any organic solvents. During the BV oxidation of an aromatic aldehyde various products can be formed depending on the catalyst and the solvent (Scheme 1). The electron donating substituents on the aromatic ring are known to favor the formation of the ester which forms the corresponding phenol on hydrolysis.[10] The BV reaction over 4-methoxybenzaldehyde (anisaldehyde) carried out in the presence of different solvents using Sn(IV)phenylphosphonate (SnPP) as the catalyst showed that as the polarity of the solvent decreased the activity of the catalyst increased (Fig. 1). No benzoic acid was detected in the reaction mixture.

This trend is opposite to what was observed over Sn-beta zeolites.[10] Amongst the different solvents used the conversion was the best for the least polar solvent toluene, which gave the aldehyde conversion of 42% and a selectivity to the phenol of 35%. We observed that in the absence of a solvent the conversion went up to 54% and the selectivity to the phenol increased to 68%. The hydrolysis of the ester to phenol is facile in the absence of a solvent. This result is extremely important in the BV oxidation as it eliminates the need to find a compatible solvent and also advances the cause of the environment as it eliminates the need for a solvent. We postulate that the SnPP materials being inorganic–organic hybrids are good hosts to both the organic reagents and H_2O_2, thus making them very active catalysts in this reaction. The effect of the catalyst characteristics on the reaction was studied by using a series of catalysts synthesized using various phosphonic acids and solvents. $Sn(C_6H_5PO_3)_2$ was synthesized using various solvent systems and it was found that the catalyst formed in H_2O-DMSO(SnPP-D) or pure H_2O (SnPP-F) was much more reactive than the one synthesized in a H_2O–EtOH (SnPP-E) mixture. 4-methoxybenzaldehyde conversions of 68–70% were observed when the catalyst prepared in H_2O or H_2O-DMSO was used in the BV reaction whereas a conversion of 48% was observed when the catalyst prepared in H_2O–EtOH was used (Table 1). The selectivity for the phenol was around 70% in all



Scheme 1 Baeyer–Villiger oxidation of an aromatic aldehyde.

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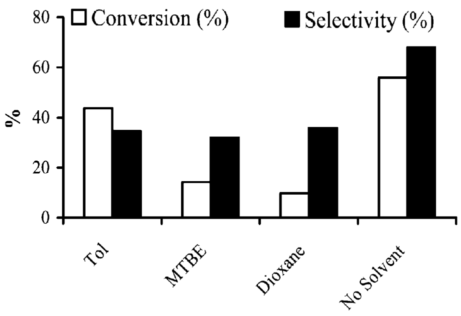


Fig. 1 Effect of solvent on the BV reaction of anisaldehyde over SnPP catalyst; Reaction conditions: 60 °C, 180 min, 3.7 mmol of aldehyde and 4.5 mmol of 30% H_2O_2; 0.025 g catalyst (SnPP-F); 3 ml solvent.

cases, the selectivity is not a function of the catalyst but that of the solvent. The surface area of catalyst prepared from H_2O–EtOH mixture was 233 $m^2\ g^{-1}$ whereas the ones made from H_2O or H_2O-DMSO was far lower than this ($\sim$50 $m^2\ g^{-1}$).

The X-ray patterns of these samples show that they have the same interlayer spacing of $\sim$15 Å, however the crystallinity of the sample prepared with EtOH is considerably lower than the other two. The SEM images of these samples reveal that in the presence of EtOH the Sn phosphonates tend to form nanoparticles which aggregate to form porous globules, whereas in the presence of only H_2O or DMSO the particles are much bigger and better defined (Fig. 2A, 4B).

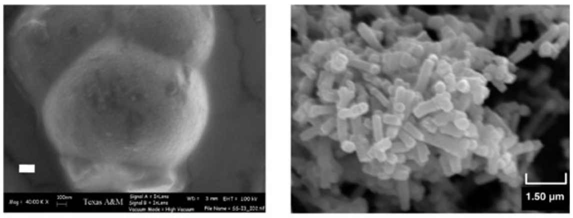
^{119}Sn Mössbauer spectroscopic studies on these samples show that all of them give essentially the same isomeric shift (IS) at 294 K: $-0.318 + 0.009$ mm s^{-1} (Fig. 3).

The quadrupole splitting (QS) is very small and nearly temperature independent. This suggests that the phenyl phosphonate ligands do not significantly influence the electronic environment around the metal atom. The line widths (fwhm) are on the order of $\sim$1.01 + 0.02 mm s^{-1}, indicating a small range of geometries of the tin atom nearest neighbor ligands. Temperature dependent Mossbauer studies on these samples indicate that the tin atom in the SnPP-E lattice is slightly more tightly bound, giving rise to a slightly higher lattice temperature than in SnPP-F. The temperature dependence of the isomer shift is essentially identical for SnPP-E and SnPP-F. This might hinder the ability of this catalyst to activate the aldehyde leading to a decreased conversion. The Mössbauer lattice temperatures, Θ_M,[13] are $\sim$128 K for SnPP-F and $\sim$143 K for SnPP-E.

Table 1 BV oxidation of 4-methoxybenzaldehyde over various SnPP catalysts[a]

Sample No.	Catalyst	Inter-layer spacing (*d*)/Å	Sn wt%	Surface area/$m^2\ g^{-1}$	Con-version %	Selectivity/phenol (%)
SnPP-A	Sn(IV)($O_3PC_6H_4$-$C_6H_4PO_3$); H_2O–DMSO	13.4	24.5	385	88	100
SnPP-B	Sn(IV) ($O_3PC_6H_5$-PO_3);H_2O–DMSO	9.4	30	399	32	70
SnPP-C	Sn(IV)($C_6H_5PO_3$) (HPO_3); H_2O–DMSO	15.4	28	285	83	75
SnPP-D	Sn(IV)($C_6H_5PO_3)_2$; H_2O	15.4	27	49	70	70
SnPP-E	Sn(IV)($C_6H_5PO_3)_2$; H_2O–EtOH	15.4	26.5	233	42	69
SnPP-F	Sn(IV)($C_6H_5PO_3)_2$; H_2O–DMSO	15.4	25.8	48	68	67

[a] Reaction conditions: 0.025 g catalyst, 60 °C, 180 min, 3.7 mmol of aldehyde and 4.5 mmol of 30% H_2O_2.



A) SnPP-E B) SnPP-F

Fig. 2 SEM images of Sn($C_6H_5PO_3)_2$: Scale for (A) 200 nm; (B) 1.50 μm.

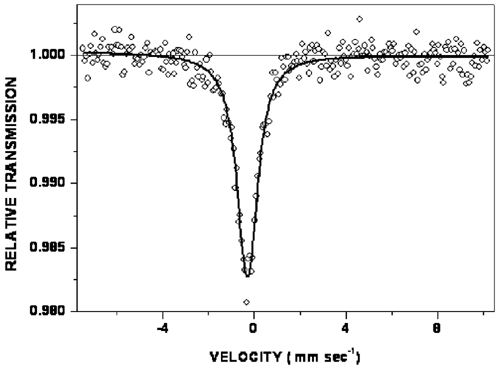
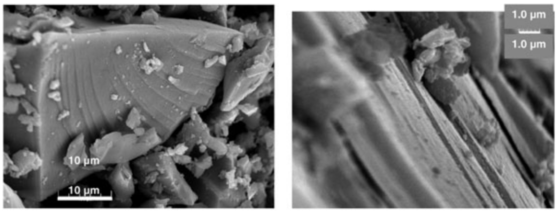


Fig. 3 Mossbauer spectra of a Sn(IV) phosphonate compound.



A) SnPP-A B) SnPP-B

Fig. 4 SEM images of crosslinked Sn phosphonates.

We have prepared a series of catalysts in H_2O–DMSO with various phosphonic acids in between the layers. The interlayer spacing, surface area and pore sizes of these materials are a function of these phosphonic acids (Table 1). The Mossbauer studies on these samples suggest that the Sn is in a nearly octahedral environment in all cases and that the environment around Sn(IV) is nearly the same. The ^{119}Sn NMR spectra do not change with the phosphonic acids and therefore the only effect the phosponic acid has is to alter pore architecture and the surface area of the Sn phosphonate. For pristine SnO_2 sample, an isotropic peak around −604 ppm flanked by sidebands is observed[9] which is characteristic of the octahedral coordination of Sn^{4+}. The NMR spectra of Sn phosphonates show a peak at −821.5 ppm which suggests that the environment around the Sn(IV) is considerably different from that of SnO_2.[12] SnO_2 is not an active catalyst for this reaction. The SEM images of these

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Table 2 BV oxidation of different 4-susbstituted benzaldehydes

Aldehyde	Conversion/%	Selectivity phenol (%)
p-Ethylbenzaldehyde	46	89
p-Tolualdehyde	52	100
p-Anisaldehyde	58	100
p-Ethoxybenzaldehyde	55	100

Reaction conditions: 0.025 g catalyst (SnPP-A) 80 °C, 60 min, 3.7 mmol of aldehyde and 4.5 mmol of 30% H_2O_2.

SnPP catalysts reveal that when the layers are cross-linked the morphology is different from the ones which are not cross-linked (Fig. 2 and 4). The cross-linked materials tend to form a larger continuous particle by the stacking of several layers and the uncross-linked ones tend to form smaller particles, which often aggregated into spheres.[11,12] The formation of pores and consequently high surface areas in the cross-linked materials can be explained analogous to the cross-linked Zr materials where the pores develop by a coming together of layers of unequal size during particle growth.[14]

We have used a series of SnPP catalysts to carry out BV oxidation on 4-methoxybenzaldehyde (Table 1). It was found that the conversion of the aldehyde was greatly influenced by the catalyst employed. When Sn(IV)($O_3PC_6H_4PO_3$) (SnPP-B) was used as the catalyst the conversion was only 32%. The conversion increased to 68% when Sn(IV)($C_6H_5PO_3$)$_2$ (SnPP-D) was used and a maximum conversion of 88% was observed over Sn(IV)($O_3PC_6H_4$–$C_6H_4PO_3$) (SnPP-A). There are two main factors determining the efficiency of the catalyst; first is the compatibility of the H_2O_2 with the catalyst and second the accessibilty of the active centres to the aldehydes. These catalysts being inorganic–organic hybrid materials are not very hydrophobic and therefore compatible with H_2O_2. The degree of accessibilty of the aldehyde to the active centers therefore decides the conversion levels in the reaction. When SnPP-F is used, the conversion of anisaldehyde is around 68% and when we introduce spacers in between the benzene ring in the form of phosphorous acid groups, the surface area goes up from 48 to 285 m^2 g^{-1} and the conversion also increases to 83%. SnPP-B has a more closely packed structure than the other catalysts leading to inaccessible active sites. We have used SnPP-A in BV oxidation reactions over various substituted benzaldehyde substrates (Table 2).

The conversion level follows the electron donating ability of the *p*-substituents; and the order of reactivity is methoxy > ethoxy > methyl > ethyl. The only product formed in all these cases was the phenol except when 4-ethylbenzaldehyde was used. In this case a small amount (∼10%) of the ester was also formed.

The catalyst SnPP-A was reused in the BV oxidation and it was found that there was no perceivable change in the activity of the catalyst. The X-ray pattern and Mossbauer spectra of this material are virtually unchanged indicating that there is no physico-chemical change to the material and there can be no leaching of the Sn(IV) because of the nature of the octahedral bonds holding the Sn within the layer. These catalysts show much higher catalytic activity compared to other heterogeneous catalysts reported in the literature (Table 3), although we must note that the amount of Sn contained in our system is much higher than in the other Sn systems.

Table 3 Comparison of catalytic activity of different Sn catalysts with 4-methoxybenzaldehyde

Catalyst	Sn wt%	Conv/ %	Sel-phenol/ %	Comments
Beta Zeolite SnO_2	∼2	56	46	Acetonitrile 50% H_2O_2 (ref. 10)
Sn Beta Zeolite	∼2	58	86	Toluene 35% H_2O_2 (ref. 9)
SnPP-A*	24.5	98	100	No solvent 30% H_2O_2

Reaction conditions: 0.05 g catalyst (* 0.025 g catalyst), 80 °C, 7 h, 3.7 mmol of aldehyde and 4.5 mmol of H_2O_2.

The BV oxidation of cyclohexanone using 0.025 g of Sn phosphonate (Sn-PPA) was carried out at 60 °C for 6 h. When the cyclohexanone to 30% H_2O_2 ratio was 1 : 1.25 the conversion of cyclohexanone was 68% with a caprolactone selectivity of 95%. When the same reaction was carried out at 90 °C for 20 h and with a cyclohexanone to 30% H_2O_2 ratio of 1 : 3 the conversion of cyclohexanone was 94% and the major product was adipic acid with a selectivity of 85%. These results show that the Sn phosphonates can be applied in the BV oxidation of a wide range of substrates from aromatic aldehydes to cyclic ketones.

In conclusion, we have developed a new catalytic system whose surface area and pore size can be tailored and tuned over a wide range and these materials can catalyze the BV reaction under facile solvent-less condition to give conversion and selectivity levels higher than those reported in the literature so far. We also believe that chiral centres can be introduced in the phosphonic acid moiety which would make this catalyst an attractive chiral catalyst for the synthesis of asymmetric lactones from racemic ketones.

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