Novel Sn(IV)phenylphosphonates as catalysts in Baeyer-Villiger oxidations

Sharath Kirumakki, Sandani Samarajeewa, Atashi Mukherjee, Robert Harwell, Abraham Clearfield*
Chemistry Department, Texas A&M University, College Station, Texas 77842, USA
clearfield@mail.chem.tamu.edu

Introduction

A new family of microporous materials, the tin(IV) phosphonates, with surface areas ranging from 100-500m^2/g and pores mostly in the microporous region, has been synthesized. The tin(IV)phosphonates are basically layered materials analogous to the zirconium phosphate with an interlayer spacing of around 15 Å. The porosity and high surface area arises from the aggregation of these nanosized particles into globular spheres. The porosity can be varied by varying the phosphonic acids and the synthesis conditions.

These materials were used as a heterogeneous catalyst for the liquid phase Baeyer-Villiger (BV) reaction with H_2O_2. An aromatic aldehyde, is converted to its corresponding phenol, with aq. H_2O_2 as the oxidant in the presence of the catalyst. Corma and co-workers have shown the remarkable activity of Sn-zeolite in this reaction[3,4]. Aromatic aldehydes and cyclic ketones were oxidized using H_2O_2 in mild solvents like dioxane and MTBE. We have been able to achieve similar activity for aromatic aldehydes under solvent free conditions and lower reaction temperatures.

Materials and Methods

$Sn(O_3PC_6H_5)_2$ was prepared hydrothermally using $SnCl_4{\cdot}5H_2O$ and phenylphosphonic acid. In a typical synthesis $SnCl_4.5H_2O$ was placed into a plastic beaker. DI water and HF were then added. In a separate beaker, $C_6H_5PO_3H_2$ was dissolved in DMSO. Once the ligand was dissolved, the two solutions were combined, leading to the immediate formation of a white suspension/gel. The mixture was then sealed and heated at 140°C for 3 days. The resulting white powder was filtered off and washed with ethanol and water. It was then dried at 60°C overnight. These Sn phosphonates were used as catalysts in B-V reaction. In a typical reaction 25mg of the catalyst was added to a round bottom flask containing the aldehyde and H_2O_2 and heated at a predetermined temperature and time. After the reaction, the catalyst was separated from the reaction mixture, and washed with acetone. Reusability of these catalysts was tested after drying them at 60°C overnight. The reaction mixture was analyzed by GC and the products were identified by GC-MS.

Results and Discussion

Tin(IV) phosphonates are nanoparticles, not by design but by their very nature. A consequence of their very small particle size is that the particles aggregate into micron-sized spheres that create tunnels that represent micropores. The cross-sectional diameters of the tunnels ranged from about 11 to 24 Å with maxima in the pore size distribution curves in the 10-27 Å range. The particles appear as micron-sized spheres, but on very high magnification, the spheres exhibit pores almost like a sponge due to the aggregation of small rods (Fig 1). The N2 sorption isotherm is a typical type-I isotherm indicative of microporous compounds (Fig 2).

These materials as catalysts were found to be active for the oxidation of a range of aromatic aldehydes(Table 1). For example in the B-V oxidation of anisaldehyde at 80°C, a conversion of 100% was achieved in 100 minutes. The selectivity to the formate ester was 65%, the other produce being the corresponding phenol from the hydrolysis of the ester. Reactions in the absence of the catalyst gave substantially low or no conversions depending on the aldehyde.

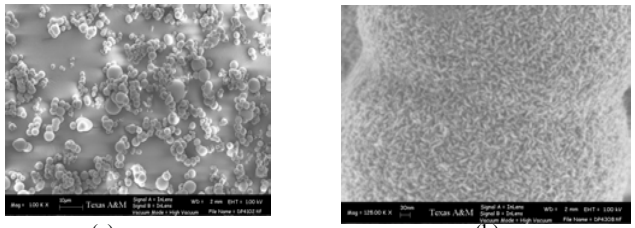
Table 1. Catalytic activity of $Sn(IV)(PhPO_3)_2$

Aldehyde	Conversion (%)	Yield of ester (%)
p-anisaldehyde	100	65
4-ethoxy benzaldehyde	85	80
p-tolualdehyde	50	75

The catalysts were reused without any significant loss of activity (>95%). We are currently working on extending the applicability of these catalysts to cyclic ketones and unactivated aromatic aldehydes.

Significance

We have been able to achieve high conversions and selectivity under solvent free conditions. These catalysts can be employed over a wide range of aromatic aldehydes and they can also be reused. These features of the catalyst combined with their high surface area and controlled pore size make them very attractive "green" heterogenous catalysts.



(a) (b)

Figure 1. (a)SEM of spherical shaped globules of $Sn(O_3PC_6H_5)_2$ and (b) an enlargement of one of the globules.

References

1. Huang, J., Subbiah, A., Pyle, D., Rowland, A., Smith, B., Clearfield, A. Chem. Mater. 18, 5213, (2006).
2. Subbiah, A., Pyle., Rowland, A., Huang, J., Narayanan, R. A., Thiyagarajan, P., Zon, J., Clearfield, A. J. Am. Chem. Soc. 127, 10826, (2005)
3. Corma, A., Nemeth, L.T., Renz, M., Valencia, S. Nature, 412, 423, (2001).
4. Renz M, Teresa Blasco T., Corma. A, Fornes, V., Jensen, R, Nemeth, .L, Chem. Eur. J. 8, 4708, (2002).