

# MANGANESE AND COBALT SALTS OF PARA- AMINO- BENZOIC ACID SUPPORTED ON SILICA GEL AS OXIDIZING CATALYSTS

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**ABSTRACT :** *Para- Aminobenzoic acid is supported on silica gel via reaction of activated silica gel and p- aminobenzoic acid which is then converted to its manganese and cobalt salts. A mixture of the manganese and cobalt salts of the acid is used to catalyze allylic and benzylic alcohols to their corresponding carbonyl compounds in reasonable yields using oxygen or air. Reactions are clean and the catalysts can be recovered easily and reused repeatedly.*

**KEY WORDS :** *Manganese and Cobalt Salts of P- aminobenzoic acid, Benzyl and Allyl Alcohols, Carbonyl Compounds, Reuseable Catalysts, Oxygen and Air.*

## INTRODUCTION :

Solid supported reagents for the organic reactions were first introduced by *Merifield* [1] and *Letsinger* [2]. Easy access to the products via a simple filtration for removing unreacted materials has rendered the method very attractive. Organic compounds such as polystyrene and its analogs have long been of interest as solid supports [3,4]. Inorganic polymers are also of

interest. For example, freshly prepared silver carbonate is an efficient oxidizing agent but difficult reaction work-up has restricted its applications. Supporting this reagent on celite has overcome the work-up problems and has made it a practical oxidizing agent for conversion of alcohols to their respective carbonyl compounds [5-7]. Alumina has also

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been used as an inorganic solid support and has been reported that chloral supported on alumina can oxidize secondary alcohols to ketones [8,9]. Silica gel another inorganic polymer, has been used widely in organic reactions [10-13]. A mixture of silica gel and ozone gas at low temperatures can oxidize saturated hydrocarbons to corresponding tertiary alcohols [14]. A great number of oxidizing agents can effect the conversion of alcohols to carbonyl compounds, particularly chromium (VI) derivatives [15,16]. The oxidation of alcohols by N- halogenoamines [17], N- halogenoamide [18] and hexamethylene-tetraaminebromide [19] have been reported recently.

We wish to report the oxidation of alcohols using silica gel as a solid support for developing new catalysts. The catalyst is prepared from reaction of activated silica gel and p- aminobenzoic acid which is then converted to its cobalt and manganese salts. Allyl and benzyl alcohols are oxidized to their corresponding carbonyl compounds in presence of oxygen or air using a mixture of these salts as catalysts. The method leads to clean reactions, recyclability of the catalysts, selective conversion of alcohols to carbonyl compounds and adaptability to fairly large scale operation.

## RESULTS AND DISCUSSION :

Silica gel is activated in a pyrolysis apparatus at 260°C in 20mm Hg to lose its water by 5.7%. P- Aminobenzoic acid is reacted with the activated silica gel. The infrared spectrum of the bound acid on the silica gel shows an absorption band at  $1561\text{cm}^{-1}$  corresponding to N-Si bending mode and N-Si vibrational modes expected at  $3300\text{-}3500\text{cm}^{-1}$  are masked due to strong Si-OH absorption band in the same region. Further evidence of the Si-N bond is obtained when the p- aminobenzoic acid bonded to silica gel is hydrolyzed with sodium hydroxide solution and the liberated p- aminobenzoic acid is recovered. The reaction of p- aminobenzoic acid bonded to silica gel with sodium bicarbonate solution afforded sodium salt of the acid, which

is converted to cobalt and manganese salts using cobalt chloride and manganese chloride solutions. Combinations of cobalt and manganese salts of p- aminobenzoic acid bonded to silica gel are used as catalysts for oxidation of alcohols in presence of oxygen or air. Low yields are obtained when acetonitrile is used as a solvent, dimethylformamide caused the salts to decompose but chlorobenzene gives high yields of expected products without decomposition of the catalysts. Allyl and benzyl alcohols are converted to their respective carbonyl compounds by these catalysts in presence of oxygen or air (Table 1). Despite many attempts, under different conditions, saturated alcohols could not be oxidized to their carbonyl compounds. The catalysts are reasonably reuseable even after four runs, only about ten percent loss in product yield is observed, (Table 2). Instead of oxygen, air has been used as the oxidant. The yields drop and reaction times become longer.

## EXPERIMENTAL :

Reagents were of commercial quality and purchased from Merck, Riedel and Fluka Chemical Companies. All oxidation products were known compounds and identified by comparison of their IR spectra and physical data with those of the authentic samples. IR spectra were taken on a FTIR Mattson 1000 Unicam. Melting points were determined in open capillaries on a Mettler FP5 apparatus and are not corrected. Silica gel was activated in a Gallen Kamp 220/240 volts amps 21AC pyrolysis apparatus. The air was bubbled through the reaction mixture by an ordinary household fish aquarium pump. The quantities of salts were determined with an XRF model 8410 ARL, RHH source 60kV. Yields reported refer to isolated products.

### Preparation of Activated Silica Gel

In a pyrolysis apparatus silica gel (5g) was heated at 260°C under reduced pressure (20mm Hg) using phosphorous pentoxide (5g) as a desiccant. The silica gel lost 0.28g of its weight after 10hrs (5.7% wt).

Table 1: Oxidation of Benzylic and Allylic Alcohols to carbonyl compounds

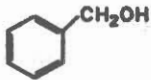
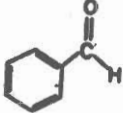
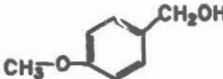
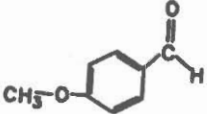
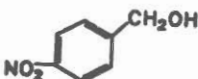
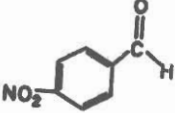
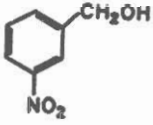
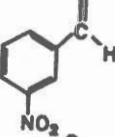
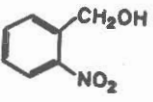
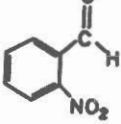
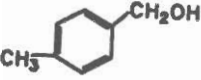
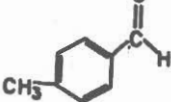
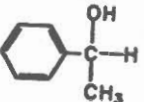
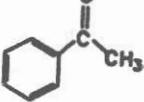
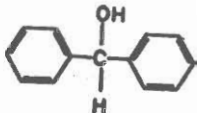
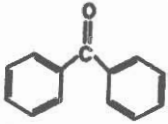
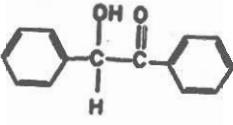
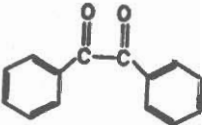
Starting Material	Product	Yield (oxygen)	Reaction Time/h	Yield (Air)	Reaction Time/h
		80	27	66	42
		85	26	68	42
		77	30	62	47
		75	30	57	47
		60	30	41	47
		83	28	65	43
		88	21	72	38
		95	20	78	32
		100	5	95	90
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$	$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	37	35	19	55

Table 1 Continued :

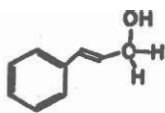
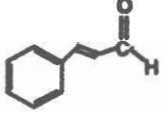
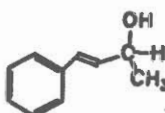
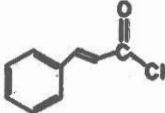
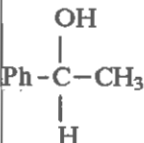
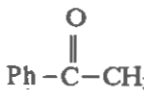
Starting Material	Product	Yield (oxygen)	Reaction Time/h	Yield (Air)	Reaction Time/h
		70	23	53	49
		74	33	56	48

Table 2: Reuseability of Catalysts.

Experimental trial	Starting material	Product	% Yield	Reaction time(.h)
First			88	21
Second	"	"	82	23
Third	"	"	80	23
Fourth	"	"	79	23

#### Reaction Between Activated Silica Gel and P- Aminobenzoic Acid

To a mixture of ethyl acetate (70 mL) and p-aminobenzoic acid (2.13g, 15mmoles) was added the activated silica gel (4.79g). The reaction mixture was then refluxed while being stirred magnetically at 80°C for 16hrs. The mixture was cooled to room temperature and filtered. The solid mass was washed with ethyl acetate by a soxhlet for 10hrs. in order to remove all unreacted p- aminobenzoic acid. The solid was then dried in an oven at 100°C to afford (6.05g) of pale yellow solid material. (1.33g of acid was reacted, 9.7mmoles). The IR spectrum showed an absorption band at 1561cm<sup>-1</sup> for Si-N bending mode and the expected Si-N vibrational mode at 300-3500cm<sup>-1</sup> could not be observed due to a strong Si - OH band in the same region.

#### Preparation of Sodium, Cobalt and Manganese Salts of the P- Aminobenzoic Acid Supported on Silica Gel

Sodium salt of the p- aminobenzoic acid (5g) supported on silica gel was prepared via a reaction of the acid and a solution of sodium carbonate to give (5.25g, 1.1mmoles, 76% wt increase) of the sodium salt. This result was verified by XRF method to show 4.47 wt increase. A mixture of saturated cobalt chloride (50mL) and sodium salt (5g) of the p- aminobenzoic acid supported on silica gel was refluxed at 100°C for 2 hrs. The mixture was then cooled to room temperature and filtered. The solid was washed with distilled water for 10 hrs (soxhlet). The solid was then dried in an oven at 110°C for 5 hrs. to give cobalt salt (5.33g) of the acid as a pink solid (60%g wt increase). This result was verified with XRF method to show 6.10% wt increase.

Similarly, manganese salt of the acid was prepared using manganese chloride solution to give 5.39g of a white solid (6.10% wt increase, XRF showed 5.97% wt increase).

#### **Oxidation of P-Methoxybenzyl Alcohol to P-Methoxybenzaldehyde. Typical Procedure**

To a solution of p- methoxybenzyl alcohol 140mg (1.0mmoles) in chlorobenzene 25ml was added the cobalt salt (460mg, 0.5mmoles cobalt) and the manganese salt (450mg, 0.5mmoles of manganese). The mixture was magnetically stirred at 110°C for 26 hrs during which oxygen was bubbled at the rate of 10mL per minute into the solution. The reaction mixture was then cooled to room temperature and diluted with the solvent (10ml). The mixture was filtered and solid material (Co and Mn salts) was washed with chlorobenzene (2×10mL). The chlorobenzene solutions were combined with the filtrate. The solvent was evaporated to give a pale yellow oil. The oil was purified by column chromatography on silica gel using carbontetrachloride and ethyl ether (1:3) as eluent ( $R_f = 0.78$ ). Evaporation of the solvent afforded p- methoxy benzaldehyde (120mg, 0.85mmoles, 85%), (Table 1). The above experiment was repeated with air instead of oxygen at a rate of 35mL per minute for 50hrs. The yield was 68% (Table 1).

#### **Reuseability of the Catalysts. Typical Procedure**

Oxidation of 1- phenylethanol to methyl-phenyl ketone was carried out as described above to give 88% yield of the desired product. The catalysts were recovered via a simple filtration and dried in an oven at 135°C for 4 hrs. The reaction was repeated using the recovered catalysts to give 82% of the product. The catalysts were recovered and reused for the third and fourth times to give 80 and 79% yields respectively. The catalysts were recovered quantitatively in each experiment (Table 2).

#### **CONCLUSION :**

Allylic and benzylic alcohols are oxidized to

their corresponding carbonyl compounds in presence of oxygen or air catalyzed by a mixture of cobalt and manganese salts of p-aminobenzoic acid supported on silica gel. The catalysts are not suitable for the oxidation of saturated alcohols. The ease of work-up, recycling of the catalysts and selectivity of the reaction are worthy of mention.

#### **REFERENCES :**

- [1] Merified, R.B., *J. Am. Chem. Soc.*, **85**, 2149 (1963).
- [2] Letsinger, R.L., and Kornet, M.J., *ibid*, **85**, 3045 (1963).
- [3] Sherrington, D.C., and Hodge, P., "*Synthesis Using Functional Polymers*", Wiley and Son, L.T.D, 192 (1988).
- [4] Yoshical, J., Ogura, K., and Kawabata, N., *J. Org. Chem.*, **49**, 3419 (1984).
- [5] Fetizon, M., Golfier, M., and Lewis, J.M., *J. Chem. Soc. Chem. Comm.*, 1118 (1969).
- [6] Babgh, V., Fetizon, M., and Golfier, M., *J. Org. Chem.*, **36**, 1339 (1971).
- [7] Fetizon, M., and Mourgnès, P., *Lett.*, **30**, 397 (1974).
- [8] Posner, G.H., Perfetti, R.B., and Runquist, A.W., *Tet. Lett.*, 3499 (1976).
- [9] Posner, G.H., and Chopdelaine, M.J., *ibid*, 3227 (1977).
- [10] Hudlicky, M., *J. Org. Chem.*, **39**, 3461 (1974).
- [11] Kato, T., Katagiri, N., Nakano, J., and Kawamura, J., *J. Chem. Soc. Chem. Comm.*, 645 (1977).
- [12] Bachi, M.D., and Vaya, J., *Tet. Lett.*, 2209 (1977).
- [13] Marshall, J.A., Andersen, N.H., and Johnson, P.C., *J. Org. Chem.*, **35**, 186 (1970).
- [14] Cohen, Z., Keinan, E., Mazur, Y., and Ulman, A., *J. Org. Chem.*, **41**, 2651 (1976).
- [15] (a): House, H.O., *Modern Synthetic Reaction*, Benyamine, W.A., New York, 2nd Ed. pp. 257-285 (1972).  
(b): Bosche, H.G., *Methoden der Organischen Chemie*. Ed., Muller, E., vol. 4-1b, Georg Thieme, Stuttgart, 4th Ed., p. 425

- (1975).
- [16] Firouzabadi, H., Sharifi, A., and Karimi, B., *Iran.J. Chem. & Chem. Eng.*, **12**(1), 39 (1993), and references cited therein.
- [17] kondo, S., Ohira, M., Kawasoe, S., Kunisada, H., and Yuki, Y., *J. Org. Chem.*, **58**, 5003 (1993).
- [18] Al-Neirabeyeh, M., Zeigler, J.C., Gross B and Caubere P., *Synthesis*, 811 (1976).
- [19] Yavari, I., and Shaabani, A., *J. Chem. Research(s)*, 274 (1994).