ChemPubSoc Europe
DOI: 10.1002/slct.201600933
ChemistrySELECT Full Papers

Catalysis

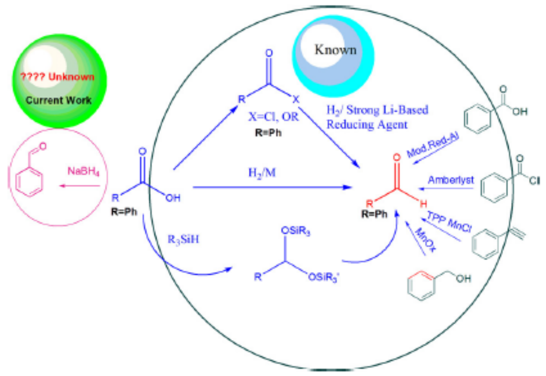
Silver-Sulphur Oxido-Vanadium Cluster: A Newly Born Catalyst for Direct Reduction of Aryl Carboxylic Acids to Aldehydes *via* Mars and van Krevelen Mechanism

Biraj Das,[a] Mukesh Sharma,[a] Lanka. Satyanarayana,[b] Galla. V. Karunakar,[c] and Kusum. K. Bania*[a]

Now no more harsh condition and expensive catalyst or reducing agent would probably be required to directly convert aromatic acids to its corresponding aldehydes. Herein, we report for a cheap and recyclable solid catalyst consist of silver (Ag), sulphur (S) and vandium (V) having a structural unit of $[Ag_2SCH_2V_2(O)_2(COO)_2]_n$. This catalyst can directly reduce aromatic carboxylic acids to aldehydes with sodium borohydride ($NaBH_4$). High chemoselectivity and selectivity was achieved specially with $-NO_2$ substituted benzoic acids. Catalytic conversion was found to be excellent in THF and methanol except the pyridine carboxylates. At room temperature and under refluxing condition no catalytic conversion was observed. However, after subjecting to microwave (MW) irradiation followed by magnetic stirring under refluxing condition gave nitro-benzaldehydes upto 90% yield. Catalytic activity of the catalyst was found to retained upto 4th consecutive cycles. The catalytic reaction was believed to proceed *via* Mars and van Krevelen mechanism.

Introduction

Direct reduction of carboxylic acids to aldehydes has remained a long challenged for researchers.[1] Number of strategies so far has been adopted to achieve selective reduction of acids to aldehydes.[2,3] Two of the most acceptable routes for such conversion are the direct route and the indirect route. In direct reduction process, aldehydes are achieved by hydrogenation under high pressure and temperature.[1] While the indirect synthetic route involved a two step processes — first the carboxylic acids are converted to a more reactive species as acid chlorides or esters which are then reduced by hydrogenation or by hydride reduction reactions, Scheme 1.[2,3] Besides these processes, aldehydes are also synthesized by oxidation of 1° alcohols, hydration of alkynes, reduction of esters and amides, acid chlorides or nitriles and also by Fridel- Craft Acylation, Scheme 1.[4–13] Industrially, CeO_2 mainly and other oxides like MnOx, ZrO are used as catalytst for production of benzaldehydes *via* hydrogenation of benzoic acids.[14] Although these reactions are useful in synthesis of aldehydes and ketones but in many cases they involved multistep process and all these methods have their own advantages and disadvantages. Both the direct and indirect synthetic routes has one major drawback i.e. they exhibit poor chemoselectivity as in both the cases some vigorous condition are employed.[15] For example, in direct hydrogenation process application of high pressure and temperature leads to the loss of control over the chemoselectivity of the reaction.[5] Besides this, some strong reducing agent involving Li is basically used.[16] Efforts has been given by the researchers to develop suitable catalyst and reducing agents to obtain the aldehydes directly from its corresponding carboxylic acids.[17–20]



Scheme 1. Some of the representative example for synthesis of aldehydes.

In recent year conversion of carboxylic acid to aldehydes *via* hydrosilylation reaction or by Fukuyama reduction[21] has at-

[a] B. Das, M. Sharma, Dr. K. K. Bania
Department of Chemical Sciences
Tezpur University
Assam, 784028, India
E-mail: kusum@tezu.ernet.in
bania.kusum8@gmail.com
[b] Dr. L. Satyanarayana
Center for NMR and Structural Chemistry
Indian Institute of Chemical Technology
Uppal Road, Tarnaka, Hyderabad, Telangana 500007, India
[c] Dr. G. V. Karunakar
Division of Crop Protection Chemicals
Indian Institute of Chemical Technology
Uppal Road, Tarnaka, Hyderabad, Telangana 500007, India

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/slct.201600933