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HETEROGENEOUS CATALYTIC CONVERSIONS WITH HYDROUS SnO₂

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ABSTRACT: Hydrous Tin oxide (SnO₂) was prepared by the action of conc. HNO₃ on tin metal. It was found to catalyse transesterification, amidation and transfer-hydrogenation in the vapour phase significantly. There was no loss in activity for at least 50 runs of the reactions.

The manufacture of speciality and fine chemicals in batch production processes are commonly associated with the production of large quantities of toxic waste materials when traditional reagents such as mineral acids, strong bases and stoichiometric oxidants are used. They also suffer from other drawbacks like handling difficulties, poor reaction selectivities and inorganic contamination of organic products. These problems can be overcome to a large extent if environmentally acceptable heterogeneous catalytic systems are developed^{1,2}.

In this aspect, hydrous oxides can emerge as a promising catalyst system. Hydrous oxides have several advantages as catalysts as they are generally very stable

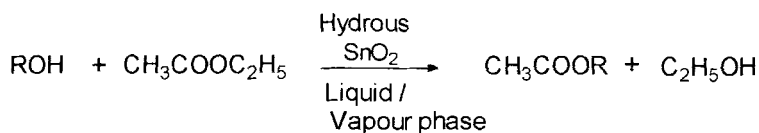
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and are not sensitive to air or water and so the reactions do not require water-free conditions. In recent years, interest in hydrous zirconium oxide for heterogeneous catalysis has greatly increased³⁻⁵

In an earlier work we carried out detailed investigation on the activity of SnO₂ catalyst modified with Lewis and Bronsted acids. It was observed that the catalyst had good activity and moderate reusability for several reactions⁶. To our knowledge, there are few reports on the catalytic activity of untreated hydrous tin oxide (SnO₂). This has prompted us to carry out preliminary studies on the catalytic efficiency of hydrous SnO₂ towards some industrially important reactions viz., transesterification, amidation and transfer-hydrogenation in liquid phase as well as in vapour phase.

Transesterification over hydrous SnO₂

The percentage yield of ester obtained by transesterification of different alcohols with ethyl acetate on hydrous SnO₂ (**Scheme I**) are given in **Tables 1 and 2** in the liquid and vapour phase respectively. The exceptional low activity observed for transesterification of octyl alcohol with ethyl acetate in the liquid as well as in the vapour phase may be due to the longer chain length and high difference in the boiling points of the parent ester and the alcohol. However, the reaction was totally selective for transesterification.



(R = Butyl, Octyl, Cyclohexyl or Benzyl)

Scheme I

Table 1. Liquid phase transesterification of various alcohols with ethyl acetate over hydrous SnO₂.

Alcohol	Time (hrs.)	Yield of Ester (%)
n-Butyl alcohol	5	36
n-Octyl alcohol	5	10
Cyclohexanol	5	0
Benzyl alcohol	5	21

Reaction conditions :

Reflux temperature, Catalyst -1.0g, Ethyl acetate - 100 mmol, Alcohol - 10 mmol

Table 2 . Vapour phase transesterification of various alcohols with ethyl acetate over hydrous SnO₂

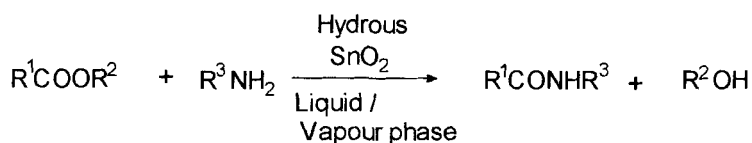
Alcohol	Temperature for maximum conversion (°C)	Ester (%)
n-Butyl alcohol	200	82
n-Octyl alcohol	210	22
Cyclohexanol	170	70
Benzyl alcohol	210	71

Reaction conditions .

Catalyst - 2.05 g, Ethyl acetate - 100 mmol, Alcohol - 10 mmol, Sample feed - 2.4 cm³ hr⁻¹

Amidation over hydrous SnO₂:

Table 3 and 4 show the catalytic efficiency of hydrous SnO₂ for the amidation of acetic acid/ ethyl acetate with aliphatic amines as well as ammonia (**Scheme II**). It was observed that the yields were better with acetic acid. Ammonia itself gave very poor yields with this catalyst.



(R¹ = Methyl, R² = H or Ethyl, R³ = H, Propyl or Butyl)

Scheme II

Table 3. Liquid phase amidation over hydrous SnO₂.

Reactants		Time (hrs.)	Yield of Amide (%)
Acetic acid	n-Propyl amine	5	0
Acetic acid	n-Butyl amine	5	38
Acetic acid	Ammonia (aq.)	5	0
Ethyl acetate	n-Butyl amine	5	6

Reaction conditions:

Reflux temperature, Catalyst -1.0g. Acetic acid (10 mmol) : Amine (50 mmol). Ethyl acetate (50 mmol) : Amine (5 mmol). Acetic acid (1 mmol) : 10 ml. Ammonia (25 %).

Table 4. Vapour phase amidation over hydrous SnO₂

Reactants		Temperature for maximum conversion (°C)	Yield of Amide (%)
Acetic acid	n-Propyl amine	170	43
Acetic acid	n-Butyl amine	200	90
Acetic acid	Ammonia (aq.)	200	3
Ethyl acetate	n-Butyl amine	200	79

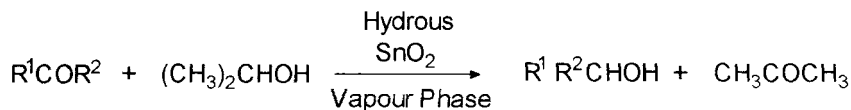
Reaction conditions :

Catalyst - 2.05 g. Acetic acid (10 mmol) : Amine (50 mmol), Ethyl acetate (50 mmol)

: Amine (5 mmol), Acetic acid (1 mmol) : 10 ml. Ammonia (25 %). Sample feed - 3.6 cm³ hr⁻¹

Transfer-hydrogenation reaction over hydrous SnO₂:

In the liquid phase, it was observed that hydrous SnO₂ could not bring about transfer-hydrogenation. Even in the vapour phase, only with cyclohexanone more than 60% of cyclohexanol was formed (**Scheme III, Table 5**).



(R¹ = Methyl, R² = Isobutyl, Phenyl or Ethyl)

Scheme III

Table 5 Vapour phase transfer-hydrogenation of
various ketones over hydrous SnO_2

Ketone	Temperature for maximum conversion ($^{\circ}\text{C}$)	Corresponding Alcohol (%)
Cyclohexanone	170	61
Methyl isobutyl ketone	170	11
Acetophenone	170	18
Ethyl methyl ketone	170	0

Reaction conditions :

Catalyst - 2.05 g. Ketone - 10 mmol. Isopropyl alcohol - 100 mmol. Sample feed - $3.6 \text{ cm}^3 \text{ hr}^{-1}$

For all these reactions the catalyst was reusable without much loss in activity for at least up to 50 runs. There is also ample scope for improving the yields or decreasing the reaction temperatures by optimising reaction parameters such as contact time and mole ratio of the reactants.

Preparation of the catalyst:

To 20 g of tin metal, 53 cm^3 of conc. HNO_3 was added in small aliquots and complete oxidation of tin metal was achieved by vigorously stirring the reaction mixture. After completion of oxidation, the white product mass was washed repeatedly with deionised water to completely remove the nitrate ions. The hydrous SnO_2 thus obtained was then dried in air at 80°C for five hours. It was observed that this process of pretreatment was adequate to get reproducible and maximum catalytic activity under the chosen reaction conditions.

General procedure for liquid phase reactions:

The liquid phase reactions were carried out in a 50cm³ three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. The reaction mixture was stirred and heated to the desired temperatures with the help of a magnetic stirrer-heater and a Teflon coated magnetic bob.

General procedure for vapour phase reactions:

The catalytic activity in the vapour phase was studied using a fixed bed continuous flow integral reactor⁷. The reactor system consisted of a Pyrex glass tube of 40 cm length and 1.25 cm inner diameter with an inlet tube of 0.8 cm diameter spiralled around the entire length. The reactants were fed into the reactor through the spiral preheater using a motor driven *syringe pump* (Sage Instruments Co. NY., Model 341) The catalyst sample was held in the reactor tube between glasswool plugs surrounded by glass beads. The reactor was kept in an electrically heated furnace. The temperature could be maintained and measured with the help of a digital temperature-controller indicator attached with a Cr-Al thermocouple.

The products of the reactions were analysed by gas chromatography with the help of a Chemito 2865 Gas Chromatograph fitted with OV 17 capillary column.

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