

# Synthesis of glycerol carbonate from glycerol and urea over tin-tungsten mixed oxide catalysts

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## ABSTRACT

Tin-tungsten mixed oxide catalysts with varying their mole ratio were prepared by co-precipitation method. The catalysts physico-chemical properties were derived from FT-infrared, Laser Raman, X-ray diffraction, UV–Vis DRS, BET surface area and temperature-programmed desorption of NH<sub>3</sub>. The catalysts activities were evaluated for the synthesis of glycerol carbonate from glycerol and urea. The activity results showed that Sn–W mixed oxide catalysts are highly active for selective formation of glycerol carbonate. Sn–W catalyst with 2:1 molar ratio exhibited about 52% of glycerol conversion with >95% selectivity towards glycerol carbonate. The active catalyst was subjected to calcination at different temperatures and evaluated for their activity in glycerol carbonate synthesis. The activity of the catalysts depends on mole ratio of Sn/W and treatment temperature which are influencing the surface-structural characteristics of the catalysts. Different reaction parameters such as glycerol to urea molar ratio, reaction temperature and catalyst loading were studied and optimum conditions were established. The catalysts showed consistent activity upon repeated use.

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## 1. Introduction

The development of biodiesel industry from biomass resource led to over plus of glycerol, produced as a byproduct in the synthesis of biodiesel. The conversion of glycerol to valuable chemicals has attracted considerable attention in recent times not only due to its availability but also for the presence of more number of functional groups [1–10]. Among different chemicals possible from glycerol, glycerol carbonate is a valuable glycerol derivative. This is being widely used in cosmetics industry, gas separation, coatings, detergents and polymers [11–15]. A number of synthetic processes are known for the preparation of glycerol carbonate from glycerol [5]. The well known methods for preparation of glycerol carbonate are the reaction from glycerol with phosgene [16] and transesterification of glycerol with a carbonate source [17]. The most interesting route to produce glycerol carbonate is from the reaction of glycerol with CO<sub>2</sub> in the presence of a catalyst [18]. This reaction requires elevated temperature, pressure and the yield of glycerol carbonate is too low to be used for practical purposes. The alternative route is

glycerolysis in which glycerol is reacted with urea in the presence of a catalyst. This approach is an indirect route for utilization of CO<sub>2</sub> as it is used in the production of urea. The synthesis of glycerol carbonate by glycerolysis is studied by different authors [17,19,20]. Mouloungui et al. patented the synthesis of glycerol carbonate by carbonylation of glycerol with urea over heterogeneous zinc catalysts such as zinc sulfate, zinc organosulfate and zinc ion exchange resins [19]. Calcined ZnSO<sub>4</sub> gave 86% of glycerol carbonate in 2 h at a reaction temperature of 150 °C and 40 mbar of pressure. The major drawback of this catalyst is that, ZnSO<sub>4</sub> salt is soluble in glycerol. There is a strong need to develop heterogeneous catalyst for strategic and environmental benefit. Heterogeneous catalysts are particularly efficient for carbonylation of glycerol with urea [17,20] affording good yield under moderate reaction conditions. Climent et al. [17] have recently reported the carbonylation of glycerol with urea at 145 °C over heterogeneous catalysts such as basic oxides (MgO and CaO), Al/Mg and Al/Li mixed oxides derived from hydro-talcites with adequate acid–base pairs. These catalysts showed about 72% of glycerol carbonate yield in 5 h of reaction time. In our previous study, we reported samarium exchanged heteropoly acid catalyst for carbonylation of glycerol with urea. The Sm<sub>0.66</sub>TPA catalyst showed good selectivity (85.4%) towards glycerol carbonate with 49.5% glycerol conversion [21]. Recently Hutchings and co-workers reported the synthesis of glycerol carbonate using gold

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and Pd based supported catalysts [22]. These catalysts are expensive and overall activity is not very high and requires long reaction time. The catalysts with acidic and basic sites such as Zn-Al hydroxalite and  $\gamma$ -zirconium phosphate were also reported [17,20]. The catalysts containing basic sites were reported for the selective synthesis of glycerol carbonate with high activity [23,24]. However, these base catalysts exhibited low activity during recycling. There is a need to develop highly active and stable catalysts for the synthesis of glycerol carbonate from glycerol and urea.

Solid acid catalysts are promising catalysts for the carbonylation of glycerol with urea [21]. Tungsten oxide based mixed oxide catalysts are known for their role in acid catalyzed reactions. Moreover these mixed oxide catalysts are known for their stability.

In the present study, a series of tin-tungsten mixed oxide catalysts were prepared with varying Sn to W molar ratio and studied for carbonylation of glycerol with urea under reduced pressure. The surface and structural properties of the catalysts were varied by treating the samples at different temperatures. The properties of the catalysts were investigated from different spectroscopic methods to establish the catalytic activities. A detailed study was undertaken to optimize the reaction parameters to achieve best results.

## 2. Experimental

### 2.1. Preparation of Sn-W mixed oxide

Sn-W mixed oxide catalysts were prepared by co-precipitation method. The preparation of Sn-W oxide with a Sn/W molar ratio of 2 is given as an example. In a typical procedure,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (4.94 g, 15 mmol) was dissolved in deionized water, followed by the addition of  $\text{SnCl}_4$  (7.815 g, 30 mmol) in a single portion. The solution stirred for 1 h at room temperature and deionized water was added to form white slurry. This slurry kept for stirring for 24 h at room temperature and the resulting white precipitate was filtered off, washed with large amount of deionized water until it is free from chlorine. The precipitate was dried in oven at 120 °C to afford Sn-W hydroxide as a white powder. SW hydroxides with different Sn/W molar ratios (Sn/W=0.5, 1, 2, 3, and 5) were successfully prepared by changing the molar ratios of the starting metal solutions. The hydroxide precursors were calcined at 500 °C for 4 h under an air atmosphere to yield final catalyst. The catalysts are denoted as SW11 where the alphabets represent the metal oxide and the numerical number related to their molar ratio.

### 2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex diffractometer using  $\text{CuK}\alpha$  radiation (1.5406 Å) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045 °C with account time of 0.5 s and in the  $2\theta$  range of 10°–80°.

Confocal Micro-Raman spectra were recorded at room temperature in the range of 200–1200  $\text{cm}^{-1}$  using a Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) Laser source of excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were loosely spread onto a glass slide below the confocal microscope for measurements.

The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded on a GBC UV-Visible Cintra 10e spectrometer in the range of 200–800 nm. BET Surface area was measured on Quadrasorb-SI instrument at relative pressure range of 0.05–0.3. Before analysis, the samples were degasified at 150 °C for 2 h to remove moisture on the surface of the catalyst.

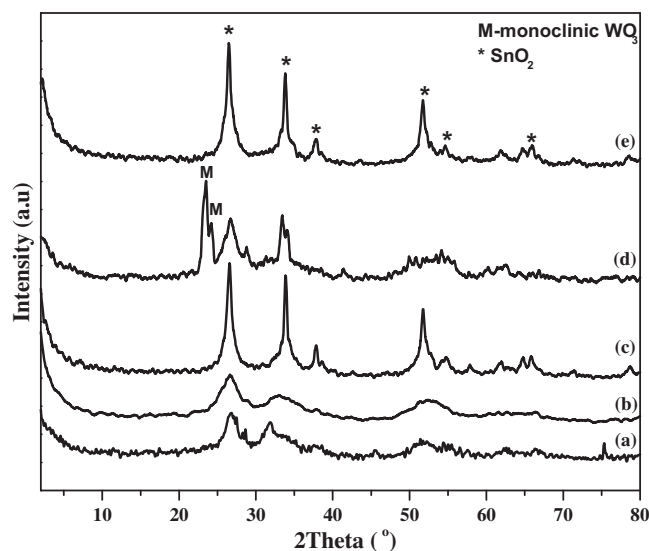


Fig. 1. XRD profiles of the SW mixed oxide catalysts calcined at 500 °C. (a) SW11, (b) SW21 (c) SW31 (d) SW51 (e) SW12.

Temperature programmed desorption of ammonia (TPD- $\text{NH}_3$ ) was carried out on a laboratory-built apparatus equipped with a gas chromatograph using TCD detector. In a typical experiment about 0.05 g of oven dried sample was taken in a quartz tube. Prior to TPD run, the catalyst sample was treated at 300 °C for 1 h by passing pure He gas (50 ml/min). After pretreatment, the sample was saturated with anhydrous ammonia (10%  $\text{NH}_3$  balance He gas) at 100 °C with a flow rate of 50 ml/min for 1 h and was subsequently flushed with He gas at the same temperature to remove physisorbed ammonia. The process was continued until a stabilized base line was obtained in the gas chromatograph. Then the TPD analysis was carried out from ambient temperature to 700 °C at a heating rate of 10 °C/min. The amount of  $\text{NH}_3$  evolved was calculated from the peak area of the already calibrated TCD signal.

### 2.3. Reaction procedure

The reactions were performed in a 25 mL two neck round-bottom (RB) flask under reduced pressures. In a typical experiment glycerol (2 g), urea (1.306 g) and catalysts (0.2 g) were taken in the round bottom flask and heated in an oil bath at 140 °C with constant stirring. One neck of the RB flask was connected to vacuum line. Reaction was run under a reduced pressure in order to remove the ammonia formed during the reaction. After completion of reaction or stipulated time, methanol was added and the catalyst was separated by filtration. The products were analyzed by a gas chromatograph (Shimadzu, 2010) equipped with flame ionization detector using inno wax capillary column (diameter: 0.25 mm, length 30 m). Products were also identified by GC-MS (Shimadzu, GCMS-QP2010S) analysis.

## 3. Results and discussion

### 3.1. Catalyst characterization

X-ray diffraction patterns of SW catalysts calcined at 500 °C are shown in Fig. 1. The XRD patterns of SW catalysts with the molar ratio of 1:1 and 2:1 were intrinsically identical to that of amorphous Sn-W hydroxide precursor. Whereas in the case of SW12, SW31 catalysts, intense diffraction peaks related to crystalline tin oxide were observed. The peaks observed at  $2\theta$  values of 26.5°, 33.9°, 37.9°, 43.5°, 51.8°, 54.7° and 61.9° are corresponding to tetragonal

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