Solvent-Free Production of Glycerol Carbonate from Bioglycerol with Urea Over Nanostructured Promoted SnO₂ Catalysts

Baithy Mallesham^{1,2} · Agolu Rangaswamy¹ · Bolla Govinda Rao¹ · Tumula Venkateshwar Rao¹ · Benjaram M. Reddy¹

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Abstract

In this study nanostructured MoO₃ and WO₃ promoted SnO₂ solid acid catalysts were explored for the production of glycerol carbonate via carbonylation of bioglycerol with urea. The investigated reference SnO₂ and promoted catalysts were synthesized by fusion and wet-impregnation methods, respectively. The physicochemical properties of the prepared catalysts were thoroughly analyzed by XRD, Raman, BET surface area, TEM, FTIR, pyridine adsorbed FTIR, NH₃-TPD, and XPS techniques. It was found from the characterization studies that integration of SnO₂ with MoO₃ and WO₃ promoters leads to remarkable structural, textural, and acidic properties. Especially, a high quantity of acidic sites were observed over the MoO₃/SnO₂ catalyst (~81.45 μ mol g⁻¹) followed by WO₃/SnO₂ (61.81 μ mol g⁻¹) and pure SnO₂ (46.47 μ mol g⁻¹), which played a key role in the carbonylation of bioglycerol with urea. The BET specific surface area and oxygen vacancies of SnO₂ were significantly enhanced after the addition of MoO₃ and WO₃ promoters. TEM images revealed the formation of nanosized particles with a diameter of around 5–25 nm for the synthesized catalysts. The MoO₃/SnO₂ catalyst exhibited a high conversion and selectivity towards glycerol carbonate in comparison to other catalysts. The observed better performance is attributed to unique properties of MoO₃/SnO₂ catalyst including smaller crystallite size, high specific surface area, abundant oxygen vacancies, and more number of acidic sites. This catalyst also exhibited remarkable stability with no significant loss of activity in the recycling experiments.

Graphic Abstract

Nanostructured MoO_3/SnO_2 solid acid catalyst exhibited an excellent catalytic activity and a high selectivity to glycerol carbonate in the carbonylation of bioglycerol with urea under solvent-free and mild conditions.



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Extended author information available on the last page of the article



Keywords Bioglycerol \cdot Urea \cdot Glycerol carbonate \cdot Acidic sites \cdot SnO₂ \cdot MoO₃/SnO₂

1 Introduction

It is now widely recognized that abundant, safe, and renewable sources of energy alternative to fossil fuels are desirable to ensure long-term economic and social stability [1, 2]. As known, the excessive consumption of fossil fuels leads to increased levels of greenhouse gas emissions, resulting in amplified global average temperatures [3-5]. At the same time, the demand for fossil fuel-based products is continuously increasing, which could further worsen the environmental pollution [6, 7]. In order to overcome the negative impacts of fossil fuels, significant efforts have been undertaken for the synthesis of platform chemicals towards a sustainable society and the economy [8-10]. Glycerol is one of the most abundant platform chemicals that can be obtained largely in the biodiesel production (~10% of glycerol) process i.e. the transesterification of vegetable oils or fats with methanol [4]. Therefore, considerable research efforts are going on for efficient transformation of surplus glycerol into valuable products.

A number of reaction procedures for the conversion of glycerol to high-value products have been reported in the literature, including oxidation, esterification, transesterification, dehydration, hydrogenolysis, etherification, acetalisation, polymerization, pyrolysis, carbonylation, and steam reforming [3-10]. Among them, the carbonylation of glycerol is considered as one of the promising processes for the synthesis of green and commercially important chemicals, such as glycerol carbonate. Particularly, glycerol carbonate is a versatile and renewable building block for organic synthesis. For example, glycerol carbonate can be converted into epichlorohydrin, surfactants, polymers and other, which have a wide range of industrial applications [11–13]. Owing to high boiling point, high flash point and low volatility characteristics, glycerol carbonate and its esters are used as solvents alternative to hazardous organic solvents for many applications [14–16]. More importantly, glycerol carbonate has a tremendous potential to become a key intermediate in the polymers production industry [17].

Different carbonyl sources, such as phosgene, CO_2 , alkyl carbonate (dimethyl carbonate, ethylene carbonate, and propylene carbonate), and urea have been used for the production of glycerol carbonate from glycerol [18–27]. Among them, the utilization of urea has received significant attention because urea is a readily available, safe, clean, and cheaper chemical. Further, urea has also drawn unequivocal attention due to the significance of indirect CO_2 chemical utilization. To remove the NH₃ formed during the reaction, two different modes are normally employed namely, reduced pressure or purging gas [13, 14, 25–27]. A number

of catalytic systems have been reported for the production of glycerol carbonate via carbonylation of glycerol with urea [21-24]. Although homogeneous catalysts are found to be effective for glycerol carbonylation reaction, the use of toxic and expensive reagents, difficulty of catalyst separation from the reaction mixture, tedious work-up procedure, and generation of large amounts of waste have restricted their application in the chemical industry. On the other hand, various heterogeneous catalysts, such as promoted metal oxides, hydrotalacites, rare earth metal oxides, zeolites, and metal oxide supported noble and/or non-noble metal catalysts have been reported for this reaction [25-31]. Among them, the promoted metal oxides exhibit quite attractive physicochemical and acidic properties and played a critical role in the stability and higher catalytic activity for the carbonylation of glycerol with urea [30, 31]. Particularly, SnO₂ is an important metal oxide due to its favorable structural, textural, and acidic properties owing to multiple oxidation states of Sn (Sn^{4+}/Sn^{2+}) and the presence of sufficient oxygen vacancy defects [4]. It is therefore anticipated that addition of MoO₃ and WO₃ promoters to the SnO₂ may lead to remarkable enhancement in the defect sites and acidic properties which could play a favorable role in the carbonylation of glycerol with urea.

The present investigation was undertaken against the aforesaid background. Accordingly, the main aim of this work was to synthesize glycerol carbonate more efficiently via carbonylation of glycerol with urea employing promoted SnO_2 -based catalysts. In this study, MoO_3 and WO_3 promoted SnO_2 catalysts were prepared and explored for the title reaction. The physicochemical properties of the prepared catalysts were intensely investigated by employing various characterization techniques, namely, X-ray diffraction (XRD), BET surface area, Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), pyridine adsorbed FTIR (Py-FTIR), NH₃-temperature programmed desorption (NH₃-TPD), and X-ray photoelectron spectroscopy (XPS). Attempts were made to correlate the structural properties of the prepared catalysts with their catalytic performance.

2 Experimental Section

2.1 Materials

Various chemicals employed for the preparation of investigated catalysts were procured from commercial vendors which include, glycerol (SRL, anhydrous extra pure AR grade), crude glycerol (obtained during biodiesel synthesis within the institute), urea, ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) (Aldrich, AR grade), ammonium metatungstate hydrate ((NH₄)₆H₂W₁₂O₄₀·xH₂O) (Aldrich, AR grade), SnCl₂·2H₂O (Aldrich, AR grade), and NaNO₃ (Aldrich, AR grade). All these chemicals were used without further purification. The crude glycerol contained 80–85% of glycerol, 15–20% of impurities such as water, phospholipids, NaCl, FAMEs, soaps, MeOH, monoglycerides, NaOH, and other.

2.2 Catalyst Preparation

A simple fusion procedure was employed for the synthesis of pure SnO₂ by using SnCl₂·2H₂O (Aldrich, AR grade) and NaNO₃ (Aldrich, AR grade) as the precursors. In a typical procedure, the desired amounts of both precursors were dissolved in deionised water under mild stirring conditions for 1 h at room temperature (NaNO₃:SnCl₂·2H₂O = ~ 1:5). The successive evaporation of excess water from the solution at 383 K resulted in a porous and foam-like solid material. Subsequently, the reaction temperature was raised to ~ 523 K and continued at the same temperature until the formation of tin oxide powder. The resulting material was washed with deionized water and dried at 373 K for 12 h and calcined at 923 K for 5 h in the presence of atmospheric air.

The promoted 10 wt% MO₃/SnO₂ (M = Mo and W) catalysts were prepared by incipient wetness impregnation method. In a typical procedure, the desired quantities of respective metal precursors $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ or $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ were dissolved in double distilled water followed by the addition of finely powdered tin oxide with stirring. The reaction mixture was placed on a hot plate (383 K) and the excess water was evaporated under vigorous stirring. The resulting materials were dried at 393 K for 12 h and finally calcined at 923 K for 5 h in atmospheric air.

2.3 Catalyst Characterization

Powder XRD patterns were recorded on a Rigaku Multiflex instrument with a nickel-filtered CuK_{α} radiation source (1.5406 Å) and a scintillation counter detector. The intensity data were collected over a 20 range of 20° to 80° with scanning at 0.01° step size and a counting time of 1 s per each point. Raman spectra were recorded at ambient temperature using a LabRam HR800UV Raman spectrometer (Horiba Jobin–Yvon) equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector. The spectra were recorded in the range of 100–1300 cm⁻¹ and at a spectral resolution of 2 cm⁻¹ using the 632.81 nm excitation line from an argon ion laser. The Ar⁺ laser was focused on the sample under a microscope with the diameter of the analyzed spot being ~ 1 μ m. The acquisition time was adjusted in relation to the intensity of Raman scattering. The specific surface areas were measured by BET analysis on a SMART SORB-92/93 instrument at liquid N₂ temperature. Prior to the experiment, catalysts were degassed at 393 K for 2 h to remove surface adsorbed residual moisture. Surface areas were obtained using the desorption data. NH₃-temperature programmed desorption (NH₃-TPD) analysis was carried out on a Micromeritics AutoChem 2910 instrument. A thermal conductivity detector was used for continuous monitoring of the desorbed NH₃. The chemisorbed amount of ammonia was analysed in flowing He gas with a flow rate of 20 mL/min from 323 to 1073 K at a heating rate of 10 K/min. The amount of desorbed NH₃ was calculated from the peak area of the TCD signal.

X-ray photoelectron spectra were recorded on a Shimadzu (ESCA 3400) spectrometer. The X-ray source utilized was Mg Ka (1253.6 eV) radiation. Analysis was done at room temperature, and the samples were mounted using double-sided adhesive tape and the binding energies were referenced to C (1 s) binding energy of adventitious carbon contamination which was taken to be 284.7 eV. The TEM studies were carried out on a JEM-2010 (JEOL) instrument equipped with a slow-scan CCD camera at an accelerating voltage of the electron beam 200 kV. The preparation of samples for TEM analysis involved crushing of the materials in an agate mortar and ultrasonically dispersing in ethanol for 15–20 min followed by deposition on a copper grid. The specimen was dried under vacuum at room temperature. The elemental analysis of the prepared catalysts was carried out by ICP-OES technique (Thermo Jarrel Ash model IRIS Intrepid II XDL, USA) following sample dissolution using acid digestion procedure.

The FTIR spectra were recorded on a Nicolet 740 FTIR spectrometer at ambient conditions using KBr disks with a nominal resolution of 4 cm⁻¹ and averaging 100 spectra. For FTIR analysis of adsorbed pyridine, the sample was oven dried at 373 K for 1 h. The oven dried sample (~ 50 mg), in a sample cup, was contacted with pyridine (~ 0.1 cm³) directly. The sample cup was then kept in a vacuum oven at 393 K for 1 h to remove the physisorbed pyridine. After cooling to room temperature, the spectrum was recorded with a nominal resolution of 4 cm⁻¹ in the spectral range of 1400–1900 cm⁻¹ using KBr background.

2.4 Activity Measurements

The catalytic evaluation experiments were conducted in a standard 25 mL two necked round bottom flask fitted with reflex condenser. The dry N_2 gas was purged through the second neck to remove the ammonia formed during the reaction. In a typical experiment, the catalytic runs were performed using 5.43 mmol of glycerol and 16.25 mmol of urea with 50 mg of catalyst at 423 K and 4 h of reaction time with constant stirring (800 rpm) under solvent-free conditions.

After completion of the reaction, methanol was added to the reaction mixture and the catalyst was separated by filtration. The obtained products were identified by GC–MS equipped with a DB-5 capillary column. Samples were taken periodically and analyzed by GC equipped with a BP-20 (wax) capillary column and flame ionization detector. The GC analyses were usually repeated three times in order to decrease the experimental error and reproducibility. In this study, each experiment was performed under the kinetically controlled region (Fig. S1, Supporting Information). The conversion and product selectivity were calculated as per the established procedures [4]. In this study, the calculated carbon balance of all the catalytic runs was always greater than 93%.

3 Results and Discussion

3.1 Catalyst Characterization

Powder X-ray diffraction patterns of pure and promoted SnO_2 samples are shown in Fig. 1. All the diffraction peaks can be readily indexed to the tetragonal structure of SnO_2 with lattice constants of a = 4.75 Å and c = 3.19 Å, which are well in agreement with the reported values (PDF #880287). It can be clearly noted from Fig. 1 that the intensity of SnO_2 peaks decreased with the incorporation of promoters into the SnO_2 lattice. It is obvious from Fig. 1 that the promoted SnO_2 samples exhibit broad peaks and shifted to higher 20

Fig. 1 Powder X–ray diffraction patterns of (a) SnO_2 , (b) WO_3/SnO_2 , and (c) MOO_3/SnO_2 samples. (*, Characteristic XRD lines of SnO_2)

values compared to that of pure SnO2. As well, no characteristic diffraction peaks corresponding to MoO₃ and WO₃ were noticed in the XRD patterns of the impregnated SnO₂ samples. This unusual observation could be either due to the incorporation of Mo and W cations into the SnO₂ lattice or the amorphous nature of the MoO_x and WO_x species. To understand this, we estimated the lattice parameters 'a' and 'c' by using the most intense lines of the XRD patterns and the calculated values are presented in Table 1. These observations, such as peak shift, difference in the lattice parameters, and absence of peaks due to MoO₃ and WO₃ noticeably confirm the formation of metal ion-doped SnO₂ solid solutions. The average crystallite sizes of all the samples were calculated using Debye-Scherrer formula and the obtained values are summarized in Table 1. It was found that the crystallite size of SnO₂ noticeably decreases after the addition of MoO₃ and WO₃, indicating the beneficial role of the promoters towards inhibition of crystal growth against the higher calcination temperatures.

Raman spectroscopy measurements were carried out to know the phases of the oxides as well as structural defects in the prepared catalysts (Fig. S2, Supporting Information). The pure SnO_2 sample exhibits primarily three fundamental Raman bands at around 474, 632, and 774 cm⁻¹, which are attributed to vibrational modes of E_g, A_{1g}, and B_{2g}, respectively [32, 33]. Interestingly, the WO₃ and MoO₃ promoted SnO₂ samples also showed the characteristic vibration modes of pure SnO₂. A closer observation of Fig. S2 reveals that Raman band (A_{1g}) of the



Table 1Crystallite size (D),Surface area (S), Pore volume(V), Acidic sites (T), andLattice parameter (A) of SnO2,WO3/SnO2, and MoO3/SnO2catalysts

Catalyst	D ^a (nm)	D ^b (nm)	$S^{c}(m^{2}/g)$	V ^c cm ³ /g)	T ^d (µmol/g)	Loading (wt%) ^e		$A^{a}(A)$	
						MoO ₃	WO ₃	a	с
SnO ₂	13.47	17.8 ± 0.4	11	0.0739	46.47	_	_	4.75	3.19
WO ₃ /SnO ₂	8.76	12.2 ± 0.3	32	0.0637	61.81	_	9.49	4.71	3.17
MoO ₃ /SnO ₂	6.06	10.1 ± 0.2	56	0.0679	81.45	9.51	-	4.69	3.16

^aFrom XRD analysis

^bFrom TEM

^cFrom BET and BJH analysis

^dFrom NH₃-TPD

^eFrom ICP-OES technique

promoted SnO₂ samples is shifted to lower wavenumbers compared to that of pure SnO₂. This is due to the doping of smaller W⁶⁺ and Mo⁶⁺ cations into the SnO₂ lattice and the consequent lattice contraction of SnO₂ as well as metal-oxygen vibration frequency that may cause a shift in the A_{1g} peak position. On the other hand, the observed E_o peak represents the presence of oxygen vacancies in the SnO₂-based materials. It can be clearly noted from Raman studies that the Mo⁶⁺ and W⁶⁺ doped SnO₂ samples exhibit higher quantities of oxygen vacancies than the pure SnO₂. Oxygen vacancy defects are a special class of point defects in many oxide materials, which could play an important role in heterogeneous catalysis [34]. As well, the observed Raman band at around 200–360 cm^{-1} can be assigned to the contributions from intrinsic lattice defects, resulting from the substitution of Sn⁴⁺ with smaller sized promoter metal ions.

Figure 2a presents the N_2 adsorption-desorption isotherms of SnO₂-based materials, which can be classified as Type IV isotherms with H1-type hysteresis loop. These isotherms are characteristic of mesoporous nature of the synthesized materials [35]. The appearance of a H1 hysteresis loop usually suggests improved pore size and pore connectivity of prepared samples with uniform distribution [35, 36]. It can be expected that pure SnO2 undergoes agglomeration and sintering at higher temperatures, resulting in larger crystallite sizes and smaller surface area. On the contrary, the promoted SnO₂ samples exhibit significant resistance towards agglomeration and sintering during high temperature treatment, which is due to the cooperative nature of the cations of both the oxides. Therefore, the MoO₃ and WO₃-doped SnO₂ samples exhibited a high specific surface area compared to that of pure SnO₂. The obtained specific surface area values of SnO₂, WO₃/SnO₂ and MoO₃/SnO₂ samples were ~11,



Fig. 2 N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of SnO₂, MoO₃/SnO₂, and WO₃/SnO₂ catalysts

32 and 56 m² g⁻¹, respectively (Table 1). Figure 2b shows the BJH pore size distribution analysis of the prepared samples. It is observed that SnO₂ and MoO₃/SnO₂ materials exhibit a unimodal pore size distribution, while the WO₃/ SnO₂ material shows a bimodal pore size distribution. The pore volume of the SnO₂ sample was also increased after the addition of MoO₃ and WO₃ species. Fig. S3 (Supporting Information) shows NH₃-TPD profiles of various catalysts. From NH₃-TPD profiles, we have calculated total amount of acidic sites of the catalysts and the results are presented in Table 1. Higher numbers of acidic sites were observed for MoO_3/SnO_2 sample (~81.45 µmol g⁻¹) followed by $WO_3/$ SnO_2 (61.81 µmol g⁻¹), and pure SnO_2 (46.47 µmol g⁻¹). It is therefore obvious that the addition of MoO₃ and WO₃ species to the SnO₂ enhances its acidic properties with BET specific surface area (Table 1).

Figure 3a shows the Sn 3d core level XP spectra of the prepared catalysts. The binding energy (BE) of the peaks observed at around 487.4 and 495.8 eV correspond to Sn $3d_{5/2}$ and Sn $3d_{3/2}$, respectively. The BE difference between the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ is equal to 8.5 eV, which is a strong evidence to identify the oxidation state of the Sn species in the sample. Appearance of these peaks indicated that the Sn is present in +4 oxidation state in the prepared materials [37–39]. Interestingly, the Sn 3d peak position of the promoted samples is shifted to higher binding energies relative to pure SnO₂. This observation indicates the presence of Mo(W)–Sn interactions, in line with the XRD and

Raman results. Figure 3b illustrates the O 1s XP spectra of SnO₂, WO₃/SnO₂, and MoO₃/SnO₂ catalysts. The O 1s spectra were fitted with two Gaussian functions, indicating the presence of two oxygen environments in the synthesized samples. The observed major peak at lower binding energy side (~530.2 eV) can be assigned to the presence of oxygen species in the SnO₂ lattice [39-42]. Another peak identified at higher binding energy side (~532.2 eV) reveals the adsorbed oxygen species (-OH, CO, CO_3^{2-} , etc.) on the catalyst surface [39-41]. Fig. S4 (Supporting Information) shows Mo 3d and W 4f spectra of the Mo- and W-promoted SnO_2 catalysts. The observed bands at ~232.7 (3d_{5/2}) and 236.2 eV $(3d_{3/2})$ in the Mo 3d spectrum indicates the presence of Mo^{6+} oxidation state [43, 44]. On the other hand, the binding energies observed at ~35.6 and 37.8 eV can be assigned to spin-orbit splitting of W 4f_{7/2} and W 4f_{5/2} components, respectively, confirming the existence of W⁶⁺ ions in WO₃/SnO₂ sample [45].

The morphology of SnO₂, WO₃/SnO₂, and MoO₃/SnO₂ catalysts were investigated by TEM analysis (Fig. 4). The presence of irregular, non-uniform, and highly agglomerated nanoparticles are observed for pure SnO₂ sample. In contrast, quite uniform sized particles were found for the promoted SnO₂ samples, which reveal the existence of strong interactions between the promoter and SnO₂. The estimated average particle sizes for SnO₂, WO₃- and MoO₃-promoted SnO₂ samples are ~17.8 ± 0.4, 12.2 ± 0.3 and 10.1 ± 0.2 nm, respectively. The obtained FTIR spectra



Fig. 3 Sn 3d XP spectra (a) and O 1s XP spectra (b) of pure SnO₂, MoO₃/SnO₂, and WO₃/SnO₂ samples



Fig. 4 TEM images of SnO₂, WO₃/SnO₂, and MoO₃/SnO₂ samples

represent the structural features of the catalysts as shown in Fig. S5 (Supporting Information). The observed major FTIR bands at ~680, 623 and 553 cm⁻¹ can be assigned to different vibration modes of O–Sn–O bridging bond and Sn–O–Sn

terminal bonds [44, 46]. The bands at ~1628 and 3410 cm⁻¹ are attributed to O–H stretching and the deformation bending vibration modes of weakly bonded water molecules, respectively. Two FTIR bands at ~947 and 860 cm⁻¹ were found for the promoted SnO_2 samples due to the stretching modes of the terminal M–O bonds with a certain amount of double bond character and typical Sn–O–M modes (where M=Mo and/or W), respectively [47, 48].

The pyridine absorbed FTIR spectroscopy analysis is used to understand the nature of the acidity of catalysts (Fig. 5). Pyridine is a basic probe molecule employed to examine the surface acidity of solid materials and also gives the possibility to differentiate the Lewis acidic sites from the Brønsted acid sites [49]. Various bands were found in the range of 1400–1700 cm^{-1} . All the samples show pyridine absorption bands at 1550 cm⁻¹ followed by a peak at around 1639 cm⁻¹ which can be assigned to the presence of Brønsted acid sites. The bands at ~ 1450 and 1610 cm^{-1} indicate Lewis acidic sites (L). An additional band was found at 1455 cm⁻¹ which can be attributed to pyridine adsorbed on the Lewis acidic sites [50, 51]. On the other hand, the band observed at around 1490 cm⁻¹ is due to the combination of both Lewis and Brønsted acid sites [4, 52]. It is evident from the figure that all the samples contain a higher amount of Brønsted acid sites compared to Lewis acid sites.

3.2 Catalytic Activity

The carbonylation of pure and crude glycerol with urea was conducted using MoO_3/SnO_2 , WO_3/SnO_2 , and SnO_2 catalysts and the results are presented in Table 2.

As shown in Scheme 1, various products are possible in the catalytic carbonylation of glycerol with urea, such as 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate), 2,3-dihydroxypropyl carbamate (glycerol urethane), and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate. The catalytic experiments were carried out at 423 K under solventfree conditions for 4 h under reflux conditions. Very low glycerol conversion (5.1%) and selectivity of glycerol carbonate (52.7%) were obtained in the absence of catalyst. The conversion of pure glycerol over MoO₃/SnO₂, WO₃/ SnO_2 and SnO_2 catalysts was observed to be ~ 69.2, 59.7 and 34.4% with glycerol carbonate selectivities of ~97.1, 95.1 and 79.2%, respectively. On the other hand, the achieved crude glycerol conversions of MoO₃/SnO₂, WO₃/SnO₂ and SnO₂ catalysts were ~65.6, 57.5 and 31.3% with glycerol carbonate selectivities of 95.3, 91.1 and 74.7%, respectively. It was obvious that similar results were found in the case of both crude glycerol and pure glycerol with urea for all the catalysts (Table 2). This observation indicates that the wide applicability of the prepared solid acid catalysts for the production of glycerol carbonate from carbonylation of glycerol with urea. Another interesting observation to be noted is that incorporation of Mo- and W-species into the SnO₂ lattice drastically improved the catalytic efficiency in both the cases of pure and crude glycerol. The calculated TOF values of SnO₂, WO₃/SnO₂, and MoO₃/SnO₂ catalysts were found to be 5.6, 10.0, and 11.2 h^{-1} , respectively. The

Fig. 5 Pyridine absorption FTIR spectra of (a) SnO_2 , (b) WO₃/SnO₂, and (c) MoO₃/SnO₂ catalysts. *B* Brønsted, *L* Lewis acidic sites







Catalysts	X _{Gly} (%)	Selectivity of products (%)			TOF $(h^{-1})^a$	C.B. (%)	
		3	3 4				
Blank	5.1	47.3	52.7	0	_	100.2	
SnO_2	34.4	20.8	79.2	0	5.6	98.7	
WO ₃ /SnO ₂	59.7	4.6	95.1	0.3	10.0	97.1	
MoO ₃ /SnO ₂	69.2	1.8	97.1	1.1	11.2	98.3	
SnO ₂ ^b	31.3	25.3	74.7	0	5.0	93.4	
WO ₃ /SnO ₂ ^b	57.5	8.7	91.1	0.2	9.7	94.1	
MoO ₃ /SnO ₂ ^b	65.6	3.9	95.3	0.8	10.6	95.7	

Reaction conditions:1:3 molar ratios of glycerol (5.43 mmol) to urea (16.25 mmol), 423 K reaction temperature, 50 mg of catalyst, 4 h of reaction time, and stirring speed=800 rpm

C.B. carbon balance

^aTOF (h^{-1}) mole of glycerol converted per hour/mole of catalyst used

^bIndicates the crude glycerol activity

promoted catalysts were found to be most efficient with a nearly two times higher activity than that of SnO_2 (5.6 h⁻¹) sample. This result reveals the beneficial role of promoter (Mo and W) in the enhancement of catalytic activity of SnO_2 for carbonylation of glycerol with urea. Among all the catalysts, the MoO₃/SnO₂ exhibited remarkable catalytic activity and selectivity. It could be explained on the basis of unique properties of MoO₃/SnO₂ catalyst including smaller crystallite size, more crystal defects, high specific surface area, and more number of acidic sites.

The plausible reaction mechanism for the production of glycerol carbonate from carbonylation of bioglycerol with

urea is shown in Scheme 2. Various theories on the reaction mechanism of carbonylation of bioglycerol with urea can be found in the literature [13, 28, 53, 54]. The catalytic reaction proceeds through adsorption, surface reaction and desorption on M–O–Sn (M = Mo and W) catalyst surface. As shown in Scheme 2, the glycerol and urea get adsorbed on the catalyst surface via hydrogen bonding and Lewis acid–base interactions. It is expected that Lewis acid sites of metal ion activates the carbonyl oxygen of urea. Subsequently, the activated urea can react with primary –OH group of the glycerol to produce the terminal glycerol urethane with the release of NH₃ [25]. Now, there are two possible pathways:



Scheme 1 Plausible reaction products for reaction between glycerol (1) and urea (2), various products such as glycerol urethane (2,3-dihy-droxypropyl carbamate) (3), 4-(hydroxymethyl)-1,3-dioxolan-2-one

(glycerol carbonate) (**4**), and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (glycerol carbamate) (**5**)



Fig. 6 Effect of reaction temperature on carbonylation of pure glycerol (a) and crude glycerol (b) with urea over MoO_3/SnO_2 catalyst. Reaction conditions: stirring speed=800 rpm; molar ratio of bioglyc-

erol to urea = 1:3; reaction time = 4 h; catalyst amount = 50 mg. *Sel. 3* selectivity of glycerol urethane (3), *Sel. 4* selectivity of glycerol carbonate (4), *Sel. 5* selectivity of glycerol carbamate (5)

(i) the $-NH_2$ group of the intermediate can again react with the glycerol carbamate to produce the product (5-hydroxymethyl-2-oxazolidinone) with the removal of water molecule. However, 5-hydroxymethyl-2-oxazolidinone product was not observed in this study. Hence, this reaction follows another pathway i.e., the secondary -OH group of the glycerol urethane reacts with carbonyl carbon of the same urea molecule to form the glycerol carbonate with the release of another molecule of ammonia [23, 25]. In addition, the produced glycerol carbonate further reacts with second molecule of urea to form (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (5). It is therefore clear that the presence of more acidic sites and higher surface area could play a key role in the carbonylation of glycerol with urea to produce glycerol carbonate.

To understand the effect of reaction temperature (383–443 K) on the carbonylation of pure and crude glycerol with urea, the reaction was performed over the MoO₂/SnO₂ catalyst and the obtained results are presented in Fig. 6a, b. Very low glycerol conversions (~21.3 and 18.1%) were noticed at 383 K for both the cases (crude and pure glycerol). Afterwards, the glycerol conversions rapidly increased with increasing of reaction temperature up to 423 K, and further increase of temperature slightly increased the conversion up to 443 K. This could be explained by low activation of reactant molecules at 383 K, hence less number of reactant molecules interacted with the catalyst and a low glycerol conversion was achieved. At lower reaction temperature, low selectivity of glycerol carbonate was found along with the formation of glycerol urethane as intermediate product. With rising of temperature the selectivity of glycerol carbonate (97.1%) gradually increased with the expense of glycerol urethane product up to 423 K and afterwards the selectivity was slowly decreased to 88.4% at 443 K. The glycerol carbonate easily reacts further with another urea molecule to produce (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (5), hence decreased selectivity of glycerol carbonate at higher reaction temperatures.

The influence of reaction time was examined for the optimization of glycerol carbonate production over the $MoO_3/$ SnO_2 catalyst and the achieved results are shown in Fig. 7. These catalytic experiments were conducted at different time intervals from 1 to 8 h and the remaining experimental conditions were kept same as shown in Table 2. The glycerol conversion was drastically increased with increasing of reaction time up to 4 h, and after that slowly increased to 92.1% with the reaction time up to 8 h. At the initial reaction time, the selectivities towards glycerol urethane and glycerol carbonate were found to be 35.8 and 64.2%, respectively. With increasing reaction time (up to 4 h) the glycerol urethane was rapidly converted into glycerol carbonate and its selectivity reached to 97.1%. Subsequently, there is a considerable decrease in the selectivity of glycerol carbonate (87.3%) after 8 h of reaction time. The selectivity of glycerol carbonate decreased with further time because glycerol carbonate reacts with excess urea to yield the byproduct (5) (Scheme 1). The best glycerol conversion and highest selectivity of glycerol carbonate achieved at 4 h of reaction time were 69.2 and 97.1% respectively.

Figure 8 shows the influence of glycerol to urea molar ratios on the carbonylation of glycerol with urea over the MoO_3/SnO_2 catalyst. The experiments were carried out by varying the glycerol to urea molar ratio from 1:1 to 1:5 at 423 K reaction temperature, 4 h of reaction time, 800 rpm of stirring speed and 10 wt% of catalyst with respect to glycerol. At 1:1 molar ratio of glycerol to urea, 35.6% of glycerol conversion and 72.2% of glycerol carbonate selectivity along with 27.8% of glycerol urethane intermediate product were obtained. It was found that the glycerol to urea molar ratio up to 1:3 and the highest selectivity of glycerol

Fig. 7 Influence of reaction time on carbonylation of bioglycerol with urea over MoO_3/SnO_2 catalyst. Reaction conditions: reaction temperature = 423 K; stirring speed = 800 rpm; molar ratio of bioglycerol to urea = 1:3; catalyst amount = 50 mg. Sel. 3 selectivity of glycerol urethane (3), Sel. 4 selectivity of glycerol carbonate (4), Sel. 5 selectivity of glycerol carbamate (5)



Fig. 8 Influence of molar ratio on carbonylation of bioglycerol with urea over MoO_3/SnO_2 catalyst. Reaction conditions: temperature =423 K; stirring speed = 800 rpm; reaction time =4 h; catalyst amount = 50 mg. *Sel.* 3 selectivity of glycerol urethane (3), *Sel.* 4 selectivity of glycerol carbonate (4), *Sel.* 5 selectivity of glycerol carbamate (5) 100

Fig. 9 Influence of catalyst amount on carbonylation of bioglycerol with urea over MoO_3/SnO_2 catalyst. Reaction conditions: reaction temperature = 423 K; stirring speed = 800 rpm; reaction time = 4 h; molar ratio of bioglycerol to urea = 1:3. *Sel. 3* selectivity of glycerol urethane (3), *Sel. 4* selectivity of glycerol carbonate (4), *Sel. 5* selectivity of glycerol carbamate (5)

80 Conversion / Selectivity (%) 60 Gly. Conv. Sel. 4 40 Sel. 5 Sel. 3 20 0 1:2 1:3 1:4 1:1 1:5 Molar Ratio (moles) 100 80 Conversion / Selectivity (%) 60 Gly. Conv. Sel. 4 40 Sel. 5 Sel. 3 20 0 10 20 30 40 50 60 70 80 90 100 Catalyst weight (mg)

carbonate (97.1%) was achieved at 1:3 molar ratio. Subsequently, the selectivity of glycerol carbonate decreased with rising of glycerol to urea molar ratios from 1:3 to 1:5. This

is primarily due to the reaction of glycerol carbonate with excess urea to produce 2-oxo-1,3-dioxolan-4-yl)methyl carbamate as the by-product at higher molar ratios of glycerol to urea. The glycerol conversions achieved were $\sim 35.6, 56.3, 69.2, 74.9, and 79.2\%$ at molar ratios of 1:1, 1:2, 1:3, 1:4, and 1:5, respectively. These observations are in line with earlier reported results [14].

We have investigated the effect of catalyst amount on the glycerol conversion and the selectivity of the products over the MoO_3/SnO_2 catalyst and the obtained results are presented in Fig. 9. The catalytic experiments were conducted by varying the catalyst amount from 10 to 100 mg, and keeping other experimental conditions same as described in Table 2. The MoO_3/SnO_2 sample exhibited superior glycerol conversion even at a low catalyst amount. The glycerol conversion and selectivity of glycerol carbonate were found to

be ~ 20 and 64.2% at 10 mg of catalyst amount, respectively. It can be observed from Fig. 9 that glycerol conversion rapidly increases with rising of catalyst amount up to 70 mg, and there after not much variation in the glycerol conversion. However, there is a remarkable change in the selectivity of glycerol carbonate with the variation of catalyst amount up to 50 mg. Then, the selectivity of glycerol carbonate slowly decreased from 97.1 to 87.3%. These results suggest that more amount of catalyst favor the conversion of glycerol as well as glycerol carbonate due to the availability of more number of active sites on the catalyst surface. Therefore, further increase in the catalyst amount could favor the formation of 2-oxo-1,3-dioxolan-4-yl)methyl carbamate (12.3%),

Fig. 10 Reusability on carbonylation of pure glycerol (a) and crude glycerol (b) with urea over MoO₃/SnO₂ catalyst. Reaction conditions: reaction temperature = 423 K; stirring speed = 800 rpm; molar ratio of bioglycerol to urea = 1:3; catalyst amount = 50 mg; reaction time = 4 h. Sel. 4 selectivity of glycerol carbonate (4)





Table 3Comparison of
performance of MoO₃/SnO₂
solid acid catalyst with reported
catalysts for carbonylation of
glycerol

Catalysts	Temperature (K)	Time (h)	X _G (%)	X _{GC} (%)	Y _{GC} (%)	Refs
MoO ₃ /SnO ₂	423	4	69	97	67	This work
Sn-beta zeolite	418	5	70	37	26	[52]
Au/Fe ₂ O ₃	423	4	80	48	38	[13]
Au/Nb ₂ O ₅	423	4	66	32	21	[13]
Co ₃ O ₄ /ZnO	418	4	60	100	60	[29]
$PS-(Im)_2ZnI_2$	413	6	72	84	60	[14]
Cu/MCM-41	418	3	66	68	45	[55]
Ni/MCM-41	418	3	60	89	53	[55]
Zn/MCM-41	418	5	73	98	71	[55]
ZMG	423	7	71	92	65	[57]

hence decreased selectivity of the glycerol carbonate at higher catalyst amounts.

The stability of MoO₃/SnO₂ catalyst was evaluated by recycling experiments for both pure and crude glycerol. For each run, the catalytic experiments were performed at 423 K of reaction temperature under solvent-free conditions with a 1:3 molar ratio of glycerol to urea, 800 rpm of stirring speed and 50 mg of catalyst for 4 h of reaction time. After completion of each cycle, the catalyst was separated by simple centrifugation, washed with de-ionized water and methanol to remove the products adhering on the surface of the catalyst. The resulting sample was dried at 373 K for 12 h, and then reused directly for the next run. The obtained results are shown in Fig. 10a,b. The obtained pure glycerol conversions were $\sim 69.2, 68.1, 67.4, 66.1,$ and 56.6% for 1st, 2nd, 3rd, 4th, and 5th cycles, respectively. These results indicate that there was no considerable change in the performance of the catalyst up to 4th run, and then the glycerol conversion and selectivity of glycerol carbonate were slightly reduced. As well, the crude glycerol conversions were found to be 65.6, 64.4, 63.2, 53.7, and 48.3% for 1st, 2nd, 3rd, 4th, and 5th runs, respectively. After 3rd run, the glycerol conversion and selectivity of glycerol carbonate were significantly decreased. To determine the reasons for the decreased catalytic efficiency of MoO₃/SnO₂ catalyst after fourth and third cycles, we performed various characterization studies namely, XRD, BET SA, and NH₃-TPD over the used MoO₃/SnO₂ catalyst (4th and 3rd cycle) and the obtained results are presented in Table ST1 (Supporting Information). The XRD profiles of the fresh and spent catalysts are shown in Fig. S6 (Supporting Information). Similar characteristic diffraction peaks were found for both spent and fresh catalysts. The estimated crystallite size of fresh and spent catalysts was found to be ~ 6.06 and 10.14 (pure glycerol), 13.25 nm (crude glycerol), respectively (Table ST1). It was clear that the spent catalyst shows relatively larger crystallite size compared to that of the fresh catalyst, which could be due to the agglomeration of smaller crystals to form larger crystals after repeated cycles. As well, it was found from BET and NH₃-TPD results that the spent MoO₃/SnO₂ sample exhibits significantly decreased specific surface area with lower pore volume and small amounts of acidic sites compared to that of fresh catalyst (Table ST1). The obtained physicochemical properties of the spent catalyst of crude glycerol reveal more deactivation than with the spent catalyst of pure glycerol. It is primarily due to easy deactivation of the catalyst surface in the presence of more impurities in the crude glycerol. As mentioned in the experiment section the crude glycerol contains various impurities that include both organic and inorganic compounds. The inorganic residues remained in the crude glycerol are expected to play a critical role in the deactivation of the catalyst. Based on the above results, it can be concluded that changes in the physicochemical properties of MoO₃/SnO₂ catalyst are the major reason for its deactivation in the recycling tests.

3.3 Comparison of MoO₃/SnO₂ with Reported Catalysts

Finally, we have made an effort to compare the catalytic activity results of MoO_3/SnO_2 solid acid with the reported catalysts (Table 3). It can be noted that MoO_3/SnO_2 catalyst shows comparable activity with the literature reported works. However, we must understand that the reaction conditions used in the present study are significantly different with respect to the literature reports. Among the various reported catalysts, the Au/Fe₂O₃ and Au/Nb₂O₅ samples exhibited a high glycerol conversion with very low yield of glycerol carbonate [13]. Copper, nickel, and zinc supported on MCM-41 materials exhibited higher glycerol conversions at low reaction times (3 h). However, the selectivity of desired glycerol carbonate product was very low [55]. In the case of PS-(Im)₂ZnI₂ and ZMG catalysts, higher glycerol

carbonate were found, but longer reaction times are required [14, 56, 57]. As well, $\text{Co}_3\text{O}_4/\text{ZnO}$ catalyst shows lower glycerol conversion with higher selectivity of glycerol carbonate [29]. The Sn- β zeolite exhibited 70% of glycerol conversion at lower reaction times [45]. In comparison to the literature reports, it can be stated that the MoO₃/SnO₂ is a promising catalyst for the carbonylation of glycerol with urea.

4 Conclusions

In summary, the carbonylation of glycerol with urea to synthesize glycerol carbonate was studied using SnO₂-based solid acid catalysts. The incorporation of MoO₃ and WO₃ species into the SnO₂ significantly improved its structural, textural, and acidic properties. It was found that MoO₃/SnO₂ catalyst shows an excellent glycerol conversion with higher glycerol carbonate yield when compared to WO₂/SnO₂ and SnO₂ catalysts. The superior activity performance of the MoO₃/SnO₂ is attributed to the presence of more number of acidic sites, higher oxygen vacancy defects, smaller particle size, and superior specific surface area. Among all the reaction parameters, the reaction temperature played a significant role in the improvement of glycerol conversion and glycerol carbonate selectivity. There is no significant variation in the catalytic activity for carbonylation of crude glycerol and pure glycerol with urea over the MoO₃/SnO₂ catalyst. As well, the MoO₃/SnO₂ catalyst showed an excellent stability up to four consecutive runs for pure glycerol and three consecutive runs for crude glycerol.

5 Supporting Information

Detailed information about the influence of stirring speed on the reaction, Raman spectra, NH_3 -TPD profiles, W 4f and Mo 3d XP spectra, FTIR spectra, and characterization results of fresh and used catalysts are provided.

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Compliance with Ethical Standards

Conflicts of interest There are no conflicts to declare.

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Affiliations

Baithy Mallesham^{1,2} · Agolu Rangaswamy¹ · Bolla Govinda Rao¹ · Tumula Venkateshwar Rao¹ · Benjaram M. Reddy¹

- Baithy Mallesham baithy.m@gmail.com
- Benjaram M. Reddy bmreddy@iict.res.in

- ¹ Catalysis and Fine Chemicals Department, CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 007, India
- ² Chemical Engineering Department, Indian Institute of Technology Hyderabad, Sangareddy, Kandi 502285, India