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Baithy Mallesham, Putla Sudarsanam, Gangadhara Raju and Benjaram M. Reddy* Development of highly promising solid acids is one of the key technologies to meet the essential challenges of economical and environmental concerns. Thus, novel molybdenum and tungsten promoted

bio-glycerolt

lenges of economical and environmental concerns. Thus, novel molybdenum and tungsten promoted SnO₂ solid acids (wet-impregnation) and pure SnO₂ (fusion method) were prepared. The synthesized catalysts were systematically analyzed using various techniques, namely, XRD, BET surface area, pore size distribution, XPS, FTIR, FTIR of adsorbed pyridine, Raman, NH₃-TPD, and H₂-TPR. XRD results suggested formation of nanocrystalline SnO₂ solid solutions due to the incorporation of molybdenum and tungsten cations into the SnO₂ lattice. All the materials exhibited smaller crystallite size, remarkable porosity, and high specific surface area. Raman measurements suggested the formation of more oxygen vacancy defects in the doped catalysts, and the TPR results confirmed facile reduction of the doped SnO₂. NH₃-TPD studies revealed the beneficial role of molybdenum and tungsten oxides on the acidic properties of the SnO₂. FTIR studies of adsorbed pyridine showed the existence of a larger number of Brønsted acidic sites compared to Lewis acidic sites in the prepared catalysts. The resulting catalysts are found to be efficient solid acids for acetalization of glycerol with acetone, furfural, and its derivatives under solventfree and ambient temperature conditions. Particularly, the Mo⁶⁺-doped SnO₂ catalyst exhibited excellent catalytic performance in terms of both glycerol conversion and selectivity of the products. The increased presence of acidic sites and enhanced specific surface area, accompanied by notable redox properties and superior lattice defects are found to be the decisive factors for better catalytic activity of the Mo⁶⁺doped SnO₂ sample. The investigated SnO₂ solid acids represent a novel class of heterogeneous catalysts useful for the transformation of glycerol to value-added products in an eco-friendly manner.

Design of highly efficient Mo and W-promoted SnO₂

solid acids for heterogeneous catalysis: acetalization of

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1 Introduction

In recent years, there has been significant attention towards the conservation of natural resources, reduction of energy consumption and adverse environmental impacts of fossil fuels.¹ On the other hand, the prices of petrochemicals have been increasing at a remarkable rate due to enormous market distortions caused by the extraordinary growth of the manufacturing industry in Asia.² Although, there is an ambiguity to envisage the precise time of the depletion of fossil fuels, some alternative solutions have been postulated including the discovery of renewable feedstocks. Among these alternatives, biodiesel is one of the most attractive clean energy sources, showing numerous advantages when compared to petroleum-

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based diesel fuel. Primarily, biodiesel is a nontoxic, biocompatible and biodegradable fuel, which reduces greenhouse gas (*e.g.*, CO₂) emissions to 78% that of diesel. For example, the nationwide organization of a 5 vol% biodiesel blend (B5) in Canada would decrease the amount of CO₂ entering the atmosphere by 2.5 metric tons.^{3,4} Additionally, biodiesel exploitation in diesel engines has shown considerable attenuation in the emission of sulfur, polyaromatics, hydrocarbons, particulate matter, smoke, noise, and carbon monoxide.^{3–5} Therefore, the European Union has aimed for 10% substitution of biofuels in the transportation industry by the end of 2020, which requires 17.4 million tons of biodiesel production per year.⁶

Biodiesel is usually produced by the transesterification of vegetable oils or fats with methanol. In this process, approximately 10% of crude glycerol is attained as a by-product.^{7,8} The global biodiesel industry is estimated to reach 37 billion gallons by 2016 with an average annual growth of 42%, which provides around 4 billion gallons of glycerol.⁹ However, the increasing prices of starting reagents and the prolonged synthesis procedure raised questions over biodiesel

commercialization.^{10,11} It is reported that the cost of raw material contributes ~70–95% of the total biodiesel production, which is predicted to further increase in future due to high biodiesel demand. Additionally, biodiesel has shown low oxidation stability and poor cold flow properties that confines its applicability as a diesel fuel additive.¹² Since glycerol is a vast biodiesel industry by-product, the development of new outlets from waste glycerol to value-added chemicals is of great importance to enhance the economic profitability of biodiesel.

Accordingly, several catalytic conversion processes of glycerol have been investigated including hydrogenolysis, oxidation, dehydration, polymerization, steam reforming, etherification, esterification, acetalization, and so on.^{13,14} Among these processes, the acetalization of glycerol is an excellent reaction for the synthesis of six- and five-membered cyclic products that exhibit a wide spectrum of commercial activities. Mainly, glycerol acetals and ketals are extensively used as additives, bases, scents, and flavors in several industries.¹⁵ They can enhance the viscosity and cold properties of biodiesel and also meet its established requirements for flash point and oxidation stability.¹⁶ Moreover, a significant reduction in the emissions of hydrocarbons, carbon monoxide, unregulated aldehydes, and particulate matter can be achieved by adding these oxygenated compounds to the standard diesel fuel.¹⁷

Traditionally, homogeneous Brønsted acids, such as, HCl, H₃PO₄, and *p*-toluenesulfonic acid have been employed for the acetalization of glycerol.¹⁸ Also, the utilization of hazardous organic solvents has been described to improve the conversion of glycerol.¹⁷ However, such procedures represent several limitations derived from the use of expensive and toxic reagents, tedious work-up procedure and generation of large amounts of waste. It has been reported that the costs for the disposal of hazardous substances and related pollution consequences are above the inflation rate in many countries.¹⁹ Moreover, GlaxoSmithKline researchers have estimated that chemicals involved in pharmaceutical industries contain about 85% solvent, hence recovery efficiencies are typically 50-80%.²⁰ Thus, numerous green strategies have been implemented in chemical synthesis to meet the essential challenges of economical and environmental concerns.²¹ It is well-known that the sustainability of green chemistry mainly depends on (i) the use of benign solvents or solvent-free conditions, (ii) the development of less toxic and promising reagents/catalysts, and (iii) the design of cost effective and reliable methodologies.²² In view of this, the application of heterogeneous catalysts for various chemical transformations is one of the greatest recent achievements in chemistry.²³ They tremendously simplify industrial processes by facilitating the separation of reactants and products, and avoid the use of large amounts of solvents. Moreover, they can be recycled multiple times without significant loss of activity and selectivity, thereby making the process economically more viable.24,25

A variety of heterogeneous catalysts have been studied, such as ion exchange resins, zeolites, heteropolyacids, and promoted metal oxides in the acetalization of glycerol.^{13,18,26} Nevertheless, ion exchange resins and heteropolyacids exhibit poor thermal stability, inadequate regeneration ability, and low specific surface area, whereas zeolites show diffusion problems related to the reactants within the microporous network, induced by mass transfer resistance.^{14,16} On the other hand, promoted metal oxides are potential heterogeneous catalysts owing to various attractive features, for instance, simple preparation, high thermal stability, strong surface acidic sites, and better catalytic activities.¹⁴ Tin dioxide (SnO₂) is a versatile metal oxide because of its two unique characteristics: variation in valence state and existence of oxygen vacancy defects.²⁷ Therefore, SnO₂ has been found widespread applications in catalysis, solar energy conversion, antistatic coatings, electrochromic devices, and transparent conductive electrodes.²⁸ However, due to inadequate thermal stability of the pure tin oxide, its application is confined to a great extent in catalysis.²⁹ Several modifications have been suggested, of which addition of metal and non-metal oxides to the tin oxide is an effective strategy. It was reported that the higher the valence of the cation of oxide, the stronger the stabilizing effect against higher temperatures.

Accordingly, in the present work, we have prepared novel molybdenum and tungsten promoted SnO₂ green solid acids by means of a wet-impregnation method. A reference pure SnO₂ was also prepared using a simple fusion method. Synthesized catalysts were characterized by various techniques namely, X-ray diffraction (XRD), BET surface area, Barrett-Joyner-Halenda (BJH) pore size distribution, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, FTIR analysis of adsorbed pyridine, ammonia-temperature programmed desorption (NH₃-TPD), and hydrogen-temperature programmed reduction (H2-TPR) to examine the physicochemical features of the prepared catalysts. An eco-friendly process was developed for the acetalization of bioglycerol with acetone, furfural and its derivatives for the first time over SnO2-based solid acids at room temperature and under solvent-free conditions. Earlier studies demonstrated that the catalytic performance of tin oxide can be substantially improved by the incorporation of heteroelements.^{29,30} To our surprise, promoted SnO₂ solid acids showed excellent catalytic performance in terms of both conversion of glycerol and selectivity to the desired products than that of pure SnO_2 . Particularly, the addition of Mo^{6+} ions to SnO₂ significantly enhanced its activity that was proved to be due to the presence of superior surface acidic sites, large BET surface area, enhanced lattice defects, and facile redox properties.

2 Experimental

2.1 Catalyst preparation

The pure SnO_2 was prepared by a simple fusion method using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, AR grade) and NaNO_3 (Aldrich, AR grade) as the precursors. In a typical procedure, the required quantities of precursors (NaNO₃: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} = \sim 1:5$) were dissolved in double distilled water and vigorously stirred for 1 h

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at room temperature. The subsequent evaporation of excess water from the solution at 383 K resulted in a porous and foam-like solid product. Afterward, the reaction temperature was increased to \sim 523 K and continued at the same temperature until the formation of white powdered tin oxide. The obtained products were cooled to room temperature, washed with deionized water and oven dried at 373 K for 12 h. Some portion of the sample was calcined at 923 K for 5 h in air.

The promoted SnO₂ solid acids containing 10 wt% of metal oxides (MoO₃ and WO₃) were synthesized by a wetimpregnation method. In brief, the desired quantities of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ or $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ (Aldrich, AR grade) were dissolved in double distilled water followed by the addition of finely powdered tin oxide. The excess water was evaporated on a hot plate under vigorous stirring. The obtained products were oven dried at 393 K for 12 h and finally calcined at 923 K for 5 h in air atmosphere. For convenience, the prepared SnO₂, MoO₃/SnO₂ and WO₃/SnO₂ catalysts are referred to as Sn, MSn and WSn, respectively, throughout the article.

2.2 Characterization studies

X-Ray diffraction measurements were carried out on a Rigaku Multiflex instrument equipped with a nickel-filtered CuKa (0.15418 nm) radiation source and a scintillation counter detector. The scattered intensity data were collected from 2θ values of 2 to 80° by scanning at 0.01° steps with a counting time of 1 s at each step. The average crystallite size of the samples was determined by means of the Scherrer equation and the lattice parameters were estimated by a standard cubic indexation method. BET surface area, pore volume, and pore size distribution measurements were made on a Micromeritics ASAP 2020 instrument. Prior to measurements, the samples were degassed at 573 K for 3 h to remove any residual moisture. The BET specific surface areas were calculated from adsorption data in the relative pressure (P/P_0) range = 0.04-0.25. Pore size and pore volume were calculated using the BJH method applied to the desorption leg of the isotherms. Williamson-Hall plots ($\beta \cos\theta / \lambda vs. \sin\theta / \lambda$) were used to separate the effects of crystallite size and lattice strain of the catalysts.31

Raman spectra were recorded at room temperature on a Horiba Jobin–Yvon HR800 Raman spectrometer equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector and a confocal microscope. The line at 632 nm of Ar⁺ ion (Spectra Physics) laser was used as an excitation source for the visible Raman spectroscopy. The 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 according to the intensity of Raman scattering. The wavenumber values reported from the spectra are accurate to within 1 cm⁻¹.

The NH₃-TPD measurements were performed on a Micromeritics AutoChem 2910 instrument. A thermal conductivity detector was used for continuous monitoring of the desorbed gas. Prior to TPD measurements, samples were pre-treated at 573 K for 1 h and then saturated with 4.95% NH₃ (balance He) with a flow rate of 20 mL min⁻¹ for 1 h, and subsequently flushed with He to remove the physisorbed gas. The chemisorbed amount of NH_3 was measured in flowing He gas with a flow rate of 20 mL min⁻¹ from 323 to 1073 K at a heating rate of 10 K min⁻¹. The FTIR spectra were recorded on a Nicolet 740 FT-IR spectrometer at ambient conditions using KBr discs 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.³²

The XPS analysis was performed using a Shimadzu (ESCA 3400) spectrometer. The X-ray source utilized was Mg K α (1253.6 eV) radiation. Analysis was done at room temperature, and the samples were maintained under rigorous vacuum typically in the order of less than 10^{-8} Pa to avoid large amount of noise in the spectra from contaminates. All binding energies measured were within a precision of ± 0.2 eV. The binding energies were corrected by setting the binding energy (BE) of the adventitious carbon (C 1s) peak at 284.6 eV.

The H₂-TPR experiments were conducted in a tubular quartz reactor coupled to a TCD of gas chromatograph (Shimadzu) and performed in a conventional apparatus by monitoring the H₂ consumed. The sample (30 mg of fresh catalyst) was heated at a rate of 10 K min⁻¹ from room temperature to 1100 K in 20 mL min⁻¹ flow of 5% H₂ in Ar. The hydrogen consumption during the reduction was calculated by passing the effluent gas through a molecular sieve trap to remove the produced water and was analyzed by gas chromatograph using the TCD.

2.3 Acetalization of glycerol with carbonyl compounds

The catalytic performance of the prepared solid acids was investigated for acetalization of glycerol with acetone, furfural and its derivatives. These experiments were performed in a 50 mL round bottom flask with a 1 : 1 molar ratio of glycerol to acetone (or furfural) under solvent-free and room temperature conditions. Catalysts were pre-activated at 423 K for 2 h before catalytic runs. After completion of the reaction, catalyst was separated from the reaction mixture by centrifugation and the liquid products were confirmed by GC-MS equipped with a DB-5 capillary column and a flame ionization detector (FID), and also by ¹H-NMR spectroscopy (solvent, CDCl₃). Samples were taken periodically and analyzed by GC equipped with BP-20 (wax) capillary column and FID. The conversion and product selectivity were calculated as per the established procedure.³³

3 Results and discussion

The XRD patterns of the SnO_2 -based catalysts calcined at 923 K are presented in Fig. 1. As shown in Fig. 1, the diffraction



Fig. 1 Powder X-ray diffraction patterns of pure SnO_2 (Sn), WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) samples.

peaks of pure SnO_2 can be indexed to (110), (101), (200), (211), (220), (002), (310), (112), (301), (202), and (321) planes that indicate the tetragonal SnO₂ (PDF #880287). Interestingly, molybdenum and tungsten impregnated SnO₂ samples also exhibited a typical tetragonal phase of SnO₂. A closer observation reveals that the XRD patterns of the impregnated SnO₂ samples are broad and shifted to higher angles compared to pure SnO₂. At this point, it must be emphasized that the broadening of the XRD peaks distinctly reflects the nanocrystalline nature of the samples which is even more pronounced in the case of MoO₃/SnO₂ catalyst. Additionally, no diffraction peaks corresponding to MoO3 and WO3 were noticed in the investigated XRD region. This notable scrutiny can be explained either due to doping of Mo and W ions into the SnO₂ lattice³⁴ or the amorphous nature of the impregnated Mo- and W-oxides.³⁵ Using the most intense line (110) of the XRD patterns, calculation of lattice parameters 'a' and 'c' was carried out and the derived values are summarized in Table 1. Evidently, the lattice parameters were found to decrease after addition of Mo and W ions to the SnO2. These disparate features, such as peak shift, variation in the lattice parameters, and absence of peaks due to MoO3 and WO3 obviously confirm the formation of metal ion-doped SnO2 solid solutions.

The shift of peaks towards higher angles can be elucidated by the ionic radii disparity of the host $(Sn^{4+} \sim 0.71 \text{ Å})$ and guest metal ions $(Mo^{6+} \sim 0.62 \text{ Å} \text{ and } W^{6+} \sim 0.56 \text{ Å})$. Hence, the doping of smaller sized Mo^{6+} and W^{6+} ions into the SnO_2 lattice is expected to cause lattice contraction (*i.e.*, smaller lattice parameters). The peak shift is more pronounced in the case of W^{6+} -doped SnO_2 sample compared to Mo^{6+} -doped SnO_2 due to the large difference in ionic radius of the respective metal ions, in agreement with lattice parameter values (Table 1). The average crystallite sizes of SnO_2 were determined using the Scherrer formula and the obtained values are

Table 1 Surface area (*S*), crystallite size (*D*), pore volume (*V*), pore size (*P*), lattice strain (ϵ), and lattice parameter (*A*) of SnO₂ (Sn), WO₃/SnO₂ (WSn), and MoO₃/SnO₂ (MSn) catalysts

	G	Da	тb	n ^b		$A^{a}\left(\mathrm{\AA}\right)$	
Entry	$(m^2 g^{-1})$	(nm)	$(cm^3 g^{-1})$	p (nm)	ε^{c}	а	с
Sn	11	13.47	0.074	9.03	0.011	4.75	3.19
WSn	32	8.76	0.064	7.75	0.020	4.71	3.17
MSn	56	6.06	0.068	4.84	0.024	4.69	3.16
a —		h					

 a From XRD spectra. b From BJH analysis. c From Williamson–Hall plots.

presented in Table 1. It is interesting to note that the crystallite size of SnO₂ substantially decreased after doping of metal ions into the SnO₂ lattice. This is certainly due to the beneficial role of dopants towards inhibition of crystal growth against higher temperatures. The average crystallite sizes of MSn, WSn and Sn samples are 6.06, 8.76 and 13.47 nm, respectively. The determined lattice strain of the prepared samples by Williamson-Hall method are presented in Table 1 (Fig. S1 in the ESI⁺). Lattice strain is a kind of metrology parameter which describes the distorted degree in a real crystalline compound.³⁶ It is found that doped tin oxide samples exhibit higher lattice strain values than that of pure tin oxide, which could be due to the lattice distortions induced by doping of Mo⁶⁺/W⁶⁺ ions into the tin oxide lattice. The lattice strain values of Sn, WSn and MSn samples are 0.0119, 0.0204 and 0.0243, respectively. Moreover, it was shown that smaller crystallite size and contraction of the SnO₂ lattice enhances the lattice strain significantly.³⁷ As stated, a linear relation between crystallite size, lattice parameters and lattice strain was found in the prepared catalysts (Table 1).

Fig. 2 shows the N₂ adsorption-desorption isotherms of SnO₂-based catalysts calcined at 923 K. According to the literature, these plots can be classified as type IV isotherms with H1-type hysteresis, which are characteristic of mesoporous materials.³⁸ The appearance of a H1 hysteresis loop generally suggests enhanced pore size as well as pore connectivity of materials with homogeneous distribution. Although no template was used in the present study, all synthesized materials displayed remarkable porosity that pointed out the significance of the preparation method. The pore volume and pore size of pure SnO₂ were 0.0739 cm³ g⁻¹ and 9.0357 nm, respectively (Table 1). Conversely, doped-SnO₂ samples exhibited lower pore volume and smaller pore size than that of pure tin oxide. Fig. 3 illustrates the pore size distribution of various catalysts. A unimodal distribution was observed in the case of Sn and MSn catalysts, whereas the WSn sample showed multimodal distribution.³⁹ Among the investigated catalysts, pure tin oxide exhibited a broad pore size distribution. The specific surface areas of all samples are presented in Table 1. Generally, the specific surface areas of the mixed oxides are considerably larger than those of the individual oxides.⁴⁰ It is wellknown that high thermal treatments are essential during the preparation of metal oxides to achieve better physicochemical

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Fig. 2 N_2 adsorption–desorption isotherms of SnO_2 (Sn), WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) catalysts.



Fig. 3 Pore size distribution profiles of SnO_2 (Sn), WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) catalysts.

properties. However, pure metal oxides usually undergo agglomeration and sintering at high temperatures that eventually leads to larger crystallite sizes and smaller surface areas, hence poor catalytic activities. Conversely, when metal oxides are combined together, the produced mixed oxides exhibit significant resistance towards agglomeration and sintering due to the cooperative nature of the cations of the mixed oxides. The mutual interaction between the metal oxides strongly inhibits their individual crystallization and particle growth resulting



Fig. 4 Visible Raman spectra of SnO_2 (Sn), WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) catalysts calcined at 923 K.

in higher specific surface areas than those of pure metal oxides.^{41–43} As stated, doped SnO_2 materials exhibited enhanced specific surface areas compared to pure SnO_2 in agreement with the crystallite size decrease (Table 1). The Sn, WSn, and MSn samples exhibited specific surface areas of 11, 32 and 56 m² g⁻¹, respectively. Catalytic reactions mostly take place on the surface of the catalysts and the reaction rates are typically in proportion to the surface area of the catalysts.⁴¹ Hence, it can be expected that the enhanced surface area of the MSn sample would be one of the vital reasons to achieve better catalytic activity in the glycerol acetalization, which is discussed in the latter paragraphs.

Raman spectroscopy, sensitive to both M–O bond arrangement and lattice defects, is an excellent technique for the investigation of SnO_2 -based materials. The Raman spectra of Sn, WSn, and MSn samples are shown in Fig. 4. SnO_2 with the tetragonal structure belongs to the space group D_{4h} .⁴⁴ On the basis of group theory, the normal lattice vibration at the point of the Brillouin zone is given as follows:

$$\Gamma = 1A_{1g} + 1A_{2g} + 1A_{2u} + 1B_{1g} + 1B_{2g} + 2B_{1u} + 1E_g + 3E_u$$

Among these vibrations, A_{1g} , B_{1g} , B_{2g} , and E_g modes are Raman active, whereas the modes A_{2u} , E_u , and B_{1u} are infrared active and optically inactive, respectively.⁴⁵ It was reported that A_{1g} , B_{1g} , and B_{2g} bands indicate the vibration modes of the Sn–O bonds in the plane perpendicular to the *c*-axis, whereas the E_g band reveals the vibration of oxygen in the direction of the *c*-axis.⁴⁶ The intensity of the B_{1g} peak (either at 87 or 123 cm⁻¹) is so weak that it could seldom be observed.^{47,48} The Raman spectrum of pure SnO₂ displayed primarily three bands at around 630, 474 and 770 cm⁻¹ which are attributed to vibration modes of A_{1g} , E_g and B_{2g} , respectively. The presence of these bands corroborates the tetragonal structure of the SnO₂ in agreement with XRD measurements. As mentioned previously, no discernible B_{1g} peak was found in

the present work. Interestingly, the prominent A1g band of doped SnO₂ samples is shifted to lower wavenumbers than that of pure SnO₂. The doping of smaller metal ions (W⁶⁺ and Mo⁶⁺) and the consequent lattice contraction of tin oxide as well as M–O vibration frequency may induce a shift in the A_{1g} peak position. The Raman bands of MSn and WSn samples are broad-influenced by the induced size effects as observed from XRD studies. Among the A_{1g} , E_g and B_{2g} bands, the E_g Raman band is very important as it represents the existence of lattice defects (i.e., oxygen vacancies) in tin oxide materials. Oxygen vacancies are a special class of point defects in many oxide materials and play an important role in catalysis.⁴⁹ It is a well established fact in the literature that the incorporation of smaller sized metal ions induces the shifting of neighboring O atoms towards dopants. The induced O distortions could enhance the lattice strain that will be relaxed by the formation of an O vacancy in the vicinity of the dopant. It is clear from the XRD and Raman studies that Mo^{6+} and W^{6+} doped SnO_2 samples show enhanced lattice strain and reasonably large amount of oxygen vacancies than that of the pure SnO₂. In addition, a broad Raman band at around 200–360 cm⁻¹ can be assigned to the contributions from intrinsic lattice defects,⁵⁰ resulting from the substitution of Sn⁴⁺ with smaller sized Mo⁶⁺ and W⁶⁺ ions. Furthermore, no Raman bands pertaining to MoO₃ and WO₃ were observed confirming the formation of SnO₂-based solid solutions supporting the observations made from the XRD results.

XPS measurements were performed to obtain the chemical state information of metal ions of various samples. Fig. 5 depicts the Sn 3d core level XP spectra of pure and doped SnO₂ catalysts. In all cases, the peaks were symmetric and appeared as a spin-orbit doublet at ~487.4 (3d_{5/2}) and ~495.8 eV (3d_{3/2}), respectively, confirming the presence of Sn4+ ions.34 The Sn 3d peak position of the MSn and WSn samples is shifted to higher binding energies relative to pure SnO₂. The displacement of Sn 3d peaks suggests the incorporation of molybdenum and tungsten ions into the SnO₂ lattice, which is consistent with the XRD and Raman results.⁵¹ The O 1s core level XPS profiles of Sn, WSn and MSn catalysts are shown in Fig. 6. All the samples exhibited predominantly one peak at ~531.8 eV, which indicates the presence of only one type of oxygen species³⁴ (*i.e.* lattice oxygen). Moreover, the estimated BE difference between the O 1s and Sn 3d_{5/2} core levels $(\Delta BE_{O-Sn} \text{ in Table 2})$ is significantly reduced for the doped SnO₂ samples, indicating the existence of strong electronic interactions between Sn and the dopants. This remarkable observation can be explained by the reduction of the interatomic spacing (i.e., contraction of the SnO₂ lattice in the doped samples) upon substitution of Sn^{4+} ion (~0.71 Å) with smaller sized Mo^{6+} (~0.62 Å) and W^{6+} (~0.56 Å) ions. As stated earlier with respect to XRD and Raman studies, contraction of the SnO₂ lattice enhances the lattice strain and oxygen vacancies. Therefore, based on the characterization results, it can be stated that the strong interaction between Sn and the dopants improves the lattice strain as well as oxygen vacancies in the doped SnO₂.

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Fig. 5 Sn 3d XP spectra of pure SnO $_2$ (Sn), WO $_3/SnO_2$ (WSn), and MoO $_3/SnO_2$ (MSn) samples.



Fig. 6 O 1s XP spectra of pure SnO $_2$ (Sn), WO $_3/SnO_2$ (WSn), and MoO $_3/SnO_2$ (MSn) samples.

Table 2 XPS data of SnO_2 (Sn), WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) catalysts

Catalyst	Sn 3d _{5/2}	O 1s	Mo 3d _{5/2}	W 4f _{7/2}	ΔBE_{O-Sn}
Sn	487.4	531.8	_		44.4
MSn	487.6 487.7	531.4 531.4	232.7	35./ —	43.8 43.7

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Fig. 7 W 4f and Mo 3d XP spectra of WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) samples, respectively.

The XP spectra of Mo 3d and W 4f of the respective metaldoped SnO₂ samples are presented in Fig. 7. As can be seen from the figure, the Mo 3d spectrum is a simple spin-doublet with the binding energies of $3d_{5/2}$ and $3d_{3/2}$ at 232.7 and 236.2 eV, respectively, corresponding to the Mo⁶⁺ oxidation state.³⁴ Moreover, no peak due to other molybdenum species, such as Mo⁴⁺ (231.4 eV) and Mo⁵⁺ (237.5 eV) ions, was noted. On the other hand, the W 4f core level spectrum exhibited the binding energies of $4f_{7/2}$ and $4f_{5/2}$ at 35.6 and 37.8 eV, respectively, demonstrating the existence of W⁶⁺ ions in agreement with earlier reported values.⁵²

The FTIR spectra of Sn, WSn, and MSn samples show three broad peaks at around 680, 623 and 553 cm⁻¹, which correspond to different vibration modes of O–Sn–O and Sn–O–Sn groups (Fig. S2 in the ESI†).³⁴ The presence of an IR band at ~947 cm⁻¹ in the MSn sample reveals the stretching modes of the terminal Mo–O bond with a certain amount of double bond character. Also, the existence of a band at 860 cm⁻¹ illustrates the typical Sn–O–Mo modes. The broad band noticed between 3600 and 3000 cm⁻¹ is attributed to H-bonded hydroxyls, which are increased in intensity for the doped SnO₂ catalysts.⁵³ Additionally, the band at 1621 cm⁻¹ is assigned to the bending vibrations of hydrogen-bonded surface OH groups of the physically adsorbed water molecules.⁵⁴

It is a well-established fact that NH₃ acts as an excellent probe molecule to examine the acidic properties of heterogeneous solid acids. The strong basicity and small molecular



Fig. 8 $\rm NH_3\text{-}TPD$ profiles of SnO_2 (Sn), WO_3/SnO_2 (WSn), and MoO_3/SnO_2 (MSn) catalysts.

size of NH₃ facilitates the easy detection of acidic sites present in the narrow pores of the solids.55 The NH₃-TPD profiles of various solid materials are depicted in Fig. 8. The TPD peaks can be defined based on earlier precedence of before and after 673 K corresponding to low-temperature (LT) and high-temperature (HT) regions, respectively.⁵⁶ The HT region peaks could be assigned to desorption of NH₃ from strong acidic sites, whereas the LT region peaks are attributed to release of NH₃ from weak acid sites. These annotations clearly signify the presence of both strong as well as weak acidic sites in the investigated SnO₂-based solid acids useful for various catalytic applications. Pure SnO₂ exhibits a weak peak at 380 K that can be assigned to the NH₃ bonded with surface hydroxyl groups, which could be considered as Brønsted acid centers.⁵⁷ Surface hydroxyl groups could be generated due to dissociative adsorption of water on the highly polar M₁-O-M₂ bonds (where M₁ and M_2 represent different cations).⁵⁸ On the other hand, the peak at 750 K represents desorption of ammonia from Lewis acid sites, which are unsaturated Sn⁴⁺ cations with the coordination number four.⁵⁷ Interestingly, the addition of molybdenum and tungsten metal ions to the tin oxide showed a promotional role on the improvement of acidic properties of tin oxide. Both weak and strong acidic sites were enhanced in the case of SnO₂ solid solutions. It has been reported that mixed oxides show much stronger acidic properties than single oxides. The enriched acidic properties of mixed oxides are considered to be the result of an excess negative charge or positive charge induced by the formation of non-equivalent M₁-O-M₂ bonds.^{59,60} Therefore, it appears that the doping of Mo^{6+} and W^{6+} into the SnO₂ lattice results in the non-equivalent Sn-O-M (M = Mo and W) bonds and thereby enriched acidic sites on the surface of the doped SnO₂ samples. Further, it is evident from the figure that the Mo⁶⁺-doped SnO₂ sample exhibits a superior concentration of acidic sites when compared to W⁶⁺-doped SnO₂ catalyst. The calculated amount of acidic sites in the LT region were found to be 18.69, 33.98 and



Fig. 9 Pyridine FTIR spectra of SnO_2 (Sn), WO_3/SnO_2 (WSn) and MoO_3/SnO_2 (MSn) catalysts. B – Brønsted and L – Lewis acidic sites.

57.06 μ mol g⁻¹ for the Sn, WSn, and MSn samples, respectively, whereas 28.05, 27.81, and 24.43 μ mol g⁻¹ of acidic sites are observed in the HT region, respectively.

Though NH₃-TPD analysis provides much information about the strength and amount of the acidic sites, it doesn't afford sufficient evidence about the nature of the acidic sites (*i.e.*, Brønsted or Lewis acid sites) and their relative proportion in the prepared solid acids. For this, we performed FTIR spectroscopic studies of pyridine over Sn, WSn, and MSn catalysts and the obtained profiles are presented in Fig. 9. FTIR analysis of adsorbed pyridine is one of the excellent techniques to distinguish Brønsted and Lewis acid sites present in solid acids.⁶¹ It can be seen from the figure that all samples exhibited a prominent peak at around 1638 cm⁻¹, which can be assigned to the pyridine adsorbed on Brønsted acidic sites.⁶² Additionally, the existence of IR bands at 1540 and 1455 cm⁻¹ can be ascribed to the pyridine adsorbed on Brønsted and Lewis acidic sites, respectively.⁶¹ The IR band at 1490 cm⁻¹ indicates the existence of both Brønsted and Lewis acidic sites. It is obvious from the figure that all the prepared catalysts exhibit a higher number of Brønsted acid sites accompanied by very low amounts of Lewis acid sites. The existence of a high percentage of Brønsted acidic sites reveals a pivotal role in the acetalization of glycerol as discussed in latter paragraphs. The estimated relative proportion of Brønsted acid sites to Lewis acid sites is presented in Table 3.

The reduction properties of Sn, WSn, and MSn samples were studied by H₂-TPR technique and the obtained TPR profiles are presented in Fig. 10. As can be seen from the figure, pure SnO₂ exhibited two prominent peaks at 789 and 1055 K, which are assigned to the reduction of Sn(4+) to Sn(2+) and Sn (2+) to Sn(0), respectively.⁶³ This observation indicates a two step reduction instead of one step reduction *i.e.*, Sn(4+) \rightarrow Sn (0). Interestingly, the substitution of Sn⁴⁺ by Mo⁶⁺ and W⁶⁺ ions leads to shifting of reduction peaks towards lower

Table 3Correlation between BET surface area (S), amount of acidic sites, ratioof Brønsted acid sites to Lewis acid sites (B/L) and catalytic activity results of SnO_2 (Sn), (WSn), and MoO_3/SnO_2 (MSn) catalysts

		h		Gly. conv.	(%)
Sample	S^{a} (m ² g ⁻¹)	Acid sites ^b (µmol g ⁻¹)	B/L ratio ^c (%)	Acetone ^d	Furfural ^e
Sn	11	46.74	>99	15	51
WSn	32	61.81	>96	55	67
MSn	56	81.45	>95	61	75

 a From BET analysis. b From NH3-TPD results. c From FTIR analysis of adsorbed pyridine. d From Fig. 11. e From Fig. 13.



Fig. 10 H_2 -TPR profiles of SnO₂ (Sn), WO₃/SnO₂ (WSn), and MoO₃/SnO₂ (MSn) catalysts.

temperature, and the total quantity of desorbed oxygen from the doped tin oxide catalysts is more than that of pure SnO₂. The 789 K peak is shifted to 735 and 680 K, while the 1055 K peak is shifted to 1038 and 1003 K in the case of WSn and MSn samples, respectively. The easy reduction of doped materials is due to structural modifications induced in the SnO_2 lattice when some Sn^{4+} cations are replaced with Mo^{6+} W⁶⁺ cations (evidenced from XRD, Raman, and XPS studies), thus favoring the diffusion of O^{2-} anions within the lattice. In the case of the MSn sample, the existence of a peak at ~875 K corresponds to the reduction of Mo⁶⁺ to Mo⁴⁺, whereas the peak at higher temperatures (~1098 K) represents the reduction of Mo⁴⁺ to Mo⁰ species.⁶⁴ The H₂-TPR profile of WSn displayed two broad peaks at 923 and 1104 K which are due to the stepwise reduction of $W^{6+} \rightarrow W^{4+}$ and $W^{4+} \rightarrow W^0$, respectively.52

3.1 Acetalization of glycerol with acetone

The prepared SnO_2 solid acids were investigated for the acetalization of glycerol with acetone and the obtained results are shown in Fig. 11. The catalytic acetalization of glycerol with



Fig. 11 Acetalization of glycerol with acetone over SnO_2 (Sn), WO_3/SnO_2 (WSn) and MoO_3/SnO_2 (MSn) catalysts. Reaction conditions: molar ratio of glycerol to acetone = 1 : 1; reaction time = 90 min; catalyst amount = 5 wt% (w.r.t. glycerol).



Scheme 1 Acetalization of glycerol with acetone to (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (solketal) and 2,2-dimethyl-1,3-dioxan-5-ol.

acetone to (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (solketal) and 2,2-dimethyl-1,3-dioxan-5-ol is presented in Scheme 1. The catalytic experiments were carried out at room temperature under solvent-free conditions with a 1:1 molar ratio of glycerol to acetone and 5 wt% of catalyst for 90 min reaction time. It was found that the conversion of glycerol significantly increases after the incorporation of molybdenum and tungsten ions into the tin oxide. Table 3 clearly reveals a linear relationship between surface area and the amount of acidic sites of the prepared SnO₂-based catalysts with the activity results. The poor activity of pure tin oxide is mainly due to the small amount of surface acidic sites and low specific surface area. The glycerol conversion over Sn, WSn and MSn catalysts was 15, 55 and 61%, respectively. Interestingly, a high selectivity of solketal (96%) was obtained irrespective of the catalysts used. The high catalytic activity of MSn solid acid is due to the presence of large amounts of acidic sites and enhanced specific surface area.

Several theoretical and experimental studies were undertaken to elucidate the reasons behind the high selectivity of solketal. It was suggested that five membered solketal can be formed selectively through a short-lived tertiary carbenium ion intermediate initiated by the Brønsted acidic sites (ketal mechanism).⁶⁵ The formed carbenium ion can be stabilized by resonance with the non-bonded electron pairs of the adjacent oxygen atom. Afterward, a quick nucleophilic attack of the



Fig. 12 Influence of reaction time on acetalization of glycerol with acetone over MoO_3/SnO_2 (MSn) catalyst. Reaction conditions: molar ratio of glycerol to acetone = 1 : 1; catalyst amount = 5 wt% (w.r.t. glycerol).

secondary hydroxyl group leads to solketal. On the other hand, Li *et al.* proposed that Lewis acidic sites play a similar role as in the Meerwein–Ponndorf–Verley reduction/Oppenauer oxidation reactions, by coordinating and activating the carbonyl group of the acetone.¹³ Then, the carbon atom of the carbonyl group can be attacked by the primary alcoholic group of glycerol followed by the formation of a bond between the carbonyl oxygen atom and the β -carbon of the glycerol. Finally, the dehydration process leads to the formation of solketal. However, the present work reveals the existence of large amounts of Brønsted acidic sites in the prepared SnO₂ solid acids (evidence from pyridine-IR studies). Therefore, without any hesitation, it can be concluded that solketal formation is due to the ketal mechanism catalyzed by Brønsted acidic sites.

In order to examine the variation of glycerol conversion and products selectivity with time, we have studied acetalization of glycerol at different time intervals (reaction time varied from 30 to 150 min) over MSn catalyst. The remaining reaction conditions were the same as described above and the obtained results are displayed in Fig. 12. It can be noted from this figure that the conversion of glycerol was considerably increased at 60 min of reaction time, with 35 and 51% of glycerol conversions obtained for 30 and 60 min of reaction time, respectively. With a further increase of reaction time, only a slight enhancement in the conversion of glycerol was noted. The conversion of glycerol was 61, 66 and 71% for 90, 120 and 150 min of reaction time, respectively. Interestingly, the selectivity of solketal did not change much with the reaction time.

3.2 Acetalization of glycerol with furfural and its derivatives

We have also explored the SnO₂-based catalysts for the acetalization of glycerol with furfural and its derivates to know the accessibility of solid acids for different carbonyl compounds. Scheme 2 shows the acetalization of glycerol with furfural and its derivatives under solvent-free and room temperature conditions. For all catalysts, the reaction conditions were fixed



Scheme 2 Catalytic acetalization of glycerol with furfural and its derivatives to cyclic acetals, (2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol and 2-(furan-2-yl)-1,3-dioxan-5-ol.



Fig. 13 Acetalization of glycerol with furfural over SnO_2 (Sn), WO_3/SnO_2 (WSn), and MOO_3/SnO_2 (MSn) catalysts. Reaction conditions: molar ratio of glycerol to furfural = 1 : 1; reaction time = 30 min; catalyst amount = 5 wt% (w.r.t. glycerol).

as follows: solvent-free, room temperature, 30 min reaction time, 5 wt% catalyst amount, and 1:1 molar ratio of glycerol to furfural. Fig. 13 shows the conversion of glycerol and selectivity of products over Sn, WSn, and MSn catalysts. Here too, high glycerol conversions were obtained for the doped SnO₂ catalysts. Accordingly, 51, 67 and 75% of glycerol conversions were noted for Sn, WSn, and MSn catalysts, respectively. As observed in the acetalization of glycerol with acetone, here also the high catalytic activity of MSn solid acid could be due to the enhanced surface area and higher amounts of surface acidic sites (Table 3). Further, it can be expected that the formation of products in the acetalization of glycerol with furfural is also due to the ketal mechanism catalyzed by Brønsted acidic sites as described in the case of acetalization of glycerol with acetone, because both acetone and furfural are typical carbonyl compounds. Contrary to the glycerol acetalization with acetone, in this instance, an insignificant variation in the selectivity of products was noted for all the catalysts.⁶⁶ The selectivity of five- and six-membered ring acetals was 64 and 36% over MSn catalyst, respectively.



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Fig. 14 Influence of reaction time on acetalization of glycerol with furfural over MoO_3/SnO_2 (MSn) catalyst. Reaction conditions: molar ratio of glycerol to furfural = 1 : 1; catalyst amount = 5 wt% (w.r.t. glycerol).

 $\label{eq:table_table_table} \begin{array}{l} \mbox{Table 4} & \mbox{Acetalization of glycerol with mono-substituted furfural compounds} \\ \mbox{over } MoO_3/SnO_2 \ (MSn) \ catalyst^a \end{array}$

		Selectivity (%)	
Aldehyde	Gly. conv. (%)	5-mem	6-mem
5-Methylfurfural	60	68	32
5-Nitrofurfural	65	85	15
5-Chlorofurfural	71	61	39
5-Hydroxymethyl furfural	63	65	35

^{*a*} Reaction conditions: molar ratio of glycerol to substituted furfurals = 1 : 1, reaction time = 30 min, catalyst amount = 5 wt% (w.r.t. glycerol).

Fig. 14 shows the time-on-stream analysis (from 30 to 120 min) for the acetalization of glycerol with furfural over MSn catalyst. The reaction conditions were kept the same as described earlier. The conversion of glycerol was \sim 75 and \sim 99% at reaction times of 30 and 120 min, respectively. On the other hand, no considerable variation in the selectivity of products was observed with reaction time. The selectivity of five membered ring acetals was \sim 64 and \sim 66% at 30 and 120 min of reaction time, respectively.

The acetalization of glycerol with mono-substituted furfurals was studied and the obtained results are presented in Table 4. It was found that all substituted compounds exhibit lower glycerol conversion than that of furfural. This observation demonstrates the influence of steric hindrance induced by the presence of substitutes rather than the electronic effects of the substituent (*i.e.*, inductive, resonance and hyper conjugation effects). Table 5 shows the characteristic ¹H-NMR signals of cyclic acetals synthesized from the acetalization of glycerol with furfural and its derivatives. Among the substituted furfurals, 5-chlorofurfural exhibited the highest glycerol conversion (71%), whereas low conversion of glycerol was obtained in the case of 5-methylfurfural (60%). Interestingly, a high selectivity of five membered products was obtained for all substituted furfural compounds, particularly 5-nitrofurfural

 Table 5
 Characteristic proton NMR signals of cyclic acetals synthesized from acetalization of glycerol with various furfural compounds

Entry	Aldehyde ^a	Cyclic acetals 5-mem : 6-mem	Chemical shift ^{b} (ppm)
1	R = H	1a:1b	6.01 (s) : 5.89 (s)
2	R = Cl	2a:2b	5.89 (s) : 5.78 (s)
3	$R = NO_2$	3a:3b	5.97 (s) : 5.81 (s)
4	$R = CH_3$	4a:4b	6.12 (s) : 5.94 (s)
5	$R = CH_2OH$	5a:5b	6.09 (s) : 5.87 (s)

^a Scheme 2. ^b Proton signal of OCH(C₆H₅)O.

showed a selectivity of 85%. These exciting findings reveal the versatile nature of the Mo-promoted SnO_2 solid acid that can be used for the acetalization of glycerol with the substituted furfural compounds.

We have also investigated the reusability of MSn catalyst to understand its stability for the acetalization of glycerol with acetone and furfural (Fig. S3 and S4 in the ESI⁺). The reaction conditions are the same as described in Fig. 11 and 13, respectively, for the acetalization of glycerol with acetone and furfural. The MSn catalyst could be used repeatedly for five catalytic runs. After each run, the catalyst was washed with methanol to remove glycerol and the products, and preactivated at 423 K for 2 h before catalytic runs. It was found that the conversion of glycerol slightly decreased after the repeated use of catalyst for up to three catalytic runs and no significant variation in the selectivity of products was observed. After the 5th catalytic run, the catalytic performance of the MSn solid acid was significantly decreased, and 29 and 38% glycerol conversion were obtained for the acetalization of glycerol with acetone and furfural, respectively. The reasons for the decrease in the activity after several recycling experiments are under further investigation. On the whole, the Mopromoted SnO₂ catalyst is quite stable and recyclable in the acetalization of glycerol under ambient reaction conditions.

4 Conclusions

In summary, we developed a green heterogeneous process to synthesize industrially useful chemicals from the acetalization of glycerol over SnO₂-based solid acids. Fusion technique and wet-impregnation method were used for the preparation of pure and promoted (molybdenum and tungsten) SnO2 catalysts, respectively. Various techniques were employed to investigate the physicochemical characteristics of the SnO₂-based materials. XRD and Raman results suggested the formation of nanocrystalline SnO2 solid solutions due to the doping of Mo⁶⁺ and W⁶⁺ ions into the SnO₂ lattice. Also, large amounts of oxygen vacancy defects were found in the prepared catalysts as confirmed by Raman studies. All the solid catalysts were characterized by smaller crystallite size, extraordinary porosity and high specific surface area. XPS analysis confirmed the existence of Sn⁴⁺, Mo⁶⁺ and W⁶⁺ oxidation states in the respective catalysts. FTIR studies showed different types of hydroxyl groups on the surface of the solid acids. TPR profiles revealed

the facile reduction of SnO_2 after addition of Mo^{6+} and W^{6+} ions to the SnO2. NH3-TPD studies demonstrated the presence of both strong as well as weak acidic sites in the investigated catalysts. FTIR studies of adsorbed pyridine clearly showed the presence of higher amounts of Brønsted acidic sites when compared to Lewis acidic sites in the prepared SnO₂ based catalysts. The catalytic results revealed that doped SnO₂ catalysts exhibit excellent catalytic performance in the acetalization of glycerol under solvent-free and room temperature conditions. The poor activity of pure SnO₂ can be explained by the small amount of surface acidic sites and low specific surface area. Among the investigated catalysts, the Mo⁶⁺ doped SnO₂ showed better catalytic activity in terms of both glycerol conversion and selectivity of the products. The high activity of Mo^{6+} -doped SnO₂ is mainly due to the presence of higher amounts of acidic sites associated with improved specific surface area, better redox properties, and superior lattice defects. These interesting findings revealed the promising role of Mo⁶⁺-doped SnO₂ solid acid in the acetalization of biodiesel-derived glycerol under environmentally benign reaction conditions.

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