

Mesoporous Sn-SBA-15 as an Efficient Catalyst for the Synthesis of Nopol by Prins Condensation

Pallavi Bhange^{1†}

¹Catalysis Division, National Chemical Laboratory, Pune – 411 008, India

[†]School of Sciences, Sanjay Ghodawat University, Atigre, Kolhapur, Pin-416 118, India

ABSTRACT

A series of Sn-incorporated mesoporous silica SBA-15 samples have been synthesized with $n_{\text{Si}}/n_{\text{Sn}}$ ratios ranging from 80 to 10 under milder acidic conditions. An expansion of the lattice (powder XRD) and an increase in mesopore area (low temperature N_2 adsorption) indicate that the hexagonal structure of the SBA-15 is maintained with no loss of long range order. Sn-SBA-15 is the most efficient for the Prins condensation reaction. The Sn-SBA-15 catalysts have proved to be an efficient and reusable catalyst, for the Prins condensation of β -pinene and paraformaldehyde.

Key Words: Sn-SBA-15; Direct synthesis of Sn-SBA-15; Prins condensation

1. INTRODUCTION

Sn-containing micro- and mesoporous materials have attracted special interest during last several years in the scientific community because of their catalytic application in a variety of organic reactions. It is well known that the Sn(IV) sites possess Lewis acidic character and is expected to play important role in the reaction by polarizing electron-rich groups such as carbonyls and alcohols. By virtue of their Lewis acidic sites, these catalysts have been extensively used in several heterogeneous catalytic organic transformations, such as the Baeyer-Villager oxidation of ketones to lactones [1–2], and the Meerwein-Ponndorf reduction of aldehydes and ketones [1-3]. Recently, these catalysts have also been successfully employed in biomass upgrading, e.g. for sugars isomerization [4–7], and the cyclization of citronellal [8]. Sn-containing catalysts has promising application in the cosmetic, fragrance and flavour industry e.g for the production of the melonal flavour through the aldol condensation of 6-methyl-5-hepten-2-one and acetaldehyde to citral, which is subsequently oxidized to melonal [2].

Sn-based both micro and mesostructured materials have been widely used for carbon-carbon coupling *via* Prins condensation reaction [9]. In particular, Sn-containing mesoporous catalysts gained significant attention for the synthesis of nopol. Nopol is an optically active bicyclic primary alcohol, (named as 6,6-dimethylbicyclo-(1,1,3)-hept-2-ene-2-ethanol) used in the agrochemical industry to produce pesticides and also in the manufacture of soaps, detergents, polishes and other household products [10-11]. This primary terpenic alcohol obtained by reacting β -pinene- a renewable feedstock from pine trees and paraformaldehyde. Commercially, Nopol is synthesized by three general methods., 1) by autoclaving para formaldehyde and β -pinene at 150 to 230°C for several hours, 2) secondly by using zinc chloride as catalyst at 115-120°C for several hours yield ~57% of nopol and 3) by using acetic acid as catalyst at 120°C, that yields nopyl acetate, which is then saponified to nopol. Kriewitz et al. have reported that pinene reacts with an alcoholic solution of paraformaldehyde at 170-175°C gives 15 % yield of Nopol [12]. Bain et al. revealed that an equimolar mixture β -pinene and formaldehyde readily condense to form Nopol [13]. Nevertheless, these processes are energy and time-consuming and utilize large amounts of corrosive chemicals which are hard to separate from the final reaction mixture and also yield low nopol selectivity.

In recent years, environmental and economic concerns have promoted process of innovation toward cleaner technologies. Therefore, there is a great challenge to use heterogeneous catalysts that can facilitate the reaction under mild reaction conditions, *i.e.* lower temperatures and pressures; avoid the use of toxic or harmful substances and minimize the generation of noxious waste. Recently, Montes de Correa et al. have described the synthesis of nopol over Sn-MCM-41 molecular sieves in the presence of toluene as a solvent at 363 K [14]. Grafting of Sn by chemical vapor deposition on MCM-41 as a catalyst gives Nopol with more than 90 % yields. More recently, a mesoporous iron phosphate catalyst has been reported for the selective synthesis of nopol at 80°C in acetonitrile solvent [15]. Jyothi et al. have reported that the grafting of tin chloride on a quaternary ammonium chloride functionalized MCM-41 yielded a catalyst with higher activity and yield of product compared to the corresponding silica analogue in the Prins condensation of isobutene and formaldehyde to isoprenol [16-17]. However, the catalyst preparation involved several steps and no report on the activity of the bare MCM-41 was given. Sn-kenyaite catalysts prepared by CVD method showed high nopol selectivity but β -pinene conversion is around 50 % [18].

However, there is a still scope for improvement especially toward developing a selective and recyclable catalyst that promotes the reaction under mild reaction. In continuation of our studies related to heterogeneous catalysis [19], we report herein our preliminary results on the synthesis of nopol from β -pinene and paraformaldehyde over Sn-SBA-15 and compared with SBA-15 and Sn grafted SBA-15 samples. A unique characteristic feature of SBA-15 including larger pore size, high degree of structural ordering, ease of synthesis and higher hydrothermal stability and the existence of micropores interconnecting hexagonally ordered mesopores, which make it more suitable for catalysis as these interconnections facilitate diffusion inside the entire porous structure. In order to utilize these materials for catalytic application, we have to inculcate the acidity by incorporating metal ions into its porous structure. The new Sn-SBA-15 catalyst is an efficient, selective and recyclable catalyst for the production of nopol by the Prins condensation of β -pinene with paraformaldehyde in the presence of toluene.

2. Experimental

2.1 Synthesis.

Sn-SBA-15 materials were synthesized according to the reported procedure [19]. The synthesis of Sn-SBA-15 molecular sieves is worked out by changing the $n_{\text{H}_2\text{O}}/n_{\text{HCl}}$ ratio and the resulting pH of the synthesis medium. The Sn-SBA-15 samples was prepared by using a fixed water to HCl molar ratio of 796 (70 mL of 0.07 M HCl) with molar gel composition was 1TEOS: 0.01–0.1 SnO₂: 0.016 P123: 0.16–0.46 HCl: 127 H₂O. The resultant solid was filtered, washed and calcined at 550°C. The Sn-SBA-15 samples were designated as Sn-X, where X denotes the input $n_{\text{Si}}/n_{\text{Sn}}$ ratio. For comparison, Sn-free SBA-15 sample was also prepared under similar condition. For comparison, Sn-SBA-15 was done by incipient-wetness impregnation method under nitrogen atmosphere [20].

2.2. Characterization.

The powder XRD patterns of calcined samples were taken from X'Pert Pro (M/s Panalytical) diffractometer using Ni filter, Cu K α radiation and proportional counter as detector. The BET surface area of the samples was determined by N₂ adsorption at -196°C by using Autosorb-1 instrument. The TEM of the samples were recorded on a JEOL Model 1200EX microscope operating at 100kV. The temperature-programmed desorption of ammonia (NH₃-TPD) was performed to determine the total amount of acidity of the catalysts. Temperature-programmed desorption (TPD) experiments were conducted on a Micromeritics AutoChem 2910 instrument.

2.3. Catalytic Activity

The reaction were carried out in a batch reactor under nitrogen atmosphere, using β -pinene (5 mmol) and para formaldehyde (10 mmol) with 0.05 g of freshly prepared catalyst in the temperature range of 50–110°C. Aliquots of the reaction mixture were collected at different time intervals and analyzed by GC equipped with a FID (Agilent Technologies, model 6890N). Identification of the products was done by GC- MS.

3. Results and discussion

3.1. Structural and textural properties

Typical powder XRD patterns of calcined Sn-SBA-15 samples exhibits well-resolved diffraction peaks at 0.8, 1.6 and 1.7° (2 θ) respectively (Fig 1). It is observed that there are no diffraction lines due to crystalline SnO₂ in the high angle region even at a high Sn loading. In Sn-SBA-15 samples, the total surface area increases from 906 to 1127 m²g⁻¹ with Sn content compared to parent SBA-15. This trend indicates the absence of pore blocking and presence of nanoparticles of SnO₂ embedded in silica matrix that contributes to the higher surface area of the samples. The transmission electron micrographs indicate the long-range order of the material is maintained without any pore blocking (Fig. 2). Thus, by adjusting the $n_{\text{H}_2\text{O}}/n_{\text{HCl}}$, a part of Sn gets incorporated into the lattice of SBA-15 at low Sn concentrations ($n_{\text{Si}}/n_{\text{Sn}} > 10$). Even at high tin loading for Sn-10, smaller tin particles are formed, which are not detectable by XRD. TPD profiles of the Sn-SBA-15 catalyst showed a broad desorption pattern indicating the surface acid strength is widely distributed (Table 1).

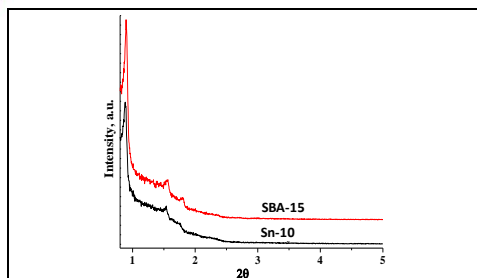


Fig. 1. Powder XRD pattern of SBA-15 and Sn-SBA-15 sample

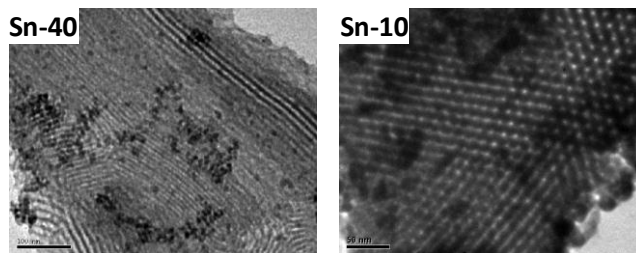
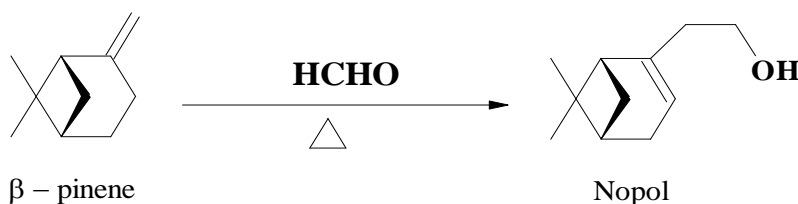


Fig. 2. Transmission electron micrographs of Sn-40 and Sn-10 samples

3.2. Catalytic studies

The formation of nopol by Prins condensation of β -pinene with para formaldehyde occurs through an addition reaction between these two reactants in the presence of Sn-SBA-15 as an acid catalyst.



Scheme 1. Reaction scheme for Prins condensation of β -pinene with *p*-formaldehyde

We verified that the reaction does not occur in the absence of catalyst. The effect of Sn-SBA-15 (with different Si/Sn ratios) on conversion of β -pinene and yield of nopol over is presented in Table 1. We observed that Si-SBA-15 showed negligible activity for the condensation of β -pinene with para formaldehyde, but the activity increases with Sn content. Sn-incorporation enhanced the catalytic activity due to the increase in number of weak and medium acid sites of Sn (IV) cations as revealed by TPD experiment. The highest acidity is attributed to the uniform distribution of Sn atoms at the atomic level throughout the mesoporous structure of SBA-15. Firstly, the Nopol conversion increases with an increase in Sn content of the SBA-15 samples (Table 1). Sn-SBA-15 is far more active and shows high efficiency and recyclability. For Sn-B-40, conversion increases to 58 % within 6 h. For Sn-B-10, the reaction is faster and almost 65 % conversion is achieved within 6 h. The selectivity for nopol is 100 % over all catalysts. The Sn-SBA-15 activity and selectivity to nopol increase with the reaction temperature from 25°C to 110°C. The comparison was also made with the Sn-impregnated SBA-15 samples. It was found that Sn-impregnated SBA-15 samples were found to be less active.

Table 1 Condensation of β -pinene and formaldehyde to nopol over Sn-SBA-15 catalysts

Sr. No	Catalyst	Total SA, to m^2g^{-1}	TPD, total acidity	Conv. (%)
1.	Sn-10	1127	0.30	65
2.	Sn-40	1042	0.23	58
3.	Sn-80	948	0.18	14
4.	SBA-15	906	-	4
5.	Sn-impregnated SBA-15-10	592	0.16	11
6.	recycle Sn-40	-	-	51

Procedure: 0.5 mmol of β -pinene, 1 mmol paraformaldehyde, 50mg catalyst, time= 6.0 h and temp. = 90°C

4. Conclusions

Sn-SBA-15 is the active catalyst for the Prins condensation of β -pinene and para formaldehyde at 90°C in the presence of toluene as solvent which is attributed to the medium acid sites of Sn^{4+} ions in the catalyst.

References

- Dijkmans, J.; Demol, J.; Houthoofd, K.; Huang, S.; Pontikes, Y.; Sels, B. Post-Synthesis Sn β : An Exploration of Synthesis Parameters and Catalysis. *J. Catal.* **2015**, 330, 545.

2. Moliner, M. State of the Art of Lewis Acid-Containing Zeolites: Lessons from Fine Chemistry to New Biomass Transformation Processes. *Dalton Trans.* **2014**, 43, 4197.
3. Conrad, S.; Verel, R.; Hammond, C.; Wolf, P.; Goltl, F.; Hermans, I. Silica-Grafted Sn IV Catalysts in Hydrogen-Transfer Reactions. *ChemCatChem* **2015**, 7, 3270. Gunther, W. R.; Wang, Y.; Ji, Y.; Michaelis, V. K.; Hunt, S. T.; Griffin, R. G.; Roman-Leshkov, Y. Sn-Beta Zeolites with Borate Salts Catalyse the Epimerization of Carbohydrates via an Intramolecular Carbon Shift. *Nat. Commun.* **2012**, 3, 1109.
4. Li, Y.-P.; Head-Gordon, M.; Bell, A. T. Analysis of the Reaction Mechanism and Catalytic Activity of Metal-Substituted Beta Zeolite for the Isomerization of Glucose to Fructose. *ACS Catal.* **2014**, 4, 1537.
5. Holm, M. S.; Saravanamurugan, S.; Taarning, E. Conversion of Sugars to Lactic Acid Derivatives Using Heterogeneous Zeotype Catalysts. *Science*. **2010**, 328 (5978), 602.
6. Tolborg, S.; Sadaba, I.; Osmundsen, C. M.; Fristrup, P.; Holm, M. S.; Taarning, E. Tin-Containing Silicates: Alkali Salts Improve Methyl Lactate Yield from Sugars. *ChemSusChem* **2015**, 8, 613.
7. Muller, P.; Wolf, P.; Hermans, I. Insights into the Complexity of Heterogeneous Liquid-Phase Catalysis : Case Study on the Cyclization of Citronellal. *ACS Catal.* **2016**, 6, 2760.
8. Ji, M.; Li, X.; Wang, J.; Zhu, J.; Zhou, L. Grafting SnCl₄ Catalyst as a Novel Solid Acid for the Synthesis of 3-Methylbut-3-En-1-ol. *Catal. Today* **2011**, 173, 28.
9. K. Bauer, D. Garbe, H. Surburg (Eds.), "Common Fragrance and Flavor Materials. Preparation Properties and Uses", VCH Verlagsgesellschaft, 59 (1990).
10. "Kirk-Othmer Encyclopedia of Chemical Technology", John Wiley, New York, (1997) Vol. 26.
11. Kriewitz, Ber. 32 (1899) 57.
12. J. P. Bain, J. Am. Chem. Soc. 68 (1946) 638.
 - a. L. Villa de P., E. Alarcon and C. Montes de Correa, Chem. Commun. (2002) 2654.
13. U. R. Pillai, E. Sahle-Demessie, Chem. Commun. (2004) 826.
14. T. M. Jyothi, M. L. Kaliya, M. Herskowitz and M. V. Landau, Chem. Commun. 11 (2001) 992.
15. T. M. Jyothi, M. L. Kaliya, M. V. Landau, V. Miron, Ange. Chemie. 40 (15) (2001) 2881.
16. Alda Luz Villa de P, Edwin Alarcon, Consuelo Montes de C, Catal. Today. 107-108 (2005) 942.
17. Shah P., Ramaswamy A.V., Lazar K., and Ramaswamy V. Direct hydrothermal synthesis of mesoporous Sn-SBA-15 materials under weak acidic condition. *Microporous and Mesoporous Materials*_100, (2007), 210-226.
18. Shah P., Ramaswamy A.V., Pasricha R., Lazar K. and Ramaswamy V. Synthesis and characterization of tin oxide-modified mesoporous SBA-15 molecular sieves and catalytic activity in transesterification reaction. *Appl. Catal. A: General*, 273 (2004) 239-248.