Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry
2023, 12 (1): 18-23
(International Peer Reviewed Journal)

Effect of MgO on supported PtSn Catalysts in n–Butane Dehydrogenation and Olefin Selectivity

Veldurthi Shashikala[1]* and B. Padma[2]

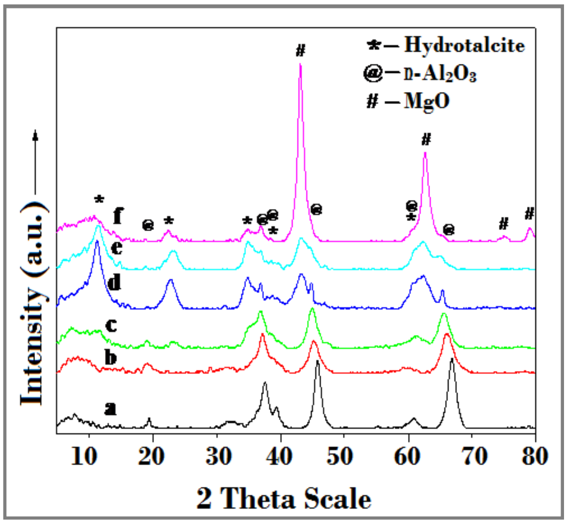
1. Department of Chemistry, University College for Women, Osmania University,
Hyderabad – 500097, Telangana, **INDIA**
2- Department of Chemistry, University Post Graduate College, Osmania University,
Hyderabad – 500003, Telangana, **INDIA**
Email: Shashikala_chem@osmania.ac.in

Accepted on 15th January, 2023

ABSTRACT

Magnesium oxide loading effect on n-butane dehydrogenation and selectivity of butenes was studied on a series of six catalysts PtSn0.5HTL, PtSn1HTL, PtSn2HTL, PtSn3HTL, PtSn7HTL and PtSn9HTL. H_2 *chemisorption studies reveal that the first four catalysts exhibit almost similar metal dispersion and metal particle sizes. However, butenes selectivity was increased with increase in the MgO loading in HTL support. This may be due to electronic effects caused by metal support interactions in PtSnxHTL catalysts. Increase in the basicity of the support increases the butenes selectivity.*

Graphical Abstract:



XRD patterns of PtSnxHTL catalysts after reduction.

Keywords: Dehydrogenation, MgO loading, Selectivity, Butenes.

INTRODUCTION

Synthesis of light olefins from dehydrogenation of lower alkanes (C1–C4) is an industrially important reaction. n-Butane dehydrogenation has been studied on PtSn catalysts supported on Al_2O_3 and $ZnAl_2O_4$ [**1–3**]. Supported bimetallic Pt-based catalysts are important for many hydrocarbon reactions. The promotion by Sn is known to increase the lifetime of these catalysts due to reduced deactivation by coking [**4, 5**]. It was found that the acidic nature of the support enhances the undesired products due to cracking, isomerization and polymerization reactions [**1-3**]. In our previous report n-butane dehydrogenation on PtSn supported on carbon modified magnesium oxide proved the decrease in undesired side products and increase in the selectivity of the n-olefins [**6**]. However, poor mechanical strength of the MgO ceases its industrial applications.

In our present work we have synthesized a series of six samples of Mg-Al hydrotalcite like materials with different MgO to Al_2O_3 ratio. PtSn active catalyst was impregnated on these supports and the effect of basicity on the dehydrogenation activity and n-olefin selectivity was studied. All the catalysts were characterized using XRD, BET – surface area, BJH – pore size, H_2 chemisorption studies. The activity of the catalysts was studied after reduction under H_2 flow.

MATERIALS AND METHODS

Preparation of xHTL supports and PtSn/HT catalysts: A series of six samples were prepared by fixing the Al_2O_3 mole ratio one and changing the mole ratio of MgO as 0.5, 1, 2, 3, 7 and 9 and are named as 0.5HTL, 1HTL, 2HTL, 3HTL, 7HTL and 9HTL respectively. Each sample was prepared as follows, corresponding weights of magnesium nitrate and aluminium nitrate salts were dissolved in distilled water and were co-precipitated with mixture of aqueous solution of sodium hydroxide (10% W/V) at a pH of 12 and treated hydrothermally at 333-338 K for 18 h. The gel so obtained was then washed with distilled water until the pH of the out let pH of 7, filtered, oven dried at 120°C for overnight and calcined at 550℃ for 18 h. Same weight ratio of PtSn were taken as reported elsewhere, i.e. 1 wt% platinum and 0.3 wt% Sn [**6**]. All the catalysts (PtSnxHTLs) were prepared by the incipient wetness impregnation of 1 wt% Pt and 0.3 wt% Sn from their aqueous solution of H_2PtCl_6 (Sigma Aldrich) and $SnCl_2$ (Sigma Aldrich). These catalysts were dried at 120°C for 12 h followed by calcination at 500°C for 5 h under N_2 atmosphere. Every catalyst was pre-reduced under H_2 flow.

Characterization: N_2 physisorption (BET surface area) was performed at a liquid nitrogen temperature using Micromeritics ASAP 2010 instrument. XRD was performed on an X-ray diffractometer (Rigaku, Japan). H_2 chemisorption was performed using BELCAT catalyst analyzer (BEJ, Japan) at 35°C. Amount of 0.4 g of each catalyst was pre-reduced at 550°C for 2 h under H_2 gas flow and evacuated for 30 min at the same temperature, which was cooled down to 35°C and then H_2 chemisorption was performed. The H/Pt atomic ratio was assumed to be 1.0 in order to calculate the dispersion of Pt.

Activity Evaluation: The activity of the catalysts was studied as reported elsewhere [**6**]. According to the procedure given there, the n-butane dehydrogenation activity tests of the PtSn0.5HTL, PtSn1HTL, PtSn2HTL, PtSn3HTL, PtSn7HTL and PtSn9HTL catalysts were conducted in a fixed-bed continuous flow reactor at 500°C temperature, 0.1 g of each catalyst was reduced in situ using the H_2 gas flow (50 $mL\ min^{-1}$) at 500°C for 2 h before the reaction. The feed gas mixture containing n-butane, H_2 and N_2 gasses with equal mole ratios (flow rate 30 $mL\ min^{-1}$) was allowed to flow through the catalyst under atmospheric pressure and a GHSV of 18,000 $mL\ g_{cat}\ h^{-1}$. The reaction products were analyzed using an on-line gas chromatography with Al_2O_3/KCl capillary column (I.D.: 0.53 mm, length: 50 m, Agilent Technologies).

RESULTS AND DISCUSSION

XRD, N_2 Physisorption, H_2 Chemisorption studies: X ray diffraction images of the reduced catalysts were given in the figure 1. Increase in the MgO phase in the expense of alumina via Mg – Al hydrotalcite phase could be clearly seen from the figure. η- Alumina phase (ICDD number 04-0875 with d spacing 1.4 (66.76), 1.97 (46.03), 2.40 (37.44)) with lower loadings of MgO was observed from sample a to d. In addition hydrotalcite phase was started forming in sample c and clear hydrotalcite (ICDD number 14.191 with d spacing 7.69(14.47), 3.88 (28.91), 2.58 (44.10)) structure was found in sample d and e. Additionally MgO (ICDD number 87-0651 with d spacing 2.43 (36.89), 2.11 (42.86), 1.49 (62.23)) peaks were started forming from sample d and intense peaks of MgO phase separated out in sample f. Because of memory effect hydrotalcite phase was observed even after reduction [7].

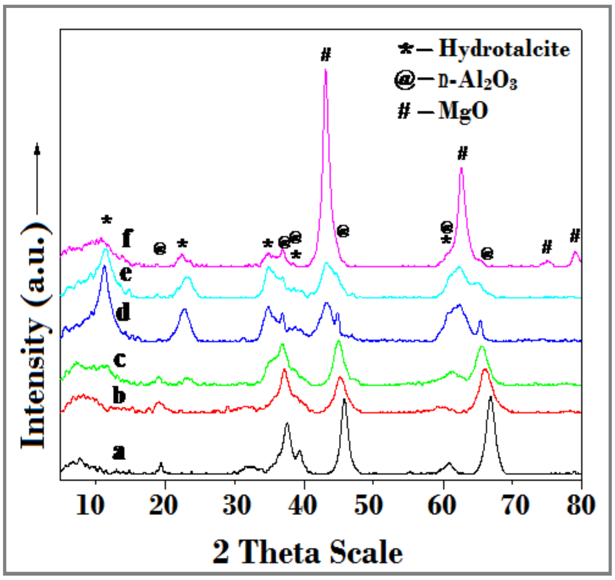


Figure 1. XRD patterns of PtSnxHTL catalysts after reduction.

a) PtSn0.5HTL b) PtSn0.5HTL c) PtSn0.5HTL d) PtSn0.5HTL e) PtSn0.5HTL f) PtSn0.5HTL

N_2 physisorption studies on all the catalysts after reduction, BET surface area, BJH Pore sizes and pore volume, were presented in table 1. Initially the surface area was increased from 192.49 m^2 g^{-1} of catalyst a to 235.47 m^2 g^{-1} of catalyst b. sudden decrease in surface area from Catalysts d to e and f was due to increase in the mole ratio of the magnesium oxide. Separation of the magnesium oxide phase can also be seen from the XRD patterns. Increase in the magnesium oxide phase obviously decreases the surface area. Irregularity in the pore size and pore volume of the catalysts from a to f are due to formation/interchanging of the phases with change in mole ratio of the alumina and magnesia. This decrease in surface area was in agreement with the mole ratio of MgO.

Table 1. N_2 physisorption studies of catalysts after reduction.
BET Surface area, Pore Volume and Pore size distribution

Code	Catalyst	BET SA (m^2 g^{-1})	Pore Vol (mL g^{-1})	Pore size (Å)
A	PtSn0.5HTL	192.49	56.71	63.08
B	PtSn1HTL	235.47	0.467	92.74
C	PtSn2HTL	191.76	0.059	64.44
D	PtSn3HTL	200.12	0.0511	57.26
E	PtSn7HTL	92.97	0.173	65.78
F	PtSn9HTL	49.37	80.02	201.86

Results of H_2 chemisorption studies, metal dispersion and metal particle sizes, were given in table 2. In catalysts from sample a to d the metal dispersion and the particle sizes are almost similar. Whereas decrease in the metal dispersion in the catalysts e and f may be due to the dissolution of MgO and the following co-precipitation during the impregnation step. This may cause partial encapsulation of metal particles by magnesium oxide [**6, 8**]. Other possibilities for low metal dispersion the MgO support are diffusion of metal particles into the support, and the presence of strong metal support interactions etc [**8-11**].

Table 2. H_2 Chemisorption studies of all the catalysts after reduction: Metal dispersion and metal particle size (nm)

Code	Catalyst	Metal dispersion	Metal particle size (nm)
a	PtSn05HTL	55.86	1.02
b	PtSn1HTL	52.78	1.13
c	PtSn2HTL	53.25	1.09
d	PtSn3HTL	51.22	1.34
e	PtSn7HTL	18.92	6.76
f	PtSn9HTL	01.31	35.42

Activity: Figure 2 presented the time on stream studies of all the catalysts at 500°C, with GHSV - 1800 mL g_{cat} h^{-1}, feed flow rate 30 mL min^{-1}. n – butane percent conversion and butenes selectivities were given in this figure. Decrease in conversion at the initial times was observed in all the catalysts. Dehydrogenation activity of PtSn on the supports with increase in the mole ratio of alumina to magnesia decrease in the conversion and increase in the butene selectivity was observed. Though the metal dispersion and the particle sizes on the catalysts were almost same in the catalysts PtSn0.5HTL to PtSn3HTL conversion of n-butane and the butenes sectivities were in the order of magnesium oxide loadings. Lower the loading of magnesium oxide higher the conversion vice versa. However the butane selectivities were increased with increase in the magnesium oxide loading. This may be explained with metal support interactions cause electronic effects which further effect on the n – butane conversion and the butenes selectivity. Further decrease in the conversion on catalysts e, PtSn7HTL and f, PtSn9HTL were due to decrease in the availability of active metal particles for the reaction. Activity comparison of the catalysts at 5th hour was given in figure 3. From this figure it was observed that increase in the basicity decreases the n – butane conversion in little proportions. And increase in selectivity of butenes was found to increase considerably by reducing undesired side reactions like cracking, isomesization and polymerization reactions.

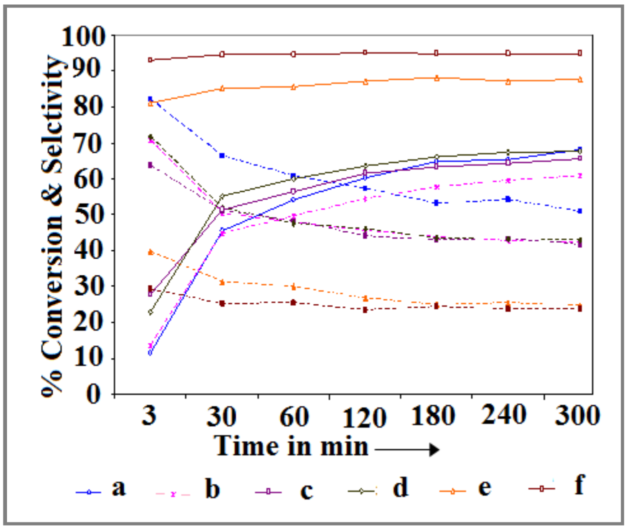


Figure 2. Time on stream studies: n – Butane dehydrogenation activity on all the catalysts (a to f) after reduction.% conversions - dotted lines, % Selectivities – solid lines.

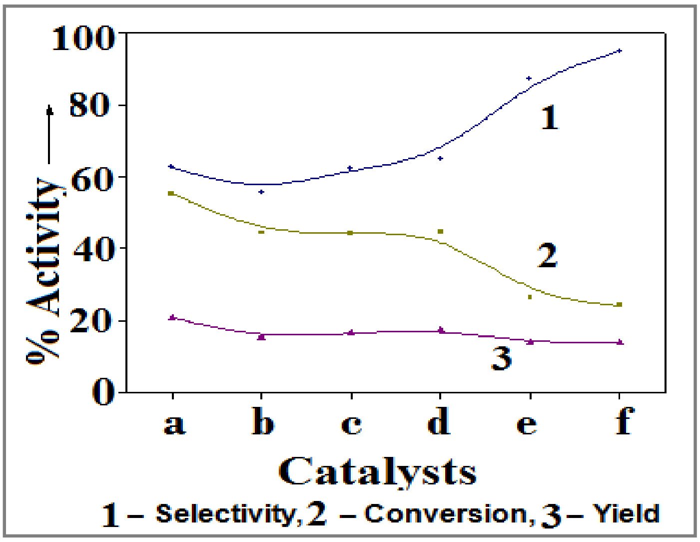


Figure 3. Comparison of activity of the catalysts at 300 min.

APPLICATION

Synthesis of light olefins from dehydrogenation of lower alkanes (C1–C4) is an industrially important reaction. Supported bimetallic Pt-based catalysts are important for many hydrocarbon reactions. Nature of support is very important in dehydrogenation reactions. Increase in selectivity of required products is more economic and many such industrial reactions.

CONCLUSION

From the activity evaluation and characterization studies performed on the catalysts PtSn0.5HTL, PtSn1HTL, PtSn2HTL, PtSn3HTL, PtSn7HTL and PtSn9HTL it was concluded that though the metal dispersion and metal particles sizes of the active catalyst were almost similar the n – butane dehydrogenation was depending on the nature of the support also. Increase in the basicity of the support increases the butenes selectivity.

ACKNOWLEDGEMENTS

This work was supported by the Energy Efficiency and Resources section of the Korea Institute of Energy Technology Evaluation and Planning, Seoul, South Korea.

REFERENCES

[1]. A. D. Ballarini, P. Zgolicz, I. M. J. Vilella, S. R. de Miguel, A. A. Castro, O. A. Scelza, n-Butane dehydrogenation on Pt, PtSn and PtGe supported on γ-Al_2O_3 deposited on spheres of α-Al_2O_3 by washcoating, *Appl Catal A.* **2010**, 381, 83–91.

[2]. S. A. Bocanegra, A. G. Ruiz, S. R. de Miguel, O. A. Scelza, Performance of PtSn catalysts supported on MAl_2O_4 (M: Mg or Zn) in *n*-butane dehydrogenation: characterization of the metallic phase, *Appl Catal* A, **2004**, 277, 11–22.

[3]. C. Larese, J. M. Campos-Martin, J. J. Calvino, G. Blanco, J. L. G. Fierro, Z. C. Kang, Alumina- and Alumina–Zirconia-Supported PtSn Bimetallics: Microstructure and Performance for the *n*-Butane ODH Reaction, *J Catal.*, **2002**, 208, 467–478

[4]. R. Butch, Platinum-tin reforming catalysts: II. Activity and selectivity in hydrocarbon reactions, *J. Catal.*, **1981**, 71, 348.

[5]. O. A. Bari, A. Holmen, E.A. Blekkan, Propane Dehydrogenation over Supported Platinum Catalysts: The Influence of Tin on the Coking Properties, *Stud. Surf. Sci. Catal*., **1994**, 88, 519.

[6]. Veldurthi Shashikala, Heon Jung, Chae-Ho Shin, Hyoung-Lim Koh, Kwang-Deog Jung, n-Butane Dehydrogenation on PtSn/Carbon Modified MgO Catalysts, Veldurthi Shashikala, Heon Jung, Chae-Ho Shin, Hyoung-Lim Koh, Kwang-Deog Jung, *Catal Lett.*, **2013**, 143, 251-256.

[7]. A.H. Padmasri, A. Venugopal, V. Siva Kumar, V. Shashikala, B. M. Nagaraja, P. Seethara mulu, B. Sreedhar, B. David Raju, P. Kanta Rao, K. S. Rama Rao, Role of hydrotalcite precursors as supports for Pd catalysts in hydrodechlorination of CCl_2F_2, *Journal of Molecular Catalysis A: Chemical*, **2004**, 223, 329–337.

[8]. M. A. Aramendia, J. A. Benitez, V. Borau, C. Jimenez, J. M. Marinas, J. R. Ruiz, F. Urbano, Study of MgO and Pt/MgO Systems by XRD, TPR, and ^{1}H MAS NMR, *Langmuir*, **1999**, 15, 1192–1197

[9]. J. K. A Clarke, M. J. Bradley, L. A. J. Garvie, A. J. Craven, T. Baird, Pt/MgO as catalyst for hydrogenolysis reactions of C5 and C6 hydrocarbons: evidence for metal-support interactions, *J Catal.*, **1993**, 143, 122–137.

[10]. N. Nava, M. A. Morales, W. Vanoni, J. A. Toledo, E. B. Saitovitch, T. Viveros, Structural behavior of Pt–Sn supported on MgO, *Hyperfine Interact*, **2001**, 134, 81–92.

[11]. L. Bednarova, C. E. Lyman, E. Rytter, A. Holmen, Effect of support on the size and composition of highly dispersed Pt–Sn particles, *J Catal.*, **2002**, 211, 335–346.