

## Synthesis of SBA-15 and Cs HPW for Trans-Esterification Reactions for Biodiesel Production

Dawn SS<sup>1</sup>, Anitha A<sup>2</sup>, Vikash Kumar, Rajat Jain, Vivek Kumar

Research Scholar, <sup>1,2</sup> Department Of Chemical Engineering, Sathyabama University

### Abstract

Equipment corrosion, complex product separation, disposal of high amount of corrosive mineral acids and difficulty in catalyst recovery has led to the replacement of homogeneous catalyst recovery with alternate heterogeneous catalyst system. Solid acid catalysts have proved to be a better substitute for Acylation and Alkylation reactions. Heteropolyacids particularly Cs-substituted keggin-type12- Tungstophosphoric acid was synthesized. SBA-15, owing to its low reactivity with the Keggin anions best suited to support Cs-HPW was prepared. Both catalyst and support were characterized for their surface area, pore volume and pore size distribution using BET method. The catalyst system made will be used for trans esterification reactions.

**Key words:** Keggin, Solid Acids, Trans-Esterification Reaction, Cs-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, SBA-15

### I. INTRODUCTION

Stringent environmental regulations, corrosive nature, high toxicity difficulties have led to the replacement of homogeneous acid catalysts with solid acid catalysts for Acylation, Alkylation, Esterification and Isomerisation reactions (1,2). Amongst the several solid acid catalysts, heteropolyacids with Keggin structures have received significant importance due to their simple preparation and strong acidity. Do deca-tungstophosphoric acid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (hereafter HPW) is the strongest acid among the heteropolyacids. Very low surface area and high affinity for polar media limits the potential catalytic performance of HPW. Attempts to overcome these drawbacks include partial neutralization of protons in HPW in different cation like Cs<sup>+</sup> and NH<sub>4</sub><sup>+</sup> in corresponding salts(2,3), embedding of HPW on support of HPW on high surface oxides(6-12). Partial neutralization of HPW with Cs salts exhibiting Cs/W ratio of >=2, makes the catalyst microporous thereby increasing the surface area. Though Cs-HPW salt formed exhibiting high catalytic activity at ratios between 2.0 and 2.5 they form colloidal suspensions in polar media causing filtration problems. To overcome this drawback Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> salt is stabilised in a porous oxide matrix. Investigation over the years recommend higher loading of catalytic phase on the porous oxide matrix with little pore blockage and improved control of its location. Large pore diameter (7-9nm) and comparable internal surface area makes SBA-15 a proper support for CsHPW relative to MCM-41(2-3 nm) and silica gel.

While only few report on CsHPW supported on SBA-15 used as catalysts for Acylation, Alkylation and Isomerisation reactions are available no reports on the same catalyst system for trans-esterification reactions are available.

The industrial process of biodiesel productions is usually carried out by heating an excess of alcohol usually methanol(or) ethanol with vegetable oils under different conditions in the presence of an inorganic catalyst. This chemical process is called Transesterification or Alcoholysis. The inorganic catalysts used can be acidic or basic in nature. Conventionally homogeneous acidic and basic catalysts like HCl, H<sub>2</sub>SO<sub>4</sub> and NaOH, KOH are used. The difficulties with these catalysts necessitates its replacement with a heterogenous catalyst system. The aim is to test the heterogeneous catalyst system for trans-esterification reactions used for bio diesel production. However this paper highlights the procedure for the synthesis of Cs-substituted HPW and SBA-15.

### II. EXPERIMENTAL

#### A. Preparation Of Catalyst:

The bulk CsHPW with Cs/W ratio between 1.5 and 2.5 was prepared from aqueous solution of Cs<sub>2</sub>CO<sub>3</sub> (Aldrich) and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Aldrich) by titration according to a previously reported procedure(5,23). An appropriate amount of aqueous solution of Cs<sub>2</sub>CO<sub>3</sub> at a rate of 0.1 ml/min is added to prepared HPW with stirring. The milky colloidal solution was aged for 20 hrs with

constant stirring and then evaporated at 318K. The remaining solid was finally calcined in air at 573K for 2 hrs.

#### B. Preparation of Support:

SBA-15 employed in this study was prepared following the procedure described elsewhere(24) via crystallization from an acidic aqueous solution of polyethylene glycol-block-poly(propylene glycol)-block poly(ethylene glycol) co polymer (Mavg=5800, hereafter P123) and TEOS 2g of surfactant (P123) was dissolved in 64 ml water and 10.5 ml conc. HCl by stirring for 1 hr. 4.2 g of tetra ethylene ortho silicate was then added. The contents were aged for 24 hrs at 30°C with stirring. During ageing at critical miscelle temperature, the typical liquid crystals of P123 get associated to form a miscelle. As the temperature is raised propylene oxide becomes hydrophilic relative with ethylene oxide and curls the miscelle to form a sphere. Silica is then condensed on the surface of the template. The sample was then placed in hot air oven for 24 hours. The contents were filtered, washed with excess water and dried over night. The dry sample was calcined at 100° C for 2 hrs at the rate of 15 deg per minute, 300° C for 2 hrs at the rate of 1 deg per minute, 400° C for 2 hrs at the rate 1 deg per minute, 500° C for 6 hrs at the rate of 1 deg per minute. Calcination is done in order to remove the surfactant leaving the silica with the required structure.

### III. CHARACTERISATION OF THE MATERIALS

Surface area and pore volume were derived from N<sub>2</sub> adsorption-desorption isotherms using the conventional BET method, for SBA-15 and bulk CsHPW. Pore size distribution was also calculated from the desorption branch of the N<sub>2</sub>-sorption isotherm. The sample was degassed under vacuum for 2 hrs at 373K.

### IV. CONCLUSION

Cs-substituted tungsto phosphoric acid as a catalyst and mesoporous siliceous SBA-15 as support were synthesized. The catalyst prepared will be loaded internally, externally and in combination on the support (SBA-15). A Comparative study on the Performance of acid catalysed Transesterification reactions used for Biodiesel Production will be done for HPW, Cs-HPW, Cs-HPW loaded internally on SBA-15, Cs-HPW loaded externally on SBA-15 and Cs-HPW loaded internally and externally on SBA-15.

### REFERENCES

- [1] Y.Izumi, K.Vrabe, M.Onaka, Zeolite, clay and heteropoly acid in organic reactions, VCH, New York, 1992, P.99
- [2] M.Misono, chem.. common, (2001), 1141
- [3] S.Tatematsu, T. Hibi, T. Okuhara, M.Misono, chem. Lett(1980)865.
- [4] A.Kukovecz, Z.Balogi, Z.Konya, M.Toha, P.Lentz, S.I.Niwa, F.Mizukami, Molnar, J.B.Nagy, I.Kiricsi, Appl. Catal.a 228(2002)83
- [5] A.Lapkin, B.Bozkaya, T.mays, L.Borello, K.edle, B.Crittenden, catal.today 81(2003)611
- [6] K.M.Rao, R.gohetto, A.Ianibello, A. Zecchina, J.catal.119(1989)512
- [7] L.R.Pizzio, C.V.Caceres, M.N.Blanco, Appl.catal.A, Gren 167(1998)283
- [8] A.Bielansi, A.lubanska, J.Pozniczek, A.Micek-Ilnicka, appl catal.A: Gen 238(2003)239
- [9] L.R.Pizzio, P.G.Vazouez, C.V.Caceres, M.N.Blanco, Appl. Catal.A: Gen 256(2003)125
- [10] F.Marme, G.Coudurier, J.C.Edwards, Appl.catal.A: Gen.183(1999)1
- [11] J.F.Knifton, J.C.Edwards, Appl. Catal. A: Gen.183(1999)1
- [12] P.Vazouez, L.Pizzio, G. Romanelli, J.Autino, C. caceres, M.Blanco, Appl.catal. A: gen 235(2002)233.
- [13] S.Tatematsu, T.Hibi, T.Okuhara, M.Misono, chem.. Lett. (1984)- 865- 868
- [14] T.okuhara, T.Nishimura, H. Watanalie, M.Misono, J.Mol.catal.A.74(1992) 247-256
- [15] L.Vnadman, M.V. Landan, M. Herskowitz, V. Ezasky, M. Talianker,
- [16] S.Nikitenko, Y.Koltypin, A. Gedanken, J.Catal.2B(2003)163-175