



STABLE, REUSABLE MoO₃/ZrO₂ SOLID ACID CATALYST FOR THE SYNTHESIS OF DIPHENYLMETHANE VIA FRIEDEL-CRAFT ALKYLATION UNDER SOLVENT FREE CONDITION

VijayaCharanGuguloth, BattuSatyanaryana *

Department of Chemistry, University College of Science, Osmania University, Hyderabad, Telangana, India.

Email: satyambchem@yahoo.co.in. Contact no: +91 9440065576

ABSTRACT: A simple method is described for the synthesis of substituted diphenylmethane derivatives in excellent yields by Friedel-Craft alkylation reaction under solvent free condition using molybdenum promoted ZrO₂ solid acid catalyst at 80°C. The MoO₃/ZrO₂ catalyst has been prepared from using impregnation method followed by calcination at 923K for 6 hours in air atmosphere. This catalyst was characterized by various techniques such as SEM, XRD, FTIR, UV DRS, and BET surface area. Zirconia has both acidic and basic properties which can be altered by incorporating suitable promoter atom like Mo which in turn increase the surface area thereby enhance the surface acidity. Impregnation of Mo ions shows a strong influence on phase modification of zirconia from thermodynamically more stable monoclinic to metastable tetragonal phase. Incorporation of promoter Mo will stabilize tetragonal phase which is active in catalysing reactions. In Friedel-Craft alkylation MoO₃/ZrO₂ catalyst was found to be stable, efficient and environmentally friendly, easily recovered by filtration, higher yield of product and can be reusable efficiently.

Keywords: Heterogeneous catalyst, MoO₃/ZrO₂, Solvent-free condition, Friedel-Craft alkylation, green chemistry.

Introduction:

In 1887 Charles Friedel and James Mason Crafts isolated amyl benzene after the treatment of amyl chloride with AlCl₃ in benzene^I. In the last decade, catalysts acting through hydrogen bond interactions have attracted great interest, and they represent a noteworthy part of the organocatalytic field.^{II-IV} One of the main families of organocatalytic structure included in this large group are the thiourea/urea derivatives, and many efforts have been devoted to the design and synthesis of new ones as appropriate catalysts in a large number of interesting processes.^V In the last few years, we have focused part of our investigation on the development of new thiourea-catalysed methods.^{VI} The Friedel-Crafts alkylation reaction has received the attention of a great number of research groups, becoming an efficient tool for carbon-carbon bond formation.^{VII} Diphenylmethane and its derivatives generally prepared via Friedel-Crafts benzoylation reactions are industrially important compounds used as

7	MoO ₃ /ZrO ₂	water	4.5	90
8	ZrO ₂	Neat	5.5	60
9	MoO ₃	Neat	6	75

^aYield refers to isolated products

EXPERIMENTAL:

Catalyst Preparation:

Zirconium Hydroxide is prepared from aqueous solutions of ZrOCl₂.8H₂O and NH₂OH, dried at 120°C 3% wt. of Ammonium heptamolybdate is dissolved in oxalic acid until clear solution is obtained, to this solution 5g of finely powdered hydrous zirconia is added. Excess water is evaporated on water bath and the resulting sample was oven dried at 393K for 24 h and calcined at 923k for 6h in air atmosphere. Pure zirconia was prepared by calcining hydrous zirconia at 923k for 6h for comparison.

Catalyst characterization:

The powder X-ray diffraction patterns were recorded on XRD 7000 Shimadzu instrument by using nickel filtered CuK_α radiation and scintillation counter detector. The scattered intensity data were recorded from 2θ values scanning range from 10 to 80° by scanning at scan speed of 2.000 (deg/min), sampling pitch 0.0200 deg and preset time .60 (sec). Debye-Scherrer equation is used to determine average crystallite size of the particle.

Scanning Electron Microscope (SEM) investigations performed on a Hitachi model SEM-EDS S3700N scanning electron microscopy at an applied voltage of 15.0 KV.

An FTIR spectrum of the catalyst was recorded on a BRUKEROPTICS model: TENSOR 27 spectrometer at ambient conditions. Self-supporting KBr pellets containing the catalyst samples were used to scan the spectra.

The BET surface area of the catalyst was determined by N₂ physisorption at 77 K by taking 0.162 nm² as the area of cross section of the N₂ molecule. The N₂ BET surface area of various samples were determined after H₂ reduction and subsequent O₂ uptake measurements. These samples were of Course evacuated for longer times in order to remove any preadsorbed O₂ in the pores of the catalyst particles.


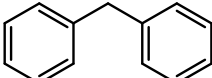
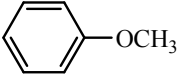
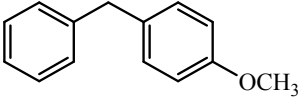
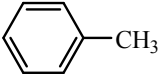
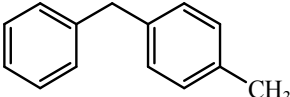

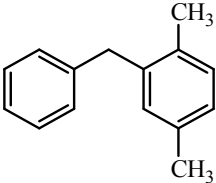
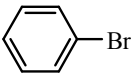
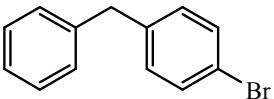
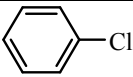
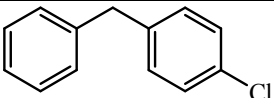
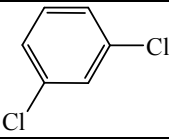
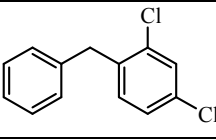
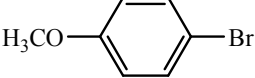
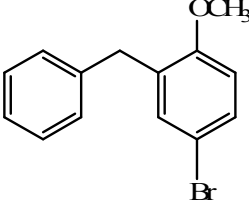
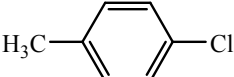
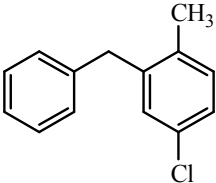
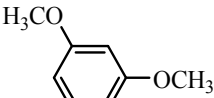
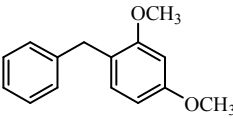
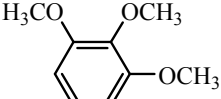
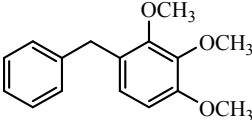
Catalyst activity:

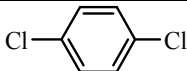
Diphenyl methane is a valuable product in chemical industry which is also known as benzyl benzene, is used in organic synthesis, the compound is also an intermediate which is used in the synthesis of benzophenone. Zirconia has both acidic and basic properties. Zirconia's acidic and basic properties can be altered by incorporating suitable promoter atom. Incorporation of promoter atoms like molybdenum, tungsten, iron, alumina and bismuth enhance the surface acidity. As part of my research program we have developed a simple and efficient procedure for Friedel-Crafts alkylation's for the synthesis of Diphenylmethanes by using an efficient catalyst, molybdenum supported zirconia in benzylation of benzene.

General procedure for the synthesis of a few substituted diphenylmethane in Friedel-Craft alkylation:

A mixture of benzyl chloride (1 g), benzene/substituted benzenes (excess) and catalyst (0.1g) was at 80°C in a round bottom flask. The progress of the reaction was monitored by TLC, after complete conversion of the reactant the catalyst was filtered and the pure compound is obtained and chromatographed on silica gel column by using the solvent Hexane. In a typical experiment, substituted benzenes and benzyl chloride were reacted in presence of MoO₃/ZrO₂ in solvent free condition as shown in scheme-I. The progress of the reaction was monitored by thin layer chromatography (TLC).

Table 1Catalytic friedel craft alkylation of diphenylmethane using MoO₃/ZrO₂

Entry	Reactant	Product	Reaction Time	Yield (%)
A			3hrs	100
B			1hr 45min	98
C			2hr 30min	95
D			2hrs	93
E			2hr 45min	93
F			1hr 30min	95
G			1hr	90
H			3hr 15min	92
I			3hr 45min	90
J			4hrs	92
K			4hr 20min	90

L		No reaction	-----	-----
---	---	-------------	-------	-------

Results and discussion:

The X-ray diffraction patterns of ZrO_2 and molybdenum promoted ZrO_2 samples calcined at 923 K are presented in fig 1.

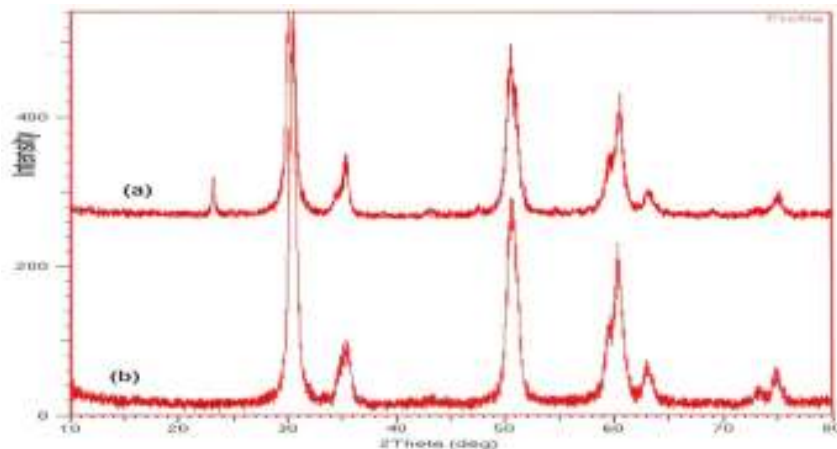


Fig .1X-ray diffraction patterns of (a) 3% MoO_3/ZrO_2 (b) Pure ZrO_2

Most of the XRD studies on metal oxide zirconia catalysts revealed the formation of tetragonal zirconia polymorphs after incorporation of metal atoms. The XRD studies on hydrous zirconia sample calcined at 923K and compared with metal oxide zirconia sample calcined at the same temperature. The hydrous zirconia sample exhibited poor crystallinity with the mixture of monoclinic and tetragonal phases. On the other hand the molybdenum promoted zirconia sample exhibited prominent lines due to tetragonal phase, indicating that the impregnated molybdenum ions shows a strong influence on the phase modification of zirconia from thermodynamically more stable monoclinic to the metastable tetragonal phase. It was also observed that the molybdenum promoted zirconia shows smaller crystallite sizes when compared to the unpromoted zirconia. It was confirmed from XRD results that the incorporated molybdenum atom related the formation of larger crystallite of zirconia and stabilize them in the metastable tetragonal phase. The unpromoted zirconia normally leads to the formation of thermodynamically more stable monoclinic forms with larger crystallites. Both the samples exhibit typical tetragonal phase of zirconia that is observed from the figure2. Pure ZrO_2 exhibits mixture of monoclinic and tetragonal phases but incorporation of promoter atom molybdenum into the zirconia lattice stabilizes the tetragonal phase^{XXI}. It is observed that sulphate ion promoted zirconia exhibits smaller crystallite size and more tetragonal phase because of which it is active in catalysis^{XXII}.

In this study both the samples ZrO_2 and molybdenum promoted ZrO_2 exhibit only the tetragonal phase but the average crystallize; size of the samples is almost same. Pure ZrO_2 and molybdenum promoted ZrO_2 do not have the same activity in friedel craft alkylation, substituted diphenylmethane derivatives in friedel craft alkylation are obtained at 80-85⁰C in 1hr 30 min - 4.0hours' time over molybdenum promoted ZrO_2 where as pure zirconia is totally inactive. Bismuth, tungsten and selenium promoted catalysts also exhibit tetragonal phase but the activity is not comparable with that of molybdenum promoted ZrO_2 catalyst.

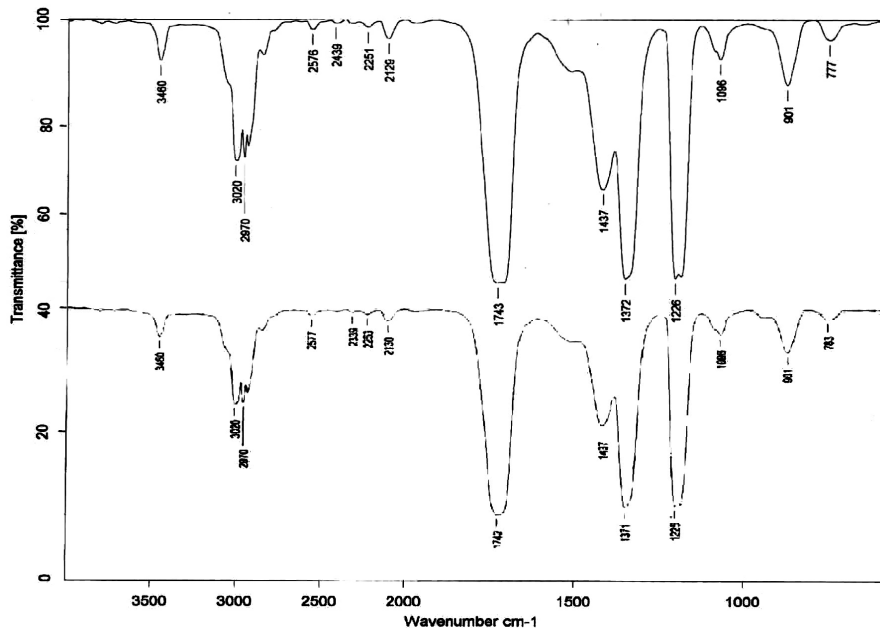


Fig.3: A. IR of pure Zirconia B. IR of $\text{MoO}_3/\text{ZrO}_2$

After calcination at 923K, the FTIR spectrum exhibits two shoulders at 1096 and 901 cm^{-1} the 3460 cm^{-1} band intensity corresponding to stretching vibration of hydroxyl groups decreased strongly and better resolved bands are observed clearly at 783, 557 cm^{-1} which are characteristic of crystalline zirconia. From this it is concluded that, because of calcination, condensation of hydroxyl groups of $\text{Zr}(\text{OH})_2$ occurred, leading to a crystallized sample of the species.

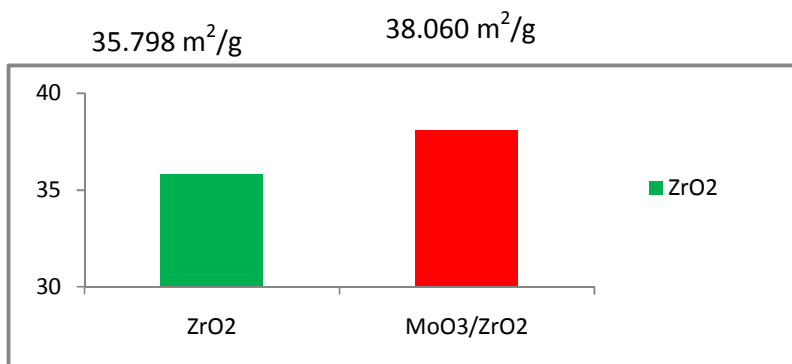


Fig 4: Surface area of ZrO_2 and $\text{MoO}_3/\text{ZrO}_2$

The specific surface area of the sample calcined at 923K for 6 hours, shows that the presence of $\text{MoO}_3/\text{ZrO}_2$, strongly influences the surface area in comparison with the pure ZrO_2 . The specific surface area of $\text{MoO}_3/\text{ZrO}_2$ samples are much larger than that of pure ZrO_2 calcined at the same temperature showing that increase in surface area increases surface acidity of the

catalyst. It is observed from the fig 4. Surface area of pure zirconia was found to be 35.798 m²/g and molybdenum promoted zirconia was 38.060m²/g it indicates that incorporation of molybdenum into the lattice of zirconia increases the surface area increasing the surface acidity and decreases the average particle size.

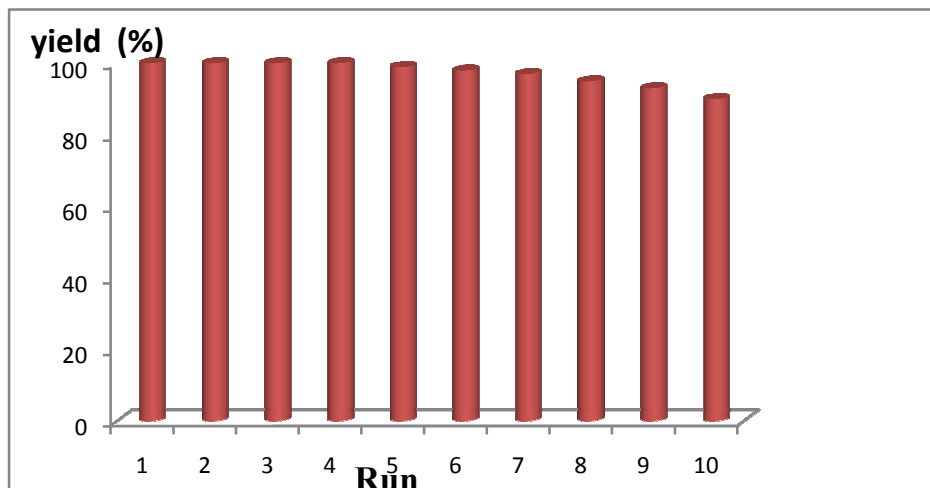


Figure 5: Yield comparison bar chart

Figure 5 Catalytic activity of 3% MoO₃/ZrO₂ in 10 cycles for Friedel-Craft alkylation. Furthermore, structural elucidation of MoO₃/ZrO₂ was performed in detail using X-ray diffraction (XRD) technique after use for five runs. XRD results for the catalyst (Figure 6) showed an ordered meso structure in large domains with no distinct defects observed for these reaction conditions. Three well-resolved diffraction peaks in the 2θ range of 0.8–20 were observed for MoO₃/ZrO₂ as an organic–inorganic hybrid material. However, the ordered structure of MoO₃/ZrO₂ remained intact, as supported by the XRD results. The patterns feature distinct Bragg peaks in the 2θ range of 20–50°, which can be indexed to (1 0 0), (1 1 0), and (2 0 0) reflections of a two-dimensional hexagonal structure of MoO₃/ZrO₂ material. The presence of these peaks indicates that the crystallographic ordering of the mesopores in MoO₃/ZrO₂ was retained after its use as a catalyst in five runs.

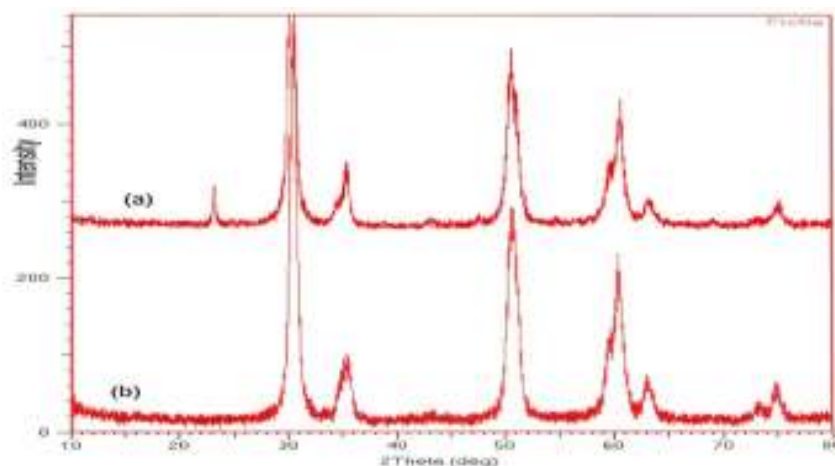


Fig .6 : X-ray diffraction patterns of (a) 3% MoO₃/ ZrO₂ (b) Pure ZrO₂

Characterization of diphenylmethane: Spectral data

Diphenylmethane (IIIa):IR (KBr, cm^{-1}): 3462, 2970, 1742, 1371, 1225, 907, 697.¹HNMR (CDCl_3 , 400MHz) δ = 4.5 (s, 2 H), 7.7 (m, 6H), 7.9 (m, 4H).

1-benzyl-4-methoxybenzene (IIIb):IR (KBr, cm^{-1}): 3458, 2970, 1740, 1368, 1215, 1033, 698.¹HNMR (CDCl_3 , 400MHz) δ = 3.9(s, 3 H), 4.1 (s, 2 H), 7.1-7.4(m, 9H).

1-benzyl-4-methylbenzene (IIIc):IR (KBr, cm^{-1}): 3461, 2969, 1742, 1371, 1225, 907, 726.¹HNMR (CDCl_3 , 400MHz) δ = 2.4 (s, 3 H), 4.0(s, 2 H), 7.1-7.3 (m, 9H).

2-benzyl-1, 4-dimethylbenzene (III d):IR (KBr, cm^{-1}): 3461, 2969, 1742, 1371, 1225, 906, 729.¹HNMR (CDCl_3 , 400MHz) δ = 2.3 (s, 3 H), 2.4 (s, 3 H), 4.1(s, 2 H), 7.1-7.5(m, 8H).

1-benzyl-4-bromobenzene (IIIe):IR (KBr, cm^{-1}): 3344, 2970, 1740, 1369, 1215, 899.¹HNMR (CDCl_3 , 400MHz) δ = 3.95(s, 2 H), 7.1-7.6(m, 9H).

1-benzyl-4-chlorobenzene (III f):IR (KBr, cm^{-1}):3451, 2969, 1742, 1371, 1224, and 1024.¹HNMR (CDCl_3 , 400MHz) δ = 4.6(s, 2 H), 7.1-7.5(m, 9H).

1-benzyl-2, 4-dichlorobenzene (IIIg):IR (KBr, cm^{-1}): 3452, 3003, 2970, 1740, 1369, 1215, and 1024.¹HNMR (CDCl_3 , 400MHz) δ = 4.1(s, 2 H), 7.1-7.4(m, 8H).

1-benzyl-4-bromo-2-methoxybenzene (IIIh):IR (KBr, cm^{-1}): 3458, 2970, 1740, 1486, 1368, 1231, 1029, 803, 697. ¹HNMR (CDCl_3 , 400MHz) δ = 3.8 (s, 3 H), 3.9(s, 2 H), 6.7(d, 2H), 7.1-7.3(m, 6H).

2-benzyl-4-chloro-1-methylbenzene (IIIi):IR (KBr, cm^{-1}): 3449, 2969, 1742, 1371, 1224, and 1024.¹HNMR (CDCl_3 , 400MHz) δ = 2.4 (s, 3 H), 4.1(s, 2 H), 6.9-7.4(m, 8H).

1-benzyl-2, 4-dimethoxybenzene (IIIj):IR (KBr, cm^{-1}):3447, 2969, 1741, 1371, 1224, 1024.¹HNMR (CDCl_3 , 400MHz) δ = 3.85 (s, 6 H), 4.1(s, 2 H), 6.5-6.6(m, 3H), 7.1-7.3(m, 5H).

1-benzyl-2, 3, 4-trimethoxybenzene (IIIk):IR (KBr, cm^{-1}): 3461, 3008, 2970, 1741, 1370, 1225, 906, 726. ¹HNMR (CDCl_3 , 400MHz) δ = 3.75 (s, 3 H), 3.80 (s, 3 H), 3.95 (s, 3 H), 4.00(s, 2 H), 6.80 (d, 1 H), 7.1 (t, 2 H), 7.3(m, 4H).

Conclusion:

The following conclusions can be drawn from the above study

1. Promoted catalyst will have higher surface area and higher acidity compared to ZrO_2 . Incorporation of promoter molybdenum oxide will stabilize tetragonal phase which is active in catalyzing the reactions.
2. $\text{MoO}_3/\text{ZrO}_2$ catalyst is environmentally friendly, easy to prepare, water tolerant and can be recycled.
3. Zirconia shows very little activity in benzylation of benzene, however its catalytic activity increased drastically because of impregnating molybdenum oxide into the lattice of Zirconia, higher activity of molybdenum promoted ZrO_2 catalyst is due to uniform distribution of spherical particles all over the zirconia lattice and creating lattice defects by changing surface and bulk properties.
4. A Green heterogeneous catalyst is developed for benzylation of benzenes to obtain diphenylmethanes in good to excellent yields.
5. Metal oxide solid acid supported zirconia catalysts like Se, W, Bi, Mo, Al, Fe, and Zn are much more promising for various organic reactions of practical significance and are expected to gain great interest in the coming years.

Acknowledgments:

One of the authors GVC thanks to University Grants Commission (UGC) for financial support of this work.

References:

- I. Friedel, C. and Crafts, J. M., *J. Chem. Soc.*, 32,(1877), 725.
- II. Kerstin, E.-E. and Berkessel, A., *Top. Curr. Chem.*, 291, (2010), 01.
- III. a) List, B. (Ed.) Springer, Heidelberg, Germany, 291, (2010). b) Dalko, P. I. (Ed.), *Catalysts, Reactions, and Applications*, Set. John Wiley & Sons., (2013), 3.
- IV. a) de-Figueiredo, R. M., and Christmann, M., *Eur. J. Org. Chem.*, (2007), 2575. b) Marques-Lopez, E., Herrera, R. P., and Christmann, M., (2010). c) Aleman, J., and Cabrera, S., *Chem. Soc. Rev.*, 42,(2013), 774.
- V. a) Schreiner, P. R., *Chem. Soc. Rev.*, 32,(2003), 289. b) Takemoto, Y., *Org. Biomol. Chem.*, 3,(2005), 4299. c) Connon, S. J., (2006), 5418.
- VI. a) Herrera, R. P., Sgarzani, V., Bernardi, L., and Ricci, A., *Angew. Chem.*, 44, (2005), 6576. b) Pettersen, D., Herrera, R. P., Bernardi, L., Fini, F., Sgarzani, V., Fernandez, R., and Ricci, A., *Synlett.*, 2,(2006), 239. c) Bernardi, L., Fini, F., Herrera, R. P., Ricci, A., and Sgarzani, V., *Tetrahedron.*, 62, (2006), 375. d) Herrera, R. P., Monge, D., Martín-Zamora, E., Fernandez, R., and Lassaletta, J. M., *Org. Lett.*, 9, (2007), 3303. e) Alcaine, A., Marques-Lopez, E., Merino, P., Tejero, T., and Herrera, R. P., *Org. Biomol. Chem.*, 9, (2011), 2777. f) Marques-Lopez, E., Alcaine, A., Tejero, T., and Raquel P. H., *Eur. J. Org. Chem.*, (2011), 3700.
- VII. a) Marques-Lopez, E., Diez -Martinez, A., Merino, P., and Herrera, R. P., *Curr. Org. Chem.*, 13, (2009), 1585. b) You, S., Cai, Q., and Zeng, M. (2009), 2190. c) Terrasson, V., De Figueiredo, R. M., and Campagne, J. M., *Eur. J. Org. Chem.*, (2010), 2552.
- VIII. Bastock, T. W., and Clark, J. H. *Speciality chemicals. Elsevier Applied Science, London and New York*, (1991), 383.
- IX. Khadilkar, B. M., and Borkar, S. D., *J. Chem. Technol. Biotechnol.*, 71,(1998), 209.
- X. Commandeur, R., Berger, N., Jay, P., and Kervennal, J., *Eur. Pat. Appl.*, EP 0440 (1991), 986.
- XI. Harford, A. D., and Vernon, H. W. *US Patent* 2, (2008), 897, 112, 1956.
- XII. Douglas, A., and Vernon, H. W. *British Petroleum Co. Ltd.*, DE-AS, 1, (1957), 35.
- XIII. Moshinskaya, N. K., Olifer V. S., and Zhuoiev, L. I., SU 137, (1960), 993.
- XIV. Siggel, E., *US Patent*, 2, (1952), 710, 849.
- XV. Stewart, M. I., and Carlson, O. K., *FMC Corp., US Patent*, 3, (1967), 593, 640.
- XVI. Leus, A. M., Ashland Oil and Refining Co., *US Patent*, 3, (1967), 529.
- XVII. Sato, Y., Yida, I., and Shimizu, *DE-OS*, 2, (1972), 210.
- XVIII. Olah, G. A., *Angew. Chem.*, 12, (1973), 173.
- XIX. Hu, X., Chuah, G. K., and Jaenicke, S., *Appl. Catal. A-Gen.*, 217, (2001), 1.
- XX. Sebti, S., Tahir, R., Nazih, R., and Boulaajaj, S., *Appl. Catal. A-Gen.*, 218, (2001), 25.
- XXI. Liu, P. N., Zhou, Z. Y., and Lau, C. P., *Chem. Eur. J.*, 13, (2007), 8610.
- XXII. Noji, M., Konno, Y., and Ishii, K., *J. Org. Chem.*, 72,(2007), 5161.

Received on May 01, 2019.