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International Conference on Environment 2010 green technologies



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13-15th December 2010
Parkroyal Hotel, Penang



LIQUID PHASE ALKYLATION OF BENZENE WITH 1-DECENE OVER SILICA SUPPORTED $H_{14}[NaP_5W_{30}O_{110}]$ AS A GREEN AND REUSABLE CATALYST

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ABSTRACT

Alkylation of benzene with 1-decene was investigated for the production of linear alkylbenzene (LAB), using silica supported and bulk preyssler and keggin type heteropoly acids. Silica supported $H_{14}[NaP_5W_{30}O_{110}]$ and $H_3PW_{12}O_{40}$ catalysts with 40% loading were calcinated at 240 and 300°C, respectively. It is found that the catalysts exhibit much higher catalytic activity than conventional HF acid. At the reaction temperature of 80°C, 2hr reaction time and atmospheric pressure of 40% $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ showed the highest conversion (84%) and good selectivity (59%) to 2-phenyl decane.

Keywords: Linear alkylbenzene; Heteropoly acid; Preyssler; Alkylation; Green catalyst

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INTRODUCTION

The alkylation of aromatic hydrocarbons with olefins is utilized on a large scale in the chemical industry. Alkylation of benzene with C_{10-14} linear alkenes is used for the synthesis of linear alkylbenzene (LAB), the primary raw material for the production of linear alkylbenzene sulfonates (LABS), which is a surfactant detergent intermediate [1]. LAB production has experienced continuous growth because of the increased per capita consumption worldwide as a result of improved health care and generally increased per capita income [2]. The world production of linear alkylbenzenes currently reaches to 3 million tons per year [2].

Currently, LAB production is carried out commercially using $AlCl_3$ and especially HF catalysts. Both of them make many drawbacks such as pollution, handling, safety, corrosion and tedious work up. Thus, many efforts have been done to substitute a solid acid catalyst in LAB production process [1]. UOP and CEPSA announced their Detal process in 1995 based on a fixed bed of solid acid catalyst [1].

Recently various catalysts like zeolites, heteropoly acids, clays, ionic liquids, sulfated zirconia and various metal oxides were tested for this reaction. For instance, Borutskii and his coworker tested different catalysts like zeolites ZSM and Y, mordenite, activated bentonite, and sulfated aluminum and zirconium for the production of LAB [3]. Shang et al. used an $AlCl_3$ catalyst immobilized on $\gamma-Al_2O_3$ [4].

Solid heteropoly acids have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts [5].

Heteropoly acids (HPAs) appeared to be appropriate catalysts for the alkylation reactions due their strong acidity, fundamentally of the Brönsted type, comparable to that of HF and H_2SO_4 acids. One of the most common types of these acids is keggin heteropoly acid with the general formula of $H_3XM_{12}O_{40}$ where X is the heteroatom (P^{5+} , Si^{4+} , etc.) and M the addendum atom (Mo^{6+} , W^{6+} , etc.). The structure of the heteropoly anion is composed of a

central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal–oxygen octahedra MO_6 [6]. Fig. 1 illustrates the structure of kegggin type heteropoly acids.

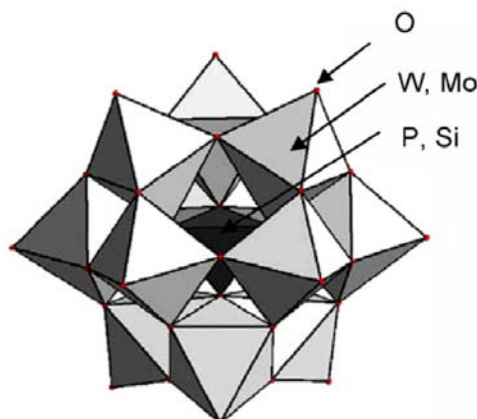


Figure 1: Keggin-Type Heteropoly Anion Structure.

Another type of polyoxometalates is preyssler heteropoly acid. Preyssler acid, $H_{14}[NaP_5W_{30}O_{110}]$, is remarkable owing to its exclusive physicochemical properties. They include strong Brönsted acidity, reversible transformations, solubility in polar and non-polar solvents, high hydrolytic stability and high thermal stability that are very important in catalytic processes [7]. The structure of Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$, is shown in Fig. 2.

However, the catalytic applicability of Preyssler's anion with exclusive properties has been largely overlooked, with only a few demonstrations of catalytic activity [8]. This heteropoly anion with 14 acidic protons, is an efficient "super acid" solid catalyst which can be used both in the homogeneous and heterogeneous phases [9].

An important problem using heteropoly acids as heterogeneous catalyst is their low surface area (7-10 m^2/g); another problem is their high solubility in polar solvents, consequently they should be supported on acidic neutral solids, which interact weakly with HPAs such as active carbon, zeolites, silica, acidic ion-exchange resin and etc. [10].

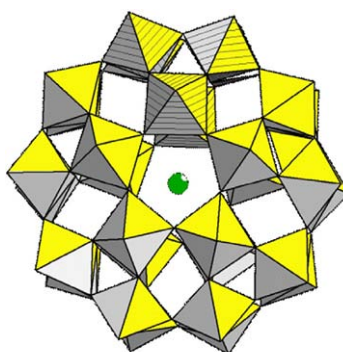


Figure 2: Preyssler's Anion Structure.

In this study, liquid phase alkylation of benzene with 1-decene was investigated over two different catalysts in supported and bulk types.

EXPERIMENTAL

Chemicals. All the chemicals were obtained from Merck Company and used as received. Yields are based on GC/mass analysis using Agilent 6890 GC system Hp-5 capillary 30m×530μm×1.5μm nominal.

Catalyst preparation. $H_{14}[NaP_5W_{30}O_{110}]$ was synthesized in our laboratory according to our previous work [11]. The SiO_2 were impregnated in an aqueous solution of required amount of $H_3PW_{12}O_{40}$ and $H_{14}[NaP_5W_{30}O_{110}]$, that are 40 wt.% referred to the total weight of the dried HPA+support. Then stirred at room temperature for 12h, followed by evaporation at 50°C and drying at 100°C over night. The particle size of SiO_2 were about 0.1(mm).

RESULTS AND DISCUSSION

Alkylation of benzene with 1-decene was carried out at atmospheric pressure in a 25-mL glass batch reactor equipped with a magnetic stirrer and a reflux condenser. In this study, $H_{14}[NaP_5W_{30}O_{110}]$ and $H_3PW_{12}O_{40}$ were used as the catalyst in bulk and supported forms. Silica supported $H_{14}[NaP_5W_{30}O_{110}]$ and $H_3PW_{12}O_{40}$ were tested with the loading of 40 wt%. Before introducing into the reactor, PW and preyssler silica supported catalysts were activated in air for 3 h at 300°C and 240°C respectively. The reaction temperature was 80°C, with typically a 5 mol/mol ratio of benzene to 1-decene and a 4 wt% of catalyst. The reaction time was 2hr. Filtration of reaction mixture was done after each run to remove catalyst particles.

The results of this reaction illustrate that supporting heteropoly acids on silica increase the conversion, although SiO_2 cannot catalyze this reaction unaccompanied and showed negligible catalytic activity. Table 1 shows the catalytic activity and selectivity of these catalysts.

Table 1: Conversion of 1-Decene and Product Distribution Over Heteropoly Acid Catalysts (Reaction Temp.=80°C; Reaction Time=2h; Benzene/1-Decene=5 Mol/Mol, Catalyst=4 Wt%). (2-P= 2-Phenyl Decane, 3-P= 3-Phenyl Decane, 4-P= 4-Phenyl Decane, 5-P= 5-Phenyl Decane)

catalyst	Conversion%	Selectivity			
		2-P	3-P	4-P	5-P
40% $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$	84	58.73	22.53	13.85	5.89
40% $H_3PW_{12}O_{40}/SiO_2$	78	60.08	23.58	9.46	6.88
$H_{14}[NaP_5W_{30}O_{110}]$	66	50.31	26.33	13.76	9.60
$H_3PW_{12}O_{40}$	39	78.91	12.04	3.1	6.05
SiO_2	0	-	-	-	-

As indicated in Table 1, silica supported $H_{14}[NaP_5W_{30}O_{110}]$ has the highest activity to catalyze this reaction with the conversion of 84% and show the selectivity of about 60% for 2-phenyl decane, which is much higher than that over HF ($\leq 20\%$), where thermodynamic equilibrium is probably reached [12].

The alkylation of benzene with olefins goes through a carbonium ion mechanism [13, 14]. In this mechanism, firstly the alkene interacts with the acid site to form an alkylcarbenium ion. This intermediary can isomerize to other olefins by hydrogen transfer, then alkylcarbenium attack to benzene ring to form phenyldecanes, which can also isomerize to form other phenyl decane isomers. Fig. 3 demonstrates this procedure.

For 1-decene, five carbonium ions are possible. The stability of carbonium ions depends on the C-number, as the C-number also increases the stability of carbonium ions. Because of very low stability of 1-phenyl isomer, it does not exist in the product. On the basis of relative stabilities of the other carbonium ions (all secondary), it is expected that the isomer content will increase with the carbon number (toward the center of the alkyl-chain).

Accordingly, the nature of anions has a considerable effect on reactivity and selectivity of the LAB production.

As seen in Fig. 4, HF has an excellent conversion of 90% but its selectivity for 2-Phenyl decene is about 20% which is very low. On the other hand, HY exhibits the selectivity of 30.7% for 2-Ph, which is also higher than that over HF [13].

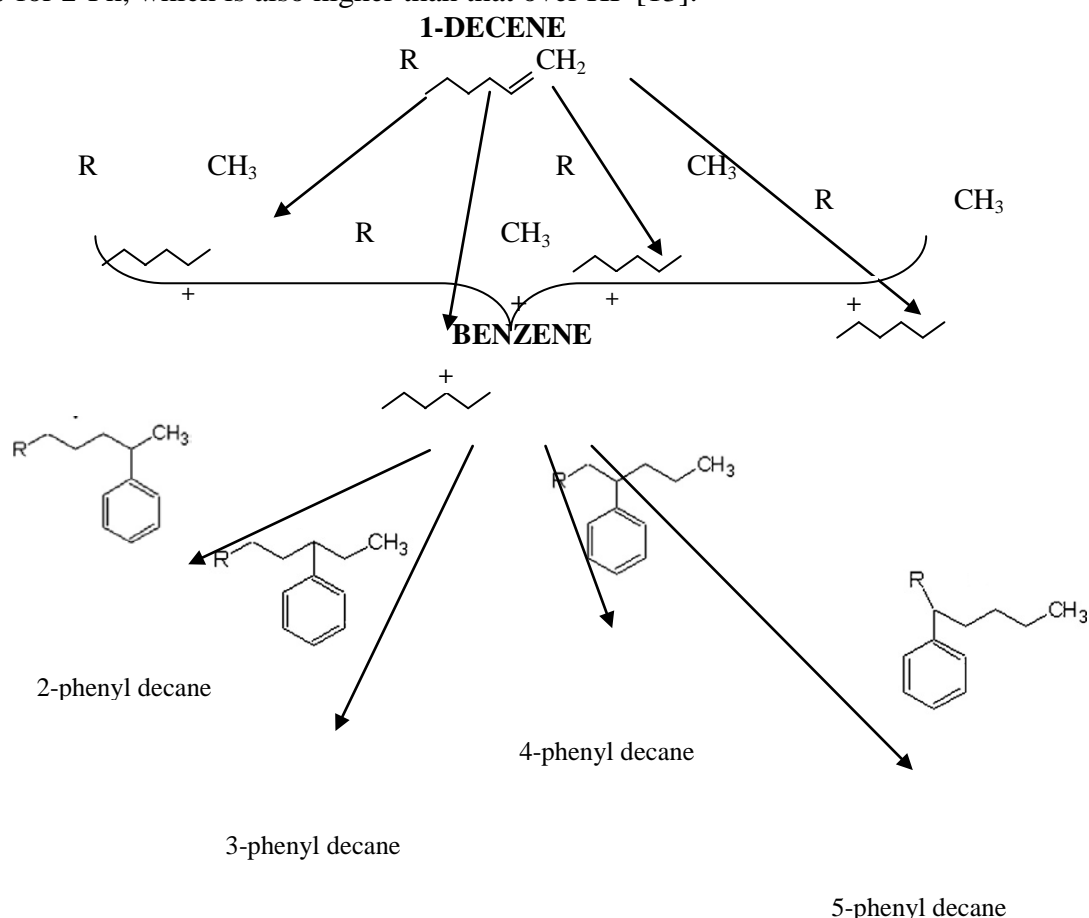


Figure 3: Mechanism of the Alkylation of Benzene with 1-Decene (R= C₅H₁₁).

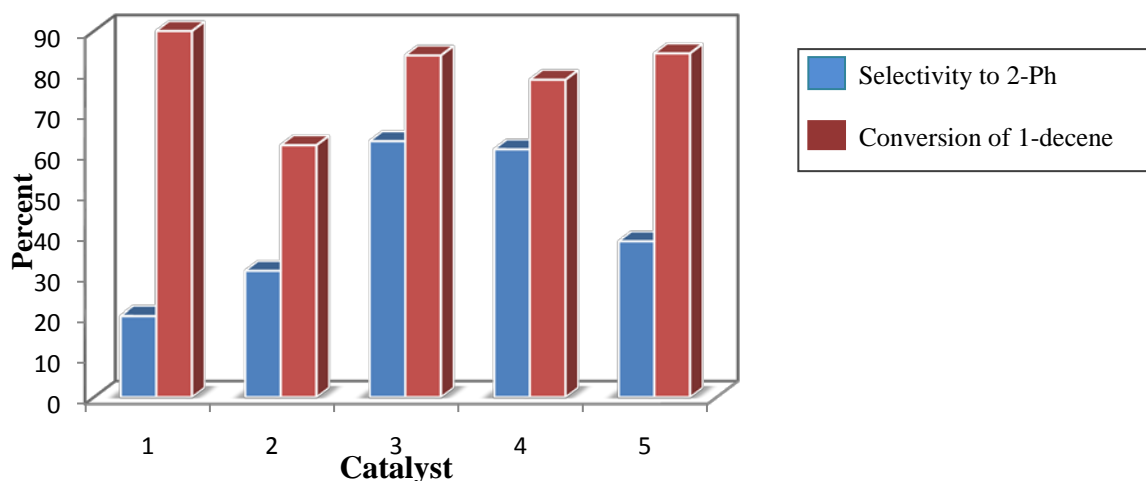


Figure 4: Comparison of Yields and Selectivity for 2-Ph on Different Catalysts in the Alkylation of Benzene. 1= HF [13], 2= HY [16], 3= 40% $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, 4= 40% $H_3PW_{12}O_{40}/SiO_2$, 5= 40% PW/SBA-15 [16].

Wang and Zhu [15] reported 84% conversion for 1-decene using 40%PW/SBA-15 and selectivity for 2-Ph was 38%, which is particularly lower than 40% on $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst.

CONCLUSIONS

In this work, we have studied alkylation of benzene with 1-decene over $H_{14}[NaP_5W_{30}O_{110}]$ and $H_3PW_{12}O_{40}$ catalysts in the supported and bulk forms. Under the reaction conditions of 80°C, 2h reaction time, benzene/1-decene ratio of 5mol/mol and catalyst wt % of 4, silica supported preyssler with the loading of 40% illustrated the highest catalytic activity among other catalysts. It showed 84% conversion of 1-decene with 2-Phenyl decane selectivity of about 63%. The results demonstrate that supporting heteropoly acids on SiO_2 increase the catalytic activity. The result found herein is believed to be potentially important for industrial production of LAB over solid acid catalysts.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Fotoohi for her help on GC/mass analysis.

REFERANCES

- [1] Kocal, J. A., B.V. Vora and T. Imai, Production of linear alkylbenzenes, *Appl. Catal. A*, Vol. 221, 2001, pp. 295-301.
- [2] Caoa, Y., R. Kessasb, C. Naccachec and Y. Ben Taarit, Alkylation of benzene with dodecene. The activity and selectivity of zeolite type catalysts as a function of the porous structure, *Applied Catalysis A: General*, Vol. 184, 1999, pp. 231-238.
- [3] Borutskii, P. N., E. G. Kozlova, N. M. Podkletnova, N. D. Gil'chenok, B. G. Sokolov, V. A. Zuev, and A. A. Shatovkin, Alkylation of Benzene with Higher Olefins on Heterogeneous Catalysts, *Petroleum Chemistry*, Vol. 47, No. 4, 2007, pp. 250-261.
- [4] Shang, L., M. Ji, T. Cai, W. Shan, M. He and S. Jiang, Highly active and stable immobilized aluminium chloride catalyst for the alkylation of benzene with 1-dodecene, *React. Kinet. Catal. Lett.*, Vol. 87, No. 1, 2006, pp.101-106.
- [5] Schwegler, M.A., H. van Bekkum and N. Munck, *Appl. Catal.*, Vol. 74, 1991, pp. 191-198.

- [6] Hernáandez-Cortez, J. G., L. Martínez , L. Soto , A. López, J. Navarrete, Ma. Manríquez, V.H. Lara, E. López-Salinas, Liquid phase alkylation of benzene with dec-1-ene catalyzed on supported 12-tungstophosphoric acid, *Catalysis Today*, accepted paper.
- [7] Heravi, M. M., V. Zadsirjan, K. Bakhtiari, H. A. Oskooie and F. F. Bamoharram , Green and reusable heteropolyacid catalyzed oxidation of benzylic, allylic and aliphatic alcohols to carbonyl compounds, *Catalysis Communications*, Vol. 8, 2007, pp. 315–318.
- [8] Harrup, M.K. and C.L. Hill, *Inorg. Chem.*, Vol. 33, 1994, pp. 5448-5455.
- [9] M. H. Alizadeh, H. Razavi, F. Farash Bamoharram, M.H. Hassanzadeh, The oxidative cleavage of carbon-tin bond catalyzed by heteropolyacids of molybdenum, *Kinet. Catal.*, Vol. 44, 2003, pp. 524-528.
- [10] Wu, Y., X. Ye, X. Yang, X. Wang, W. Chu and Y. Hu, *Ind. Eng. Chem. Res.*, Vol. 35, 1996, pp. 25-36
- [11] Heravi, M. M., S. Sajadi, H.A. Oskooie, R. Hekmat Shoar, F.F. Bamoharram, A direct oxidative route for the synthesis of pyrimidines using heteropolyacids, *S. Afr. J. Chem.*, Vol. 62 , 2009, pp. 1-4.
- [12] Olson, A.C., *Ind. Eng. Chem.*, Vol. 52, 1960, pp. 833-839.
- [13] Venuto, P. B., L. A. Hamilton, and P. S. Landis, Heterogeneous catalysis by solid superacids. 3. Alkylation of benzene and transalkylation of alkylbenzenes over graphite-intercalated Lewis acid halide and perfluorinated resin sulfonic acid (Nafion-H) catalysts *J. Catal.*, Vol. 5, No. 21, 1960, pp. 103-110.
- [14] Patinkin, S. H. and B. S. Friedman, Friedel- Crafts and Related Reactions, G. Olah, Ed., Vol. II, Chap. 14, p. 3. Int. Publishers, New York, 1964.
- [15] Wang, J. and H. Zhu, Alkylation of 1-dodecene with benzene over H₃PW₁₂O₄₀ supported on mesoporous silica SBA-15, *Catalysis Letters*, Vol. 93, No. 3–4, 2004, pp. 209-212.