3rd International Congress on Nanoscience and Nanotechnology (ICNN 2010)

9 - 11 November 2010 / Shiraz University, Shiraz, Iran

Certificate Of Attendance

This is to certify that Mr. / Mrs. **A.Hafizi**

participated in the 3rd International Congress on Nanoscience and Nanotechnology (ICNN2010), held by Shiraz University in co-operation with the Iranian Nano Society (INS), on 9-11 Nov. 2010, by presenting a paper entitled:

LIQUID PHASE ALKYLATION OF BENZENE WITH 1-DECENE CATALYZED BY NANO SiO2 SUPPORTED 12-TUNGSTOPHOSPHORIC ACID

as poster/oral presentation.

Co-Authors: **A. Ahmadpour, M.M. Heravi, F.F bamoharram**

Prof. M. H. Sheikhi
Congress Chairman
M. H. Sheikhi

Prof. M. Shariaty – Niassar
INS Chairman
M. Shariaty Niassar

Web Site: www.ICNN2010.com E-mail: ICNN2010@shirazu.ac.ir
Nanotechnology Research Institute, Shiraz University
Mollasadra St. Shiraz, Iran
Tel & Fax: +98 (711) 647 30 55

LIQUID PHASE ALKYLATION OF BENZENE WITH 1-DECENE CATALYZED BY NANO SiO_2 SUPPORTED 12-TUNGSTOPHOSPHORIC ACID

A. Hafizi[1*], A. Ahmadpour[1], M.M. Heravi[2] , F.F bamoharram[3]
[1]Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[2]Department of Chemistry, School of Sciences, Azzahra University, Iran
[3]Department of Chemistry, Azad University of Mashad, Mashad, Iran

* *alih271@yahoo.com*

KEYWORDS
Linear alkylbenzene, nano catalyst, nano SiO_2, green catalyst, alkylation

ABSTRACT
Liquid phase alkylation of benzene with 1-decene was investigated with supported keggin heteropoly acid to produce linear alkylbenzene (LAB). $H_3PW_{12}O_{40}$ was supported on Nano SiO_2 and SiO_2 with 20% loading and thermally treated at 250˚C. the catalyst was characterized with IR. At the reaction temperature of 80˚C and atmospheric pressure the nano SiO_2 supported $H_3PW_{12}O_{40}$ showed higher activity and selectivity than SiO_2 supported $H_3PW_{12}O_{40}$ catalyst.

INTRODUCTION

Alkylation of benzene with C_{10}-C_{14} linear alkenes is used for the synthesis of linear alkylbenzene (LAB), which is the primary raw material of biodegradable detergents. 2-phenylalkane is the best biodegradable linear alkylbenzene due to its fast biodegradation. Nowadays, LAB production is mostly based on homogeneous catalytic reaction with HF as catalyst. Using HF makes many problems such as environmental pollution, safty, separation difficulty and equipment corrosion [1,2]. To solve this problem solid acid catalysts such as zeolites [3] , heteropoly acids [4] , clays [5] , fluorided silica-alumina [6] and ionic liquids [7] have been investigated for this reaction.

The use of heteropolyacids (HPAs), has recently received considerable attention as nontoxic, eco-friendly and environmentally benign catalysts for alkylation reactions. [4].

The Keggin type heteropoly acids are the most important of this family in catalysis, because of their high acidic strength and relatively high thermal stability. These are strong Br nsted acids and their strength of acidity is higher than that of the conventional solid acids like zeolites and mixed oxides [1].

Because of their low surface area (8-10 m^2/gr) they should be supported on acidic or neutral solids, such as silica, active carbon, and acidic ion-exchange resin for better accessibility of reactants to the active sites. SiO_2 is a good candidate for this purpose because of its weakly interact with HPAs, high surface area and its high thermal stability [8]. The long history of successful commercialization of catalysis is accompanied by the development of many different methods to prepare catalysts in an attempt to optimize their properties. However, in spite of the effort, the ability to custom design active sites and site environments for perfect selectivity and desirable activity continues to be a goal yet to be reached. New techniques made available by nanotechnology have resulted in some progress toward achieving this goal.

Making uniform nano-sized SiO_2 supported keggin particles is also of interest. Such particles could have a higher specific surface area and a higher density of surface defects than conventionals. This could be beneficial to their catalytic properties.

We immobilized keggin HPA into the SiO_2 and SiO_2 nano particles (with the particle size of about 20nm) and investigated the catalytic behavior of these new catalysts.[9]

EXPERIMENTAL

Catalyst preparation

The two kinds of SiO_2 (E. Merck) were impregnated in an aqueous solution of required amount of $H_3PW_{12}O_{40}$ (E. Merck, 99%), that is 20 wt.% referred to the total weight of the dried WP+support. Then stirred at room temperature for 12 h, followed by evaporation at 50°C and drying at 100°C over the night. The particle size of SiO_2 were about 0.1(mm) and 20 (nm).

Catalytic activity experiments

The liquid phase alkylation of benzene with 1-decene was carried out at atmospheric pressure in a 100-mL glass batch reactor equipped with a magnetic stirrer and a reflux condenser. The catalysts were calcinated in air for 4 h at 300 ˚C. The reaction temperature was 80 ˚C. The molar ratio of benzene (E.merck, 99%) to 1-decene (E.merck, 99%) was 5 and a 20 ml/g ratio of 1-decene to catalyst. After 3 h, as indicated, the reaction was stopped and the catalyst was separated. The filtrate was analyzed using a Varian CP-3800 gas chromatograph equipped with an capillary column (crosslinked 5% ME silicone, 30 m × 0.53 mm × 1.5 µm film thickness), coupled with a Flame Ionization detector. Products were identified by GC-MS.

RESULTS AND DISCUSSION

Under the reaction conditions employed, the conversion of 1-decene reached the plateau value over PW/nano SiO_2 and PW/SiO_2 after 3 hr of reaction time, respectively. The catalytic activities of PW/nano SiO_2 and PW/SiO_2 catalysts in the steady reaction compared in Table 1.

Table 1. Conversion of 1-decene and product distribution over PW/nano SiO_2 and PW/SiO_2 catalysts (reaction temperature = 80°C; reaction time = 3 h; benzene/1-decene = 5 mol/mol; 1-decene/catalyst =20 ml/g).

Catalyst	Conversion	Product selectivity			
		2-P	3-P	4-P	5-P
Nano SiO_2	0.0	-	-	-	-
SiO_2	0.0	-	-	-	-
PW	32	65.2	23.5	7.8	3.5
PW/Nano SiO_2	75	73.5	4.3	7.2	15
PW/SiO_2	68.5	54.6	7.5	5.3	32.6

Results show that not impregnated SiO_2 has no catalytic activity in this reaction. Catalyst activity increases by using nano SiO_2 as support. The increase in conversion of 1-decene is because of increasing the surface area of catalyst in nano form. The other important result is the increase of 2-phenyldecane which is the best form of linear alkylbenzene for biodegradation.

CONCLUSIONS

silica-supported 12-tungstophosphoric acid acts as an effective solid acid catalyst for the synthesis of linear alkylbenzenes. By using nano SiO_2 as the support of catalyst under the reaction temperature of 80°C and reaction time of 3hr the conversion of 1-decene increases compared with larger SiO_2 particles because of its higher surface area. The selectivity to 2-phenyldecane increases to 73.5% by using nano SiO_2 which is a good improvement in green catalysis.

REFERENCES

[1] J.A. Kocal, B.V. Vora, T. Imai: *Appl. Catal. A: General*, **221**, 295 (2001).

[2] C. Perego, P. Ingallina: *Catal. Today*, **73**, 3 (2002).

[3] B. Wang , C.W. Lee, T. Cai, S.E. Park: Catalysis Letters Vol. 76, 2001

[4] A. Nociar, P. Hudec, T. Jakubik, A. Smieskova, Z. Zidek, Petroleum Coal 45 (3–4) (2003) 184.

[5] S.R. Guerra, L.M.O.C. Merat, R.A.S. San Gil, L.C. Dieguez, Catal. Today 133–135(2008) 223.

[6] A. Ghanbari-Siahkali, A. Philippou, J. Dwyer, M.W. Anderson: *Appl. Catal. A: General*, **192**, 57 (2000).

[7] H. Xin, Q. Wu, M. Han, D. Wang, Y. Jin, Appl. Catal. A: Gen. 292 (2005) 354.

[8] S. Damyanova, L.M. Gomez, M.A. Banares, J.L.G. Fierro, Chem. Mater. 12 (2000) 501.

[9] Majid M. Heravi, S. Sadjadi , S. Sadjadi , H.A. O ,F.F. Bamoharram, Ultrasonics Sonochemistry 16 (2009) 718–720