12-2020

Alkylation of Benzene on Immobilized Phosphotungstic Acid

Kofi Kankam
East Tennessee State University

Recommended Citation

Kankam, Kofi, "Alkylation of Benzene on Immobilized Phosphotungstic Acid" (2020). *Electronic Theses and Dissertations.* Paper 3847. https://dc.etsu.edu/etd/3847

Alkylation of Benzene on Immobilized Phosphotungstic Acid

A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

by

Kofi Kankam

December 2020

Dr. Aleksey Vasiliev, Chair

Dr. Ismail Kady

Dr. Hua Mei

Keywords: alkylbenzenes, sol-gel synthesis, phosphotungstic acid, catalyst

ABSTRACT

Alkylation of Benzene on Immobilized Phosphotungstic Acid

by

Kofi Kankam

Linear alkylbenzenes (LAB) are key intermediates in the synthesis of linear alkylbenzene sulfonate surfactants that are used in the manufacture of detergents. Production of LAB with traditional Lewis acids as catalysts, such as hydrofluoric acid, results in the formation of large amounts of toxic wastes and corrosion of industrial equipment. Phosphotungstic acid (PTA) has gained much attention in recent years as a solid catalyst for various alkylation reactions. This research work aims to develop a novel material based on PTA-containing silica gel, which can effectively catalyze LAB synthesis. Sol-gel synthesis of silica gel in the presence of PTA and tetraethyl orthosilicate as precursors produced a mesoporous aterial containing covalently embedded PTA clusters. Obtained superacidic catalyst demonstrated high catalytic activity in liquid-phase alkylation of benzene by various alkenes. Covalent embedding of catalytically active HPA clusters prevents their leaching from the catalyst surface, which enabled its excellent catalytic properties.

DEDICATION

This work is dedicated to my family and loved ones.

ACKNOWLEDGEMENTS

I would like to express my sincerest gratitude to Dr. Vasiliev, my research advisor for the opportunity to be a part of his research group and also for his guidance and patience throughout this journey.

I would like to thank Dr. Ismail Kady and Dr. Hua Mei for accepting to be a part of my Advisory committee and for their help on my thesis.

I would like to thank Dr. Reza Mohseni for his help with instrumentations and analysis for my research work.

I am grateful to Maria Kalis for her help in administrative and organizational aspects throughout my time in graduate school.

I would also like to thank Anastasia Kuvaysakaya, my research colleague for her help and support during the entire project.

Special gratitude to the American Chemical Society Petroleum Research Fund for supporting this research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ARCO	Atlantic Richfield Company
BET	Brunauer-Emmett-Teller theory
DI	Deionized water
FT-IR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography with mass-spectrometry detector
H-PTA/SiO_2	Phosphotungstic acid embedded in silica gel
HPA	Heteropolyacid
HPMo	Molybdophosphoric acid
HPW	Tungstophosphoric acid
HSiW	Tungstosilic acid
LAB	Linear alkylbenzene
LAS	Linear alkylbenzene sulfonate
NMR	Nuclear magnetic resonance
PTA	Phosphotungstic acid
SEM	Scanning electron microscope
TEOS	Tetraethyl orthosilicate
TON	Turnover numbers
UOP	Universal Oil Products

CHAPTER 1. INTRODUCTION

Linear Alkylbenzenes

Linear alkylbenzenes (LAB) are essential intermediates in the manufacture of linear alkylbenzene sulfonates, which are used as surfactants. They are used worldwide in household detergents and personal care products, industries like polymers, textiles, oil recovery, paints, and pharmaceuticals[1].

Linear alkylbenzene sulfonates (LAS), alkylphenol ethoxylates, alkyl ethoxy sulphates, and quaternary ammonium compounds are the most common commercial surfactants available. LAS, which are the most anionic surfactants, are used for over 45 years with an estimated worldwide consumption of 1.5 to 2 million tons per year[2]. Regardless, LAS and other surfactants may have a bad impact on the environment. Production and usage of surfactants, especially LAS deserve special attention because they are used in very large amounts and they also impact terrestrial/aquatic ecosystems after being utilized[3].

Linear alkylbenzene sulphonates (LAS) are mixtures of skeletal isomers represented by a general formula $C_6H_4C_xH_{2x+1}SO_3Na$, where x is 8-16. Fig. 1 shows a general linear alkylbenzene sulphonate structure. The long alkyl chain and phenyl group positions are very important as they contribute to the biodegradability and solubility of the LAS[4].

There are many skeletal isomers named according to the number of carbons attached to the benzene ring. For example, the molecular structures of six phenyldodecane skeletal isomers are shown in Fig. 2[5]. Among LAS isomers, sodium 2-phenylalkane sulfonates (Na-2-LAS) have the greatest biodegradability but the lowest solubility[6]. Therefore, the optimum composition of Na-2-LAB is a compromise of biodegradability and solubility.

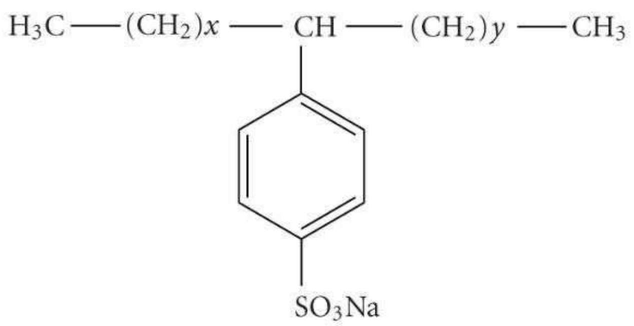
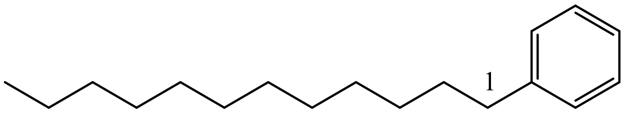
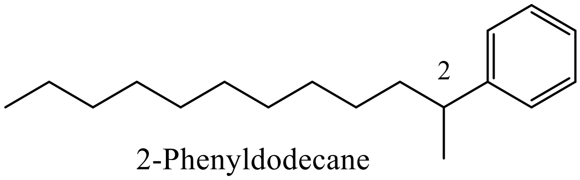


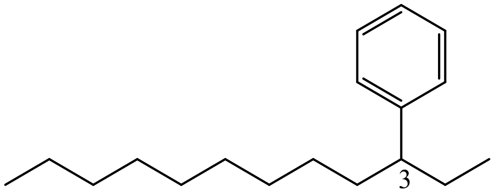
Figure 1. General linear alkylbenzene sulphonate structure.



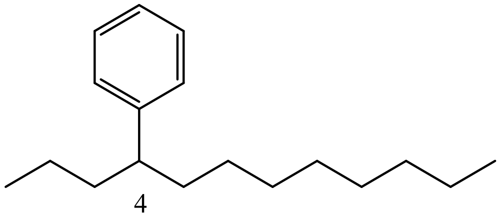
1-Phenyldodecane



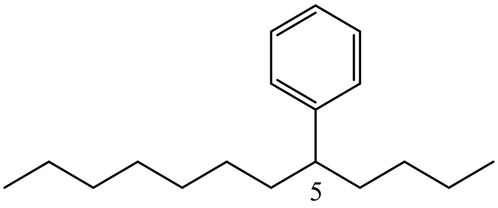
2-Phenyldodecane



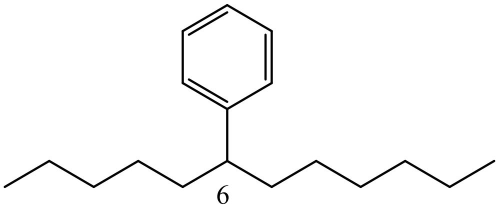
3-Phenyldodecane



4-Phenyldodecane



5-Phenyldodecane



6-Phenyldodecane

Figure 2. Skeletal isomers of phenyldodecane

Current Technologies in LAB Manufacture

The production of LAB has been accomplished through several paths. Linear paraffins (C_{10}-C_{14}) must first be isolated from oil gas fractions and many recovery techniques and adsorptive separations have been developed. Some of the liquid phase commercial process technologies include Molex^{TM}, which utilizes a hydrocarbon adsorbent and a moving simulated bed technology (UOPs Sorbex^{TM}). GDR Parex and Exxon Ensorb are vapor phase processes[7]. In each of these commercial process technologies, the linear paraffins are recovered at over 98% purity. They are converted into alkylated benzenes (producing LAB), and alkyl olefins or chlorides[8].

Some technologies and routes developed include the formation of mono-chloroparaffins by the chlorination of paraffins, and used commercially by industries. The mono-chloroparaffins produced is used for benzene alkylation catalyzed by aluminum chloride. This path has been developed and used commercially by ARCO Technology Inc[7].

Dehydrochlorination after chlorination of linear paraffins are being used to form olefins which are used as alkylating agents are also being explored[9]. Lewis acids are mostly used as catalysts for the alkylation of benzenes with linear olefins. Companies such as Shell and Chevron produce olefins by ethylene oligomerization, and alkylation of benzene is also done in the presence of hydrofluoric acid catalyst[6].

In the late 1960s, the hydrofluoric acid alkylation path became more known and used than the aluminum chloride catalyzed alkylation, which was prominent in the early 1960s. Hydrofluoric acid alkylation became popular because it produced high-quality products with economic advantages such as lower cost of kerosene as a feedstock for the route in the dehydrogenation of paraffins[10]. However, most the technologies used to produce LAB are currently based on the use of Lewis acids even though hydrofluoric acid is an excellent catalyst.

There are some concerns about environmental safety with the use of hydrofluoric acids and therefore measures are being taken to minimize the release of toxic substances. In recent years, solid catalysts have been developed and the Detal^{TM} process that utilizes non-corrosive solid catalysts was commercialized in the early 1990s. A technology, which uses solid acidic catalyst commercially, is under test and review in India to date. It is other than a zeolite-based one, although not much information is known about this technology and it has not been fully commercialized[7].

Detal^{TM} process, which is provided by UOP, is currently the only modern technology that has been commercialized and uses a solid catalyst that has been made especially for this technology. It has two major parts in operation. An example flow scheme is shown in Fig. 3[11]. Linear olefins are first produced by dehydrogenation technology by the UOP. The olefin feed and recycled benzene, before they are introduced to the fixed bed reactor, are mixed with the make-up benzene. The fixed bed reactor contains a solid acid catalyst. The reaction proceeds under mild conditions in the liquid phase to obtain optimum product quality. The flow of the effluent from the reactor is directed into the fractionation region of the system and it is very much similar to the process involving hydrofluoric acid. Two extra components help to improve the quality of the product and its yield. The Define^{TM} compartment, which selectively hydrogenates diolefins to mono olefins, and the other unit, which is a PEP^{TM} aromatics elimination unit help to remove all remaining aromatics from the olefin feed stream[11].

As stated earlier, the use of homogenous catalysts such as hydrofluoric acid for these processes is not environmentally friendly due to the large amount of toxic acidic wastes produced. These catalysts are also very corrosive and wear out industrial equipment. These problems can be eliminated by switching to heterogenous solid acidic catalysts that are reusable.

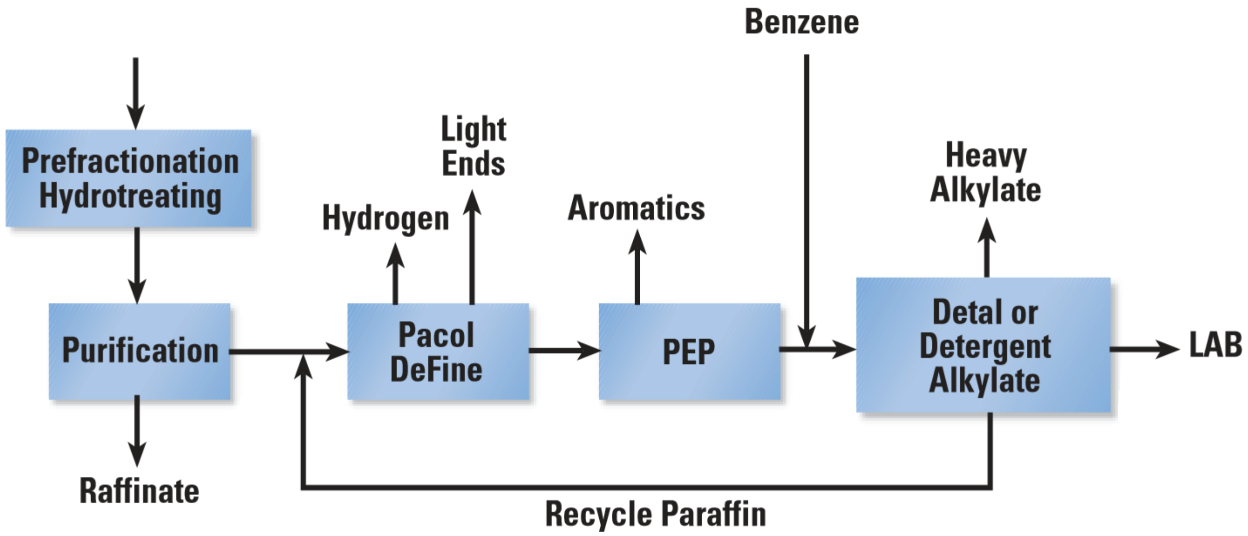


Figure 3. UOP industrial LAB process scheme

Heterogeneous Catalysts

The use of traditional Brönsted and Lewis acids such as H_2SO_4, HCl, HF, $AlCl_3$, BF_3, and $ZnCl_2$ presents dangers in handling, disposal, containment, and regeneration, which has to do with their toxic and corrosive nature[12]. There are countless acid-catalyzed organic reactions and there is a pressing need to do away from mineral acid-catalyzed processes. Solid acid catalysts are very important in environmentally friendly industrial processes. The use of heterogeneous (solid) catalysts in organic reaction synthesis and chemical manufacturing industries is progressively important as they provide green substitutes to homogeneous catalysts[13]. In the past few years, the evolution of inorganic solid-catalyzed organic reactions is attaining much significance owing to definite advantages of heterogeneous catalysts, such as mild reaction conditions, simplified product isolation, reduced generation of waste byproducts, easy catalyst recovery and reuse[14,15]. Heterogeneous catalysts are used thoroughly in protection and deprotection processes in organic synthesis[16].

Many heterogeneous processes of alkylation, trans-alkylation, and disproportionation of aromatics involve the use of solid acidic catalysts or supported acidic catalytic complexes. The use of catalytic complexes that are liquid super-acids, for example, based on metal chlorides or metal fluorides, is attributed to the fact that they tend to catalyze unwanted and side reactions as a result of isomerization, polymerization, and degradation of olefins, to a degree creating stirring, catalyst isolation and recovery problems, and causing corrosion of industrial equipments[17]. Liquid acids are active in benzene alkylation at temperatures well below 100 °C and supported catalyst acids are active at up to 200 °C, whereas catalytic systems made of aluminosilicate require high pressures because they are usually effective at higher temperatures[18]. In the early 1940s, the alkylation of benzene using activated clay and synthetic aluminosilicates[1] was welcomed and established. Clay and synthetic aluminosilicates are more active and thermally stable than ion-exchange resins at a temperature range between 120–140 °C in the alkylation of phenol using C_9−C_{12} olefins.

Benzene alkylation with higher olefins C_8−C_{10} was also accomplished with heterogeneous catalysts made of Ta(V) and Nb(V) halides deposited on the solid support[19]. The utilization of silicotungstic acid supported on aluminosilicate or silica gel to perform benzene alkylation with C_{11}−C_{14} olefins has also been reported. They proved that the molar ratio between Al_2O_3: SiO_2 also affects the activity of the silicotungstic catalyst supported on aluminosilicate, thus it does not depend on the surface area only. The reaction rate is relatively low, despite its low activation energy (12−13 kJ mol^{-1}), because of the slow internal diffusion of the reactants.

Aluminium-magnesium with the zeolite or clay structure, which was treated by various acids, was used to catalyze the alkylation of benzenes[20]. This catalyst can result in higher olefin conversion of more than 90% with a selectivity of around 85% for linear alkylbenzenes[20], and also a catalyst made up of this clay with cerium nitrate and air-steamed at a temperature of 600 °C was studied in the alkylation of benzene reaction under a pressure of 3.5 MPa at 150 °C. The conversion rate was up to 99% for C_{10}–C_{14} olefins with a yield of 95% for linear alkylbenzenes. In benzene alkylation by C_{10}–C_{18} α-olefins at 180 °C, the molar ratio between benzene-olefins up to 100:1 and space velocity of 0.25 per hour on zeolite Y modified by rare-earth elements, the yield of monoalkylbenzene was up to 85%-90%. It should be noted that other phenylalkane isomers are formed together with 2-phenylalkanes, which was preferred due to its biodegradability[21].

On lanthanide promoted zeolite, benzene alkylation at 180 °C yielded 94% of undecylbenzene[21]; there was an increase in the conversion rate from 30% to 69% when alkylation was done at 220 °C with dodecene using a high silica pentasil type zeolites with increased molar ratio Si/Al.

Even though zeolites show relatively high acidity and activity, the discovery of more efficient catalysts and processes for the production of linear alkylbenzenes is on the rise. The necessity in other catalysts is caused mainly by the fact that zeolite catalysts have microporous structure creating some steric hindrances in the diffusion of reactants to the active sites and desorption of large byproducts during regeneration. Zeolites are also thermally and chemically unstable.

Heteropolyacids (HPAs)

Heteropolyacid (HPA) catalysts and related compounds are a branch in catalysis, in which their importance worldwide is ascending. Numerous developments were carried out in basic research as well as in fine chemistry processes[22]. HPAs exhibit a very strong acidity and significant redox properties, which can be altered by changing the chemical composition of heteropolyanion. Reactions that are catalyzed by both homogenous and heterogeneous systems have been investigated by many researchers. The reactions, in which they can be utilized, from alkylation, cyclization, dehydration up to oxidation of amines or epoxidation of olefins, may draw numerous applications in fine chemical production, which includes fragrances, pharmaceutical, and food industries[23]. There are numerous structural types of HPAs, but the majority of the catalytic applications involve the most common Keggin-type HPAs[24] due to their availability and chemical stability. Other catalysts such as Preyssler and Wells-Dawson heteropolyacids are also being explored.

Heteropolycompounds are classified as condensates of differing oxoacids and the ones with Keggin-type structure are polynuclear complexes typically made of molybdenum, vanadium, or tungsten as polyatoms (M), and phosphorus, silicon, or germanium as heteroatom or central atom (X) (Fig. 4)[25]. The Keggin structure is made up of a central tetrahedral XO_4 surrounded by twelve octahedral MO_6[26]. The general formula of the Wells–Dawson heteropolyanion is $[X^{n+}{}_2M_{18}O_{62}]^{n-}$, where X^{n+} denotes a central atom such as sulfur(VI), phosphorous(V), or arsenic(V) surrounded by addenda atoms M, including, molybdenum(VI), tungsten(VI), a mixture of elements with each of them consisting of MO_6 (M-oxygen) octahedral blocks. The structure, known as alpha isomer, has two similar “half units” of the central atom surrounded by nine octahedral units XM_9O_{31} bound through oxygen atoms[27]. The Preyssler polyanion is made up of a cyclic assemble of five PW_6O_{22} units, with each being developed from Keggin anion, $[PW_{12}O_{40}]^{3-}$, by the elimination of two sets of three corner shared WO_6 octahedra[28].

There is a relative evaluation of the properties of catalyst samples based on $H_3PW_{12}O_{40}$ and zeolite Y[29]. Compared with zeolite, a higher selectivity, activity, and stability of the deposited phosphotungstic catalyst in benzene alkylation with 1-dodecene was observed. At 80 °C, the olefin conversion was approximate 90%, the s5electivity for linear alkylbenzenes was near 100%, and that for 2-phenyldodecane was about 40%. There are various reports on the synthesis of catalytic systems made of superacids, which are based on zirconium oxide.

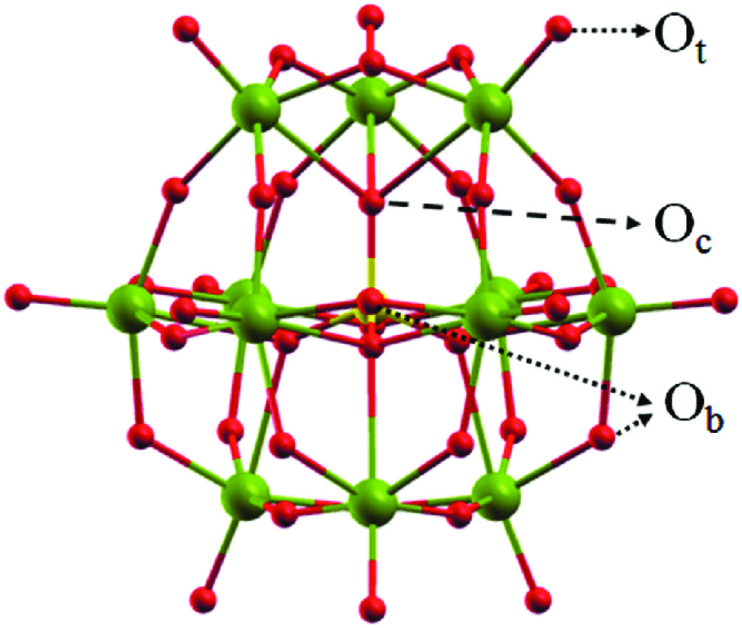


Figure 4. Keggin's anion $[PW_{12}O_{40}]^{3-}$ (tungsten in green, oxygen in red and phosphorus in yellow).

Catalysts made of sulfated zirconium oxide especially in the isomerization of lighter alkanes are extensively being studied and these catalysts are being promoted by tetragonal modification of the structure of sulfated zirconia which makes it more active catalytically than monoclinic structure[30]. Tungsten-containing zirconium oxide catalysts also show high activity in alkane isomerization[31].

The use of pure HPA, however, has some drawbacks in homogenous catalyses such as difficulty in separation from the reaction mixture and its recycling. Also, there are some limitations caused by high solubility of HPAs in polar solvents and their low surface area.

Immobilized Heteropolyacids

An important group of catalysts that gained significant attention is immobilized acids used in catalysis. HPAs being supported on solids with a large surface area are very favorable in developing great catalytic performance in heterogeneous reactions. The application of silicated acids such as silicated perchloric and polyphosphoric acids in organic synthesis is on the rise because of distinct advantages. They have relatively high efficiency due to large surface area, thermal stability, recoverability and reusability, reduced toxicity, high selectivity and they are easy to handle[32]. The use of polymers as acid support in catalysis has also been established and utilized along with the use of silica. Regardless, using silica support is being elected over the other solid supports including the use of polymers because of their limitations.

There are numerous ways to prepare mesoporous silica materials for catalysis. They include sol-gel techniques, ion-exchange, impregnation, covalent grafting, and electrostatic interactions[33]. Immobilization of HPAs onto porous support can be conducted by two main processes that have been reported: co-condensation by sol-gel technique, and impregnation[34]. HPAs being introduced to an already assembled silica structure are termed as impregnation and this approach is very simple. Due to changes in structure, this method usually results in the loss of homogeneity and it is difficult to have high loading. Leaching is also very high at this technique because HPAs are not being embedded inside the silica structure, but it is being loaded onto the surface that results in reduced activity and stability[35].

The second method is co-condensation synthesis using the sol-gel technique, which involves the formation of sol and then, after cross-linking, a gel. Condensation and hydrolysis reactions of organosilica precursors (Fig. 5)[36] are the primary reactions that occur, and this process needs to be carried out in polar solvents. There is an increase in molecular weight as polymerization occurs repeatedly, which produces a highly cross-linked 3D network. Upon the addition of a base or an acid catalyst into the reaction system, the process speeds up rapidly and goes into completion. Acidic conditions are preferred as HPAs are very unstable in basic conditions[35].

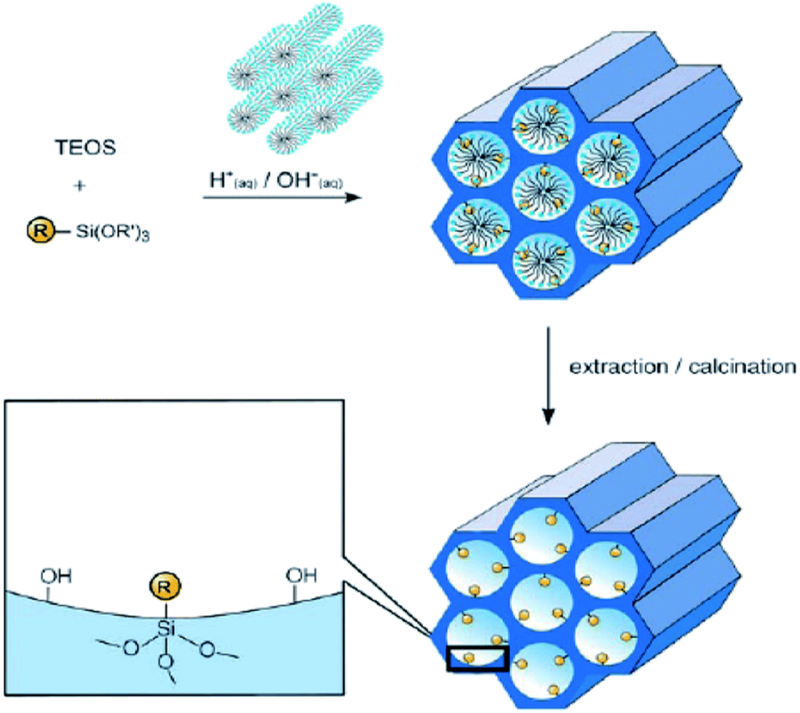


Figure 5. Hydrolysis and condensation of TEOS in a sol-gel process

HPAs are introduced into the silica network by co-condensation of an oxide precursor with clusters of HPA by the sol-gel method. They are embedded in the framework of the silica material by forming Si-O-W bonds covalently. Highly mesoporous substances can be achieved by introducing surfactants which will be necessary for desired large surface areas. Active sites are distributed evenly with this type of direct synthesis. It yields highly porous materials that are relatively more stable with improved materials' performances[37]. Homogeneity and porosity can be controlled and due to the HPA being relatively more stable on the prepared porous material, the sol-gel method is a much more convenient and advantageous technique to use.

Due to the high acidity of HPAs and the numerous advantages when on solid supports, silicated HPAs tend to be very useful in catalysis. Various reactions including productive use of silicated heteropolyacids $H_3PW_{12}O_{40}/SiO_2$ (PW/SiO_2) in the synthesis of 3,4-dihydropyrimidones from urea, an aldehyde, and a keto ester in acetonitrile has been described for the first time[38]. Comparing with other classical methods, such as the Biginelli reaction conditions, using the silicated HPA has the advantage of ease of workup, excellent product yield, tolerance to different functional groups, and mild reaction conditions. Alkylation of phenol in the gas-phase by *tert*-butanol on silicated PTA gave high selectivity on para-*tert*-butylphenol product[39]. Alkylation of toluene with oct-1-ene on silicated HPA was studied on an MCM-41 support[40].

This liquid phase alkylation, which was efficiently catalyzed by HPAs of Keggin's type on MCM-41 support, gave a high yield of monoalkylation product and a conversion rate of nearly 100% for oct-1-ene. Tungstosilicic acid (HSiW), molybdophosphoric acid (HPMo), and tungstophosphoric acid (HPW) were the HPAs that were studied. The supported catalysts on MCM-41, specifically HPW and HSiW, showed significantly better activity than bulk HPAs. The conversion rate was close to 100% with the supported catalysts and yielded monoalkylation products only. The supported catalysts exhibited better efficiency in catalysis than bulk HPA and this goes to show that the surface area on the supported catalysts was the difference. The efficiency of the catalyst for alkylation was dependent on the type of HPA with HSiW on MCM-41 support having the highest activity in their work[40]. The supported catalysts can be recovered and reused[40].

Research Objectives

Catalytic performance of impregnated catalysts is the most studied even though embedded catalysts are excellent. The objective of this work is to study the catalytic activity of

HPA, which is covalently embedded into the silica matrix in liquid-phase alkylation of benzene with various alkenes. The reaction mixture composition will be analyzed using gas chromatography with a mass spectrometry detector (GC-MS).

CHAPTER 2. EXPERIMENTAL METHODS

Chemicals and Reagents

Chemicals used in the synthesis of the catalyst and alkylation studies are listed in Table 1.

Table 1. Chemicals Used

Name of Reagent	**Chemical formula**	**Supplier**	**Use**
Phosphotungstic acid hydrate (PTA)	$H_3[P(W_3O_{10})_4].xH_20$	Acros Organics (Morris Planes, NJ)	Catalyst, precursor
Benzene	C_6H_6	EMD Millipore corp. (Darmstadt, Germany)	Reactant
Dec-1-ene	$CH_3(CH_2)_7CH=CH_2$	Acros Organics (Morris Planes, NJ)	Reactant
Oct-1-ene	$CH_3(CH_2)_5CH=CH_2$	Acros Organics (Morris Planes, NJ)	Reactant
Octadec-1-ene	$CH_3(CH_2)_{15}CH=CH_2$	Alfa Aesar (Tewksbury, MA)	Reactant
Hexane	C_6H_{14}	J.T. Baker (Phillipsburg, NJ)	Solvent
Nitric Acid	HNO_3	Fisher Chemical (Pittsburgh, PA)	Reagent
Tetraethoxysilane (TEOS)	$Si(OC_2H_5)_4$	Acros Organics (Morris Planes, NJ)	Precursor
Pluronic P123	$HO[CH_2CH_2O]_{20}[CH_2CH\text{-}(CH_3)O]_{70}[CH_2CH_2O]_{20}H$	Sigma-Aldrich (St. Louis, MO)	Surfactant

Preparation of Catalyst

Catalyst H-PTA/SiO_2 was synthesized using the sol-gel method. 50 g of Pluronic P123 was added to 150 mL of ethanol. Another solution contained 72 g of TEOS and 18 g of PTA dissolved in ethanol (50 mL). The PTA/TEOS solution and 150 mL of 20% HCl were simultaneously added dropwise to the surfactant solution under continuous stirring. The resulting reaction mixture was refluxed for 24 h. The gel formed was filtered and washed with deionized water to completely remove the acid. The resulting gel was rinsed with acetone and dried overnight. The product was calcined for 5 h at 500 °C to make sure that the surfactant is completely removed[41].

Alkylation of Benzene

General Procedure

Catalysts were dehydrated for 2 h in a vacuum at 400 °C before the alkylation reaction proceeded. Then the dehydrated catalysts were added to 40 mL of a mixture of benzene and an alkene in a Parr stainless steel high-pressure reactor. The reactor was placed in a hot oil bath at a constant temperature with continuous stirring for 2 h (Fig 6). After the reaction, samples were decanted from the catalyst and analyzed.

Effect of Alkylation Conditions

The effect of temperature was studied for oct-1-ene, dec-1-ene, and octadec-1-ene. The reaction was conducted at 150, 160, 170, 180, 190, and 200 °C respectively, the molar ratio of benzene to alkene is 4:1, and 40 mg of the catalyst. In the alkylation of octadec-1-ene, only 180, 190, and 200 °C temperature was used. Effect of ratio benzene: alkene was studied for dec-1-ene.

The reaction was conducted with 2:1 and 8:1 molar ratio. The effect of the catalyst amount was studied in the reaction between benzene and dec-1-ene with 30, 20, 10, and 5 mg of the catalyst.

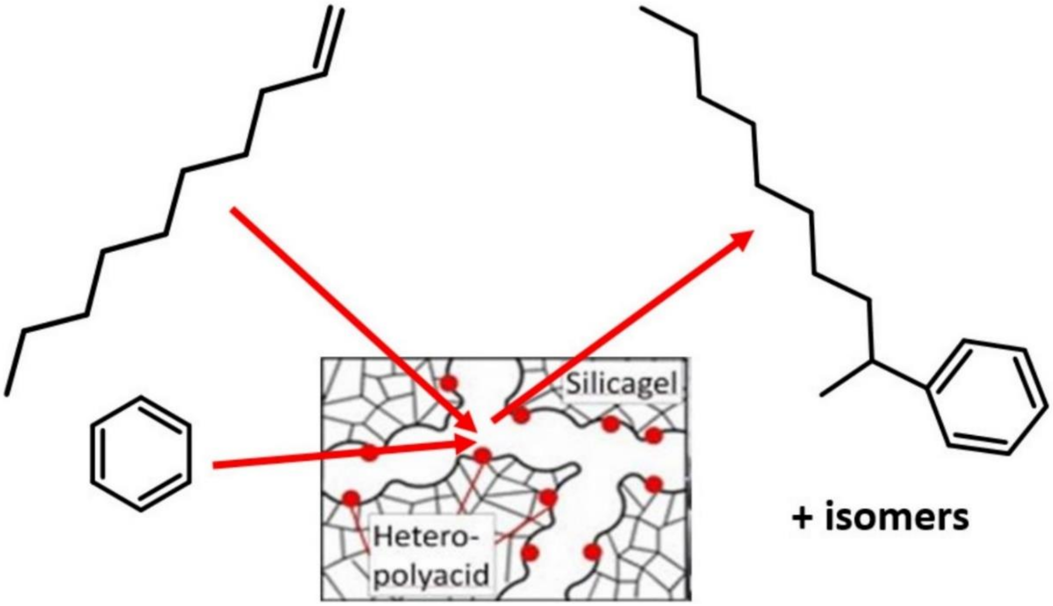


Figure 6. Benzene alkylation by dec-1-ene.

Study of Deactivation and Regeneration of the Catalyst

After the reaction of benzene with dec-1-ene (4:1 molar ratio) at 200 °C, the catalyst was recovered by decanting the liquid from the solid catalyst. The recovered catalyst was washed with small amounts of hexane and dehydrated for 2 h in a vacuum at 400 °C.

The second procedure was based on the oxidation of carbon on the catalyst by concentrated nitric acid. The recovered catalyst was treated by 15 mL of nitric acid for 2 h at 120 °C, filtered, washed by DI water, and dried on air. The catalyst was dehydrated for 2 h in a vacuum at 400 °C.

Instrumental Characterization

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of pure and used catalysts were obtained in KBr pellets on a Mattson Genesis II spectrometer (Madison, WI). Before recording spectra, the samples were grinded into a uniform powder with KBr in a mortar.

Elemental Analysis

The elemental analysis of total organic carbon content was provided by Robertson Microlit Laboratories (Ledgewood, NJ)

Scanning Electron Microscopy

SEM images of the catalyst were taken on a Zeiss DSM 940 scanning electron microscope (Oberkochen, Germany) at 20 kV. The sample was coated with gold before imaging.

Porosity

Porous characteristics were determined by using Quantachrome Nova 2200e porosimeter (Boynton Beach, FL). Samples were degassed under vacuum for 2 h at 400 °C. N_2 was used as an adsorbate for determining adsorption/desorption isotherms at -196 °C. The branch of adsorption isotherms in the range of $P/P_o = 0.2$-0.4 was used to measure the Brunauer-Emmett-Teller (BET) surface area and calculations were done using NovaWin v.11.02 software.

Particle Size Distribution

Particle size analyzer Zetasizer Nano ZS90 (Melvin, UK), was used to determine particle sizes by dynamic light scattering. Samples were dispersed in deionized water by sonication for 5 minutes before measurements.

GC-MS Analysis

After reactions were completed, the liquid phases were separated by decantation from the solid catalysts. 1 μL of liquid samples was dissolved in 5 mL of hexane and analyzed by gas chromatography on a Shimadzu GCMS-QP20210 Plus (Kioto, Japan). Rtx-5MS capillary column (30m x 0.25mm) was used with He as a carrier gas at a flow rate of 21.9 mL/min. For liquid samples obtained after alkylation of benzene by dec-1-ene and oct-1-ene (Fig 7), column oven temperature was set at 50 °C while injector temperature was set at 280 °C. For samples obtained after alkylation of benzene by octadec-1-ene, column oven temperature and injector temperature were set at 70 and 295 °C, respectively. The isomers were seperated in accordance with their boiling points.

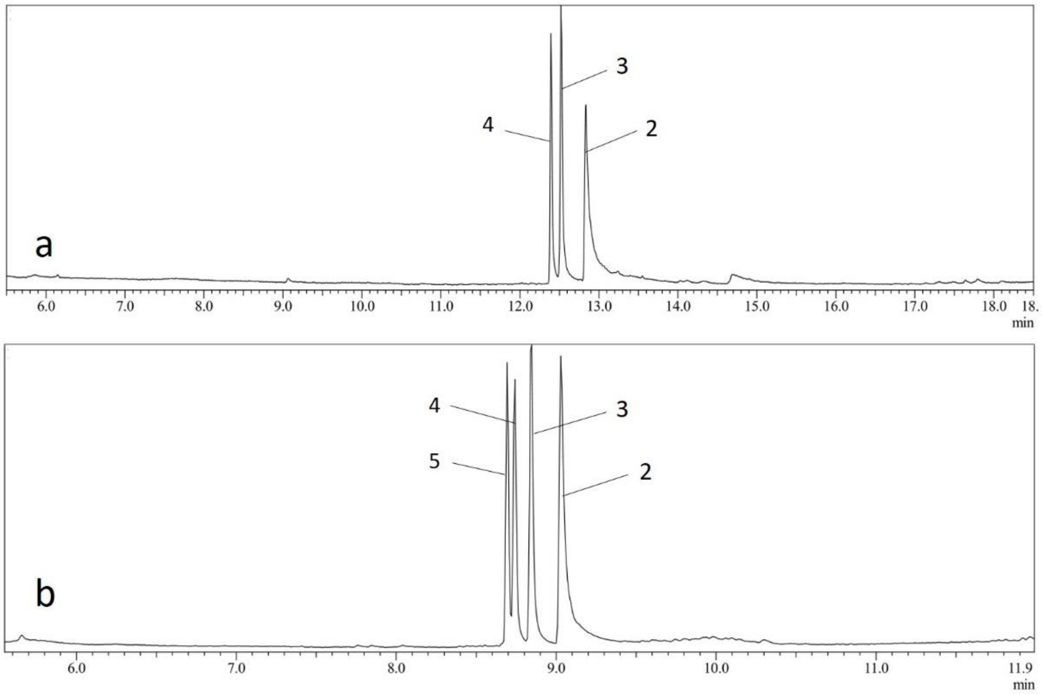


Figure 7. GC chromatograms of products after alkylation of benzene by oct-1-ene (a), and dec-1-ene (b). Numbers on peaks represent positions of phenyl ring in the alkyl chain.

CHAPTER 3. RESULTS AND DISCUSSION

Alkylation of Benzene

Effect of Temperature

PTA/SiO_2 demonstrated high catalytic activity in the conversion of alkenes into alkylbenzenes than non-immobilized pure PTA. Figure 8 illustrates the catalytic activity of pure PTA and PTA/SiO_2 in the conversion of different alkenes at various temperatures.

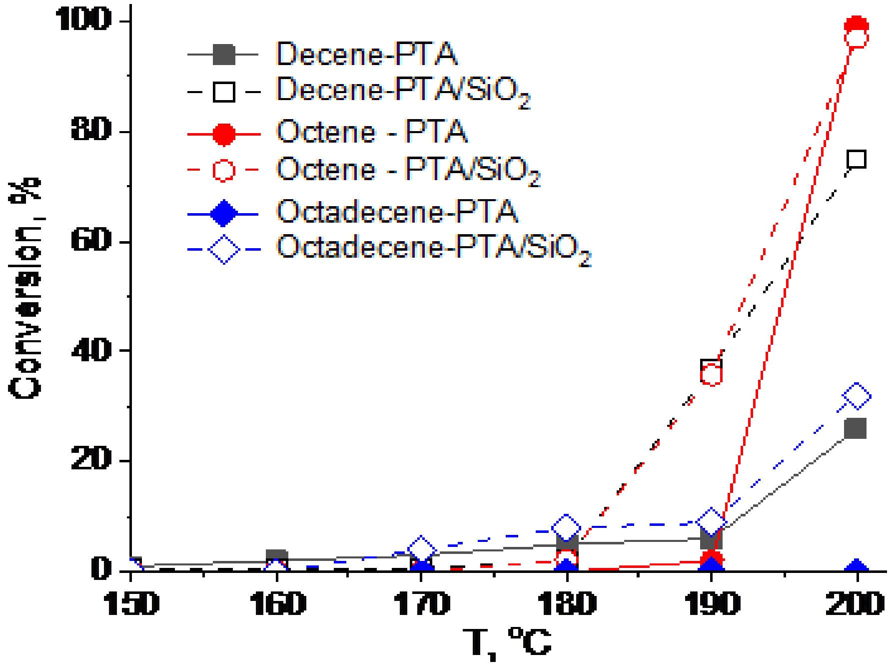


Figure 8. Comparative catalytic activity of pure PTA and PTA/SiO_2 at various temperatures

Conversion of alkenes, oct-1-ene, and dec-1-ene, to the products catalyzed by pure PTA and PTA/SiO_2 began at 150 °C followed by a steady increase to higher conversion rates at 200 °C. For oct-1-ene and dec-1-ene, conversion reached 97% and 75%, respectively. Octadec-1-ene showed notable catalytic activity (32% conversion) only at 200 °C. These experiments demonstrated that the conversion of alkenes to the products depends on the alkene and the state of the catalytically active substance.

Effect of the Amount of Catalyst

Benzene alkylation with dec-1-ene at 200 °C was carried out at various amounts of pure PTA and PTA/SiO_2. Figure 9 shows the effect of the catalyst amount on the conversion of dec-1-ene to the products. PTA/SiO_2 demonstrated higher catalytic activity with an increase of conversion when the amount of catalyst was increased. The same can effect was observed for pure PTA: the conversion rate dropped to a negligible value when the amount of catalyst was reduced.

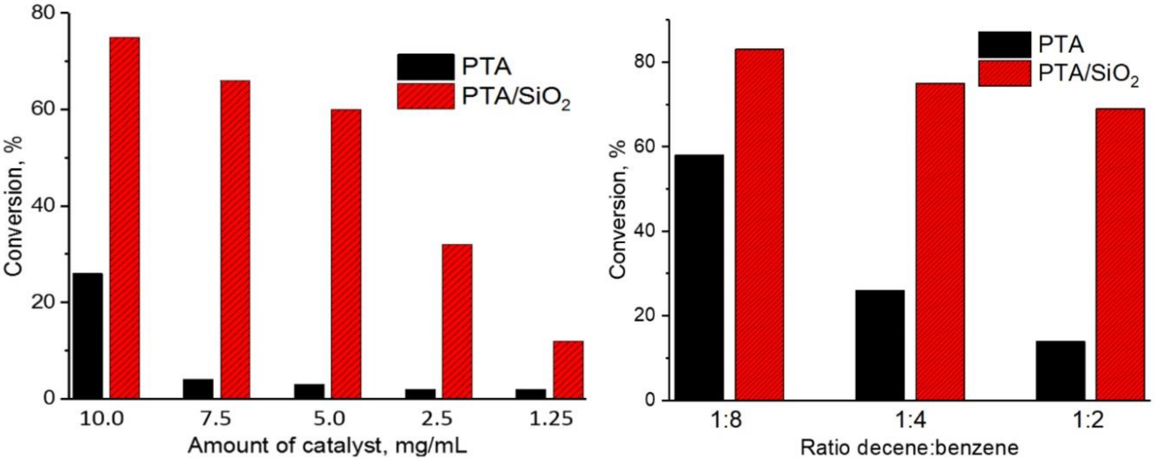


Figure 9. Effect of the catalyst amount (left) and alkene to benzene ratio (right)

Effect of Alkene to Benzene Molar Ratio

Benzene alkylation reaction with dec-1-ene at 200 °C was carried out with different molar ratios of decene to benzene. Catalytic activities of pure PTA and PTA/SiO_2 were compared. It was found that the conversion of dec-1-ene rises with an increase of the content of benzene in the reaction mixture for both catalysts. As shown in Figure 9, 1:8 molar ratio of decene to benzene resulted in the highest conversion for both catalysts. Overall, PTA/SiO_2 demonstrated higher catalytic activity with the highest conversion of 83% for 8:1 molar ratio between benzene:decene. The highest conversion rate for pure PTA was 58% at the same conditions.

Phenylalkane Isomers Distribution

Alkylation of benzene by oct-1-ene and dec-1-ene produced all linear phenylalkane isomers except 1-phenyl isomers. Obtained products were analyzed with GC-MS and it showed that pure PTA had higher selectivity on 2-phenyloctane compared with PTA/SiO_2, 53% vs. 49% for phenyloctane isomers as shown in Figure 10. For phenyldecane isomers, PTA/SiO_2 had higher selectivity on 3-phenyldecane compared with pure PTA, where 2-phenyldecane was a major product.

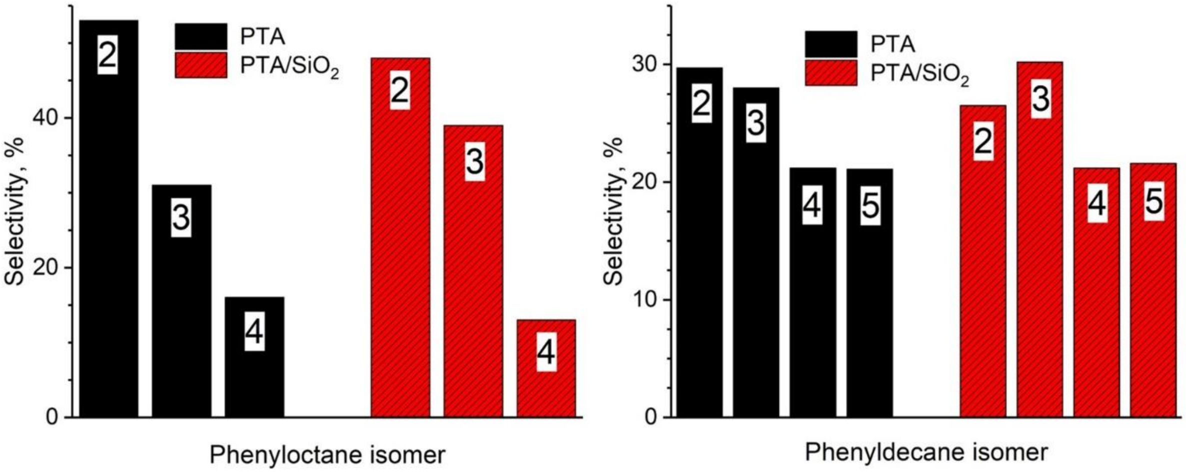


Figure 10. Isomers distribution of alkylated products: phenyloctane (left) and phenyldecane (right) isomers

4-and 5-phenyldecanes were formed in almost equal amounts on both catalysts. Contents of eight isomeric phenyloctadecenes were not calculated due to the partial overlap of their peaks.

Isomerization of Alkenes

GC-MS analysis showed the isomerization of oct-1-ene and dec-1-ene during the reaction. Almost all oct-1-ene and dec-1-ene isomerized into other isomers, mostly oct-2-ene and dec-2-ene.

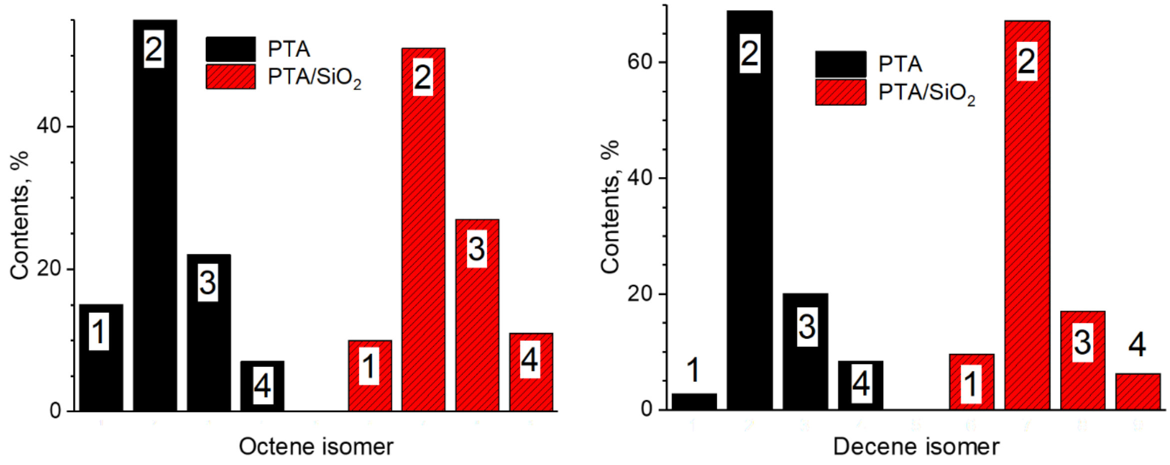


Figure 11. Distribution of octene (left) and decene (right) isomers

Regeneration of the Catalyst

After separation of the catalyst from the reaction mixture and washing by hexane, its activity in the second cycle was significantly reduced. The conversion of decene reached only 4%. In the case of treatment by nitric acid, it was only 3.4%. Thus, the activity of the catalyst was not fully recovered.

Instrumental Characterization

SEM Imaging

PTA/SiO$_2$ consisted of spherical particles and formed large agglomerates of 1-5 μm in diameter, as shown in Figure 12. Smaller particles of silica with irregular shapes were also found. The sizes of the small particles of silica varied in the range of 300-500 nm.

Particle Size Distribution

PTA/SiO_2 particles before alkylation reaction, as shown in Figure 13, had sizes between 300 and 600 nm, with the mean particle size at 417 nm. It significantly decreased after alkylation reaction at 200 °C. They had smaller sizes between 150 nm and 400 nm with the mean particle size at 253 nm.

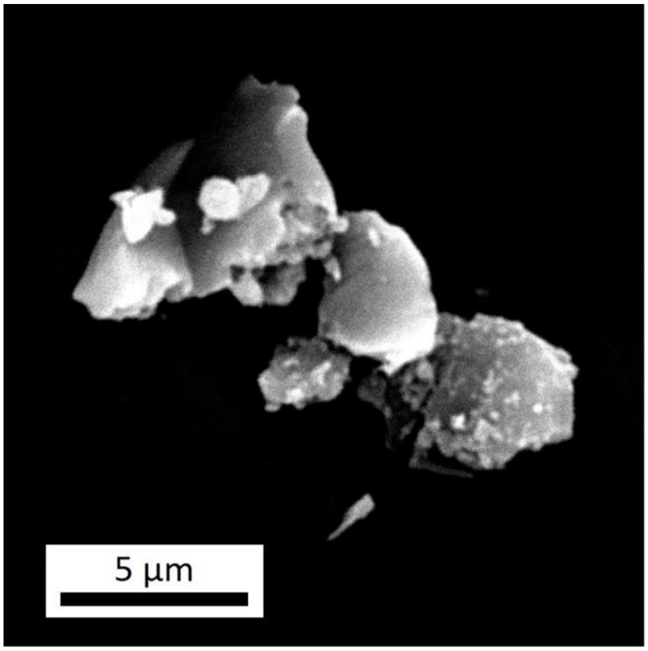


Figure 12. SEM image of PTA/SiO_2

Formation of Carbon Deposits on the Catalyst

Carbon deposits were formed on the catalyst PTA/SiO_2 during the alkylation reaction of benzene by dec-1-ene at all studied temperatures (Table 1). Their formation resulted from a side reaction of cationic alkene polymerization on acidic active sites. Alkylation at 190 °C produced the highest content of carbon on the catalyst. Conducting reaction at temperatures below 180 °C produced lower contents of carbon deposits.

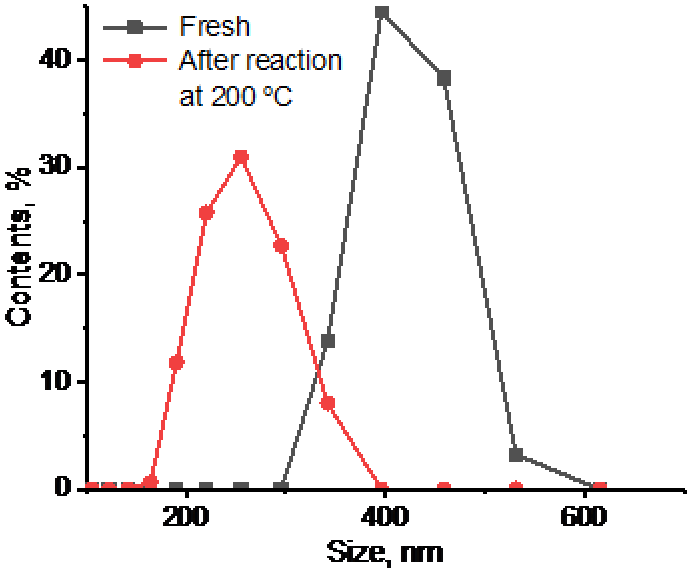


Figure 13. Particle size distribution for PTA/SiO$_2$ particles before (black) and after (red) alkylation of dec-1-ene at 200 °C

BET Surface Area

BET surface area decreased significantly after the alkylation reaction of dec-1-ene at 200 °C (Table 2). The amount of carbon deposits formed on the catalyst after the alkylation reaction corresponds to these data.

FT-IR Spectroscopy

Figure 14 shows FT-IR spectra of PTA/SiO$_2$ before and after the alkylation reaction. The spectra of silica gel have characteristic bands at 805, 1080 (υ_{SiO}), 1654 (H_2O), and 3480 cm^{-1} (υ_{OH}). A broad band at 962 cm^{-1} corresponds to O-W-O stretching vibrations from the Keggin structure of the PTA.

Table 2. Characteristics of Fresh and Used Catalyst PTA/SiO_2

Reaction temperature, °C	Carbon contents, wt.%	BET surface area, m^2/g	Mean particle size, nm
Fresh	-	585	417
150	3.92	423	322
160	3.81	339	244
170	2.93	334	239
180	3.80	364	252
190	8.30	328	262
200	7.22	270	253

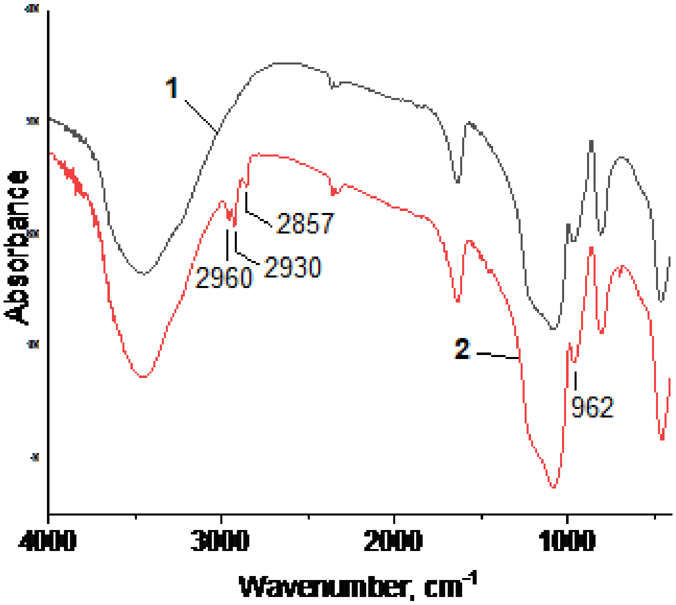


Figure 14. FT-IR spectra of PTA/SiO_2 before (black) and after (red) alkylation

After the alkylation reaction, new bands at 2960, 2930, and 2857 cm^{-1} (υ_{CH}) indicated the presence of traces of hydrocarbons deposited on the catalyst.

Discussion

The presence of immobilized PTA in the silica matrix was confirmed by FT-IR spectroscopy (Fig. 14) and atomic adsorption spectroscopy[42]. Covalent bonding of PTA was evident from ^{29}Si NMR study[41].

In all experiments, the catalytic activity of PTA/SiO_2 was higher than pure PTA. As shown in Fig. 8, PTA did not catalyze the conversion of octadec-1-ene even at 200 °C. It demonstrates the effect of porosity and, as a result, higher surface area of immobilized catalyst on the catalytic activity. As was found by the porosimetry study, its BET surface area was 585 m^2/g compared to 0.3 m^2/g for PTA. The content of PTA in the catalyst was 0.2 mg/g[42]. Even though the total amount of PTA in the reaction mixture was lower in the case of PTA/SiO_2, better accessibility of its active sites provided a higher conversion of alkenes to phenylalkanes.

Comparative conversions of different alkenes at the same temperature are in agreement with literature data, which reported a decrease of conversion with an increase of alkene chain length[43]. While oct-1-ene almost completely converted to phenyloctanes, conversion of octadec-1-ene reached only 32% at the same conditions. Thus slow diffusion of bulky alkene molecules to the active sites limits their conversion. Differences in activity of the catalyst are evident from the comparison of turnover numbers (TON) for different alkenes and their molecular volumes calculated using Spartan v.6.1.8 software (Table 3).

Table 3. Molecular Volumes and TON of Alkenes on Pure and Immobilized Catalyst at 200 °C

Alkene	Molecular volumes, Å^3	TON	
		PTA	PTA/SiO$_2$
Oct-1-ene	158	216	2829
Dec-1-ene	194	51	1875
Octadec-1-ene	341	0	686

Increasing the catalyst amount in the reaction mixture resulted in an increase of alkene conversion (Fig. 9). At lower catalyst loading, conversion increased linearly, which proved fast external diffusion of the reagents to the active sites[44]. Although the relationship between the amounts of available active sites on the reaction rate was evident at any loading, their excess at higher loading of the catalyst produced some leveling effect[43]. Interestingly, pure PTA had very low catalytic activity at reduced loadings. A possible explanation of this unusual fact can be the agglomeration of dispersed hydrophilic PTA particles in a non-polar solvent system. It reduces their surface area and, as a result, accessibility of active sites. In contrast, PTA/SiO$_2$ particles deagglomerate during the reaction (Fig. 13).

Low ratio alkene to benzene favored its high conversion (Fig. 9). This effect was expected from Le Chatelier principle in the reaction mixture at equilibrium. In addition, a large excess of benzene prevents a side reaction of dialkylation.

All linear isomeric phenylalkanes were found in the mixture of products (Fig. 10). In the case of phenyloctanes, the major isomer was 2-phenyloctane. For phenyldecane isomers, 2- and 3-phenyldecanes were major products. It should be noted that PTA/SiO$_2$ had a higher isomerizing ability than PTA. Respective amounts of 3-substituted isomers were higher than on PTA. Among phenyldecanes, 3-phenyl isomer was even a major product. 2- and 3-phenyl isomers are both formed from 2-alkenes, depending where the alkene was protonated and what carbon atom (2 or 3) has (+). They both are secondary carbenium ions. Also 3-phenyl isomer can be formed from 3-alkenes that are products of isomerization of 2-alkenes.

The mechanism of benzene alkylation consists of several steps[42]. First, alkenes form carbenium ions on acidic active sites. Obtained ion can isomerize with the migration of (+) along the chain. The most thermodynamically stable carbenium ions have (+) in the middle of the chain. Then carbenium ions react with benzene producing corresponding phenylalkanes. Finally, phenylalkanes can isomerize on the same active sites[17].

As it can be seen in Fig. 11, oct-2-ene and dec-2-ene are major alkene isomers in the reaction mixture. Higher contents of 3-, 4- and 5-phenyl isomers in the reaction mixture with respect to corresponding alkene isomers cannot be explained by isomerization of corresponding alkenes on the catalyst. Evidently, it resulted from secondary isomerization of primarily formed alkylation products. It is known that weakly acidic catalysts, such as HF or H_2SO_4, do not isomerize phenylalkanes[17]. Their isomerization requires stronger acidic sites. Thus the composition of the products confirms the high acidity of PTA/SiO_2.

Although the notable conversion of alkenes to phenylalkanes started after 180 °C, the isomerization of alkenes occurred even below this point. In the range of temperatures between 150 and 180 °C, 5-50% of starting terminal alkenes converted to internal isomers. Thus the catalyst was sufficiently acidic to produce carbenium ions from alkenes. It explains the formation of carbon deposits on the catalyst at any studied conditions by side reactions of cationic alkene polymerization on active sites[45]. Bands at 2857-2960 cm^{-1} indicate the presence of solid polymeric hydrocarbons after polymerization of alkenes on the catalyst. These deposits cannot be extracted by solvents. The amounts of carbon at temperatures 150-180 °C varied between 2.93 and 3.92 wt.%. At higher temperatures, it increased up to 8.30 wt.%.

Considering still an insufficient success in the recovery of initial catalytic activity of the used catalyst, further efforts should be made to determine optimal conditions for the catalyst regeneration.

CONCLUSIONS

Polycondensation of tetraethyl orthosilicate with phosphotungstic acid resulted in the formation of structurally stable porous material with high surface acidity. This material demonstrated catalytic activity in liquid phase alkylation of benzene by long-chain alkenes. Yields of alkylbenzenes significantly exceeded corresponding values for pure phosphotungstic acid. Conversion of alkenes to the products depended on their length and was the highest in the case of oct-1-ene. During the reaction, the formation of carbon deposits on the catalyst was observed with the deagglomeration of larger particles.

REFERENCES

(1) Kocal, J. A.; Vora, B. V.; Imai, T. Long-Chain Alkylbenzenes: Their Analytical Chemistry, Environmental Occurrence and Fate. *Int. J. Environ. Anal. Chem.* 1**986**, *26* (3–4), 241–263. https://doi.org/10.1021/es00115a006

(2) Elsgaard, L, Petersen, S. O.; Debosz, K. Effects and Risk Assessment of Linear Alkylbenzene Sulfonates in Agricultural Soil. Short-Term Effects on Soil Microbiology. *Environ. Toxicol. Chem*. **2001**, 20 (8), 1656–1663. https://doi.org/10.1002/etc.5620200806

(3) Mungary, A. K.; Kumar, P. Fate of Linear Alkylbenzene Sulfonates in the Environment: A Review. *Int. Biodeterior. Biodegrad.* **2009**, *63* (8), 981–987. https://doi.org/10.1016/j.ibiod.2009.03.012

(4) Bellussi, G.; Perego, C. New Catalysts and New Processes in the Industrial Alkylation of Aromatics. *Catal. Today* **2002**, *73* (1-2), 3–22. https://doi.org/10.1016/S0920-5861(01)00511-9

(5) Wang, J. J.; Chuang, Y. Y.; Hsu, H. Y.; Tsai, T. C. Toward Industrial Catalysis of Zeolite for Linear Alkylbenzene Synthesis: A Mini Review. *Catal. Today* **2017**, 109–116. https://doi.org/10.1016/j.cattod.2017.05.046

(6) Scheibel, J. J.The Evolution of Anionic Surfactant Technology to Meet the Requirements of the Laundry Detergent Industry. *J. Surfactants Deterg.* **2004**, *7* (4), 319–328. https://doi.org/10.1007/s11743-004-0317-7

(7) Kocal, J. A.; Vora, B. V.; Imai, T Production of Linear Alkylbenzenes. *Appl. Catal. A Gen.* **2001**, *221* (1–2), 295–301. https://doi.org/10.1016/S0926-860X(01)00808-0

(8) Kolesnikov, I. M.; Vinokurov, V. A.; Gushchin, P. A.; Ivanov, E. V.; Kolesnikov, S. I.; Lyubimenko, V. A. Efficient Catalysts for Benzene Alkylation with Olefins. *Catal. Commun.* **2016**, *82,* 1–6. https://doi.org/10.1016/j.catcom.2016.04.001

(9) Bai, S.; Dai, Q.; Chu, X.; Wang, X. Dehydrochlorination of 1,2-Dichloroethane over Ba-Modified Al_2O_3 Catalysts. *RSC Adv*. **2016**, 6, 52564–52574. https://doi.org/10.1039/C6RA08855D

(10) Jones, E. K. Commercial Alkylation of Paraffins and Aromatics. In "Advances in Catalysis", Elsevier, **1958**, 165–195. https://doi.org/10.1016/S0360-0564(08)60407-1

(11) UOP Linear Alkylbenzene (LAB) Complex. UOP, A Honywell Company, **2007**. https://www.honeywell-uop.cn/wp-content/uploads/2011/02/UOP-LAB-Complex-Data-Sheet.pdf (accessed May 20, 2020)

(12) Reddy, B. M.; Sreekanth, P. M.; Lakshmanan, P. Sulfated Zirconia as an Efficient Catalyst for Organic Synthesis and Transformation Reactions. *J. Mol. Catal. A Chem.* **2005**, *237* (1–2), 93–100. https://doi.org/10.1016/j.molcata.2005.04.039

(13) Ledneczki, I.; Dárányi, M.; Fülöp, F.; Molnár, Á. SAC-13 Silica Nanocomposite Solid Acid Catalyst in Organic Synthesis. *Catal. Today* **2005**, *100* (3–4), 437–440. https://doi.org/10.1016/j.cattod.2004.09.076

(14) Wilson, K.; Clark, J. H. Solid Acids and Their Use as Environmentally Friendly Catalysts in Organic Synthesis. *Pure Appl. Chem.* **2000**, *72* (7), 1313–1319. https://doi.org/10.1351/pac200072071313

(15) Nikoonahad, A, Djahed, B.; Norzaee, S.; Eslami, H.; Derakhshan, Z.; Miri, M.; Fakhri, Y.; Hoseinzadeh, E.; Ghasemi, S. M.; Balarak, D.; Fallahzadeh, R. A.; Zarrabi, M.;Taghavi, An Overview Report on the Application of Heteropoly Acids on Supporting Materials in the Photocatalytic Degradation of Organic Pollutants from Aqueous Solutions. *PeerJ* **2018**, (9). https://doi.org/10.7717/peerj.5501

(16) Sartori, G.; Ballini, R.; Bigi, F.; Bosica, G.; Maggi, R.; Righi, P. Protection (and Deprotection) of Functional Groups in Organic Synthesis by Heterogeneous Catalysis. *Chem. Rev.* **2004**, *104* (1), 199–250. https://doi.org/10.1021/cr0200769

(17) Ren, Y.; De Almeida, J. L. G.; Dufaux, M.; Taarit, Y. B.; Naccache, C. Linear Alkylbenzene. *J. Am. Oil Chem. Soc*. **1994**, 71 (7), 675–694. https://doi.org/10.1007/BF02541423

(18) Zhang, Z.; Han, Y.; Zhu, L.; Wang, R.; Yu, Y.; Qiu, S.; Zhao, D.; Xiao, F.-S. Strongly Acidic and High-Temperature Hydrothermally Stable Mesoporous Aluminosilicates with Ordered Hexagonal Structure. *Angew. Chem. Int. Ed. Engl.* **2001**, 40 (7), 1258–1262. https://doi.org/10.1002/1521-3773(20010401)40:7%3C1258::AID-ANIE1258%3E3.0.CO;2-C

(19) Nowak, I.; Ziolek, M. Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis. *Chem. Rev.* **1999**, 99 (12), 3603–3624. https://doi.org/10.1021/cr9800208

(20) Tejero, J. L. B.; Danvilla, A. M. Alkylation of Aromatic Hydrocarbons in Fixed Bed Catalytic Process. *U.S. Patent* 5,146,026, September 8, **1992**.

(21) Borutskii, P. N.; Kozlova, E. G.; Podkletnova, N. M.; Gil’Chenok, N. D.; Sokolov, B. G.; Zuev, V. A.; Shatovkin, A. A. Alkylation of Benzene with Higher Olefins on Heterogeneous Catalysts. *Pet. Chem*. **2007** , 47 (4), 250–261. https://doi.org/10.1134/S0965544107040044

(22) Misono, M.; Nojiri, N. Recent Progress in Catalytic Technology in Japan. *Appl. Catal.* **1990**, *64* (C), 1–30. https://doi.org/10.1016/S0166-9834(00)81550-X

(23) Vázquez, P.; Pizzio, L.; Romanelli, G.; Autino, J.; Cáceres, C.; Blanco, M. Mo and W Heteropolyacid Based Catalysts Applied to the Preparation of Flavones and Substituted Chromones by Cyclocondensation of O-Hydroxyphenyl Aryl 1,3-Propanediones. *Appl. Catal. A Gen.* **2002**, *235* (1–2), 233–240. https://doi.org/10.1016/S0926-860X(02)00266-1

(24) Kozhevnikov, I. V. Heteropoly Acids and Related Compounds as Catalysts for Fine Chemical Synthesis. *Catal. Rev.* **1995**, *37* (2), 311–352. https://doi.org/10.1080/01614949508007097

(25) Wen, S.; Guan, W.; Wang, J.; Lang, Z.; Yan, L.; Su, Z. Theoretical Investigation of Structural and Electronic Properties of $[PW_{12}O_{40}]^{3-}$ on Graphene Layer. *Dalton Trans.* **2012**, *41* (15), 4602–4607. https://doi.org/10.1039/C2DT12465C

(26) Kozhevnikov, I. V. Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions. *Chem. Rev.* **1998**, *98* (1), 171–198. https://doi.org/10.1021/cr960400y

(27) Briand, L. E.; Baronetti, G. T.; Thomas, H. J. The State of the Art on Wells-Dawson Heteropoly-Compounds: A Review of Their Properties and Applications. *Appl. Catal. A Gen.* **2003**, *256* (1–2), 37–50. https://doi.org/10.1016/S0926-860X(03)00387-9

(28) Romanelli, G.; Autino, J. Recent Applications of Heteropolyacids and Related Compounds in Heterocycles Synthesis. *Mini Rev. Org. Chem.* **2009**, 6 (4), 359–366. https://doi.org/10.2174/157019309789371578

(29) Zhu, H.-O.; Ren, X.-Q.; Wang, J. A Comparative Study of the Catalytic Behavior of SBA-15 Supported Heteropoly Acid $H_3PW_{12}O_{40}$ and H-Y Catalysts in the Alkylation of

Benzene with 1-Dodecene. *React. Kinet. Catal. Lett*. **2004**, 83 (1), 19–24. https://doi.org/10.1023/B:REAC.0000037371.31835.60

(30) Bardin, B. B.; Davis, R. J. A Comparison of Cesium-Containing Heteropolyacid and Sulfated Zirconia Catalysts for Isomerization of Light Alkanes. *Top. Catal*. **1998**, 6 (1/4), 77–86. https://doi.org/10.1023/A:1019174624875

(31) Larsen, G.; Petkovic, L. M. Effect of Preparation Method and Selective Poisoning on the Performance of Platinum Supported on Tungstated Zirconia Catalysts for Alkane Isomerization. *Appl. Catal. A Gen*. **1996**, 148 (1), 155–166. https://doi.org/10.1016/S0926-860X(96)00232-3

(32) Faghihian, H.; Mohammadi, M. H. A Novel Catalyst for Alkylation of Benzene. *Comptes Rendus Chim.* **2012**, *15* (11–12), 962–968. https://doi.org/10.1016/j.crci.2012.08.007.

(33) Li, K.; Hu, J.; Li, W.; Ma, F.; Xu, L.; Guo, Y. Design of Mesostructured $H_3PW_{12}O_{40}$-Silica Materials with Controllable Ordered and Disordered Pore Geometries and Their Application for the Synthesis of Diphenolic Acid. *J. Mater. Chem.* **2009**, *19* (45), 8628–8638. https://doi.org/10.1039/b910416j

(34) Yang, L.; Qi, Y.; Yuan, X.; Shen, J.; Kim, J. Direct Synthesis, Characterization and Catalytic Application of SBA-15 Containing Heteropolyacid $H_3PW_{12}O_{40}$. *J. Mol. Catal. A Chem.* **2005**, *229* (1–2), 199–205. https://doi.org/10.1016/j.molcata.2004.11.024

(35) Dufaud, V.; Lefebvre, F. Inorganic Hybrid Materials with Encapsulated Polyoxometalates. *Materials (Basel).* **2010**, *3* (1), 682–703. https://doi.org/10.3390/ma3010682

(36) Rath, D.; Rana, S.; Parida, K. M. Organic Amine-Functionalized Silica-Based Mesoporous Materials: An Update of Syntheses and Catalytic Applications. *RSC Adv.* **2014**, *4* (100), 57111–57124. https://doi.org/10.1039/C4RA08005J

(37) Guo, Y.; Li, K.; Yu, X.; Clark, J. H. Mesoporous $H_3PW_{12}O_{40}$-Silica Composite: Efficient and Reusable Solid Acid Catalyst for the Synthesis of Diphenolic Acid from Levulinic Acid. *Appl. Catal. B Environ.* **2008**, *81* (3–4), 182–191. https://doi.org/10.1016/j.apcatb.2007.12.020

(38) Rafiee, E.; Shahbazi, F. One-Pot Synthesis of Dihydropyrimidones Using Silica-Supported Heteropoly Acid as an Efficient and Reusable Catalyst: Improved Protocol Conditions for the Biginelli Reaction. *J. Mol. Catal. A Chem.* **2006**, *250* (1–2), 57–61. https://doi.org/10.1016/j.molcata.2006.01.049

(39) Kumar, G. S.; Vishnuvarthan, M.; Palanichamy, M.; Murugesan, V. SBA-15 Supported HPW: Effective Catalytic Performance in the Alkylation of Phenol. *J. Mol. Catal. A Chem.* **2006**, *260* (1–2), 49–55. https://doi.org/10.1016/j.molcata.2006.07.050

(40) Liu, Y.; Xu, L.; Xu, B.; Li, Z.; Jia, L.; Guo, W. Toluene Alkylation with 1-Octene over Supported Heteropoly Acids on MCM-41 Catalysts. *J. Mol. Catal. A Chem.* **2009**, *297* (2), 86–92. https://doi.org/10.1016/j.molcata.2008.09.007

(41) Seaton, K.; Little, I.; Tate, C.; Mohseni, R.; Roginskaya, M.; Povazhniy, V.; Vasiliev, A. Adsorption of Cesium on Silica Gel Containing Embedded Phosphotungstic Acid. *Micropor. Mesopor. Mater.* **2017**, *244*, 55–66. https://doi.org/10.1016/j.micromeso.2017.02.025

(42) Kuvayskaya, A.; Garcia, S.; Mohseni, R.; Vasiliev, A. Superacidic Mesoporous Catalysts Containing Embedded Heteropolyacids. *Catal. Lett*. **2019**, *149* (7), 1983-1990. https://doi.org/10.1007/s10562-019-02738-2

(43) Yadav, G. D.; Doshi, N. S. Synthesis of Linear Phenyldodecanes by the Alkylation of Benzene with 1-Dodecene over Non-Zeolitic Catalysts. *Org. Proc. Res. Dev*. **2002**, *6* (3),

263–272. https://doi.org/10.1021/op000044s

(44) Yadav, G. D.; Siddiqui, M. I. N. I. UDCaT-5: A Novel Mesoporous Superacid Catalyst in the Selective Synthesis of Linear Phenyldodecanes by the Alkylation of Benzene with 1-Dodecene. *Ind. Eng. Chem. Res*. **2009**, *48* (24), 10803–10809. https://doi.org/10.1021/ie900610b

(45) Sengar, A.; van Santen, R. A.; Kuipers, J. A. M. Deactivation Kinetics of the Catalytic Alkylation Reaction. *ACS Catal.* **2020**, *10* (13), 6988–7006. https://doi.org/10.1021/acscatal.0c00932

VITA

KOFI KANKAM

Education: M.S. Chemistry, East Tennessee State University, Johnson City, Tennessee, 2020

B.S. Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, 2016

Professional Experience: Graduate Assistant, East Tennessee State University; College of Arts and Sciences, 2018-2020

Teaching Assistant, Kwame Nkrumah University of Science and Technology, Chemistry department, 2016-2017

Presentations**:** **Kofi Kankam**, Abbas Shilabin, The search for highly selective and potent CB1 and CB2 inhibitors: Synthesis and characterization of Benzodiazepine derivatives.

The 71st Southeastern Regional Meeting of American Chemical Society. Savannah, GA, 2019.

Eastman-NETSACS Student Research Symposium. Kingsport, TN, 2019.

Grants Received: Kofi Kankam and Vasiliev A. American Chemical Society Petroleum Research Fund 58891-UR5. ACS-PRF