ALKYLATION OF BENZENE WITH LONG CHAIN OLEFINS OVER SOLID-ACID CATALYST

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ABSTRACT

This investigation is concerned with the linear alkylbenzene production reaction by the alkylation of benzene with long chain olefins C_{10}-C_{13} over various prepared solid acid catalysts. The alkylation process was studied at different reaction temperature, Weight hourly space velocities and with constant pressure and benzene/olefin ratio. The liquid-phase of alkylation of benzene with olefins carried out over prepared tungstophosphoric acid supported on S_iO_2 with 5, 10, 20 and 30 wt. % loading catalysts in a fixed bed reactor. Prepared tungstophosphoric acid supported over silica catalyst with 30 % loading gave the highest conversion of olefin to linear alkylbenzene (94% conversion) at 398K and $5h^{-1}$. The study of the kinetics of benzene alkylation with olefins over these prepared catalysts reveals that the reaction is second order. The value of Thiele modulus for each prepared catalysts is lower than 0.4 which means that diffusion free regime and the surface reaction is the limiting step for the alkylation process.

INTRODUCTION

The alkylation of benzene with higher n-alkenes, basically in the range of C_{10} to C_{13}, is preformed industrially in the manufacture of linear alkylbenzene (LAB), an intermediate used in the production of linear alkylbenzenesulphonate (LAS), the most important biodegradable surfactant in the detergency sector.

LAB is industrially produced by one of three technologies of benzene alkylation from alkenes with hydrofluoric acid or aluminum trichloride as catalysts or from chloroalkanes in the presence of aluminum trichloride as a catalyst (1). These two Friedel-Crafts catalysts (hydrofluoric acid and aluminum trichloride) give different phenyl isomer distributions in the LAB produced. Alkylation using homogeneous catalysts such as sulphric acid, hydrofluoric acid and aluminum trichloride has been investigated by Alul (2) and Olson (3).

Since homogeneous acid catalysts are a source of pollution, industrial hazard and equipment corrosion, a good deal of effort has been into research and development to replace hydrofluoric acid HF and aluminum trichloride $AlCl_3$ by a non-corrosive solid catalyst having acid properties. A Wide variety of heterogeneous catalysts has been investigated so far, such as rare earth X and Y zeolites (4), silicotungstic acid supported on alumina and on silica-alumina (5), ZSM-4, ZSM-5, ZSM-20, ZSM-38, ZSM-12, mordenite and offertite (6-11), Ca, NaY (12), HNaY zeolites (13), MCM-22 (14) and with aluminum silicate and/ or magnesium silicate (15-16). Sivasanker and Thangaraj (17) and Sivasanker et al. (18) have studied the alkylation of benzene with an industrial mixture of higher alkenes for the production of LAB over β-zeolite, mordenite and ZSM-12 catalysts. Universal Oil Products (UOP/ Petresa) have announced new process in Canada using a solid acid catalyst and the first industrial plant using this solid acid catalyst technology operated in Canada in 1995 (19-20).

To measure how much the reaction rate is lowered because of the resistance to pore diffusion, the quantity ε called effectiveness factor must be defined (21).

$$Eff.Factor\ \varepsilon = \frac{(actual\ mean\ reaction\ rate\ within\ pore}{(rate\ if\ not\ slowed\ by\ pore)} \quad \text{.... (1)}$$

$$= \frac{r_A,\ with\ diffusion}{r_A,\ without\ diffusion\ resist.} \quad \text{.... (2)}$$

Thiele modulus can be estimated for each catalyst type depending on its physical properties and process operation condition. For first order surface reaction Thiele modulus can be estimated in Eqn. (3).

$$M_T = L * \sqrt[2]{k''' / D_e} \quad \text{…. (3)}$$

The aim of this work is the production linear alkylbenzene by alkylation of benzene with long chain olefins over prepared solid acid catalysts such as tungstophosphoric acid supported on silica with 5, 10, 20 and 30 wt. % loading catalysts in a fixed bed reactor. Study the effect of various range of temperature and weight hourly space velocity (WHSV). Then studying the reaction kinetics and developing the mathematical model to describe the rate of reaction and estimate all parameters of this model.

EXPERIMENTAL WORK

Experimental Equipment

The experimental equipment used in this study is shown in the Figure (1). Benzene and olefins were charged in a feed conical vessel. Dosing pump flows the mixture of olefin and benzene to the reactor at volumetric flow rate (0- 1000) cm^3/h and discharge pressure 10 bar. The reactor is stainless steel tube with 19 mm inside diameter, 800 mm length and 2mm thickness (Catatest Model BL-2 supplied by Geomecanique, France). The reactor supplied with four heaters (150 mm length for each) and 2 insulators (100 mm length). These heaters were controlled by a temperature indicators and controllers to set the desired temperature for each one automatically. The temperature reading along the full length of reactor was obtained by chromel-alumel thermocouples (K type). For each experiment 10 g of catalyst was charged in the middle zone of the reactor between upper and lower zone filled with inert glass beads.

Fig. (1) Alkylation Reaction Unit (Photographic View)

Process flow diagram of the alkylation process

The alkylation process was examined at reaction temperatures varied from 353-398 K, while the weight hourly space velocities from 5-20h^{-1}. The pressure and benzene /olefin ratio were kept constant at 10 bar and 10/1, respectively. Before the alkylation reaction was started, the catalyst was activated at 423 K and atmospheric pressure in nitrogen flow of (1 liter/h) for 2 h. Then the catalyst bed was cooled to about 333 K and N_2 flow was adjusted at 10 ml /min to keep the system at the required pressure 10 bar. The mixture of benzene and olefins were charged from the conical vessel to the reactor through check valve. The flow rate of reactants was adjusted to the desired value for each particular experiment. The mixture of reactants (Benzene and Olefins) and N_2 is entering the preheating zone and then passed the catalyst bed. As soon as the flow rate of reactants was stabilized, the temperature of the reaction section was adjusted to the desired for each particular experiment. The liquid product was collected in a liquid receiver, which was drained at the end of the run to collection flask.

Preparation of tungstophosphoric acid supported on SiO_2 catalyst

Series of tungstophosphoric acid catalysts supported on silica with different texture properties were prepared by impregnation method. Supports were impregnated with aqueous solutions of the acid using the incipient wetness technique. After impregnation the catalysts were dried at about 393K for 2.5h. The obtained material was then calcined at 523K for 3h, in an electrical furnace.

Test method

The weight percentage of SiO_2 was determined by fusion method (22). The fusion mixture in this method was (K_2CO_3+Na_2CO_3).

An off-line gas chromatograph (Packard 438A, USA) flame ionization detector (FID) was used to analysis the composition of linear alkylbenzene in the liquid product. The apparatus consists of a stainless steel capillary column with 50m long and 0.25 mm inside diameter. The column was open tube coated (SE–30) name type.

RESULT &DISCUSSION

Effect of temperature

The effect of reaction temperature in the range of 353- 398 K on olefin conversion at different space velocities was studied. As expected, Figure 2 shows that the increasing of temperature will increase the olefin conversion. The olefin conversion at WHSV= 20h^{-1} was not significantly affected by the increasing of the temperatures from (355- 398K). it was found that no dialkylated product was found even when the temperature was increased from (355-398K). This was because of excess benzene in the reaction mixture. In contrast, at 15, 10 and 5 h^{-1} the conversion was significantly increased with increasing the temperatures. In addition, high reaction temperature (≥ 433K) can lead to the comparatively quick deactivation of catalyst. It could be expected that the tendency of the polymerization of olefin would be raised by high reaction temperature (≥ 433K)[23].

Effect of WHSV

The effect of weight hourly space velocity between 5-20h^{-1}on olefin conversion at different reaction temperatures was studied. The results of this investigation were presented in Figure (3). This figure show that the decreasing of WHSV will increase the olefin conversion, because the decreasing in WHSV of the feed results to increasing in the residence time, which leads to aplenty of contact time of the feed (reactants) with the catalyst inside reactor, and this means effectives conversions of olefin to linear alkylbenzene. All the results indicate that low WHSV is favored alkylation process.

Kinetic of alkylation process

The kinetic of alkylation process of olefin and benzene was studied. For second order kinetic reaction, the performance equation for reactors containing porous catalyst particles for plug flow type, which represented the solid catalyzed reactions (21), the performance equation may be obtained in Eq.(1).

$$k' \cdot C_{A_\circ} \cdot \tau' = \frac{X_A}{(1 - X_A)} \qquad \ldots.\ (4)$$

A plot of $\frac{X_A}{1 - X_A}$ $vs\ \tau' C_{A_\circ}$ gives straight lines with slopes equal to alkylation rate constant for linear alkylbenzene produced over various types of catalysts. The statistical analysis of these straight lines was computed to identify significant. The correlation coefficients (ρ^2) for all the straight lines of second order kinetic reaction are > 0.95 which is statistically significant. The alkylation rate constants for linear alkylbenzene tabulated in Table (1). These results indicated that the alkylation rate constant increased with increasing reaction temperature.

Thiele Modulus and Effectiveness factor

For second order kinetic reaction, Thiele modulus was obtained by eqn. (5).

$$M_T = L \cdot \sqrt{\frac{(k''' \cdot C_A)_{obs}}{D_e}} \qquad \ldots.\ (5)$$

Effective diffusivity for a porous solid can be estimated by using eqn. (6) (24).

$$D_e = 19400 \frac{\theta^2}{\tau_m \cdot S_g \cdot \rho_p} \sqrt{\frac{T}{M}} \qquad \ldots\ldots (6)$$

The effective diffusivities as well as Thiele modulus values were calculated and presented in Table (2).

The effectiveness factor for all types of catalyst was near to be 1 because Thiele modulus values were very small ($M_T < 0.4$) as mentioned by H.Scott Fogler (25), Levenspiel (21) and Hougen and Watson (26) that indicates the concentration of reactant doesn't drop appreciably within the pore, thus pore diffusion offers negligible resistance. This can also be verified by noting that values for M_T means either short pore, slow reaction or rapid diffusion, all three factors tending to lower the resistance to diffusion.

CONCLUSIONS

The liquid-phase of alkylation of benzene with olefins was examined by tungstophosphoric acid supported on S_iO_2 with 5, 10, 20 and 30 wt. % loading catalysts in a fixed bed reactor. Alkylation conversion increased with increasing temperature of reaction 353-398K and decreasing with increasing WHSV 5- 20h^{-1}. Prepared tungstophosphoric acid supported over silica catalyst with 30 % loading gave the highest conversion of olefin to linear alkylbenzene (94% conversion) at 398K and 5h^{-1}The alkylation reaction of benzene with olefins is well represented by second order performance equation for reactor containing porous catalyst particles as plug type. The values of Thiele modulus for each prepared catalysts are (< 0.4) which means that diffusion free regime and the chemical surface reaction is the limiting step for alkylation process.

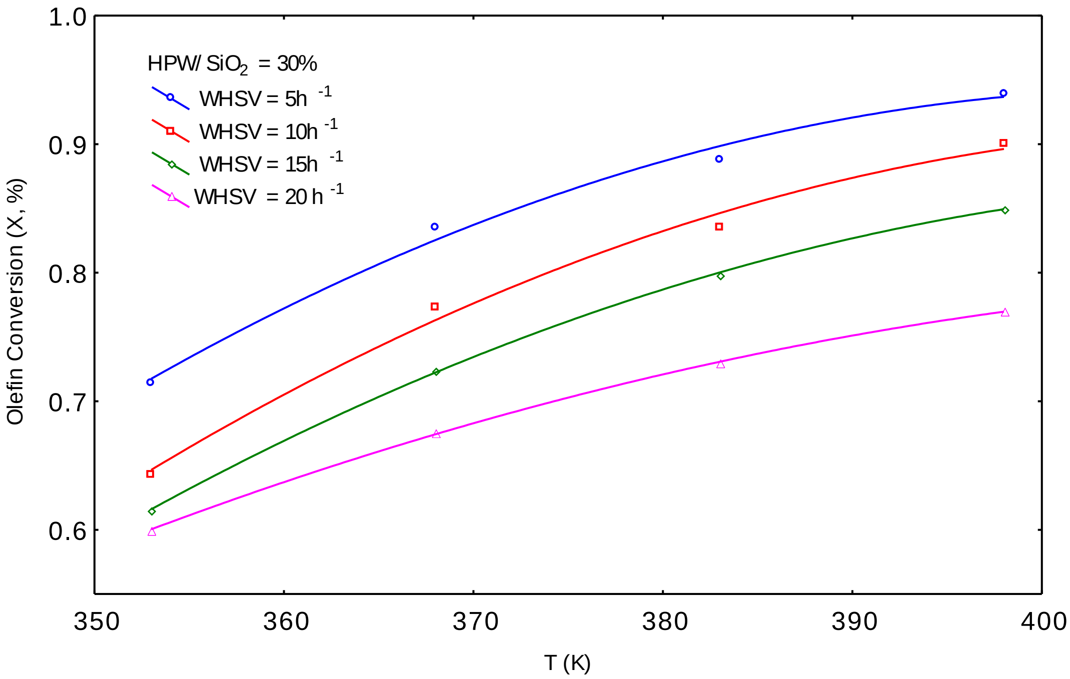

Fig. (2) Effect of Temperatures on the Olefins Conversion at Various WHSV for HPW/SiO_2= 30 wt. % Catalyst.

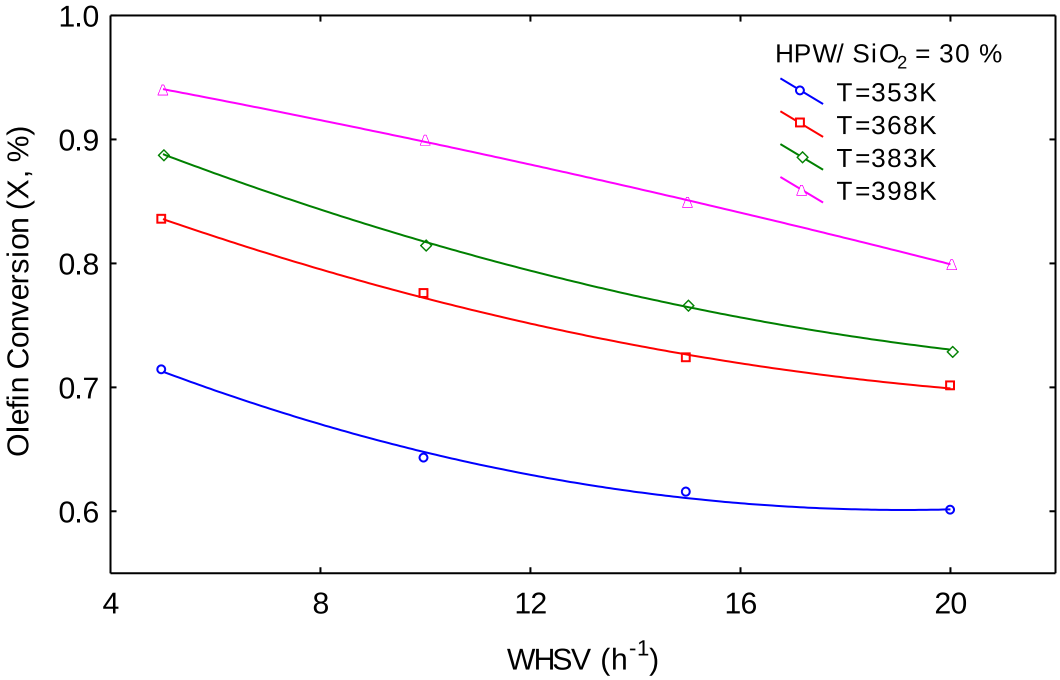

Fig. (3) The Effect of Weight Hourly Space Velocity on the Olefin Conversion at various temperatures for HPW/SiO_2 = 30 wt. % Catalyst.

Table (1) The alkylation rate constants for linear alkylbenzene production

HPW / SiO_2- 5 wt.%	
Temperature (K)	k' $(lit^2 / Kg.mol.h)$
353	32.00
368	43.30
383	65.00
398	68.00
HPW / SiO_2- 10 wt.%	
Temperature (K)	k' $(lit^2 / Kg.mol.h)$
353	39.87
368	53.50
383	66.20
398	82.00
HPW / SiO_2- 20 wt.%	
Temperature (K)	k' $(lit^2 / Kg.mol.h)$
353	59.00
368	117.00
383	172.00
398	228.50
HPW / SiO_2- 30 wt.%	
Temperature (K)	k' $(lit^2 / Kg.mol.h)$
353	167.00
368	451.10
383	859.00
398	1806.00

Table (A-6) Thiele Modulus with relative properties

HPW / SiO_2- 5 wt.%		
Temperature (***K***)	$D_e * 10^3$ (cm^2/s)	$M_T * 10^3$
353	1.43	2.88
368	1.46	3.25
383	1.49	3.84
398	1.51	3.82
HPW / SiO_2- 10 wt.%		
Temperature (***K***)	$D_e * 10^3$ (cm^2/s)	$M_T * 10^3$
353	1.47	3.25
368	1.50	3.63
383	1.53	3.78
398	1.56	4.16
HPW / SiO_2- 20 wt.%		
Temperature (***K***)	$D_e * 10^3$ (cm^2/s)	$M_T * 10^3$
353	1.68	3.50
368	1.71	4.50
383	1.74	5.25
398	1.78	5.38
HPW / SiO_2- 30 wt.%		
Temperature (***K***)	$D_e * 10^3$ (cm^2/s)	$M_T * 10^3$
353	1.74	4.47
368	1.78	5.97
383	1.81	7.34
398	1.85	8.29

Nomenclature

D_e	Effective diffusivity	cm^2 / s
k'	Catalytic reaction rate constant	$lit^2/mol.kgcat\ s$
k'''	Catalytic reaction rate constant.	$lit^2/mol.h.m^3cat$
L	Characterization length of catalyst particle	m
M	Molecular weight.	g / mol
M_T	Thiele modulus	
S_g	Surface area of catalyst.	cm^2 / g
T	Temperature	K
X	Olefin conversion.	…..

ABBREVIATION

FID	Flame ionization detector.
GC	Gas chromatography
HPW	Tungstophosphoric acid
LAB	Linear alkylbenzene.
LAS	Linear alkylbenzenesulphonate
UOP	Universal Oil Product.
WHSV	Weight hourly space velocity.
ZSM-12	Zeolite Socony Mobile-12
ZSM-5	Zeolite Socony Mobile-5

GREEK SYMBOLS

ε	Effectiveness factor.	---
θ	Void fraction	---
τ_m	Tortuosity factor	---
ρ^2	Correlation Coefficient	---
ρ_P	Solid density	g/cm^3

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