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**ALKYLATION OF BENZENE WITH 1-OCTENE OVER TITANIA
PILLARED MONTMORILLONITE**

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Abstract

Linear alkylbenzene sulfonic acid, the largest-volume synthetic surfactant, in addition to its excellent performance, is important due to its biodegradable environmental friendliness, as it has a straight chain and is prepared by the sulphonation of linear alkylbenzenes (LAB). To ensure environmental protection, the commercial benzene alkylation catalysts HF or AlCl_3 are replaced and we have developed a clean LAB production process using a pillared clay catalyst capable of not only replacing the conventional homogeneous catalysts, but also having high selectivity for the best biodegradable 2-phenyl LAB isomer. Pillared clay catalysts having high Brønsted acidity show efficient conversion in gas phase alkylation of benzene with 1-octene with a good 2-phenyl octane selectivity.

Keywords: Linear alkyl benzene, 1-octene, titania pillared clay, Brønsted acidity

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INTRODUCTION

One of the largest users of chemistry is the detergent industry which continues to use linear alkylbenzene sulfonates (LAS) on an enormous scale. The increasing use of detergents by households discharges large quantities of alkylbenzene and its sulfonated derivatives. Rapid biodegradation of the disposed organic compounds is important to keep pollution levels as low as possible. Among the isomers of linear alkylbenzene, 2-phenyl LAB is the best biodegradable, making it an environmentally favorable isomer. Commercially, benzene alkylation to form LAB is done using HF or AlCl_3 catalysts. The HF acid has high efficiency, superior product and is more often used as compared to the alternative AlCl_3 catalyst. With HF, there is an even isomer distribution with all the phenyl isomers present at approximately 17 to 20% [1].

However, the potential application of heterogeneous catalysts have long been recognized, principally because of the concern about handling concentrated HF and the disposal of fluorinated neutralization products [2]. Thus, as these homogenous catalysts are very corrosive and polluting, a great effort is made for their substitution by solid acid catalysts such as zeolites, clays, *etc.* that do not have these inconvenience. In addition to solve the above problems, the heterogeneous catalytic process is capable not only of replacing the conventional homogeneous catalysts, but also has high selectivity for the 2-phenyl LAB isomer.

The efficient use of eco-friendly clays is restricted due to their low thermal stability, which makes them less suitable for high temperature reactions. Modifications are done to improve the stability and activity. The catalytic properties of montmorillonite clays can be greatly manipulated by pillaring, among which pillaring by using polyoxocations of titanium gives a considerably larger interlayer spacing in comparison with other metal oxide pillared clays (PILCs) [3]. This offers the opportunity to apply heterogeneous catalysis to the organic reactions for bulky substrates, while maintaining the easy product diffusion from the catalytic site obtained in homogeneous catalysis. The present study uses titania PILC for the alkylation of benzene with 1-octene. Titania pillaring solution is prepared from the sol obtained from titanyl sulphate [4]. Effects of reaction variables such as flow rate, temperature and arene/alkylating agent molar ratio are optimized to get good catalytic results. Pillaring shows efficient conversion and selectivity when compared with the parent montmorillonite and the Na^+ -exchanged montmorillonite. The catalytic activity is correlated to the total acidity obtained from TPD of NH_3 , and Brønsted acidity obtained from cumene cracking reactions.

EXPERIMENTAL

Na^+ -exchanged and titania pillared clays are prepared from montmorillonite KSF (Aldrich). The experimental details regarding the preparation of the

catalyst samples and the methods of characterization such as XRD analysis, FTIR analysis, surface area and pore volume measurements, elemental analysis (ICP-AES), TG analysis ^{29}Si and ^{27}Al MAS NMR analysis have been described in our earlier paper [4]. The same is the case with the experimental details of the acidity measurement using temperature programmed desorption of ammonia. The samples, after 12 h drying at 110°C , were calcined for 5 h at 500°C . The sample notation M stands for parent montmorillonite, NM for the Na^+ -exchanged one and TM for the titania PILC.

Catalytic gas phase benzene alkylation reactions, as well as cumene cracking reactions are carried out at atmospheric pressure in a fixed bed, vertical, down-flow glass reactor placed inside a double-zone furnace under a continuous flow of nitrogen. Exactly 0.5 g of the sample is sandwiched between the layers of inert silica beads. A thermocouple detector monitors the temperature of the catalyst. The reactants are fed into the reactor by means of a syringe pump (Cole palmer®) at a required flow rate, molar ratio and temperature. The products and the unreacted reactant are condensed by means of a water condenser, collected and subjected to gas chromatographic analysis using a Chemito GC 1000 gas chromatograph with BP1 capillary column and FID detector. The 1-octene conversion (wt.%) (cumene conversion in the case of cracking), and product selectivity (wt.%) are noted. Catalysts were kept at 500°C for 2 h prior to each reaction for activation.

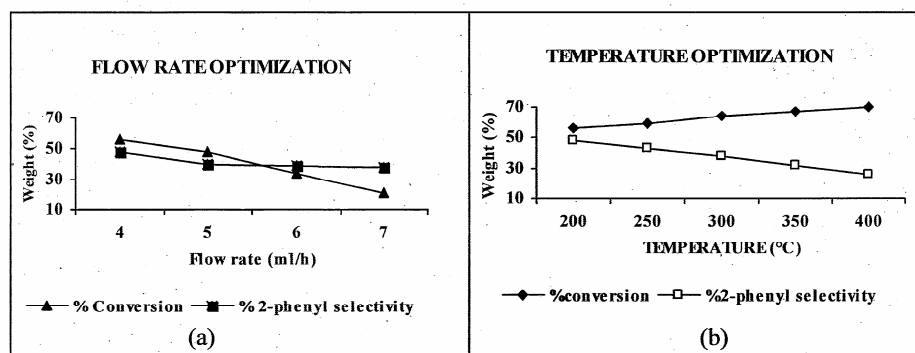


Fig. 1. (a) Effect of flow rate at a temperature of time on stream 2 h, and catalyst weight 0.5g. (b) effect of temperature on the conversion and selectivity at a flow rate of 4 mL/h, time on stream 2 h and catalyst weight 0.5 g

RESULTS AND DISCUSSION

Benzene alkylation using 1-octene is often used as a model reaction in LAB synthesis. For getting maximum catalytic results the reaction conditions are optimized over titania PILC.

The reaction is performed at 200°C on the catalyst, at flow rates of 4 mL/h – 7 mL/h. The catalytic activity shows a decreasing trend with increasing flow rate as shown in Fig. 1(a). The 2-phenyl octane selectivity is also decreased and thus the selected flow rate is 4 mL/h. It is reported that a decrease in the conversion is observed at higher flow rates due to a smaller contact time, where the kinetics get affected [5]. Temperature has a paramount influence in the conversion, as well as in the product distribution for alkylation of benzene (Fig. 1(b)). Conversion increases, whereas selectivity drops with increasing temperature from 200-400°C at a temperature interval of 50°C. The decreased selectivity may be due to the fast hydride shifts of the carbonium ion intermediate to produce the isomer ions [6]. This increases the probability of the formation of other phenyl isomers, 3- and 4-phenyloctane. The total conversion increases at the expense of selectivity, which is also due to cracking and higher substitution. Thus 200°C is selected for further studies. As the benzene/octane molar ratio is increased, conversion, 2-phenyl selectivity and monoalkylation selectivity increases, whereas the possibility of higher substitution becomes smaller. This is due to the solvation effect of benzene in higher molar ratios [7]. Thus a molar ratio of 20 is selected for a comparison of the different systems. The results of catalytic activity over various systems are shown in Table 1. The improved conversion, 2-phenyl selectivity and high amount of monoalkylation upon pillaring are seen. The decreased amount of other products is a result of the porous structure of the PILC.

Table 1

Catalytic activity of benzene alkylation with 1-octene over clay systems

Catalyst	Conversion (wt.%)	Selectivity ((wt.%)			
		Monoalkyl Benzene	2-phenyl octane	Higher substitution	Others
M	20.9	66.2	25.4	12.3	21.5
NM	36.1	76.8	28.6	10.9	12.3
TM	55.7	86.6	47.9	4.4	9.0

Temperature 200°C, flow rate 4 mL/h, benzene/1-octene molar ratio 20:1 time on stream 2 h and catalyst weight 0.5 g

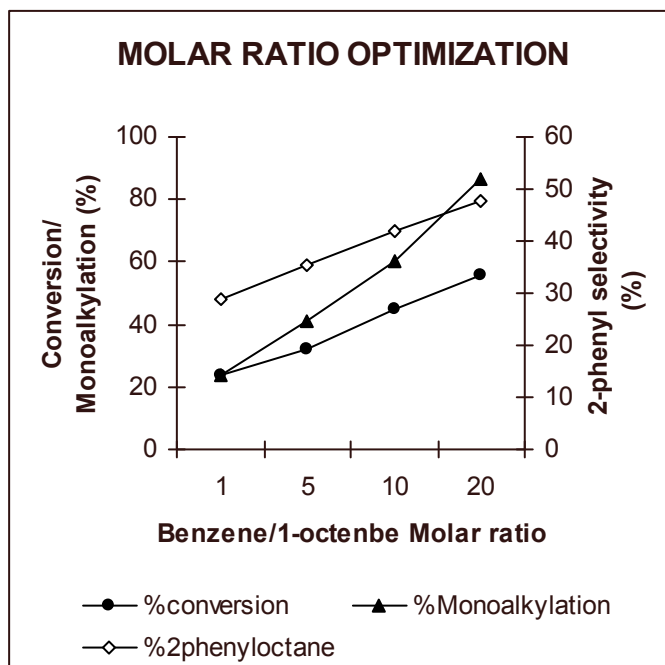


Fig. 2. Optimization of the molar ratio at a temperature of 200°C, flow rate of 4 mL/h, time on stream 2 h, and catalyst weight 0.5g

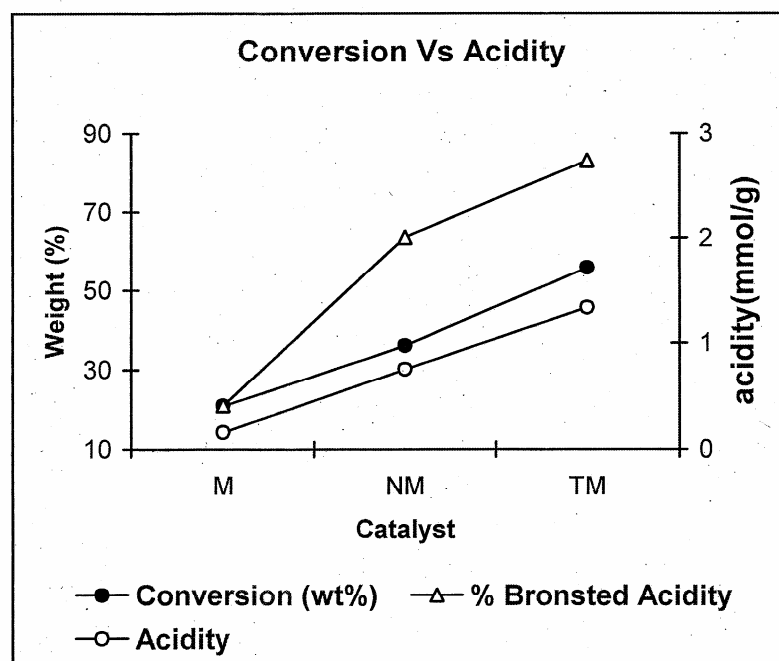
The alkylation of benzene with olefin takes place via a carbonium ion mechanism [8]. The mechanism of alkylation of 1-alkenes over heterogeneous zeolite catalyst suggests the role of Brønsted acidity in the conversion. Thus we have carried out cumene cracking reaction over the selected catalysts, in which the cracking of cumene, producing benzene and propene, are generally attributed to the action of Brønsted acid sites, following a carbonium ion mechanism. It is commonly used as a model reaction for characterizing the presence of this type of site on a catalyst surface. The formation of α -methyl styrene during cumene cracking, due to dehydrogenation, has been ascribed to Lewis acidity [9, 10]. A comparison of the relative amounts of these two products over the different systems provide some information about the relative effectiveness of the cracking and dehydrogenation sites *i.e.* Brønsted and Lewis acid sites on the catalysts respectively [11-13]. From the selectivity to cracked products, the % Brønsted acidity is calculated. The cumene conversion results are shown in Table 2.

Table 2

Result of cumene conversion reaction to test the acidity

Catalyst	Cumene conversion (wt.%)	Selectivity (wt.%)			Cracked product (wt.%)	% Brönsted acidity
		Benzene	α -Methyl Styrene	Others		
M	6.7	12.8	0.3	86.9	6.6	23.0
NM	21.1	62.8	4.9	32.3	19.5	67.8
TM	28.7	75.7	7.3	17.0	26.3	91.5

Temperature 450°C, flow rate 4 mL/h, time on stream 2 h and catalyst weight 0.5 g

**Fig. 3.** Correlation diagram of acidity vs. conversion in the optimized conditions at a time on stream 2 h and catalyst weight 0.5 g

We tried to correlate the conversion to Brönsted acidity, as well as to total acidity obtained from TPD of NH_3 , and got a perfect correlation supporting the

role of acidic sites as is evident from Fig. 3. From cumene cracking it is clear that the major acidity is from Brönsted acid sites which are needed in the LAB synthesis. The increased acidity upon pillaring is a result of exposure of the layer structure and the presence of the metal oxide pillar. This proves the efficiency of pillaring in improving the catalytic activity as a result of improved structural, as well as textural properties such as surface area-pore volume, interlayer distance, acidity, *etc.* with the retention of the basic clay layer structure [4].

CONCLUSIONS

This work studied alkylation of benzene with 1-octene over pillared, ion exchanged and unmodified montmorillonite clays. Similar to earlier investigations over various catalysts, the parent montmorillonite sample displayed decreased conversion and selectivity. The effects of various reaction parameters on the conversion over titania PILC were studied in the LAB reaction, and correlated to the total acidity obtained by TPD of ammonia, and Brönsted acidity obtained from cumene cracking reactions. In addition, selectivity of the 2-phenyl substituted isomer over the PILC is very high in comparison with the parent and ion exchanged clay, as well as the commonly used homogeneous HF acid catalyst. The reaction selectivity over PILC can be attributed to its shape selectivity of product isomers.

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