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Friedel-Crafts alkylation of benzene with 1-dodecene over ion exchanged bentonite catalysis

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ABSTRACT

The liquid - phase alkylation of benzene with 1-dodecene has been investigated in the presence ion- exchanged bentonite. The comparison of the activities of Fe^{3+}, Al^{3+}, and Zr^{4+} exchange bentonite indicate that the best results were obtained with Fe^{3+} exchange bentonite. The influence of various reaction parameters such as reaction temperature, reactant feed ratio and catalyst amount affecting the activity and selectivity of Fe^{3+}exchanged bentonite have been studied. The reactions were found to proceed under relatively mild conditions with excellent conversions, and a simple product isolation procedure was achieved. Fe^{3+} exchange could also be recycled and reused effectively for several times, thus rendering green characteristic to this reaction.

Key words: Alkylation, catalyst, bentonite, benzene, 1-dodecene

INTRODUCTION

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry. Alkylation of benzene with C10-14 linear alkenes is used for the synthesis of linear alkyl benzenes (LABs), which are the primary raw material for the production of LAB sulfonates, a surfactant detergent intermediate[1-2]. Generally, such reactions were carried out using strong homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$ and H_2SO_4[1-3], which are highly toxic, generate a substantial amount of waste, and cause severe corrosion problems. The new environmental legislation pushes for the replacement of all liquid acids by solid acid catalysts which are environmentally more friendly catalysts and which lead to minimal Pollution and waste[4]. UOP and CEPSA announced their Detal process in early 1990s based on a fixed bed of solid acid catalyst[5]. Alkylation of benzene with long chain olefins has been reported over a wide variety of heterogeneous catalysts such as X and Y zeolites[6,7] silicotungstic acid supported on alumina[8], montmorillonite clay, various pentasil zeolites[9], HBEA[10], , HY[11,12] and alumina-pillared clay[13],. The alkylation of benzene with long chain olefins is a commercially important process for the production of linear alkyl benzenes (LAB), a raw material, used in the production of biodegradable detergent[14]. Then, the main purpose of the present work was to explore the catalytic properties of the Khaluys bentonite for the alkylation of benzene with 1-dodeceneby using Fe^{3+}-exchanged bentonite. The catalyst was used to study the effect of various reaction parameters such as molar ratio, temperature and catalyst weight on 1-dodecene conversion.

EXPERIMENTAL

The Khaluys bentonite was kindly supply by Saudi Geological Survey (SGS) (Saudi Arabia, Jeddah). The starting material was purified by sedimentation. The sedimented clay, shows a surface area equal to 90 m^2/g, the average pore sizes equal to 1.1 nm and the cation exchange

capacity was 0.89 meq/g. This sample was further treated by diluted sulphuric acid to eliminate the carbonates[15] s wich shows the surface area equal to 213 m2/g, the average pore sizes equal to 0.85 nm and the cation exchange capacity was 0.74 meq/g. The natural clay was ground, sieved to 140 mesh and dried at 378 K. The sample was then dispersed into 1 l of distilled water for 2 h and allowed to settle for 16 h. The $^{+}$,Fe^{3+} exchange bentonite was prepared[15] by using solutions of $FeCl_3.6H_2O$. The exchange clay was repeatedly washed and centrifuged before drying in a vacuum oven at 60 °C 12h . It was then ground and sieved at 140 mesh (ASTM). The material was then stored in a dry - air container.

General Reaction Procedure

The reactions were carried out mainly in a small stainless steel -pressure vessel (Ca. 20 cm^3 capacity) and fitted with a threaded cap and a PTFE seal. The alkylation of benzene with 1-dodecene was added in the required molar ratio to the activated catalyst. The pressure vessel was sealed and heated in oven at different temperatures[16]. After the desired heating period, the reactor was removed and quenched in cold water. At the end of the reaction, the organic layer could be easily decanted from the catalyst and any organic residues were removed by extraction with a proper solvent. The products were analyzed quantitatively by Gas Chromatography (GC) using a SRI 8310 G.C.

RESULTS AND DISCUSSION

Catalytic activity

1-Dodecene undergoes double bond shift isomerization and benzene alkylation in presence of catalyst. The different isomers of dodecene react with benzene to form different dodecylbenzene isomers. The formation of dialkylated and olefin olegomerized products was not observed in the reaction .The conversion was expressed as the percentage of alkene converted into alkylated products . The Fe^{+3}, Al^{+3} and Zr^{+4} -exchanged bentonite catalyzing the alkylation of benzene with 1-dodecene at 80 °C were shown in (Fig. 1). The Fe^{+3} exchanged bentonite catalyst was found to be superior to the other catalysts. The alkylation activity of the metal exchanged bentonite catalysts was in the following order: Fe^{+3} exchange > Al^{+3} exchange >Zr^{+4} exchange. Therefore ,all the futher experiments were carried out using Fe^{+3} exchanged bentonite catalyst.

The effect of catalyst loading was studied at 100 °C using benzene/1-dodecene molar ratio of 10 in the range of 0.25 - 1.5g by using Fe^{+3} exchanged bentonite. As the catalyst loading was increased from 0.25 to 1.0g, the reaction rate increased substantially while further increase in catalyst loading to 1.0g, there was a slight increase in the conversion was shown in (Fig. 2). Further increase in the catalyst loading did not result in the

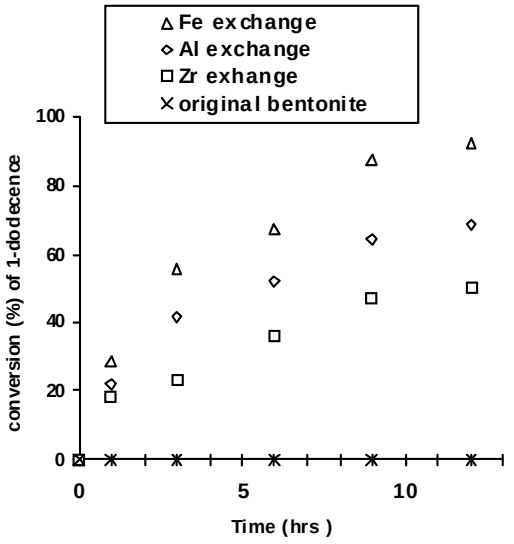

Fig. 1: Alkylation of benzene with 1-dodecence in presence of different ion-exchanged bentonite catalysts.

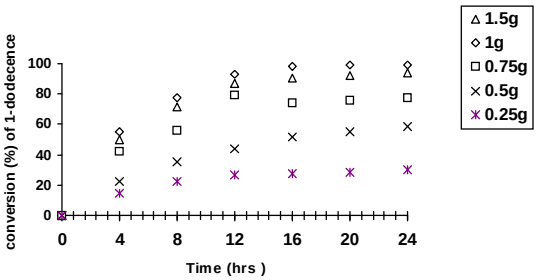

Fig. 2: Effect of catalyst weight on the conversion of 1-dodecene in the alkylation of benzene over Fe^{+3} exchanged bentonite

increase in conversion. With an increase in the catalyst loading, opportunity for the reaction on external acid sites increased and consequently the conversion of alkene increased. Therefore, all the further experiments were carried out using 1g of catalyst.

In general, the reaction temperature has an important effect on the kinetics and thermodynamics of the alkylation reaction. Therefore, the effect of reaction temperature on the results of alkylation reactions catalyzed by Fe^{+3} - exchanged bentonite catalyzing the alkylation of benzene and with 1-dodecene in the range of temperatures from 60^{0}C -120^{0}C as shown in (Fig. 3). At 60°C, 1-dodecene conversion was 29% and increased to 88% at 120 ^{0}C for 12h. Further increase in reaction temperature to 100 ^{0}C had no appreciable effect on 1-dodecene conversion.

The influence of the molar ratio of benzene to 1-dodecene for the alkylation reaction as shown in (Fig. 4) . As the benzene/1-dodecene molar ratio increased from 2 to 15, 1-dodecene conversion decreased from 53% to 93% The maximum conversion 92 % is observed when this ratio was 10 if this ratio is further increased, the carbonium ions will be greatly diluted and much reactant moisture is introduced into the reaction system. The low concentration of carbonium ions and the loss of the acidic species may give rise to the decrease of 1-dodecene conversion. Besides, the reduced concentration of the carbonium ions could inhibit the hydrogen shift reactions and so result in a slight enhancement of 2-dodecylbenzene selectivity. However, a higher molar ratio of benzene to 1-dodecene will cause a larger amount of benzene to be separated from the product and recycled. For this reason, the optimal molar ratio of benzene to 1-dodecene 10 is preferable. under identical conditions. In order to study the recyclability of the catalyst, the reaction was studied at 120 æ%C with 1.0 g catalysts using Fe^{+3} exchanged bentonite catalyst, benzene/1-dodecene molar ratio 10 for 12 h. Fresh catalyst showed 78% dodecene conversion. For recycling, after first use, the catalyst was separated by filtration, washed with methanol and dried at 100 æ%C for 3 h and used with fresh reaction mixture in the second run. The methanol washed catalyst showed 65% dodecene conversion and the decease in conversion with the used catalyst

Table 1: Effect of recycling of the catalysts in alkylation of benzene with 1-dodecene over Fe^{3+}exchanged bentonite

Catalyst	dodecene conversion wt(%)	dodecylbezene selectivity (%)
first run	98	38
1 reuse	91	38
2 reuse	39	36
2 reuse	20	32

Reaction condition: reaction temperature at 80^{0}C, reaction time of 4 h

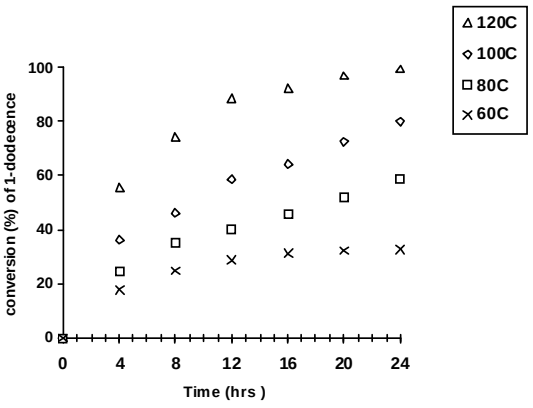

Fig. 3: Effect of reaction temperature on the conversion of 1- dodecene over Fe^{+3} exchanged bentonite

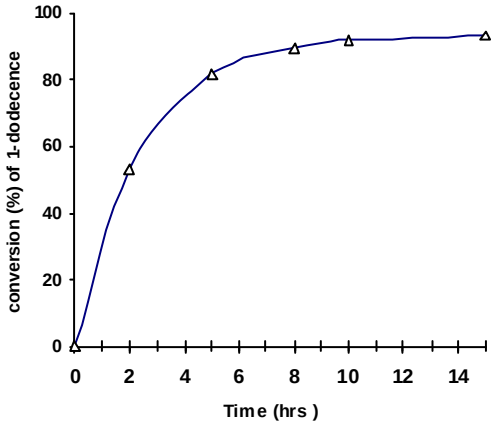

Fig. 4: Effect of molar ratio of benzene to 1-dodecence

could be due to the blockage of active sites of the catalyst by heavy aromatics and oligomerised dodecene [17]. However, after regeneration of the catalyst by calcination at 450 æ%C for 6 h, dodecene conversion increased to 73%. The small activity loss observed with the regenerated catalyst could be due to partial loss of acid sites of the catalyst during regeneration.

Conclusions

The catalytic activity of the different (Fe^{3+}-, Al^{3+}-, and Zr^{4+}) exchanged bentonite catalyst was studied in the alkylation of benzene with and 1-dodecene. Among all catalyst studied Fe^{3+}exchanged bentonite was the most active, showing high 1-dodecene conversion. The influence of various reaction parameters such as reaction temperature, reactant feed ratio and catalyst amount affecting the activity and selectivity of Fe^{3+}exchanged bentonite have been studied. The reactions were found to proceed under relatively mild conditions with excellent conversions; and a simple product isolation procedure was achieved. The catalyst was reusable without the loss of the activity for their recycling.

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