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Review Paper

## Investigation of solid acid catalysts for alkylation of isobutane-butene process

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### 1. ABSTRACT

Automotive exhaust emission is the predominant source of air pollution. With the increasingly stringent environmental protection requirements, the standards of gasoline are constantly upgrading via reducing the content of olefins, sulfur and aromatics. Alkylation of isobutane with butene is one of the most important ways for production of gasoline with high octane number. Although, the isobutane with olefins alkylation refinery process based on liquid acid catalysts such as sulfuric acid and hydrofluoric acid has been commercially successful but the use of these catalysts in the process of alkylation has environmental, health and high operatin costs problems. Solid acid catalysts especially zeolites due to their high operability and lower cost of equipment, no environmental problems and outstanding structural properties, are more suitable candidates for improving the isobutane/butene process. So, replacing these catalysts with solid acid catalysts is one of the most important research goals in the field of catalysts.

**Keywords:** Alkylate, Octane Number, Zeolite, Liquid Acid Catalysts, Olefins.

### 2. INTRODUCTION

Because the distillation of the petroleum fractions does not meet the fuel demand, processes such as reforming, isomerization and alkylation have provided the market demand for producing gasoline as a fuel. Among the mentioned processes, alkylation is one of the important method to produce gasoline with high octane number. Alkylation is a chemical process in the petroleum industry which light paraffins such as isobutane react with light olefins such as butene to produce branched paraffins called alkylates.

TMP is the desired product of this process because it has a high octane number ( $\geq 100$ ). DMH is the secondary product of  $C_8$  and octane number is between 55 and 82. In addition  $C_8$ , alkylate also includes  $C_5-C_7$  and  $C_9^+$ . The complexity of the products shows that series and parallel reactions such as isomerization, cracking, oligomerization and hydride transfer occur in alkylation process. (Figure 1).

$H_2SO_4$  and HF are common liquid catalysts in this process. These catalysts have environmental and economic problems. So, replacing liquid acid catalysts with solid catalysts is one of the most important research goals in the field of catalysts.

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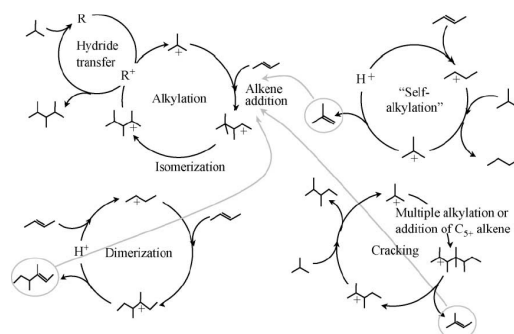
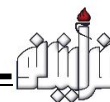


Figure 1. Alkylation process mechanism and side reactions [1]

### 3. RESULTS AND DISCUSSION

So far, various catalysts such as zeolite, metal oxides, sulfated zirconia, heteropolyacids, etc. have been studied for isobutane-butene alkylation process. In this part, briefly, discuss the common catalysts and researches that have been done in this process.

#### 3.1. Zeolites

Among the solid catalysts, zeolites due to non-corrosive, eco-friendly and low- cost properties, are suitable option for isobutane-butene alkylation process. Also the pores of zeolites have an extremely high order in shape and size. The concentration and strength of active sites are very high level. [2]

#### 3.2. Metal Oxides

Catalysts based on metal oxides have important role in isobutane-butene alkylation process. Synthesis method and particle size are two essential factors in increasing the performance of these catalysts.  $\text{MoO}_3/\text{TiO}_2$ ,  $\text{WO}_3/\text{ZrO}_2$  and  $\text{MoO}_3/\text{ZrO}_2$  are examples of metal oxide catalysts. [3]

#### 3.3. Sulfated Metal Oxides

These catalysts are as promising candidate for heterogeneous alkylation. metals/mixed metals are considered as a non-corrosive, non-toxic and low- cost. Sulfated Zirconia (SZ) is the most favorite sulfated metal oxide in this process. The catalytic performance of this catalyst depends on many factors such as nature of the precursors, sulfation methods, water content, surface area and calcination temperature. [4]

#### 3.4. Heteropolyacids

HPAs are nonporous solids with strong acidity that consist of heteropoly anions with metal-oxygen octahedral as the basic structural unit. The remarkable aspect of these catalysts is their strong acidity compare to other solid acid catalysts. However, the high price of these catalysts has reduced their attractiveness in this process.  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  are examples of HPA. [5]

### 4. CONCLUSION

Optimizing the structural features and developing effective methods to activate alkylation catalysts are most important advantages of solid acid catalysts in comparison with liquid acid catalysts. Sulfated zirconia as solid catalyst has low coking capacity and deactive very fast. Heteropolyacids have good performance but they are not economical. Zeolites are more suitable candidates for isobutane-butene alkylation due to eco-friendly, low- cost and outstanding structural properties.

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