

Alkylation of isobutane with butenes using OSDA-free zeolite Beta

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Abstract: The alkylation of isobutane by propene and butane is an important reaction for obtaining high quality fuels. Decades of research did not bring up a suitable solid catalyst, although trends, such as the need of high acid site density were proposed. Herein we explore the use of OSDA-free zeolite Beta for the alkylation of isobutane. This material is a highly active, aluminum rich zeolite. Different dealumination treatments showed that the most Al-rich OSDA-free zeolite Beta is the ideal catalyst, even outperforming state-of-the-art conventional zeolites.

Keywords: OSDA free zeolite beta, alkylation, dealumination.

1. Introduction

Highly branched C₇ and C₈ alkanes exhibit excellent fuel properties and can be produced by the alkylation of isobutane using propene or butenes (Figure 1).¹ This alkylation is currently based on hydrofluoric or sulfuric acid; so far no solid catalyst was found to replace the liquid acids.² Although

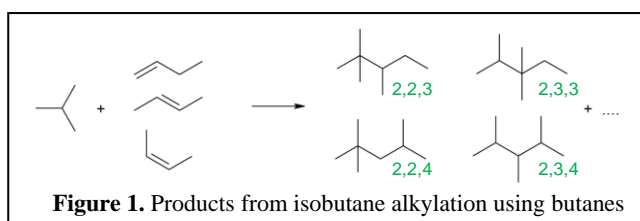


Figure 1. Products from isobutane alkylation using butanes

several active solid catalysts were found, stability is still the major challenge. So far the most promising catalysts are La- and Ce- exchanged FAU type zeolites and different H-form zeolites, where zeolite beta shows excellent results.^{1,3,4} A major challenge is to balance the acid strength, as too strong acid sites promote cracking and too weak acid sites elicit the dimerization of the olefin. Further, a high acid site density was shown to be beneficial for high productivity.³ For these reasons, zeolite Beta with a high density of acid sites would be an ideal catalyst. OSDA-free zeolite Beta provides a platform of strong acid sites with high density and easy modification by dealumination.⁵ It can be utilized for a broad spectrum of reactions and is therefore employed successfully in the alkylation of isobutane in this study.

2. Experimental

Zeolite catalysts were either used as received or transformed from the Na-form to the H-form by exchange with NH₄NO₃ and subsequent calcination. The catalysts (500 mg) were activated at 250 °C and subsequently placed in a 100 mL Parr reactor that was closed immediately and purged with nitrogen. The reactor was cooled on ice and liquid isobutane was added via a 31.4 mL compressed air driven plunger that was cooled at 15 °C to ensure that isobutane is in its liquid state. Subsequently gaseous 1-butene was added using a 49.1 mL plunger that was not cooled. The lines were subsequently purged with nitrogen to ensure that the entire olefin was transferred to the reactor. Reactions were carried out at 70 °C to 100 °C while

stirring the slurry. After completion of the reaction, the reactor was cooled on ice and the gases were released. Subsequently n-decane was added to the reactor to dilute the reaction products. Reactions were analyzed using a GC-FID instrument with tetradecane as standard.

3. Results and discussion

The alkylation of isobutane with 1-butene was tested with a relatively high olefin/paraffin ratio (1/50). This in fact promotes deactivation and allows to rapidly identify the most robust catalysts. Initially, conventional zeolite Beta was tested, where the best catalyst provided 149 mg_{product}/g_{cat} at 42 % C₈ selectivity. Remarkably, OSDA-free zeolite beta (Si/Al=4.5-5.2) provided higher activity with up to 407 mg_{product}/g_{cat} (Figure 2). All Al-rich catalysts provided excellent C₈ selectivity (>65 %, Figure 3), which can be rationalized by the high acid site density. Dealumination of these zeolites resulted in lower activity and lower C₈ selectivity than for the untreated Al-rich zeolites. There is a clear decreasing trend observed with increasing Si/Al ratio, irrespective of the origin of the catalyst (Figure 2, Figure 3). Samples that showed lower crystallinity or lower micropore volume, i.e. pore blocking by extra-framework aluminum did not follow this trend, and gave a lower yield. NH₃-TPD and FTIR using pyridine as probe molecule showed that the trend in Si/Al ratio is directly coupled to the less abundant strong acid sites for dealuminated OSDA-free and conventional zeolites compared to the OSDA-free zeolite Beta. By changing reaction parameters, such as temperature or olefin concentration, it is possible to fine-tune the product mixture, such as decreasing the amount of cracked products ($\leq C_7$) by lowering the reaction temperature. We will also discuss the performance in continuous mode, allowing lifetime evaluation.

4. Conclusions

The alkylation of isobutane with 1-butene was successfully performed using OSDA-free zeolite beta. The high acid site density of rather strong acid sites was responsible for the outstanding activity of the system. Dealuminated samples as well as conventional zeolite Beta are less performant in this reaction, which is caused by the lower density of strong acid sites.

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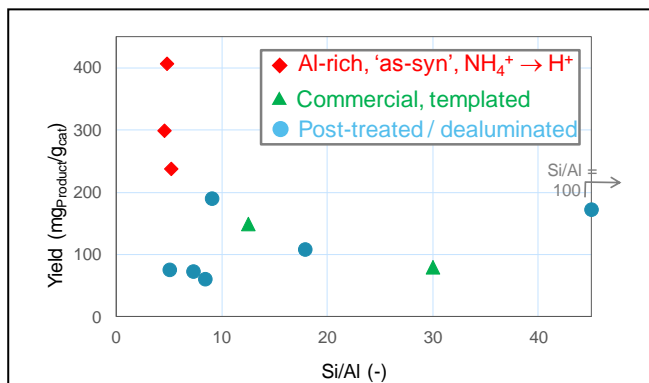


Figure 2. Product yield for zeolite beta with different Si/Al.

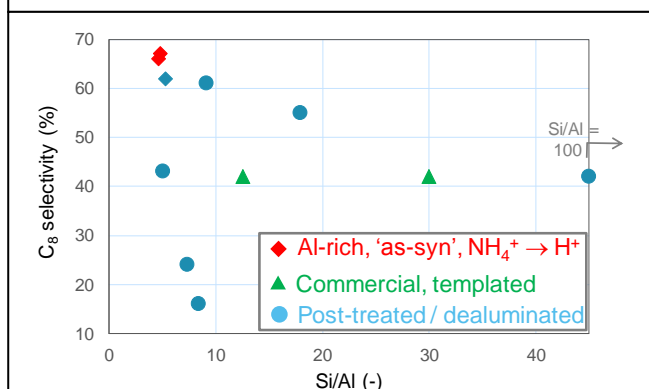


Figure 3. C₈ selectivity for zeolite beta with different Si/Al