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Alkylation of isobutane with butenes using OSDA-free zeolite Beta

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PURPOSE OF THE ABSTRACT

As awareness of climate change is growing, also the chemical industry is heavily looking for ways to diminish its environmental burden. As these processes are often performed at large scales, even slight improvements lead to significant benefits. Therefore, even from a green chemistry perspective, investigating these processes remains very relevant.
One such example is the production of gasoline. Gasoline is still very important, as transportation still heavily depends on it and this is not likely to change in the next decade. However, as legislation on fuel additives and aromatics content in gasoline becomes more stringent, the demand for branched alkylate as high octane blendstock is growing. This branched alkylate is obtained by alkylating isobutane with butenes. Historically, most alkylation plants were either based on sulfuric or hydrofluoric acid. Although used at large scale, issues concerning safety and disposal of spent acid urge a transition to implement solid acids in alkylation. For example, in the sulfuric acid-based plants, 100 kg spent acid (+ acid-soluble waxes) are produced per tonne alkylate, showing the tremendous environmental burden. These solid acids circumvent the use of these polluting acids and thus make the alkylation process much more environmental friendly (e.g. avoiding discharge of spent acid, leakage of highly corrosive acids into the environment...) Hereto, Albemarle developed the Alkyclean® technology, using La-exchanged faujasites.[1] However, these Al-rich faujasites were found to be more prone to deactivation than zeolite Beta.[2] However no decent, Al-rich Betas have been tested yet, as their OSDA-based syntheses were inadequate (e.g. low crystallinity).[3,4] In that sense, the OSDA-free routes towards Beta zeolites paved the way towards highly crystalline Al-rich Betas.[5] In this work, different OSDA-free Betas were evaluated for alkylation.

First of all, OSDA-free Beta samples were synthesized, using syntheses varying in type of seeds and silica source. These different OSDA-free Beta batches were compared both among each and also with OSDA-based Betas. These experiments already gave glimpses of the beneficial properties of the OSDA-free Betas.
In a following step, a La-HY reference was synthesized according to patent literature[6], as a benchmark. Also here, OSDA-free Beta was found to be most resistant to catalyst deactivation.

Now the OSDA-free Beta was found to be an interesting alkylation catalyst, an extensive characterization of the different OSDA-free Beta batches was performed to identify the origin of the subtle differences in catalytic performance. Herein N_2-physisorption, NH_3-TPD, XRD and SEM yielded important insights in what drives catalytic performance of the OSDA-free Beta. Furthermore, solid state Al NMR measurements were performed to probe differences in aluminum speciation. Also this parameter differed, depending on the synthesis method.

In a final step, catalyst regeneration was investigated by comparing both oxidative and hydrogenative regeneration methods, of which the latter yielded complete regeneration of the catalyst. For this sample, the evolution in acidity and particle size of the platinum particles was followed over multiple runs. Herein, the acidity did not diminish and the Pt particles remained homogeneously distributed on the zeolite material.

FIGURES

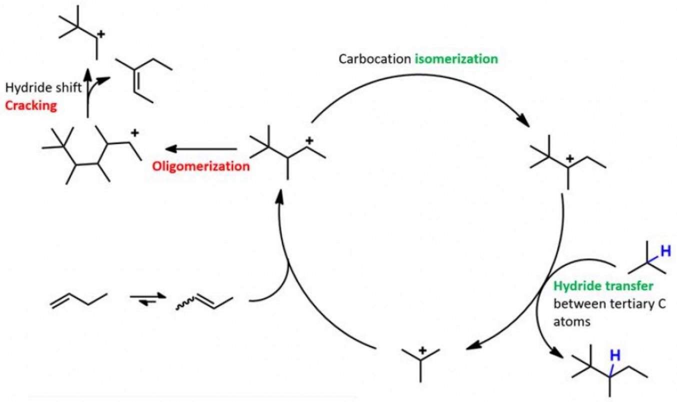

Figure 1. Mechanism for alkylation of isobutane with butenes.

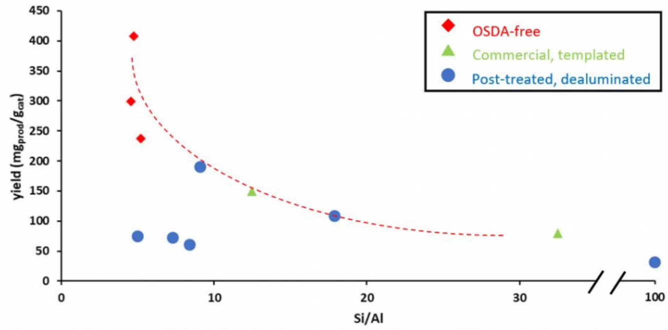

Figure 2. Product yield (C_{5+}) for Betas with different Si/Al ratio. Reaction conditions: 0.5 g catalyst was dried *in situ*. Hereto, a mixture of 31.4 mL isobutane and 360 mg *n*-butene was added (P/O = 50). Reactions were performed at 100°C for 20 h.

FIGURE 1

Mechanism alkylation

FIGURE 2

zeolite screening

KEYWORDS

alkylation | hydrocarbons | zeolites | petrochemistry

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