

Isobutane/2-butene alkylation over lanthanum exchanged faujasite type zeolites

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Introduction

Isobutane/2-butene alkylation is an important refining process for the production of a complex mixture of high-octane alkanes, which is an ideal blending component of gasoline. Nowadays, commercial alkylation units use H₂SO₄ and HF as catalysts, which suffer from many drawbacks such as corrosiveness and handling hazards. Therefore, it is desirable to replace them by solid catalysts. Zeolites, in particular lanthanum exchanged faujasites, show a great potential [1].

Materials and Methods

La-exchanged zeolites X and Y were prepared from NaX (Si/Al = 1.1) and NaY (Si/Al = 2.4) by the same ion exchange procedure consisting of five ion exchange steps with aqueous La(NO₃)₃ solution and two calcination steps. Prior to alkylation, the catalysts were activated *in situ* at 180°C for 14 h under H₂. The alkylation reaction was performed in a CSTR at 75 °C and 20 bar, by feeding a mixture of 10/1 isobutane/2-butene with an olefin space velocity of 0.2 g_{butene}·g_{catalyst}⁻¹·h⁻¹. The products were analyzed using an HP 6830 gas chromatograph. The ²⁷Al (MQ)MAS NMR measurements were performed on a Bruker AV500 spectrometer.

Results and Discussion

In agreement with previous studies, it was found that the catalyst lifetime of LaX was significantly longer than that of LaY [2]. Deactivation started after 14.3 and 7.5 h, respectively. The total integral yield of C₈ products was 6.2 and 2.4 g·g_{cat}⁻¹ for LaX and LaY, respectively. These results indicate that LaX is among the best solid catalysts tested for isobutane/2-butene alkylation. In the reaction over LaY, consumption of the products was observed when deactivation started. This may be explained by deprotonation followed by oligomerization or by cracking to isobutane. The product distribution indicated that the hydride transfer activity of LaX was significantly higher than that of LaY.

The active species in isobutane/2-butene alkylation can be described as carbenium ions or alkoxy groups [4]. However, the conversion of these species occurs *via* a carbenium ion transition state involving a charge separation, which is achieved easier the stronger the acid site is. In agreement with previous studies, the concentration of strong Brønsted acid sites was identified as the key property for a high hydride transfer activity [2]. Although the same concentration of Brønsted acid sites was found for both catalysts, the concentration of strong Brønsted acid sites was significantly higher in LaX. This is an apparent contradiction to the general trend that the strength of Brønsted acid sites decreases with increasing aluminum concentration. There are two possible explanations for this observation: While almost complete

ion exchange was observed for LaX (99.3%), the ion exchange degree of LaY was only 87%. It has been reported that residual sodium cations selectively poison the strongest Brønsted acid sites [5]. Additionally, the incorporation of polyvalent lanthanum cations leads to distortion of the zeolite framework by increasing the Si-O-T (T = Si, Al) angles in the zeolite lattice. An increase of the Si-O-T bond angle leads to an increasing s character of the T-O bonds. Consequently, the p character of the OH bonds in bridging hydroxyl groups increases making them more acidic. Framework aluminum atoms, which are affected by this distortion, give rise to a peak at 46.4 and 43.5 ppm in the ²⁷Al MAS NMR spectra of LaX and LaY (Figure 1), respectively [3]. The effect was much more pronounced for LaX, because the incorporation of a trivalent cation like La³⁺ is most favorable when three framework aluminum atoms and, thus, three lattice charges are found close to each other. Due to its higher content of lattice aluminum, LaX offers a significantly larger number of these sites. In LaY lanthanum is predominantly present as [La(OH)]²⁺ and [La(OH)₂]⁺ cations. In particular the latter species only induces a weak distortion on nearby framework aluminum nuclei.

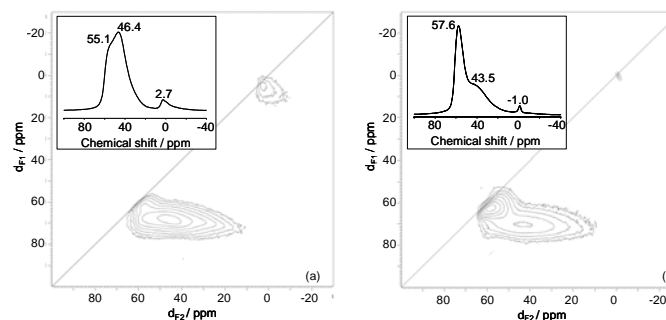


Figure 1. ²⁷Al MQMAS NMR and MAS NMR (inserts) spectra of hydrated samples: (a) LaX and (b) LaY

Significance

Lanthanum exchanged faujasite type zeolite show great potential for HF and H₂SO₄ as catalysts in industrial isobutane/2-butene alkylation plants. The present work provides detailed insight in the performance and properties of these materials. The results will help to develop the next generation of solid alkylation catalysts.

References

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