Communication

Isobutane/2-Butene Alkylation with Zeolite Y without Brønsted Acidity

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Foi estudada a alquilação de isobutano com 2-buteno catalisada por zeólitas Y trocadas com cátions metálicos, usando um cloreto de alquila com iniciador de carbocátions. Os resultados indicaram que, comparavelmente a uma zeólita protônica, a desativação foi significativamente mais lenta e a produção de tri-metilpentanos foi maior nas zeólitas trocadas com metais. Os cátions agem como sítios ácidos de Lewis, interagindo com o cloreto e iniciando as reações de carbocátions. Os resultados suportam a hipótese de que os sítios protônicos favorecem a adsorção das olefinas, aumentando a velocidade de oligomerização.

Alkylation of isobutane with 2-butene was performed on metal-exchanged Y zeolites, using an alkylchloride as carbocation initiator. The results indicated that, compared with a protonic zeolite, the deactivation was significantly slower and the production of trimethylpentanes was higher on the metal-exchanged zeolites. The metal cations act as Lewis acids, interacting with the chloride initiating the carbocationic reactions. The results also support the view that protonic sites on the catalyst favor adsorption of the olefin, thus increasing oligomerization rate.

Keywords: alkylation, zeolite, Brønsted acidity, gasoline

Introduction

The alkylation of isobutane with 2-butene is a reaction normally catalyzed by Brønsted acids. The primary function of the acid system is to protonate the hydrocarbons to generate small concentrations of carbocations. Nevertheless, as the reaction begins it becomes autocatalytic[1-3] due to a hydride transfer step as shown in Scheme 1. Alkylation has been used since the 1930's to produce high octane gasoline.[4,5] However, due to environmental concerns, it will grow in importance in oil refining in the next years. The alkylate, predominantly with eight carbon atoms, is a valuable blending for the adjustment of the gasoline composition to attain the environmental requirements.[3]

Alkylation is normally catalyzed by H_2SO_4 or HF. However, these acid systems present severe environmental problems, especially HF, whose use in new alkylation plants is forbidden in the USA.[6] Today, these acids account for about 30% of the refining catalyst market, but this share tends to increase, as alkylation grows in importance.[3]

The search for a solid catalyst to replace HF and H_2SO_4 in alkylation has been a long-standing challenge for chemists.[6-8] Many materials are active for alkylation, but

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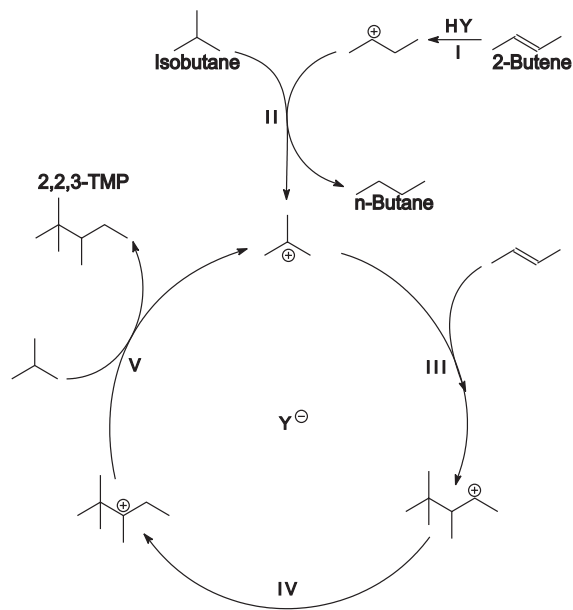
Scheme 1. Isobutane/2-butene alkylation on HY zeolite.

they show rapid deactivation, due to oligomerization,[9] impairing the development of a commercial solid catalyst for this process. Some studies tend to overcome this problem, by working on process engineering solutions.[10] According to some authors, the rapid deactivation of solid

acid catalysts is due to a preferred adsorption of the olefins on the surface.[3,11] This favors successive alkylation reactions, forming the oligomers, which do not desorb from the catalyst surface.

Zeolites are among the best solid catalysts tested in alkylation. One of the main features of the zeolites is their ability to catalyze hydride transfer.[11] Notwithstanding, they still show a fast deactivation during alkylation. We have recently shown that metal-exchanged zeolites can give rise to carbocationic reactions through the interaction with an alkyl halide.[12] The metal cation acts as a Lewis acid site, coordinating with the alkylhalide to form a metal-halide species and an alkoxide bonded to the zeolite structure, that acts as an adsorbed carbocation[12] (Scheme 2). It is not completely clear however, that ionic reactions on zeolites take place directly through the involvement of alkoxides, or there occurs a rapid equilibrium between alkoxides and free carbocations. We were able to show[13] that they can catalyze Friedel-Crafts reactions and we wish to present now, preliminary results indicating that this approach can be used in isobutane/2-butene alkylation, with a superior performance than a protonic catalyst.

Scheme 2. Reaction of an alkylchloride with a metal-exchanged zeolite. Formation of alkoxides.

The preparation and characterization of the metal-exchanged zeolites were described elsewhere.[12] The degree of exchange was approximately 25%, relative to the original sodium cations. The catalysts were named AgY, CuY and FeY (framework Si/Al = 2.6 and surface area of 704 m^2 g^{-1}). For comparative purposes a HUSY zeolite, (framework Si/Al = 4.5 and surface area of 566 m^2 g^{-1}) was also tested in the alkylation experiments.

The reaction was carried out in a stainless steel unit with a tubular reactor (fixed bed). The system was connected to a gas chromatograph and operated in continuous flow mode. The alkylations were carried out in liquid phase at 50 °C, 450 lb in^{-2} and olefin WHSV of 0.1 h^{-1}. A liquid mixture of isobutane/trans-2-butene, with a molar ratio of 10:1, was used as feed and introduced by means of a high precision metering pump. The zeolites (2 g) were initially pre-treated at 450 °C (3.5 °C min^{-1}) under flowing air (30 mL min^{-1}) to prevent metal reduction. The reactor was then cooled to 50 °C, still

under flowing air, and pressurized with nitrogen to 450 lb in^{-2}. Except for the HUSY, a mixture of the isobutane/trans-2-butene, with an amount of 2-butylchloride equivalent to the metal content in the zeolite, was introduced during the first 5 minutes of reaction. After this period, the addition of the halide was stopped and only the isobutane/trans-2-butene mixture was fed to the reactor. It is important to stress that no reaction was observed on the metal-exchanged zeolites, if the chloride was not fed in the initial moments. The effluent was vaporized and diluted with N$_2$ (30 mL min^{-1}), prior to on line analysis by gas chromatography. The main reaction products, trimethylpentanes, were assigned by comparison with standard samples. All the activity and selectivity data were taken from the gas chromatography analysis.
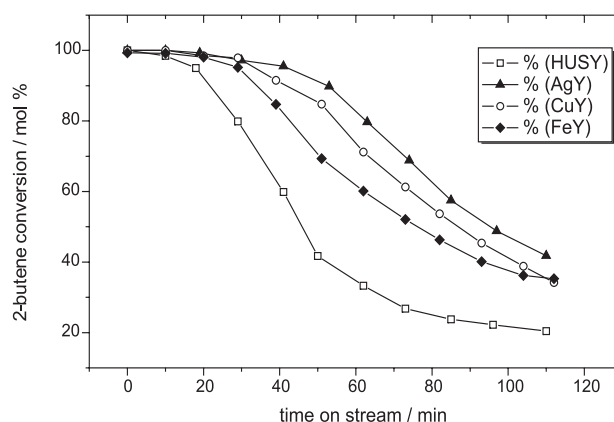
Figure 1. Conversion of 2-butene against time on stream.

Figure 1 shows the conversion of 2-butene against time-on-stream. All the metal-exchanged zeolites showed a slower deactivation rate than the HUSY zeolite. These results are in agreement with the hypothesis that oligomerization is favored on protonic solid catalysts, due to the preferred adsorption of the olefins.[3,11] Once the protons are eliminated or partially removed from the surface, the rate of oligomerization decreases.

Figure 2 shows the selectivity to trimethylpentanes in the C$_8$ fraction, against time-on-stream. Again, all the metal-exchanged zeolites showed a superior performance than the HUSY, indicating that they are selective to the desired product. The catalytic performance of AgY was superior to the performance of CuY and FeY. A possible explanation is that zeolites exchanged with di and especially trivalent cations, show some Brønsted acid sites, associated with the cleavage of water molecules,[14] showing a behavior closer to the protonic zeolite.

The metal-exchanged zeolites still deactivated, indicating that formation of oligomers was not completely

eliminated. However, we cannot rule out other possibilities to account for the slower deactivation. Depletion of the adsorbed intermediates, the alkoxides, can also lead to a decrease in the 2-butene conversion. These species can either abstract a hydride from isobutane or eliminate a proton, yielding an olefin (Scheme 3).
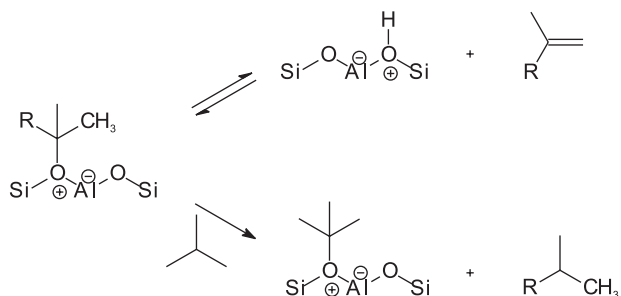
Scheme 3. Schematic representation of proton elimination and hydride transfer reactions on zeolites.

The first reaction is influenced by the relative concentration of isobutane on the surface and favored as the Si/Al ratio decreases. On the other hand, the proton elimination is mainly driven by the relative acid/base strength between the zeolite and the alkoxide. It is normally accepted that decreasing zeolite Si/Al ratio, acid strength also decreases, as the sites become closer. This favors elimination, which contributes to the depletion of the intermediate on metal-exchanged zeolites. Preliminary experiments, reintroducing the alkylhalide during the decay period, restore the full conversion, indicating that, at least part of the deactivation process is due to the decrease of alkoxides on the catalyst surface. Once they are restored, the activity reaches the maximum. Nevertheless, one cannot rule out the formation of oligomers.

Same behavior is observed in the selectivity of these catalysts to trimethylpentanes. As we can see in Figure 2, it decreases with time-on-stream, especially in HUSY. In addition, the selectivity of this zeolite to hydrocarbons with eight carbon atoms is lower, compared to the metal-exchanged zeolites, at the initial moments of the reaction, when the 2-butene conversion is higher. This result suggests that side reactions, responsible for the deactivation of the catalyst, are more effective in HUSY than in AgY, CuY and FeY.

As shown in Figure 2, the trimethylpentanes (TMP) constitute the main components of the C_8 hydrocarbons at the initial moments of the reaction. However, their concentration decreases with time-on-stream, which can be attributed to the reduction of the hydride transfer rate. This behavior is well established in alkylation with zeolites.[3] The distribution of the trimethylpentanes at

the beginning of the reaction is similar for all zeolites (38% 2,3,3 TMP; 32% 2,2,4 TMP; 30% 2,3,4 TMP). This indicates that the metal-exchanged zeolites do not alter the isomerization rate of the trimethylpentyl cations, thus acting on the hydride transfer. At the beginning of the reaction, the remaining C_8 hydrocarbons are mostly dimethylhexanes, but as deactivation occurs unsaturated C_8 hydrocarbons are also formed. These results indicate that the same intermediates are formed on the protonic and on the metal-exchanged zeolites. Hence, the isomerization rate of the trimethylpentyl cations, that governs the TMP distribution, is not affected. The major role of the metal cations on the zeolite is to provide a small concentration of the intermediates, through the interaction with the alkylhalide.
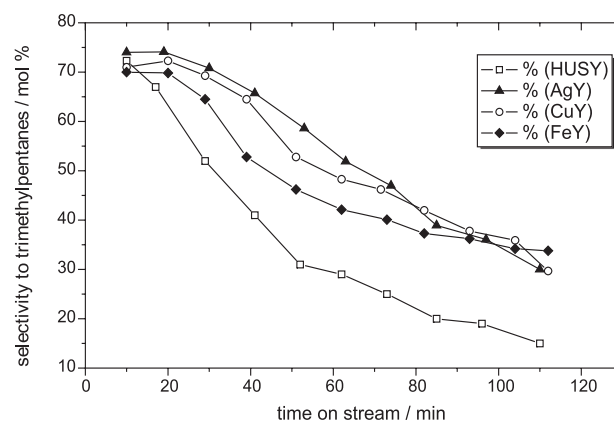

Figure 2. Selectivity to trimethylpentanes in the C_8 fraction.

It is widely known[11,15] that the rate of hydride transfer increases as the framework Si/Al ratio decreases. On the other hand, the acid strength goes in the opposite direction. Hence, one must balance the Si/Al ratio in order to optimize acid strength and hydride transfer when using protonic zeolites. Our approach of generating the adsorbed carbocations by interacting an alkyl halide with a metal-exchanged zeolite permits the use of lower Si/Al ratio, thus improving the hydride transfer rate, which is essential for alkylation. The absence of protonic acid sites also reduces the oligomerization rate, thus making this system an interesting approach for developing a solid catalyst process[16] for alkylation.

Acknowledgments

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