Part 1. Catalyst Development

Introduction

Steep reductions in sulfur levels allowed in gasoline and the recent ban on MTBE in several states (California, New York and Connecticut) have made it difficult for refiners to prepare gasoline blends that meet state and federal guidelines. While ethanol is being touted as a viable oxygenate alternative to MTBE, a recent study published by the National Commission on Energy Policy concludes that corn-based ethanol has limited potential as a viable blendstock since it costs twice more than gasoline and does not have any advantages in reducing CO₂ emissions over traditional gasoline blending agents. Furthermore, the higher vapor pressure of ethanol limits the amount that can be blended in gasoline – especially during the summer months.

EIA (Energy Information Administration) reports that the volume of total gasoline production can easily be restored to MTBE-free volume levels with alkylate. High-octane alkylate is the cleanest gasoline blending stream produced in refineries. Alkylate is an ideal clean fuel component because it has a high octane rating, low vapor pressure and low toxicity. Alkylate has been blended into gasoline for decades to improve octane and thus the antiknock properties of gasoline. Therefore, it is one of the most important and cost effective blendstocks of the gasoline pool. It is anticipated that the amount of alkylate blended into either the CARB gasoline or the East-Coast RFG blend will increase to 20-25% by volume in the near future. Alkylate is currently made using corrosive liquid acids as catalysts. Refiners typically use either hydrofluoric acid (HF), which can be deadly if spilled, or sulfuric acid (H₂SO₄), which is also potentially harmful and increasingly costly to recycle.

Exelus has developed an innovative iso-paraffin alkylation technology ExSact, as an economically viable alternative to HF/H₂SO₄ processes. The two main components of ExSact are:

1. A unique solid-acid catalyst that converts light hydrocarbons into alkylates and
2. A novel fixed-bed reactor that is designed to enhance the performance of this catalyst.

The synergistic integration of the “green” solid acid catalyst with the novel reactor is expected to provide refiners with a cleaner-by-design alternative to produce a high-octane gasoline component to meet both state and Federal requirements. This four-part series describes the successful development of this new “green” technology to produce alkylate.
Alkylation Reactions

Alkylation of isobutane with light (C₃ –C₅) olefins in the presence of a strong acid catalyst involves a series of consecutive and simultaneous reactions occurring through carbocation intermediates. The addition of proton to an olefin, followed by hydride abstraction from iso-butane, leads to a t-butyl cation. The t-butyl cation then combines with an olefin (say, C₄) to give the corresponding C₈ carbocation: These C₈ carbocations may isomerize via hydride transfer and methyl shifts to form more stable cations. These C₈ cations undergo rapid hydride transfer as iso-butane regenerates the t-butyl cation to perpetuate the chain sequence.

Unfortunately, these are not the only reactions occurring during alkylation. There are a number of secondary reactions that, in general, tend to reduce the quality of alkylate. The C₈⁺ can continue to react with olefins and form larger cations. The successive addition of olefins to carbocations, or olefin polymerization, is the primary route to formation of large hydrocarbon residue or “coke”, leading to catalyst deactivation.

- **Alkylation**
  - iC₄H₁₀ + C₄H₈ → iC₈H₁₈
  - isobutane + butene → iso-octane (alkylate)
- **Polymerization**
  - n (C₄H₈) → CₙH₂ₙ
  - n (butene) → oligomers
- **Product Degradation**
  - iC₈H₁₈ + C₄H₈ → iC₁₂H₂₆
  - Iso-octane + butene → heavy paraffins

Figure 2. Iso-paraffin alkylation reactions

Solid acid catalysts have been investigated as alternatives to liquid catalysts for isobutane alkylation for over 30 years. These include AlCl₃; promoted zirconia; heteropolyacids, such as tungstates; liquid acids immobilized on silica, polymers, or other solid supports; and natural and synthetic zeolites. Solid catalysts can improve selectivity and reduce production costs, but their tendency to deactivate rapidly during alkylation has prevented virtually every known solid-acid alkylation catalyst from becoming commercially viable.
Problems with Solid-Acid Catalysts

Catalyst Activity: A catalytic process is not commercially viable unless the chemical transformation is achieved within practical limits of space-time yields. Economic necessities determine the lower limit for industrial catalysis – too long a reactor residence time will make the reactor costs too high. The upper limit is imposed by achievable rates of heat and mass transfer. When one switches from a liquid-acid catalyzed process to one catalyzed by solid-acids, there is a significant decrease in the number of available acid sites. 1 gram of sulfuric acid contains roughly 20x10^{-3} moles of acid sites; 1 gram of solid-acid catalysts (e.g. zeolite or promoted zirconia) on the other hand, contains at most 10^{-3} moles of acid sites of which only 20-30% are strong enough to catalyze the alkylation reaction. In other words, there are 100 times more active acid sites in a gram of liquid-acid compared to a gram of solid-acid catalyst. This is the case for solid acid catalysts having very large surface areas (and hence small pores); the situation is worse with catalyst formulations having lower surface areas and larger pores. One can use a large excess of catalyst to compensate for the lower acid site density for solid acid catalysts – but that would greatly reduce the space-time yields making it economically unattractive. This is one major reason why replacing liquid acids with solid-acid catalysts has proved to be so elusive a goal.

Figure 3. Rates of reactions for industrial alkylation processes

Catalyst Stability: All liquid acids produce conjunct polymers as alkylation by-products. These polymers are called acid-soluble oil (ASO) or red oil. The oil is a complex mixture of unsaturated hydrocarbons having molecular weights in the range of 250-300. They dilute the acid and thus lower the acid strength. In commercial scale operations, a small slip-stream of used acid has to be withdrawn and replenished by fresh acid. In solid-acid catalysts, this polymer (“coke”) builds up on acid sites eventually blocking the catalyst pore mouth and deactivating the catalyst. Pore-mouth plugging typically occurs when the catalyst suffers from severe intra-particle diffusional limitations. The problem of rapid deactivation via pore-mouth plugging, leading to very short catalyst lifetimes (on the order of minutes), has prevented virtually every known solid-acid alkylation catalyst from being a commercially viable and environmentally superior alternative to conventional liquid-acid alkylation processes.

Increasing the pore size increases catalyst life, but affects the catalyst site density adversely. Decreasing the pore size increases the number of active sites per unit volume, and hence the initial activity, but leads to quicker plugging of the pores.
Exelus’s approach

Using grants from the US Department of Energy and the National Science Foundation, Exelus started work on developing a viable solid-acid catalyst alternative to liquid acid catalyzed iso-paraffin alkylation technologies in 2001. Our goal was to develop a simple swing fixed-bed reactor process using a benign solid-acid catalyst. Our desire to use a fixed-bed reactor was influenced by two issues: a) to simplify process scale-up and b) to keep both capital costs and operating expenses as low as possible. This, however, is easier said than done for alkylation reactions. Iso-paraffin alkylation reactions are very fast and they suffer from severe pore diffusion limitations. As a result when catalyst particle sizes are increased from 100 µm (for slurry reactors) to 1.6 mm for fixed-bed reactors, the catalyst activity reduces by 50-fold as shown in figure 4 below. To match the catalyst productivity of a slurry reactor, one would need to build a fixed-bed reactor with 50-times the volume – which is not practical for commercial scale system.

In addition to using a fixed-bed reactor, we wanted to ensure that the solid-acid catalyst was both robust as well as benign i.e. environmentally friendly. We rejected right at the outset replacement of a liquid acid with a liquid-acid supported on solid particles or co-feeding toxic halogens to a solid-acid catalyst to maintain its activity.

![Graph showing reduction in catalyst activity with increasing particle size](image)

Figure 4: Reduction in catalyst activity with increasing particle size

Our development approach was to first understand the dynamics of the alkylation reaction by systematically studying the effect of both physical and chemical aspects of the solid-acid catalyst system design on product distribution and catalyst deactivation characteristics. Several different catalyst formulations encompassing a wide range of acid functions, number of acid sites and acid strengths were evaluated as part of this study. Many of our findings were in stark contrast to conventional (widely held) beliefs about solid-acid catalyzed alkylation reactions.
Through this systematic study, Exelus was able to identify an optimal “window” of design parameter values that were then used to develop the ExSact system. By judicious manipulation of the active material composition (number of sites and acid site strength), researchers at Exelus have developed a unique solid-acid catalytic system that has roughly 400% more active sites than a typical solid-acid catalyst. The catalyst activity of the solid acid was found to be higher than a typical liquid acid catalyst, which means that much lower amounts of catalyst are required to catalyze the isoparaffin alkylation reaction, allowing one to design alkylation reactors with significantly lower volumes (hence cost).

Figure 5: Exelus solid-acid catalyst performance compared to other commercially available systems

By integrating optimized acid-sites with superior mass transport characteristics and a pore architecture that reduces pore-mouth plugging, Exelus has developed a truly revolutionary solid acid catalyst. As shown in figure 5 above, the new catalyst system is easily able to achieve a quantum jump in performance over conventional solid-acid catalysts. All isoparaffin alkylation tests were run in the same reactor, under identical feed composition (isobutane to olefin ratio and 2-butene as olefin), space velocity, reactor pressures and particle sizes but over a range of temperatures since the modified zirconia and chlorinated alumina catalysts work best at 20-30°C while the zeolite catalysts work best around 70-90°C.
Solid-Acid Catalyst Performance

The robust solid-acid catalyst produces alkylate with a superior octane rating over a wide range of operating temperatures (50-100°C), olefin space velocities (0.1 to 1.0 1/hr) and feed composition (I/O ratios from 6 to 30). Its robustness minimizes the requirement for extensive feed pre-treatment. The technology (catalyst stability/product octane/alkylate yield) has been proven on a bench scale reactor as shown below. Catalyst stability was confirmed by measuring the catalyst performance through multiple cycles of alkylation and regeneration using hydrogen. Figure 6 shows data from a bench-scale evaluation (using a back-mixed reactor) of a single catalyst loading that processed a number of different feedstocks under a variety of process conditions. The data shown are for periods of operation that used similar feed and operating conditions. Feedstocks ranging from pure 2-butylene and isobutylene to butylene mixtures were tested in this run.

![Figure 6: Results of the stability test with using the new solid-acid catalyst](image)

The octane rating (RON) is the same when using 1 or 2-butene but drops by a point when using 30% iso-butylene olefin feed source. Raising the reaction temperature by 30°C reduces the product octane marginally by 1 octane point in contrast to the liquid acid processes, which are penalized severely. The catalyst effectiveness factor also has a large effect on both product slate and catalyst lifetimes. By carefully studying the effect of Thiele Modulus on catalyst life and product octane values, Exelus was able to tune the catalyst diffusional characteristics to further optimize the solid-acid catalyst performance.
Conclusions

Exelus has developed a revolutionary refinery process (ExSact) that is designed to produce high-octane alkylate without the use of toxic liquid acids. The strength and distribution of its acid sites reduce olefin dimerization and paraffin cracking, while enhancing isobutane alkylation. Furthermore, the controlled pore structure of the catalyst reduces deactivation by coke formation and pore mouth plugging. The paraffin alkylation process using ExSact catalyst is fundamentally safer and cleaner than conventional liquid-acid catalyzed processes, eliminating the use and generation of toxic chemicals. The new solid-acid catalyst promises significantly improved yields and selectivities, minimizing waste by-products and disposal problems associated with spent catalysts and regeneration of large quantities of liquid acids. Given the current push for eco-friendly processes to produce ultra-clean fuels, The ExSact technology is poised to fill a large void in the gasoline market for decades to come.

Figure 7: Innovations in the Exelus solid-acid catalyst design

Next month the second-part of this 4-part series will summarize the development of the novel fixed-bed reactor for iso-paraffin alkylation.

More information on the Exelus alkylation process can be found at our website www.exelusinc.com