



Nanoporous materials forge a path forward to enable sustainable growth: Technology advancements in fluid catalytic cracking



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ABSTRACT

An overview is presented on the central role that zeolites and other nanoporous materials currently play in the Fluid Catalytic Cracking (FCC) process as well as how this role evolved over the course of the years since its inception. Today, utilization in FCC constitutes the vast majority of global zeolite catalyst consumption by volume. FCC is the main conversion process in a typical fuels refinery, and as the most critical ingredient of the catalyst, zeolites are responsible for producing majority of the gasoline used around the world as well as taking an important role in the production of other transportation fuels (e.g., diesel, jet fuel) and building blocks for the petrochemical industry (e.g., propylene, butylenes). Therefore, it can be stated that zeolite catalysts fuel our industrialized society and provide the building blocks for its advancement; consequently, zeolites have a direct impact on the future of the global economy and its sustainability. Strategies that involve zeolites and other nanoporous materials for improving performance of FCC operation and ensuring its environmental sustainability were reviewed. Zeolite modifications were examined with each leading to an improvement in zeolite stability under severe conditions in an FCC unit. The importance of diffusion pathways within an FCC catalyst particle, leading to higher accessibility of the active zeolite sites, were explored, and the importance of a well-designed catalyst architecture, allowing FCC feed, intermediates, and final products to diffuse freely in and out of the catalyst particle were discussed. The role of contaminant metals in FCC was investigated, and some mitigation strategies for the most common FCC contaminants, nickel and vanadium, were presented. The impact of contaminant iron was discussed alongside catalyst architecture, particularly surface porosity of the catalyst particle. Utilization of other nanoporous materials in FCC, especially as environmental additives, was summarized. Testing considerations were screened with an emphasis on matching laboratory deactivation to refinery FCC observations.

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1. Introduction

The fluid catalytic cracking (FCC) process represents an integral part of a refinery complex, providing the majority of gasoline consumed throughout the world in addition to other important transportation fuels. The FCC, in its current design, utilizes a well-fluidizable catalyst that is continually added and withdrawn (and/or lost). The catalyst facilitates the cracking of crude oil into

important products including gasoline, diesel, jet fuel, and liquefied petroleum gases (LPGs).

The FCC has been utilized in the industry for over 70 years, going from a single FCC unit in the USA to over 400 in operation today around the world. Since FCC's inception, the technology has undergone major transformations, including changes in both hardware and catalyst technologies. Importantly, these transformations have ripple effects – as a result of the flexibilities afforded by technology changes, the FCC is continually being pushed to its limits. Ancillary units have been implemented and have undergone dramatic changes as well, including crude oil desalters and particulate matter collectors. Regulatory requirements have been put

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in place to push FCC limits even harder. For instance, improvements in hardware and catalyst technologies have enabled increased control of emissions, including particulate matter, NO_x, and SO_x.

Hardware changes over the years have allowed for step changes by improved feed atomization and catalyst distribution and fluidization. Catalyst changes over the years have allowed for step changes in conversion and selectivities. The two, hardware, and catalyst, have constantly undergone iterative changes as the other has allowed. For instance, improved catalyst activity through enhancements in zeolitic cracking led to drastically different unit designs such as the short contact time unit configuration.

Hardware and catalyst changes not only respond to each other, but also to the market. The availability and diversity of crude oils on the market represents another force to which FCC technology must adapt. Processing of residue-containing (i.e. resid) and shale-derived (i.e. tight oil) feeds require optimized hardware and catalyst technologies. Product demand, such as diesel over gasoline, also drives hardware revamps and catalyst selection criteria.

The past 70 years demonstrate the compounding improvements in FCC catalyst and additive technologies – a result of both push and pull forces in the market and from process licensors, hardware vendors, catalyst suppliers, and government agencies. The goal of this contribution is to review FCC catalyst and additive technology developments in detail starting with the inception of the FCC concept.

2. FCC background and history

The FCC process was a result of the combination of an urgent global need, political dynamics of that period, focused collaboration, and scientific advancements in related fields (fluidization, heterogeneous catalysis, materials science, etc.). In 1938, a consortium called Catalytic Research Associates (CRA) was formed between multiple firms with varying functions (operating, licensing, chemical manufacturing) in order to develop a catalytic cracking process [1]. Houdry held patents that covered fixed-bed cracking using oxides of silicon and aluminum; the consortium was tasked with inventing a novel process that did not infringe on these patents. Houdry's patent was industrially important because of the regeneration ability of the catalyst via coke burning. Two years later, the structure and members of the consortium were reorganized amid World War II politics [2].

Early on, the transfer of fluidized solids was investigated at a Baton Rouge pilot plant. Shortly after, investigations into fluidized catalysts over catalyst pellet systems commenced. In 1940, with political and national pressures to provide jet fuel during World War II, funds to build the first powdered/fluidized catalyst plant were approved. The first catalyst used at the Louisiana plant, called PCLA for powdered catalyst Louisiana, was an amorphous alumina-based catalyst. The operation was publicly announced, albeit carefully with political tensions world-wide, on February 11, 1941, in which a new “continuous catalytic cracking process” was unveiled [3]. Within three years, 34 additional units were built and commissioned due to its overwhelming success in producing high quality gasoline and aviation fuel, among other products.

Since the first continuous catalytic cracking process, hundreds of FCC units have been built around the world. Major hardware and catalyst changes have taken place during that time. On the catalyst side, changes have also occurred since the 1940's. Originally, Houdry utilized acid-activated bentonite. Natural and synthetic aluminosilicates had good cracking properties and strong Lewis acid sites. Early catalysts had low alumina content, around 13%, and by the 1950's, this figure increased to about 25% [4]. The early FCC catalysts were finely ground materials, i.e. no spray-drying process was employed. Spray drying was first utilized in FCC catalyst

production in 1948 and improved the fluidization and attrition properties of the catalyst via sphericity improvements. However, the biggest technological change in the history of the FCC catalyst was the implementation of zeolites. Zeolites were first introduced to FCC catalysts in 1964 and represented a major step change in catalyst stability and selectivity as a result of their strong Brønsted and Lewis acid sites. Zeolites not only provided strong solid acidity for high activity and stability, but also introduced a high surface area pore/channel network that brought size and shape selectivity as well as higher density of acid sites (per unit weight of catalyst).

By the late 1990's, additional modifications were being made to the FCC catalyst. Special alumina matrices for nickel passivation and additional metals traps for vanadium passivation were introduced. The stability of the zeolite was improved for maximum conversion via the introduction of rare earth oxides. Ion exchange technology in the FCC catalyst manufacturing process allowed for the reduction of sodium, a catalyst poison for the acid sites. Lower sodium enabled higher catalyst activity and stability. Finally, attention to catalyst porosity was heightened in order to take advantage of resid processing [5]. Resid processing became important in the 1980's with the oil crisis at the time, when refiners were looking to take advantage of opportunity (i.e. low cost) crude oils.

In the 2000's, FCC catalyst additives aimed at improving not only yields off the FCC unit, but also at minimizing its environmental impacts. ZSM-5, which was patented and introduced by Mobil much earlier, was being employed for octane improvement by increasing light olefins [6]. Other additives developed targeted emissions and product specifications, such as SO_x, NO_x, and gasoline sulfur reduction additives. Also in the 2000's, DMS (distributed matrix structures) technology represented another breakthrough for the FCC catalyst with improved pore architecture for the most advanced zeolitic cracking in the industry, which is explained in more detail in section 5.1. This resulted in immediate market acceptance via utilization at numerous refineries around the world as shown in Fig. 1 below. DMS technology provided a step out in performance via state of the art porosity modifications, partially enabled by a novel technique of *in situ* zeolite crystallization. The new technique allowed for optimized porosity, including surface porosity and channel modifications.

Activity impacts of the major catalyst and hardware improvements are summarized in Fig. 2, as estimated by historical conversion levels in FCC units. The second order activity as a function of major step change technologies improved dramatically from 1950 when amorphous catalysts were still used. Subsequent improvements via zeolites, ultra-stable Y-zeolite (USY), short contact time (SCT) unit designs, and DMS are illustrated.

The proceeding sections of this manuscript detail the important catalyst and hardware improvements described in this section with an emphasis on advancements in materials science and chemistry that were integral in FCC improvements.

3. Hardware developments

The first commercial FCC operation commenced in 1942 when the Model I FCC unit started in Baton Rouge, Louisiana, processing 13,000 barrels of crude oil per day [7]. Since this first FCC unit, hundreds of FCC units have been built and designs have evolved to adapt to changing market demands. These changes effectively enabled the FCC to maintain its dominance as the key conversion process for gasoline and light olefins production within a refinery complex.

In recent years, the use of opportunistic crude feeds, the greater emphasis on light olefins production, and the concerns around environmental emission regulations have driven a host of

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