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Opportunities for Catalysts in the Refining and Petrochemical Industries: An Eight-Year Forecast

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Executive Summary

E.1 Introduction

Refining catalysts fare well in both good and bad economic environments. During good times, refiners look to catalysts to increase output so they can sell more product at high prices. During bad times, for example the weak economy we are currently experiencing, refiners look to catalysts to increase efficiency, thus reducing raw materials and energy consumption.

This is not to say that the current economic situation will have no impact on catalyst demand, because it will. The world has changed drastically over the past six months, with oil prices going from record highs of $145/bbl in July 2008 to about $45/bbl at the end of 2008, and it would be impossible for the industry not to feel some kind of impact. Many predict that growth in fuel demand for the next year or two will be less than previously expected—a result of consumers cutting down on traveling to save money combined with reduced growth in developing countries, which was responsible for a lot of the transportation fuel-use growth. That being said, fuel demand is expected to grow, and many believe that this growth will get prices back to semi-normal levels after one to two years; the U.S. Department of Energy's Energy Information Administration expects oil prices to rise to $60/bbl in 2009 and then to continue climbing up to $130/bbl by 2030 (these values are in 2007 dollars).

NanoMarkets believes that there are substantial opportunities for both existing catalyst producers, and for technology firms looking to get into this industry. We expect several overall trends from the past few years to continue throughout this eight-year forecast, driving demand for energy catalysts. However, the growth over the next two years will not be as high as previously thought due to the current recession in the U.S. and other countries.

E.2 Summary of Emerging Opportunities for Catalyst Producers

E.2.1 Refinery Catalysts

Three key trends describe the landscape for catalysts used to produce fuels. First, while there is a lot of talk about alternative fuels such as ethanol and about vehicles powered by fuel cells and electricity, most industry players agree that liquid hydrocarbon-based fuels will dominate the energy mix for the foreseeable future. Inherent in the demand for these fuels is the need for modern catalysts, without which the refining industry would not be able to produce the quantity of fuel the world is expected to consume over decades to come.

Second, there is a trend toward processing heavier and dirtier feedstock; light, easy-to-process crude oil is becoming less and less available, and therefore refiners are finding ways to process more abundant and accessible feedstock such as tar sands, shale oil, and heavy oils. The contaminants in these heavier feedstocks are what poison the catalysts used to process the feedstock, rendering them "spent" much sooner than they would have been with yesterday's lighter crude oil. As a result, refiners are forced to use more catalysts, either changing out the catalysts more frequently or just adding a higher concentration of catalysts to a reactor.

The third point has to do with environmental mandates that require lower and lower levels of sulfur in the final fuel product. These requirements are tightening, as well as spreading to fuels other than gasoline (such as diesel and jet fuel). Reducing the sulfur concentration requires more catalysts, as well as more specialized catalysts, especially when the level gets down to parts-per-million.

The interaction of these key trends has created real opportunities for catalyst materials. These opportunities exist for catalysts used in traditional refining processes (fluid catalytic cracking, hydrocracking, hydrotreating, and reforming) and in new processes, such as the conversion of synthesis gas via Fischer-Tropsch into fuels and chemicals.

What are refiners looking for in catalysts? In general, refiners are always looking for catalysts that offer higher selectivity, improved productivity, and better energy and raw material utilization. NanoMarkets expects new catalyst developments to address these desires through tweaks and modifications rather than with a significantly new approach as occurred with the discovery of synthetic zeolites (although the industry would certainly welcome a catalyst with higher performance than the current y-type zeolite). In order to make these tweaks and modifications, it is important to know how refiners and fuels producers are operating their facilities.

Each of the key trends discussed above is in some way dictating how refiners are operating their refineries, and thus offers an indication of what type of catalysts they are looking for. Here’s how the main trends in refining/fuel demand are expected to play out for catalyst producers.

The fact that refiners are processing dirtier feedstocks, which contain higher levels of contaminants and impurities, affects most of the refining units but in particular increases the need for hydrotreating capacity. To preserve catalysts in the main refining units, hydrotreaters are being added to the front- and back-end of these units. As a result, refiners are looking for catalysts with longer lifetimes or that can stand up to the higher level of contaminants.

Next, refiners are operating units to minimize the amount of gasoline produced and maximize diesel and propylene production. This affects the FCC units, which traditionally produce the majority of gasoline in a refinery; hydrocrackers, which make most of the diesel; and the reforming and isomerization units, which upgrade gasoline. As a result, refiners are looking for the following types of catalysts: diesel-selective FCC catalysts, propylene-selective FCC catalysts, diesel-maximizing hydrocracking catalysts, and hydrogen-maximizing reforming catalysts. The demand for reforming catalysts that maximize hydrogen production is a result of both the decreased demand for gasoline (reformers typically are used to upgrade gasoline streams) and the increase in hydrotreating, which consumes hydrogen.

FCC Catalysts: Demand for FCC catalysts was growing over the last few years because of the global growth in gasoline demand. However, the demand growth for gasoline has slowed and is expected to continue to decrease or flatten out. Over the next five to ten years, demand for FCC catalysts will be driven by: (1) demand from petchem producers for propylene; (2) demand for diesel; and (3) the trend toward processing heavier feedstocks. Even though we do not expect to see a lot of new FCC unit construction, FCC catalyst consumption is still expected to increase, although only modestly.

Refiners are looking for catalyst technologies that will allow them to run their FCC units to decrease gasoline production while increasing propylene and diesel production.

Maximizing propylene production in FCC units is driven by minimizing hydrogen-transfer reactions—a bimolecular exchange that favors the production of light alkanes and coke at the expense of propylene. There are several ways to modify FCC catalysts to suppress hydrogen transfer. One way is to reduce the volume of strong acid sites by reducing the amount of zeolite. Another is to decrease the zeolite unit cell size, which is typically done by reducing the rare earth oxide (REO) content. The downside to reducing the REO content is that it leads to a reduction in catalyst activity. The other way to suppress the unwanted hydrogen transfer reaction is to prevent the molecules from contacting one another for long enough to allow the reaction to occur. This can be done by modifying the zeolite pore structure, by shape, size, or both, so that the molecules diffuse through the catalyst very quickly, reducing the residence time of the olefins in the catalyst.

One way to maximize diesel production from FCC units is to operate the units at lower temperatures. The problem with this scenario, however, is that the lower temperatures negatively impact the slurry yield.

There are other areas of interest for FCC catalyst development as well. One such focus is developing catalysts that are less susceptible to deactivation by contamination of metals, primarily vanadium. Metals in FCC feed act as poison to the catalysts and therefore lower the catalyst's lifetime. Producers have developed catalysts that include passivators, such as antimony and barium compounds, which "partially offset" the effects of nickel on the catalyst; catalysts incorporating tin, barium, and strontium titanates, as well as magnesium oxide have been found to act as metal traps for vanadium.

Hydrocracking Catalysts: The hydrocracker is similar to the FCC in that it catalytically cracks heavy hydrocarbons into lighter products; however, it uses a different type of catalyst, operates at lower temperatures and pressure, and involves the use of hydrogen gas. Compared to hydrotreating catalysts, hydrocracking catalysts require less metals loading but are much more complex because they have two functions: to remove contaminants and crack molecules.

Research and development in hydrocracking catalysts centers around: (1) catalysts that selectively produce diesel; (2) catalysts that improve hydrogen utilization; and (3) catalysts that lower sulfur content to meet the ULSD mandates.

There are several types of hydrocracking catalysts used, each tailored to the feed material, desired product slate, and operating conditions. Typical hydrocracking catalysts are amorphous silica-alumina and Y-type zeolites with varying Si/Al2 framework ratios. These catalysts also contain a small amount of uniformly distributed rare earth metals, most commonly nickel, palladium, platinum, and tungsten.

Amorphous hydrocracking catalysts have lower cracking activity. They are typically used to maximize distillates and lube base production. Some commonly used amorphous catalysts are: silica-alumina, silica-magnesia, silica-titania, and silica-zirconia. The most frequently used is SiO2-Al2O3.

For higher cracking activity in the hydrocracking unit, crystalline catalysts are used, with the most common being zeolite Y. Zeolite Y is synthesized by reacting sodium silicate or colloidal silica with sodium aluminate in the presence of sodium hydroxide and an amorphous sodium aluminosilicate nucleating agent. This structure, which is sometimes referred to as Na-Y zeolite, must be further treated to obtain an optimal acidity level. The sodium-form zeolite goes through an ion-exchange process to exchange sodium ions for ammonium.

There are several ways to modify zeolite catalysts to achieve the optimal activity for different applications. Just as with the FCC catalysts, the unit cell size of the zeolite can be modified to change the cracking activity of the hydrocracking catalyst. Catalysts with higher unit cell size typically have higher cracking activity, which favors the production of naphtha. Smaller unit cell size, which can be achieved by hydrothermally treating the catalyst to further reduce the sodium content, typically leads to higher distillate production.

Hydrotreating Catalysts: Much of the focus in the hydrotreating catalyst area today centers around processing heavier feedstocks without decreasing throughput, while at the same time meeting the ever tightening sulfur reduction requirements.

Conventional hydrotreating catalysts are made of tungsten and molybdenum sulfides on alumina modified with the addition of cobalt or nickel sulfides. The most economical catalysts used for sulfur removal contain cobalt and molybdenum (CoMo) sulfides on an alumina support. For nickel removal, nickel-cobalt-molybdenum or nickel-molybdenum compounds on alumina supports are used. However, because nitrogen is more difficult to remove than sulfur, a catalyst that can sufficiently remove nitrogen will most likely be able to effectively remove sulfur.

Other Refining Catalysts: The primary purpose of reforming, isomerizatin, and alkylation is to boost octane in gasoline. However, because there is an over-supply of gasoline worldwide, refiners are looking at other ways to operate these units for increased profitability.

The reformer is also a major source of hydrogen in a refinery; for some refiners it is the only source. Legislation requiring increased sulfur reduction for gasoline has led to an increase in hydrotreating, and thus to a higher consumption of hydrogen. As a result, refiners are looking for catalysts that maximize the production of hydrogen from their reformers.

Typical reforming catalysts consist of silica-alumina supports with platinum and, sometimes, the addition of halogen, typically chloride. Several reactions take place in the reformer, with the components of the catalyst dictating the balance between these reactions.

E.2.2 Fischer-Tropsch Catalysts

Most industry players will agree that meeting the projected demand for transportation fuel will require a diverse range of commercially viable fuel sources. Petroleum-based fuels will continue to dominate the market. However, as crude oil becomes ever harder to access and the demand for fuel continues to rise, biomass, coal, and natural gas will be needed to fill the gap.

One technology that is getting a lot of attention today is gas-to-liquids (XTL)—a process that makes synthetic fuels and chemicals. (XTL is the generic term referring to gas-to-liquids technologies. Specific variations are GTL when referring to natural gas, CTL for coal-to-liquids, and BTL for biomass-to-liquids.) While these technologies have been around since the 1950s, there is renewed interest today motivated by declining availability of easy-to-access crude oil; an abundance of natural gas and coal in some regions; growing demand for “clean” fuels; and advances in technology, among other issues. As oil becomes increasingly scarce and more expensive, the demand for catalysts used for these technologies will continue to rise, especially in regions with high deposits of natural gas and coal, including China, the Middle East, Russia, and the U.S.

One major benefit of XTL fuels is their compatibility with existing vehicle technologies and fuel distribution systems. These fuels could be transported through existing pipelines, dispensed at existing fueling stations, and used to fuel today’s vehicles.

GTL: The most widely used XTL feedstock today is natural gas, which is the most cost-effective route to syngas. The commercial production of fuels and chemicals via GTL is still in its early stages, however, and several of these GTL projects have either been delayed or canceled over the past year, largely because (1) investment costs have typically been higher than expected, and (2) there are not enough engineers/construction units on the ground to build the facilities. The projects (existing, in construction, and planned) are outlined below:

One of the major challenges facing GTL technologies is the large capital investment required to produce syngas. The cost of these plants does not look so bad when oil is above $120/barrel. However, at the current price of oil, cost improvements will be required to make this process competitive with traditional crude-oil based technologies. Technological breakthroughs, both in reactor design and catalyst development, are needed to address the cost concern. Economy of scale will lower this cost, but not enough to make GTL economically feasible outside of special cases.

CTL: CTL is of particular interest for countries with large reserves of coal, including China, Russia, and the U.S. (Illinois, Kentucky, Pennsylvania, and West Virginia). Several announcements have been made over the last few years for CTL plants in these regions. For instance, China’s largest coal producer, Shenhua Group, announced plans in 2007 for eight CTL projects with a combined capacity to produce 30 million m.t./year of synthetic fuel and chemicals by 2020.

This flurry of activity appears to be slowing down, however, as environmental and capital cost concerns come center stage. One of the things that makes coal so attractive—its high carbon content and thus its high energy density—also makes it problematic. Because of coal's high carbon content, it releases a lot of carbon dioxide. As a result, several projects have been either canceled or delayed.

Many believe that CTL interest will return as a result of technological advances, including the development of carbon capture and sequestration (CCS) technology compatible with CTL. Improvements in process and catalyst design are expected to address capital cost concerns as well.

BTL: Unlike CTL and GTL technologies, which have been around for some time, BTL technologies are relatively new and are still in the developmental stages. Compared to GTL and CTL, BTL brings with it some extra challenges (as well as benefits, including the advantage of being carbon dioxide neutral). One such issue centers around feedstock handling and preparation. One of the challenges with BTL is that it requires approximately one ton of biomass to produce one barrel of liquid fuel. Transporting large quantities of biomass to a central location would be uneconomical. One approach to address this issue is the development of small-scale Fischer-Tropsch reactors to convert biomass locally. While this does not directly relate to the catalysts used to process the biomass, it does impact the resulting syngas and thus the catalysts needed to treat this syngas.

F-T: The major focus of catalyst producers involved in XTL is the development of Fischer-Tropsch catalysts. While F-T has several benefits it also has one particularly troublesome problem: it produces a wide product distribution. Improving (or narrowing) this distribution to maximize a particular product is arguably one of the key characteristics that needs to be addressed. Catalyst design is one of the knobs being used to solve this issue.

The choice of active metal has important implications for the selectivity of the catalyst. Cobalt, iron (under F-T conditions iron is converted to iron carbide), nickel, and ruthenium are all active catalysts for the F-T synthesis. Nickel catalysts are too hydrogenating and therefore produce a high yield of the undesired product methane. Ruthenium is not available in quantities that would be needed for large-scale applications and is also very expensive. This leaves iron and cobalt. While cobalt is much more expensive than iron, it is about three-to-five times more active on an equivalent surface area basis than iron, which makes it the metal of choice. However, cobalt is extremely sensitive to contaminants, such as H_2S; therefore iron is typically used when the syngas stream contains high levels of impurities (typically when coal is the syngas source), because it is relatively inexpensive and can be replaced frequently.

There are other ways to alter the catalyst performance besides the choice of active metal. These include: addition of promoters, catalyst preparation and formulation, pretreatment and reduction, and selective poisoning.

The basic composition of cobalt catalysts is as follows: Inorganic oxide support such as aluminum, silica or titania, with about 15–30 wt percent cobalt; 0.05–0.1 percent noble metal promoter; and 1–10 wt percent oxide promoter such as zirconia, lantania, or cerium oxide.

The F-T catalyst consists of cobalt metal particles distributed on a support. The size of these particles appears to play a role in catalyst performance. It is widely accepted that for cobalt particles larger than 8 nm, the rate of reaction is proportional to the number of cobalt surface sites, which is dependent on particle size, morphology, and stability, as well as the extent of metal reduction. Various studies suggest that smaller particles, less than 6–8 nm in diameter, have lower specific apparent activity than larger particles, and appear to result in higher methane selectivity and higher yields of olefinic products. A study done at the Unité de Catalyse et de Chimie du Solide explained this phenomenon with the following reasons: (1) catalyst deactivation at FT conditions (cobalt oxidation, coking, sintering, formation of mixed cobalt-support compounds, catalyst attrition, etc.), (2) different electronic structure of smaller and larger cobalt particles, which would affect intrinsic activity of cobalt metal sites.

Several studies have found that adding small amounts of noble metal promoters such as platinum, palladium, rhodium, and ruthenium, can have a significant impact on the properties of cobalt catalysts. Promoters are typically added by co-impregnating the porous support with an aqueous solution of cobalt salt and noble metal precursors, which include perrhenic acid, ruthenium nitrosyl nitrate, and tetraammineplatinum (II) nitrate.

The impact of these promoters has been found to vary with the type of support, noble metal, and reaction conditions. The most noticeable impact has been an increase in carbon monoxide conversion at steady state conditions, with the most dramatic effect seen for noble metal promoted alumina-supported cobalt catalysts. This effect is less pronounced for silica and titania supported catalysts.

The impact of noble metal promotion on hydrocarbon selectivity seems to be an open question. Most of the literature finds that the addition of noble metals to cobalt catalysts results in higher selectivity for methane and lower selectivity for the desired high molecular weight hydrocarbons. However, this effect seems to be more apparent at high levels of noble metals, >0.1 percent.

Iron-based FT catalysts are less active than cobalt-based catalysts. However, iron catalysts exhibit a high water-gas shift activity and therefore are suitable for use with syngas that has a low H_2/CO ratio. The basic composition of iron FT catalysts consists of bulk iron oxide with the addition of several promoters. Copper is typically present as a reducing agent at 1–4 wt percent. Other common promoters include potassium-, aluminum-, and silicon-oxides. The objective of these promoters is to increase the basicity of the catalyst surface, which tends to increase CO adsorption, and to decrease the hydrogenation reaction, which improves chain growth resulting in higher molecular weight product distribution. Potassium has been found to increase CO adsorption, as well as to decrease hydrogenation. However, it is also known to increase water-gas shift activity leading to a faster rate of catalyst deactivation because of the increased rate of carbon deposition on the surface of the catalyst.

Silicon oxide seems to work synergistically with potassium in that it appears to slow down the rate of degradation.

E.3 Summary of Eight-Year Forecast

The following forecasts are based on what NanoMarkets believes will be the most-likely scenario to play out over the next eight years. We expect a short-term recession that will last through 2009 and perhaps much of 2010, followed by a long-term inflation as a result of recent attempts made by governments to provide emergency finance for financial institutions around the world. This will likely be reflected in inflationary pressures in a year or two.

As the world economy grows at a much slower pace over the next year or two, the growth in fuel demand previously anticipated as a result of growing GDP in developing countries will decline. Given the decrease in growth for fuel demand, the demand growth for catalysts used to produce these fuels will also be less than previously expected.

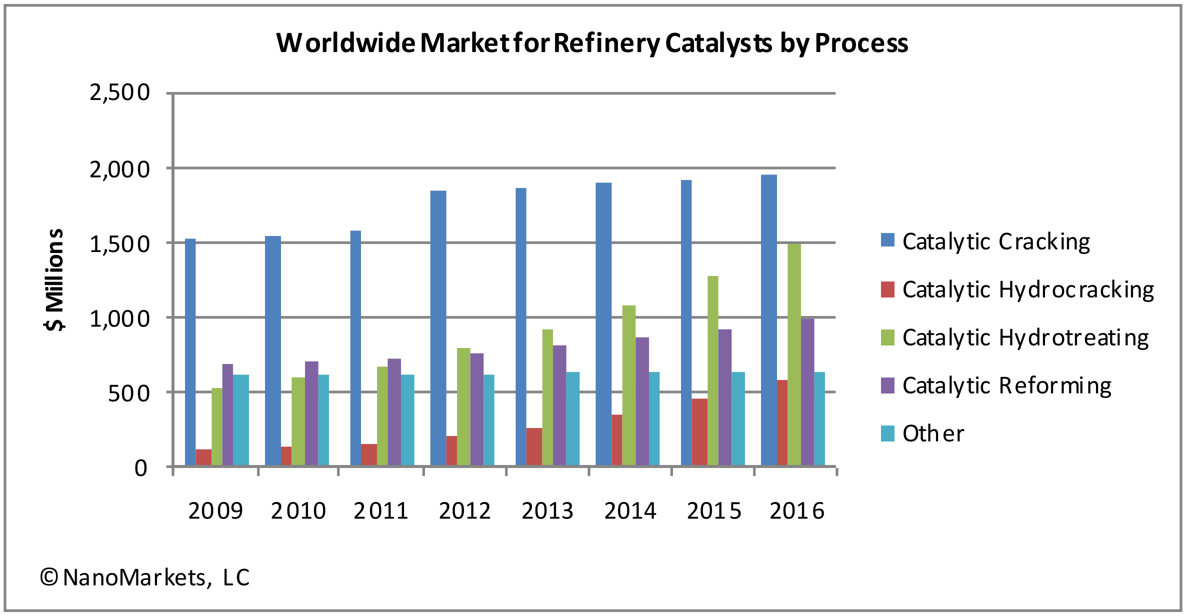
In addition to a slower pace of fuels demand growth, the recession will also impact planned expansions as well as investment in R&D. In a recession, it is difficult to get funding, and, therefore, companies will most likely delay plans for new facilities or facility expansions. In addition, during an economic crisis, especially one in which the future is uncertain, companies tend to focus on the short term. This would mean that companies are likely to forego investing in research on riskier technologies.

E.3.1 Forecasts for Refining Catalysts

While the current economic environment does not look good for fuel consumption, longer-term trends suggest that fuels demand will continue to increase, but at a lower growth rate. In evaluating the market for catalysts used in refineries to produce fuel, we have considered the fact that catalysts are sold into two markets—new units being built to meet the additional demand and existing units that continue to reload catalysts. There will be continual addition of new units to meet the growth in fuels demand, so the market overall is expanding to meet the expanding global demand of fuels. There is also a secondary effect in that the market is expanding because of the environmental effect—more catalysts as well as more frequent re-loading of catalysts to meet reduced sulfur restrictions.

Exhibit E-1 summarizes NanoMarkets' forecasts for refining catalysts broken out by process unit. The numbers are based on average overall refining capacity growth of 1 percent, with a slightly lower growth of 0.5 percent for FCC capacity; average capacity growth for hydrocracking of 5 percent; hydrotreating at 1.75 percent; and reforming at 0.5 percent. We then estimated the price and amount of catalysts consumed per capacity of feedstock processed in each of the units. These numbers are based on both the technical literature and interviews with catalyst producers. We have assumed that the amount of catalyst consumed per weight of feedstock processed will continue to increase over the next eight years to account for the increasing use of heavier and dirtier feedstock.

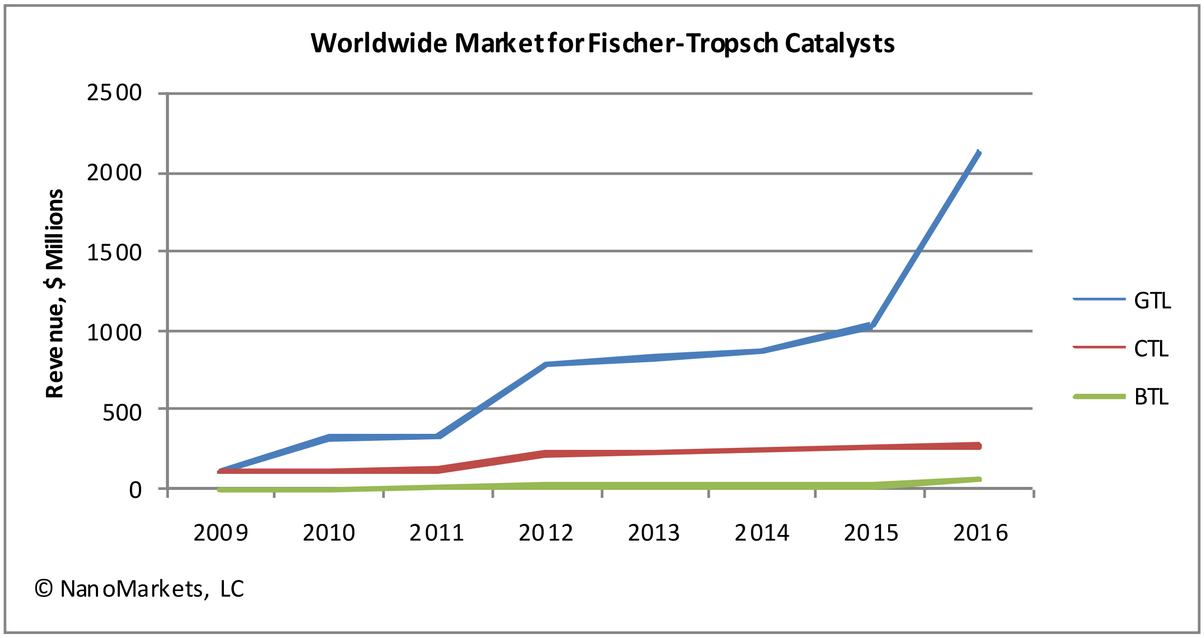
The price of these catalysts remains relatively flat over 2009 and 2010 in line with NanoMarkets' economic forecast (recession over the next one to two years followed by inflation). After 2011, we assume that the catalyst prices will begin to rise (the rate of increase is different for each of the catalysts and is dependent both on the cost of the materials used to make the catalysts and on how new the technology is, which dictates the premium that a producer can obtain).



E.3.2 Forecasts for Fischer-Tropsch

The forecasts for catalysts used in the Fischer-Tropsch process are also based on what we believe will be the most-likely scenario. While we used a similar method to determine these forecasts, the market for these catalysts is not a mature market, unlike the market for traditional fuels.

Exhibit E-2 summarizes NanoMarkets' forecasts for Fischer-Tropsch catalysts. The forecasts assume that GTL and BTL will rely on cobalt-based catalysts and CTL will use iron-based catalysts. Our forecasts are based on company and government announcements for the construction of new gasification and Fischer-Tropsch facilities. Due to the current economic environment, as well as announced delays and cancelations of projects due to higher-than-expected costs, NanoMarkets has pushed out these projects by one to two years. However, all three technologies are expected to see a rise in capacity over the next eight years, with GTL leading the way.



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