UOP is the world’s leading supplier of catalysts, adsorbents and process technology to the hydrocarbon processing industry. UOP has been in the petrochemical and refining business for 95 years and is the world’s leading supplier of molecular sieve adsorbents. Because of UOP’s long history and background in refining industries, we offer a multitude of products to meet many needs for contaminant removal in a number of refining and petrochemical processes.

There are numerous applications for UOP MOLSIV™, activated alumina based and composite adsorbents within the refining and petrochemical industries. UOP has products to remove many different contaminants within these various processes. Some of these processes are catalytic...
Continued from page one

reforming (recycle H₂, net H₂, reformate), HF alkylation (feed treatment and defluorination), isomerization (feed treatment and make-up gas treatment), light ends fuel recovery, and sulfur recovery. Within these areas, UOP adsorbents can help remove many contaminants, including: H₂O, H₂S, RSH, CO₂, COS, HF, HCl, NH₃, alcohols, carbonyls, ethers and ketones. UOP adsorbents extend catalyst life, protect equipment and ensure that product specifications are met.

UOP adsorbents are used both in regenerative and non-regenerative services, even in the same unit. In cyclic catalytic reformers, regenerative adsorbers are used to remove impurities from the recycle hydrogen stream. In CCR Platforming™, CLR-204 adsorbent is UOP’s high capacity product used for net gas treating and LPG treating. If green oil is an issue, CLR-454 adsorbent makes no green oil and has good capacity in net gas treating. If organic chlorides are a problem, PCL-100 adsorbent can be used in stabilizer feed treating to remove both organic chlorides and trace HCl. Talk with your UOP representative to determine which chloride scavenging adsorbent is the best fit for your application.

Feed and make-up H₂ dryers are installed in paraffin isomerization units to protect the catalyst. PDG-418 adsorbent can be used in the make-up H₂ dryers for moisture removal, whereas HPG-250 adsorbent is used for both moisture removal and removal of CO₂, H₂S, or methanol. ADS-106 adsorbent is available for removal of carbon monoxide (CO) from make-up hydrogen gas, again to reduce catalyst deactivation. For liquid feed driers in paraffin isomerization units UOP’s HPG-250 and HPG-429 are premier commercially proven products that have the highest capacity for trace contaminant removal. For sulfur removal, ADS-120 adsorbent is a cost-effective, non-regenerable product available for removing sulfur from both Penex and Reforming feed streams. UOP GB-217 and GB-220 non-regenerable absorbents are used for H₂S scavenging in hydrocarbon streams.

Feed dryers are also installed in HF alkylation units to reduce HF acid consumption. To help remove fluoride from the product streams, various UOP non-regenerative adsorbents can be used. The industry standard for defluorination adsorbents is UOP A-202 HF activated alumina and is widely used. For longer bed life, UOP offers P-188 adsorbent, the premier, highest capacity defluorination adsorbent. If you have alkylation feedstocks and need to purify etherification raffinate streams, use UOP ORG-E adsorbent. For light ends recovery, adsorbents are used to dehydrate hydrocarbons prior to the cryogenic plant. AZ-300 adsorbent has a high capacity for a wide range of polar molecules, including H₂O, oxygenates, organic sulfur, and nitrogen compounds. It also has high selectivity and capacity for light acid gases such as CO₂, H₂S, and COS. UOP adsorbents are also used to purify the recovered hydrocarbons by removing sulfur compounds, CO₂, various alcohols and oxygenates. If mercury is your contaminant, UOP has both regenerative and non-regenerative products that can be used individually or in combination with our other adsorbent products depending on your needs. UOP GB-238 absorbent is very effective in removing arsine in propylene streams to very low levels. Our regenerative HgSIV™ adsorbents remove both water and mercury and can be added directly to an existing dehydrator system. Our non-regenerative GB alumina absorbents can be used to permanently capture mercury for either liquid or gas treatment. Your UOP representative can help you decide what approach is best for you.
UOP CLR-204 Adsorbent

UOP CLR-204 is UOP’s latest generation chloride adsorbent for improved capacity, lower reactivity and lower costs for your unit.

Features:
- Currently installed in 12 operating units
- Multiple successful commercial manufacturing campaigns
- Produced using a novel manufacturing process
- Utilizes nano-sized crystals for the formation of active sites

Benefits:
- Increased chloride capacity for less frequent change-out and lower annual disposal costs
- Lower reactivity results in less green oil and organic chloride formation leading to longer adsorbent life

UOP CLR-204 adsorbent can be a drop-in replacement for UOP 9139A activated alumina since it has identical physical properties

- HCl adsorption testing indicates 25-40% capacity improvement over UOP 9139A activated alumina
- UOP reactivity testing indicates ~50% lower green oil formation than UOP 9139A activated alumina

<table>
<thead>
<tr>
<th>9139A</th>
<th>CLR-204</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product type</td>
<td>Promoted alumina</td>
</tr>
<tr>
<td>Typical chloride breakthrough capacity, Wt%</td>
<td>Base high capacity (best promoted alumina product commercially available)</td>
</tr>
<tr>
<td>Bead size</td>
<td>5x8 and 7x12</td>
</tr>
<tr>
<td>Operating temperatures</td>
<td>All (low and high)</td>
</tr>
<tr>
<td>Green oil formation</td>
<td>Low</td>
</tr>
<tr>
<td>Organic chloride formation</td>
<td>Low</td>
</tr>
<tr>
<td>Mass transfer rating</td>
<td>Good</td>
</tr>
<tr>
<td>Density</td>
<td>47 lb/ft³ (753 kg/m³)</td>
</tr>
</tbody>
</table>

Chloride Removal in Catalytic Reforming

– By Vlado Kanazirev

Look to UOP’s specialty aluminas and molecular sieves for effective scavengers in removing chlorides from various gas and liquid process streams. If not removed, they can ultimately lead to equipment corrosion and ammonium chloride salt deposition in downstream compressors and fuel-gas systems.

Adsorbents are most commonly used in removing chlorides from catalytic reformer hydrogen off-gases. These adsorbents feature optimum surface area and macroporosity to ensure high capacity for chloride adsorption. In addition, UOP has developed an effective specialty molecular sieve to treat the liquid reformate stream to remove trace chlorides.

Adsorbents from UOP provide the only cost-effective chloride management solution that’s based on more than 50 years of catalytic reforming experience.

The most common applications for chloride adsorbents in catalytic reforming—whether continuous catalyst regeneration unit, semi-regenerative unit or cyclic fixed bed unit—are:
- HCl removal from net gas
- Chloride removal from stabilizer feed or overhead product

Adsorbent selection plays a major role in chloride removal effectiveness. Improper selection can lead to premature chloride breakthrough and undesirable side reactions, resulting in the formation of green oil or organic chlorides. Downstream of chloride treaters, organic chlorides can revert to HCl in the compressors or the stabilizer column. Each of the chloride adsorbents used in reforming operations must have certain key characteristics to provide the best possible performance.
Increased use of propylene feed stocks for petrochemical processes such as polypropylene, cumene, and oxo alcohol has necessitated propylene yield maximization in petroleum refinery fluid catalytic cracking (FCC) processes. UOP has been designing and licensing FCC technology (Figure 1) for nearly 60 years and offers FCC, resid FCC, and PetroFCC processes to convert straight-run atmospheric gas oils, vacuum gas oils, atmospheric residues, and heavy stocks recovered from other refinery operations into high-octane gasoline, light fuel oils and olefin-rich light gases such as propylene. An integral component of a UOP licensed FCC process for production of chemical and polymer grade propylene is the Propylene Recovery Unit (PRU) on the propylene-propane (C₃⁻, C₃) stream exiting the FCC unit. These PRUs utilize proprietary UOP process equipment as well as high performance and low reactivity absorbents for contaminant removal. These absorbents improve the operation of the downstream units as well as improve the properties of the intermediate and final products.

**Adsorption Technology**

UOP manufactures a wide range of molecular sieve (zeolite), activated alumina-based, and composite (alumina-zeolite) adsorbents. Adsorbents typically have a porous structure with a high surface area. Molecular sieves have a crystalline structure with uniform pore openings that determine which molecules are adsorbed and which are rejected.

On the other hand, activated alumina-based adsorbents are amorphous in nature with a wide range of pore openings. Adsorption is the preferred separations technology for trace contaminant (typically polar or polarizable) removal from vapor or liquid phase streams. Adsorption can occur via a number of different mechanisms including physisorption, chemisorption, a combination of physisorption and chemisorption, and ion exchange. Physisorbed contaminants on molecular sieves and UOP’s composite adsorbent, AZ-300, are preferentially adsorbed via the concept of selectivity. Adsorbents have the ability to remove contaminants to ultra low (ppb) effluent specifications to assure protection of downstream processes, equipment, and catalysts. The final attainable effluent specification for each contaminant depends on the adsorption mechanism and properties of the product utilized in a specific application. Adsorbents and catalysts share key attributes: porosity, surface area, and surface functionality. The reactivity (leading to side reactions) of an adsorbent is of utmost importance when treating reactive streams such as olefins.

In process facilities, the solid adsorbent is loaded into a pressure vessel and the contaminated process stream passes through the packed bed. Dynamic adsorption takes place across a mass transfer zone that progresses through the adsorbent bed as a stable wave or “front” until contaminant breakthrough occurs. Adsorbent requirements must be sufficient to accommodate the equilibrium section as well as the mass transfer zone’s length. An
adsorbent’s equilibrium capacity for a contaminant is dependent on the concentration of the contaminant in the feed stream as well as its temperature. Adsorbent regeneration is accomplished via a thermal and/or pressure swing driving force. Thermal regeneration of molecular sieves, activated aluminas and composite adsorbents are typically conducted by passing a hot (150-290°C) gas such as N₂ or contaminant free light hydrocarbon through the packed bed to desorb the contaminants. The heating step is followed by a cooling step (utilizing a contaminant-free gas or liquid stream). Some UOP products use the mechanism of a chemical reaction for contaminant removal and are operated in a non-regenerative mode. The contaminants are tightly bound to the absorbent and remain on the material through the useful life of the product and proper disposal following recharge of the vessel.

**Contaminants of Concern in PRU’s and Appropriate Adsorbents for their Removal**

Contaminants of concern in the propylene-propane (C₃⁻, C₃) stream exiting a FCC process include H₂O, oxygenates (such as alcohols and ketones), NH₃, other nitrogen-based compounds (such as amines, nitriles and amides), organic sulfur compounds (mercaptans (RSH), dimethyl sulfide (DMS)), dimethyl disulfide (DMDS), H₂S, CS₂, CO₂, COS, AsH₃ (arsine), PH₃ (phosphine), and Hg (metallic mercury). These contaminants must be removed from the propylene-propane stream to:

- Prevent deactivation of petrochemical process catalysts that utilize the recovered propylene as a feedstock
- Minimize environmental concerns
- Meet product specifications for polymer grade propylene

Of particular concern in regard to polypropylene production polymerization catalysts (Ziegler-Natta and metallocene types) and propylene hydrogenation processes are sensitivity to contaminants such as H₂S, COS, CS₂, AsH₃, PH₃ and Hg which must be removed to levels well below 30 ppbw in order to maximize yield and catalyst life. Cumene production processes also require that the propylene feedstock be purified to assure low levels of nitrogen-based contaminants, AsH₃, PH₃ and Hg, for the same reasons. Adsorbents are commonly used in a PRU to remove these contaminants. While the adsorbents are purifying the propylene stream, it is essential that they are not reactive with the olefins or the contaminants themselves. Low reactivity adsorbents prevent conversion of the olefin to oligomers, prevent conversion of the contaminants and minimize coking of the adsorbent during its thermal regeneration, thereby, maximizing the effective adsorption capacity and adsorbent life. UOP’s products have been tested and compared to other commonly used purification materials. UOP’s products show less reactivity and less coking when analyzed.

UOP has a broad portfolio of molecular sieve, activated alumina-based and composite adsorbents appropriate for propylene-propane stream purification in FCCU PRUs. Several of these adsorbent products are shown in the table below.

<table>
<thead>
<tr>
<th>Product Name &amp; Type</th>
<th>Operating Mode*</th>
<th>Contaminants Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLSIV ODG-442 Adsorbent Molecular sieve</td>
<td>R</td>
<td>H₂O</td>
</tr>
<tr>
<td>UOP AZ-300 Adsorbent Composite</td>
<td>R or NR</td>
<td>H₂O, oxygenates, H₂S, COS, CS₂, RSH, DMDS, NH₃, amines, nitriles, CO₂</td>
</tr>
<tr>
<td>UOP SG-731 Adsorbent Promoted activated alumina</td>
<td>R or NR</td>
<td>H₂S, CS₂, COS</td>
</tr>
<tr>
<td>UOP GB-238 Absorbent Metal oxide on alumina</td>
<td>NR</td>
<td>H₂S, COS, AsH₃, PH₃</td>
</tr>
<tr>
<td>UOP GB-346 Absorbent and UOP GB-346S Absorbent Metal oxide on alumina</td>
<td>NR</td>
<td>Hg</td>
</tr>
</tbody>
</table>

* R = regenerative, NR = non-regenerative

FCCU sourced propylene can be an excellent feedstock for petrochemical processes provided the contaminants of concern are removed with the proper adsorbents in a PRU. UOP has the products and product application technology to protect petrochemical process catalysts from deactivation to help minimize plant upsets, ensure longer catalyst life and aid in worry-free operation.
Use of Molecular Sieves and other Adsorbents for Contaminant Removal in Ethylene and Propylene Production

– By Jay Gorawara

Adsorbents such as molecular sieves and activated aluminas are widely used in the processing industries to remove water and other contaminants from feed streams. In recent years there has been a growing need for the removal of other contaminants in ethylene and propylene production. This article highlights the capability of these adsorbents to remove many contaminants in reactive streams using both regenerative and non-regenerative adsorbents and helps processors identify potential applications to improve their operation or upgrade the quality of their products.

Zeolite Molecular Sieves

Zeolite adsorbents are synthetically produced molecular sieves that are microporous, crystalline, metal aluminosilicates. Metal cations contained in the crystalline structure of molecular sieve adsorbents balance the negative charge of the framework. These metal cations create an electrical field resulting in a strong attraction for polar molecules. Higher polarity generally results in a higher attraction for a molecular sieve. Because of its high polarity, water can be removed by molecular sieves from most process streams.

The size of the pore opening on each face into the internal structure where the contaminants pass through is determined during manufacturing by the type of crystal and occupying cation. Thus some molecules can be readily adsorbed or completely excluded (even highly polar molecules) according to their relative molecular size.

The table below lists the two types of molecular sieve adsorbents most commonly used for olefin processing and the molecules that they will adsorb and exclude.

<table>
<thead>
<tr>
<th>*General Type</th>
<th>Molecules Adsorbed</th>
<th>Molecules Excluded</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>&lt;3 angstroms effective pore diameter H₂O, NH₃,</td>
<td>&gt;3 angstroms effective diameter acetylene, ethylene, propylene and larger hydrocarbons</td>
</tr>
<tr>
<td>13X</td>
<td>&lt;8 angstroms effective diameter H₂O, NH₃, CH₃OH, H₂S, CO₂, C₂H₄, C₃H₆</td>
<td>&gt;8 angstroms effective diameter – All common contaminants and hydrocarbons in ethylene and propylene processing are smaller than 8 angstroms</td>
</tr>
</tbody>
</table>

**Larger Oxygenate and Sulfur compounds**

* Chart depicts basic molecular sieve types only. In all applications, these basic forms are customized for specific use.

** Typically found in C₄+ olefins present in refinery streams

Type 3A molecular sieve is highly effective for removal of water and ammonia to extremely low levels from reactive streams in ethylene plants because of the polarity of these contaminants and the fact that the reactive carrier stream components are excluded. As long as a non-reactive binder with high breakup resistance is used to form the finished molecular sieve product, long life is expected.

Because Type 13X zeolite molecular sieve has one of the highest capacities of any molecular sieve for most polar compounds and will adsorb larger contaminants such as branched chain oxygenates and sulfur compounds, it is frequently used for contaminant removal from olefinic streams. Type 13X and other large pore molecular sieves require special operating procedures when used in an olefin stream where they readily adsorb the carrier stream. When a molecular sieve adsorbs a compound, heat is released. Most contaminants are at low enough levels that the heat release is minimal. But when the adsorbed compound is at high level such as in a stream containing significant olefins, a large amount of heat can be released triggering possible exothermic reactions that endanger equipment and personnel. To prevent this situation, a preload step is used before the initial exposure of a fresh or regenerated adsorbent to the olefin containing stream.

It is also possible to use type 4A and 5A molecular sieves to dry and purify olefin streams. However, there is typically no advantage over 13X since they adsorb the reactive components such as ethylene and propylene, have lower overall capacity, and cannot adsorb larger oxygenate and sulfur compounds.

Promoted Aluminas

Modified activated alumina adsorbents are synthetically produced, transitional phase aluminas. Unlike zeolites, activated aluminas have a pore
system that is accessible to practically all compounds present in ethylene, propylene and polymer plants. Hence, the size exclusion phenomenon cannot be used in alumina based adsorption processes. Instead, the complex surface chemistry of aluminas offers tremendous opportunities for designing adsorbents for particular applications. The modification of surface functionality by inorganic additives, or promoters, during manufacturing is an especially useful method for enhancing adsorbent performance. The promoted aluminas have excellent performance for removal of specific contaminants to very low levels.

In olefinic streams, light acid gases such as CO$_2$, H$_2$S and COS are common contaminants that can be most effectively removed with this type of modified activated alumina. As these aluminas rely on chemisorption to remove CO$_2$, H$_2$S and COS, they exhibit high capacities for these contaminants even at very low concentrations. In addition, the chemisorption mechanism assures that ultra low (ppb levels) contaminant effluent specifications can be attained in properly designed adsorption systems utilizing promoted aluminas for CO$_2$, H$_2$S, and COS removal.

These promoted alumina adsorbents also have the additional advantage in that unlike molecular sieves, they do not have a strong affinity for reactive, polar compounds such as olefins. With little or no selective capacity for olefins, there is a very low heat of adsorption when olefins are exposed to promoted aluminas, hence a preload step is not required. In addition, these adsorbents exhibit very low reactivity towards the main carrier stream. The formation of additional contaminants, such as olefin oligomers, is practically non-existent at typical process conditions.

**Hybrid Adsorbent**

By combining high selectivity and capacity for light acid gases with low reactivity and heat of adsorption of hydrocarbons, a properly modified activated alumina is very suitable for the purification of olefinic streams. Correspondingly, molecular sieves have a high capacity for polar molecules. Ideally, one adsorbent could exhibit the properties of both zeolitic and promoted alumina adsorbents. A hybrid adsorbent, a homogenous combination of a promoted alumina and a large pore molecular sieve adsorbent can take advantage of the complementary performance characteristics of both materials. A properly designed high quality hybrid adsorbent can simultaneously have good capacity for light acid gases as well as a broad range of polar molecules.

Though a hybrid adsorbent contains zeolite, when properly produced it typically may not require a preload step when processing olefinic hydrocarbons. The elimination of the preload step, while retaining the effective removal of polar compounds and light acid gases, provides the olefins producer and polymer manufacturer with significant process advantages. The unique properties of a hybrid adsorbent may enable the processor to use a single product for the adsorptive removal of the broadest range of contaminants without a preload step. The result is an adsorbent that provides additional protection against unanticipated contaminants with a simplified and safer process.

**Metal Oxide Containing Adsorbents**

This class of adsorbents is a “must have” for propylene purification, where the removal of contaminants such as AsH$_3$, PH$_3$, COS to low part per billion (ppb) levels is critical for the economic production of polypropylene. These trace contaminants adversely effect performance of the very sensitive modern polymerization catalysts. The metal oxide component in these adsorbents irreversibly binds the hydride contaminants via an oxidation-reduction mechanism; hence water is a by-product of the reaction.

It is critical for these advanced metal oxide adsorbents to have high contaminant capacity combined with low reactivity towards the carrier stream. An optimized pore structure is also essential for this liquid phase application. A high binder surface area can help to retain the water produced in the arsine and phosphine scavenging reactions.

**Note:** There is a potential for the metal oxide products to form hazardous (potentially explosive compounds) in the presence of acetylene under certain conditions. Consult your adsorbent supplier for recommendation of the proper adsorbent, as well as operating procedures for your operations.
In net gas treaters, the adsorbent must provide:

- Rapid reaction rate of HCl with the adsorbent to minimize the time necessary for adsorption/reaction to occur thereby increasing dynamic adsorbent capacity
- Low effluent HCl concentrations to reduce the HCl level to less than 1 ppmv, significantly reducing corrosion in downstream equipment
- Low coke buildup to maximize dynamic capacity
- Acceptable pressure drop

In liquid adsorption systems designed to remove HCl and organic chlorides from liquid hydrocarbon streams, stabilizer feed and/or overhead from liquid hydrocarbon streams, to remove HCl and organic chlorides in the stabilizer net overhead gas, since the concentrations in the stabilizer overhead stream are an order of magnitude higher. These adsorbent characteristics are extremely important, since inefficient chloride management adds significantly to the operating cost of any catalytic reforming unit. Untreated streams can cause major corrosion problems in downstream equipment.

**Design Considerations**

To determine the size and configuration of an adsorber system designed to remove the chlorides from any of the various catalytic reforming vapor or liquid phase streams, certain conditions must be considered:

- Gas or liquid flow rate
- Temperature of the feed
- Pressure
- Feed stream composition
- Type and level of chlorides to be removed
- Type and level of any other contaminants present
- Bed dimensions for an existing unit
- Bed life desired
- Pressure drop desired
- Effluent chloride specification (typically less than 1 ppmv)

With this information and the design parameters that have been developed and confirmed commercially for each of our products, UOP can recommend bed size and configuration as well as the expected life and pressure drop. These designs are tailored to provide optimum performance for chloride removal in your specific application.

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**UOP in the News**

**UOP to Offer Albemarle NEBULA® Catalyst for Ultra-Low-Sulfur Diesel through Hydroprocessing Alliance**

UOP will offer the Albemarle NEBULA hydrotreating catalyst for the production of high-quality, ultra-low-sulfur diesel (ULSD) as part of the Hydroprocessing Alliance, UOP’s strategic alliance with Albemarle Corp. NEBULA catalyst is an innovative material jointly discovered by ExxonMobil Research and Engineering Company and co-developed with Albemarle that offers greater catalyst activity and can enhance diesel yield and quality. The Hydroprocessing Alliance will now offer the catalyst for reloads and revamps of hydroprocessing units.

“The NEBULA catalyst can be used as a drop-in for hydrocracker reloads to allow them to produce more ULSD without costly modifications to the unit,” said UOP Alliance Director Jim Kennedy. “This is a distinct advantage as the demand for diesel continues to grow and environmental specifications get stricter. We are very pleased that through the Hydroprocessing Alliance, we can now make this important product available to our customers.”

The NEBULA catalyst is a base-metal catalyst with higher activity than conventional hydrotreating catalysts. In addition to supporting production of ULSD without additional capital investment, NEBULA can enhance hydrotreating unit revamps to reach higher throughputs or achieve higher product quality standards. Additionally, NEBULA’s high denitrogenation (HDN) and hydroaromatization (HDA) activities can debottleneck hydrocrackers that have limited hydrotreating activity. It has been used in more than 40 applications since its introduction in 2001.

“NEBULA’s proven operational flexibility and superior performance is a strong addition to the Alliance’s portfolio of cost effective solutions required in today’s market,” said Marc Nicolas, Director of Albemarle’s Alliance activities. “In just three years Alliance efforts have resulted in the licensing of 61 hydrotreating units. We look forward to our continued work with UOP to provide advanced products, technologies and consultative services that bring significant value and support to the long-term business objectives of our clients.”

UOP and Albemarle formed the Hydroprocessing Alliance in 2006 to support the production of clean transportation fuels worldwide. The alliance combines the strengths of UOP, a leading developer of hydrotreating and hydrocracking process technology and hydrocracking catalysts, and Albemarle, a leading developer and supplier of innovative refinery hydrotreating catalysts and technologies, to provide the refining industry with a broad portfolio of process and catalyst offerings for middle distillate hydrotreating, vacuum gas oil hydrotreating, mild hydrocracking, hydrocracking, and fixed-bed residue hydrotreating.