



DOWEX DR-2030 and DOWEX MONOSPHERE DR-2030 Catalysts

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Dry acid catalysts for chemical processing

Homogeneous acid catalysis is the most common method for converting reactants to products in use by the chemical process industry. There are several problems with bulk addition of acids. The reaction is often not under control, going beyond the desired reaction, producing unwanted by-products. Bulk acid reactions have limited stereospecificity in product formation. Finally, the product isolation often requires neutralization of the acid and results in salts, with product recovery problems and added expense.

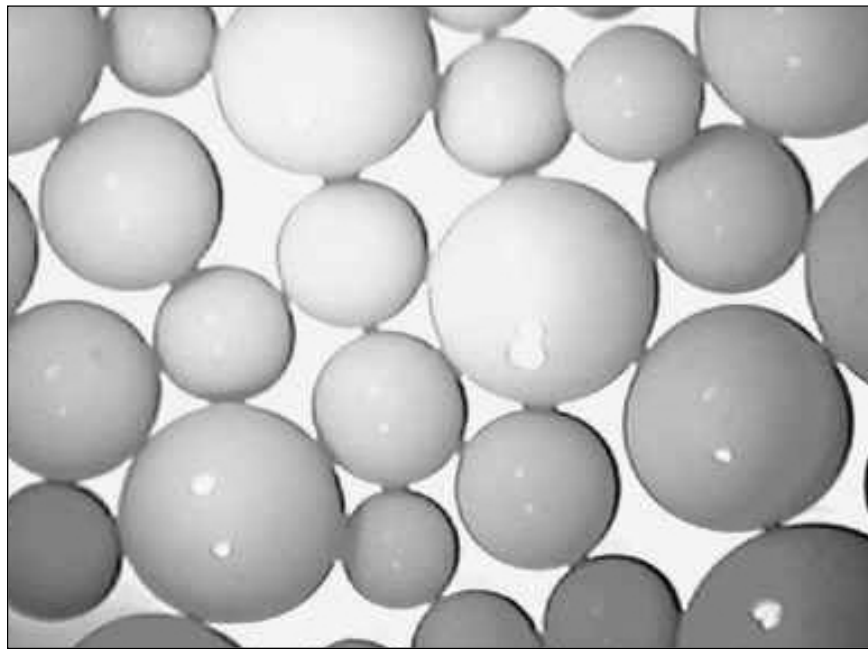
An attractive alternative is an immobilized, solid phase catalyst. Heterogeneous acid catalysts offer controlled contact time, improved stereospecificity and replace the problem of acid neutralization with simple filtration.

Heterogeneous Catalysis

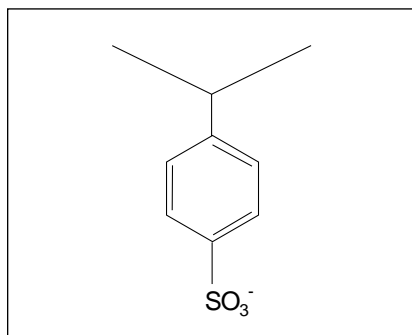
- Excellent capacity equivalent to 2M acid
- Ease of separation, simple filtration
- Acid neutralization elimination
- Fixed bed reactors under better temperature and contact time control
- Polymer matrix that excludes larger molecules (>1500-2000 MW) from further reaction
- Product selectivity often increases

DOWEX* DR-2030 catalyst is styrenic plastic bead, functionalized with sulfonic acid groups. These tough plastic beads are insoluble in organic solvents, strong acids or base. The high level of functionality of the beads results in an acid concentration of >2M. The effective acidity is enhanced by the hydrophobic nature of the plastic backbone. The polymer matrix often stereochemically orients the reactants for greater selectivity or reduced by-product formation.

Figure 1. DOWEX DR-2030



Sulfonic acid functionality of DOWEX DR-2030 catalysts



Moisture Content – Many acid catalyzed reactions are anhydrous so DOWEX DR-2030 is produced in the dry form. For many reactions a low level of moisture is suitable for good interaction with reaction solvent. In other cases further moisture removal may be required. Further catalyst drying is best performed by washing the catalyst with a dry, water miscible solvent (alcohol or ketone).

It is important to verify the moisture content of the catalyst during evaluation and operations. A convenient way to measure moisture content is with Karl Fisher titration, using a known volume of catalyst in dry solvent.

DOWEX DR-2030 catalysts are also available in the fully water hydrated form as DOWEX M-31 and DOWEX MONOSPHERE* M-31 catalysts.

Temperature Limits – Because of the hydrophobic nature of the catalyst and spatial restriction of the groups, many reactions occur at lower temperatures than they would with a homogeneous acid catalyst. DOWEX DR-2030 is based on a styrenic plastic matrix so the upper limit for safe operation is set at 130°C. Higher temperatures can be temporarily experienced but are not advised as desulfonation can start at these temperatures.

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Macroporous Structure –

DOWEX DR-2030 is a highly porous, synthetic catalyst. High porosity and surface area (see Figure 4) are important requirements for fast diffusional kinetics. A photomicrograph of a split bead attests to the high surface area of the catalyst (Figure 2).

Co-solvents – Sometimes a solvent is added to the reaction mixture to enhance molecular transport to and from the reaction site. Polar solvents will form a solvation sphere around the sulfonic acid groups, swelling the catalyst and enhancing transport of the reactants and products. The order of solvent addition should be considered in catalyst preparation to optimize performance.

Testing – Evaluation of dry acid catalysts can be done in a batch reaction or as a column study. The investigator needs to consider the ratio of catalyst to solution, the temperature, catalyst swelling (solvation), order of reactant addition, reaction time and the role moisture might play in the reaction. Batch reaction evaluation is convenient because the beads can be easily filtered out of the reaction mixture.

Operations – Typically, solid catalysts are used in packed beds where reactants are pumped through the catalyst at the desired temperature. For more information on operations for DOWEX catalyst, see the Fuel Oxygenate Newsletters referenced on Page 3.

DOWEX MONOSPHERE DR-2030 –

Continuous catalyst operations in packed beds must be optimized for maximum throughput. Kinetic limitations for diffusion of reactants into the catalyst sites and diffusion of product back out into the bulk solution should be considered. Because of their relatively long diffusion paths, the largest beads are the most kinetically limited with an effective “dead zone” present at the interior of the bead.

Figure 2. Split bead shows macropores of DOWEX DR-2030

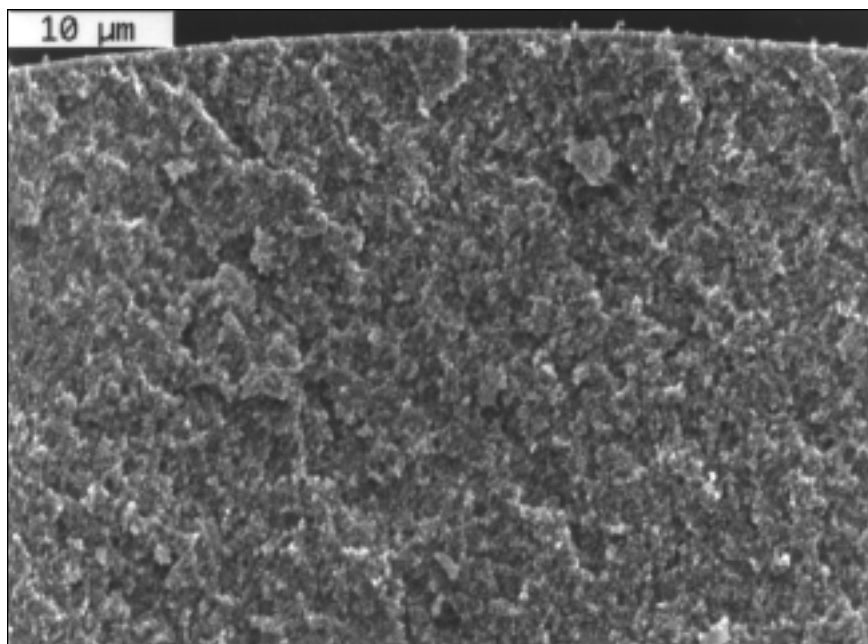
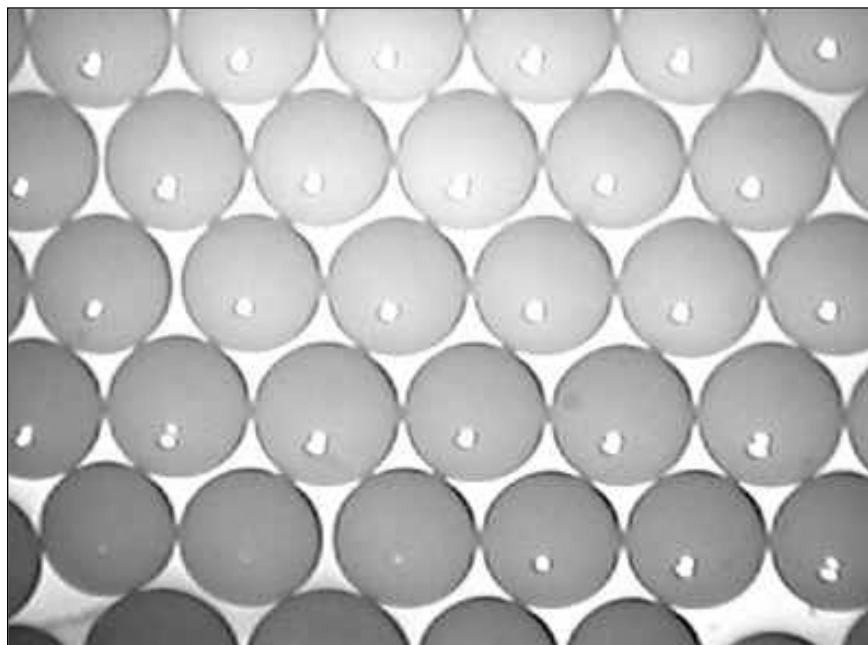


Figure 3. DOWEX MONOSPHERE DR-2030



Pressure drop through the bed is another potential limitation. While the smallest beads have very fast diffusion kinetics, they contribute more to pressure drop. DOWEX MONOSPHERE DR-2030 is made by a patented process resulting in excellent uniformity of bead size (see Figure 3). Many customers have experienced as much as 15% increase in productivity when switching from a standard bead size to uniform particles like DOWEX MONOSPHERE DR-2030.

Applications – DOWEX dry catalysts are used for a wide variety of applications including phenol alkylation, aldol condensations, ester hydrolysis, esterification and isomerization to name a very few. Additional selectivity is introduced by the polymeric matrix due to exclusion of larger molecules (1500 to 2000 MW) from the reaction sites. A current listing of literature references is available from Dow.

Immobilized Metal Catalysts – Precious and non-precious metals can be immobilized on synthetic catalysts to take advantage of the high surface areas and high acidity offered by synthetic supports. Some examples are Al, Ag, Cd, Cu, Co, Cr, Fe, La, Mn, Mo, Mg, Ni, Pt, Pd, Rh, Sn, Va and Zn. A current listing of literature references titled “Immobilized Metals on Catalysts” is available upon request.

Low residual acidity of DR-2030 – Some reactions, particularly during start-up, are very sensitive to catalysts that are “too hot”, where higher levels of by-products are formed. Often these symptoms go away with further use. In some cases this problem is due to residual acid left in the catalyst from manufacture. DOWEX DR-2030 catalysts are specially prepared to reduce the levels of residual acidity thereby reducing by-product formation in sensitive reactions.

Figure 4.

Typical Properties	DOWEX DR-2030	DOWEX MONOSPHERE DR-2030
Dry weight capacity	>4.7 meq/g	>4.7 meq/g
Moisture content	<3%	<3%
Whole beads	>95%	>95%
Particle size	16 to 40 mesh	425-525 microns
Fines content (as wet beads)	<5% are less than 40 mesh	<1% are less than 297 microns
Porosity	0.33 cc/g	0.35 cc/g
Surface area	30 m ² /g	31 m ² /g
Density	0.59 cc/g 37 lbs/cubic foot	

Other DOWEX Catalysts – A wide variety of other functional chemistries are available that include weak acids, strong base and weak base groups. In addition to macroporous supports, continuous, gel type supports are also available. For additional information, see “DOWEX Ion Exchange Resins – Powerful Chemical Processing Tools”. Custom made catalysts are also available through Dow Contract Manufacturing. Inquiries are welcome, contact the Customer Information Group at 1-800-447-4369.

For more information...

To receive additional information or pricing and availability of dry catalysts, contact the Customer Information Group in your respective area. Telephone numbers for each area can be found on the last page of this literature.

For technical assistance with your catalyst development efforts, contact Dr. H. Robert Goltz at 989-636-2023 or by e-mail at HRGOLTZ@DOW.com.

For additional information on chemical processing, see “DOWEX Ion Exchange Resins – Powerful Chemical Processing Tools” Form No. 177-01395/CH 171-426-E.

Fuel Oxygenate Newsletters for DOWEX M-31 Catalyst

- *Catalyst Properties in Perspective.* Form No. 177-01508.
- *Catalyst Loading and Dewatering.* Form No. 177-01511.
- *Process Problems in MTBE/TAME/ETBE Production.* Form No. 177-01513.
- *MTBE/TAME/ETBE Catalyst Deactivation.* Form No. 177-01516.

Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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